3RD EDITION

FLUID CATALYTIC CRACKING HANDBOOK

An Expert Guide to the Practical Operation, Design, and Optimization of FCC Units





REZA SADEGHBEIGI

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W.R. Grace v. Cochise Technology - IPR 2023-01063

Fluid Catalytic Cracking Handbook

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Dedication

To my family and the great friends I have made over the years.

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Third Edition

Reza Sadeghbeigi



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Preface to the Third Edition

Coming from Iran, I have been extremely blessed and fortunate in being educated and working in the United States of America. From my days of working as roustabout and roughneck on offshore drilling rigs in the early 1970s, to nearly 40 years later, my goal has been to share my hard-learned experience and knowledge with others. I have accomplished this through publishing technical articles and books, conducting seminars, and providing customized training. *My main objective of writing this book is simply to give back a fraction of the good will that so many great folks have provided to me throughout my professional journey.*

The refining industry has been downsizing in the United States for many years. The crop of aging refinery technical experts is fast disappearing, with no "farm system" to replace them. Attending annual conferences used to be beneficial in providing this technology transfer. In the past 10 years, these conferences are becoming restrained by political correctness and influenced by commercial interests. In many cases, the speakers/presenters have limited knowledge for offering practical "lessons learned" on the spot. Furthermore, many attendees are reluctant to challenge the status quo or raise new ideas in a public forum.

This third edition truly provides a transfer of my 35 years of experience in the cat cracking process. There are no other publications available that deliver comprehensive discussions of the cat cracking field without any commercial interest interference, while at the same time offering tangible and practical information that can be used in making the "right" decisions in an ever-challenged industry. Examples of these decisions would be processing suitable feedstock, purchasing appropriate fresh catalyst and/or additive, designing or ensuring that FCC equipment is designed appropriately, and being able to troubleshoot/optimize the operations of the unit effectively.

Several new chapters have been added since the second edition, and the original chapters have been extensively updated. The new chapter on *refractory lining* contains a great deal of practical information that is essential to enhancing the long-term mechanical reliability of the FCC components. The new chapter on *residue cracking* provides insights into achieving optimum yields, while sustaining long-term unit run length. The new chapter on *flue gas emissions* provides various effective options to better comply with emission requirements, without going overboard.

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I am proud of this third edition. For one, I received input/feedback from our valued clients, industry "experts," as well as my colleagues at RMS Engineering, Inc. Each chapter was reviewed carefully for accuracy and completeness. The emphasis has been on providing tools to maximize the profitability and reliability of existing operations without major capital project expenditures. I hope this book will serve as a handy reference resource for anyone associated with the fluid catalytic cracking process.

I plan to continue sharing my technical expertise and know-how for the next few years.

Reza Sadeghbeigi
Houston, Texas
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Acknowledgments

I am grateful to the following individuals who played key roles in this book's completion:

My colleagues at RMS Engineering, Inc., *Shari Glazier*, *Lee Kittleson*, and *Larry Gammon*, who went the "extra mile" to ensure the book flows well. I would also like to thank Doug Hogue, Refractory Consultant of HRCI, for his major contribution to the chapter on refractory.

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About the Author

Mr. Reza Sadeghbeigi has extensive experience with fluid cat crackers, having worked with more than 100 FCC units since 1977. Reza received his BS in chemical engineering from Iowa State University and his MS from Oklahoma State University. He is a registered professional engineer in Texas and Louisiana.

Reza established RMS Engineering, Inc. (RMS) in January 1995 to provide independent engineering services to the refining industry in the area of fluid catalytic cracking. RMS provides expertise and know-how in delivering services such as FCC equipment design, troubleshooting, unit optimization, and customized operator/engineer training.

Should you have any questions or comments on this book, or if you would like to tap into our services, please feel free to contact Reza at (281) 333-0464 (US) or by e-mail (reza@rmsfcc.com).

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CHAPTER 1

Process Description

Global demand for transportation fuels will continue to grow and this demand will be met largely by gasoline and diesel fuels. The fluid catalytic cracking (FCC) process continues to play a key role in an integrated refinery as the primary conversion process of crude oil to lighter products. In the next two decades, the FCC process will be likely used for biofuels and possibly for reducing CO_2 emissions. For many refiners, the cat cracker is the key to profitability because the successful operation of the unit determines whether or not the refiner can remain competitive in today's market.

Since the start-up of the first commercial FCC unit in 1942, many improvements have been made to enhance the unit's mechanical reliability and its ability to crack heavier, lower value feedstocks. The FCC has a remarkable history of adapting to continual changes in market demands. Tables 1.1 and 1.1A highlight some of the major developments in the history of the FCC process.

The FCC unit uses a "microspherical" catalyst that behaves like a liquid when it is properly fluidized. The main purpose of the FCC unit is to convert high-boiling petroleum fractions called *gas oil* to high-value transportation fuels (gasoline, jet fuel, and diesel). FCC feedstock is often the gas oil portion of crude oil that commonly boils in the 650°F+ to 1,050°F+ (330−550°C) range. Feedstock properties are discussed in Chapter 3.

Approximately 350 cat crackers are operating worldwide (102 in the United States), with a total processing capacity of over 14.7 million barrels per day [1]. Most of the existing FCC units have been designed or modified by six major technology licensors:

1. UOP (Universal Oil Products)
2. Kellogg Brown & Root—KBR (formerly The M.W. Kellogg Company)
3. ExxonMobil Research and Engineering (EMRE)
4. The Shaw Group Inc.
5. CB&I Lummus
6. Shell Global Solutions International.

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Table 1.1: The Evolution of Catalytic Cracking—Pre FCC Invention.

1915	Almer M. McAfee of Gulf Refining Co. discovered that a Friedel—Crafts aluminum chloride catalyst could catalytically crack heavy oil. However, the high cost of catalyst prevented the widespread use of McAfee's process.
1922	The French mechanical engineer named Eugene Jules Houdry and a French pharmacist named E.A. Prodhomme set up a laboratory to develop a catalytic process for conversion of lignite to gasoline. The demonstration plant in 1929 showed the process is not economical. Houdry had found that fuller's earth, a clay containing aluminosilicate (Al_2SiO_6), could convert oil from lignite to gasoline.
1930	The Vacuum Oil Company invited Houdry to move his laboratory to Paulsboro, NJ.
1931	The Vacuum Oil Company merged with Standard Oil of New York (Socony) to form Socony-Vacuum Oil Company.
1933	A small Houdry unit processing 200 bpd of petroleum oil was commissioned because of the economic depression of the early 1930s. Socony-Vacuum could not support Houdry's work and granted him permission to seek help elsewhere. Sun Oil Company joined in developing Houdry's process.
1936	Socony-Vacuum converted an old thermal cracker to catalytically crack 2,000 bpd of petroleum oil using the Houdry process.
1936	Use of natural clays as catalyst greatly improved cracking efficiency.
1937	Sun Oil began operation of Houdry unit processing 12,000 bpd. The Houdry process used reactors with a fixed bed of catalyst and it was a semi-batch operation. Almost 50% of the cracked products were gasoline.
1938	With the commercial successes of the Houdry process, Standard Oil of New Jersey resumed research of the FCC process as part of the consortium that included five oil companies (Standard Oil of New Jersey, Standard Oil of Indiana, Anglo-Iranian Oil, Texas Oil, and Dutch Shell), two engineering construction companies (M.W. Kellogg and Universal Oil Products), and a German chemical company (I.G. Farben). This consortium was called Catalyst Research Associates (CRA), and its objective was to develop a catalytic cracking process that did not impinge on Houdry's patents. Two MIT professors (Warren K. Lewis and Edwin R. Gilliand) had suggested to CRA researchers that a low gas velocity through a powder might lift the powder enough to flow like liquid. Standard Oil of New Jersey developed and patented the first fluid catalyst cracking process.
1938—1940	By 1938 Socony-Vacuum had 8 additional units under construction, and by 1940 there were 14 Houdry units in operation processing 140,000 bpd of oil. The next step was to develop a continuous process rather than Houdry's semi-batch operation. Thus came the advent of a moving-bed process known as thermofor catalytic cracking (TCC), which used a bucket conveyor elevator to move the catalyst from the regenerator kiln to the reactor.
1940	M.W. Kellogg designed and constructed a large pilot plant at the Standard Oil Baton Rouge, Louisiana, refinery.
1941	A small TCC demonstration unit was built at Socony-Vacuum's Paulsboro refinery.
1943	A 10,000 bpd TCC unit began operation at Magnolia Oil Company in Beaumont, TX (an affiliate of Socony-Vacuum's Paulsboro refinery).
1945	By the end of World War II, the processing capacity of the TCC units in operation was about 300,000 bpd.

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Table 1.1A: The Evolution of the FCC Process.

1942	The first commercial FCC unit (Model I upflow design) started up at the Standard of New Jersey Baton Rouge, Louisiana, refinery, processing 12,000 bpd.
1943	First down-flow design FCC unit was brought online. First TCC brought online.
1947	First Universal Oil Products (UOP)-stacked FCC unit was built. M.W. Kellogg introduced the Model III FCC unit.
1948	Davison Division of W.R. Grace & Co. developed microspheroidal FCC catalyst.
1950s	Evolution of bed cracking process designs.
1951	M.W. Kellogg introduced the Orthoflow design.
1952	Exxon introduced the Model IV.
1954	High alumina (Al_2O_2) catalysts were introduced.
Mid-1950s	UOP introduces side-by-side design.
1956	Shell invented riser cracking.
1961	Kellogg and Phillips developed and put the first resid cracker onstream at the Borger, TX, refinery.
1963	The first Model I FCC unit was shut down after 22 years of operation.
1964	Mobil Oil developed ultrastable Y (USY) and rare earth exchanged ultrastable Y zeolite (ReY) FCC catalyst. Last TCC unit completed.
1972	Amoco Oil invented high-temperature regeneration.
1974	Mobil Oil introduced CO promoter.
1975	Phillips Petroleum developed antimony for nickel passivation.
1981	TOTAL invented two-stage regeneration for processing residue.
1983	Mobil reported first commercial use of ZSM-5 octane/olefins additive in FCC.
1985	Mobil started installing closed cyclone systems in its FCC units.
1994	Coastal Corporation conducted commercial test of ultrashort residence time, selective cracking (MSCC).
1996	ABB Lummus Global acquired Texaco FCC technologies.

Figures 1.1–1.9 contain sketches of typical unit configurations offered by the FCC technology licensors. Although the mechanical configuration of individual FCC units may differ, their common objective is to upgrade low-value feedstock to the more valuable products used for transportation and petrochemical industries. Worldwide, about 45% of all gasoline comes from FCC and ancillary units such as the alkylation unit.

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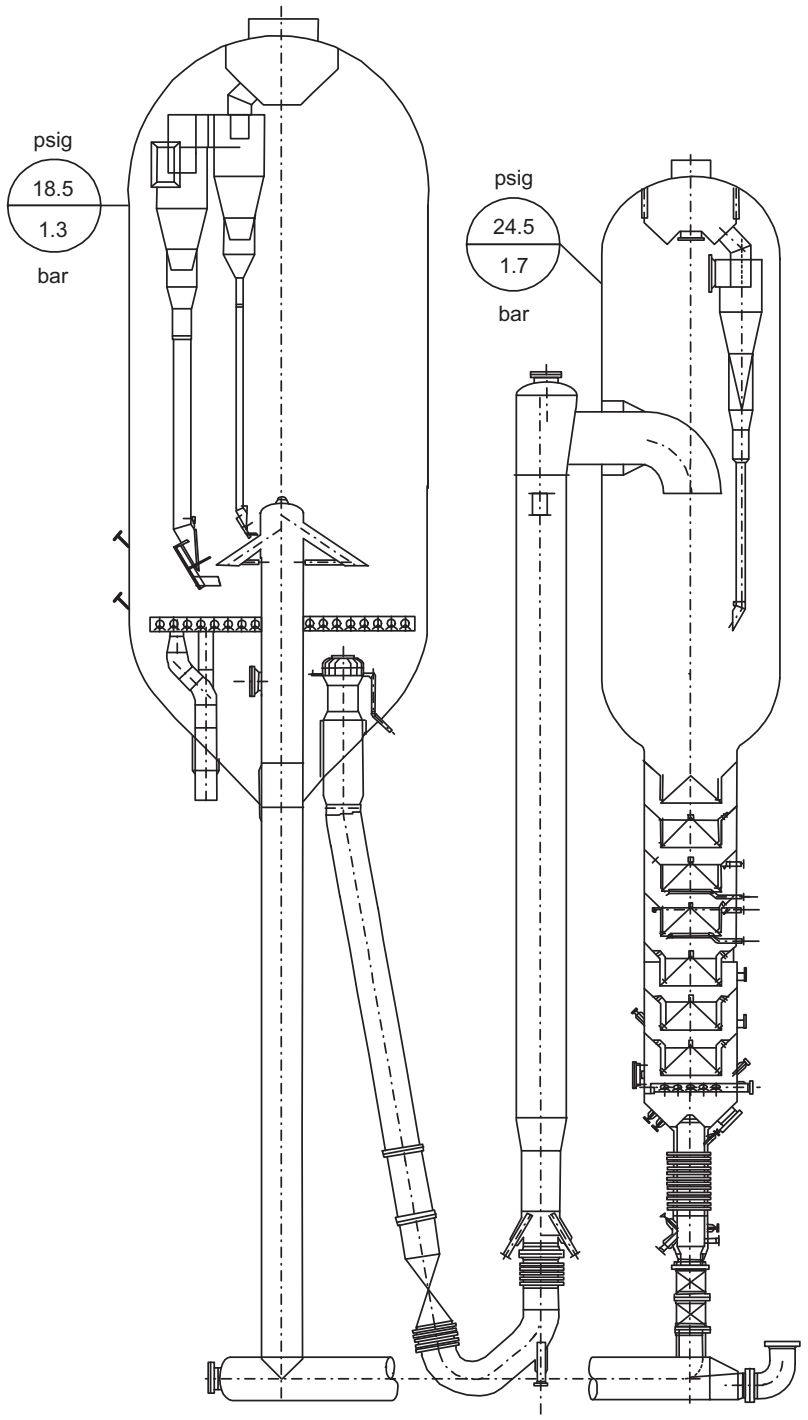


Figure 1.1: Example of a Model II cat cracker with enhanced RMS design internals.

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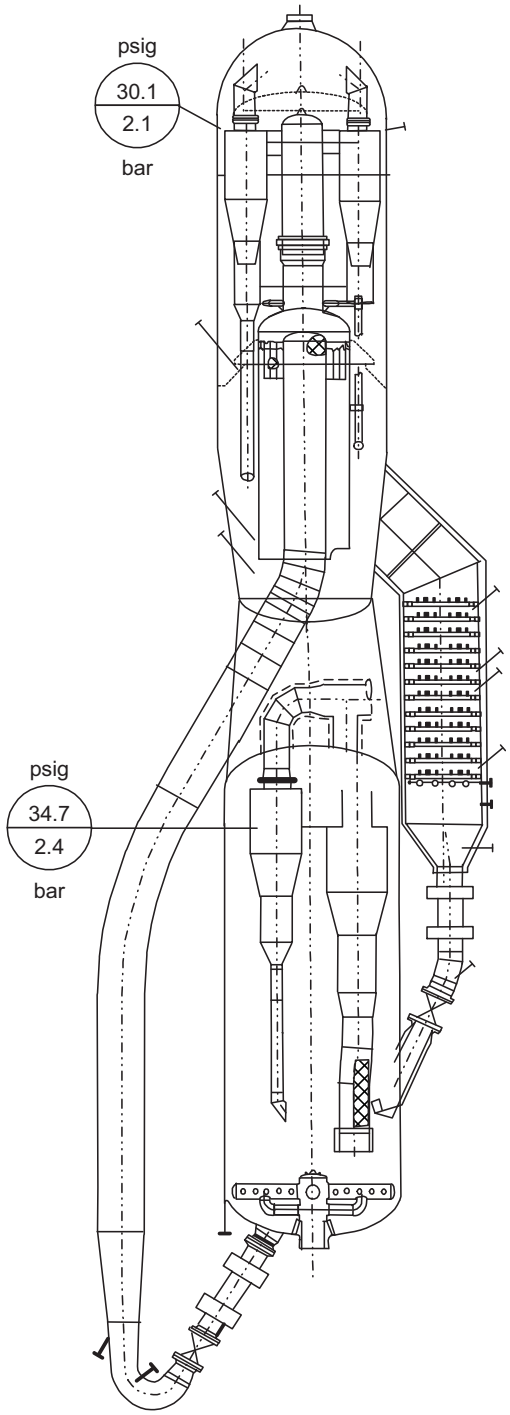


Figure 1.2: Example of a UOP stack design FCC unit.

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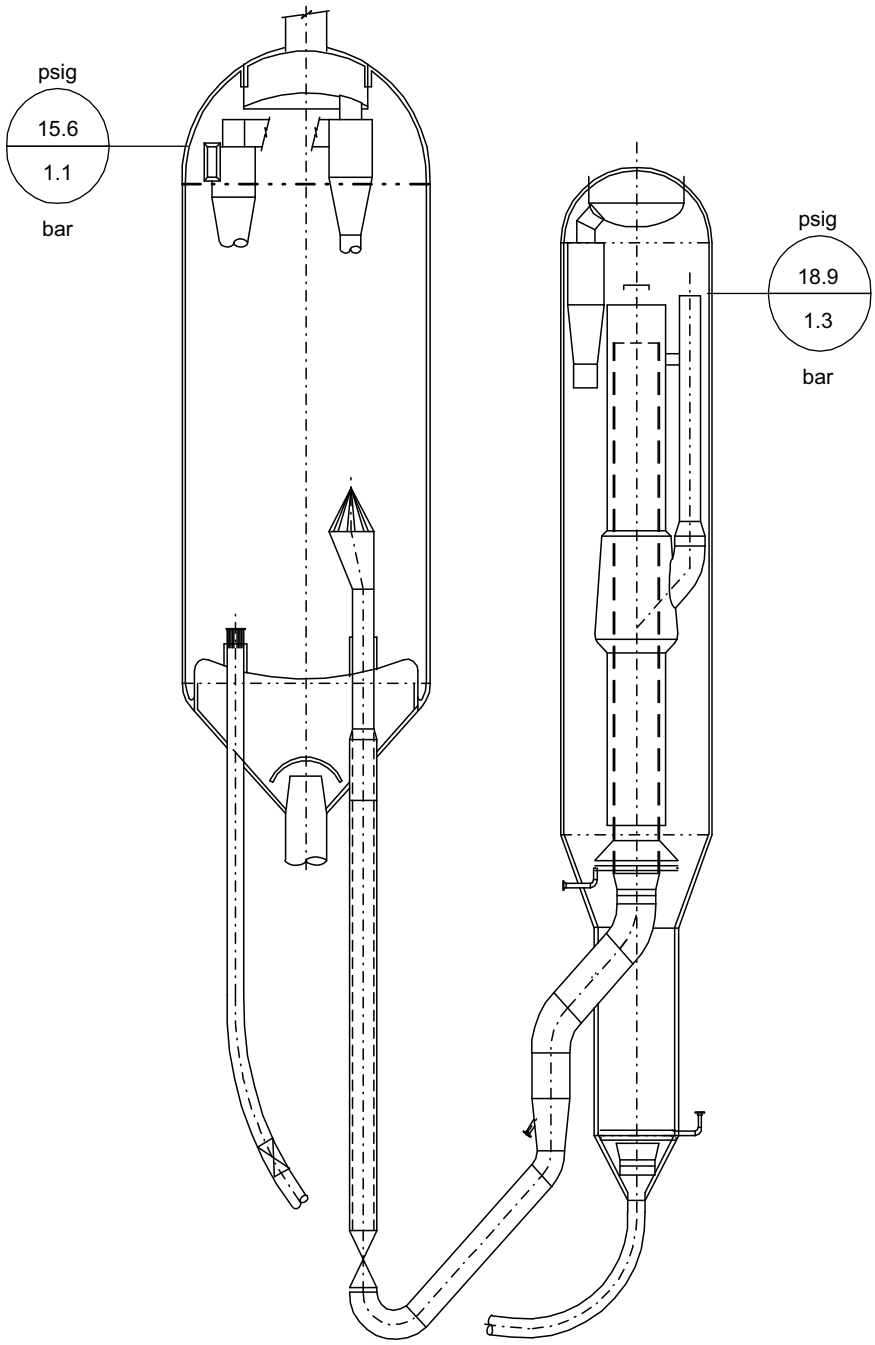


Figure 1.3: Example of a Model IV design FCC unit.

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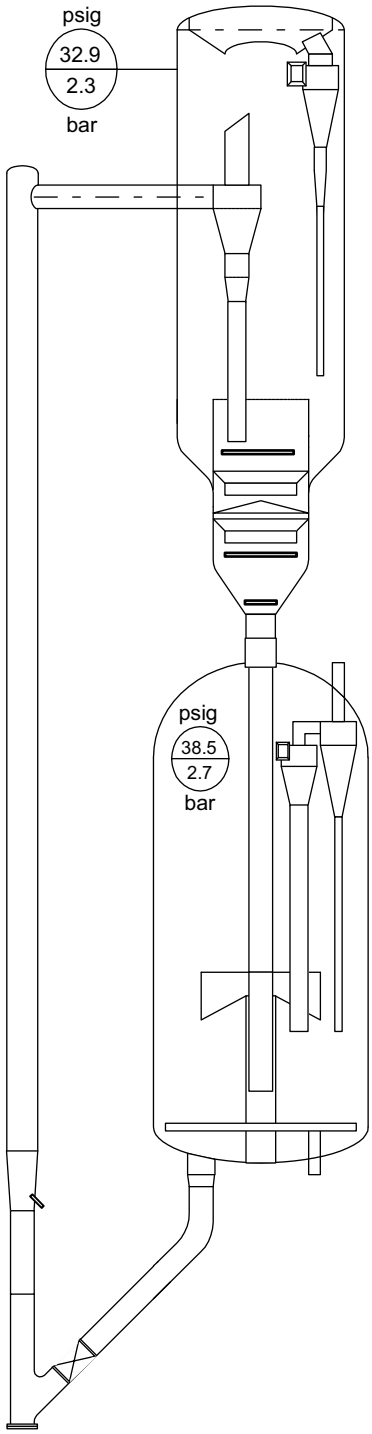


Figure 1.4: Example of KBR Orthoflow design FCC unit.

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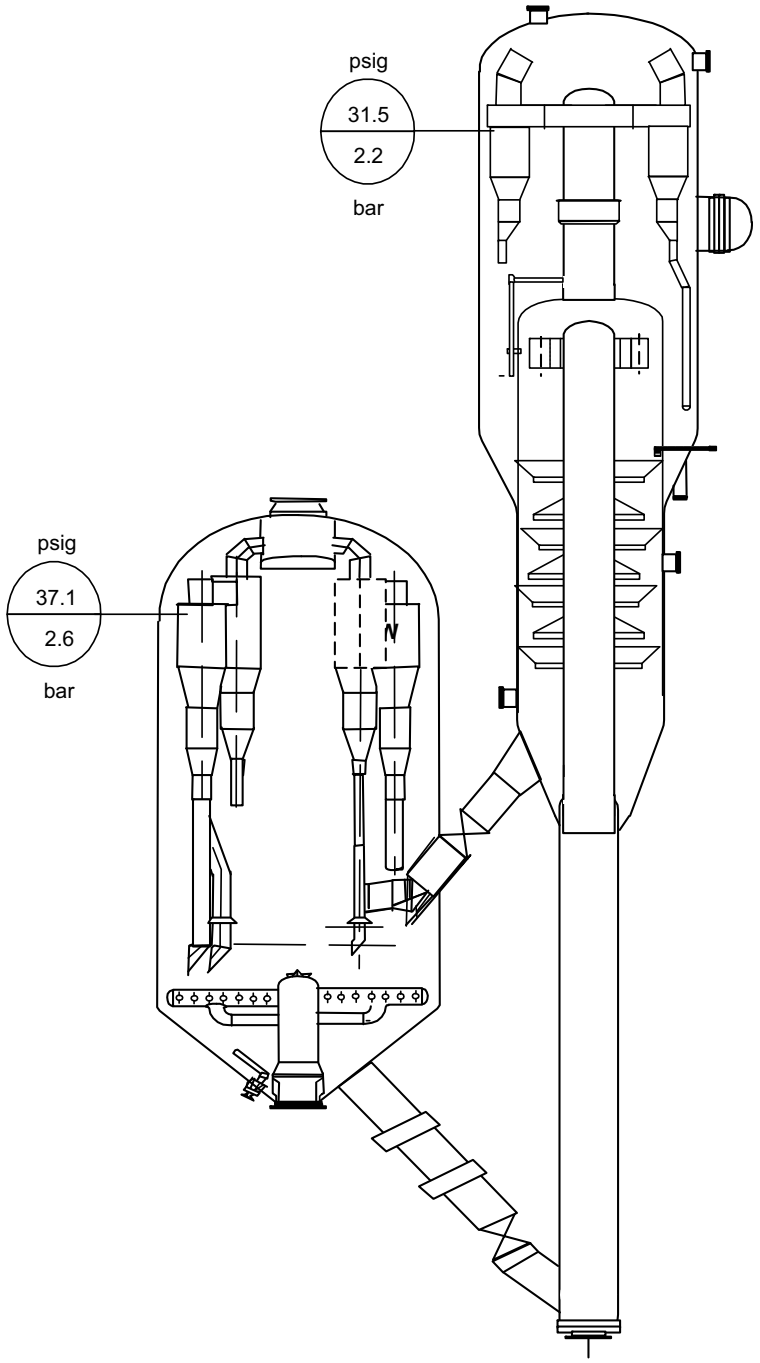


Figure 1.5: Example of a side-by-side design FCC unit.

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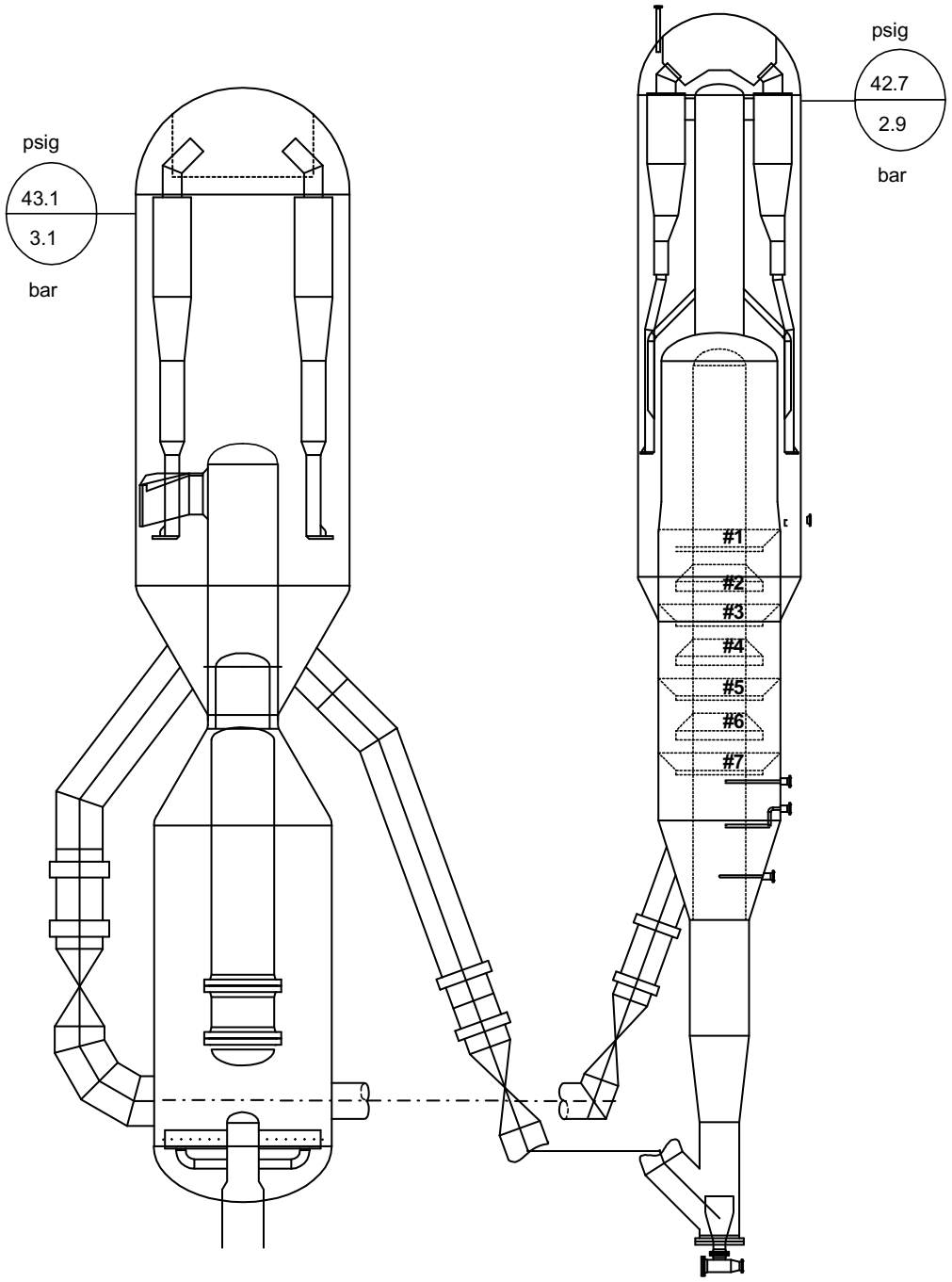


Figure 1.6: Example of a UOP high-efficiency design FCC unit.

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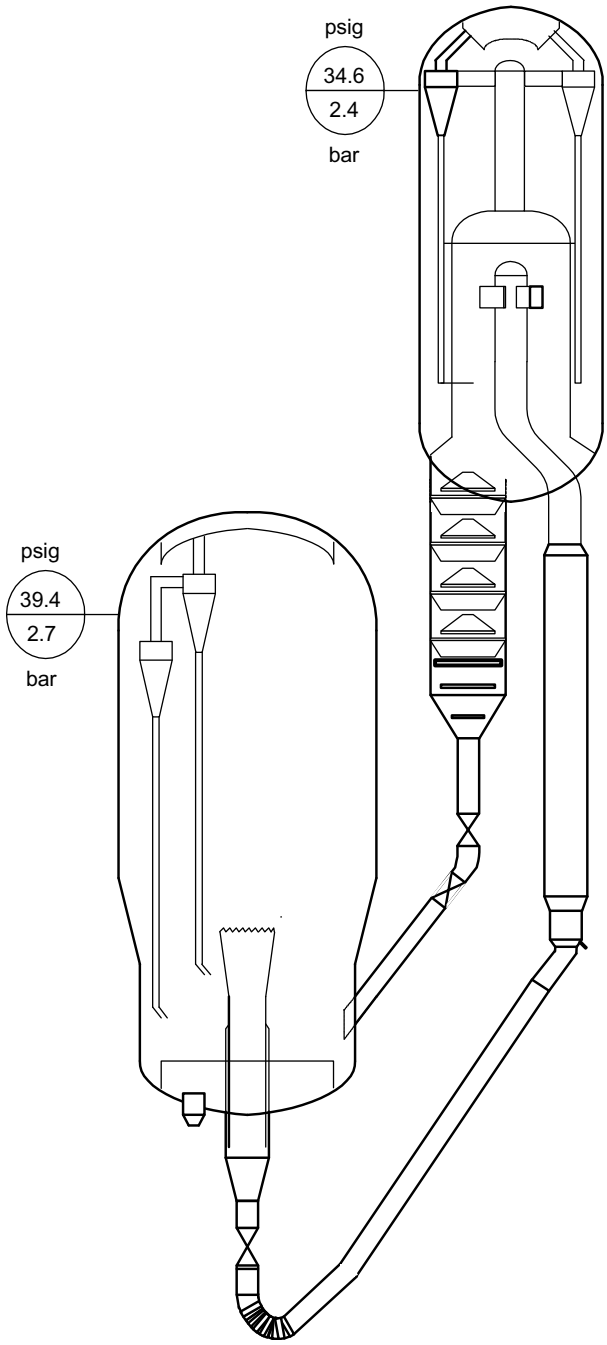


Figure 1.7: Example of a Flexicracker.

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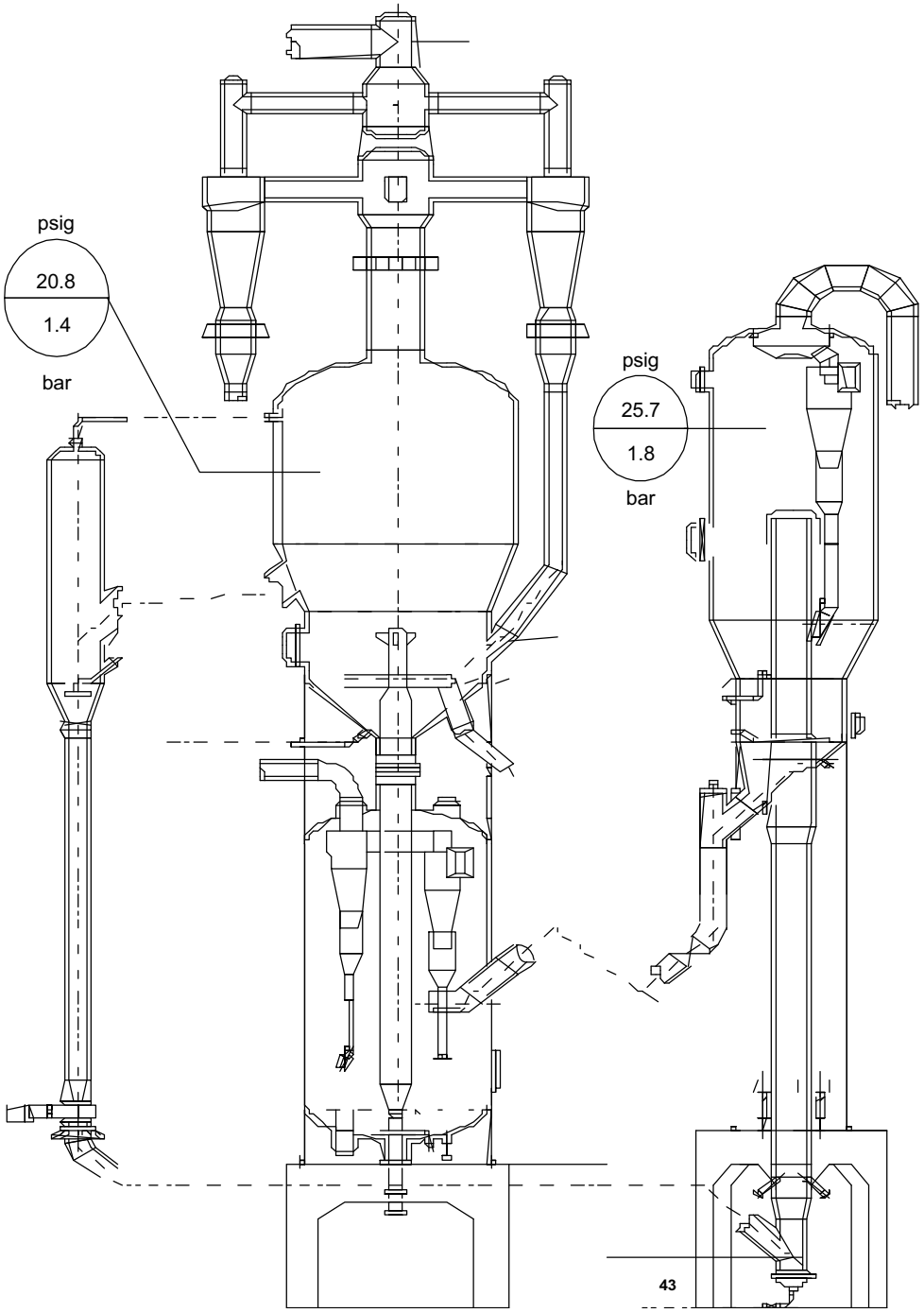


Figure 1.8: Example of The Shaw Group Inc. design FCC unit.

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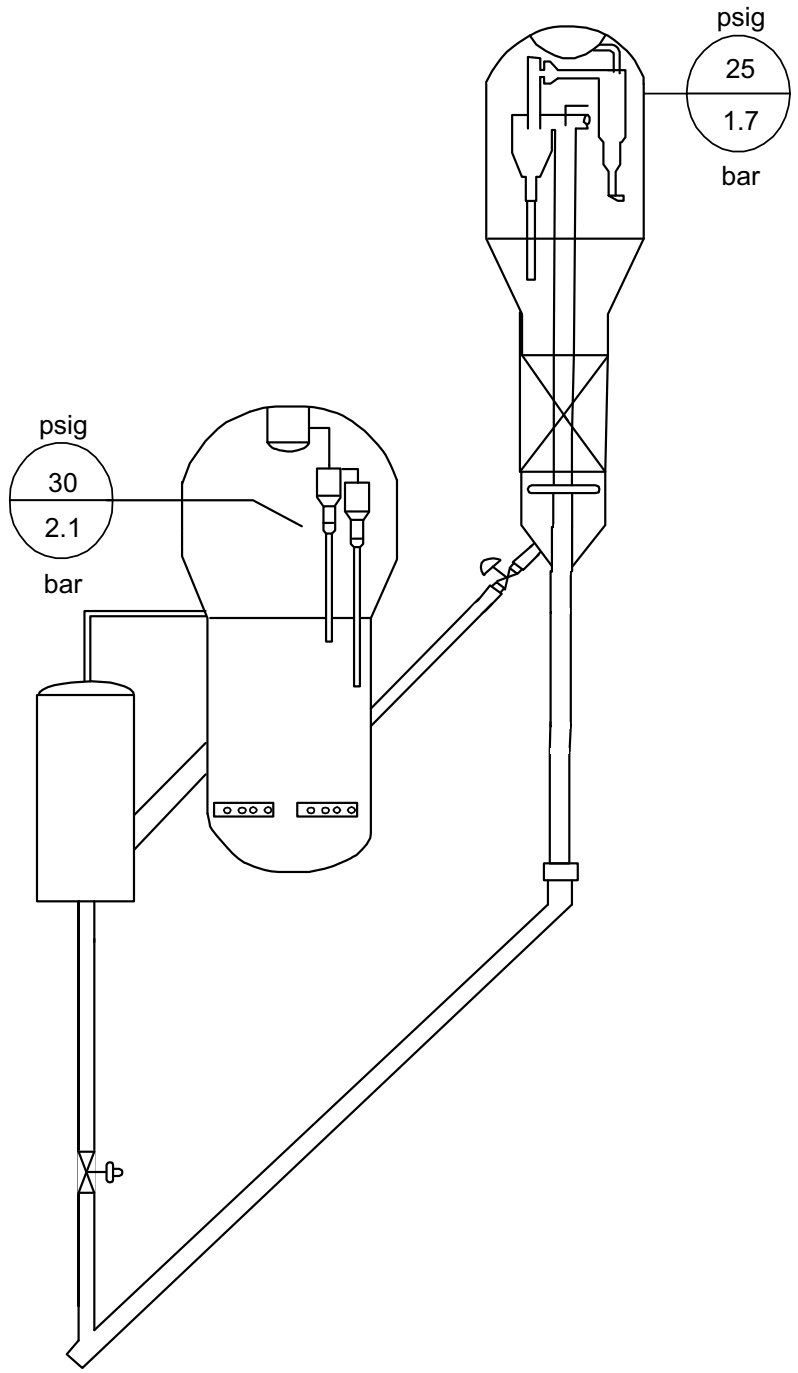


Figure 1.9: Example of Lummus Technology Inc. FCC unit.

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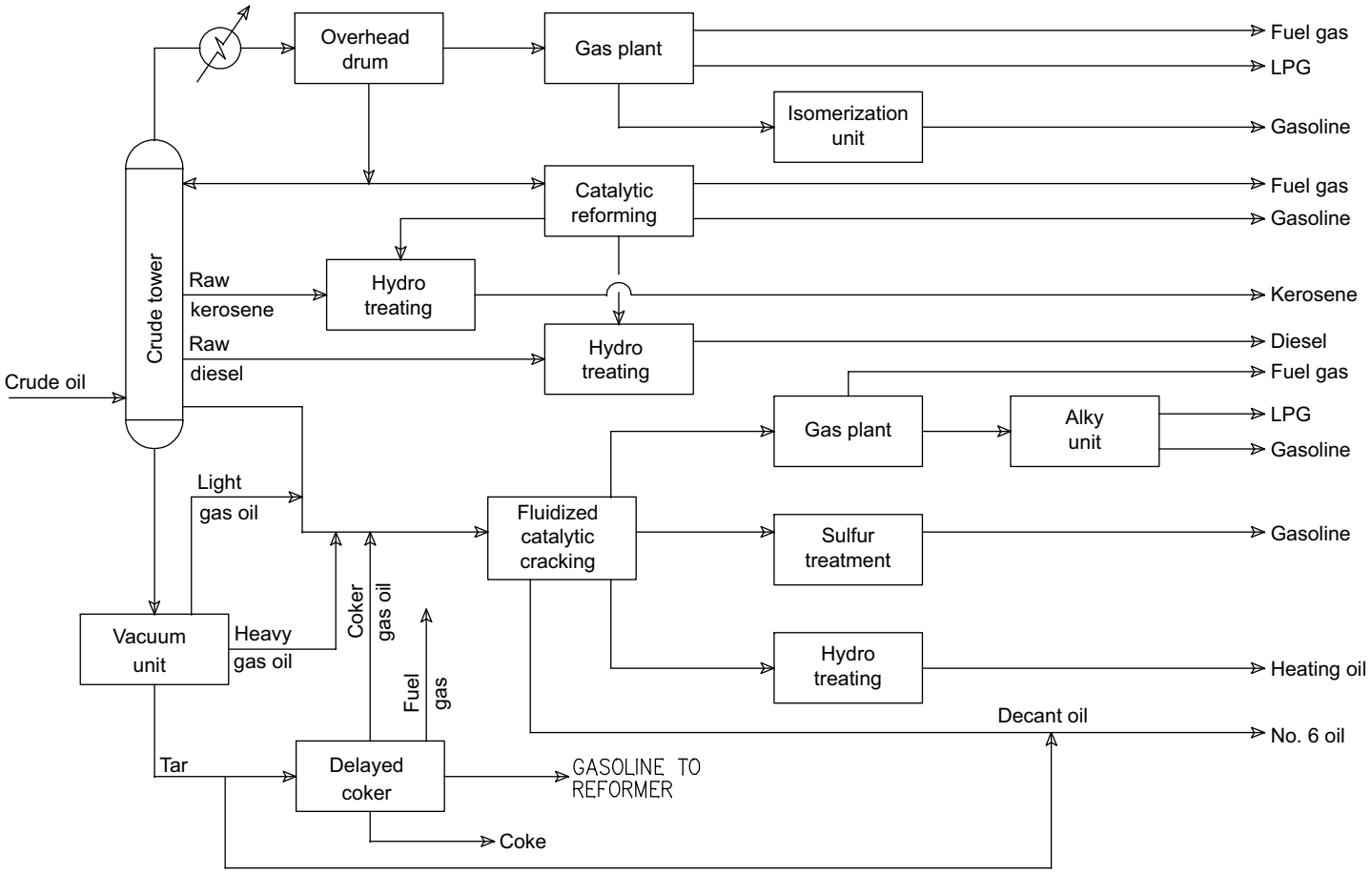


Figure 1.10: A typical high-conversion refinery.

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Before proceeding, it is helpful to understand how a typical cat cracker fits into the refining process. A petroleum refinery is composed of several processing units which convert the raw crude oil into usable products such as gasoline, diesel, jet fuel, and heating oil (Figure 1.10).

The crude unit is the first unit in this refining process. Here, the raw crude is distilled into several intermediate products: naphtha, kerosene, diesel, and gas oil. The heaviest portion of the crude oil, which cannot be distilled in the atmospheric tower, is heated and sent to the vacuum tower where it is split into gas oil and residue. The vacuum tower bottoms (residue) can be sent to be processed further in units such as the delayed coker, deasphalting unit, visbreaker, or residue cracker, or is sold as fuel oil or road asphalt.

The gas oil feed for the conventional cat cracker comes primarily from the atmospheric column, the vacuum tower, and the delayed coker. In addition, a number of refiners blend some atmospheric or vacuum resid into their feedstocks to be processed in the FCC unit. The charge to the FCC unit can be fully hydrotreated, partially hydrotreated, or totally unhydrotreated.

The FCC process is very complex. For clarity, the process description has been broken down into the following separate sections:

- Feed preheat
- Feed nozzles—riser
- Catalyst separation
- Stripping section
- Regenerator—heat/catalyst recovery
- Partial versus complete combustion
- Regenerated catalyst standpipe/slide valve
- Flue gas heat and pressure recovery schemes
- Catalyst handling facilities
- Main fractionator
- Gas plant
- Treating facilities.

Feed Preheat

Most refineries produce sufficient gas oil to meet the cat crackers' demand. However, for those refineries in which the gas oil produced does not meet the cat cracker capacity, it may be economical to supplement feed by purchasing FCC feedstocks or blending some residue. The refinery-produced gas oil and any supplemental FCC feedstocks are generally combined and sent to a surge drum that provides a steady flow of feed to the charge pumps. This drum can also separate any water or vapor that may be in the feedstocks.

In most FCC units, the gas oil feed from storage and/or from other units is preheated prior to reaching the riser. The source of this preheat is often main fractionator pumparound streams, main fractionator products, and/or a dedicated gas-fired furnace (Figure 1.11).

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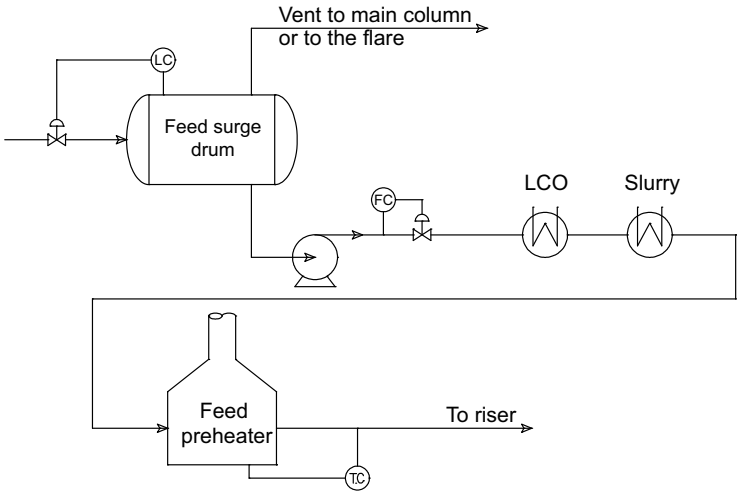


Figure 1.11: Typical feed preheat system (*FC = flow control, LC = level control, TC = temperature control, LCO = light cycle oil*).

Typical feed preheat temperature is in the range of 400−750°F (205−400°C). The feed is first routed through heat exchangers using hot streams from the main fractionator. The main fractionator top pumparound, light cycle oil (LCO) product, and bottoms pumparound are commonly used (Figure 1.11). Removing heat from the main fractionator is at least as important as preheating the gas oil feed.

The majority of FCC units use fired heaters to maximize the FCC feed preheat temperature. The gas-fired feed preheater provides several operating advantages. For example, in units where the air blower capacity and/or catalyst circulation is constrained, increasing the preheat temperature allows increased throughput. Additionally, for units in which deep hydrotreated feed is processed, the ability to increase the feed preheat temperature is an excellent option to control the regenerator bed temperature. The effects of feed preheat are discussed in Chapter 8.

Feed Nozzles—Riser

The reactor−regenerator is the heart of the FCC process. In today's cat cracking, the riser is the reactor (see Figure 1.12 for a typical riser Wye feed section).

Efficient contacting of the feed and regenerated catalyst is critical for achieving the desired cracking reactions. Feed nozzle(s) are used to atomize the feed with the help of dispersion or atomizing steam. Smaller oil droplets increase the availability of feed at the reactive acid sites on the catalyst. With high-activity zeolite catalyst, virtually all of the cracking reactions take place in 3 seconds or less.

In most FCC units, the feed nozzles are an "elevated" type, in which they are located about 15−40 ft (5−12 m) above the base of the riser. Depending on the FCC feed rate and riser diameter, the number of feed nozzles can range from 1 to 15.

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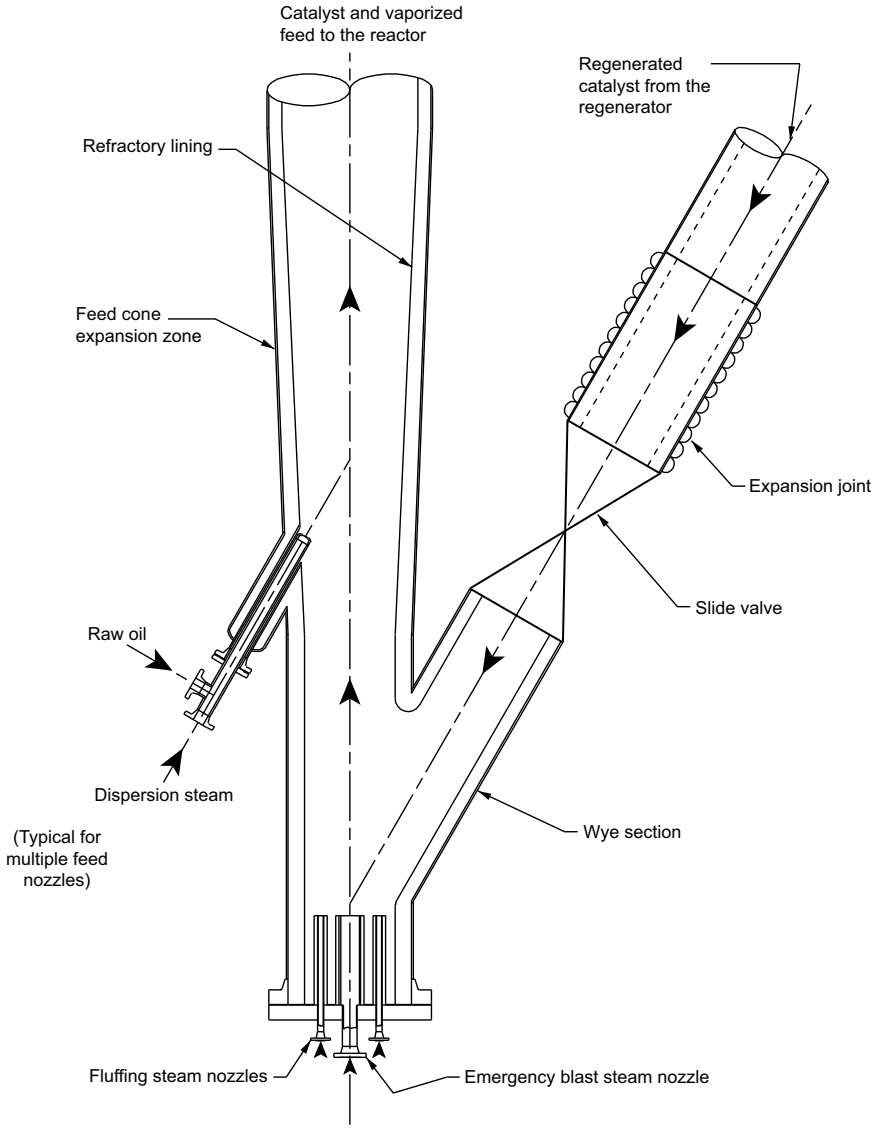


Figure 1.12: Typical riser Wye feed section.

The cracking reactions ideally occur in the vapor phase. Cracking reactions begin as soon as the feed is vaporized by the hot regenerated catalyst. The expanding volume of the vapors is the main driving force that is used to carry the catalyst up the riser.

The hot regenerated catalyst will not only provide the necessary heat to vaporize the gas oil feed and bring its temperature to the desired cracking temperature, but also compensate for the "internal cooling" that takes place in the riser due to endothermic heat of reaction.

Depending on the feed preheat, regenerator bed, and riser outlet temperatures, the ratio of catalyst to oil is normally in the range of 4:1 to 10:1 by weight. The typical regenerated

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catalyst temperature ranges between 1,250°F and 1,350°F (677−732°C). The cracking or reactor temperature is often in the range of 925−1,050°F (496−565°C).

The riser is often a vertical pipe. Typical risers are 2 to 7 feet (61 to 213 cm) in diameter and 75 to 120 feet (23 to 37 meters) long. The ideal riser simulates a plug flow reactor, where catalyst and vapor travel the length of the riser, with minimum back mixing.

Some risers are fully external, in which they are mostly cold-wall design with 4- to 5-in. (10−13 cm) thick internal refractory lining, for insulation and abrasion resistance. The section of the riser that is internal to the reactor vessel is of a hot-wall design, often having 1-in. (2.5 cm) thick internal refractory lining. The material of construction for the cold-wall riser is carbon steel and low chrome alloy for the hot-wall design.

Risers are normally designed for an outlet vapor velocity of 40−60 ft/s (12−18 m/s). The average hydrocarbon and catalyst residence times are about 2 and 3 s, respectively (based on riser outlet conditions). As a consequence of the cracking reactions, a hydrogen-deficient material called "coke" is deposited on the catalyst, reducing catalyst activity.

Catalyst Separation

After exiting the riser, catalyst enters the reactor vessel. In today's FCC operations, the reactor vessel serves as housing for the cyclones and/or a disengaging device for catalyst separation. In the early application of FCC, the reactor vessel provided further bed cracking, as well as being a device used for additional catalyst separation.

Nearly every FCC unit employs some type of inertial separation device connected on the end of the riser to separate the bulk of the catalyst from the vapors. A number of units use a deflector device to turn the catalyst direction downward. On some units, the riser is directly attached to a set of cyclones. The term "rough cut" cyclones generally refers to this type of arrangement. These schemes separate ~75−99.9% of the catalyst from product vapors.

Most FCC units employ either single- or two-stage cyclones (Figure 1.13) to separate the remaining catalyst particles from the cracked vapors. The cyclones collect and return the catalyst to the catalyst stripper via the diplegs and flapper/trickle valves (Figures 1.14A and 1.14B). The product vapors exit the upper cyclones and flow to the main fractionator tower. The efficiency of a typical riser termination device and upper cyclone system is often 99.999+%.

It is important to separate catalyst and vapors as soon as they enter the reactor, especially if the cracking temperature is >950°F (510°C). If not, the extended contact time of the vapors with the catalyst in the reactor housing will allow for nonselective catalytic recracking of some of the desirable products. The extended residence time also promotes thermal cracking of the desirable products. These recracking reactions can be extensive if the reactor temperature is more than 950°F (510°C). Most refiners have modified their riser termination devices to minimize these reactions.

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Figure 1.13: A typical two-stage cyclone system.

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Counterweighted flapper valve



Secondary cyclone trickle valve

Figure 1.14A: Photos of a typical counterweighted flapper valve, and a secondary cyclone trickle valve.

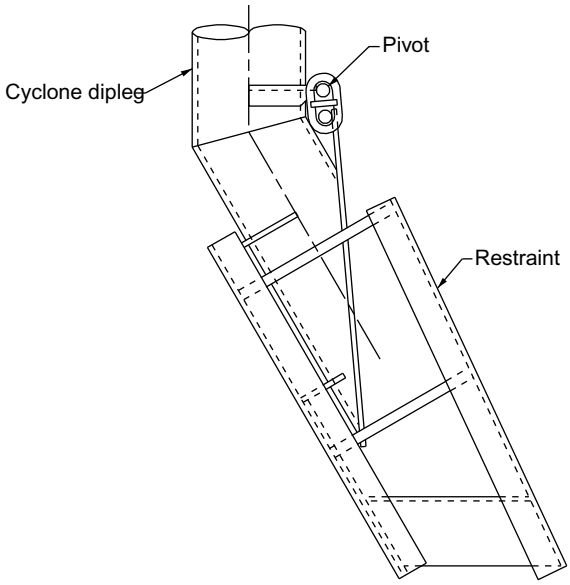


Figure 1.14B: Typical trickle valve drawing.

Stripping Section

The "spent catalyst" entering the catalyst stripper has hydrocarbons that are adsorbed on the surface of the catalyst; there are hydrocarbon vapors that fill the catalyst's pores, and hydrocarbon vapors that are entrained with the catalyst. Stripping steam is used primarily to remove the entrained hydrocarbons between individual catalyst particles. The stripping steam does not often address hydrocarbon desorption or the hydrocarbons that have filled the catalyst's pores. However, cracking reactions do continue to occur within the stripper. These reactions are driven by the reactor temperature and the catalyst residence time in the stripper. The higher temperature and longer residence time allow conversion of adsorbed hydrocarbons into "clean lighter" products. Shed trays, disk/donut baffles, and structural packing are the most common devices in commercial use for providing contact between down-flowing catalyst and upflowing steam (for stripper example, see Figure 1.15).

An efficient catalyst stripper design provides the intimate contact between the catalyst and steam. Reactor strippers are commonly designed for a steam superficial velocity of about 0.75 ft/s (0.23 m/s) and a catalyst mass flux rate at approximately 700 lb/min/ft^2 (3,418 kg/min/m^2). At too high a flux rate, the falling catalyst tends to entrain steam, thus reducing the effectiveness of stripping steam. A typical stripping steam rate is in the range of 2−5 lb of steam per 1,000 lb (2−5 kg per 1,000 kg) of circulating catalyst.

It is important to minimize the amount of hydrocarbon vapors carried over to the regenerator, but not all the hydrocarbon vapors can be displaced from the catalyst pores in the stripper. A fraction of them are carried with the spent catalyst into the regenerator.

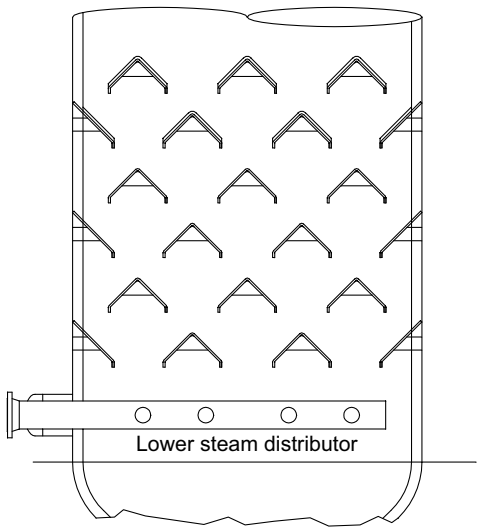


Figure 1.15: An example of a catalyst stripper.

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These hydrocarbon vapors/liquid have a higher hydrogen to carbon ratio than the "hard" coke on the catalyst. The drawbacks of allowing these hydrogen-rich hydrocarbons to enter the regenerator are as follows:

- *Loss of liquid product*: Instead of the hydrocarbons burning in the regenerator, they could be recovered as liquid products.
- *Loss of throughput*: The combustion of hydrogen to water produces 3.7 times more heat than the combustion of carbon to carbon dioxide. The increase in the regenerator temperature caused by excess hydrocarbons could exceed the temperature limit of the regenerator internals and force the unit to reduce the feed rate.
- *Loss of catalyst activity*: The higher regenerator temperature combined with the presence of steam in the regenerator reduces catalyst activity via destroying the catalyst's crystalline structure.

The flow of spent catalyst to the regenerator is often regulated by either a slide or plug valve (Figure 1.16A). The slide or plug valve maintains a desired level of catalyst in the stripper. In all FCC units, an adequate catalyst level must be maintained in the stripper to prevent reversal of hot flue gas into the reactor.

In most FCC units, the spent catalyst gravitates to the regenerator. In others, lift or carrier air is used to transport the catalyst into the regenerator. The uniform distribution of the spent catalyst is extremely critical to achieve efficient combustion that minimizes any afterburning and NO_x emissions. Figure 1.16B shows an example of a properly designed spent catalyst distribution system, and Figure 1.16C shows an example of the spent catalyst entering the regenerator through the sidewall using a ski-jump distributor, which unfortunately does not provide uniform catalyst distribution.



Example of a slide valve



Example of a plug valve

Figure 1.16A: Example of a typical slide valve and a typical plug valve.

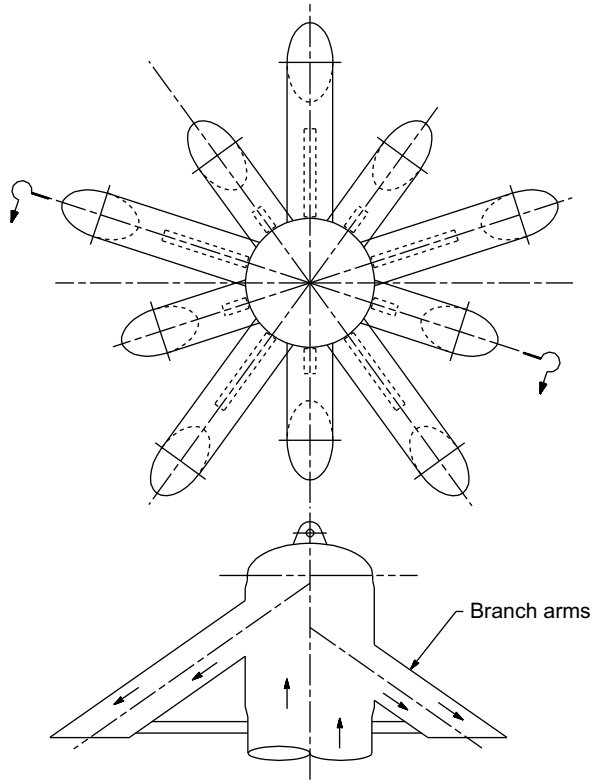


Figure 1.16B: Example of a spent catalyst distribution system (courtesy of RMS Engineering, Inc.).

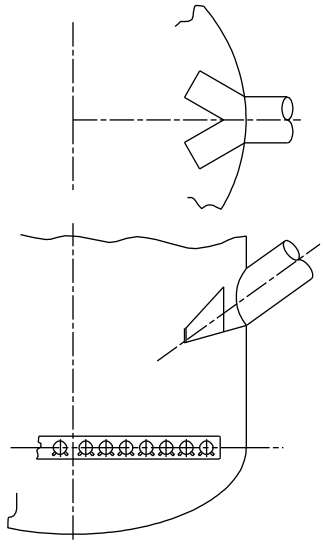


Figure 1.16C: Example of a hockey stick style catalyst distributor.

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Regenerator—Heat/Catalyst Recovery

The regenerator has three main functions:

1. It restores catalyst activity.
2. It supplies heat for cracking reactions.
3. It delivers fluidized catalyst to the feed nozzles.

The spent catalyst entering the regenerator usually contains between 0.5 and 1.5 wt% coke. Components of coke are carbon, hydrogen, and trace amounts of sulfur and organic nitrogen molecules. These components burn according to the reactions given in Table 1.2.

Air provides oxygen for the combustion of this coke and is supplied by one or more air blowers. The air blower provides sufficient air velocity and pressure to maintain the catalyst bed in a fluidized state. In some FCC units, purchased oxygen is used to supplement the combustion air. The air/oxygen enters the regenerator through an air distribution system (Figure 1.17) located near the bottom of the regenerator vessel. The design of the air distributor is important in achieving efficient and reliable catalyst regeneration. Air distributors are often designed for a 1.0- to 2.0-psi (7−15 kPa) pressure drop to ensure positive air flow through all nozzles.

Table 1.2: Heat of Combustion.

			kcal/kg of C, H_2, or S	BTU/lb of C, H_2, or S	
$C + 1/2O_2$	→	CO	2,200	3,968	(1.1)
$CO + 1/2O_2$	→	CO_2	5,600	10,100	(1.2)
$C + O_2$	→	CO_2	7,820	14,100	(1.3)
$H_2 + 1/2O_2$	→	H_2O	28,900	52,125	(1.4)
$S + xO$	→	SO_x	2,209	3,983	(1.5)
$N + xO$	→	NO_x			(1.6)



Figure 1.17: Examples of air distributor designs (*courtesy of RMS Engineering Inc.*).

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In traditional bubbling bed regenerators, there are two regions: the *dense phase* and the *dilute phase*. At velocities common in these regenerators, 2−4 ft/s (0.6−1.2 m/s), the bulk of catalyst particles are in the dense bed, immediately above the air distributor. The dilute phase is the region above the dense phase up to the cyclone inlet and has a substantially lower catalyst concentration.

Partial Versus Complete Combustion

Catalyst can be regenerated over a range of temperatures and flue gas composition with inherent limitations. Two distinctly different modes of regeneration are practiced: *partial combustion* and *complete combustion.* Complete combustion generates more energy and the coke yield is decreased; partial combustion generates less energy and the coke yield is increased. In complete combustion, the excess reaction component is oxygen, so more carbon generates more combustion. In partial combustion, the excess reaction component is carbon, all the oxygen is consumed, and an increase in coke yield means a shift from CO_2 to CO.

FCC regeneration can be further subdivided into low-, intermediate-, and high-temperature regeneration. In low-temperature regeneration (about 1,190°F or 640°C), complete combustion is impossible. One of the characteristics of low-temperature regeneration is that at 1,190°F, all three components (O_2, CO, and CO_2) are present in the flue gas at significant levels. Low-temperature regeneration was the mode of operation that was used in the early implementation of the catalytic cracking process.

In the early 1970s, high-temperature regeneration was developed. High-temperature regeneration meant increasing the temperature until all the oxygen was burned. The main result was low carbon on the regenerated catalyst. This mode of regeneration required maintaining, in the flue gas, either a small amount of excess oxygen and no CO or no excess oxygen and a variable quantity of CO. If there was excess oxygen, the operation was in full burn. If there was excess CO, the operation was in partial burn.

With a properly designed air/spent catalyst distribution system and potential use of CO combustion promoter, the regeneration temperature could be reduced and still maintain full burn mode of catalyst regeneration.

Table 1.3 contains a matrix summarizing various aspects of catalyst regeneration. Regeneration is either partial or complete at low, intermediate, or high temperatures. At low temperatures, regeneration is always partial, carbon on regenerated catalyst is high, and increasing combustion air results in afterburn. At intermediate temperatures, carbon on regenerated catalyst is reduced. The three normal “operating regions” are indicated in Table 1.3.

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Table 1.3: A Matrix of Regeneration Characteristics.

Operating Region Regenerator Combustion	Partial Combustion Mode	Full Combustion Mode
Low temperature (nominally 1,190°F/640°C)	Stable (small afterburning); O_2, CO, and CO_2 in the flue gas	Not achievable
Intermediate temperature (nominally 1,275°F/690°C)	Stable (with combustion promoter), tends to have high carbon on regenerated catalyst	Stable with combustion promoter
High temperature (nominally 1,350°F/730°C)	Stable operation	Stable operation

There are some advantages and disadvantages associated with full as compared with partial combustion:

- Advantages of full combustion:
  - Energy efficient
  - Heat balances at low coke yield
  - Minimum hardware (no CO boiler)
  - Better yields from clean catalyst
  - Environmentally friendlier
- Disadvantages of full combustion:
  - Narrow range of coke yields, unless a heat removal system is incorporated
  - Greater afterburn, particularly with an uneven air or spent catalyst distribution system
  - Low catalyst/oil ratio.

The choice of partial versus full combustion is dictated by FCC feed quality. With "clean feed," full combustion is the choice. With low-quality feed or resid, partial combustion, possibly with heat removal, is the choice.

Regenerated Catalyst Standpipe/Slide Valve

During regeneration, the coke level on the catalyst is typically reduced to $<0.10\%$. From the regenerator, the catalyst flows down a transfer line, commonly referred to as a standpipe. The standpipe provides the necessary pressure head to circulate the catalyst around the unit. Some standpipes are short and some are long. Some standpipes extend into the regenerator and employ an internal cone, and the top section is often called a *catalyst hopper*. In some units, regenerated catalyst is fed into an external withdrawal well hopper.

Standpipes are typically sized for a catalyst flux rate in the range of 150−300 lb/s/ft^2 (750−1,500 kg/s/m^2) of circulating catalyst. In most short standpipes, sufficient flue gas is carried down with the regenerated catalyst to keep it fluidized. However, longer standpipes

will require external aeration to ensure that the catalyst remains fluidized. A gas medium, such as air, steam, or nitrogen, is injected at intervals along the length of the standpipe to achieve this. The catalyst flowing density in a well-designed standpipe is in the range of 35−45 lb/ft^3 (560−720 kg/m^3).

The flow rate of the regenerated catalyst to the riser is commonly regulated by either a slide or a plug valve. The operation of a slide valve is similar to that of a variable orifice. Slide valve operation is often controlled by the reactor temperature. Its main function is to supply enough catalyst to heat the feed and achieve the desired cracking temperature. In the ExxonMobil Model IV (see Figure 1.3) and Flexicracker designs (see Figure 1.7), the regenerated catalyst flow is controlled by adjusting the pressure differential between the reactor and regenerator.

Regenerator Catalyst Separation

As flue gas leaves the dense phase of the regenerator, it entrains catalyst particles. The amount of entrainment depends largely on the flue gas superficial velocity in the regenerator. The larger catalyst particles, 50−90 μm, fall back into the dense bed. The smaller particles, 0−50 μm, are suspended in the dilute phase and carried into the cyclones.

Most FCC unit regenerators employ 2−20 pairs of primary and secondary cyclones. These cyclones are designed to recover catalyst particles >15 μm diameter. The recovered catalyst particles are returned to the regenerator via the diplegs.

The distance above the catalyst bed at which the flue gas velocity has stabilized is referred to as the transport disengaging height (TDH). At this height, the catalyst concentration in the flue gas stays constant; none will fall back into the bed. The centerline of the first-stage cyclone inlets should be at TDH or higher; otherwise, excessive catalyst entrainment will cause extreme catalyst losses.

Flue Gas Heat and Pressure Recovery Schemes

The flue gas exits the cyclones to a plenum chamber in the top of the regenerator. The hot flue gas holds an appreciable amount of energy. Various heat recovery schemes are used to recover this energy. In some units, the flue gas is sent to a CO boiler where both the sensible and combustible heat is used to generate high-pressure steam. In other units, the flue gas is exchanged with boiler feed water to produce steam via the use of a shell/tube or box-type heat exchanger.

In most units without turbo expanders, the flue gas pressure is let down via a double-disk slide valve and an orifice chamber. Approximately one-third of the flue gas pressure is let down across the double-disk valve, with the remaining two-thirds via an orifice chamber. The orifice chamber is either a vertical or horizontal vessel containing a series of perforated plates, designed to maintain a reasonable pressure drop across the flue gas valve.

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In some medium-to-large FCC units, a turbo expander can be used to recover this pressure energy. Associated with this pressure recovery, there is also about a 200°F (93°C) drop in the flue gas temperature.

To protect the expander blades from being eroded by catalyst, flue gas is first sent to a third-stage separator to remove the catalyst fines. Depending on the design, the third-stage separator, which is external to the regenerator, can contain a large number of small cyclones, swirl tubes, or several large cyclones. The third-stage separators are designed to separate 70−95% of the incoming particles from the flue gas.

A power recovery train (Figure 1.18) employing a turbo expander usually consists of four parts: the expander, a motor/generator, an air blower, and a steam turbine. The steam turbine is primarily used for start-up and often to supplement the expander to generate electricity.

The motor/generator works as a speed controller and flywheel; it can produce or consume power. In some FCC units, the expander horsepower exceeds the power needed to drive the air blower and the excess power is output to the refinery electrical system. If the expander generates less power than what is required by the blower, the motor/generator provides the power to hold the power train at the desired speed.

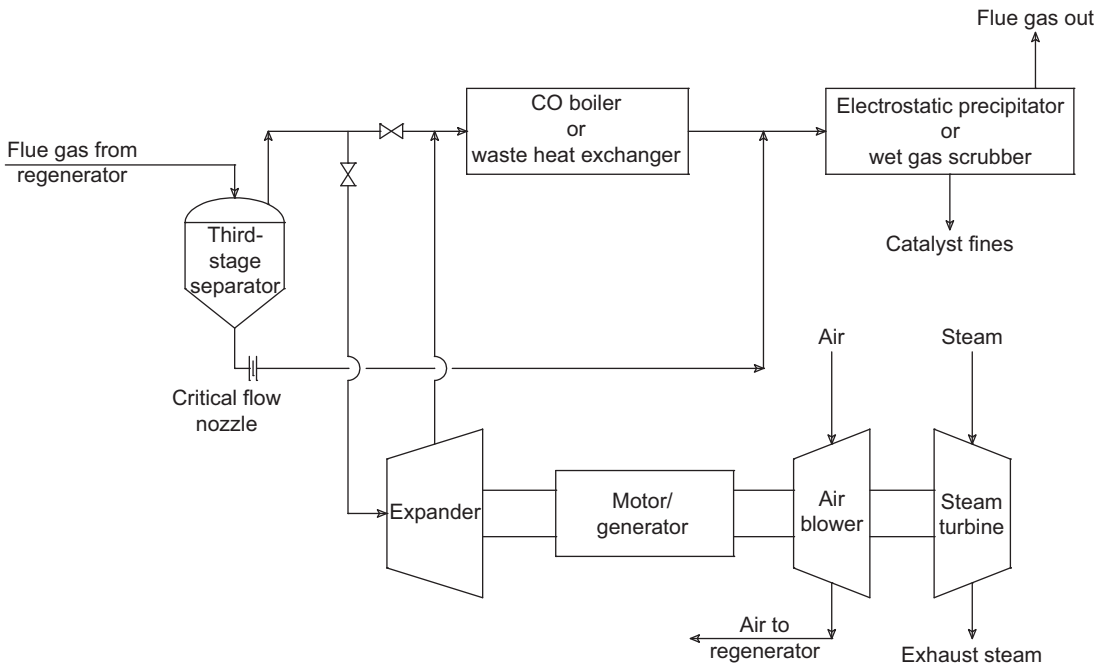


Figure 1.18: A typical flue gas power recovery scheme.

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From the expander, the flue gas goes through a steam generator to recover thermal energy. Depending on local environmental regulations, an electrostatic precipitator (ESP) or a wet gas scrubber may be placed downstream of the waste heat generator prior to release of the flue gas to the atmosphere. Some units use an ESP to remove catalyst fines in the range of 5−20 μm from the flue gas. Some units employ a wet gas scrubber to remove both catalyst fines and sulfur compounds from the flue gas stream.

Catalyst Handling Facilities

The activity of catalyst degrades with time. The loss of activity is primarily due to impurities in the FCC feed and from thermal and hydrothermal deactivation mechanisms that occur in the regenerator. To maintain the desired activity, fresh catalyst is continually added to the unit. Fresh catalyst is stored in a fresh catalyst hopper and, in most units, is added automatically to the regenerator via a catalyst loader.

The circulating catalyst in the FCC unit is often called equilibrium catalyst or simply E-cat. Periodically, quantities of equilibrium catalyst are withdrawn and stored in the E-cat hopper for future disposal. A refinery that processes residue feedstocks can also use good-quality E-cat from a refinery that processes light sweet feed. Residue feedstocks contain large quantities of impurities, such as metals, and require high rates of fresh catalyst to maintain the desired activity. The use of a good-quality E-cat, in conjunction with fresh catalyst, can be cost-effective in maintaining low catalyst costs.

Even with proper operation of the reactor and regenerator cyclones, catalyst particles smaller than 20 μm still escape from both of these vessels. In most FCC units, the catalyst fines from the reactor cyclones are sent with the slurry oil product into the storage tanks. Few units employ tertiary recovery devices (slurry settler, Gulftronics, Dorrclone, etc.), in which the recovered catalyst is recycled to the riser.

The residual catalyst fines from the regenerator flue gas are often removed through a flue gas scrubber, an ESP, or a properly designed third-/fourth-stage cyclone system.

Main Fractionator

The purpose of the main fractionator, or main column (Figure 1.19), is to desuperheat and recover liquid products from the reactor vapors. The hot vapors from the reactor flow into the main fractionator near the base. Fractionation is accomplished by condensing and revaporizing hydrocarbon components as the vapor flows upward through trays and/or packing in the tower.

The operation of the main column is similar to the crude tower, but with two differences. First, the reactor effluent vapors must be cooled before any fractionation begins. Second, large quantities of gases will go overhead with the unstabilized gasoline for further separation.

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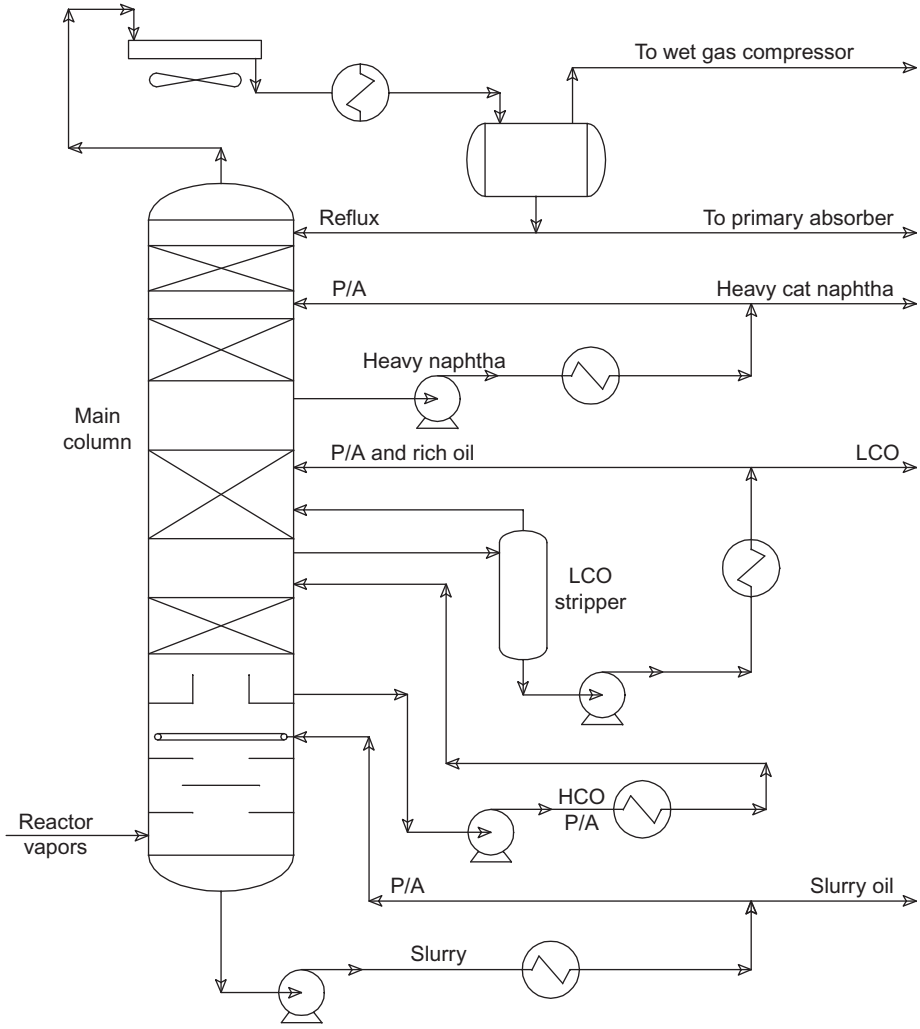


Figure 1.19: A typical FCC main fractionator circuit (*HCO = heavy cycle oil, P/A = pumparound*).

The bottom section of the main column provides a heat transfer zone. Shed decks, disk/donut trays, and grid packing are among some of the contacting devices used to promote vapor/liquid contact. The reactor vapor is desuperheated and cooled by several pumparound streams. The cooled pumparound also serves as a scrubbing medium to wash down catalyst fines entrained in the vapors.

Pool quench (see also Figure 13.12) can be used to maintain the fractionator bottoms temperature below the coking temperature, usually at about 680°F (360°C).

The recovered heat from the main column bottoms is commonly used to preheat the fresh feed, generate steam, serve as a heating medium for the gas plant reboilers, or some combination of these services.

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The heaviest bottoms product from the main column is commonly called slurry, clarified, or decant oil (DO) (in this book, these terms are used interchangeably). The slurry oil is often used as a "cutter stock" with vacuum bottoms to make No. 6 fuel oil. High-quality slurry oil (low sulfur, low metals, low ash) can be used for carbon black feedstocks.

Early FCC units had soft catalyst and inefficient cyclones, with substantial carryover of catalyst to the main column, where it was absorbed in the bottoms. Those FCC units controlled catalyst losses in two ways. First, they used high recycle rates to return slurry to the reactor. Second, the slurry product was routed through slurry settlers, either gravity or centrifugal, to remove catalyst fines. A slipstream of FCC feed was used as a carrier to return the collected fines from the separator to the riser. Since then, improvements in the physical properties of FCC catalyst and in the reactor cyclones have lowered catalyst carryover. Most units today operate without separators. The slurry oil is sent directly to the storage tank. Catalyst fines accumulate in the tank and are disposed of periodically. Some units continue to use some form of slurry settler to minimize the ash content of the slurry oil.

Above the bottoms product, the main column is often designed for three possible sidecuts:

1. Heavy cycle oil (HCO), used as a pumparound stream, sometimes as recycle to the riser, rarely as a product
2. LCO, used as a pumparound stream, sometimes as absorption oil in the gas plant, stripped as a product for diesel/heating oil blending
3. Heavy naphtha, used as a pumparound stream, sometimes as absorption oil in the gas plant, and possible blending in the gasoline pool.

In many units, the LCO is the only sidecut that leaves the unit as a product. LCO is withdrawn from the main column and routed to a side stripper for flash control. LCO is often treated for sulfur removal prior to being blended into the heating oil pool. In most units, a slipstream of LCO, either stripped or unstripped, is sent to the sponge oil absorber in the gas plant. In other units, sponge oil is the cooled heavy naphtha.

HCO, heavy naphtha, and other circulating side pumparound streams are used to remove heat from the fractionator. They supply reboil heat to the gas plant and generate steam. The amount of heat removed at any pumparound point is set to distribute vapor and liquid loads evenly throughout the column and to provide the necessary internal reflux.

Unstabilized gasoline and light gases pass up through the main column and leave as vapor. The overhead vapor is cooled and partially condensed in the fractionator overhead condensers. The stream flows to an overhead receiver, typically operating at $<$15 psig ($<$1 bar). Hydrocarbon vapor, hydrocarbon liquid, and water are separated in the overhead drum.

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The hydrocarbon vapors flow to the wet gas compressor (WGC). This gas stream contains not only ethane and lighter gases but also more than 95% of the C_3's/C_4's and about 10% of the naphtha. The phrase "wet gas" refers to condensable components of the gas stream.

The hydrocarbon liquid from the overhead receiver is split. Some is pumped back to the main column as reflux and some is pumped forward to the gas plant. Condensed water is also split. Some is pumped back as wash water to the overhead condensers and some is pumped away to treating. In some units, the sour water from the overhead receiver is also used as wash to the WGC discharge coolers.

Gas Plant

The FCC gas plant (Figure 1.20) separates the unstabilized gasoline and light gases into:

- Fuel gas
- C_3's and C_4's
- Gasoline.

C_3's and C_4's (or debutanizer overhead products) include propane, propylene, normal butane, isobutane, and butylenes. Most refiners either alkylate the C_3's/C_4's or use a depropanizer tower to split C_3's from C_4's and process C_4's stream into the alkylation unit. Most FCC gas plants also include treating facilities to remove sulfur from these products.

The gas plant starts at the WGC. A two-stage centrifugal compressor is often employed. This type of compressor generally incorporates an electric motor, or a multistage turbine, that is typically driven by high-pressure steam. The steam is often exhausted to a surface condenser operating under vacuum. It should be noted that there are FCC units in which single-stage WGCs are employed.

In most two-stage systems, the vapors from the compressor's first-stage discharge are partially condensed and flashed in an interstage drum. The liquid hydrocarbon is pumped forward to the gas plant, either to the high-pressure separator (HPS) or directly to the stripper.

The vapor from the interstage drum flows to the second-stage compressor. The second-stage compressor discharges through a cooler to the HPS. Gases and light streams from other refinery units are often included for recovery of liquefied petroleum gas (LPG). Recycle streams from the stripper and the primary absorber also go to the HPS. Wash water is injected to dilute contaminants, such as ammonium salts, that can cause equipment fouling. This mixture is partially condensed and flashed in the HPS.

The vapor from the HPS flows to the primary absorber and the liquid is pumped to the stripper. The HPS is essentially a separation stage with an external cooler located between the primary stripper and absorber. In some units, they are a single tower.

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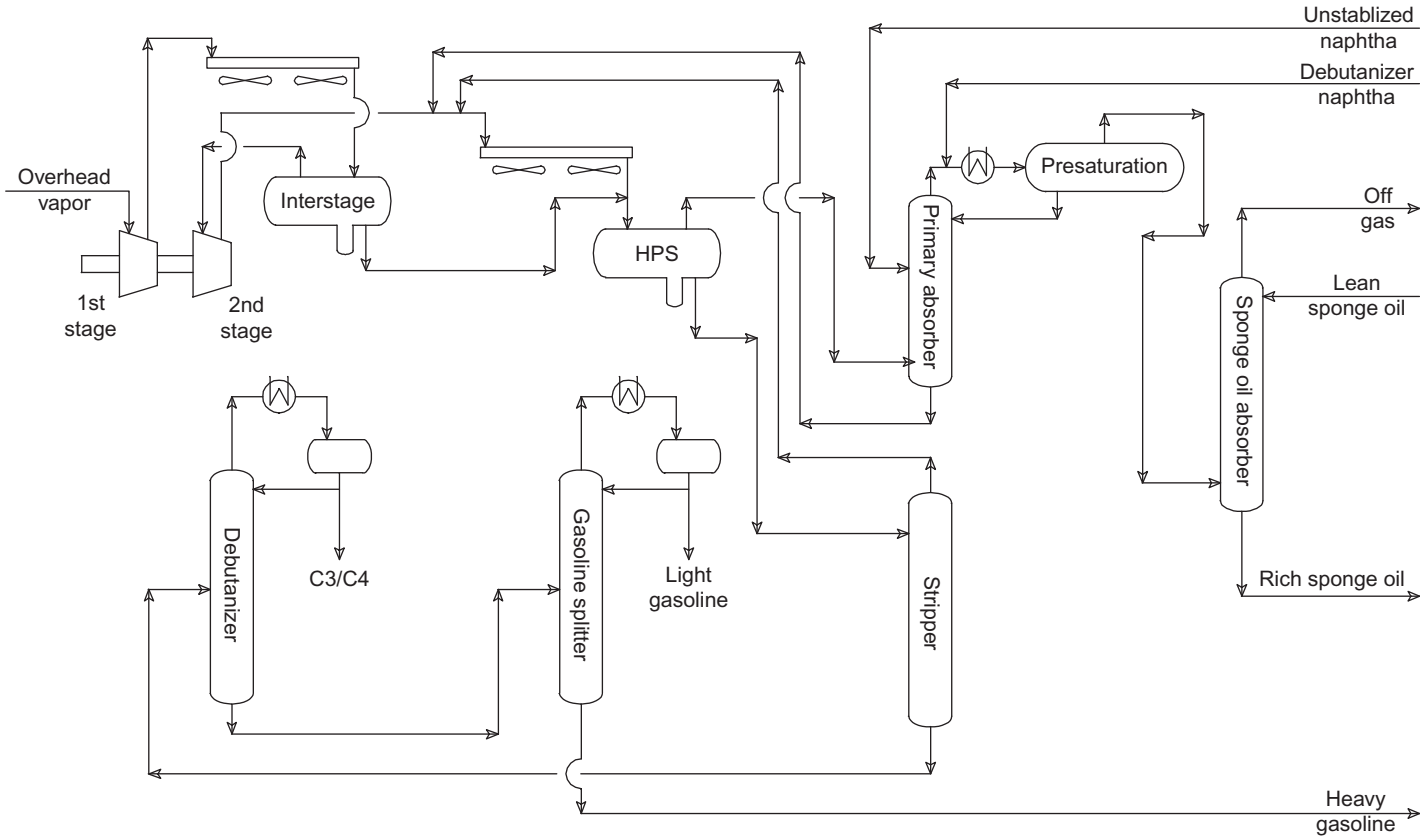


Figure 1.20: A typical FCC gas plant (*HPS = high-pressure separator*).

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Primary Absorber

The HPS overhead vapor contains appreciable amounts of C_3's and heavier components. The primary absorber recovers these components. The HPS vapor enters below the bottom tray and proceeds up the tower contacting absorption oil. Heavy components are absorbed in the oil.

Two sources of absorption oil are normally utilized in this tower. The first is the hydrocarbon liquid from the main fractionator overhead receiver. This stream, often called "wild," or unstabilized naphtha, enters the absorber a few trays below the top tray. The second absorbent is cooled debutanized gasoline, which generally enters on the top tray. It has a lower vapor pressure and can be considered a trim absorbent. The expression "lean oil" generally refers to the debutanized gasoline plus the unstabilized naphtha from the overhead receiver.

The absorption process is exothermic. To improve C_3+ recovery, liquid from one or more of the middle trays is pumped through an intercooler and returned to the tray below. In some FCC units, the lean oil feed is chilled.

To enhance C_3+ recovery, some units have installed presaturator drums that function as an additional absorption stage. In this operation, the cooled debutanized gasoline is mixed (presaturated) with the absorber overhead gas. The mixture is cooled and flashed in the presaturator drum. The liquid from this drum is then pumped to the top of the primary absorber.

Sponge Oil or Secondary Absorber

The vapor from the primary absorber or the presaturator contains a small quantity of gasoline. The sponge oil or secondary absorber recovers this gasoline. "Sponge oil" is often stripped or unstripped LCO. It is used for final absorption of the dry gas stream. Instead of LCO, a few FCC units use cooled heavy naphtha from the main column as sponge oil.

The lean sponge oil enters the absorber on the top tray. The gas from the presaturator or from the primary absorber enters below the bottom tray. The rich sponge oil from the bottom is then returned to the main fractionator. The lean gas leaves the top of the absorber to an amine unit for H_2S removal prior to entering the refinery fuel gas system.

Stripper or De-ethanizer

The HPS liquid consists mostly of C_3's and heavier hydrocarbons; however, it also contains small fractions of C_2's, H_2S, and entrained water. The stripper removes these light ends. The liquid enters the stripper on the top tray. The heat for stripping is provided by an external reboiler, using steam or debutanizer bottoms as the heat medium. The vapor from the reboiler rises through the tower and strips the lighter fractions from the descending liquid. The rich overhead vapor flows to the HPS via the condenser and is fed on to the primary absorber. The stripped naphtha leaves the tower bottoms and goes to the

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debutanizer. Few de-ethanizer towers have dedicated water draw trays to remove the entrained water.

Debutanizer

The stripper bottoms contain C_3's, C_4's, and gasoline; the debutanizer separates the C_3's and C_4's from the gasoline. In some units, the hot stripper bottoms can be further preheated before entering the debutanizer. In a number of units, the stripper bottoms are sent directly to the debutanizer. The feed enters about midway in the tower. Debutanizer feed is always partially vaporized because the debutanizer operates at a lower pressure than the stripper. A control valve that regulates the stripper bottoms' level is the means of this pressure drop. As a result of this drop, part of the feed is vaporized across the valve.

The debutanizer separates the feed into two products. The overhead product contains a mixture of C_3's and C_4's. The bottoms product is the stabilized gasoline. Heat for separating these products comes from an external reboiler. The heating source is usually the main fractionator HCO or slurry. Steam can also be used.

The overhead product is totally liquefied in the overhead condensers. A portion of the overhead liquid is pumped and returned to the tower as reflux. The remainder is sent to a treating unit to remove H_2S and other sulfur compounds. The mixed C_3's and C_4's stream can then be fed to either an alkylation unit or is fed to a depropanizer tower where the C_3's are separated from C_4's. The C_3's are processed for petrochemical feedstock and the C_4's are alkylated.

The debutanized gasoline is cooled, first by supplying heat to the stripper reboiler or by preheating the debutanizer feed. This is followed by a set of air or water coolers. A portion of the debutanizer bottoms can be pumped back to the presaturator or to the primary absorber as lean oil. The balance is treated for sulfur and blended into the refinery gasoline pool.

Gasoline Splitter

A number of refiners split the debutanized gasoline into "light" and "heavy" gasoline. This optimizes the refinery gasoline pool when blending is constrained by sulfur and aromatics. In a few gasoline splitters, a third "heart cut" is withdrawn. This intermediate cut is low in octane, and it is processed in another unit for further upgrading.

Water Wash System

The cat cracker feedstock contains concentrations of organic sulfur and nitrogen compounds. Cracking of organic nitrogen compounds liberates hydrogen cyanide (HCN), ammonia (NH_3), and other nitrogen compounds. Cracking of organic sulfur compounds produces hydrogen sulfide (H_2S) and other sulfur compounds.

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A wet environment exists in the FCC gas plant. Water comes from the condensation of process steam in the main fractionator overhead condensers. In the presence of H_2S, NH_3, and HCN, this environment is conducive to corrosion attack. The corrosion attack can be any or all of the following types [2]:

- General corrosion from ammonium bisulfide
- Hydrogen blistering and/or embrittlement
- Pitting corrosion under fouling deposits.

Ammonium bisulfide is produced by the reaction of ammonia and hydrogen sulfide [2]:

$$\begin{aligned} &NH_3 + H_2S \rightarrow (NH_4)HS \\ &MW = 17, \quad MW = 34 \\ &\text{Weight ratio: } NH_3/H_2S = 0.5 \end{aligned} \tag{1.1}$$

Ammonium bisulfide is extremely corrosive to steel. The corrosion product is hydrogen gas and iron sulfide. The reaction is normally self-terminating because iron sulfide coats the metal surface with a protective film that inhibits further corrosion. However, if cyanide is present, the iron sulfide is removed and bisulfide corrosion is no longer self-terminating. Hydrogen cyanide (HCN) is formed in the riser from the reaction of ammonia (NH_3) and CO. Ammonium cyanide is formed from the reaction of hydrogen cyanide (HCN) and ammonia (NH_3). The ammonium cyanide will dissolve in a wet environment and ionize into cyanide and ammonium ions. The cyanide ion reacts with the insoluble iron sulfide to form a soluble ferrocyanide complex. This destroys the iron sulfide protective film and exposes fresh metal to further attack. As this corrosion proceeds, it produces hydrogen atoms which penetrate into the metal surfaces causing hydrogen blistering. This leads to stress corrosion cracking (SCC).

The chemical reactions are as follows:

1. Generation of hydrogen cyanide

$$CO + NH_3 \rightarrow HCN + H_2O \tag{1.2}$$

2. Formation of ammonium cyanide

$$HCN + NH_3(aq) \rightarrow NH_4CN(aq) \tag{1.3}$$

3. Ionization in water

$$NH_4CN \rightarrow NH_4^+ + CN^- \tag{1.4}$$

4. Cyanide corrosion

$$FeS + CN^- \rightarrow Fe(CN)_6 + (NH_4)_2S \tag{1.5}$$

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Ammonia can also react with hydrogen sulfide to form ammonium sulfide:

$$2NH_3 + H_2S \rightarrow (NH_4)_2S$$
$$\text{MW } 2NH_3 = 34, \quad \text{MW } H_2S = 34, \tag{1.6}$$
$$\text{weight ratio } 2NH_3/H_2S = 1.0$$

Ammonium sulfide is not corrosive, but it can precipitate. Under-deposit corrosion and pitting can occur.

Typically, sour water from the FCC contains a mixture of ammonium sulfide and ammonium bisulfide with an ammonia-to-hydrogen sulfide ratio between 0.5 and 1.0.

Most refiners employ continuous water wash as the principal method of controlling corrosion and hydrogen blistering. The best source of water is either steam condensate or well-stripped water from a sour water stripper. A number of refiners use ammonium polysulfate to neutralize hydrogen cyanide and to control hydrogen stress cracking.

In the gas plant, corrosive agents (H_2S, HCN, and NH_3) are most concentrated at high-pressure points. Water is usually injected into the first- and second-stage compressor discharges. The water contacts the hot gas and scrubs these agents. There are two common injection methods: *forward cascading* and *reverse cascading*.

In forward cascading (Figure 1.21), the water is normally injected into the discharge of the first-stage compressor and condenses in the interstage cooler. From the interstage drum, the

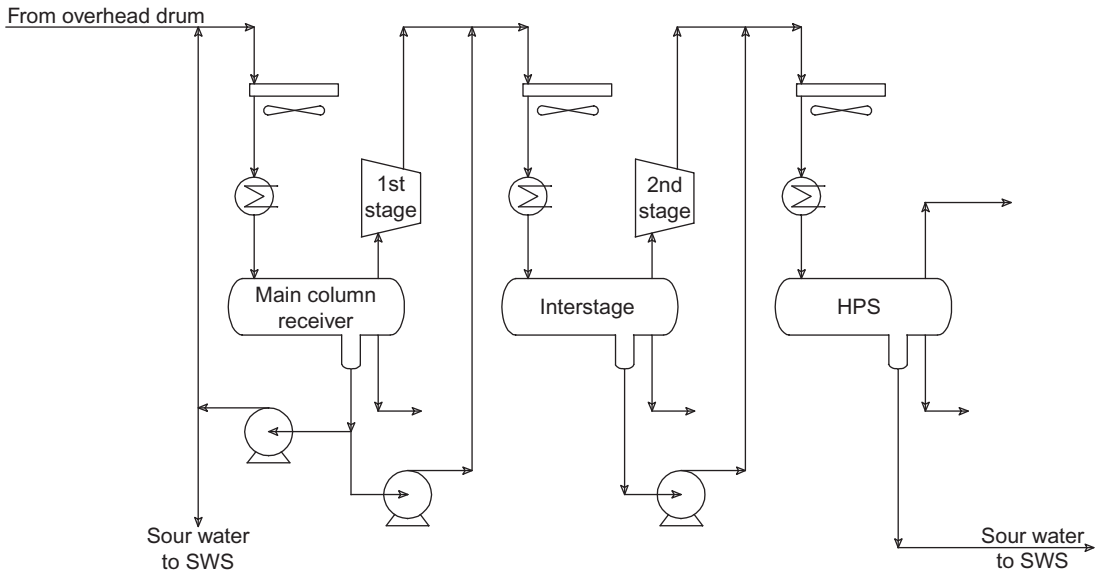


Figure 1.21: A typical forward cascading water wash system (*SWS = sour water stripper*).

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water is pumped to the second-stage discharge, condenses in the cooler, and collects in the HPS. From the HPS, the water is then pressured to the sour water stripper (SWS).

In reverse cascading (Figure 1.22), fresh water is injected into the second-stage discharge. The water containing corrosive agents is pressured to the first-stage discharge and then back to the main fractionator overhead. From the overhead receiver, the water is then pumped to the sour water stripper. Reverse cascading requires one less pump, but a portion of cyanide captured in the second stage is released in the interstage, forming a cyanide recycle. Consequently, forward cascading is more effective in minimizing cyanide attack.

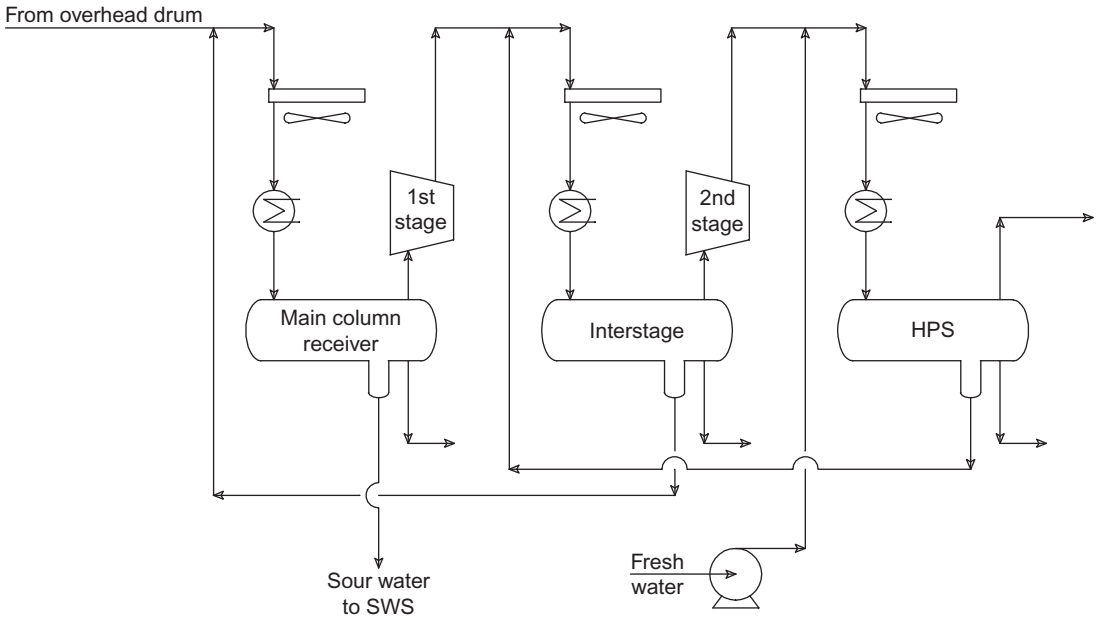


Figure 1.22: A typical reverse cascading scheme for water wash.

Treating Facilities

The gas plant products, namely fuel gas, C_3's, C_4's, and gasoline, contain sulfur compounds that require treatment. Impurities in the gas plant products are acidic in nature. Examples include hydrogen sulfide (H_2S), carbon dioxide (CO_2), mercaptan (R—SH), phenol (ArOH), and naphthenic acids (R—COOH). Carbonyl and elemental sulfur may also be present in the above streams. These compounds are acidic.

Amine and caustic solutions are used to remove these impurities. The amine solvents known as alkanolamines remove both H_2S and CO_2. Hydrogen sulfide is poisonous and toxic. For refinery furnaces and boilers, the maximum H_2S concentration is normally about 160 ppm.

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Amines remove the bulk of the H_2S; primary amines also remove the CO_2. Amine treating is not effective for removal of mercaptan. In addition, it cannot remove enough H_2S to meet the copper strip corrosion test. For this reason, caustic treating is the final polishing step downstream of the amine units. Table 1.4 illustrates the chemistry of some of the important caustic reactions.

Table 1.4: Acid/Base Reactions Encountered Most Frequently by Oil Industry Caustic Treaters.

Carbon dioxide		
$CO_2 + 2NaOH$	→	$Na_2CO_3 + H_2O$
Hydrogen sulfide		
$H_2S + 2NaOH$	→	$Na_2S + 2H_2O$
Mercaptan sulfur		
$RSH + NaOH$	→	$RSNa + H_2O$
Naphthenic acid		
$RCOOH + NaOH$	→	$RCOONa + H_2O$

Sour Gas Absorber

An amine absorber (Figure 1.23) removes the bulk of H_2S from the sour gas. The sour gas leaving the sponge oil absorber usually flows into a separator that removes and liquefies hydrocarbon from vapors. The gas from the separator flows to the bottom of the H_2S contactor where it contacts a countercurrent flow of the cooled lean amine from the regenerator. The treated fuel gas leaves the top of the H_2S absorber, goes to a settler drum for the removal of entrained solvent, and then flows to the fuel system.

Rich amine from the bottom of the H_2S contactor goes to a flash separator to remove dissolved hydrocarbons from the amine solution. The rich amine is pumped from the separator to the amine regenerator.

In the amine regenerator, the rich amine solution is heated to reverse the acid−base reaction that takes place in the contactor. The heat is supplied by a steam reboiler. The hot, lean amine is pumped from the bottom of the regenerator and exchanges heat with the rich amine in the lean-rich exchanger and a cooler, before returning to the contactor.

A portion of the rich amine flows through a particle filter and a carbon bed filter. The particle filters remove dirt, rust, and iron sulfide. The carbon filter, located downstream of the particle filters, removes residual hydrocarbons from the amine solution.

The sour gas, containing small amounts of amine, leaves the top of the regenerator and flows through a condenser to the accumulator. The sour gas is sent to the sulfur unit, while the condensed liquid is refluxed to the regenerator.

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For many years, nearly all the amine units were using monoethanolamine (MEA) or diethanolamine (DEA). However, in recent years, the use of tertiary amines such as methyl diethanolamine (MDEA) has increased. These solvents are generally less corrosive and require less energy to regenerate. They can be formulated for specific gas recovery requirements.

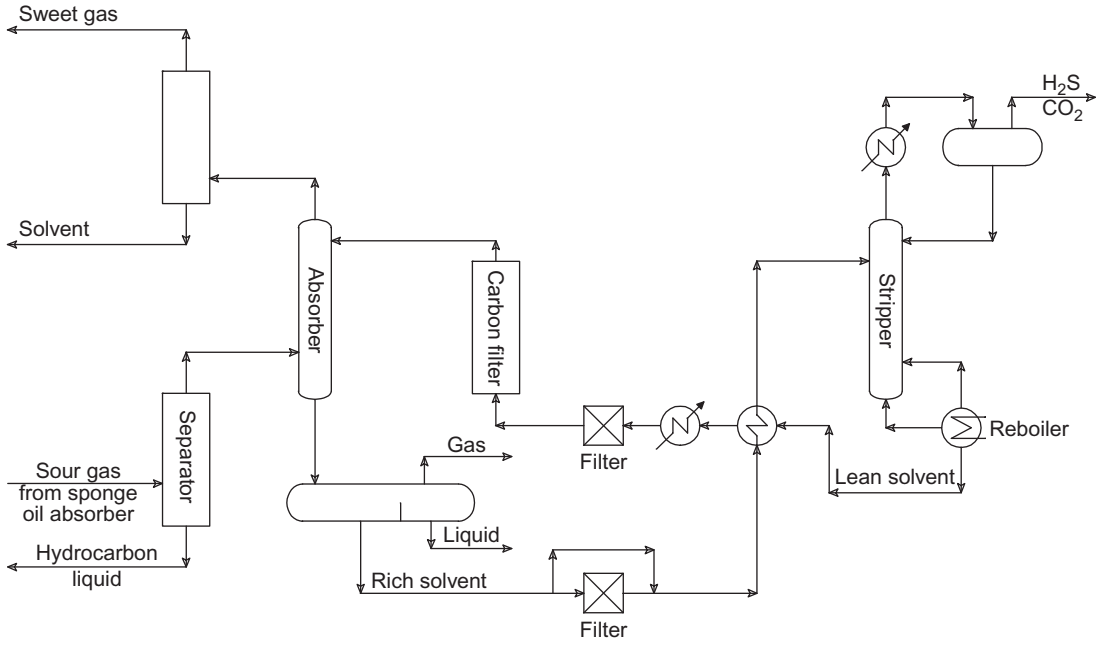


Figure 1.23: A typical amine treating system.

LPG Treating

The LPG stream containing a mixture of C_3's and C_4's must be treated to remove hydrogen sulfide and mercaptan. This produces a noncorrosive, less odorous, and less hazardous product. The C_3's and C_4's from the debutanizer accumulator flow to the bottom of the H_2S contactor. The operation of this contactor is similar to that of the fuel gas absorber, except that this is a liquid−liquid contactor.

In the LPG contactor, the amine is normally the continuous phase with the amine−hydrocarbon interface at the top of the contactor. This interface level controls the amine flow out of the contactor. (Some liquid/liquid contactors are operated with the hydrocarbon as the continuous phase. In this case, the interface is controlled at the bottom of the contactor.) The treated C_3/C_4 stream leaves the top of the contactor. A final coalescer is often installed to recover the carryover amine.

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Caustic Treating

Mercaptans are organic sulfur compounds having the general formula of R—S—H. As stated earlier, amine treating is not effective for the removal of mercaptan. There are two options for treating mercaptans. In each option, the mercaptans are first oxidized to disulfides. One option, extraction, dissolves the disulfides in caustic and removes them. The other option, sweetening, leaves the converted disulfides in the product. Extraction removes sulfur, sweetening just removes the mercaptan odor. Extraction is used for light products (up to light naphtha) and sweetening for heavy products (gasoline through diesel).

Both sweetening and extraction processes (Figure 1.24) commonly use caustic and catalyst. If the LPG and the gasoline contain high levels of H_2S, a caustic prewash is needed to protect the catalyst.

The sweetening process utilizes a caustic solution, catalyst, and air. Mercaptans are converted to disulfides in a mixing vessel or fiber film contactor. The reactions take place according to the following equations:

$$RSH + NaOH + \text{catalyst} \rightarrow RSNa + H_2O \tag{1.7}$$

$$2RSNa + \tfrac{1}{2}\, O_2 + H_2O + \text{catalyst} \rightarrow RSSR + 2NaOH \tag{1.8}$$

The mixture of caustic and disulfides is transferred to a settler. From the settler, the treated gasoline flows to a coalescer, sand filter, or wash water tower, before going to storage. The caustic solution is recirculated to the mixing vessel/fiber film contactor.

In the extraction process, the LPG from the prewash tower enters the bottom of an extractor column. The extractor is a liquid/liquid contactor in which the LPG is countercurrently contacted by a caustic solution. Another option is the use of a fiber film contacting device. The mercaptans dissolve in the caustic (Eq. (1.7)). The treated LPG leaves the top of the extractor and goes on to a settler, where entrained caustic is separated.

From the bottom of the extractor, the caustic solution, containing sodium mercaptide, enters the regenerator. Plant air supplies oxygen to react with the sodium mercaptide to form disulfide oil (Eq. (1.8)), which is insoluble in caustic. The oxidizer overhead stream flows to a disulfide separator. A hydrocarbon solvent, such as naphtha, washes the disulfide oils out of the regenerated caustic. The regenerated caustic is returned to the extractor and the solvent containing disulfide oil is disposed in other units.

Summary

FCC is one of the most important conversion processes in a petroleum refinery. The process incorporates most phases of chemical engineering fundamentals, such as fluidization, heat/mass transfer, and distillation. The heart of the process is the reactor—regenerator, where most of the innovations have occurred since 1942.

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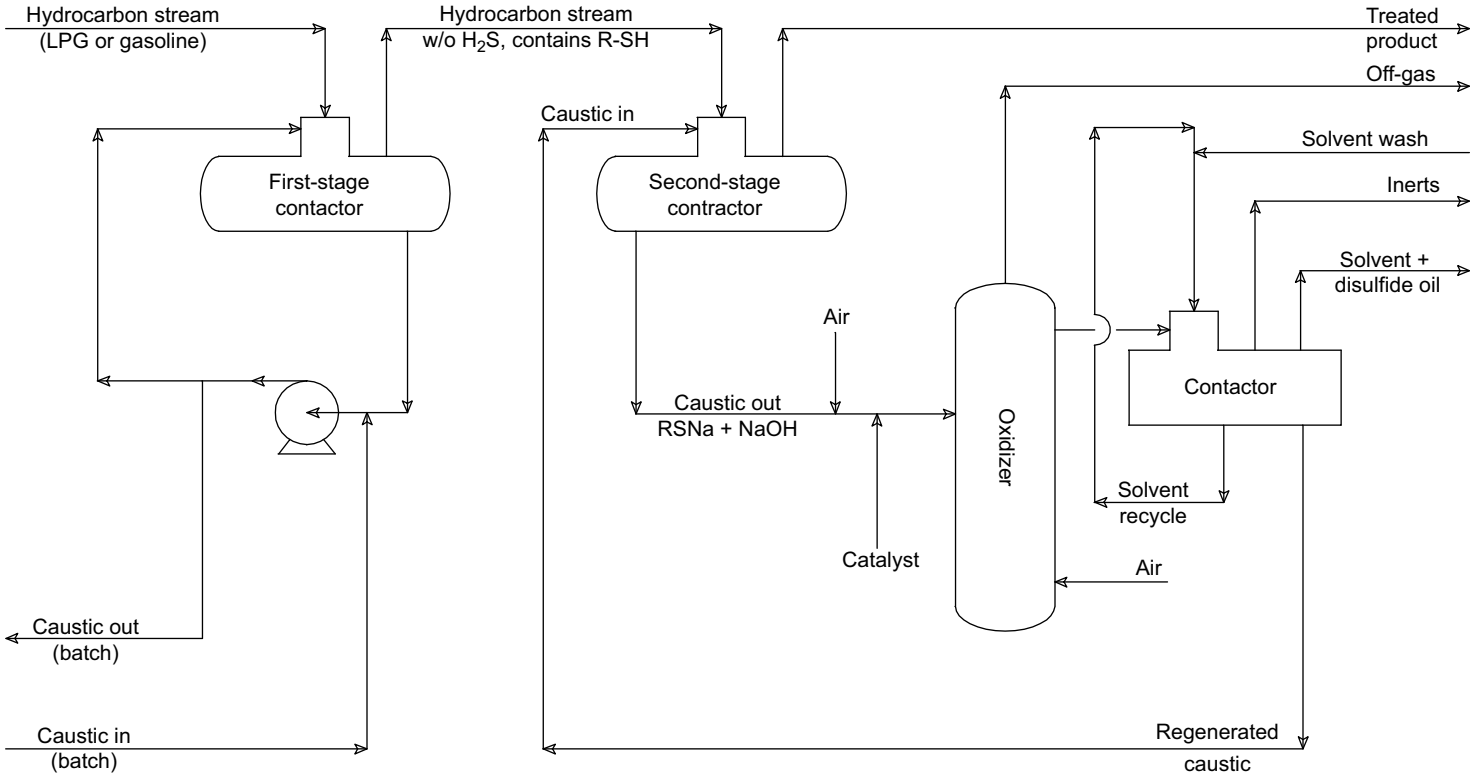


Figure 1.24: Caustic sweetening and extraction processes (*adapted from Merichem Company—Houston, TX*).

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The FCC unit converts low-value, high-boiling feedstocks into valuable products such as gasoline and diesel. The FCC is extremely efficient, with only about 5% of the feed used as fuel in the process. Coke is deposited on the catalyst during the reaction and burned off in the regenerator, supplying all the heat for the reaction.

Products from the reactor are recovered in the main fractionator and the gas plant. The main fractionator recovers the heaviest products, such as LCO and DO, from the gasoline and lighter products. The gas plant separates the main fractionator overhead vapors into gasoline, C_3's, C_4's, and fuel gas. The products contain sulfur compounds and need to be treated prior to being used. A combination of amine and caustic solutions are employed to sweeten these products.

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[1] R. Mari Lyn, Worldwide refining, Oil Gas J. 108(46) (2010) 52.
[2] Fluid Catalytic Cracking Information, Fluid catalytic cracking reference articles. <http://www.Canadaspace.com>

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CHAPTER 2

Process Control Instrumentation

An FCC unit is a "pressure balance" operation that behaves similarly to a water manometer. Differential pressure between the regenerator and reactor vessels is the driving force that allows for the fluidized catalyst to circulate between the regenerator and reactor vessels. The slide or butterfly valve located in the regenerator flue gas line is used to regulate the differential pressure between the regenerator and reactor vessels. The reactor pressure is controlled by the wet gas compressor (WGC).

Fresh catalyst must be added to make up for the catalyst losses from the reactor/regenerator vessels, as well as to compensate for the loss of catalyst activity. The catalyst inventory in the unit is controlled by periodic withdrawal of the excess catalyst from the regenerator vessel. The catalyst level in the regenerator vessel fluctuates and is controlled within a "desirable" level by withdrawal of the catalyst. The catalyst level in the reactor/stripper vessel is controlled by manipulating the spent catalyst slide or plug valve. This slide or plug valve allows enough catalyst to flow into the regenerator in order to maintain the desired catalyst level. Differential pressure indicators across the reactor and regenerator vessels are used to measure the catalyst's "raw" levels and the catalyst's flowing densities.

In most cat crackers, the flow of "clean" catalyst from the regenerator is automatically regulated via a reactor or riser outlet temperature set point. In very few FCC units, this function is performed manually. In Model IV and Flexicracker designs, the reactor–regenerator differential pressure is used to regulate the catalyst circulation rate.

In FCC regenerators that operate in complete combustion mode, the total air to the regenerator is adjusted to achieve a desired level of excess oxygen in the regenerator flue gas. The regenerator bed temperature often fluctuates and it is manually adjusted by manipulating feed quality, preheat temperature, the use of recycle streams to the riser, stripping steam rate, and possible adjustments to the fresh catalyst addition rate and/or activity.

In partial burn mode of catalyst regeneration, the regenerator temperature and carbon on the catalyst are often controlled by regulating air rate to the regenerator and/or targeting a desired concentration of CO in the regenerator flue gas.

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Operating Variables

The key operating parameters in the reactor−regenerator section include the following:

- Fresh feed rate
- LCO, HCO, or slurry recycle to the riser
- Riser outlet or reactor cyclones outlet temperature
- Feed preheat temperature
- Reactor and/or regenerator pressures
- Flue gas excess oxygen
- CO concentration of regenerator flue gas (partial combustion)
- Regenerator dense bed temperature (partial combustion)
- Coke on regenerated catalyst (partial combustion)
- Stripping steam rate
- Feed nozzle atomization steam
- Catalyst addition rate or fresh catalyst surface area.

Process Control Instrumentation

Process control instrumentation controls the FCC unit in a safe, monitored mode with limited operator intervention. Two levels of process control are used:

- Basic supervisory control
- Advanced process control (APC).

Basic Supervisory Control

The primary controls in the reactor−regenerator section are flow, temperature, pressure, and catalyst level.

The flow controllers are often used to set desired flows for the fresh feed, recycle, air rate, stripping steam, dispersion steam, and so on. Each flow controller usually has three modes of control: manual, auto, and cascade. See Figure 2.1 for a typical process flow diagram (PFD). In manual mode, the operator manually opens or closes a valve to the desired percent opening. In auto mode, the operator enters the desired flow rate as a set point. In cascade mode, the controller set point is an input from another controller.

The reactor temperature is controlled by a temperature controller that regulates the regenerated catalyst slide valve. The regenerator temperature is not automatically controlled but depends on its mode of catalyst regeneration. In partial combustion, the regenerator

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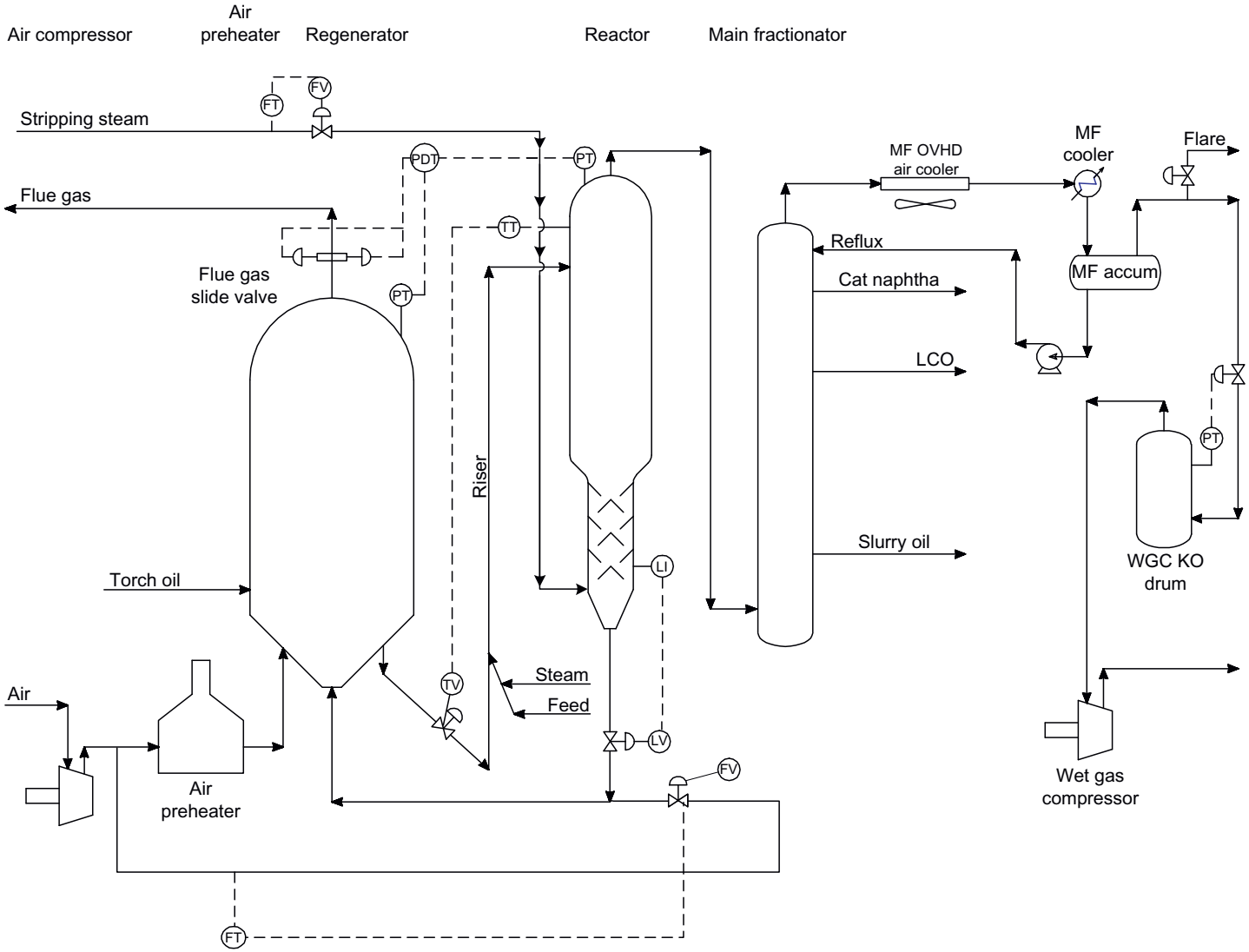


Figure 2.1: Typical FCC unit process flow diagram (PFD) (*FV = flow control valve, FT = flow transmitter, KO = knock out, LI = level indicator, LV = level control valve, MF = main fractionator, OVHD = overhead, PDT = pressure differential transmitter, PT = pressure transmitter, TV = temperature control valve*).

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temperature is controlled by adjusting the flow of air to the regenerator. In full burn, the regenerator temperature is a function of several variables, including feedstock quality, catalyst properties, use of recycle, stripping steam rate, and mechanical conditions of the feed injection system and the catalyst stripper.

The reactor pressure is not directly controlled, instead it floats on the main column overhead receiver. A pressure controller on the overhead receiver controls the WGC and indirectly controls the reactor pressure. The regenerator pressure is often controlled directly by regulating the flue gas slide or butterfly valve. (In some cases, the flue gas slide or butterfly valve is used to control the differential pressure between the regenerator and reactor.)

The reactor or stripper catalyst level is maintained with a level controller that regulates the movement of the spent catalyst slide valve. The regenerator level is manually controlled to maintain catalyst inventory.

Regenerated and Spent Catalyst Slide Valve

Low Differential Pressure Override

Normally, the reactor temperature and the stripper level controllers regulate the movement of the regenerated and spent catalyst slide valves. The algorithm of these controllers can drive the valves either fully open or fully closed if the controller set point is unobtainable. It is extremely important that a positive and stable pressure differential be maintained across both the regenerated and spent catalyst slide valves. For safety, a low differential pressure controller overrides the temperature/level controllers, should these valves open too much. The shutdown is usually set at 2 psi (14 kPa). An example of a typical shutdown matrix is shown in Table 2.1.

The direction of the catalyst flow must always be from the regenerator to the reactor and from the reactor back to the regenerator. A negative differential pressure across the regenerated catalyst slide valve can allow hydrocarbons to backflow into the regenerator. This is called a “flow reversal” and can result in an uncontrolled afterburn and possible equipment damage. A negative pressure differential across the spent catalyst slide valve can allow air to backflow from the regenerator into the reactor with equally disastrous consequences.

To protect the reactor and the regenerator against a flow reversal, pressure differential controllers (PDICs) are used to monitor and control the differential pressures across the slide valves. If the differential pressure falls below a minimum set point, the PDIC overrides the process controller and closes the valve. Only after the PDIC is satisfied will the control of the slide valve return to the process.

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Table 2.1: Typical Shutdown Matrix.

Cause	RCSV	Riser Emergency Steam	Feed to Riser	Slurry Recycle	HCO Recycle	SCSV	Regenerator Emergency Steam	Alarm Only
Normal	Process	Closed	Process	Process	Process	Process	Closed	
RCSV low differential pressure								X
RCSV low/low differential pressure	Close	Open	Close	Close	Close			
SCSV low differential pressure								X
SCSV low/low differential pressure						Close	Open	
Air blower low/low air flow	Close	Open	Close	Close	Close		Open	
Riser low/low feed flow		Open	Close					
Low reactor temperature			Close					X
Reactor/stripper high catalyst level	Close	Open	Close	Close	Close			X
Manual shutdown	Close	Open	Close	Close	Close	Close	Open	

RCSV = regenerated catalyst slide valve; SCSV = spent catalyst slide valve.

Advanced Process Control

To maximize the unit's profit, one must operate the unit simultaneously against as many constraints as possible. Examples of these constraints are limits on the air blower, WGC, reactor/regenerator temperatures, slide valve differentials, and so on. The conventional regulatory controllers work only one loop at a time and they do not talk to one another. A skilled operator can "push" the unit against more than one constraint at a time, but the constraints often change. To operate closer to multiple constraints, a number of refiners have installed an APC package either within their distributed control system (DCS) or in a host computer.

The primary advantages of an APC are as follows:

- It provides more precise control of the operating variables against the unit's constraints and therefore obtains incremental throughput or cracking severity.

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- It is able to respond quickly to ambient disturbances, such as cold fronts or rainstorms. It can run a day/night operation, taking advantage of the cooler temperatures at night.
- It pushes against two or more constraints rather than one single constraint. It can maximize the air blower and WGC capacities.

As mentioned above, there are two options for installing an APC. One option is to install an APC within the DCS framework, and the other is to install a multivariable modeling/control package in a host computer. Each has advantages and disadvantages, as indicated below.

Advantages of Multivariable Modeling and Control

The multivariable modeling/control package is able to hold more tightly against constraints and recover more quickly from disturbances. This results in an incremental capacity used to justify multivariable control. An extensive test run is necessary to measure the response of unit variables.

In APC on a DCS framework, the control structure has to be designed, configured, and programmed for each specific unit. Modifying the logic can be an agonizing process. Wiring may be necessary. It is difficult to document the programming and difficult to test.

With a host computer framework, the control package is all in the software. Changing the program can still be agonizing, but the program can be tested off-line. There is more flexibility in the computer system, which can be used for many other purposes, including online heat and weight balances.

Disadvantages of Multivariable Modeling and Control

A multivariable model is like a "black box." The constraints go in and the signals come out. Operators do not trust a system that takes the unit away from them. Successful installations require good training and continual communication. The operators must know the interconnections in the system.

The model may need expensive work if changes are made during a turnaround. If the feed gets outside the range the unit was modeled for, results can be at best unpredictable. An upset can happen for which the system was not programmed.

The DCS-based APC is installed in a modular form, meaning operators can understand what the controlled variable is tied to a little more easily.

The host computer-based system may have its own problems, including computer-to-computer data links.

In any APC the operator has to be educated and brought into it before he or she can use it. The control has to be properly designed, meaning the model has to be configured and "tuned" properly. The operators need to be involved early and all of them need to be consulted. All four shifts may be running the unit differently.

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Summary

In most FCC units, the instrumentations that are shown in the piping and instrumentation diagrams (P&IDs) are often the minimum needed to operate the FCC unit. Many FCC units do not take advantage of DCS capabilities for efficient and reliable operations of the cat cracker. Instrument diagnostics can be used to detect accuracy and status of the transmitters. These diagnostics features can alert console operators with the accuracy of the measuring process variables, such as catalyst level, slide valve differentials, and cracking temperatures (see Table 2.1). DCS screens can be configured to display items such as cyclone velocities, cyclone pressure drops, actual catalyst bed levels, rate-of-change alarms, regenerator superficial velocity, and many other parameters.

An APC package (whether within the DCS framework or as a host-based multivariable control system) provides more precise control of operating variables against the unit's constraints. It will gain incremental throughput or cracking severity. A properly designed APC operates the unit safely and yet continually, while optimizing feed rate, operating severity, product qualities, and environmental controls, as well as staying within the unit's constraints.

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CHAPTER 3

FCC Feed Characterization

Refiners process many different types of crude oil. As market conditions and crude quality fluctuate, so does cat cracking feedstock. Often the only constant in FCC operations is the continual change in feedstock quality.

Feed characterization is the process of determining the physical and chemical properties of the feed. Two feeds with similar boiling point ranges may exhibit dramatic differences in cracking performance and product yields.

FCC feed characterization is one of the most important activities in monitoring the cat cracking operation. Understanding feed properties and knowing their impact on unit performance are essential. Troubleshooting, catalyst selection, unit optimization, and subsequent process evaluations all depend on the feedstock.

Feed characterization relates product yields and qualities to feed quality. By knowing the effects of a feedstock on unit yields, a refiner can purchase the feedstock that maximizes profitability. It is not uncommon for refiners to purchase raw crude oils or FCC feedstocks without knowing their impact on unit operations. This lack of knowledge can be expensive.

Sophisticated analytical techniques, such as mass spectrometry, high-pressure liquid chromatography (HPLC), near-infrared spectroscopy (NIR), and chemometrics, can be used to measure aromatic and saturate contents of the FCC feedstock. For example, American Society for Testing Materials (ASTM) methods D2549, D2786, and D3239 can be used to measure total paraffin, naphthene, and aromatic ring distributions. Unfortunately, only a few refinery laboratories either directly or indirectly use any of the methods to characterize their FCC feedstock. This is largely because these analysis techniques are time consuming, costly, and do not provide practical insight that a unit can use on a daily basis to evaluate and improve its performance. Consequently, simpler empirical correlations are more often used. They require only routine tests commonly performed by the refinery's laboratory. These empirical correlations are good alternatives to determine total paraffin, naphthene, and aromatic molecules, plus they provide practical tools for monitoring the FCC unit's performance. As with the sophisticated analytical techniques, the empirical correlations assume an olefin-free feedstock.

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The two primary factors that affect feed quality are:

1. Hydrocarbon classification
2. Impurities.

Hydrocarbon Classification

The hydrocarbon types in the FCC feed are broadly classified as paraffins, olefins, naphthenes, and aromatics (PONA).

Paraffins

Paraffins are straight- or branched-chain hydrocarbons having the chemical formula C_nH_{2n+2}. The name of each member ends with *−ane*; examples are propane, isopentane, and normal heptane (Figure 3.1).

In general, FCC feeds are predominately paraffinic. The paraffinic carbon content is typically between 50 and 65 wt% of the total feed. Paraffinic stocks are easy to crack and normally yield the greatest amount of total liquid products. Normal paraffins will crack mostly to olefin and other paraffin molecules. They yield a fair amount of light gasoline (C_5 and C_6 molecules), though the octane of the gasoline is rather low.

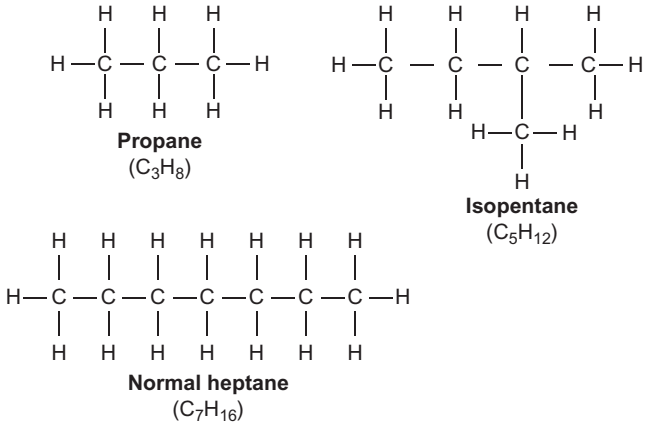


Figure 3.1: Examples of paraffins.

Olefins

Olefins are unsaturated compounds with a formula of C_nH_{2n}. The names of these compounds end with *−ene*, such as ethene (ethylene) and propene (propylene). Figure 3.2 shows typical examples of olefins. Compared to paraffins, olefins are unstable and can react with

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themselves or with other compounds such as oxygen and bromine solution. Olefins do not occur naturally; they show up in the FCC feed as a result of preprocessing the feeds elsewhere. These processes include thermal cracking and other catalytic cracking operations.

Olefins are not the preferred feedstocks to an FCC unit. This is not because olefins are inherently bad, but because olefins in the FCC feed indicate thermally produced oil. They often polymerize to form undesirable products such as slurry and coke. The typical olefin content of FCC feed is <5 wt%, unless unhydrotreated coker gas oils are being charged.

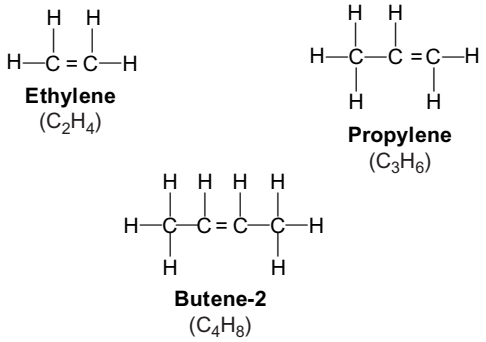


Figure 3.2: Examples of olefins.

Naphthenes

Naphthenes (C_nH_{2n}) have the same formula as olefins, but their characteristics are significantly different. Unlike olefins, which are straight-chain compounds, naphthenes are paraffins that have been "bent" into a ring or a cyclic shape. Naphthenes, like paraffins, are saturated compounds. Examples of naphthenes are cyclopentane, cyclohexane, and methylcyclohexane (Figure 3.3).

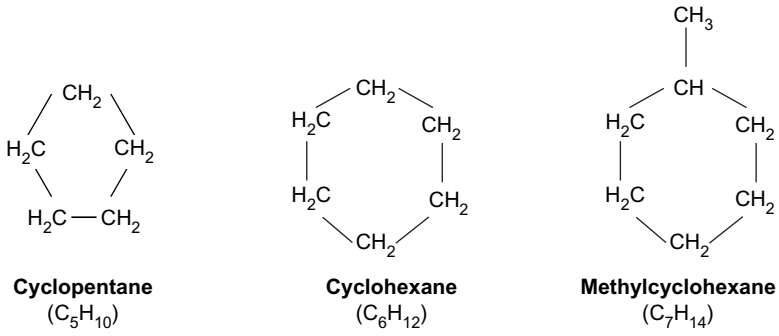


Figure 3.3: Examples of naphthenes.

Naphthenes are desirable FCC feedstocks because they produce high-octane gasoline. The gasoline derived from the cracking of naphthenes has more aromatics and is heavier than the gasoline produced from the cracking of paraffins.

Aromatics

Aromatics (C_nH_{2n-6}) are similar to naphthenes, but they contain a resonance-stabilized unsaturated ring core. Aromatics (Figure 3.4) are compounds that contain at least one benzene ring. The benzene ring is very stable and does not crack to smaller components. Aromatics are not a preferred feedstock because few of the molecules will crack. The cracking of aromatics mainly involves breaking off the side chains resulting in excess fuel gas yield. In addition, some of the aromatic compounds contain several rings (polynuclear aromatics, PNAs) than can "compact" to form what is commonly called "chicken wire." Figure 3.5 illustrates three examples of a PNA compound. Some of these compacted aromatics will end up on the catalyst as carbon residue (coke), and some will become slurry product. In comparison with cracking paraffins, cracking aromatic stocks results in lower conversion, lower gasoline yield, and less liquid volume gain, but with higher gasoline octane.

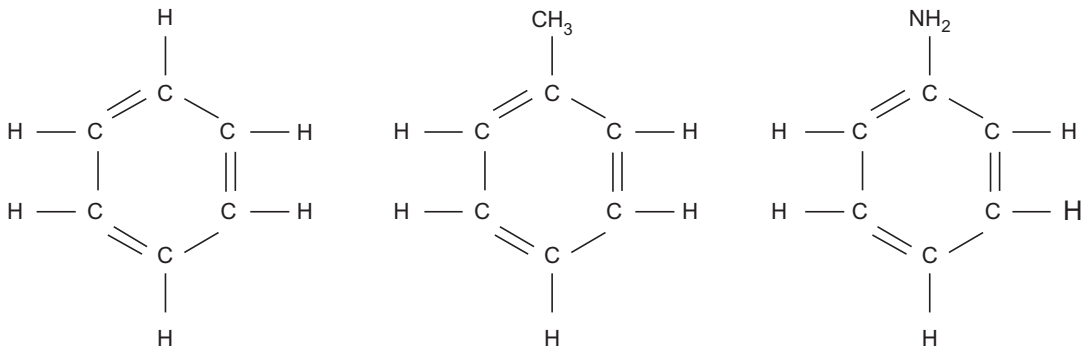


Figure 3.4: Examples of aromatics.

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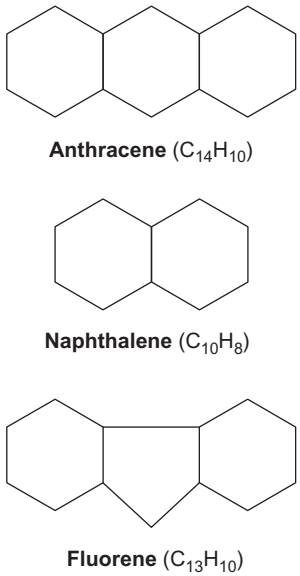


Figure 3.5: Examples of PNA molecules.

Feedstock Physical Properties

Characterizing an FCC feedstock involves determining both its chemical and physical properties. Because sophisticated analytical techniques are not practical on a daily basis, physical properties are used. They provide qualitative measurement of the feed's composition. The refinery laboratory is usually equipped to carry out these physical property tests on a routine basis. The most widely used properties are as follows:

- American Petroleum Institute (API) gravity
- Distillation
- Aniline point
- Refractive index (RI)
- Bromine number (BN) and bromine index (BI)
- Viscosity
- Conradson, Ramsbottom, microcarbon, and heptane insoluble.

API Gravity

The American Petroleum Institute gravity or API gravity is a measure of how heavy or light a hydrocarbon liquid is compared to water. The API gravity is a measure of the relative density of petroleum liquid to the density of water. Specific gravity (SG) is another common measurement of density. The liquid SG is the relative weight of a volume of sample to the weight of the same volume of water at 60°F (15.5°C).

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Compared with SG, API gravity magnifies small changes in the feed density. For example, going from 24°API to 26°API changes the SG by 0.011 and the density by 0.72 lb/ft^3 (0.0115 g/cm^3). Neither is very significant, but a two-number shift in API gravity can have significant effects on yields.

The SG relates to API gravity by the following equations:

$$SG_{(\text{at } 60^\circ F)} = \frac{141.5}{131.5 + \text{API gravity}} \tag{3.1}$$

$$\text{API gravity} = \frac{141.5}{SG_{(\text{at } 60^\circ F)}} - 131.5 \tag{3.2}$$

Since API gravity is inversely proportional to SG, the higher the API gravity, the lighter the liquid sample. In petroleum refining, API gravity is routinely measured for every feed and product stream. The ASTM D287 is a hydrometer test typically performed by a lab technician or unit operator. The method involves inserting a glass hydrometer into a cylinder containing the sample and reading the API gravity and the fluid temperature on the hydrometer scale. Standard tables similar to Table 3.1 convert the API at any temperature back to 60°F. The API gravity is always reported at 60°F (15.5°C).

For a highly paraffinic (waxy) feed, the sample should be heated to about 120°F (49°C) before immersing the hydrometer for testing. Heating ensures that the wax is melted, eliminating erroneous readings.

Table 3.1: API Gravity at Observed Temperature Versus API Gravity at 60°F.

Observed Temperature (°F)	18.0	19.0	20.0	21.0	22.0	23.0	24.0	25.0	26.0	27.0
70	17.5	18.4	19.4	20.4	21.4	22.4	23.4	24.4	25.4	26.3
75	17.2	18.2	19.1	20.1	21.1	22.1	23.1	24.1	25.0	26.0
80	16.9	17.9	18.9	19.8	20.8	21.8	22.8	23.7	24.7	25.7
85	16.6	17.6	18.6	19.6	20.5	21.5	22.5	23.4	24.4	25.4
90	16.4	17.3	18.3	19.3	20.2	21.2	22.2	23.1	24.1	25.1
95	16.1	17.1	18.0	19.0	20.0	20.9	21.9	22.8	23.8	24.8
100	15.9	16.8	17.8	18.7	19.7	20.6	21.6	22.5	23.5	24.4
105	15.6	16.5	17.5	18.7	19.4	20.3	21.3	22.2	23.2	24.1
110	15.3	16.3	17.2	18.2	19.1	20.1	21.0	21.9	22.9	23.8
115	15.1	16.0	17.0	17.9	18.8	19.8	20.7	21.6	22.6	23.5
120	14.8	15.8	16.7	17.6	18.6	19.5	20.4	21.3	22.3	23.2
125	14.6	15.5	16.4	17.4	18.3	19.2	20.1	21.1	22.0	22.9
130	14.3	15.2	16.2	17.4	18.0	18.9	19.9	20.8	21.7	22.6
135	14.1	15.0	15.9	16.8	17.7	18.7	19.6	20.5	21.4	22.6
140	13.8	14.7	15.6	16.6	17.5	18.4	19.3	20.2	21.1	22.0

Source: ASTM D1250-80, Tables 5A and 5B.

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Daily monitoring of API gravity provides the operator with a tool to predict changes in unit operation. For the same distillation range, the 26°API feed cracks more easily than the 24°API feed because the 26°API feed has more long-chain paraffinic molecules. In contact with the 1,300°F (704°C) catalyst, these molecules are easier to rupture into valuable products.

The simple API gravity test provides valuable information about the quality of a feed. But the shift in API gravity usually signals changes in other feed properties such as carbon residue and aniline point. Additional tests are needed to fully characterize the feed. In general, as the feed API gravity is decreased, so does the unit conversion. For example, one number decline in the feed API gravity will lower the unit conversion by about 2%.

Distillation

Boiling point distillation data also provides information about the quality and composition of a feed. Its significance is discussed later in this chapter. Distillation indicates molecular weight and carbon number. It indicates whether the feed contains any "clean" products that could be sold "as is." Before discussing the data, the different testing methods and their limitations need to be reviewed.

In a typical refinery, the feed to the cat cracker is a blend of *gas oils* from operating units such as the crude, vacuum, solvent deasphalting, and coker. Some refiners purchase outside FCC feedstocks to keep the FCC feed rate maximized. Other refiners process atmospheric or vacuum residue in their cat crackers. Residue is often defined as the fraction of feed that boils above 1,050°F (565°C). The fraction of FCC feed hydrotreating varies among the refiners. Some FCC feeds are 100% hydrotreated and some none. The majority of the FCC feeds are partially hydrotreated. Each FCC feed stream has different distillation characteristics.

The frequency and method of testing feed streams varies from one refiner to another. Some refiners analyze daily, others two or three times a week, and some once a week. The frequency depends on how the distillation results are applied, the variation in crude slates, and the availability of lab personnel.

The fractional distillation test conducted in the laboratory involves measuring the temperature of the distilled vapor at the initial boiling point (IBP), as volume and/or weight percent fractions 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 95 are collected, and at the end point (EP). The ASTM methods that are commonly used to determine the boiling range of FCC feedstock include D86, D1160, D2887, and D7169.

D86 is one of the oldest distillation test methods used in refineries to determine the boiling range of a liquid sample. The distillation is done at atmospheric pressure and it is used for samples with an EP <750°F (400°C). Above this temperature, the sample can begin to

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crack. Thermal cracking is identified by a drop in the temperature of the distilled vapor, the presence of brown smoke, and a rise in the system pressure. Above 750°F liquid temperature, the distilling flask begins to deform. All of today's FCC feeds are too heavy to use the D86 method, but it is used for light products such as gasoline, kerosene, and distillates.

As with D86, D1160 is also one of the original test methods to measure boiling fractions for heavier liquid hydrocarbon samples. D1160 is run under vacuum (1 mm of mercury). The results are converted to atmospheric pressure, using standard correlations. Some newer apparatuses have built-in software that will perform the conversion automatically. D1160 is limited to a maximum EP temperature of about 1,000°F (538°C) at atmospheric pressure. Above this temperature, the sample begins to crack thermally.

However, most refiners use simulated distillation (SIMDIS) methods to determine boiling range distribution of heavier streams such as FCC feedstock, LCO, and slurry oil products. The two common test methods are ASTM D2887 and ASTM D7169.

D2887 is a low-temperature SIMDIS method that determines the wt% of boiling range distribution using gas chromatography (GC). Its use is limited to a maximum EP temperature of about 1,000°F (538°C). ASTM D7169 extends the SIMDIS application to boiling point temperatures as high as 1,328°F (720°C). The boiling points obtained from these methods are supposed to be equivalent to true boiling point (TBP) distillation by using ASTM D2892.

Distillation data provides information about the light fraction of feed boiling at <650°F (343°C). Light virgin feed, the fraction that boils below 650°F, often results in a greater LCO yield and lower unit conversion. Sources of these fractions are atmospheric gas oil, light vacuum gas oil, light coker gas oil, and absence of adequate fractionation in the backend of hydrotreaters. Lower conversion of light virgin feed is caused by:

1. Lower molecular weight, which means the oil is more difficult to crack
2. Light aromatics, which have fewer crackable side chains
3. Often, the presence of light coker stocks, which are very aromatic.

Economics and unit configuration dictate whether to include 650°F material in the FCC feed. As a general rule, this fraction should be minimized. Minor improvements in the operation of the upstream distillation columns can substantially reduce the amount of light gas oil in the FCC feed. However, including light gas oil in FCC feed reduces the amount of coke laid on the catalyst. Less coke means a lower regenerator temperature. Light gas oil can be used as a "quench" to decrease the regenerator temperature and to increase the catalyst to oil ratio.

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The distillation test also provides information about the fractions that boil over 900°F (482°C). These fractions provide an indication of the coke-making tendency of a given feed. Associated with this 900+ °F fraction is a higher level of contaminants such as metals and nitrogen. As discussed later in this chapter (see "Impurities" section), these contaminants deactivate the catalyst and produce less liquid product and more coke and gas.

Distillation data is the backbone of FCC feed analyses. Published correlations use distillation data to determine the chemical composition of FCC feed.

Aniline Point

Aniline is an aromatic amine ($C_6H_5NH_2$). When used as a solvent, it is selective to aromatic molecules at low temperatures, paraffins and naphthenes at higher temperatures. Aniline is used to determine the aromaticity of oil products, including FCC feedstocks. Aniline point is the minimum temperature for complete solubility of an oil sample in aniline.

ASTM D611 involves heating a 50/50 mixture of the feed sample and aniline until there is only one phase. The mixture is then cooled, and the temperature at which the mixture becomes suddenly cloudy is the aniline point. The test senses solubility via a light source that penetrates through the sample.

The aniline point increases with paraffinicity and decreases with aromaticity. It also increases with molecular weight. Naphthenes and olefins show values that lie between those for paraffins and aromatics. Typically, an aniline point higher than 200°F (93°C) indicates paraffinicity, and an aniline point lower than 150°F (65°C) indicates aromaticity.

Aniline point is used in some correlations to estimate the aromaticity of gas oil and light stocks. TOTAL's [1] correlation uses aniline point and RI. Other methods, such as $n-d-M$ [2], employ RI to characterize FCC feed.

Refractive Index

Similar to aniline point, RI shows how refractive or aromatic a sample is. The higher the RI of the taken sample, the more aromatic and less crackable will be the sample. A feed having an RI of 1.5105 is more difficult to crack than a feed with an RI of 1.4990. The RI can be measured in a laboratory (ASTM D1747) or predicted using correlations such as the one published by TOTAL.

In the laboratory, RI is measured using a refractometer. The instrument has two prisms and a light source. The technician spreads a small amount of sample on the faces of both prisms in the refractometer. The light is then directed at the sample and the scale is read. The observed scale is then converted to an RI with tables supplied with the instrument and corrected for the sample temperature.

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Both RI and aniline point tests qualitatively measure the aromaticity of a liquid hydrocarbon sample. With dark and viscous samples, both methods have their limitations. For darker samples, the aniline point test is slightly more accurate because of its larger scale over the same range of aromatics. The industry does not agree as to which method is more accurate. The three published correlations that will be discussed later use the RI at 68°F (20°C) for calculating feed composition. But at 68°F, most FCC feeds are solid and their RIs cannot be determined accurately. Both the TOTAL and API [3] correlations predict RI values using feed properties such as SG, molecular weight, and average boiling point.

Bromine Number and Bromine Index

Bromine number (ASTM D1159) and bromine index (ASTM D2710) are qualitative methods to measure the reactive sites of a sample. The bromine number (D1159) method should be used for heavy materials such as FCC feedstock.

Bromine reacts not only with olefin bonds but also with basic nitrogen molecules and some aromatic sulfur derivatives. Nevertheless, olefins are the most common reactive sites, and the bromine number is used to indicate olefinicity of the feed.

Bromine number is the number of *grams* of bromine that will react with 100 g of the sample. Typical bromine numbers are:

- less than 5 for hydrotreated feeds
- 10 for heavy vacuum gas oil
- 50 for coker gas oil.

A general rule of thumb is that the olefin fraction of the sample is 1/2 of its bromine number.

Alternatively, the bromine index is the number of *milligrams* of bromine that will react with 100 grams of the sample and is used mostly by the chemical industry for stocks that have very low olefin contents.

Viscosity

Viscosity indicates the chemical composition of an oil sample. As the viscosity of a sample increases, paraffins increase, hydrogen content increases, and the aromatic fraction decreases.

Viscosity is normally measured at two different temperatures: typically 100°F (38°C) and 210°F (99°C). For many FCC feeds, the sample is too thick to flow at 100°F and the

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sample is heated to about 130°F. The viscosity data at two temperatures are plotted on a viscosity–temperature chart (see Appendix 1) which shows viscosity over a wide temperature range [4]. Viscosity is not a linear function of temperature, and the scales on these charts are adjusted to make the relationship linear.

Viscosity is a measurement of resistance to flow. Although the unit of absolute viscosity is *poise*, its measurement is difficult. Instead, kinematic (flowing) viscosity is determined by measuring the time for a given flow through a capillary tube of specific diameter and length. The unit of kinematic viscosity is *stoke*. However, in general practice, *centistoke* is used. Poise is related to stoke by the equation:

$$\text{Centistoke (cSt)} = \frac{\text{Centipoise}}{\text{Density}} \tag{3.3}$$

ASTM method D445 is used to measure kinematic viscosity. The kinematic viscosity values are reported in millimeters squared per second (mm^2/s), where 1 mm^2/s equals 1 cSt. ASTM D2161 method can be used to convert kinematic viscosity to Saybolt Universal seconds (SUS) at the same temperature and also to Saybolt Furol viscosity at 122°F and 210°F (50°C and 98.9°C). Kinematic viscosity values are based on water being 1.0034 mm^2/s (cSt) at 68°F (20°C).

Conradson, Ramsbottom, Microcarbon, and Heptane Insolubles

One area of cat cracking not fully understood is the proper determination of carbon residue of the feed and how it affects the unit's coke make. Carbon residue is defined as the carbonaceous residue formed after thermal destruction of a sample. Cat crackers are generally limited in coke burn capacity; therefore, the inclusion of residue in the feed produces more coke and forces a reduction in FCC throughput. Conventional gas oil feeds generally have a carbon residue <0.5 wt%; for feeds containing resid, the number can be as high as 15 wt%.

Four popular tests are presently used to measure carbon residue or concarbon of FCC feedstocks:

1. Conradson carbon residue (CCR)
2. Ramsbottom carbon residue (RCR)
3. Microcarbon residue (MCR)
4. Heptane insolubles.

The object is to indicate the relative coke-forming tendency of feedstocks. Each test has advantages and disadvantages, but none of them provide a rigorous definition of carbon residue or asphaltenes.

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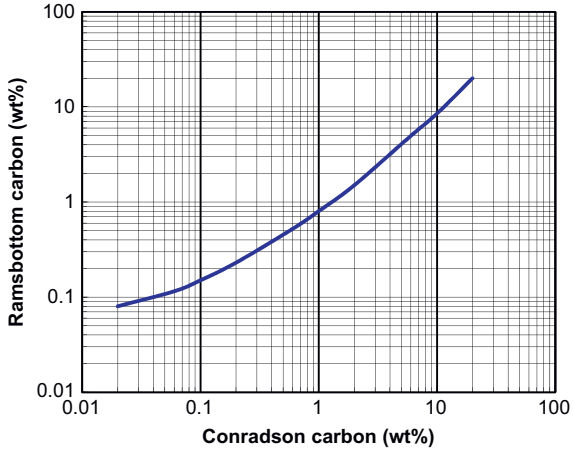


Figure 3.6: Ramsbottom carbon residue versus CCR. (*Copyright ASTM D524. Reprinted with permission.*)

The CCR test (ASTM D189) measures carbon residue by evaporative and destructive distillation. The sample is placed in a preweighed sample dish. The sample is heated, using a gas burner, until vapor ceases to burn and no blue smoke is observed. After cooling, the sample dish is reweighed to calculate the percent carbon residue. The test, though popular, is not a good measure of the coke-forming tendency of FCC feed. It indicates thermal, rather than catalytic, coke. In addition, the test is labor intensive and is usually not reproducible, and the procedure tends to be subjective.

The RCR test (ASTM D524) is also used to measure carbon residue. The test calls for introducing 4 g of sample into a preweighed glass bulb, then inserting the bulb in a heated bath for 20 min. The bath temperature is maintained at 1,027°F (553°C). After 20 min, the sample bulb is cooled and reweighed. Compared with the Conradson test, Ramsbottom is more precise and reproducible. Both tests produce similar results and often are interchangeable (Figure 3.6).

The MCR method uses an analytical instrument to measure Conradson carbon in a small automated set. The MCR (ASTM D4530) gives test results that are equivalent to the CCR test (ASTM D189). The purpose of this test is to provide some indication of the relative coke-forming tendency of such material.

The heptane insoluble (ASTM D3279) method is commonly used to measure the asphaltene content of the feed. Asphaltenes are clusters of PNA sheets, but no one has a clear understanding of their molecular structure. They are insoluble in C_3 to C_7 paraffins. The amount of asphaltenes that precipitates varies from one solvent to another, so it is important that the reported asphaltenes values be identified with the appropriate solvent. Both normal heptane and pentane insolubles are widely used for measuring asphaltenes.

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Although they do not provide rigorous definitions of asphaltenes, they provide practical ways of assessing coke precursors in FCC feedstocks. It should be noted that the traditional definition of asphaltenes is that they are heptane insoluble. Pentane insoluble minus heptane insoluble is the definition of resins. Resins are molecules larger than aromatics and smaller than asphaltenes.

Impurities

The concentration of impurities in the FCC feedstock largely depends on the crude oil quality, gas oil EP, and the severity of hydrotreating. The cat cracker, as the main conversion unit, is designed to handle a variety of feedstocks. However, these impurities have negative effects on unit performance. Understanding the nature and effects of these contaminants is essential in feed and catalyst selection as well as troubleshooting the unit.

Most of the impurities in the FCC feed exist as components of large organic molecules. The most common contaminants are:

- Nitrogen
- Sulfur
- Metals (nickel, vanadium, potassium, iron, calcium, copper).

Except for sulfur, all these contaminants poison the FCC catalyst, causing it to lose its ability to produce valuable products. Sulfur in the feed increases operating costs because additional feed and product treatment facilities are required to meet product specifications and comply with environmental regulations. Generally speaking, a higher concentration of sulfur within the feed correlates to greater fractions of aromatic molecules in the FCC feedstock.

Nitrogen

Nitrogen in the FCC feed refers to organic nitrogen compounds. The nitrogen content of FCC feed is often reported as *basic* and *total* nitrogen. Total nitrogen is the sum of basic and *nonbasic* nitrogen. Basic nitrogen is about one-fourth to one-half of total nitrogen.

The word “basic” denotes molecules that react with acids. Basic nitrogen compounds will neutralize acid sites on the catalyst. This causes a temporary loss of catalyst activity and a drop in unit conversion (Figure 3.7). However, nitrogen is a temporary poison. The burning of nitrogen in the regenerator restores the activity of the catalyst. In the regenerator, about 95% of the nitrogen in the coke is converted to elemental nitrogen. The remaining nitrogen is converted to nitrogen oxides (NO_x). The NO_x leaves the unit with the flue gas.

Catalyst poisoning from the presence of basic nitrogen in the FCC feedstock is significant, and unfortunately very little attention is often given to the deleterious effects of basic nitrogen. Virtually all the basic nitrogen ends up in coke. As shown in Figure 3.7, each 125 ppm of basic nitrogen lowers the unit conversion by 1 wt%. To compensate for nitrogen poisoning, the reactor temperature can be increased. In addition, an FCC catalyst with a high zeolite and active matrix content can be used to minimize the deleterious effects of the organic nitrogen.

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For some refiners, hydrotreating the feed may be an appropriate economical approach. Except for most of the California crudes and a few others, feeds with high nitrogen also have other impurities. Therefore, it is difficult to evaluate deleterious effects of nitrogen alone. Hydrotreating the feed reduces not only the nitrogen content but also most other contaminants.

Aside from catalyst poisoning, nitrogen is detrimental to the unit operation in several other areas. In the riser, some of the nitrogen is converted to ammonia and cyanide (H—CN). Cyanide accelerates the corrosion rate of the FCC gas plant equipment; it removes the protective sulfide scale and exposes bare metal to further corrosion. This corrosion generates atomic hydrogen that ultimately results in hydrogen blistering. Cyanide formation tends to increase with cracking severity.

In addition, some of the nitrogen compounds end up in LCO as pyrroles and pyridines [5]. These compounds are easily oxidized and will affect color stability. The amount of nitrogen in the LCO depends on the conversion. An increase in conversion decreases the percentage of nitrogen in the LCO and increases the percentage on the catalyst.

The source and gravity range of raw crude greatly influence the amount of nitrogen in the FCC feed (Table 3.2). Generally speaking, heavier crudes contain more nitrogen than the lighter crudes. In addition, nitrogen tends to concentrate in the residue portion of the crude. Figure 3.8 shows examples of nitrogen compounds found in crude oil.

UOP Test Method 269 is commonly employed to determine the basic nitrogen content of FCC feed. The feed sample is first mixed 50/50 with acetic acid. The mixture is then titrated with perchloric acid.

ASTM Method D5762 is often employed to measure the total nitrogen of the FCC feedstock in the range 40—10,000 ppm. For hydrocarbon liquid containing <100 ppm total nitrogen, D4629 test method is used.

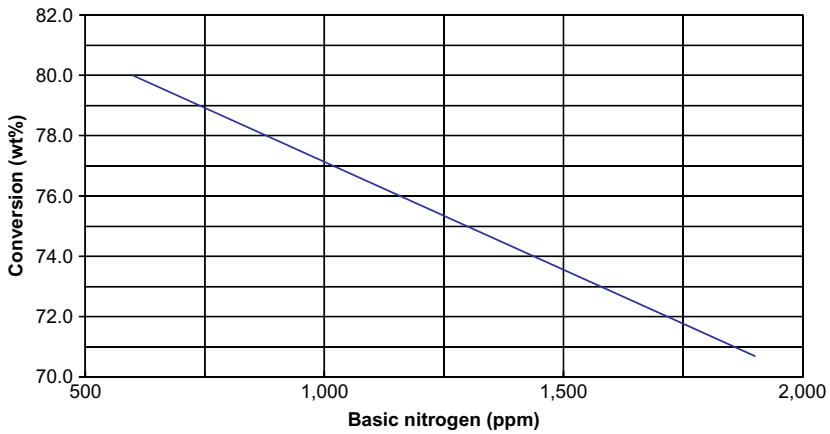
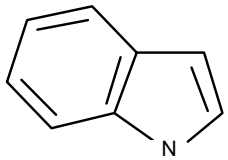


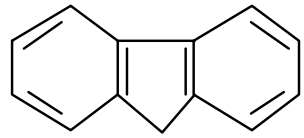
Figure 3.7: Effect of FCC feed nitrogen on unit conversion.

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(A) Neutral N–compounds

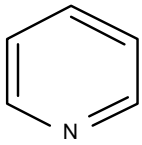


Indole

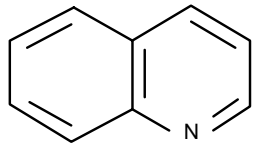


Carbazole

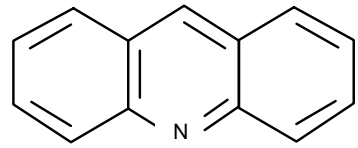
(B) Basic N–compounds



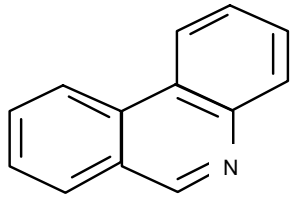
Pyridine



Quinoline

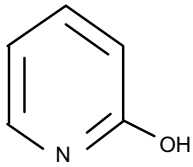


Acridine

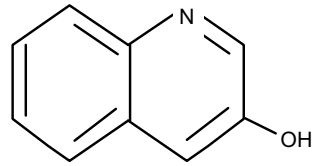


Phenanthridine

(C) Weakly basic N–compounds



Hydroxipyridine



Hydroxiquinilone

Derivatives with R = H, Alkyl-, phenyl-, naphthyl-

Nitrogen distribution in several Middle Eastern oils

Content: 20–25% of nitrogen in 225–540°C gas oil fraction
75-80% of nitrogen in 540°C plus vacuum resid fraction

Type: 225–540°C gas oil fraction: 50% of nitrogen as neutral nitrogen compounds, 33% as basic, 17% as weakly basic
540°C plus vacuum resid fraction: 20% of nitrogen in asphaltenes, 33% as neutral, 20% as basic, 27% as weakly basic

Figure 3.8: Types of nitrogen compounds in crude oil [6].

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Table 3.2: API Gravity, Residue, and Nitrogen Content of Typical Crudes.

Crude Source	API Gravity	Vacuum Bottoms (vol %)	Total Nitrogen* of Heavy Vacuum Gas Oil (ppm)
Maya	21.6	33.5	2,498
Alaska North Slope (ANS)	28.4	20.4	1,845
Arabian Medium	28.7	23.4	829
Forcados	29.5	7.6	1,746
Cabinda	32.5	23.1	1,504
Arabian Light	32.7	17.2	1,047
Bonny Light	35.1	5.3	1,964
Brent	38.4	11.4	1,450
West Texas Intermediate Cushing (WTIC)	38.7	10.6	951
Forties	39.0	10.1	1,407

*Nitrogen level varies with crude source and residue content.

Sulfur

FCC feedstocks contain sulfur in the form of organic sulfur compounds such as mercaptan, sulfide, and thiophenes. Frequently, as the residue content of crude oil increases, so does the sulfur content (Table 3.3). Total sulfur in FCC feed is determined by the wavelength dispersive X-ray fluorescence spectrometry method (ASTM D2622). The results are expressed as elemental sulfur.

Although desulfurization is not the goal of cat cracking operations, $\sim$30–50% of sulfur in the feed is converted to H_2S. In addition, the remaining sulfur compounds in the FCC products are lighter and can be desulfurized by low-pressure hydrodesulfurization processing.

In the FCC, H_2S is formed principally by the catalytic decomposition of nonthiophenic (nonring) sulfur compounds. Table 3.4 shows the effects of feedstock sulfur compounds on H_2S production.

As with H_2S, the distribution of sulfur among the other FCC products depends on several factors, which include feed quality, catalyst type, conversion, and operating conditions. Feed type and residence time are the most significant variables. Sulfur distribution in FCC products of several feedstocks is shown in Table 3.5. Figure 3.9 illustrates the sulfur distribution as a function of the unit conversion.

For nonhydrotreated feeds at 78 vol% conversion, about 50 wt% of the sulfur in the feed is converted to hydrogen sulfide (H_2S). The remaining 50% of the sulfur is distributed approximately as follows:

- 6 wt% in gasoline
- 23 wt% in LCO
- 15 wt% in DO
- 6 wt% in coke.

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Table 3.3: API Gravity, Residue, and Sulfur Content of Some Typical Crudes.

Crude Source	API Gravity	Vacuum Bottoms (vol %)	Sulfur Content of Vacuum Gas Oil (wt%)*
Maya	21.6	33.5	3.35
Alaska North Slope (ANS)	28.4	20.4	1.45
Arabian Medium	28.7	23.4	3.19
Forcados	29.5	7.6	0.30
Cabinda	32.5	23.1	0.16
Arabian Light	32.7	17.2	2.75
Bonny Light	35.1	5.3	0.25
Brent	38.4	11.4	0.63
West Texas Intermediate Cushing (WTIC)	38.7	10.6	0.63
Forties	39.0	10.1	0.61

*Sulfur level varies with crude source and residue content.

Table 3.4: Effects of Feedstock Sulfur Compounds on H_2S Production.

Cracking Conditions: 7 Cat/Oil Ratio, 950°F, Zeolite Catalyst			
Feed Source	Conversion (vol%)	% of Feed Sulfur which is Mercaptan or Sulfide and not Aromatic in Nature	Vol% of Sulfur Converted* to H_2S
Mid Continent	72	38	47
West Texas	69	33	41
Coker Gas Oil	56	30	35
Hydrotreated West Texas HCO	77	12	26
	50	6	16

*The % sulfur converted to H_2S depends largely on the type of sulfur in the feed and the residence time of the hydrocarbons in the riser [1].
Source: Wollaston [7].

Adding residue to the feed increases the sulfur content of coke proportional to the incremental sulfur in the feed (Table 3.6). Thiophenic (ring-type) sulfur compounds crack more slowly, and the uncracked thiophenes end up in gasoline, LCO, and DO.

Hydrotreating reduces the sulfur content of all the products. With hydrotreated feeds, more of the feed sulfur goes to coke and heavy liquid products. The same sulfur atoms that were converted to H_2S in the FCC process are also being removed first in the hydrotreating process. The remaining sulfur compounds are harder to remove. The heavier and more aromatic the feedstock, the greater the level of sulfur in the coke (Table 3.7).

Although hydrotreating increases the percentage of sulfur in coke and slurry, the actual amount of sulfur is substantially less than in the nontreated feeds. Sulfur still plays a minor role in unit conversion and yields. Its effect on processing is minimal. Some aromatic sulfur compounds do not convert, but this is no different from other aromatic compounds. They become predominately cycle oil and slurry. This tends to lower conversion and reduce maximum yields.

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Table 3.5: Sulfur Distribution in FCC Products.

Feedstock Sources				
Feedstock	**West Texas Virgin Gas Oil**	**West Texas Virgin Gas Oil (HDT)**	**California Gas Oil**	**Kuwait DAO & Gas Oil Blend (HDT)**
Sulfur content (wt%)	1.75	0.21	1.15	3.14
Conversion (vol%)	77.8	77.8	78.7	80.1
Sulfur Distribution (wt% of Feed Sulfur)				
H_2S	42.9	19.2	60.2	50.0
Light gasoline	0.2	0.9	1.6	1.9
Heavy gasoline	3.3	1.9	7.9	5.0
LCO	28.0	34.6	20.7	17.3
DO	20.5	34.7	6.8	15.3
Coke	5.1	8.7	2.8	10.3

Source: Huling [8].

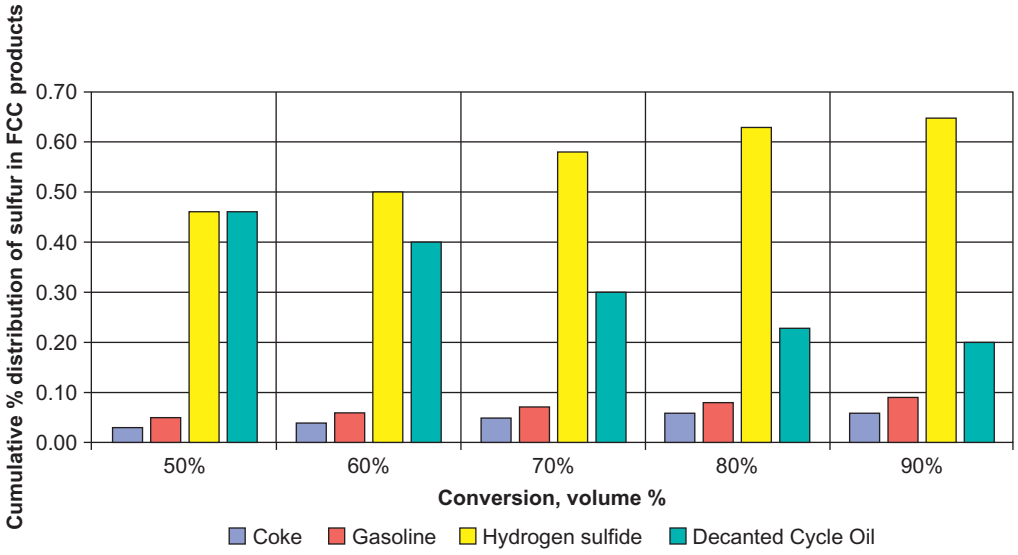


Figure 3.9: Sulfur distribution of the FCC products as a function of unit conversion.

Table 3.6: Sulfur Content of Coke Versus Quantity of Residue in FCC Feed.*

Pilot Plant Data, Riser Cracking for Maximum Liquid Recovery		
Feedstock Source	**Feed Sulfur (wt%)**	**Sulfur in Coke (wt% of Feed Sulfur)**
Gas oil	0.7	3.5
Gas oil +10% of West Texas Sour VTB	1.0	13.8
Gas oil +20% of West Texas Sour VTB	1.32	18.6

*As the residue content of the feed is increased, there is a marked increase in the coke's sulfur due to higher coke yield and a higher sulfur content of the coke precursors.

Source: Campagna [9].

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Table 3.7: Sulfur Content of Coke Versus Hydrotreated* FCC Quality.

Pilot Plant Data, Riser Cracking for Maximum Liquid Recovery			
Feedstock Source	**Feedstock Sulfur (wt%)**	**Hydrocarbon Type % Triaromatics***	**Sulfur in Coke (wt% of Feed Sulfur)**
Light Arabian HDS	0.21	7.3	28.1
Heavy Arabian HDS	0.37	17.6	48.2
Maya HDS	0.70	5.0	43.7

*In a hydrotreated feed, the more polyaromatic type sulfur compounds, the more sulfur ends up in coke.
Source: Campagna [9].

Metals

Metals, such as nickel, vanadium, and sodium, are present in crude oil. These metals are often concentrated in the heavy boiling range of atmospheric bottoms or vacuum residue, unless they are carried over with the gas oil by entrainment.

These metals are catalysts themselves and promote undesirable reactions such as dehydrogenation and condensation. Dehydrogenation means the removal of hydrogen; condensation means polymerization, which is the formation of "chicken wire" aromatic molecules. Hydrogen and coke yields are increased, and gasoline yields are reduced. Metals reduce the catalyst's ability to produce the desired products.

These metals permanently poison the FCC catalyst by lowering the catalyst activity, thereby reducing its ability to produce the desired products. Virtually all the metals in the FCC feed are deposited on the cracking catalyst. Paraffinic feeds tend to contain more nickel than vanadium. Each metal has negative effects.

Nickel (Ni)

As discussed in Chapter 4, an FCC catalyst has two parts:

1. The nonframework structure called matrix
2. The crystalline structure called zeolite.

In contact with the catalyst, nickel deposits on the matrix. Nickel promotes dehydrogenation reactions, removing hydrogen from stable compounds and making unstable olefins, which can polymerize to heavy hydrocarbons. These reactions result in high hydrogen and coke yields. The higher coke causes higher regenerator temperatures. This lowers the catalyst to oil ratio and lowers conversion.

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High nickel levels are normally encountered when processing heavy feed. Neither excess hydrogen nor excess regenerator temperature is desirable. Excess hydrogen lowers the molecular weight of the wet gas; since the compressor is usually centrifugal, this limits the discharge pressure. Lower pressure means less capacity and this can force a reduction in charge or operation at lower conversion.

A number of indices relate metal activity to hydrogen and coke production. (These indices predate the use of metal passivation in the FCC process but are still reliable.) The most commonly used index is 4 × nickel + vanadium. This indicates that nickel is four times as active as vanadium in producing hydrogen. Other indices [10] used are:

$$\text{Jersey nickel equivalent index} = 1{,}000 \times (\text{Ni} + 0.2 \times \text{V} + 0.1 \times \text{Fe}) \tag{3.4}$$

$$\text{Shell contamination index} = 1{,}000 \times (14 \times \text{Ni} + 14 \times \text{Cu} + 4 \times \text{V} + \text{Fe}) \tag{3.5}$$

$$\text{Davison index} = \text{Ni} + \text{Cu} + \frac{\text{V}}{4} \tag{3.6}$$

$$\text{Mobil index} = \text{Ni} + \frac{\text{V}}{4} \tag{3.7}$$

In every equation, nickel is the most active. These indices convert all metals to a common basis, generally either vanadium or nickel.

Metals are most active when they first deposit on the catalyst. With time, they lose their initial effectiveness through continuous oxidation−reduction cycles. On the average, about one-third of the nickel on the equilibrium catalyst will have the activity to promote dehydrogenation reactions.

A small amount of nickel in the FCC feed has a significant influence on the unit operation. In a "clean" gas oil operation, the hydrogen yield is about 40 standard cubic feet (scf) per barrel of feed (0.07 wt%). This is a manageable rate that most units can handle. If the nickel level increases to 1.5 ppm, the hydrogen yield increases up to 100 scf per barrel (0.17 wt%). Note that in a 50,000 barrel/day unit, this corresponds to a mere 16 pounds (7.3 kg) per day of nickel. Unless the catalyst addition rate is increased or the nickel in the feed is passivated (see Chapter 4), the feed rate or conversion may need to be reduced. The wet gas will become lean and may limit the pumping capacity of the WGC.

In most units, the increase in hydrogen make does not increase coke yield; the coke yield in a cat cracker is constant (Chapter 7). The coke yield does not go up because of other unit constraints, such as the regenerator temperature and/or WGC which require the operator to reduce charge or severity. High hydrogen yield also affects the recovery of C_3+ components in the gas plant. Hydrogen works as an inert and changes the liquid−vapor ratio in the absorbers.

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On a wt% basis, the increase in hydrogen is negligible, but the sharp increase in gas volume impacts unit performance.

Catalyst composition and feed chloride have a noticeable impact on hydrogen yield. Catalysts with an active alumina matrix tend to increase the dehydrogenation reactions. Chlorides in the feed reactivate aged nickel, resulting in high hydrogen yield.

Two common indicators track the effects of nickel on the catalyst. These are:

1. Hydrogen/methane ratio
2. Volume of hydrogen per barrel of feed.

The H_2/CH_4 ratio is an indicator of dehydrogenation reactions. But the ratio is sensitive to the reactor temperature and the type of catalyst. A better indicator of nickel activity is the volume of hydrogen per barrel of fresh feed. The typical H_2/CH_4 mole ratio for a gas oil having $<$0.5 ppm nickel is between 0.25 and 0.35. The equivalent H_2 make is between 30 and 40 scf/bbl of feed.

It is usually more accurate to back-calculate the feed metals from the equilibrium catalyst data than to analyze the feed regularly. If nickel will be a regular component of the feed, passivators are available. If nickel affects operation and margins, it is often beneficial to use antimony to passivate the nickel. This can be particularly attractive if the nickel on the equilibrium catalyst is $>$1,000 ppm.

Vanadium

Vanadium also promotes dehydrogenation reactions, but less than nickel. Vanadium's contribution to hydrogen yield is 20−50% of nickel's contribution, but vanadium is a more severe poison. Unlike nickel, vanadium does not stay on the surface of the catalyst. Instead, it migrates to the inner (zeolite) part of the catalyst and destroys the zeolite crystal structure. Catalyst surface area and activity are permanently lost.

Vanadium occurs as part of organometallic molecules of high molecular weight. When these heavy molecules are cracked, coke residue containing vanadium is left on the catalyst. During regeneration, the coke is burned off and vanadium is converted to vanadium oxides such as vanadium pentoxide (V_2O_5). V_2O_5 melts at 1,274°F (690°C) which allows it to destroy zeolite under typical regenerator temperature conditions. V_2O_5 is highly mobile and can go from one particle to another.

There are several theories about the chemistry of vanadium poisoning. The most prominent involves conversion of V_2O_5 to vanadic acid (H_3VO_4) under regenerator conditions. Vanadic acid, through hydrolysis, extracts the tetrahedral alumina in the zeolite crystal structure, causing it to collapse.

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The severity of vanadium poisoning depends on the following factors:

1. *Vanadium concentration:* In general, vanadium concentrations above 2,000 ppm on the E-cat can justify passivation.
2. *Regenerator temperature:* Higher regenerator temperatures (>1,250°F or 677°C) exceed the melting point of vanadium oxides, increasing their mobility. This allows vanadium to find zeolite sites. This deactivation is in addition to the hydrothermal deactivation caused by higher regenerator temperature alone.
3. *Combustion mode:* Regenerators operating in full combustion and producing "clean" catalyst (Figure 3.10) increase vanadium pentoxide formation because of the excess oxygen.
4. *Sodium:* Sodium and vanadium react to form sodium vanadates. These mixtures have a low melting point (<1,200°F or 649°C) and increase vanadium mobility.
5. *Steam:* Steam reacts with V_2O_5 to form volatile vanadic acid. Vanadic acid, through hydrolysis, causes collapse of the zeolite crystal.
6. *Catalyst type:* The alumina content, the amount of rare earth, and the type and amount of zeolite affect catalyst tolerance to vanadium poisoning.
7. *Catalyst addition rate:* A higher catalyst addition rate (fresh and/or purchased E-cat) dilutes the concentration of metals and allows less time for the vanadium to get fully oxidized.

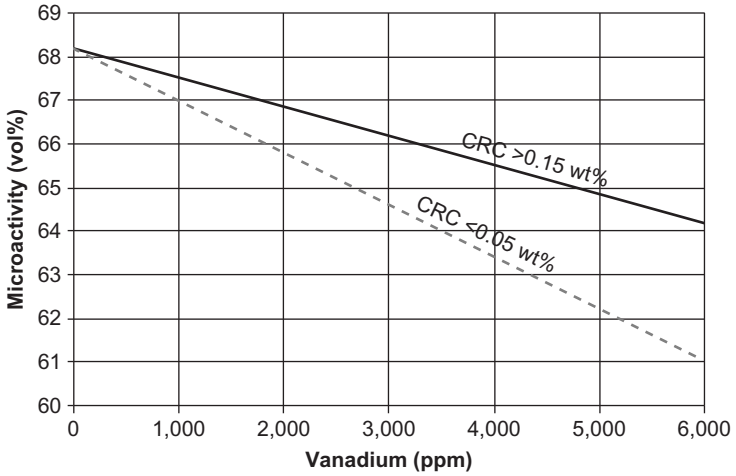


Figure 3.10: Vanadium deactivation varies with regenerator severity [11].

Alkaline Earth Metals

Alkaline earth metals in general and sodium in particular are detrimental to the FCC catalyst. Sodium permanently deactivates the catalyst by neutralizing its acid sites. In the regenerator, it causes the zeolite to collapse, particularly in the presence of vanadium. Sodium comes from two prime sources:

1. Sodium in the fresh catalyst
2. Sodium in the feed.

Fresh catalyst contains sodium as part of the manufacturing process. Chapter 4 discusses the drawbacks of sodium that are inherent in the fresh catalyst.

Sodium in the feed is called *added sodium*. For all practical purposes, the adverse effects of sodium are the same regardless of its origin.

Sodium usually appears in the form of sodium chloride. Chlorides tend to reactivate aged metals by redistributing the metals on the equilibrium catalyst and allowing them to cause more damage.

Sodium originates from the following places:

- *Caustic that is added downstream of the crude oil desalter.* Caustic is injected downstream of the desalter to control overhead corrosion. Natural chloride salts in crude decompose to HCl at typical unit temperatures. Caustic reacts with these salts to form sodium chloride. Sodium chloride is thermally stable at the temperature found in the crude and vacuum unit heaters. This results in sodium chloride being present in either atmospheric or vacuum resids. Most refiners discontinue caustic injection when they process residue to the FCC unit. However, it can still be present in purchased feedstocks.
- *Water-soluble salts that are carried over from the desalter.* An effective desalting operation is more important than ever when processing heavy feedstocks to the cat cracker. Chloride salts are usually water soluble and are removed from raw crude in the desalter. However, some of these salts can be carried over with desalted crude.
- *Processing of the refinery "slop."* A number of refiners process the refinery slop in their desalter. This can adversely affect the desalter and carry over salts with the desalted crude. Slop can be fed to the coker or FCC main fractionator with the same result.
- *Purchased FCC feedstock can be exposed to salt water as ballast.*
- *The use of atomizing steam and/or water that contain sodium.* Just about every refiner practices some type of feed atomization using either steam or water. The steam or water can contain varying amounts of sodium depending on the quality of water treatment used in the refinery.

Other Metals

Iron is usually present in FCC feed as *tramp iron* and is not catalytically active. Tramp iron refers to various corrosion by-products from upstream processing and handling. Potassium and calcium are also metals that can deactivate the FCC catalyst.

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Copper is another poison to the FCC catalyst that has more than twice the activity of nickel in dehydrogenation. Some NO_x-reducing additives contain copper, which adversely impacts the FCC reactor yields.

Summary

The metals in the FCC feed have many deleterious effects. Nickel and copper cause excess hydrogen production, forcing eventual loss in the conversion or throughput. Both vanadium and sodium destroy catalyst structure, causing losses in activity and selectivity. Solving the undesirable effects of metal poisoning involves several approaches:

- Hydrotreating the FCC feed
- Increasing the makeup rate of fresh catalyst
- Adding good-quality equilibrium catalysts to flush the metals
- Employing some type of metal passivation (antimony for nickel and metal trap for vanadium).

Empirical Correlations

The typical refinery laboratory is not equipped to conduct PONA and other chemical analyses of the FCC feed on a routine basis. However, physical properties such as API gravity and distillation are easy to measure. As a result, empirical correlations have been developed by the industry to determine chemical properties from these physical analyses.

Characterizing FCC feed provides quantitative and qualitative estimates of the FCC unit's performance. Process modeling uses the feed properties to predict FCC yields and product qualities. The process model should be used in daily unit monitoring, catalyst evaluations, optimization, and process studies.

There are no standard correlations. Some companies have proprietary correlations, but this does not mean that these correlations do a better job at predicting yields. Nonetheless, they all incorporate most or some of the same physical properties. Today, the most widely published correlations in use are:

- *K*-factor
- TOTAL
- $n-d-M$ method
- API method.

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K-*Factor*

The *K*-factor is a very useful indication of feed crackability. The *K*-factor relates to the hydrogen content of the feed. It is normally calculated using feed distillation and gravity data, and measures aromaticity relative to paraffinicity. Higher *K*-values indicate increased paraffinicity and more crackability. A *K*-value above 12.0 indicates a paraffinic feed; a *K*-value below 11.0, aromatic.

Like aniline point, the *K*-factor differentiates between the highly paraffinic and aromatic stocks. However, within the narrow range $K = 11.5-12.0$, the *K*-factor does not correlate between aromatics and naphthenes. Instead, it relates fairly well to the paraffin content (Figure 3.11). The *K*-factor does not provide information as to the ratio of naphthene and paraffin contents. The ratio of naphthenes to paraffins can vary considerably with the same *K*-values (Table 3.8).

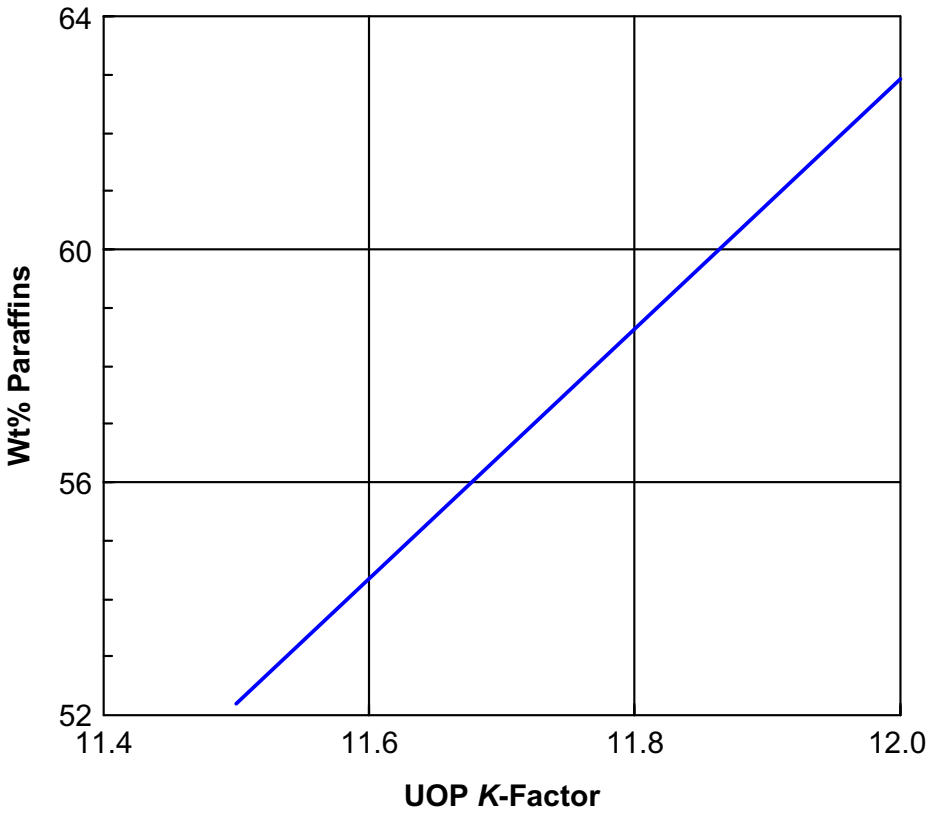


Figure 3.11: Weight percent paraffins at various K_{UOP} factors.

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Table 3.8: Variation of C_N/C_P as a Function of K_{UOP} Factor.*

Sample No.	K_{UOP} Factor	$C_A + C_N$ (wt%)	C_N/C_P
1	11.70	46	0.47
2	11.69	45	0.44
3	11.70	46	0.44
4	11.67	45	0.43
5	11.70	45	0.39
6	11.70	44	0.35
7	11.70	42	0.33

*The *K*-factor relates well to aromatics + naphthenes, but not to naphthenes.
C_A = aromatic content, C_N = naphthenic content, C_P = paraffin content. Source: Andreasson [12].

K-value is the ratio of the cube root of a boiling temperature to gravity. There are two widely used methods to calculate the *K*-factor: K_W (the Watson method) and K_{UOP}. The equations used for calculating both factors are shown below (see Eqs. (3.8)−(3.14)):

$$K_W = \frac{(\text{MeABP} + 460)^{1/3}}{\text{SG}} \tag{3.8}$$

$$K_{\text{UOP}} = \frac{(\text{CABP} + 460)^{1/3}}{\text{SG}} \tag{3.9}$$

$$K_{\text{UOP}} = \frac{(\text{VABP} + 460)^{1/3}}{\text{SG}} \tag{3.10}$$

where:

MeABP = mean average boiling point (°F);
MABP = molar average boiling point (°F);
CABP = cubic average boiling point (°F);
SG = specific gravity at 60°F;
VABP = volumetric average boiling point (°F);
f_{mi} = mole fraction of component *i*;
TB_i = normal boiling point of pure component *i* (°F);
f_{vi} = volume fraction of component *i*;
T = temperature (°F).

$$\text{MeABP} = \frac{(\text{MABP} + \text{CABP})}{2} \tag{3.11}$$

$$\text{MABP} = \sum (f_{mi} \times \text{TB}_i) \tag{3.12}$$

$$\text{CABP} = \sum (f_{vi} \times \text{TB}_i^{1/3})^3 \tag{3.13}$$

$$\text{VABP} = \frac{(T(10\%) + T(30\%) + T(50\%) + T(70\%) + T(90\%))}{5} \tag{3.14}$$

The UOP method uses CABP, which, for all practical purposes, is the same as VABP, as shown in Appendix 2. The K_{UOP} factor is more popular than K_W because the VABP data are readily available. The use of MeABP in the Watson method generally results in a lower K-value than that of UOP. Example 3.1 illustrates steps to calculate the K_{UOP} and K_W factors.

In summary, the K-factor can provide information about the aromaticity or paraffinicity of the feed. However, within the narrow range $K = 11.5-12.0$, it cannot differentiate between the ratio of paraffins, naphthenes, and aromatics. To determine these ratios, other correlations, such as TOTAL or $n-d-M$, should be employed.

Example 3.1

Determine K_{UOP} and Watson K_W using the following FCC feed properties:

Feed Properties

		°F	°C
API gravity	23.5	60	15.6
SG	0.913	60	15.6
Density	0.900	68	20
Refractive index	1.4810	152.6	67
Viscosity (SUS)	137.0	130	54.4
Viscosity (SUS)	50.0 (7.27 cSt*)	210	98.9
Sulfur (wt%)	0.48		
Aniline point		192.0	88.9

**See ASTM D2161-10 to convert SUS to cSt.*

D1160 at 1 atm

Vol%	Temperature (°F)	Temperature (°C)
10	652	344
30	751	399
50	835	446
70	935	502
90	1,080	582

Procedure (steps provided below)

1. Calculate VABP from distillation data.
2. Calculate the 10 −90% slope.
3. Calculate MeABP and CABP by adding corrections from Appendix 2 to VABP.
4. Calculate K_{W} and K_{UOP}.

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Step 1: VABP = 1/5(652 + 751 + 835 + 935 + 1,080)

$$\text{VABP} = 851^\circ\text{F} = 455^\circ\text{C} = 728.2^\circ\text{K}$$

Step 2: 10−90% slope

$$\text{Slope} = \frac{T_{90} - T_{10}}{80} = \frac{1,080 - 652}{80}$$

$$\text{Slope} = 5.35\%$$

Step 3: From Appendix 2, corrections to VABP are ∼−34°F for MeABP and −10°F for CABP.

Therefore:

$$\begin{aligned}\text{MeABP} &= 851 - 34 = 817^\circ\text{F} = 436^\circ\text{C}\\ \text{CABP} &= 851 - 10 = 841^\circ\text{F} = 449.4^\circ\text{C}\end{aligned}$$

Step 4:

$$K_W = \frac{(817 + 460)^{1/3}}{0.913} = 11.88$$

$$K_{\text{UOP}} = \frac{(841 + 460)^{1/3}}{0.913} = 11.96$$

Instead of using Appendix 2, the MeABP can be determined from the following equation [6]:

$$\text{MeABP} = \text{VABP} + 2 - \left(\frac{(T_{90} - T_{10})}{170 + 0.075 \times \text{VABP}} + 1.5\right)^3$$

$$\text{MeABP} = 851 + 2 - \left(\frac{1,080 - 652}{170 + (0.075 \times 851)} + 1.5\right)^3$$

$$\text{MeABP} = 816^\circ\text{F}\ (435^\circ\text{C})$$

In the absence of full distillation data, the *K*-factor can be estimated using the 50% point in place of MeABP.

TOTAL

The TOTAL correlations calculate aromatic carbon content, hydrogen content, molecular weight, and RI using routine laboratory tests. The TOTAL correlations are listed below and are also in Appendix 3. Example 3.2 illustrates the use of TOTAL correlations [1].

For FCC feeds, particularly the ones containing residue, the TOTAL correlation is more accurate at predicting aromatic carbon content than the *n*−*d*−*M* correlation. Table 3.9 illustrates this comparison. One option is to calculate MW, $\text{RI}_{(20)}$, C_A, and H_2 from the

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Table 3.9: Comparison of TOTAL Correlations with Other Methods.

Correlation	Average Deviation	Absolute Average Deviation	Bias Maximum Deviation
Carbon content (% C)			
n−*d*−*M*	5.14	4.67	12.99
API	2.88	2.53	9.13
TOTAL	0.93	0.00	3.45
Hydrogen content (% H)			
Linden	0.31	−0.05	1.57
Fein−Wilson−Winn	0.36	0.19	1.43
Modified Winn	0.19	0.07	0.86
TOTAL	0.10	0.00	0.42
Molecular weight (MW)			
API	62.0	−62.0	180.9
Maxwell	63.3	−63.6	175.0
Kester−Lee	61.5	−61.1	176.9
TOTAL	10.6	−0.20	44.4
Refractive index (RI)			
API at 20°C	0.0368	−0.0367	0.0993
Lindee−Whitter at 20°C	0.0315	−0.0131	0.0303
TOTAL at 20°C	0.0021	0.0	0.0074
TOTAL at 60°C	0.0021	0.0	0.0074

Source: Dhulesia [1].

TOTAL correlation, and use either the *n*−*d*−*M* or API method to calculate the wt% naphthene (C_N) and wt% paraffin (C_P).

Example 3.2

Molecular weight (MW)

$$\begin{aligned} MW &= 7.8312 \times 10^{-3} \times SG^{-0.09768} \times (AP, {}^{\circ}C)^{0.1238} \times (VABP, {}^{\circ}C)^{1.6971} \\ MW &= 7.8312 \times 10^{-3} \times (0.913)^{-0.0978} \times (88.9)^{0.1238} \times (455)^{1.6971} \\ MW &= (7.8312 \times 10^{-3}) \times (1.0089) \times (1.7429) \times (32{,}427) \\ MW &= 446.6 \end{aligned} \tag{3.15}$$

RI at 20°C (68°F)

$$\begin{aligned} RI_{(20)} &= 1 + 0.8447 \times SG^{1.2056} \times (VABP, {}^{\circ}C + 273.16)^{-0.0557} \times MW^{-0.0044} \\ RI_{(20)} &= 1 + 0.8447 \times (0.913)^{1.2056} \times (728.2)^{-0.0557} \times (446.6)^{-0.0044} \\ RI_{(20)} &= 1 + 0.8447 \times 0.8961 \times 0.6927 \times 0.97351 \\ RI_{(20)} &= 1.5105 \end{aligned} \tag{3.16}$$

RI at 60°C (140°F)

$$\begin{aligned} RI_{(60)} &= 1 + 0.8156 \times SG^{1.2392} \times (VABP, {}^{\circ}C + 273.16)^{-0.0576} \times MW^{-0.0007} \\ RI_{(60)} &= 1 + 0.8156 \times (0.913)^{1.2392} \times (728.2)^{-0.0576} \times (446.6)^{-0.0007} \\ RI_{(60)} &= 1 + 0.8156 \times 0.8933 \times 0.6841 \times 0.9957 \\ RI_{(60)} &= 1.4963 \end{aligned} \tag{3.17}$$

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Hydrogen (H_2) content (wt%)

$$H_2 = 52.825 - 14.26 \times RI_{(20)} - 21.329 \times SG - 0.0024 \times MW - 0.052 \times S + 0.757 \times \ln(V)$$
$$H_2 = 52.825 - 14.26 \times 1.5105 - (21.329 \times 0.913) - (0.0024 \times 446.6) - (0.052 \times 0.48) + (0.757 \times \ln(7.27))$$
$$H_2 = 12.22\text{wt\%} \quad (3.18)$$

Aromatic (C_A) content (wt%)

$$C_A = -814.136 + (635.192 \times RI_{(20)}) - (129.266 \times SG) + (0.013 \times MW) - (0.34 \times S) - (6.872 \times \ln(V))$$
$$C_A = -814.136 + (635.192 \times 1.5105) - (129.266 \times 0.913) + (0.013 \times 446.6) - (0.34 \times 0.48) - (6.872 \times \ln(7.27))$$
$$C_A = 19.31\text{wt\%} \quad (3.19)$$

where:

SG = specific gravity at 20°C (68°F);
AP = aniline point (°C);
VABP = volumetric average boiling point (°C);
S = sulfur (wt%);
V = viscosity at 98.9°C (210°F) (cSt).

n−d−M Method

The $n-d-M$ correlation is an ASTM (D3238) method that uses RI (n), density (d), average molecular weight (MW), and sulfur (S) to estimate the percentage of total carbon distribution in the aromatic ring structure ($\%C_A$), naphthenic ring structure ($\%C_N$), and paraffin chains ($\%C_P$). Both RI and density are either measured or estimated at 20°C (68°F). Appendix 4 shows formulas used to calculate carbon distribution. Note that the $n-d-M$ method calculates, for example, the percent of carbon in the aromatic ring structure. For instance, if there was a toluene molecule in the feed, the $n-d-M$ method predicts six aromatic carbons (86%) versus the actual seven carbons.

ASTM D2502 is one of the most accurate methods of determining molecular weight. The method uses viscosity measurements; in the absence of viscosity data, molecular weight can be estimated using the TOTAL correlation.

The $n-d-M$ method is very sensitive to both RI and density. It calls for measurement or estimation of the feed RI at 20°C (68°F). The problem is that the majority of FCC feeds are virtually solid at 20°C and the refractometer is unable to measure the RI at this temperature. To use the $n-d-M$ method, RI at 20°C needs to be estimated using published correlations. For this reason, the $n-d-M$ method is usually employed in conjunction with other correlations such as TOTAL. Example 3.3 can be used to illustrate the use of the $n-d-M$ correlations.

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Example 3.3

Using the feed property data in Example 3.1, determine MW, C_A, C_N, and C_P using the *n*–*d*–*M* method (see Appendix 4).

Step 1: Molecular weight determination by ASTM method.

1. Obtain viscosity at 100°F (37.8°C):
   a. Plot cSt viscosities at 130°F (54.4°C) 137 SUS (27.9 cSt) and 210°F (98.89°C) 50 SUS (7.27 cSt), using Appendix 1
   b. Extrapolate to 100°F, viscosity = 280 SUS (60.2 cSt).
2. Convert viscosities from centistoke (cSt) to SUS:
   a. From Appendix 6, viscosity at 100°F = 60.2 cSt
   b. Viscosity at 210°F = 7.27 cSt.
3. Obtain molecular weight:
   a. From Appendix 5, H function = 372 and MW = 440.

Step 2: Calculate RI at 20°C from the TOTAL correlation.

$$\begin{aligned} RI_{(20)} &= 1 + 0.8447 \times SG^{1.2056} \times (VABP, {}^\circ C) + 273.16)^{-0.0557} \times MW^{-0.0044} \\ RI_{(20)} &= 1 + 0.8447 \times (0.913)^{1.2056} \times (728.2)^{-0.0557} \times (446.6)^{-0.0044} \\ RI_{(20)} &= 1.5105 \end{aligned} \tag{3.20}$$

Step 3: Calculate *n*–*d*–*M* factors.

$$\begin{aligned} \nu &= 2.51 \times (RI_{(20)} - 1.4750) - (d_{20} - 0.8510) \\ \nu &= 2.51 \times (1.5105 - 1.4750) - (0.90 - 0.8510) \\ \nu &= 0.0401 \text{ positive} \\ \omega &= (d_{20} - 0.8510) - 1.11\,(RI_{(20)} - 1.4750) \\ \omega &= (0.90 - 0.8510) - 1.11 \times (1.5105 - 1.4750) \\ \omega &= 0.0096 \text{ positive} \end{aligned} \tag{3.21}$$

Because ν is positive, calculate % aromatic ring structures:

$$\begin{aligned} \%C_A &= (430 \times \nu) + 3{,}600/MW \\ \%C_A &= (430 \times 0.0401) + (3{,}600/440) \\ \%C_A &= 25.6 \end{aligned} \tag{3.21a}$$

Because ω is positive, calculate % ring compounds in crude:

$$\begin{aligned} \%C_R &= 820 \times \omega - (3 \times S) + \frac{10{,}000}{MW} \\ \%C_R &= 820 \times 0.0226 - 3 \times 0.48 + \frac{10{,}000}{430} \\ \%C_R &= 29.2 \end{aligned} \tag{3.21b}$$

Calculate % of naphthenic compounds in crude:

$$\begin{aligned} \%C_N &= \%C_R - \%C_A \\ \%C_N &= 29.2 - 25.6 \\ \%C_N &= 3.6 \end{aligned} \tag{3.21c}$$

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Calculate % of paraffin chains in crude:

$$\%C_P = 100 - \%C_R$$
$$\%C_P = 100 - 29.2 \qquad (3.21d)$$
$$\%C_P = 70.8$$

API Method

The API method is a generalized method that predicts mole fraction of paraffinic, naphthenic, or aromatic compounds for an olefin-free hydrocarbon. The development of the equations is based on dividing the hydrocarbon into two molecular ranges: heavy fractions (200<MW<600) and light fractions (70<MW<200). Appendix 7 contains API correlations applicable to the FCC feed. Example 3.4 can be used to illustrate the use of the API correlations.

Example 3.4

Use the feed property data in Example 3.1 to calculate MW, $RI_{(20)}$, X_A, X_N, and X_P (the mole fractions of aromatics, naphthenes and paraffins, respectively), employing API correlations (see Appendix 7).

Calculate MW

$$\begin{aligned} MW &= a \times \exp(b \times MeABP + c \times SG + d \times MeABP \times SG) \times MeABP^e \times SG^f \\ MW &= 20.486 \times \exp(1.165 \times 10^{-4} \times 1,277 - 7.787 \times 0.913 + 1.1582 \times 10^{-3} \\ &\quad \times 0.913 \times 1,277) \times (1,277)^{1.26807} \times (0.913)^{4.98308} \\ &= 20.486 \times \exp(0.14877 - 7.10953 + 1.3503) \times 8,686.95 \times 0.6354 \\ &= 20.486 \times 0.00365955 \times 8,686.95 \times 0.6354 \\ MW &= 413.8 \end{aligned} \qquad (3.22)$$

Constants

$a = 20.486$;
$b = 1.165 \times 10^{-4}$;
$c = -7.787$;
$d = 1.1582 \times 10^{-3}$;
$e = 1.26807$;
$f = 4.98308$;
MeABP = 1,277°R = (817°F +460);
(°R = *degree Rankine*).

Calculate RI

$$\begin{aligned} I &= a \times \exp(b \times MeABP \times c \times SG + d \times MeABP \times SG) \times MeABP^e \times SG^f \\ I &= 2.341 \times 10^{-2} \times \exp(6.464 \times 10^{-4} \times 1,277 + 5.144 \times 0.913 - 3.289 \times 10^{-4} \\ &\quad \times 1,277 \times 0.913) \times (1,277)^{-0.407} \times (0.913)^{-3.333} \\ I &= 0.294 \end{aligned} \qquad (3.23)$$

I = index in refractive index

$$\begin{aligned} \mathrm{RI}_{(20)} &= (1 + 2 \times I/1 - I)^{1/2} \\ \mathrm{RI}_{(20)} &= \left(\frac{1 + 2 \times 0.294}{1 - 0.294}\right)^{1/2} \\ \mathrm{RI}_{(20)} &= 1.500 \end{aligned} \tag{3.24}$$

Viscosity gravity constant (VGC)

$$\begin{aligned} \mathrm{VGC} &= \frac{\mathrm{SG} - 0.24 - 0.022 \times \log(\nu_{210} - 35.5)}{0.755} \\ \mathrm{VGC} &= \frac{0.913 - 0.24 - 0.022 \times \log(50 - 35.5)}{0.755} \\ \mathrm{VGC} &= 0.8575 \end{aligned} \tag{3.25}$$

where:

SG = 0.913;
ν_{210} = 50 SUS.

Calculate refractivity intercept (*R*i)

$$\begin{aligned} R\mathrm{i} &= \mathrm{RI}_{(20)} - d/2 \\ R\mathrm{i} &= 1.5000 - (0.913/2) \\ R\mathrm{i} &= 1.0435 \end{aligned} \tag{3.25a}$$

where:

Density (d) = 0.913;
$\mathrm{RI}_{(20)}$ = 1.5000.

Calculate mole fractions (mol%) of paraffins (X_P), naphthenes (X_N), and aromatics (X_A) where:

a = 2.5737;
b = 1.0133;
c = −3.573;
d = 2.464;
e = −3.6701;
f = 1.96312;
g = −4.0377;
h = 2.6568;
i = 1.60988.

Use the feed property data in Example 3.1 to calculate MW, $\mathrm{RI}_{(20)}$, X_A, X_N, and X_P, employing API correlations (see Appendix 7).

Mol fraction of paraffins (X_P)

$$\begin{aligned} X_\mathrm{P} &= a + b(R\mathrm{i}) + c(\mathrm{VGC}) \\ X_\mathrm{P} &= 2.5737 + 1.0133\ (1.0435) + (-3.573 \times 0.8575) \\ X_\mathrm{P} &= 2.5737 + 1.0574 + (-3.064) \\ X_\mathrm{P} &= 0.5736 = 56.7\ \mathrm{mol\%} \end{aligned} \tag{3.26}$$

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Mol fraction of naphthenes (X_N)

$$\begin{aligned} X_N &= d + e(Ri) + f(VGC) \\ X_N &= 2.464 + (-3.6701 \times 1.0435) + (1.96312 \times 0.8575) \\ X_N &= 2.464 + (-3.8297) + (1.6835) \\ X_N &= 0.2939 = 31.8 \text{ mol\%} \end{aligned} \tag{3.27}$$

Mol fraction of aromatics (X_A)

$$\begin{aligned} X_A &= g + h(Ri) + i(VGC) \\ X_A &= -4.0377 + (2.6568 \times 1.0435) + (1.60988 \times 0.8575) \\ X_A &= -4.0377 + 2.7724 + 1.38055 \\ X_A &= 0.1325 = 11.5 \text{ mol\%} \end{aligned} \tag{3.28}$$

The findings from TOTAL, *n*−*d*−*M*, and API are summarized in Table 3.10. The comparison illustrates how sensitive the predicted feed composition is to the RI at 20°C. For instance, using the TOTAL correlation, there is a 35% drop in the aromatic content in using $RI_{(20)} = 1.5000$ instead of $RI_{(20)} = 1.5105$. When using these correlations, every effort should be made to obtain accurate and consistent values for the RI at 20°C.

With the RI at any given temperature, the $RI_{(20)}$ can be calculated from the following equation (Example 3.5 illustrates the use of the equation).

$RI_{(20)}$ at (any temperature):

$$\begin{aligned} RI_{(20)} &= RI(t) + 6.25 \times (t - 20) \times 10^{-4} \\ t &= \text{temperature } (^\circ\text{C}) \end{aligned} \tag{3.29}$$

Table 3.10: Comparison of the Findings Among the Three Correlations.

	API	*n*−*d*−*M*	TOTAL
Refractive index at 20°C	1.5000		1.5105
Molecular weight	413.8	440	446.6
Carbon Content	mol%	wt%	wt%
Aromatic	11.5 (14.3)*	(20.2)*, (8.8)†	19.3 (12.5)†
Naphthene	31.8 (27.9)*	(20.2)*, (41.1)†	
Paraffin	56.7 (57.8)*	(57.8)*, (59.6)†	

*Uses $RI_{(20)}$ from *n*−*d*−*M* correlation to determine composition.
†Uses $RI_{(20)}$ from API correlation to determine composition.

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Example 3.5

With the RI at 78°C = 1.4810, determine the RI at 20°C.

$$RI_{(20)} = 1.4810 + 6.25 \times (67 - 20) \times 10^{-4}$$
$$RI_{(20)} = 1.5104$$

(*Note that the calculated $RI_{(20)}$ closely matches that using the TOTAL correlation.*)

Benefits of Hydroprocessing

Pretreatment of FCC feedstock through hydroprocessing has a number of benefits including:

- Hydrodesulfurization (HDS)
- Hydrodenitrogenation (HDN)
- Hydrodemetallization (HDM)
- Aromatic reduction
- Conradson carbon removal.

Desulfurization of FCC feedstocks reduces the sulfur content of FCC products and SO_x emissions. In the United States, road diesel sulfur can be 500 ppm (0.05 wt%). In some European countries, for example in Sweden, the sulfur of road diesel is 50 ppm or less. In California, the gasoline sulfur is required to be <40 ppm. The Environmental Protection Agency (EPA)'s complex model uses sulfur as a controlling parameter to reduce toxic emissions. With hydroprocessed FCC feeds, about 5% of feed sulfur is in the FCC gasoline. For nonhydroprocessed feeds, the FCC gasoline sulfur is typically 10% of the feed sulfur.

The nitrogen compounds in the FCC feed deactivate the FCC catalyst activity, resulting in an increase in coke and dry gas. Hydrodenitrogenation (HDN) reduces nitrogen compounds in FCC feeds. In the regenerator, the nitrogen and the attached heterocyclic compounds add unwanted heat to the regenerator causing a low unit conversion.

Hydrodemetallization (HDM) reduces the amount of nickel and, to a lesser extent, vanadium in FCC feeds. Nickel dehydrogenates feed to molecular hydrogen and aromatics. Removing these metals allows heavier gas oil cut points.

PNAs do not react in the FCC and tend to remain in coke. Adding hydrogen to the outer ring clusters makes them more crackable and less likely to form coke on the catalyst.

Hydroprocessing reduces the CCR of heavy oils. CCR becomes coke in the FCC reactor. This excess coke has to be burned in the regenerator, increasing regenerator air requirements.

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Summary

It is important to characterize FCC feeds as to their molecular structure. Once the molecular configuration is known, kinetic models can be developed to predict product yields. The simplified correlations above do a reasonable job of defining hydrocarbon type and distribution in FCC feeds. Each correlation provides satisfactory results within the range for which it was developed. Whichever correlation is used, the results should be trended and compared with unit operation.

A clear understanding of feed physical properties is essential for successful work in the areas of troubleshooting, catalyst selection, unit optimization, and any planned revamp.

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CHAPTER 4

FCC Catalysts

The introduction of zeolite in commercial FCC catalysts in the early 1960s was one of the most significant advances in the history of cat cracking. Zeolite catalysts provided a greater profit with little capital investment. Simply stated, zeolite catalysts have been and still are the biggest bargain of all time for the refiner. Improvements in catalyst technology have continued, enabling refiners to meet the demands of their market with minimum capital investment.

Compared to amorphous silica–alumina catalyst, the zeolite catalysts are more active and more selective. The higher activity and selectivity translates to more profitable liquid product yields and additional cracking capacity. To take full advantage of the zeolite catalysts, refiners have revamped older units to crack more of the heavier, lower value feedstocks.

A complete discussion of FCC catalysts would fill another book. This chapter provides enough information to allow the reader to be able to troubleshoot the unit's operation and to select the optimum catalyst formulation. The key topics discussed are as follows:

- Catalyst components
- Catalyst manufacturing techniques
- Fresh catalyst properties
- Equilibrium catalyst analysis
- Catalyst management
- Catalyst evaluation.

Catalyst Components

FCC catalysts are in the form of fine powders with a typical particle size of 75 μm. A modern cat cracking catalyst has four major components:

1. Zeolite
2. Matrix
3. Filler
4. Binder.

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Zeolite

Zeolite, or more properly faujasite, is the key ingredient of the FCC catalyst. It provides product selectivity and much of the catalytic activity. The catalyst's performance depends largely on the nature and quality of the zeolite. Understanding the zeolite structure, types, cracking mechanism, and properties is essential in choosing the "right" catalyst to produce the desired yields.

Zeolite Structure

Zeolite is sometimes called molecular sieve. It has a well-defined lattice structure. Its basic building blocks are silica and alumina tetrahedra (pyramids). Each tetrahedron (Figure 4.1) consists of a silicon or aluminum atom at the center of the tetrahedron, with oxygen atoms at the four corners.

Zeolite lattices have a network of very small pores. The pore diameter of nearly all of today's FCC zeolite is $\sim$8.0 angstroms (Å). These small openings, with an internal surface area of roughly 600 m^2/g, do not readily admit hydrocarbon molecules that have a molecular diameter $>8.0-10$ Å.

The elementary building block of the zeolite crystal is a unit cell. The unit cell size (UCS) is the distance between the repeating cells in the zeolite structure. One unit cell in a typical fresh Y zeolite lattice contains 192 framework atomic positions: 55 atoms of aluminum and 137 atoms of silicon. This corresponds to a silica (SiO_2) to alumina (Al_2O_3) molal ratio (SAR) of 5. The UCS is an important parameter in characterizing the zeolite structure.

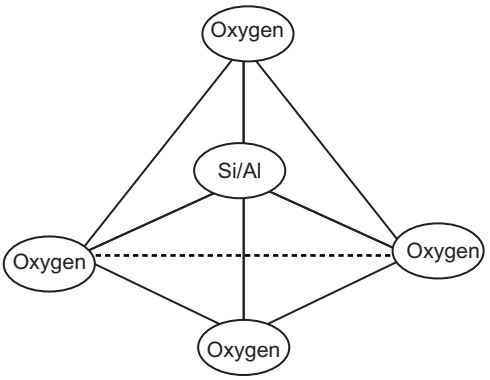


Figure 4.1: Silicon/aluminum–oxygen tetrahedron.

Zeolite Chemistry

As stated above, a typical zeolite consists of silicon and aluminum atoms that are tetrahedrally joined by four oxygen atoms. Silicon is in a +4 oxidation state; therefore, a

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tetrahedron containing silicon is neutral in charge. In contrast, aluminum is in a +3 oxidation state. This indicates that each tetrahedron containing aluminum has a net charge of −1, which must be balanced by a positive ion.

Solutions containing sodium hydroxide are commonly used in synthesizing the zeolite. The sodium serves as the positive ion to balance the negative charge of the aluminum tetrahedron. This zeolite is called soda Y or NaY. The NaY zeolite is not hydrothermally stable because of the high sodium content. The ammonium ion is frequently used to displace sodium. Upon drying the zeolite, ammonia is vaporized. The resulting acid sites are both the Bronsted and Lewis types. The Bronsted acid sites can be further exchanged with rare earth materials such as cerium and lanthanum to enhance their strengths. The zeolite activity comes from these acid sites.

Zeolite Types

Zeolites employed in the manufacture of the FCC catalyst are synthetic versions of naturally occurring zeolites called faujasites. There are about 40 known natural zeolites and over 150 zeolites which have been synthesized. Of this number, only a few have found commercial applications. Table 4.1 shows properties of the major synthetic zeolites.

The zeolites with applications to FCC are Type X, Type Y, and ZSM-5. Both X and Y zeolites have essentially the same crystalline structure. The X zeolite has a lower silica−alumina ratio than the Y zeolite. The X zeolite also has a lower thermal and hydrothermal stability than the Y zeolite. Some of the earlier FCC zeolite catalysts contained X zeolites; however, virtually all of today's catalysts contain Y zeolite or variations thereof (Figure 4.2).

ZSM-5 is a versatile zeolite that increases olefin yields and octane. Its application is further discussed in Chapter 5.

Until the late 1970s, the NaY zeolite was mostly ion exchanged with rare earth components. Rare earth components such as lanthanum and cerium were used to replace sodium in the crystal. The rare earth elements, being trivalent, simply form "bridges" between two to three acid sites in the zeolite framework. Bridging protects acid sites from being ejected and stabilizes the zeolite structure. Rare earth exchange adds to the zeolite activity and thermal and hydrothermal stability.

The reduction of lead in motor gasoline in 1986 created the need for a higher FCC gasoline octane. Catalyst manufacturers responded by adjusting the zeolite formulations, an alteration that involved expelling a number of aluminum atoms from the zeolite framework. The removal of aluminum increased SAR, reduced UCS, and in the process, lowered the

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sodium level of the zeolite. These changes increased the gasoline octane by raising its olefinicity. This aluminum-deficient zeolite was called *ultrastable* Y, or simply USY, because of its higher stability than the conventional Y.

Table 4.1: Properties of Major Synthetic Zeolites.

Zeolite Type	Pore Size Dimensions (Å)	Silica to Alumina Ratio	Applications
Zeolite A	4.1	2–5	Detergent manufacturing
Faujasite	7.4	3–6	Catalytic cracking and hydrocracking
ZSM-5	5.2 × 5.8	30–200	Xylene isomerization, benzene alkylation, catalytic cracking, catalyst dewaxing, and methanol conversion
Mordenite	6.7 × 7.0	10–12	Hydro-isomerization and dewaxing

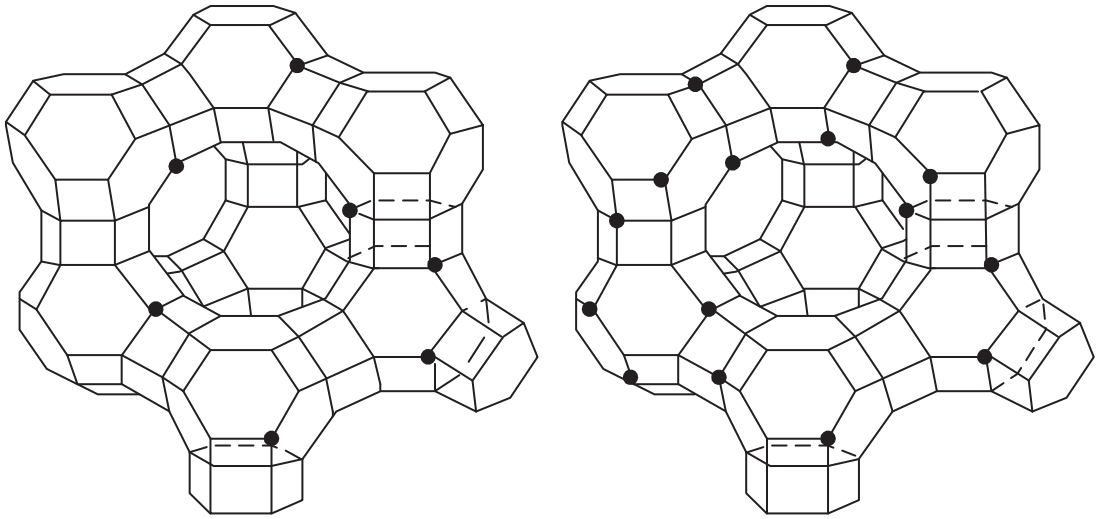


Figure 4.2: Geometry of USY and REY zeolites [1].

Zeolite Properties

The properties of the zeolite play a significant role in the overall performance of the catalyst. Understanding these properties increases our ability to predict catalyst response to changes in unit operation. From its inception in the catalyst plant, the zeolite must retain its catalytic properties under the hostile conditions of the FCC operation. The reactor/regenerator environment can cause significant changes in chemical and structural composition of the zeolite. In the regenerator, for instance, the zeolite is subjected to

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thermal and hydrothermal treatments. In the reactor, it is exposed to feedstock contaminants such as vanadium and sodium.

Various analytical tests determine zeolite properties. These tests supply information about the strength, type, number, and distribution of acid sites. Additional tests can also provide information about surface area and pore size distribution. The three most common parameters governing zeolite behavior are as follows:

- UCS
- Rare earth level
- Sodium content.

UCS: This is a measure of aluminum sites or the total potential acidity per unit cell. The negatively charged aluminum atoms are sources of active sites in the zeolite. Silicon atoms do not possess any activity. The UCS is related to the number of aluminum atoms per cell (N_{Al}) by [2]:

$$N_{Al} = 111 \times (\text{UCS} - 24.215) \tag{4.1}$$

The number of silicon atoms (N_{Si}) is:

$$N_{Si} = 192 - N_{Al} \tag{4.2}$$

The SAR of the zeolite can be determined either from the above two equations or from a correlation such as the one shown in Figure 4.3.

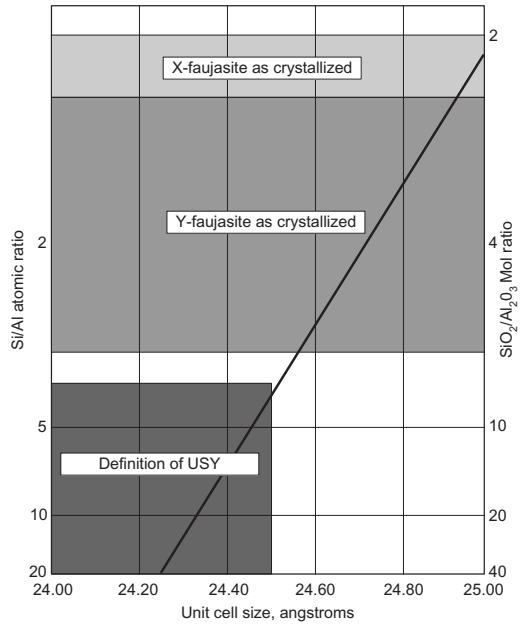


Figure 4.3: Silica–alumina ratio versus zeolite UCS.

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The UCS is also an indicator of zeolite acidity. Because the aluminum ion is larger than the silicon ion, as the UCS decreases, the acid sites become farther apart. The strength of the acid sites is determined by the extent of their isolation from the neighboring acid sites. The close proximity of these acid sites causes destabilization of the zeolite structure. Acid distribution of the zeolite is a fundamental factor affecting zeolite activity and selectivity. In addition, the UCS measurement can be used to indicate octane potential of the zeolite. A lower UCS presents fewer active sites per unit cell. The fewer acid sites are farther apart and therefore inhibit hydrogen transfer reactions, which in turn increase gasoline octane, as well as the production of C_3 and lighter components (Figure 4.4). The octane increase is due to a higher concentration of olefins in the gasoline.

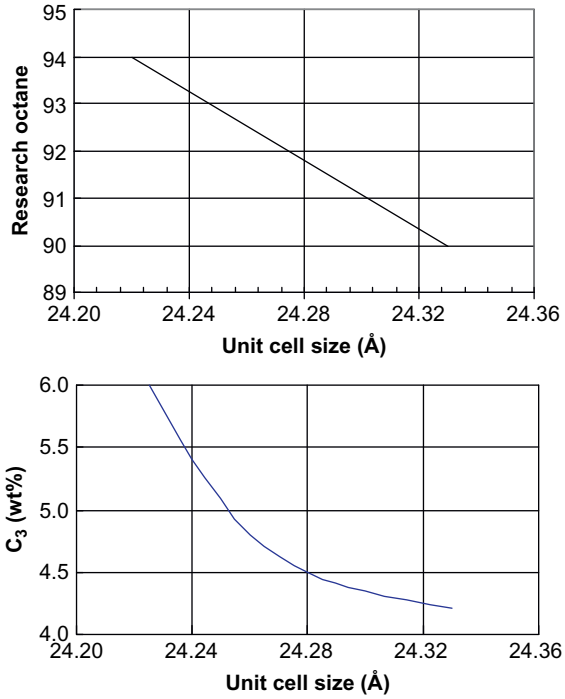


Figure 4.4: Effects of UCS on octane and C_3-yield [3].

Zeolites with lower UCS are initially less active than the conventional rare earth-exchanged zeolites (Figure 4.5). However, the lower UCS zeolites tend to retain a greater fraction of their activity under severe thermal and hydrothermal treatments, hence the name USY.

A freshly manufactured zeolite has a relatively high UCS in the range of 24.50–24.75 Å. The thermal and hydrothermal environment of the regenerator extracts alumina from the zeolite structure and therefore reduces its UCS. The final UCS level depends on the rare earth and sodium level of the zeolite. The lower the sodium and rare earth content of the fresh zeolite, the lower the UCS of the equilibrium catalyst (E-cat).

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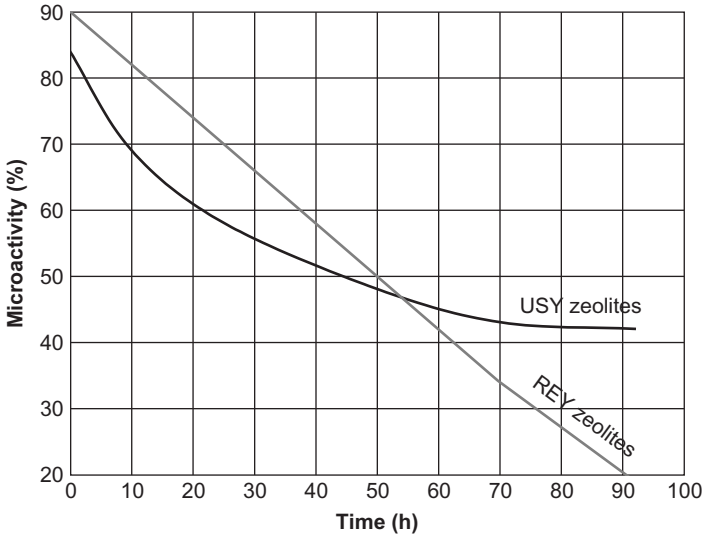


Figure 4.5: Comparison of activity retention between rare earth-exchanged zeolites versus USY zeolites [4].

Rare earth level: Rare earth (RE) elements such as lanthanum and cerium serve as a "bridge" to stabilize aluminum atoms in the zeolite structure. They prevent the aluminum atoms from separating from the zeolite lattice when the catalyst is exposed to high temperature steam in the regenerator.

A fully rare earth-exchanged zeolite equilibrates at a high UCS, whereas a non-rare earth zeolite equilibrates at a very low UCS of approximately 24.25 Å [5]. All intermediate levels of rare earth-exchanged zeolite can be produced. The rare earth increases zeolite activity and gasoline selectivity with a loss in octane (Figure 4.6). The octane loss is due to promotion of hydrogen transfer reactions. The insertion of rare earth maintains more and closer acid sites, which promotes hydrogen transfer reactions. In addition, rare earth improves thermal and hydrothermal stability of the zeolite. To improve the activity of a USY zeolite, the catalyst suppliers frequently add some rare earth to the zeolite.

Sodium content: The sodium on the catalyst originates either from zeolite during its manufacture or from the FCC feedstock. It is important for the fresh zeolite to contain very low amounts of sodium.

Sodium decreases the hydrothermal stability of the zeolite. It also reacts with the zeolite acid sites to reduce catalyst activity. In the regenerator, sodium is mobile. Sodium ions tend to neutralize the strongest acid sites. In a dealuminated zeolite, where the UCS is low (24.22−24.25 Å), the sodium can have an adverse affect on the gasoline octane (Figure 4.7). The loss of octane is attributed to the drop in the number of strong acid sites.

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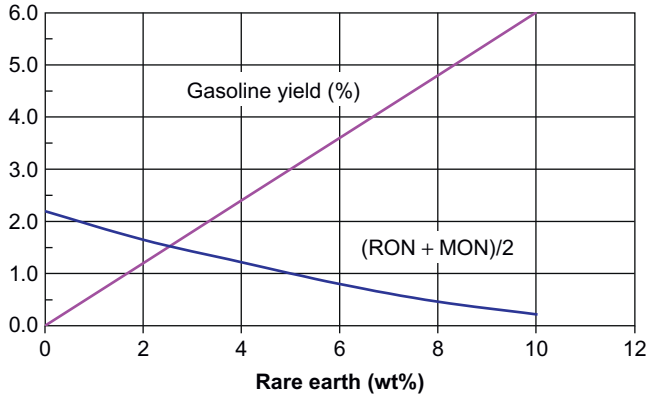


Figure 4.6: Effects of rare earth on gasoline octane and yield (*RON = research octane number, MON = motor octane number*).

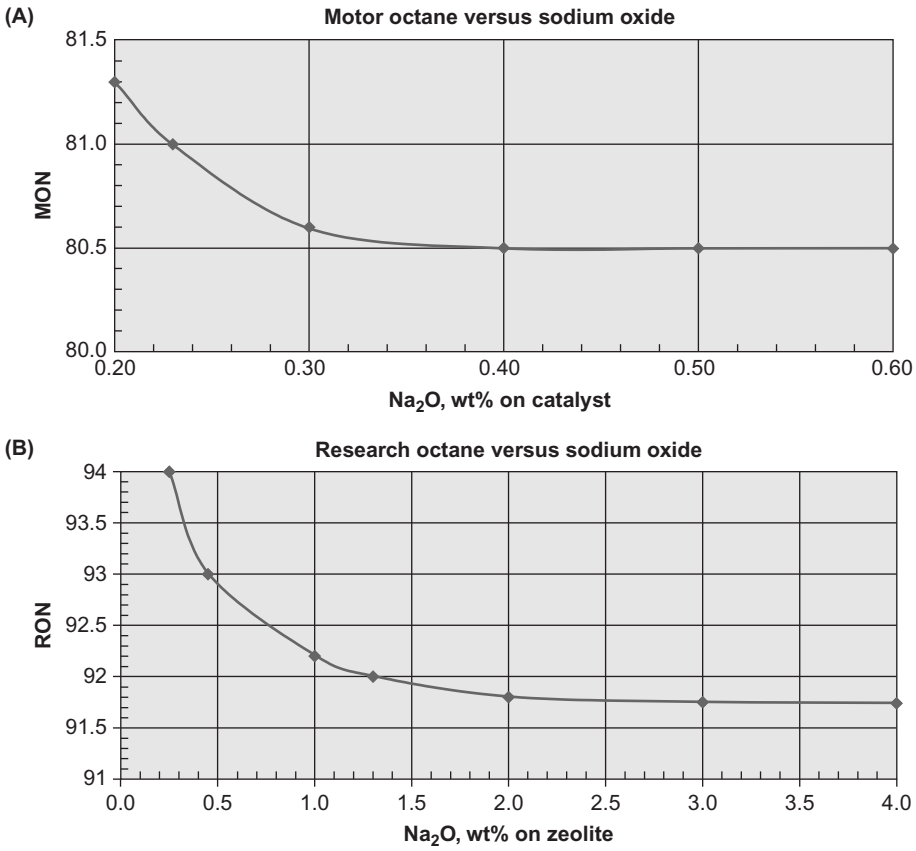


Figure 4.7: Effects of soda on motor and research octanes: motor octane versus sodium oxide [6]; research octane versus sodium oxide [3].

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FCC catalyst vendors are now able to manufacture catalysts with a sodium content of <0.20 wt%. Sodium is commonly reported as the weight percent of sodium or soda (Na_2O) on the catalyst. The proper way to compare sodium is the weight fraction of sodium in the zeolite. This is because FCC catalysts have different zeolite concentrations.

UCS, rare earth, and sodium are just three of the parameters that are readily available to characterize the zeolite properties. They provide valuable information about catalyst behavior in the cat cracker. If required, additional tests can be conducted to examine other zeolite properties.

Matrix

The term *matrix* has different meanings to different people. For some, matrix refers to components of the catalyst other than the zeolite. For others, matrix is a component of the catalyst, aside from the zeolite, having catalytic activity. Yet for others, matrix refers to the catalyst binder. In this chapter, matrix means components of the catalyst other than zeolite, and the term *active matrix* means the components of the catalyst other than zeolite having catalytic activity.

Alumina is the source for an active matrix. Most active matrices used in FCC catalysts are amorphous. However, some of the catalyst suppliers incorporate a form of alumina that also has a crystalline structure.

Active matrix contributes significantly to the overall performance of the FCC catalyst. The zeolite pores are not suitable for cracking of large hydrocarbon molecules generally having an end point >900°F (482°C); they are too small to allow diffusion of the large molecules to the cracking sites. An effective matrix must have a porous structure to allow diffusion of hydrocarbons into and out of the catalyst.

An active matrix provides the primary cracking sites. The acid sites located in the catalyst matrix are not as selective as the zeolite sites but are able to crack larger molecules that are hindered from entering the small zeolite pores. The active matrix precracks heavy feed molecules for further cracking at the internal zeolite sites. The result is a synergistic interaction between matrix and zeolite in which the activity attained by their combined effects can be greater than the sum of their individual effects [7].

An active matrix can also serve as a trap to catch some of the vanadium and basic nitrogen. The high-boiling fraction of the FCC feed usually contains metals and basic nitrogen that

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poison the zeolite. One of the advantages of an active matrix is that it guards the zeolite from becoming deactivated prematurely by these impurities.

Filler and Binder

The filler is a clay incorporated into the catalyst to dilute its activity. Kaoline [$Al_2(OH)_2$, Si_2O_5] is the most common clay used in the FCC catalyst. One FCC catalyst manufacturer uses kaoline clay as a skeleton to grow the zeolite in situ.

The binder serves as a glue to hold the zeolite, matrix, and filler together. Binder may or may not have catalytic activity. The importance of the binder becomes more prominent with catalysts that contain high concentrations of zeolite.

The functions of the filler and the binder are to provide physical integrity (density, attrition resistance, particle size distribution (PSD), and so on), a heat transfer medium, and a fluidizing medium in which the more important and expensive zeolite component is incorporated.

In summary, zeolite will affect activity, selectivity, and product quality. An active matrix can improve bottoms cracking and resist vanadium and nitrogen attacks. But a matrix containing very small pores can suppress strippability of the spent catalyst and increase hydrogen yield in the presence of nickel. Clay and binder provide physical integrity and mechanical strength.

Catalyst Manufacturing Techniques

The manufacturing process of modern FCC catalyst is divided into two general groups—incorporation and "in situ" processes. All catalyst suppliers manufacture catalyst by an incorporation process that requires making zeolite and matrix independently and using a binder to hold them together. In addition to the incorporation process, BASF also manufactures FCC catalyst using an "in situ" process in which the zeolite component is grown within the preformed microspheres. The following sections provide a general description of zeolite synthesis.

Conventional Zeolites (REY, REHY, and HY)

NaY zeolite is produced by digesting a mixture of silica, alumina, and caustic for several hours at a prescribed temperature until crystallization occurs (Figure 4.8). Typical sources of silica and alumina are sodium silicate and sodium aluminate. Crystallization of Y zeolite

typically takes 10 h at about 210°F (100°C). Production of a quality zeolite requires proper control of temperature, time, and pH of the crystallization solution. NaY zeolite is separated after filtering and water-washing of the crystalline solution.

A typical NaY zeolite contains ~13 wt% Na_2O. To enhance activity and thermal and hydrothermal stability of NaY, the sodium level must be reduced. This is normally done by the ion-exchanging of NaY with a medium containing rare earth cations and/or hydrogen ions. Ammonium sulfate solutions are frequently employed as a source for hydrogen ions.

At this state of the catalyst synthesis, there are two approaches for further treatment of NaY. Depending on the particular catalyst and the catalyst supplier, further treatment (rare earth exchange) of NaY can be accomplished either before or after its incorporation into the matrix. Post-treatment of the NaY zeolite is simpler but may reduce ion exchange efficiency.

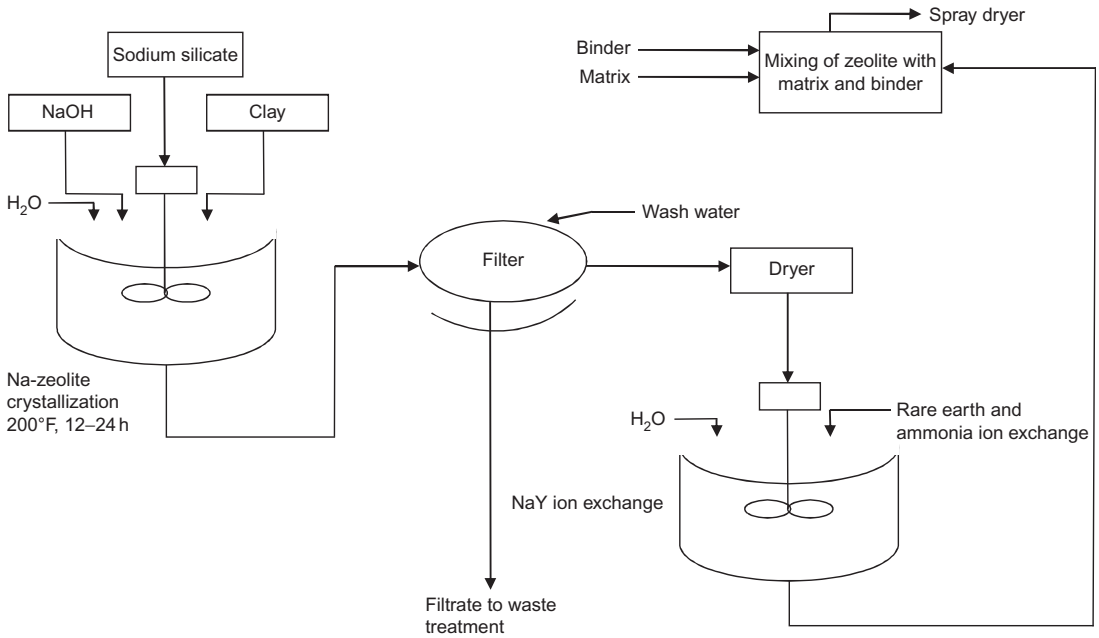


Figure 4.8: Typical manufacturing steps to produce FCC catalyst.

USY Zeolite

A USY or a dealuminated zeolite is produced by replacing some of the aluminum ions in the framework with silicon. The conventional technique (Figure 4.9) includes the use of a high-temperature (1,300−1,500°F (704−816°C)) steam calcination of HY zeolite.

Acid leaching, chemical extraction, and chemical substitution are all forms of dealumination that have become popular in recent years. The main advantage of these processes over conventional dealumination is the removal of the nonframework or occluded alumina from the zeolite cage structure. A high level of occluded alumina residing in the crystal is thought to have an undesirable impact on product selectivity by yielding more light gas and LPG; however, this has not been proven commercially.

In the manufacturing of USY catalyst, the zeolite, the clay, and the binder are slurried together. If the binder is not active, an alumina component, having catalytic properties, may also be added. The well-mixed slurry solution is then fed into a spray dryer. The function of a spray dryer is to form microspheres by evaporating the slurry solution, through the use of atomizers, in the presence of hot air. The type of spray dryer and the drying conditions determine the size and distribution of catalyst particles.

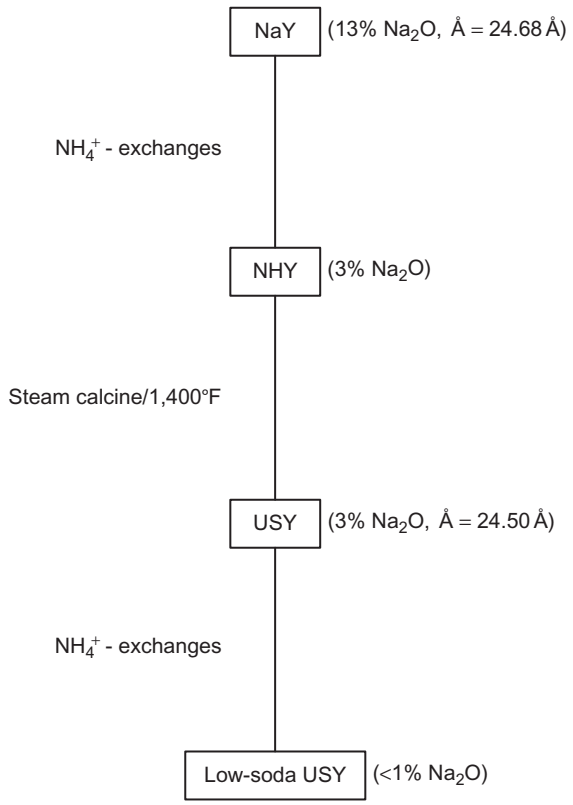


Figure 4.9: Synthesis of USY zeolite (NaY). (*Source: Filtron FCC Seminar, 1984.*)

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BASF Process

BASF's "in situ" FCC catalyst technology is based mainly on growing zeolite within the kaolin-based particles. The aqueous solution of various kaolins is spray dried to form microspheres. The microspheres are hardened in a high-temperature (1,300°F/704°C) calcination process. The NaY zeolite is produced by digestion of the microspheres that contain metakaolin and mullite with caustic or sodium silicate. Simultaneously, an active matrix is formed with the microspheres. The crystallized microspheres are filtered and washed prior to ion exchange and any final treatment.

Fresh Catalyst Properties

With each shipment of fresh catalyst, the catalyst suppliers typically mail refiners an inspection report that contains data on the catalyst's physical and chemical properties. This data is valuable and should be monitored closely to ensure that the catalyst received meets the agreed specifications. A number of refiners independently analyze random samples of the fresh catalyst to confirm the reported properties. In addition, quarterly review of the fresh catalyst properties with the catalyst vendor will ensure that the control targets are being achieved. The PSD, sodium (Na), rare earth (RE), and surface area (SA) are some of the parameters in the inspection sheet that require close attention.

Particle Size Distribution

The PSD is an indicator of the fluidization properties of the catalyst. In general, fluidization improves as the fraction of 0–40 μm particles is increased; however, a higher percentage of 0–40 μm particles will also result in greater catalyst losses.

The fluidization characteristics of an FCC catalyst depend largely on the unit's mechanical configuration. The percentage of <40 μm in the circulating inventory is mainly a function of cyclone efficiency. In units with good catalyst circulation, it may be economical to minimize the fraction of <40 μm particles. This is because after a few cycles, most of the 0–40 μm will escape the unit via the cyclones.

The catalyst manufacturers control PSD of the fresh catalyst, mainly through the spray-drying cycle. In the spray dryer, the catalyst slurry must be atomized effectively to achieve proper distribution. As illustrated in Figure 4.10, the PSD does not have a normal distribution shape. The average particle size (APS) is not actually the average size of the catalyst particles but rather the median value.

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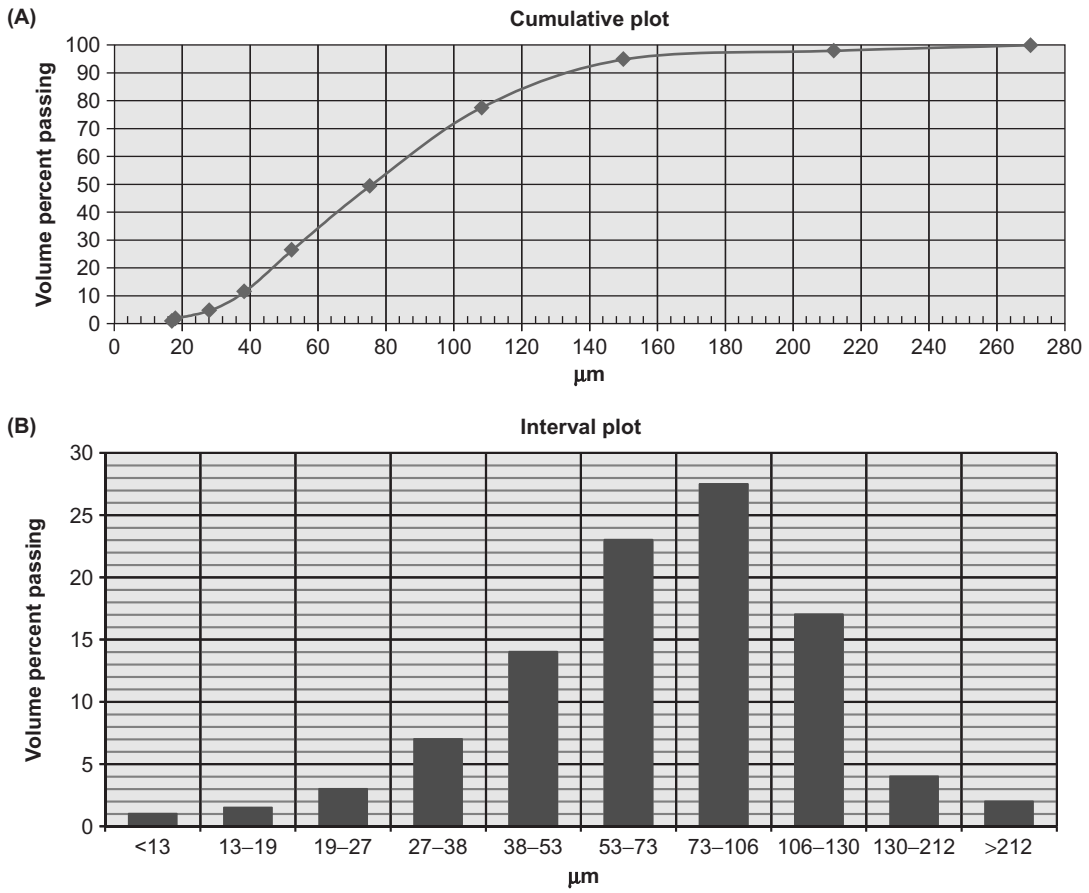


Figure 4.10: PSD of a typical FCC catalyst.

Surface Area (m^2/g)

The reported surface area is the combined surface area of zeolite and matrix. In zeolite manufacturing, the measurement of the zeolite surface area is one of the procedures used by catalyst suppliers to control quality. The surface area is commonly determined by the amount of nitrogen adsorbed by the catalyst. It should be noted that there are different methods used to measure surface area, and the reported values are different from one catalyst vendor to another.

The surface area correlates fairly well with the fresh catalyst activity. Upon request, catalyst suppliers can also report the zeolite surface area. This data is useful in that it is proportional to the zeolite content of the catalyst.

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Sodium (Na) (wt%)

Sodium plays an intrinsic part in the manufacturing of FCC catalysts. Its detrimental effects are well known, and because it deactivates the zeolite and reduces the gasoline octane, every effort should be made to minimize the amount of sodium in the fresh catalyst. The catalyst inspection sheet expresses sodium or soda (Na_2O) as the weight percent on the catalyst. When comparing different grades of catalysts, it is more practical to express the sodium content on the zeolite.

Rare Earth (wt%)

Rare earth (RE) is a generic name for 14 metallic elements of the lanthanide series. These elements have similar chemical properties and are usually supplied as a mixture of oxides extracted from ores such as bastnaesite or monazite.

Rare earth improves the catalyst activity (Figure 4.11) and hydrothermal stability. Catalysts can have a wide range of rare earth levels, depending on the refiner's objectives. Similarly to sodium, the inspection sheet shows rare earth or rare earth oxide (RE_2O_3) as the weight percent of the catalyst. Again, when comparing different catalysts, the concentration of RE on the zeolite should be used.

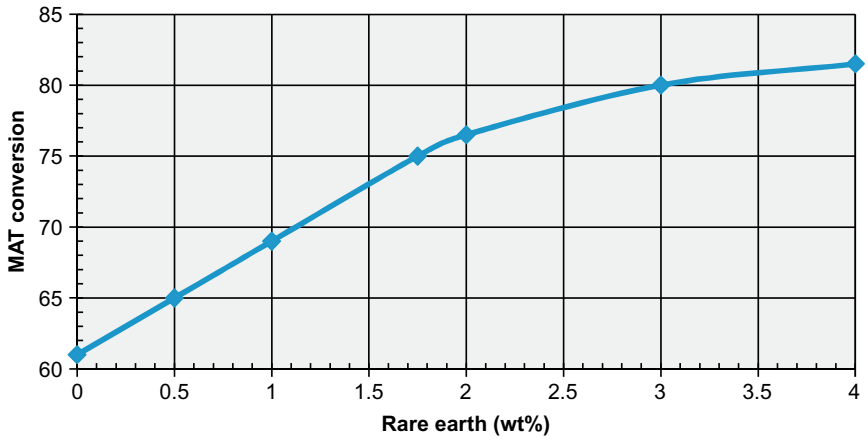


Figure 4.11: Effect of rare earth on catalyst activity (*MAT = microactivity test*).

E-Cat Analysis

Refiners send E-cat samples to catalyst manufacturers on a regular basis. As a service to the refiners, the catalyst suppliers provide analyses of the samples in a form similar to the one shown in Figure 4.12. Although the absolute E-cat results may differ from one vendor to another, the results are useful as a trend indicator.

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Sample	MAT (%)	CF	GF	SA (m^2/gm)	PV (cc/gm)	ABD (gm/cc)	0–20 (wt%)	0–40 (wt%)	0–80 (wt%)	APS	Al_2O_3 (ppm)	
11/7/2011	69	1.3	2.2	147	0.30	0.83	0	10	63	70	28.9	
11/10/2011	69	1.2	1.9	148	0.28	0.83	0	7	61	72	29.1	
11/14/2011	70	1.2	3.1	147	0.29	0.84	0	8	67	69	29.2	
11/21/2011	69	1.3	2.6	148	0.29	0.83	2	9	69	68	28.7	
11/24/2011	68	1.4	3.2	148	0.28	0.83	0	6	65	70	28.7	
11/28/2011	69	1.3	2.6	150	0.29	0.84	0	9	67	69	28.7	
12/1/2011	69	1.2	2.3	148	0.28	0.85	2	10	71	67	28.7	
12/5/2011	67	1.4	2.8	148	0.29	0.85	0	7	64	71	28.8	
12/12/2011	70	1.2	2.9	148	0.28	0.84	4	10	67	69	28.8	

	Na (ppm)	Fe (ppm)	C (wt%)	V (ppm)	Ni (ppm)	Cu (ppm)	Sb (ppm)	UCS	RE_2O_3	Z	M	Sn (ppm)
11/7/2011	4,900	5,600	0.23	4,106	1,997	25	416	24.27	1.79	130	17	902
11/10/2011	4,800	5,600	0.23	4,093	1,948	23	446		1.80	130	18	909
11/14/2011	4,600	5,600	0.16	4,051	1,940	24	440	24.27	1.79	130	17	910
11/21/2011	4,600	5,600	0.23	4,099	1,974	24	446		1.80	130	18	932
11/24/2011	4,600	5,600	0.22	4,017	1,942	24	445	24.25	1.79	130	18	939
11/28/2011	4,600	5,600	0.20	3,962	1,910	23	420		1.80	132	18	931
12/1/2011	4,800	5,600	0.24	3,892	1,893	24	458	24.27	1.79	131	18	
12/5/2011	4,600	5,600	0.15	3,893	1,885	25	432		1.79	130	18	932
12/12/2011	4,500	5,600	0.24	3,875	1,873	24	409	24.27	1.76	130	18	

Figure 4.12: Typical E-cat analysis (*CF = coke factor, GF = gas factor, PV = pore volume, ABD = apparent bulk density, Z = zeolite, M = matrix surface area*).

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The tests performed on E-cat samples provide refiners with valuable information on unit conditions. The data can be used to pinpoint potential operational, mechanical, and catalyst problems because the physical and chemical properties of the E-cat provide clues on the environment to which it has been exposed.

The following discussion describes each test briefly and examines the significance of these data to the refiner. The E-cat results are divided into catalytic properties, physical properties, and chemical analysis.

Catalytic Properties

The activity, coke, and gas factors are the tests that reflect the relative catalytic behavior of the catalyst.

Conversion (activity)

The first step in E-cat testing is to burn the carbon off the sample. The sample is then placed in a MAT unit (Figure 4.13), the heart of which is a fixed bed reactor. A certain amount of a standard gas oil feedstock is injected into the hot bed of catalyst. The activity is reported as the conversion to 430°F (221°C) material. The feedstock's quality, reactor temperature, catalyst to oil ratio, and space velocity are four variables affecting MAT results. Each catalyst vendor uses slightly different operating variables to conduct microactivity testing, as indicated in Table 4.2.

In commercial operations, catalyst activity is affected by operating conditions, feedstock quality, and catalyst characteristics. The MAT separates catalyst effects from feed and process changes. Feed contaminants, such as vanadium and sodium, reduce catalyst activity. E-cat activity is also affected by fresh catalyst makeup rate and regenerator conditions.

Some suppliers use an accelerated cracking evaluation (ACE TECHNOLOGY™) apparatus, developed by Kayser Technology Inc., to analyze E-cat activity. This method breaks out all of the component yields for each sample, which has the added advantage of allowing the refiner to evaluate yield shifts due solely to changes in catalyst properties.

Coke Factor and Gas Factor

The coke factor (CF) and gas factor (GF) represent the coke- and gas-forming tendencies of an E-cat compared to a standard steam-aged catalyst sample at the same conversion. The CF and GF are influenced by the type of fresh catalyst and the level of metals deposited on the E-cat. Both the CF and GF can be indicative of the dehydrogenation activity of the metals on the catalyst. The addition of amorphous alumina to the catalyst will tend to increase the nonselective cracking, which forms coke and gas.

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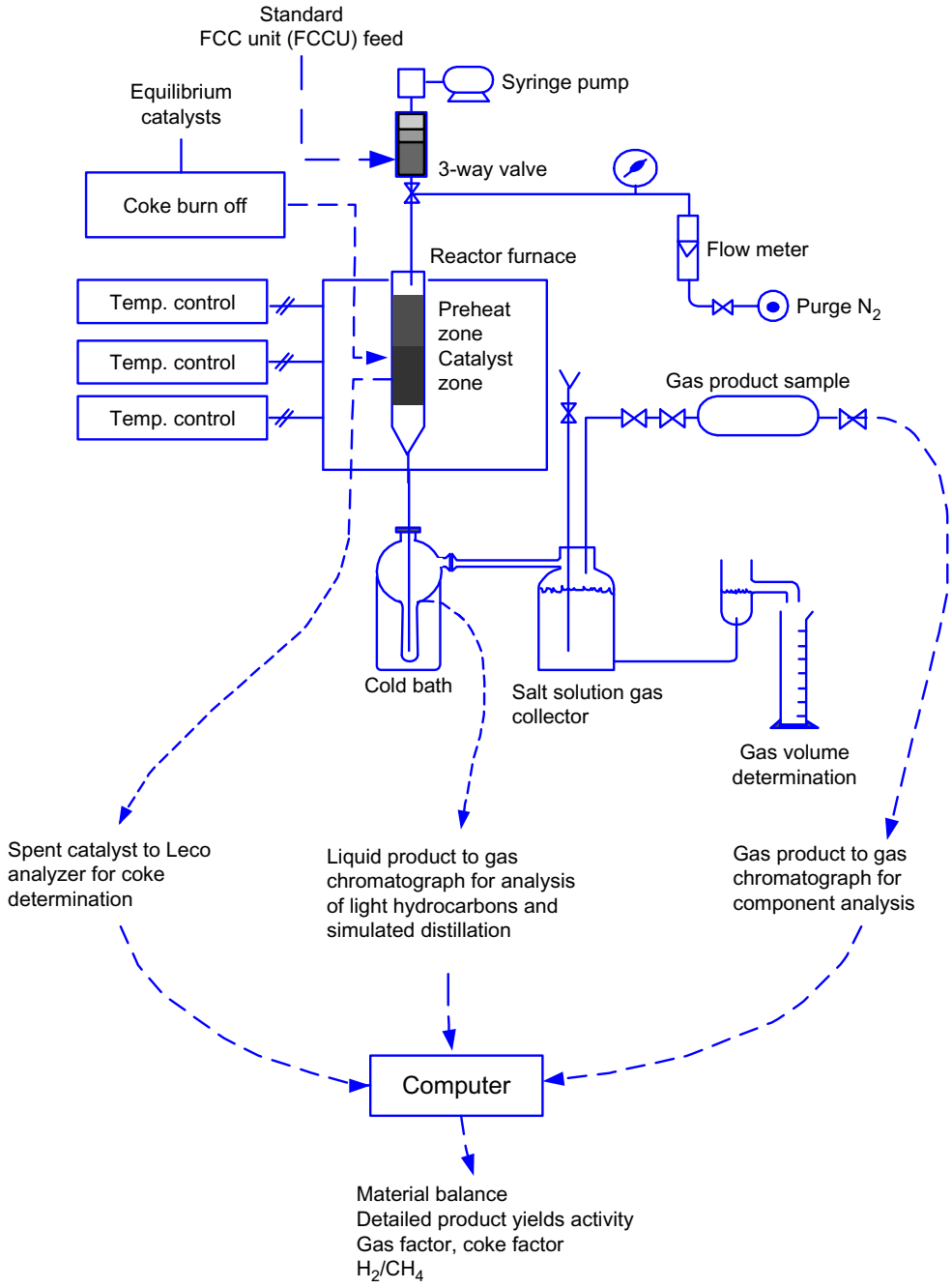


Figure 4.13: Typical MAT equipment [5].

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Table 4.2: Equilibrium Microactivity Test Conditions.

Tester (United States)	Temperature (°F/°C)	Catalyst to Oil Weight Ratio	WHSV (h^{-1})	Catalyst Contact Time (s)	Feed Source	Reactor Type
Albemarle*	998/537	3.0	NA	1	Kuwait vacuum gas oil	Isothermal
Grace Davison	980/527	4.0	30	30	Sour import heavy gas oil	Isothermal
BASF	910/488	5.0	15	48	Mid-continent	Isothermal

MAT Gas Oil Properties			
Properties	**Albemarle†**	**Davison‡**	**BASF§**
API gravity	20.4	22.5	28.6
D1160			
IBP (°F)	674	423	373
50% (°F)	883	755	732
90% (°F)	934	932	899
Concarbon (wt%)	0.17	0.25	0.22
Sulfur (wt%)	3.18	2.59	0.52
Total nitrogen (ppmv)	1,009	860	675
API procedure 2B4.1			
Aromatics (vol%)	21.9	21.7	30
Naphthenes (vol%)	25.4	19.6	28
Paraffins (vol%)	52.6	58.7	42

(*WHSV = weighted hourly space velocity, ppmv = parts per million by volume*)
*Albemarle uses a fluid bed testing unit.
†Albemarle Private Communication, July 1997.
‡Grace Davison Catalagram, No. 79, 1989.
§BASF Catalyst Report, No. TI-825.

Physical Properties

The tests that reflect physical properties of the catalyst are surface area, average bulk density, pore volume (PV), and PSD.

Surface Area (m^2/g)

For an identical fresh catalyst, the surface area of an E-cat is an indirect measurement of its activity. The SA is the sum of zeolite and matrix surface areas. Hydrothermal conditions in the cat cracker destroy the zeolite cage structure, thus reducing its surface area. They also dealuminate the zeolite framework. Hydrothermal treatment has less effect on the matrix surface area, but the matrix surface area is affected by the collapse of small pores to become larger pores.

Apparent Bulk Density (g/cc)

Bulk density can be used to troubleshoot catalyst flow problems. A too-high apparent bulk density (ABD) can restrict fluidization, and a too-low ABD can result in excessive catalyst

loss. Normally, the ABD of the E-cat is higher than the fresh catalyst ABD due to thermal and hydrothermal changes in pore structure that occur in the unit.

Pore Volume (cc/g)

Pore volume is an indication of the quantity of voids in the catalyst particles and can be a clue in detecting the type of catalyst deactivation that takes place in a commercial unit. Hydrothermal deactivation has very little effect on pore volume, whereas thermal deactivation decreases pore volume.

Pore Diameter (Å)

The average pore diameter (APD) of a catalyst can be calculated from the E-cat analysis sheet by using the following equation:

$$\text{APD (Å)} = \frac{\text{PV} \times 4 \times 10,000}{\text{SA}} \tag{4.3}$$

Example 4.1

For an E-Cat with a PV = 0.40 cc/g and SA = 120 m^2/g, determine APD:

APD = 133 Å

Particle Size Distribution

PSD is an important indicator of the fluidization characteristics of the catalyst, cyclone performance, and the attrition resistance of the catalyst. A drop in fines content indicates the loss of cyclone efficiency.

This can be confirmed by the particle size of fines collected downstream of the cyclones. An increase in fines content of the E-cat indicates increased catalyst attrition. This can be due to changes in fresh catalyst binder quality, steam leaks, and/or internal mechanical problems, such as those involving the air distributor or slide valves.

Chemical Properties

The key elements that characterize chemical composition of the catalyst are alumina, sodium, metals, and carbon on the regenerated catalyst (CRC).

Alumina (Al_2O_3)

The alumina content of the E-cat is the total weight percent of alumina (active and inactive) in the bulk catalyst. The alumina content of the E-cat is directly related to the alumina

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content of the fresh catalyst. When changing catalyst grades, the alumina level of the E-cat is often used to determine the percent of new catalyst in the unit.

Sodium (Na)

The sodium in the E-cat is the sum of sodium added with the feed and sodium on the fresh catalyst. A number of catalyst suppliers report sodium as soda (Na_2O). Sodium deactivates the catalyst acid sites and causes collapse of the zeolite crystal structure. Sodium can also reduce the gasoline octane, as discussed earlier.

Nickel (Ni), Vanadium (V), Iron (Fe), and Copper (Cu)

These metals, when deposited on the E-cat catalyst, increase coke and gas-making tendencies of the catalyst. They cause dehydrogenation reactions, which increase hydrogen production and decrease gasoline yields. Vanadium can also destroy the zeolite activity and thus lead to lower conversion. The deleterious effects of these metals also depend on the regenerator temperature: the rate of deactivation of a metal-laden catalyst increases as the regenerator temperature increases.

These contaminates originate largely from the heavy (1,050+ °F/566+ °C), high molecular weight fraction of the FCC feed. The quantity of these metals on the E-cat is determined by their levels in the feedstock and the catalyst addition rate. Essentially, all these metals in the feed are deposited on the catalyst. Most of the iron on the E-cat comes from metal scale from piping and from the fresh catalyst.

Metals content of the E-cat can be determined fairly accurately by conducting a metals balance around the unit:

$$\text{Metals}_{\text{in}} - \text{Metals}_{\text{out}} = \text{Metals accumulated} \tag{4.4}$$

This is a first-order differential equation. Its solution is as follows:

$$M_{\text{e}} = A + [M_0 - A] \times \text{e}\frac{(C_{\text{a}} \times t)}{I} \tag{4.5}$$

At steady state, the concentration of any metal on catalyst is as follows:

$$M_{\text{e}} = A = \frac{(W \times M_{\text{f}})}{C_{\text{a}}}$$

$$M_{\text{e}} = \frac{\dfrac{141.5}{131.5 + \text{API}_{\text{feed}}} \times 350.4 \times M_{\text{f}}}{B} \tag{4.6}$$

where:

M_e = E-cat metals content (ppm);
$A = (W \times M_f)/C_a$;
W = feed rate (lb/day);
M_f = feed metals (ppm);
C_a = catalyst addition rate (lb/day);
M_0 = initial metals on the E-cat (ppm);
t = time (day);
I = catalyst inventory (lb);
B = catalyst addition rate (pounds of catalyst per barrel of feed).

Figure 4.14 is the graphical solution to the above equation and can be employed to estimate metals content of the E-cat, based on feed metals and catalyst addition rate.

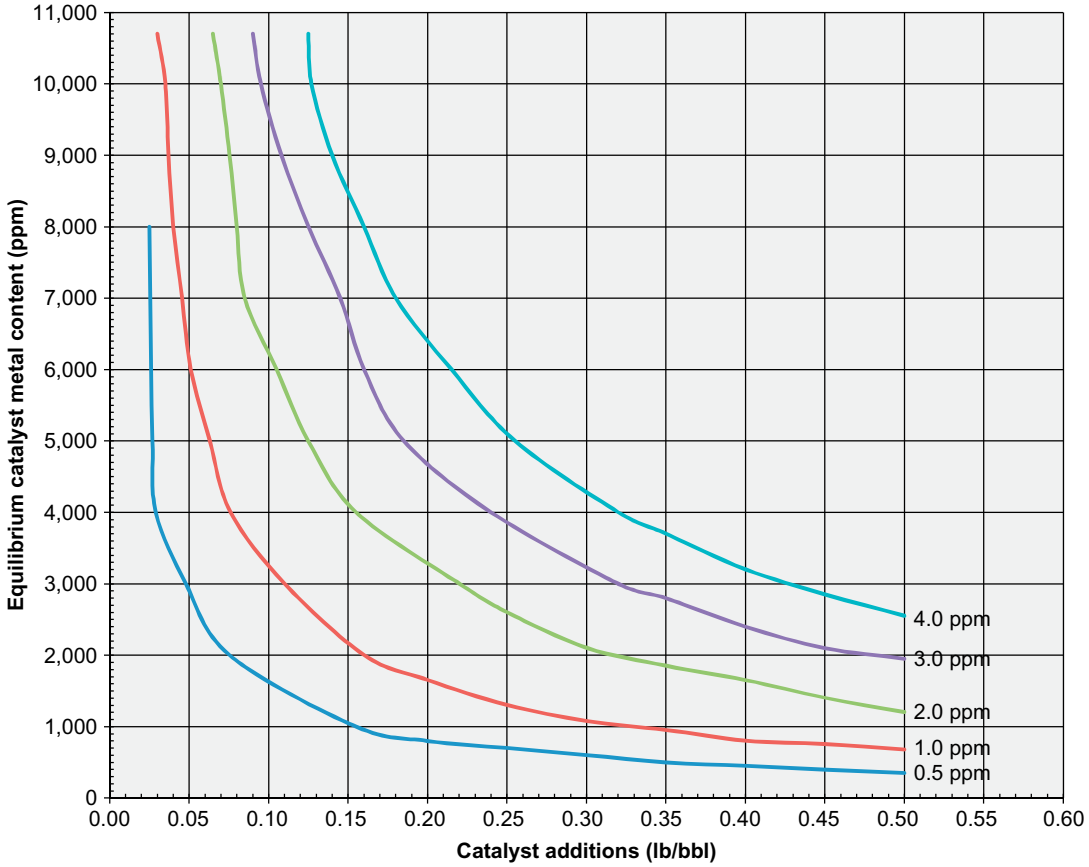


Figure 4.14: Catalyst metals content versus catalyst addition rate for 22 API gravity feed. (*Source: Katalystics' Regional Technology Seminar, New Orleans, LA, December 15, 1998.*)

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Carbon (C)

The deposition of carbon on the E-cat during cracking will temporarily block some of the catalytic sites. The CRC, or, more accurately, the coke, will lower the catalyst activity and, therefore, the conversion of feed to valuable products (Figure 4.15).

The CRC is an important parameter for a unit operator to monitor periodically. Most FCC units check for CRC on their own, usually daily. The CRC is an indicator of regenerator performance. If the CRC shows signs of increasing, this could reveal malfunction of the regenerator's air/spent catalyst distributors. It should be noted that the MAT numbers reported on the E-cat sheet are determined after the CRC has been completely burned off.

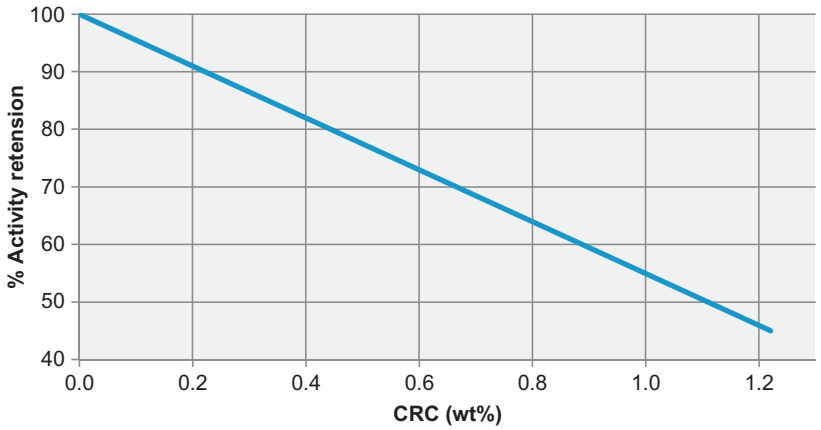


Figure 4.15: Catalyst activity retention versus CRC [8].

Catalyst Management

Depending on the design of a cat cracker, the circulating inventory can contain 30−1,200 tons of catalyst. Fresh catalyst is added to the unit continually to replace the catalyst lost by attrition and to maintain catalyst activity. The daily makeup rate is typically 1−2% of inventory or 0.1−1.0 lb (0.045−0.45 kg) of catalyst per barrel of fresh feed. In cases where the makeup rate for activity maintenance exceeds catalyst losses, part of the inventory is periodically withdrawn from the unit to control the catalyst level in the regenerator. Catalyst fines leave the unit with the regenerator flue gas and the reactor vapor.

As the catalyst ages in the unit, it loses activity and selectivity. The deactivation in a given unit is largely a function of the unit's mechanical configuration, its operating condition, the type of fresh catalyst used, and the feed quality. The primary criterion for adding fresh

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catalyst is to arrive at an optimum E-cat activity level. A too-high E-cat activity will increase delta coke on the catalyst, resulting in a higher regenerator temperature. The higher regenerator temperature reduces the catalyst circulation rate, which tends to offset the activity increase.

The amount of fresh catalyst added is usually a balance between catalyst cost and desired activity. Most refiners monitor the MAT data from the catalyst vendor's E-cat data sheet to adjust the fresh catalyst addition rate. It should be noted that MAT numbers are based on a fixed-bed reactor system and, therefore, do not truly reflect the dynamics of an FCC unit. A catalyst with a high MAT number may or may not produce the desired yields. An alternate method of measuring catalyst performance is dynamic activity. Dynamic activity is calculated in the following equations:

$$\text{Dynamic activity} = \frac{(\text{second-order conversion})}{(\text{coke yield, wt\% of feed})} \tag{4.7}$$

where

$$\text{Second-order conversion} = \frac{(\text{MAT conversion, vol\%})}{(100 - \text{MAT conversion, vol\%})} \tag{4.8}$$

For example, a catalyst with a MAT number of 70 vol% and a 3.0 wt% coke yield will have a dynamic activity of 0.78. However, another catalyst with a MAT conversion of 68 vol% and 2.5 wt% coke yield will have a dynamic activity of 0.85. This could indicate that in a commercial unit, the 68 MAT catalyst could outperform the 70 MAT catalyst due to its higher dynamic activity. Some catalyst vendors have begun reporting dynamic activity data as part of their E-cat inspection reports. The reported dynamic activity data can vary significantly from one test to another, mainly due to the differences in feedstock quality between MAT and actual commercial application. In addition, the coke yield, as calculated by the MAT procedure, is not very accurate, and small changes in this calculation can affect the dynamic activity appreciably.

The most widely accepted model to predict E-cat activity is based on a first-order decay type [9]. Example 4.2 illustrates the use of the following equations:

$$A_{(t)} = A_0 \times e^{-(S+K)t} + \frac{A_0 \times S}{S+K} \times (1 - e^{-(K+S)t}) \tag{4.9}$$

At a steady state, the above equation reduces to:

$$A_\infty = \frac{A_0 \times S}{S+K} \tag{4.10}$$

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where:

$A_{(t)}$ = catalyst microactivity at time t;
A_0 = catalyst microactivity at starting time;
t = time after changing catalyst or makeup rate;
S = daily fractional replacement rate = addition rate/inventory;
K = deactivation constant = $\ln(A_{(t)} - A_0)/-t$.

The above equation assumes no vanadium contamination. As shown in Table 4.3, vanadium contamination deactivates the catalyst exponentially.

Table 4.3: Effects of Vanadium Poisoning.

	Fresh Catalyst	Hydrothermal Deactivation	1,000 PPM Vanadium	2,500 PPM Vanadium	3,200 PPM Vanadium
Total surface area (m^2/g)	303	184	173	136	111
UCS (Å)	24.56	24.25	24.24	24.22	24.20

Example 4.2

Use of Eqs. (4.9) and (4.10) to predict E-cat activity is based on a first-order decay type.

Assume:

50,000 bpd cat cracker with:

- Catalyst inventory of 300 tons
- Makeup rate of 4.0 tons/day
- Fresh catalyst MAT number of 80 vol%
- E-cat MAT number of 71.5 vol%.

Determine:

New E-cat MAT conversion if the addition rate is reduced to 3.0 tons/day:

$$S = \frac{4.0}{300} = 0.01333 \text{ day}^{-1}$$

$$t = 300/4 = 75 \text{ days}$$

$$\text{Deactivation constant} = K = \frac{\ln(71.5) - \ln(80)}{-75.0} = 0.001498 \text{ day}^{-1}$$

$$\text{New fractional replacement} = \frac{3.0}{300} = 0.01 \text{ day}^{-1}$$

$$\text{The revised E-cat} = \frac{80 \times 0.01}{0.01333 + 0.001498} = 69.5 \text{ vol\%}$$

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Determine:

The new E-cat MAT conversion if the fresh catalyst MAT number is reduced from 80 to 75 vol%:

$$\text{Activity} = \frac{75 \times 0.01333}{0.01333 + 0.001498} = 67.4 \text{ vol\%}$$

When a refiner changes the FCC catalyst, it is often necessary to determine the percent of the new catalyst in the unit. The following equation, which is based on a probability function, can be used to estimate the percent changeover.

$$P = 1 - e^{-f \times S \times t} \tag{4.11}$$

where:

P = fractional changeover;
f = retention factor, usually in the range 0.6–0.9;
S = replacement rate = addition rate/inventory;
t = time (day).

Example 4.3

The 300-ton inventory unit in Example 4.2 is changing catalyst type and planning to add 3.5 tons/day of new catalyst. Determine the percent of changeover after 60 days of operation. Assume a retention factor of 0.7.

$P = 1 - e^{-0.7 \times 0.0117 \times 60}$
$P = 1 - e^{-490014}$
$P = 1 - 0.612618$
$P = 0.387$ or 38.7%.

Another way of calculating the percent changeover is by the use of *alumina balance*, as shown in Example 4.4.

Example 4.4

For the same 300-ton inventory unit, assume the alumina (Al_2O_3) contents of the present and new fresh catalysts are 48 and 38 wt%, respectively. Sixty days after the catalyst switch, the alumina content of the E-cat is 43 wt%.

Determine percent changeover:

$$\text{Functional changeover} = 1 - \frac{Al_2O_3(\text{new}) - Al_2O_3(\text{equil.})}{Al_2O_3(\text{new}) - Al_2O_3(\text{old})}$$

$$\text{Fractional changeover} = 1 - \frac{38 - 43}{38 - 48} = 0.5 \equiv \rightarrow\rangle 50\%$$

This method can also be used to calculate the catalyst retention factor. The above equations assume steady-state operation, constant unit inventory, and constant addition and loss rates.

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Catalyst Evaluation

Catalyst management is a very important aspect of the FCC process. Selection and management of the catalyst, as well as how the unit is operated, are largely responsible for achieving the desired product. Proper choice of a catalyst will go a long way toward achieving a successful cat cracker operation. Catalyst change-out is a relatively simple process and allows a refiner to select the catalyst that maximizes the profit margin. Although catalyst change-out is physically simple, it requires a lot of homework as discussed later in this section.

As many catalyst formulations are available, catalyst evaluation should be an ongoing process; however, it is not an easy task to evaluate the performance of an FCC catalyst in a commercial unit because of continual changes in feedstocks and operating conditions, in addition to inaccuracies in measurements. Because of these limitations, refiners sometimes switch catalyst without identifying the objectives and limitations of their cat crackers. To assure that a proper catalyst is selected, each refiner should establish a methodology that allows identification of "real" objectives and constraints and ensures that the choice of the catalyst is based on well-thought-out technical and business merits. In today's market, there are many different formulations of FCC catalysts. Refiners should evaluate catalyst mainly to maximize profit opportunity and to minimize risk. The "right" catalyst for one refiner may not necessarily be "right" for another.

A comprehensive catalyst selection methodology will have the following elements:

1. Optimize unit operation with current catalyst and vendor
   a. Conduct test run
   b. Incorporate the test run results into an FCC kinetic model
   c. Identify opportunities for operational improvements
   d. Identify unit's constraints
   e. Optimize incumbent catalyst with vendor
2. Issue technical inquiry to catalyst vendors
   a. Provide test run results
   b. Provide E-cat sample
   c. Provide processing objectives
   d. Provide unit limitations
3. Obtain vendor responses
   a. Obtain catalyst recommendation
   b. Obtain alternate recommendation
   c. Obtain comparative yield projection

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4. Obtain current product price projections
   a. For present and future four quarters
5. Perform economic evaluations on vendor yields
   a. Select catalysts for MAT evaluations
6. Conduct MAT of selected list
   a. Perform physical and chemical analyses
   b. Determine steam deactivation conditions
   c. Deactivate incumbent fresh catalyst to match incumbent E-cat
   d. Use same deactivation steps for each candidate catalyst
7. Perform economic analysis of alternatives
   a. Estimate commercial yield from MAT evaluations
8. Request commercial proposals
   a. Consult at least two vendors
   b. Obtain references
   c. Check references
9. Test the selected catalysts in a pilot plant
   a. Calibrate the pilot plant steaming conditions using incumbent E-cat
   b. Deactivate the incumbent and other candidate catalysts
   c. Collect at least two or three data points on each by varying the catalyst to oil ratio
10. Evaluate pilot plant results
   a. Translate the pilot plant data
   b. Use the kinetic model to heat-balance the data
   c. Identify limitations and constraints
11. Make the catalyst selection
   a. Perform economic evaluation
   b. Consider intangibles-research, quality control, price, steady supply, manufacturing location
   c. Make recommendations
12. Postselection
   a. Monitoring transition-percent changeover
   b. Post-transition test run
   c. Confirm computer model
13. Issue the final report
   a. Analyze benefits
   b. Evaluate selection methodology.

There is a redundancy of flexibility in the design of FCC catalysts. Variation in the amount and type of zeolite, as well as the type of active matrix, provides a great deal of catalyst options that the refiner can employ to fit its needs. For smaller refiners, it may not be

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practical to employ pilot plant facilities to evaluate different catalysts. In that case, the above methodology can still be used with emphasis shifted toward using the MAT data to compare the candidate catalysts. It is important that MAT data are properly corrected for temperature, "soaking time," and catalyst strippability effects.

In evaluating FCC catalyst, one must also pay special attention to the catalyst physical properties (e.g. PSD and attrition index) as well as long-term pricing.

Summary

The introduction of zeolite into the FCC catalyst in the early 1960s was one of the most significant developments in the field of cat cracking. The zeolite greatly improved selectivity of the catalyst, resulting in higher gasoline yields and indirectly allowing refiners to process more feed to the unit.

With the rare earth (lanthanum and cerium oxide), prices skyrocketing by more than 2,000% in the past 4 years; the catalyst manufacturers are becoming creative to arrive at new catalyst formulations to deliver similar results with lower rare earth content.

For cat crackers that process "tough" feedstock, the challenge would be to arrive at a zeolite formulation that would sustain high levels of feedstock impurities, as well as hydrothermal deactivation in the regenerator. For FCC units that process deep hydrotreated feedstock, the catalyst choice should include maximum activity while having excellent physical properties.

Since there are so many different FCC catalyst formulations in the market today, it is important that the refinery personnel involved in cat cracker operations have some fundamental understanding of catalyst technology. This knowledge is useful in areas such as proper troubleshooting and customizing a catalyst to match the refiner's needs. The additive technology will be expanding in coming years.

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CHAPTER 5

Catalyst and Feed Additives

Many FCC units use additive compounds for enhancing cat cracker performance. The main benefits of these additives (catalyst and feed additives) are to alter the FCC yields and reduce the amount of pollutants emitted from the regenerator. The reliable design of an automated multicomponent catalyst/additive system has allowed refiners to optimize the unit's performance and in some cases bring the unit into environmental compliance.

The additives discussed in this chapter are as follows:

- CO combustion promoter
- SO_2-reducing additive
- NO_x-reducing additive
- ZSM-5 additive
- Metal passivation
- Bottoms conversion.

CO Combustion Promoter

Most FCC units use a CO promoter to assist in the combustion of CO to CO_2 in the regenerator. The CO promoter is added to accelerate the CO combustion in the regenerator's dense phase and to minimize the higher temperature excursions which occur as a result of afterburning in the dilute phase and across the cyclones. The CO promoter enhances uniform burning of coke, particularly if there is an uneven distribution of spent catalyst within the regenerator contacting the combustion air.

Regenerators operating in full or partial combustion mode can often realize the benefits of a CO promoter. Currently, the most effective CO promoter is one that uses platinum as the active ingredient. The platinum, in the concentration range of 300−800 ppm, is typically dispersed on a support. Unfortunately, platinum-based CO promoters sometimes increase the NO_x concentration in the regenerator flue gas. For this reason, as part of a consent decree, many refiners in the United States add nonplatinum-based CO promoters.

The amount and frequency of CO promoter additions varies from one FCC unit to another. It often depends largely on the comfort zone of the console operator. In some units, a CO

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promoter is added to the regenerator two to three times a day, normally at a rate of 3−5 lb (1.36−2.27 kg) CO promoter per ton of fresh catalyst. In other FCC units, CO promoter is added only if the regenerator dilute phase and/or flue gas temperatures exceed the refinery set limit. Adding a CO promoter often increases oxygen in the flue gas, and thus allows the unit to increase the feed rate and/or conversion. During unit start-ups and prior to torch oil injection, the use of a CO promoter can improve the stability of the catalyst regeneration operation. However, not every cat cracker can justify a combustion-promoted operation. For example, in FCC units operating with low oxygen levels and partial combustion mode, a CO-promoted system could increase the coke on regenerated catalyst (CRC). This is because the CO combustion reaction competes with the carbon burning reaction for the available oxygen. In the full combustion mode of catalyst regeneration, the combustion of CO to CO_2 will also increase NO_x emissions. This is largely due to the oxidation of intermediates such as ammonia and cyanide gases into nitrogen oxide (NO). For regenerators operating in partial burn, the use of a platinum-based CO promoter may not have any impact on NO_x production and in some cases could actually lower the NO_x emissions of the CO boiler stack.

SO_x Additive

The coke on the spent catalyst entering the regenerator contains sulfur compounds. In the regenerator, the sulfur within the coke is converted to SO_2 and SO_3. This mixture of SO_2 and SO_3 is commonly referred to as SO_x. In most FCC regenerators, more than 95% of SO_x is SO_2, with the remainder being SO_3. The SO_x leaves the regenerator with the flue gas and is eventually discharged to the atmosphere. Several factors impact the concentration of SO_x in the regenerator flue gas. They include coke yield, thiophenic sulfur content of the feed, the regenerator operating conditions, and the FCC catalyst formulation.

In the United States, the SO_2 emissions compliance varies from one FCC unit to another. Some limits are based on the concentration of SO_2 in the regenerator flue gas and/or flue gas stack emissions. Other limits are based on the amount of SO_2 per 1,000 barrels of feed rate, and yet others have no meaningful bases. The current trend is to limit the SO_2 concentration to $<$25 ppm (at 0.0% oxygen).

There are three common methods for SO_x abatement. These are flue gas scrubbing, feedstock desulfurization, and SO_x additive. The use of an SO_x additive is often the most cost-effective alternative, which is the approach practiced by some refiners.

The SO_x additive is a microsphere powder that is added directly to the regenerator. Its three main active ingredients are magnesium oxide, cerium oxide, and vanadium oxide. The cerium oxide, and to a lesser extent vanadium oxide, promotes oxidation of SO_2 to SO_3 in the regenerator. The magnesium oxide is chemically bonded with the SO_3 in the

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regenerator. This stable sulfate species is carried with the circulating catalyst to the riser, where it is reduced or "regenerated" by hydrogen or water to yield H_2S and metal oxide. The vanadium oxide helps in this reaction. Table 5.1 shows the postulated chemistry of SO_2 reduction by an SO_x agent. The FCC units which use SO_2-reducing additives have a highly variable usage rate. However, the maximum amount is often <12% of the fresh catalyst addition rate. When analyzing the properties of the circulating catalyst, one must recognize that a portion of the vanadium and magnesium does not come from FCC feedstock, and also some of the rare earth concentrations are derived from cerium in the additive.

To achieve the highest efficiency of SO_x additive, it is important that:

- Excess oxygen be available to promote the SO_2 to SO_3 reaction
- There is a uniform air and catalyst distribution within the regenerator
- There is a sufficient concentration of magnesium, cerium, and vanadium oxides in the additive
- The regenerator temperature be lower; a lower temperature favors $SO_2 + ½\ O_2 \rightarrow SO_3$
- The capturing agent be physically compatible with the FCC catalyst and be easily regenerated in the riser and stripper
- Operation of the reactor stripper be as efficient as possible. The stripper efficiency is very important to allow the release of sulfate and the formation of H_2S.

Since most of the regenerators operating in a full combustion mode usually have a 1−3% excess oxygen content, the capturing efficiency of the SO_x additive is often greater in full combustion than in partial combustion units.

Table 5.1: Mechanism of Catalytic SO_2 Reduction.

A.	In the regenerator		
	Sulfur in coke (S) + O_2	→	$SO_2 + SO_3$
	$SO_2 + ½\ O_2$	→	SO_3
	$MgO + SO_3$	→	$MgSO_4$
B.	In the riser and stripper		
	$MgSO_4 + 4H_2$	→	$MgS + 4H_2O$
	$MgSO_4 + 4H_2$	→	$MgO + H_2S + 3H_2O$
	$MgS + H_2O$	→	$MgO + H_2S$

NO_x Additive

Nitrogen oxides include nitric oxide (NO), nitrogen dioxide (NO_2), and nitrous oxide (N_2O). Total $NO + NO_2$ concentration is usually referred to as NO_x. As part of the cracking reactions in the riser, ~55% of the FCC feed organic nitrogen is deposited on the spent

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catalyst. In a typical full-burn regenerator, the combustion of coke converts about 7% of the incoming organic nitrogen to NO_x (predominantly NO). The resulting NO in the regenerator flue gas is about 15 wt% of coke nitrogen. In "traditional" partial-burn regenerators, NO_x in the regenerator flue gas is essentially nonexistent (<15 ppm). Instead, NO_x precursors such as NH_3 and HCN are present.

FCC catalyst and additive suppliers offer various NO_x-reducing catalyst additives that are designed to reduce NO_x emissions in full-burn regenerators. Some of these additives employ copper, zinc, and/or rare earth metal-based catalysts to reduce NO_x in the regenerator. The success of their applications has been mixed. The copper-based additive increases hydrogen yield of the absorber off-gas.

ZSM-5 Additive

ZSM-5 is Mobil Oil's proprietary shape-selective zeolite, which has a different pore structure from that of Y zeolite. The pore size of ZSM-5 is smaller than that of Y zeolite (5.1−5.6 Å versus 8−9 Å). In addition, the pore arrangement of ZSM-5 is different from that of Y zeolite, as shown in Figure 5.1. The shape selectivity of ZSM-5 allows preferential cracking of long-chain, low-octane normal paraffins, as well as some olefins, in the gasoline fraction.

ZSM-5 additive is added to the unit to boost gasoline octane and to increase light olefin yields. ZSM-5 accomplishes this by upgrading low-octane components in the gasoline boiling range (C_7−C_{10}) into light olefins (C_3, C_4, C_5), as well as isomerizing low-octane linear olefins to high-octane branched olefins. ZSM-5 inhibits paraffin hydrogenation by cracking the C_7+ olefins. The gasoline aromatic content also goes up with the use of ZSM-5 additive [2].

ZSM-5's effectiveness depends on several variables. The cat crackers that process highly paraffinic feedstock and have lower base octane will receive the greatest benefits from using ZSM-5. ZSM-5 will have little effect on improving gasoline octane in units that process naphthenic feedstock or operate at a high conversion level.

When using ZSM-5, there is almost an even trade-off between FCC gasoline volume and LPG yield. For a one-number increase in the research octane of FCC gasoline, there is a 1−1.5 vol% decrease in the gasoline and an almost corresponding increase in the LPG. This again depends on feed quality, operating parameters, and base octane.

The decision to add ZSM-5 depends on the objectives and constraints of the unit. ZSM-5 application will increase the load on the WGC, FCC gas plant, and other downstream units. Most refiners who add ZSM-5 do it on a seasonal basis, again depending on their octane need and unit limitations.

The concentration of the ZSM-5 additive should be >1% of the catalyst inventory to see a noticeable increase in the octane. An octane boost of one research octane number (RON) will

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typically require a 2–5% ZSM-5 additive in the inventory. It should be noted that the proper way of quoting percentage should be by ZSM-5 concentration, rather than the total additive, because the activity and attrition rate can vary from one supplier to another. There are new generations of ZSM-5 additives that have nearly twice the activity of the earlier additives.

In summary, ZSM-5 provides the refiner the flexibility to increase gasoline octane and light olefins. With the introduction of reformulated gasoline (RFG), ZSM-5 could play an important role in producing isobutylene, used as the feedstock for production of methyl tertiary butyl ether (MTBE).

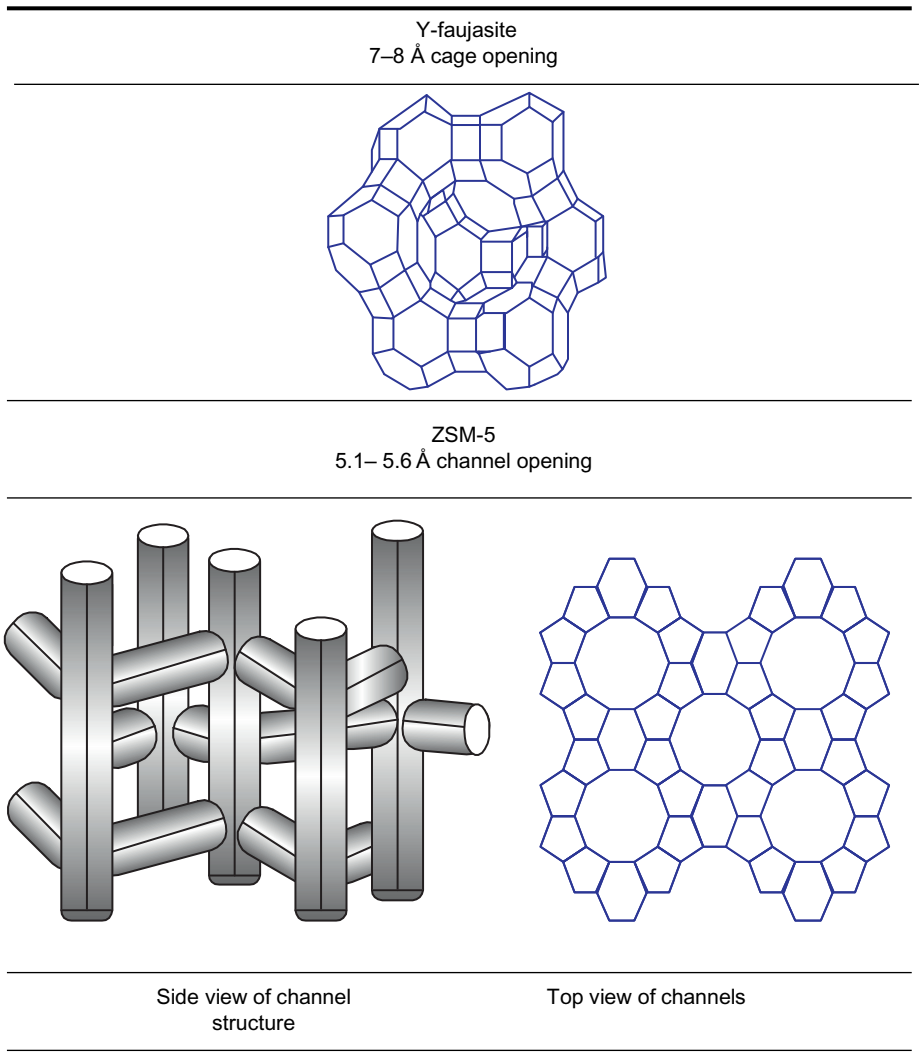


Figure 5.1: Comparison of Y-faujasite and ZSM-5 zeolites [1].

Metal Passivation

As discussed in Chapter 3, nickel, vanadium, iron, and sodium are the metal compounds usually present in the FCC feedstock. These metals deposit on the catalyst, thus poisoning the catalyst active sites. Some of the options available to refiners for reducing the effect of metals on catalyst activity are as follows:

- Increasing the fresh catalyst makeup rate
- Using outside E-cat
- Employing metal passivators
- Incorporating metal trap into the FCC catalyst
- Using demetalizing technology to remove the metals from the catalyst
- The MagnaCat separation process (demetalizing technology) that allows discarding the "older" catalyst particles containing higher metal levels.

Metal passivation in general and antimony in particular are discussed in the following section (see "Antimony" section).

In recent years, several methods have been patented for chemical passivation of nickel and vanadium. Some of the tin-based compounds have had limited commercial success in passivating vanadium. Although tin has been used by some refiners, it has neither been proven nor is it as widely accepted as antimony. In the case of nickel, antimony-based compounds have been most effective in reducing the detrimental effects of nickel poisoning. It should be noted that, although the existing antimony-based technology is the most effective method of reducing the deleterious effects of nickel, antimony is fugitive and can be considered hazardous. In this case, a bismuth-based passivator may be a better choice.

Antimony

Antimony-based passivation was introduced by Phillips Petroleum in 1976 to passivate nickel compounds in the FCC feed. Antimony is injected into the fresh feed, usually with the help of a carrier fluid such as LCO. If there are feed preheaters in the unit, antimony should be injected downstream of the preheater to avoid thermal decomposition of the antimony solution in the heater tubes.

The effects of antimony passivation are usually immediate. By forming an alloy with nickel, the dehydrogenation reactions that are caused by nickel are often reduced by 40−60%. This is evidenced by a sharp decline in dry gas and hydrogen yield.

Nickel passivation can be economically attractive when the nickel content of the E-cat is >500 ppm. The antimony solution should be added in proportion to the amount of nickel present in the feed. The optimum dosage normally corresponds to an antimony to nickel

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ratio of 0.3−0.5 of the E-cat. Antimony's retention efficiency on the catalyst is in the range of 75−85% without the recycling of slurry oil to the riser. If slurry recycle is being practiced, the retention efficiency is usually >90%. Any antimony not deposited on the circulating catalyst ends up in the DO and the catalyst fines from the regenerator. It is often a good practice to discontinue antimony injection about 1 month prior to a scheduled unit shutdown to ensure that the exposure to catalyst dust containing antimony is reduced to a minimum when wearing a half-faced respirator.

Bottoms-Cracking Additive

In situations where one of the key objectives is to maximize LCO production without producing too much slurry oil, one option worth evaluating would be the use of a bottoms-upgrading catalyst additive. These additives employ concentrated alumina catalysts that can selectively precrack large feed molecules.

Summary

In summary, with automated and reliable loading systems, the use of catalyst additives has allowed refiners' to improve the FCC unit performance and meet the required environmental compliances. The FCC unit engineers and supervisors must pay close attention to the catalyst additives' usage rate versus the pricing for these additives. An FCC unit's margins can be greatly impacted if these usage rates are not closely monitored.

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[1] R.J. Madon, J. Spielman, Increasing gasoline octane and light olefin yields with ZSM-5, Catal. Rep. 5(9) (1990).

[2] C. Liu, Effects of ZSM-5 on the aromatization performance in cracking catalyst, J. Mol. Catal. 215 (2004) 195−199.

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CHAPTER 6

Chemistry of FCC Reactions

A complex series of reactions (Table 6.1) take place when a large gas oil molecule comes in contact with a 1,200−1,400°F (650−760°C) FCC catalyst. The distribution of products depends on many factors, including the nature and strength of the catalyst acid sites. Although most cracking in the FCC is catalytic, thermal cracking reactions also occur. Thermal cracking is caused by factors such as nonideal mixing in the riser and poor separation of cracked products in the reactor.

The purpose of this chapter is:

- To provide a general discussion of the chemistry of cracking (both thermal and catalytic)
- To highlight the role of the catalyst and, in particular, the influence of zeolites
- To explain how cracking reactions affect the unit's heat balance.

Whether thermal or catalytic, cracking of a hydrocarbon means the breaking of a carbon-to-carbon bond. But catalytic and thermal cracking proceed via different routes. A clear understanding of the different process mechanisms involved is beneficial in the following unit operations:

- Selecting the "right" catalyst for a given operation
- Troubleshooting unit operation
- Developing a new catalyst formulation.

Topics discussed in this chapter are as follows:

- Thermal cracking
- Catalytic cracking
- Thermodynamic aspects.

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Table 6.1: Important Reactions Occurring in the FCC Unit.

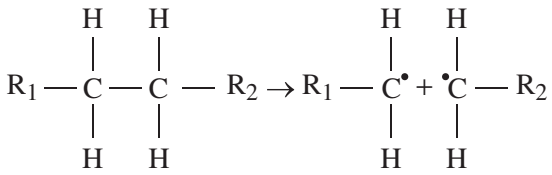
1.	Cracking:	
	Paraffins cracked to olefins and smaller paraffins	$C_{10}H_{22} \rightarrow C_4H_{10} + C_6H_{12}$
	Olefins cracked to smaller olefins	$C_9H_{18} \rightarrow C_4H_8 + C_5H_{10}$
	Aromatic side-chain scission	$ArC_{10}H_{21} \rightarrow ArC_5H_9 + C_5H_{12}$
	Naphthenes (cycloparaffins) cracked to olefins and smaller ring compounds	Cyclo-$C_{10}H_{20} \rightarrow C_6H_{12} + C_4H_8$
2.	Isomerization:	
	Olefin bond shift	1-$C_4H_8 \rightarrow$ trans-2-C_4H_8
	Normal olefin to iso-olefin	*n*-$C_5H_{10} \rightarrow$ iso-C_5H_{10}
	Normal paraffin to isoparaffin	*n*-$C_4H_{10} \rightarrow$ iso-C_4H_{10}
	Cyclohexane to cyclopentane	$C_6H_{12} + C_5H_9CH_3$
3.	Hydrogen transfer:	Naphthene + olefin $\rightarrow$ aromatic + paraffin
	Cycloaromatization	$C_6H_{12} + 3C_5H_{10} \rightarrow C_6H_6 + 3C_5H_{12}$
4.	Transalkylation/alkyl-group transfer	$C_6H_4(CH_3)_2 + C_6H_6 \rightarrow 2C_6H_5CH_3$
5.	Cyclization of olefins to naphthenes	$C_7H_{14} \rightarrow CH_3$-cyclo-$C_6H_{11}$
6.	Dehydrogenation	*n*-$C_8H_{18} \rightarrow C_8H_{16} + H_2$
7.	Dealkylation	Iso-C_3H_7-$C_6H_5 \rightarrow C_6H_6 + C_3H_6$
8.	Condensation	Ar-CH$=$$CH_2 + R_1CH=CHR_2 \rightarrow$ Ar—Ar + 2H

Thermal Cracking

Before the advent of the catalytic cracking process, thermal cracking was the primary process available to convert low-value feedstocks into lighter products. Refiners still use thermal processes such as delayed coking and visbreaking for cracking of residual hydrocarbons.

Thermal cracking is a function of temperature and time. The reaction occurs when hydrocarbons in the absence of a catalyst are exposed to high temperatures in the range of 800−1,200°F (425−650°C).

The initial step in the chemistry of thermal cracking is the formation of free radicals. They are formed upon splitting the C—C bond. A free radical is an uncharged molecule with an unpaired electron. The rupturing produces two uncharged species which share a pair of electrons. Equation (6.1) shows formation of a free radical when a paraffin molecule is thermally cracked.



(6.1)

Free radicals are extremely reactive and short-lived. They can undergo alpha-scission, beta-scission, and polymerization. (Alpha-scission is a break one carbon away from the free radical; beta-scission, two carbons away.)

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Beta-scission produces an olefin (ethylene) and a primary free radical (Eq. (6.2)) which has two fewer carbon atoms [1]:

$$R-CH_2-CH_2-{}^{\bullet}C-H_2 \rightarrow R-{}^{\bullet}C-H_2 + H_2C{=}CH_2 \tag{6.2}$$

The newly formed primary free radical can undergo further beta-scission to yield more ethylene.

Alpha-scission is not favored thermodynamically but does occur. Alpha-scission produces a methyl radical, which can extract a hydrogen atom from a neutral hydrocarbon molecule. The hydrogen extraction produces methane and a secondary or tertiary free radical (Eq. (6.3)).

$$\begin{aligned} &H_3C^{\bullet} + R-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3 \\ &\rightarrow CH_4 + R-CH_2-CH_2-CH_2-CH_2-{}^{\bullet}CH-CH_2-CH_3 \end{aligned} \tag{6.3}$$

This radical can undergo beta-scission. The products will be an alpha-olefin and a primary free radical (Eq. (6.4)).

$$\begin{aligned} &R-CH_2-CH_2-CH_2-CH_2-{}^{\bullet}CH-CH_2-CH_3 \\ &\rightarrow R-CH_2-CH_2-{}^{\bullet}CH_2 + H_2C{=}CH-CH_2-CH_3 \end{aligned} \tag{6.4}$$

Similar to the methyl radical, the $R-{}^{\bullet}CH_2$ radical can also extract a hydrogen atom from another paraffin to form a secondary free radical and a smaller paraffin (Eq. (6.5)).

$$\begin{aligned} &R_1-{}^{\bullet}CH_2 + R-CH_2-CH_2-CH_2-\ CH_2-CH_2-CH_2-CH_3 \\ &\rightarrow R-CH_3 + R-CH_2-CH_2-CH_2-CH_2-CH_2-{}^{\bullet}CH-CH_3 \end{aligned} \tag{6.5}$$

$R-{}^{\bullet}CH_2$ is more stable than $H_3{}^{\bullet}C$. Consequently, the hydrogen extraction rate of $R-{}^{\bullet}CH_2$ is lower than that of the methyl radical.

This sequence of reactions forms a product rich in C_1 and C_2, and a fair amount of alpha-olefins. Free radicals undergo little branching (isomerization).

One of the drawbacks of thermal cracking in an FCC is that a high percentage of the olefins formed during intermediate reactions polymerize and condense directly to coke.

The product distribution from thermal cracking is different from catalytic cracking, as shown in Table 6.2. The shift in product distribution confirms the fact that these two processes proceed via different mechanisms.

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Table 6.2: Comparison of Products of Thermal and Catalytic Cracking.

Hydrocarbon Type	Thermal Cracking	Catalytic Cracking
n-Paraffins	C_2 is major product, with much C_1 and C_3, and C_4 to C_{16} olefins; little branching	C_3 to C_6 is major product; few *n*-olefins above C_4; much branching
Olefins	Slow double-bond shifts and little skeletal isomerization; H-transfer is minor and nonselective for tertiary olefins; only small amounts of aromatics formed from aliphatics at 932°F (500°C)	Rapid double-bond shifts, extensive skeletal isomerization, H-transfer is major and selective for tertiary olefins; large amounts of aromatics formed from aliphatics at 932°F (500°C)
Naphthenes	Crack at slower rate than paraffins	If structural groups are equivalent, crack at about the same rate as paraffins
Alkyl-aromatics	Crack within side chain	Crack next to the ring

Source: Venuto [2].

Catalytic Cracking

Catalytic reactions can be classified into two broad categories:

1. Primary cracking of the gas oil molecules
2. Secondary rearrangement and recracking of cracked products.

Before discussing mechanisms of the reactions, it is appropriate to review FCC catalyst development and examine its cracking properties. An in-depth discussion of FCC catalyst is presented in Chapter 4.

FCC Catalyst Development

The first commercial FCC was acid-treated natural clay. Later, synthetic silica–alumina materials containing 10–15% alumina replaced the natural clay catalysts. The synthetic silica–alumina catalysts were more stable and yielded superior products.

In the mid-1950s, alumina–silica catalysts, containing 25% alumina, came into use because of their higher stability. These synthetic catalysts were amorphous; their structure consisted of a random array of silica and alumina, tetrahedrally connected. Some minor improvements in yields and selectivity were achieved by switching to catalysts such as magnesia–silica and alumina–zirconia–silica.

Impact of Zeolites

The breakthrough in FCC catalyst was the use of X and Y zeolites during the early 1960s. Addition of these zeolites substantially increased catalyst activity and selectivity. Product distribution with a zeolite-containing catalyst is different from the distribution with an amorphous silica–alumina catalyst (Table 6.3). In addition, zeolites are 1,000 times more active than the amorphous silica–alumina catalysts. The higher activity comes from greater strength and organization of the active sites in the zeolites.

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Zeolites are crystalline alumina silicates having a regular pore structure. Their basic building blocks are silica and alumina tetrahedra. Each tetrahedron consists of silicon or aluminum atoms at the center of the tetrahedron with oxygen atoms at the corners. Because silicon and aluminum are in a +4 and +3 oxidation state, respectively, a net charge of −1 must be balanced by a cation to maintain electrical neutrality.

The cations that replace the sodium ions determine the catalyst's activity and selectivity. Zeolites are synthesized in an alkaline environment such as sodium hydroxide, producing a soda-Y zeolite. These soda-Y zeolites have little stability, but the sodium can be easily exchanged. Ion exchanging sodium with cations, such as hydrogen or rare earth ions, enhances acidity and stability. The most widely used rare earth compounds are lanthanum (La^{3+}) and cerium (Ce^{3+}).

The catalyst acid sites are both Bronsted and Lewis type. The catalyst can have either strong or weak Bronsted sites or strong or weak Lewis sites. A Bronsted-type acid is a substance capable of donating a proton. Hydrochloric and sulfuric acids are typical Bronsted acids. A Lewis-type acid is a substance that accepts a pair of electrons. Lewis acids may not have hydrogen in them, but they are still acids. Aluminum chloride is the classic example of a Lewis acid. Dissolved in water, it will react with hydroxyl, causing a drop in solution pH.

Catalyst acid properties depend on several parameters, including method of preparation, dehydration temperature, silica to alumina ratio, and the ratio of Bronsted to Lewis acid sites.

Table 6.3: Comparison of Yield Structure for FCC of Waxy Gas Oil over Commercial Equilibrium Zeolite and Amorphous Catalysts.

Yields, at 80 vol% Conversion	Amorphous, High Alumina	Zeolite, XZ-25	Change from Amorphous
Hydrogen (wt%)	0.08	0.04	−0.04
C_1's + C_2's (wt%)	3.8	2.1	−1.7
Propylene (vol%)	16.1	11.8	−4.3
Propane (vol%)	1.5	1.3	−0.02
Total C_3's	17.6	13.1	−4.5
Butenes (vol%)	12.2	7.8	−4.4
i-Butane (vol%)	7.9	7.2	−0.7
n-Butane (vol%)	0.7	0.4	−0.3
Total C_4's	20.8	15.4	−5.4
C_5-390 at 90% ASTM gasoline (vol%)	55.5	62.0	+6.5
Light fuel oil (vol%)	4.2	6.1	+1.9
Heavy fuel oil (vol%)	15.8	13.9	−1.9
Coke (wt%)	5.6	4.1	−1.5
Gasoline octane number	94	89.8	−4.2

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Mechanism of Catalytic Cracking Reactions

When feed contacts the regenerated catalyst, the feed vaporizes. Then positive-charged atoms called *carbocations* are formed. Carbocation is a generic term for a positive-charged carbon ion. Carbocations can be either *carbonium* or *carbenium* ions.

A carbonium ion, CH_5^+, is formed by adding a hydrogen ion (H^+) to a paraffin molecule (Eq. (6.6)). This is accomplished via direct attack of a proton from the catalyst Bronsted site. The resulting molecule will have a positive charge with five bonds to it.

$$\begin{aligned} &R{-}CH_2{-}CH_2{-}CH_2{-}CH_3 + H^+ \text{ (proton attack)} \\ &\rightarrow R{-}C^+H{-}CH_2{-}CH_2{-}CH_3 + H_2 \end{aligned} \tag{6.6}$$

The carbonium ion's charge is not stable, and the acid sites on the catalyst are not strong enough to form many carbonium ions. Nearly all the cat cracking chemistry is carbenium ion chemistry.

A carbenium ion, $R{-}CH_2^+$, comes either from adding a positive charge to an olefin or from removing a hydrogen and two electrons from a paraffin (Eqs. (6.7) and (6.8)).

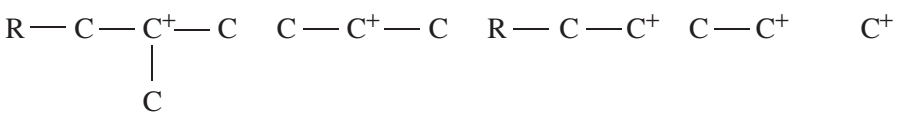
$$\begin{aligned} &R{-}CH{=}CH{-}CH_2{-}CH_2{-}CH_3 + H^+ \text{ (a proton at Bronsted site)} \\ &\rightarrow R{-}C^+H{-}CH_2{-}CH_2{-}CH_2{-}CH_3 \end{aligned} \tag{6.7}$$

$$\begin{aligned} &R{-}CH_2{-}CH_2{-}CH_2{-}CH_3 \text{ (removal of } H^- \text{ at Lewis site)} \\ &\rightarrow R{-}C^+H{-}CH_2{-}CH_2{-}CH_3 \end{aligned} \tag{6.8}$$

Both the Bronsted and Lewis acid sites on the catalyst generate carbenium ions. The Bronsted site donates a proton to an olefin molecule and the Lewis site removes electrons from a paraffin molecule. In commercial units, olefins come in with the feed or are produced through thermal cracking reactions.

The stability of carbocations depends on the nature of alkyl groups attached to the positive charge. The relative stability of carbenium ions is as follows [2], with tertiary ions being the most stable:

Tertiary > Secondary > Primary > Ethyl > Methyl



One of the benefits of catalytic cracking is that the primary and secondary ions tend to rearrange to form a tertiary ion (a carbon with three other carbon bonds attached). As will be discussed later, the increased stability of tertiary ions accounts for the high degree of branching associated with cat cracking.

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Once formed, carbenium ions can form a number of different reactions. The nature and strength of the catalyst acid sites influence the extent to which each of these reactions occur. The three dominant reactions of carbenium ions are:

1. The cracking of a carbon−carbon bond
2. Isomerization
3. Hydrogen transfer.

Cracking Reactions

Cracking, or beta-scission, is a key feature of ionic cracking. Beta-scission is the splitting of the C−C bond two carbons away from the positive-charged carbon atom. Beta-scission is preferred because the energy required to break this bond is lower than that needed to break the adjacent C−C bond, the alpha bond. In addition, short-chain hydrocarbons are less reactive than long-chain hydrocarbons. The rate of the cracking reactions decreases with decreasing chain length. With short chains, it is not possible to form stable carbenium ions.

The initial products of beta-scission are an olefin and a new carbenium ion (Eq. (6.9)). The newly formed carbenium ion will then continue a series of chain reactions. Small ions (four-carbon or five-carbon) can transfer the positive charge to a big molecule, and the big molecule can crack. Cracking does not eliminate the positive charge; it stays until two ions collide. The smaller ions are more stable and will not crack. They survive until they transfer their charge to a big molecule.

$$\begin{aligned} &R-C^{+}H-CH_2-CH_2-CH_2-CH_3 \\ &\rightarrow CH_3-CH{=}CH_2 + C^{+}H_2-CH_2-CH_2R \end{aligned} \tag{6.9}$$

Because beta-scission is monomolecular and cracking is endothermic, the cracking rate is favored by high temperatures and is not equilibrium-limited.

Isomerization Reactions

Isomerization reactions occur frequently in catalytic cracking, infrequently in thermal cracking. In both, breaking of a bond is via beta-scission. However, in catalytic cracking, carbocations tend to rearrange to form tertiary ions. Tertiary ions are more stable than secondary and primary ions; they shift around and crack to produce branched molecules (Eq. (6.10)). (In thermal cracking, free radicals yield normal or straight-chain compounds.)

$$CH_3-CH_2-C^{+}H-CH_2-CH_2R \rightarrow CH_3-\underset{\displaystyle H}{\overset{\displaystyle |}{\underset{\displaystyle |}{C^{+}}}}-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{\underset{\displaystyle |}{CH}}}-CH_2R$$

$$\text{or}$$

$$C^{+}H_2-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{\underset{\displaystyle |}{CH}}}-CH_2-CH_2R \tag{6.10}$$

Some of the advantages of isomerization are as follows:

- Higher octane in the gasoline fraction. Isoparaffins in the gasoline boiling range have higher octane than normal paraffins.
- High-value chemical and oxygenate feedstocks in the C_3/C_4 fraction. Isobutylene and isoamylene are used for the production of MTBE and tertiary amyl methyl ether (TAME). MTBE and TAME can be blended into the gasoline to reduce auto emissions.
- Lower cloud point in the diesel fuel. Isoparaffins in the LCO boiling range improve the cloud point.

Hydrogen Transfer Reactions

Hydrogen transfer is more correctly called hydride transfer. It is a bimolecular reaction in which one reactant is an olefin. Two examples are the reaction of two olefins and the reaction of an olefin and a naphthene.

In the reaction of two olefins, both olefins must be adsorbed on active sites that are close together. One of these olefins becomes a paraffin and the other becomes a cyclo-olefin as hydrogen is moved from one to the other. Cyclo-olefin is now hydrogen transferred with another olefin to yield a paraffin and a cyclodiolefin. Cyclodiolefin will then rearrange to form an aromatic. The chain ends because aromatics are extremely stable. Hydrogen transfer of olefins converts them to paraffins and aromatics (Eq. (6.11)).

$$\begin{array}{ccccccc} 4C_nH_{2n} & \rightarrow & 3C_nH_{2n+2} & + & C_nH_{2n-6} \\ \text{olefins} & \rightarrow & \text{paraffins} & + & \text{aromatic} \end{array} \tag{6.11}$$

In the reaction of naphthenes with olefins, naphthenic compounds are hydrogen donors. They can react with olefins to produce paraffins and aromatics (Eq. (6.12)).

$$\begin{array}{ccccccccc} 3C_nH_{2n} & + & C_mH_{2m} & \rightarrow & 3C_nH_{2n+2} & + & C_mH_{2m-6} \\ \text{olefins} & + & \text{naphthene} & \rightarrow & \text{paraffins} & + & \text{aromatic} \end{array} \tag{6.12}$$

A rare earth-exchanged zeolite increases hydrogen transfer reactions. In simple terms, rare earth forms bridges between two to three acid sites in the catalyst framework. In doing so, the rare earth protects those acid sites. Because hydrogen transfer needs adjacent acid sites, bridging these sites with rare earth promotes hydrogen transfer reactions.

Hydrogen transfer reactions usually increase gasoline yield and stability. The reactivity of the gasoline is reduced because hydrogen transfer produces fewer olefins.

Olefins are the reactive species in gasoline for secondary reactions; therefore, hydrogen transfer reactions indirectly reduce “overcracking” of the gasoline.

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Some of the drawbacks of hydrogen transfer reactions are as follows:

- Lower gasoline octane
- Lower light olefin in the LPG
- Higher aromatics in the gasoline and LCO
- Lower olefin in the front end of gasoline.

Other Reactions

Cracking, isomerization, and hydrogen transfer reactions account for the majority of cat cracking reactions. Other reactions play an important role in unit operation. Two prominent reactions are dehydrogenation and coking.

Dehydrogenation: Under ideal conditions, i.e. a "clean" feedstock and a catalyst with no metals, cat cracking does not yield any appreciable amount of molecular hydrogen. Therefore, dehydrogenation reactions will proceed only if the catalyst is contaminated with metals such as nickel and vanadium.

Coking: Cat cracking yields a residue called coke. The chemistry of coke formation is complex and not very well understood. Similar to hydrogen transfer reactions, catalytic coke is a "bimolecular" reaction. It proceeds via carbenium ions or free radicals. In theory, coke yield should increase as the hydrogen transfer rate is increased. It is postulated [3] that reactions producing unsaturates and multiring aromatics are the principal coke-forming compounds. Unsaturates such as olefins, diolefins, and multiring polycyclic olefins are very reactive and can polymerize to form coke.

For a given catalyst and feedstock, catalytic coke yield is a direct function of conversion. However, an optimum riser temperature will minimize coke yield. For a typical cat cracker, this temperature is about 950°F (510°C). Consider two riser temperatures, 850°F and 1,050°F (454°C and 566°C), at the extreme limits of operation. At 850°F, a large amount of coke is formed because the carbenium ions do not desorb at this lower temperature. At 1,050°F, a large amount of coke is formed, largely due to olefin polymerization. The minimum coking temperature is within this range.

Thermodynamic Aspects

As stated earlier, catalytic cracking involves a series of simultaneous reactions. Some of these reactions are endothermic and some are exothermic. Each reaction has a heat of reaction associated with it (Table 6.4). The overall heat of reaction refers to the net or combined heat of reaction. Although there are a number of exothermic reactions, the net reaction is still endothermic.

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Table 6.4: Some Thermodynamic Data for Idealized Reactions of Importance in Catalytic Cracking.

Reaction Class	Specific Reaction	Log K_E (Equilibrium Constant)			Heat of Reaction Btu/mole
		850°F	950°F	980°F	950°F
Cracking	n-$C_{10}H_{22} \rightarrow n$-$C_7H_{16} + C_3H_6$	2.04	2.46	–	32,050
	1-$C_8H_{16} \rightarrow 2C_4H_8$	1.68	2.10	2.23	33,663
Hydrogen transfer	$4C_6H_{12} \rightarrow 3C_6H_{14} + C_6H_6$	12.44	11.09	–	109,681
	cyclo-C_6H_{12} +3 1-$C_5H_{10} \rightarrow$ $3n$-$C_5H_{12} + C_6H_6$	11.22	10.35	–	73,249
Isomerization	1-$C_4H_8 \rightarrow$ trans-2-C_4H_8	0.32	0.25	0.09	−4,874
	n-$C_6H_{10} \rightarrow$ iso-C_4H_{10}	−0.20	−0.23	−0.36	−3,420
	o-$C_6H_4(CH_3)_2 \rightarrow m$-$C_6H_4(CH_3)_2$	0.33	0.30	–	1,310
	Cyclo-$C_6H_{12} \rightarrow$ CH_3-cyclo-C_5H_9	1.00	1.09	1.10	6,264
Transalkylation	$C_6H_6 + m$-$C_6H_4(CH_3)_2 \rightarrow 2C_6H_5CH_3$	0.65	0.65	0.65	−221
Cyclization	1-$C_7H_{14} \rightarrow$ CH_3-cyclo-C_6H_{11}	2.11	1.54	–	−37,980
Dealkylation	Iso-C_3H_7-$C_6H_5 \rightarrow C_6H_6 + C_3H_6$	0.41	0.88	1.05	40,602
Dehydrogenation	n-$C_6H_{14} \rightarrow$ 1-$C_6H_{12} + H_2$	−2.21	−1.52	–	56,008
Polymerization	$3C_2H_4 \rightarrow$ 1-C_6H_{12}	–	–	−1.2	–
Paraffin alkylation	1-C_4H_8 + iso-$C_4H_{10} \rightarrow$ iso-C_8H_{18}	–	–	3.3	–

Source: Venuto [2].

The regenerated catalyst supplies enough energy to heat the feed to the riser outlet temperature, to heat the combustion air to the flue gas temperature, to provide the endothermic heat of reaction, and to compensate for any heat losses to atmosphere. The source of this energy is the burning of coke produced from the reaction.

It is apparent that the type and magnitude of these reactions have an impact on the heat balance of the unit. For example, a catalyst with less hydrogen transfer characteristics will cause the net heat of reaction to be more endothermic. Consequently, this will require a higher catalyst circulation and, possibly, a higher coke yield to maintain the heat balance.

Summary

Although cat cracking reactions are predominantly catalytic, some nonselective thermal cracking reactions do take place. The two processes proceed via different chemistry. The distribution of products clearly confirms that both reactions take place but that catalytic reactions predominate.

The introduction of zeolites into the FCC catalyst in the early 1960s drastically improved the performance of the cat cracker reaction products. The catalyst acid sites, their nature and strength, have a major influence on the reaction chemistry.

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Catalytic cracking proceeds mainly via carbenium ion intermediates. The three dominant reactions are cracking, isomerization, and hydrogen transfer. Finally, the type and degree of reactions occurring will influence the unit heat balance.

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[3] G. Koermer, M. Deeba, The chemistry of FCC coke formation, Catal. Rep., Engelhard Corporation, 7(2) (1991).

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CHAPTER 7

Unit Monitoring and Control

The proper way to monitor the performance of a cat cracker is by periodic material and heat balance surveys on the unit. By carrying out these tests frequently, one can collect, trend, and evaluate the unit's operating data. Additionally, meaningful technical service to optimize the unit's operation should be based on regular test runs.

Understanding the operation of a cat cracker also requires in-depth knowledge of the unit's heat balance. Any changes to feedstock quality, operating conditions, catalyst, or mechanical configuration will impact the heat balance. Heat balance is an important tool in predicting and evaluating the changes that will affect the quantity and the quality of FCC products.

Finally, before the unit can produce a single barrel of product, it must circulate the catalyst smoothly and, therefore, one must be quite familiar with the dynamics of pressure balance.

The main topics discussed in this chapter are as follows:

- Material balance
- Heat balance
- Pressure balance.

In the material balance and heat balance sections, the discussions include the following:

- Two methods for performing test runs
- Some practical steps for carrying out a successful test run
- A step-by-step method for performing a material and heat balance survey
- An actual case study.

In the pressure balance section, the significance of the pressure balance in debottlenecking the unit is discussed.

This chapter presents the entire procedure for performing heat and weight balances.

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Material Balance

Complete data collection should be carried out weekly. Since changes in the unit are continuous, regular surveys permit distinction among the effects of feedstock, catalyst, and operating conditions. An accurate assessment of a cat cracker operation requires reliable plant data. A reasonable weight balance should have a 98−102% closure.

In any weight balance exercise, the first step is to identify the input and output streams. This is usually done by drawing an envelope(s) around the input and output streams. Two examples of such envelopes are shown in Figure 7.1.

One of the key objectives of conducting the mass balance exercise is to determine the composition of products leaving the reactor. The reactor effluent vapors entering the main fractionator contain hydrocarbons, steam, and inert gases. By weight, the hydrocarbons in the reactor overhead stream are equal to the fresh feed plus any recycle minus the portion of the feed that was converted to coke. The main sources of steam in the reactor vapors are lift steam to the riser, atomization steam to the feed nozzles, reactor dome steam, and stripping steam. Some FCC units may purposely inject water into the feed injection system as part of heat removal from the regenerator. Depending on the reactor pressure and catalyst circulation rate, ~25−50% of the stripping steam is entrained with the spent catalyst flowing to the regenerator and should be deducted.

Inert gases such as nitrogen, carbon monoxide, and carbon dioxide enter the riser and are carried down with the regenerated catalyst. The quantity of these inert gases is proportional to the catalyst circulation rate. These inert gases flow through the FCC gas plant and leave the unit with the off-gas from the sponge oil absorber column. When performing mass balance, the flow rates of these inert gases should be deducted. Additionally, the absorber off-gas samples are often taken after amine treatment; therefore, one must adjust the chromatograph analyses of the treated gas to account for H_2S and CO_2. Depending on the feedstock quality and operating conditions, about 30−50% of the feed's sulfur is converted to H_2S as part of the cracking FCC feedstock.

FCC products are commonly reported, on an inert-free basis, as the volume and weight fractions of the fresh feed. In a rigorous weight balance, gasoline, LCO, slurry oil yields, and unit conversion are reported based on fixed cut points. The common cut points are 430°F (221°C) TBP cut point for gasoline and 670°F (354°C) TBP cut point for LCO. Using fixed cut points isolates the reactor yields from the distillation system performance.

Conversion is defined as the volume or weight percent of feedstock converted to gasoline and other lighter products, including coke. However, conversion is typically calculated by subtracting the volume percent or weight percent of liquid products heavier than gasoline from fresh feed and dividing by the volume or weight of fresh feed. This is shown as follows:

$$\text{Conversion } \% = \frac{\text{Fresh feed} - (\text{LCO product} + \text{HCO product} + \text{slurry oil product})}{\text{Feed}} \times 100 \tag{7.1}$$

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Depending on seasonal demands, the gasoline end point can range from 360°F to 450°F (182−232°C). Undercutting of gasoline increases the LCO product and can appear as low conversion. Therefore, it is necessary to distinguish between the *apparent* and *true* conversion. The apparent conversion is calculated before adjustments are made to gasoline, LCO, and slurry oil distillations. True conversion is calculated after the cut-point adjustments to gasoline, LCO, and slurry oil products.

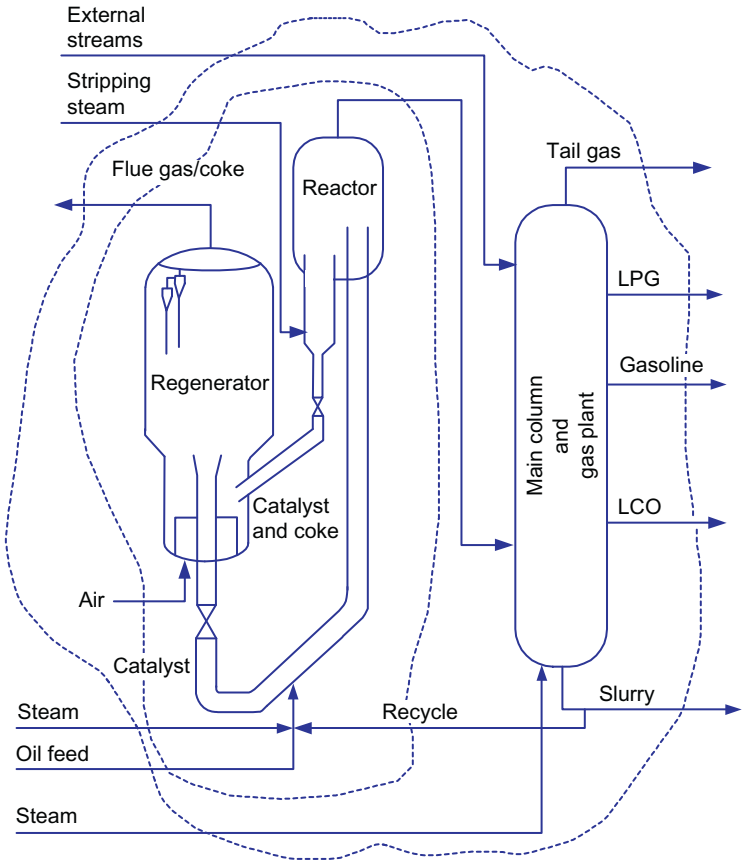


Figure 7.1: FCC unit input/output streams.

Testing Methods

The material balance around the riser requires the reactor effluent composition. Two techniques are used to get this composition. Both techniques require that the coke yield be calculated.

The first technique is to draw an envelope with the reactor effluent as the inlet stream and the product flows as the outlet streams. Included in this envelope must be any external streams that are entering into the main fractionator and/or FCC gas plant circuits. The reactor yields and its composition are determined by subtracting the products from the main fractionator and gas plant from the external streams. This is the method practiced by most refiners.

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The second technique involves direct sampling of the reactor effluent (Figure 7.2). In this technique, a sample of reactor effluent is collected in an aluminized polyester bag for separation and analysis.

There are several advantages and disadvantages to reactor effluent sampling, which are as follows.

Advantages of Reaction Mix Sampling

- Allows data gathering on different sets of conditions without waiting for the recovery side to equilibrate
- Eliminates concern about correcting for end points because the effluent sample is cut at the desired TBP end point
- Eliminates concern about obtaining a 100% weight balance.

Disadvantages of Reaction Mix Sampling

- Possible leaks during sampling
- Possible inaccurate measurement of volume of gas and weight of liquid
- Requires qualified individuals to perform the test
- Requires separate lab to perform analyses
- Can require special procedures and be expensive.

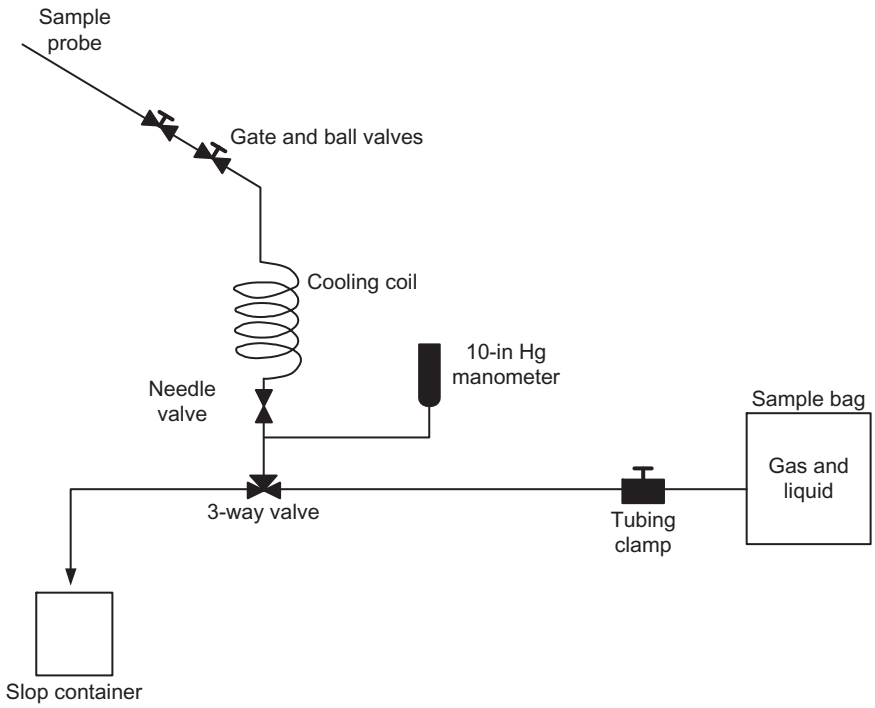


Figure 7.2: Reaction mix sampling [1].

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Recommended Procedures for Conducting a Test Run

A successful test run requires a clear definition of objectives, careful planning, and proper interpretation of the results. The following steps can be used as a guide to ensure a smooth and successful test run.

Prior to the Test Run

1. Issue a memo to the involved departments: operations, laboratory, maintenance, and oil movement. Communicate the purpose, duration, and scope of the test run. Include a list of samples and the required analyses (Table 7.1).
2. Inform the units feeding the FCC. The composition of FCC feedstock should remain relatively constant during the test run.
3. Accounting and air-flow meters should be zeroed and calibrated.
4. Sample taps should be checked, particularly those that are not used regularly.
5. The sample bombs used to collect gas, LPG, and gasoline products should be purged, marked, and ready.

Table 7.1: Typical Laboratory Analysis of FCC Streams.

FCC Feed Properties	
• API gravity • Full distillation, SIMDIS • Nitrogen (basic and total) • Refractive index (at 20°C and 67°C)	• Aniline point (°F) • Sulfur (wt%) • Viscosity (at 100°F and 210°F), Cp • Concarbon or Ramsbottom • Metals

Product Properties								
	API Gravity	**Sulfur**	**Octane RON/MON**	**RVP***	**Nitrogen**	**Ash**	**SIMDIS**	**Asphaltenes**
Gasoline	X	X	X	X	X		X	
LCO	X	X			X		X	
Slurry oil	X	X			X	X	X	X

Flue Gas Analysis	
• O_2 (mol%) • CO (ppm or mol%)	• CO_2 (mol%) • NO_x (ppm) • SO_2 (ppm)

GC Analyses	
• FCC sponge absorber off-gas (before amine treater) • LPG (before treater)	• Gasoline • External streams

RVP = Reid vapor pressure.

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Data Collection

1. The duration of a test run is usually 12–24 h.
2. Operating parameters should be specified. It should be documented which constraints (i.e. blower, WGC, etc.) the unit is operating against.
3. The sample taps must be bled adequately before samples are collected. A reliable flue gas analysis is important; an extra sample can be collected. The laboratory should retain the unused samples until all analyses are verified.
4. Absorber off-gas and C_3/C_4 samples must be collected upstream of the amine treaters (if possible) to ensure proper fractions of H_2S are reported.
5. Pertinent operating data must be collected. A form similar to the one shown in Table 7.2 can be used to gather the data.

Table 7.2: Operating Data.

Feed and Product Rates	
Fresh feed rate, bpd/(m^3/h)	50,000/(331)
Coker off-gas, scfd/(m^3/h)	3,000,000/(3,540)
FCC tail gas, scfd/(m^3/h)	16,000,000/(18,878)
LPG product, bpd/(m^3/h)	11,565/(77)
Gasoline product, bpd/(m^3/h)	30,000/(199)
LCO, bpd/(m^3/h)	10,000/(66)
Slurry oil product, bpd/(m^3/h)	3,000/(20)
Other Pertinent Flow Rates	
Dispersion steam, lb/h/(kg/h)	9,000/(4,082)
Reactor stripping steam, lb/h/(kg/h)	13,000/(5,897)
Reactor dome steam, lb/h/(kg/h)	1,200/(544)
Air to regenerator, scfm/(m^3/h)	90,000/(152,912)
Temperature, °F/(°C)	
Feed preheat (riser inlet)	594/(312)
Reactor	972/(522)
Blower discharge	374/(190)
Regenerator dense phase	1,309/(709)
Regenerator dilute phase	1,320 (716)
Regenerator flue gas	1,330/(721)
Ambient	80/(27)
Pressure, psig/(kPa)	
Regenerator	34/(234)
Reactor	33(227)
Flue Gas Analysis (mol%)	
O_2	1.5
CO_2	15.4
CO	0.0
SO_2	0.05
$N_2 + Ar$	83.05
Miscellaneous Data	
Relative humidity	80%

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Mass Balance Calculations

1. The orifice plate meter factors should be adjusted for actual operating parameters. For liquid streams, the flow meters should be adjusted for API gravity, temperature, and viscosity. For gas streams, the flow rate should be adjusted for the operating temperature, pressure, and molecular weight.
2. Chromatographs of each stream must be normalized to 100%. The GC of the off-gas must include accurate analysis of hydrogen sulfide (H_2S).
3. The coke yield should be calculated using air rate and flue gas composition.
4. The flow rate of each stream should be converted to weight units.
5. The quantity of inert gases and extraneous streams should be subtracted from the FCC gas plant products.
6. The raw mass balance should be reported, including the error. Then the feed/products should be normalized to 100%. The error will be distributed in proportion to flow rates or a known inaccurate meter will be adjusted.
7. Gasoline, LCO, and slurry flow rates will be adjusted to standard cut points.
8. The feed characterization correlations discussed in Chapter 3 should be used to determine the composition of fresh feed.

Analysis of Results

1. The yields and quality of the desired products should be reported and compared with the unit targets.
2. The results of this test run should be compared with the results of previous test runs; any significant changes in the yields and/or operating parameters should be highlighted.
3. The final step is to perform simple economics of the unit operation and make recommendations that improve unit operation short and long terms.

The following case study demonstrates a step-by-step approach to performing a comprehensive material and heat balance.

Case Study

A test run is conducted to evaluate the performance of a 50,000 bpd (331 m^3/h) FCC unit. The feed to the unit is gas oil from the vacuum unit. No recycle stream is processed; however, the off-gas from the delayed coker is sent to the gas recovery section. Products from the unit are fuel gas, LPG (debutanizer overhead), gasoline, LCO, and slurry oil. Tables 7.2, 7.3, and 7.3A contain stream flow rates, operating data, and laboratory analyses. The meter factors have been adjusted for actual operating conditions.

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Table 7.3: Feed and Product Inspections.

	Feed	Gasoline	LCO	Slurry Oil
API gravity	25.2	58.5	21.5	2.4
Sulfur (wt%)	0.5			
Aniline point (°F/°C)	208/97.8			
RI at 67°C	1.4854			
Viscosity (SSU)				
At 150°F (65.5°C)	109			
At 210°F (98.9°C)	54			
Watson *K*-factor	11.89			
Distillation (wt%)	D7169 (°F)	D7096* (°F)	D2887 (°F)	D7169 (°F)
0%	366	46	279	401
5%	560	81	414	628
10%	615	88	445	676
30%	694	144	509	755
50%	773	201	563	808
70%	856	280	625	888
90%	958	393	702	940
95%	994	427	736	988
99.5%	1,041	475	736	1,110
EP	1,139	493	822	1,328

**D7096 reported in vol%.*

Table 7.3A: Composition of FCC Gas Plant Streams.

Components	FCC Tail Gas	LPG	FCC Gasoline	Coker Off-Gas
H_2	15.5			8.0
CH_4	35.8			47.2
C_2	17.1			14.9
$C_2^=$	11.0			2.5
C_3	1.6	17.9		8.4
$C_3^=$	4.7	31.3		4.4
IC_4	0.7	16.1	0.1	0.9
NC_4	0.2	10.9	0.4	3.2
C_4 olefins	1.3	23.8	0.1	3.4
IC_5	0.4		8.7	2.6
NC_5	0.1		2.8	1.5
C_5 olefins	0.0		7.3	1.0
C_6+	0.5		80.6	
H_2S	2.1			2.0
N_2	7.2			
CO_2	1.3	.	.	0.0
CO	0.5			
Total	100.0	100.0	100.0	100.0
Specific gravity	0.78	0.55		0.94

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The mass balance is performed as follows:

1. Identification of the input and output streams used in the overall mass balance equation
2. Calculation of the coke yield
3. Conversion of the flow rates to weight units, e.g. lb/h
4. Normalization of the data to obtain a 100% weight balance
5. Determination of the component yields
6. Adjustment of the gasoline, LCO, and slurry oil yields to standard cut points.

Input and Output Streams in the Overall Mass Balance

As shown in Envelope 1 of Figure 7.1, the input hydrocarbon streams are fresh feed and coker off-gas. The output streams are FCC tail gas (minus inert gases), LPG, gasoline, LCO, slurry oil, and coke.

Coke Yield Calculations

As discussed in Chapter 1, a portion of the feed is converted to coke in the riser/reactor. This coke is carried into the regenerator with the spent catalyst. The combustion of the coke produces H_2O, CO, CO_2, SO_2, and traces of NO_x. To determine the coke yield, the amount of dry air to the regenerator and the analysis of the regenerator flue gases are needed. It is essential to have an accurate analysis of the flue gas. The hydrogen content of coke relates to the amount of volatile hydrocarbons that are carried under with the spent catalyst into the regenerator and is an indication of the reactor−stripper performance. Example 7.1 shows a step-by-step calculation of the coke yield.

Example 7.1

Determination of the unit's coke yield

Given:

Wet air = 90,000 SCFM

Relative humidity = 80%

Ambient temperature = 80°F (26.7°C)

Figure 7.3 can be used to obtain percent dry air as a function of ambient temperature and relative humidity. For this example, the percentage of dry air is 97.2% or

$$\text{Dry air} = 0.972 \times \frac{90,000\ \text{SCF}}{\text{Min}} \times \frac{1\ \text{mole}}{379.5\ \text{SCF}} \times \frac{60\ \text{min}}{1\ \text{h}} = 13,834\ \text{moles/h}$$

Flue gas rate (dry basis) is calculated from the dry air rate using nitrogen and argon as tie elements.

$$\text{Flue gas rate (dry basis)} = \frac{(13,834\ \text{moles/h} \times 0.79)}{0.8305} = 13{,}160\ \text{moles/h}$$

where 0.79 and 0.8305 are concentrations of (nitrogen + argon) in atmospheric dry air and flue gas (from analysis), respectively.

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The flow rates of each component in the dry flue gas stream are:

- O_2 out = 0.015 × 13,160 moles/h = 197 moles/h
- CO_2 out = 0.154 × 13,160 moles/h = 2,027 moles/h
- SO_2 out = 0.00052 × 13,160 moles/h = 6.8 moles/h
- (N_2 + Ar) out = 0.8305 × 13,160 moles/h = 10,929 moles/h

An oxygen balance can be used to calculate the water formed by the combustion of coke.

- O_2 out = 197 + 2,027 = 2,224 moles/h
- O_2 in = 0.2095 × 13,834 moles/h = 2,898 moles/h
- O_2 used for combustion of hydrogen = 2,898 − 2,228 = 670 moles/h

Since for each mole of O_2 two moles of water are formed, the amount of water is:

- H_2O formed = 670 × 2 = 1,340 moles/h

Components of coke are carbon, hydrogen, and sulfur. Their rates are calculated as follows:

- Carbon = 2,027 moles/h × 12.01 lb/mole = 24,344 lb/h
- Hydrogen = 1,340 moles/h × 2.02 lb/mole = 2,707 lb/h
- Sulfur = 6.6 moles/h × 32.06 lb/mole = 212 lb/h
- Coke = 24,344 + 2,707 + 212 = 27,263 lb/h
- H_2 content of coke (wt%) = $\frac{2{,}707 \text{ lb/h}}{27{,}263 \text{ lb/h}} \times 100 = 9.9$

(The hydrogen content of coke indicates the amount of volatile hydrocarbons carried through the stripper with the spent catalyst.)

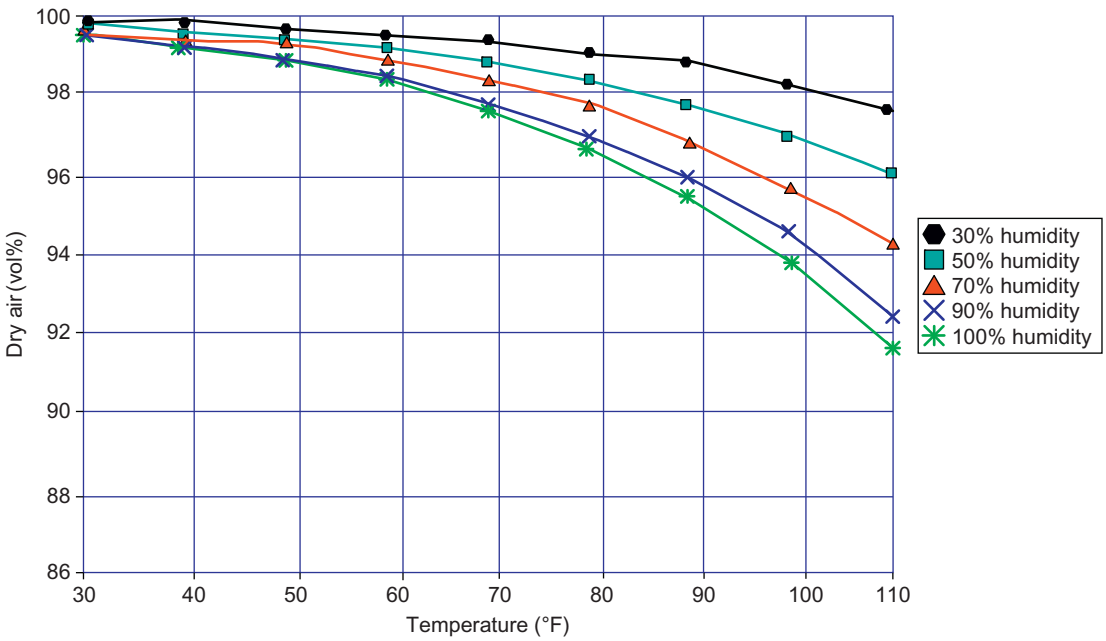


Figure 7.3: Dry air versus relative humidity and temperature.

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Conversion to Unit of Weight (lb/h)

The next step is to convert the flow rate of each stream in the overall mass balance equation to the unit of weight, e.g. lb/h. Example 7.2 shows these conversions for gas and liquid streams.

Example 7.2

Conversion of input and output streams to the unit of weight (lb/h)

$$\text{Fresh feed} = \frac{50{,}000\ \text{bbl}}{\text{day}} \times \frac{1\ \text{day}}{24\ \text{h}} \times \frac{141.5}{(131.5 + 25.2)} \times \frac{350.16\ \text{lb}}{\text{bbl}} = 658{,}964\ \text{lb/h}$$

$$\text{Coker off-gas} = \frac{3{,}000{,}000\ \text{SCF}}{\text{day}} \times \frac{1\ \text{day}}{24\ \text{h}} \times \frac{1\ \text{mole}}{379.5\ \text{SCF}} \times \frac{27.26\ \text{lb}}{1\ \text{mole}} = 9{,}156.8\ \text{lb/h}$$

$$\text{FCC tail gas} = \frac{16{,}000{,}000\ \text{SCF}}{\text{day}} \times \frac{1\ \text{day}}{24\ \text{h}} \times \frac{1\ \text{mole}}{379.5\ \text{SCF}} \times \frac{22.26\ \text{lb}}{1\ \text{mole}} = 39{,}586\ \text{lb/h}$$

The amount of inert gas in the FCC tail gas is:

$$N_2 = \frac{16{,}000{,}000\ \text{SCF}}{\text{day}} \times \frac{1\ \text{day}}{24\ \text{h}} \times 0.072 \times \frac{1\ \text{mole}}{379.5\ \text{SCF}} \times \frac{28.01\ \text{lb}}{1\ \text{mole}} = 3{,}543\ \text{lb/h}$$

$$CO_2 = \frac{16{,}000{,}000\ \text{SCF}}{\text{day}} \times 0.018 \times \frac{1\ \text{day}}{24\ \text{h}} \times \frac{1\ \text{mole}}{379.5\ \text{SCF}} \times \frac{44.01\ \text{lb}}{1\ \text{mole}} = 1{,}392\ \text{lb/h}$$

$$\text{Inert-free FCC tail gas} = 39{,}586 - (3{,}5432 + 1{,}392) = 34{,}651\ \text{lb/h}$$

$$\text{LPG} = \frac{11{,}565\ \text{bbl}}{\text{day}} \times \frac{1\ \text{day}}{24\ \text{h}} \times \frac{141.5}{(131.5 + 123.5)} \times \frac{350.16\ \text{lb}}{\text{bbl}} = 93{,}652\ \text{lb/h}$$

$$\text{Gasoline} = \frac{30{,}000\ \text{bbl}}{\text{day}} \times \frac{1\ \text{day}}{24\ \text{h}} \times \frac{141.5}{(131.5 + 58.5)} \times \frac{350.16\ \text{lb}}{\text{bbl}} = 325{,}974\ \text{lb/h}$$

$$\text{LCO} = \frac{10{,}000\ \text{bbl}}{\text{day}} \times \frac{1\ \text{day}}{24\ \text{h}} \times \frac{141.5}{(131.5 + 21.5)} \times \frac{350.16\ \text{lb}}{\text{bbl}} = 134{,}934\ \text{lb/h}$$

$$\text{Slurry oil} = \frac{3{,}000\ \text{bbl}}{\text{day}} \times \frac{1\ \text{day}}{24\ \text{h}} \times \frac{141.5}{(131.5 + 2.4)} \times \frac{350.16\ \text{lb}}{\text{bbl}} = 46{,}124\ \text{lb/h}$$

Table 7.4 shows the "raw" overall mass balance.

Some of the key findings of the overall mass balance are as follows:

- The overall mass balance closure of 99.25% is excellent and above industry average.
- The coke yield of 4.14 wt% is below industry average largely due to an above-average feed preheat temperature, a below-average reactor temperature, and an above-average amount of volatile hydrocarbon with the spent catalyst.

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Table 7.4: Raw Overall Mass Balance.

	lb/h	bpd	Wt%	Vol%	API Gravity
Absorber off-gas	39,586		6.01		
LPG (C_3's + C_4's)	93,652	11,600	14.22	23.20	123.5
Gasoline	325,971	30,000	49.48	60.00	58.50
LCO	134,934	10,000	20.48	20.00	21.50
Slurry oil	46,254	3,000	7.02	6.00	2.40
Coke	27,283		4.14		
Total	667,681	54,600	101.35	109.20	
Inert gases	4,934				
External streams	8,979	1,507			
Total FCC hydrocarbon	653,767	53,093	99.25	106.20	
Apparent conversion			72.50	74.00	
Fresh feed rate	658,738	50,000	100.00	100.00	25.2
Mass balance closure			99.25		

Component Yield

The reactor yield is determined by performing a component balance. The amount of C_5+ in the gasoline boiling range is calculated by subtracting the C_4 and lighter components from the total gas plant products. Example 7.3 shows the step-by-step calculation of the component yields.

In this case study, the mass balance closure was 99.25%, indicating the sum of the products was 0.75% less than the fresh feed rate. To achieve 100% closure, the product rates (except for the coke yield) are adjusted upward in proportion to their rates. The summary of the results, normalized but unadjusted for the cut points, is shown in Table 7.4A.

Example 7.3

Calculation of individual components

$$H_2S = \frac{0.021 \times 16\ \text{MMSCFD} \times 34.08}{379.5 \times 24} - \frac{0.02 \times 3\ \text{MMSCFD} \times 34.08}{379.5 \times 24} = 1{,}033\ \text{lb/h}$$

$$H_2 = \frac{0.155 \times 16\ \text{MMSCFD} \times 2.02}{379.5 \times 24} - \frac{0.08 \times 3\ \text{MMSCFD} \times 2.02}{379.5 \times 24} = 497\ \text{lb/h}$$

$$CH_4 = \frac{0.358 \times 16\ \text{MMSCFD} \times 16.04}{379.5 \times 24} - \frac{0.472 \times 3.0\ \text{MMSCFD} \times 16.04}{379.5 \times 24} = 7{,}594\ \text{lb/h}$$

$$C_2 = \frac{0.171 \times 16\ \text{MMSCFD} \times 30.07}{379.5 \times 24} - \frac{0.149 \times 3\ \text{MMSCFD} \times 30.07}{379.5 \times 24} = 7{,}557\ \text{lb/h}$$

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$$C_2^{=} = \frac{0.11 \times 16\ \text{MMSCFD} \times 28.05}{379.5 \times 24} - \frac{0.025 \times 3\ \text{MMSCFD} \times 28.05}{379.5 \times 24} = 5{,}189\ \text{lb/h}$$

$$C_3 = \frac{0.016 \times 16\ \text{MMSCFD} \times 44.1}{379.5 \times 24} + \frac{0.179 \times 11{,}600\ \text{bpd} \times 177.5}{24} - \frac{0.084 \times 3\ \text{MMSCFD} \times 44.1}{379.5 \times 24} = 15,376\ \text{lb/h}$$

$$C_3^{=} = \frac{0.047 \times 16\ \text{MMSCFD} \times 42.02}{379.5 \times 24} + \frac{0.313 \times 11{,}600\ \text{bpd} \times 182.4}{24} - \frac{0.044 \times 3\ \text{MMSCFD} \times 42.02}{379.5 \times 24} = 30{,}464\ \text{lb/h}$$

$$NC_4 = \frac{0.002 \times 16\ \text{MMSCFD} \times 58.12}{379.5 \times 24} + \frac{0.109 \times 11{,}600\ \text{bpd} \times 204.5}{24} + \frac{0.004 \times 30{,}000\ \text{bpd} \times 204.5}{24} - \frac{0.032 \times 3\ \text{MMSCFD} \times 58.12}{379.5 \times 24} = 11{,}387\ \text{lb/h}$$

$$IC_4 = \frac{0.007 \times 16\ \text{MMSCFD} \times 58.12}{379.5 \times 24} + \frac{0.161 \times 11{,}600\ \text{bpd} \times 197.1}{24} + \frac{0.001 \times 30{,}000 \times 197.1}{24} - \frac{0.009 \times 3\ \text{MMSCFD} \times 58.1}{379.5 \times 24} = 16{,}124\ \text{lb/h}$$

$$C_4^{=} = \frac{0.013 \times 16\ \text{MMSCFD} \times 56.1}{379.5 \times 24} + \frac{0.238 \times 11{,}600\ \text{bpd} \times 213.7}{24} + \frac{0.001 \times 30{,}000 \times 213.7}{24} - \frac{0.034 \times 3\ \text{MMSCFD} \times 56.1}{379.5 \times 24} = 25{,}508\ \text{lb/h}$$

$$C_5's = \frac{0.005 \times 16\ \text{MMSCFD} \times 72.1}{379.5 \times 24} + \frac{0.0 \times 11{,}600\ \text{bpd} \times 219.8}{24} + \frac{0.188 \times 30{,}000 \times 219.8}{24} - \frac{0.041 \times 3\ \text{MMSCFD} \times 72.1}{379.5 \times 24} = 52{,}026\ \text{lb/h}$$

$$C_6+ = 272{,}541\ \text{lb/h}$$

Adjustment of Gasoline and LCO Cut Points

As discussed earlier in this chapter, gasoline, LCO, and slurry oil yields are generally corrected to a constant boiling range basis. The most commonly used bases are 430°F (221°C) TBP gasoline and 670°F (354°C) TBP LCO cut points.

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Table 7.4A: Normalized FCC Weight Balance Summary.

	Wt%	Vol%	API Gravity	lb/h	bpd
H_2S	0.16			1,054	
H_2	0.08			527	
C_1	1.16			7,641	
$C_2^=$	0.79			5,204	
C_2	1.16			7,641	
Total H_2-C_2	3.19			21,014	
$C_3^=$	4.66	8.08	140.09	30,697	4,040
C_3	2.35	4.19	147.65	15,480	2,095
IsoC_4	2.47	3.96	119.92	16,271	1,980
NC_4	1.74	2.69	110.79	11,462	1,345
$C_4^=$	3.90	5.77	100.32	25,691	2,885
Total $C_3 + C_4$	15.12	24.69	124.33	99,601	12,345
Gasoline (C_5+)	49.70	60.26	58.5	327,370	30,129
LCO	20.61	20.12	21.5	135,779	10,062
Slurry oil	7.08	6.06	2.4	46,637	3,025
Coke	4.14			27,283	
Total	100.00	111.13		658,738	55,515
Conversion	72.31	73.82			

The adjustments to the cut points involve the following:

- Adding to the "raw" LCO product all the 430°F+ in the "raw" gasoline product and subtracting the 430°F− from the LCO product
- Adding to the "raw" LCO product all the 670°F− in the "raw" slurry oil product and subtracting the 670°F− from the slurry oil product
- Adding to the "raw" gasoline all the 430°F− that are in the "raw" LCO product, while subtracting the 430°F+ in the gasoline product
- Adding to the "raw" slurry oil product all the 670°F+ in the "raw" LCO product and subtracting the 670°F− in the slurry oil product.

Since TBP distillations are not routinely performed, they are usually calculated using published correlations. The earlier methods to calculate TBP distillation were based on using ASTM D86 boiling fractions. However, these days, few refiners use the D86 method. Instead, the popular tests employ simulative, GC-based distillation techniques. Following are the most common methods employed:

- ASTM D7169 for FCC feed and slurry oil product
- ASTM D2887 for LCO and HCO products
- ASTM D7096 or D3710 for gasoline product.

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Since gasoline contains "known" components, the boiling fractions are reported in vol%, and it is a common practice to use the findings as TBP. However, the reported analyses for other SIMDIS are in wt%.

The advantages of carrying out SIMDIS versus D86 and/or D1160 include the following [1]:

- Repeatability over physical distillation techniques
- D86 and D1160 have less than one theoretical separation stage and it is thus difficult to arrive at meaningful correlation to TBP
- Safety of performing the test.

The main drawback of SIMDIS method is that it is based on equivalent paraffin boiling points. Therefore, in samples having high aromatic concentrations (e.g. LCO, HCO, and slurry oil), the aromatic compounds tend to come out earlier than nonaromatic compounds. Consequently, it gives false boiling points. At temperatures above 400°F (204°C), the presence of highly aromatic compounds will shift the boiling point by about 50°F (28°C) across the entire boiling curve.

Table 7.5: Conversion of SIMDIS to TBP LCO and Slurry Oil Products.

LCO Product (SIMDIS 2887 to TBP)							
Wt%	**Temperature (°F)**		***C***	***D***	**ΔSD (°F)**	**ΔTBP (°F)**	**TBP**
0	276	100−95%	0.0217	1.9733	80	124*	276
5	428	95−90%	0.9748	0.8723	32	20	453
10	447	90−70%	0.3153	1.2938	77	87	464
30	511	70−50%	0.1986	1.3975	53	51	518
50	**565**	50−30%	0.0534	1.6988	54	47	565
70	618	30−10%	0.0119	2.0253	64	54	616
90	695	10−5%	0.1578	1.4296	19	11	703
95	727						723
99.5	807						847
Slurry Oil Product (SIMDIS D7169 to TBP)							
Wt%	**Temperature (°F)**		***C***	***D***	**ΔSD (°F)**	**ΔTBP (°F)**	**TBP**
0	380	100−95%	0.0217	1.9733	249	**1,162**	380
5	611	95−90%	0.9748	0.8723	117	62	621
10	660	90−70%	0.3153	1.2938	111	140	662
30	741	70−50%	0.1986	1.3975	58	58	749
50	**793**	50−30%	0.0534	1.6988	52	44	793
70	851	30−10%	0.0119	2.0253	81	87	851
90	962	10−5%	0.1578	1.4296	49	41	990
95	1,079						1,053
99.5	1,328						2,215

C and D are used as constants, SD = simulated distillation (SIMDIS)

**These numbers are somewhat unrealistic, indicating the shortcomings of these correlations*

Bold text indicates that this correlation assumes that the 50% SD value is the same as 50% TBP.

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Table 7.6: Normalized and Cut-Point-Adjusted FCC Weight Balance Summary.

	Wt%	Vol%	API Gravity	lb/h	bpd
H_2S	0.16			1,054	
H_2	0.08			527	
C_1	1.16			7,641	
$C_2^=$	0.79			5,204	
C_2	1.16			7,641	
Total H_2-C_2	**3.19**			21,014	
$C_3^=$	4.66	8.08	140.09	30,697	4,040
C_3	2.35	4.19	147.65	15,480	2,095
IsoC_4	2.47	3.96	119.92	16,271	1,980
NC_4	1.74	2.69	110.79	11,462	1,345
$C_4^=$	3.90	5.77	100.32	25,691	2,885
Total $C_3 + C_4$	15.12	24.69	124.33	99,601	12,345
Gasoline ($C_5 \rightarrow 430°F$ TBP)	48.54	59.06	59.15	319,752	29,530
LCO ($430 \rightarrow 670°F$ TBP)	18.42	18.41	25.08	121,340	9,205
Slurry oil ($670°F+$ TBP)	10.43	8.88	1.89	68,706	4,440
Coke	4.14			27,283	
Total	100.00	111.04		658,738	55,515
Conversion ($430°F+$ TBP)	71.15	72.71			

Appendix 10 contains correlations to convert ASTM D86 and SIMDIS data to TBP. Table 7.5 shows the steps to convert LCO and slurry oil SIMDIS data to TBP. Table 7.6 shows the normalized FCC weight balance with the adjusted cut points.

Analyses of Mass and Heat Balance Data

Reviewing Table 7.6, the key findings are as follows:

- At 3.2 wt%, the C_2 and lighter yield is above industry average
- At 24.7 vol%, the C_3/C_4 yield is below industry average
- At 59.1 vol%, the gasoline yield is within industry average
- At 8.9 vol%, the slurry yield is above industry average
- At 72.7 vol%, the "true" conversion is below industry average.

Heat Balance

A cat cracker is a coke rejection process. It continually adjusts itself to stay in heat balance. This means that the reactor and regenerator heat flows must be equal (Figure 7.4). Simply stated, the unit produces and burns enough coke to provide energy to:

- Vaporize fresh feed and any recycle streams
- Increase the temperature of the fresh feed, recycle, and atomizing steam from their preheated states to the reactor temperature
- Provide the endothermic heat of cracking

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- Increase the temperature of the combustion air from the blower discharge temperature to the regenerator dilute phase temperature
- Make up for heat losses from the reactor and regenerator to the surroundings
- Provide for miscellaneous heat sinks, such as stripping steam and catalyst cooling.

A heat balance can be performed around the reactor, around the stripper–regenerator, and as an overall heat balance around the reactor–regenerator. The stripper–regenerator heat balance can be used to calculate the catalyst circulation rate and the catalyst to oil ratio.

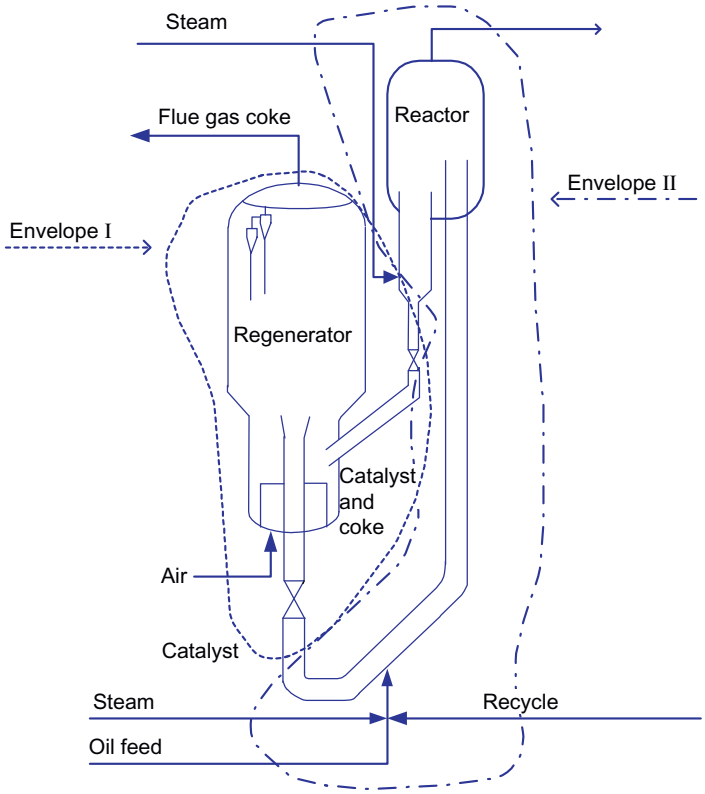


Figure 7.4: Reactor–regenerator heat balance.

Heat Balance Around Stripper–Regenerator

If a reliable spent catalyst temperature is not available, the stripper is included in the heat balance envelope (II) as shown in Figure 7.4. The combustion of coke in the regenerator satisfies the following heat requirements:

- Heat to raise air rate from the blower discharge temperature to the regenerator dilute phase temperature.
- Heat to desorb the coke from the spent catalyst.

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- Heat to raise the temperature of the stripping steam to the reactor temperature.
- Heat to raise the coke on the catalyst from the reactor temperature to the regenerator dense-phase temperature.
- Heat to raise the coke products from the regenerator dense temperature to flue gas temperature.
- Heat to compensate for regenerator heat losses.
- Heat to raise the spent catalyst from the reactor temperature to the regenerator dense-phase temperature.

Using the operating data from the case study, Example 7.4 shows heat balance calculations around the stripper–regenerator. The results are used to determine the catalyst circulation rate and the delta coke. Delta coke is the difference between coke on the spent catalyst and coke on the regenerated catalyst.

Example 7.4

Stripper–regenerator heat balance calculations

I. Heat generated in the regenerator:
C to CO_2 = 24,344 lb/h × 14,087 Btu/lb = 342.9×10^6 Btu/h
H_2 to H_2O = 2,707 lb/h × 51,571 Btu/lb = 139.6×10^6 Btu/h
S to SO_2 = 212 lb/h × 3,983 Btu/lb = 0.84×10^6 Btu/h
Total heat released in the regenerator:
$342.9 + 139.6 + 0.84 = 483.3 \times 10^6$ Btu/h

II. Required heat to increase air temperature from blower discharge to the regenerator flue gas temperature. (From Figure 7.5, enthalpies of air at 374°F and 1,330°F (190°C and 721°C) are 80 and 350 Btu/lb, respectively.)
Therefore, the required heat is:
434,657 lb/h × (350 − 80) Btu/lb = 117.4×10^6 Btu/h

III. Energy to desorb coke from the spent catalyst:
Desorption of coke = 27,263 lb/h × 1,450 Btu/lb = 39.5×10^6 Btu/h

IV. Energy to heat the stripping steam:
Enthalpy of 50 psig-saturated steam = 1,179 Btu/lb
Enthalpy of 50 psig at 972°F = 1,519 Btu/lb
Change of enthalpy = 13,000 lb/h × (1,519 − 1,179) Btu/lb = 4.4×10^6 Btu/h

V. Energy to heat the coke on the spent catalyst:
27,263 lb/h × 0.4 Btu/lb-°F × (1,309 − 972)°F = 3.7×10^6 Btu/h

VI. Heat loss to surrounding:
Assume heat loss from the stripper–regenerator (due to radiation and convection) is 4% of total heat of combustion, i.e. 0.04 × 483.3 MM Btu/h = 19.3×10^6 Btu/h

VII. Energy left that must go into catalyst:
$483.3 - 117.4 - 39.5 - 4.4 - 3.7 - 19.3 = 299.0 \times 10^6$ Btu/h

VIII. Calculation of catalyst circulation:

$$\text{Catalyst circulation} = \frac{299.1 \times 10^6 \text{ Btu/h}}{(0.285 \text{ Btu/°F} - \text{lb}) \times (1,309 - 969)\text{°F}}$$
$$= 3.087 \times 10^6 \text{ lb/h} = 25.7 \text{ short tons/min}$$

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where:
0.285 is the catalyst heat capacity (see Figure 7.6)
Cat/oil ratio = $3.1087 \times 10^6/658{,}914 = 4.68$.

$$\Delta\text{Coke} = \frac{\text{Coke yield (wt\%)}}{\text{Cat/oil ratio}} = \frac{4.14}{4.68} = 0.88 \text{ wt\%}$$

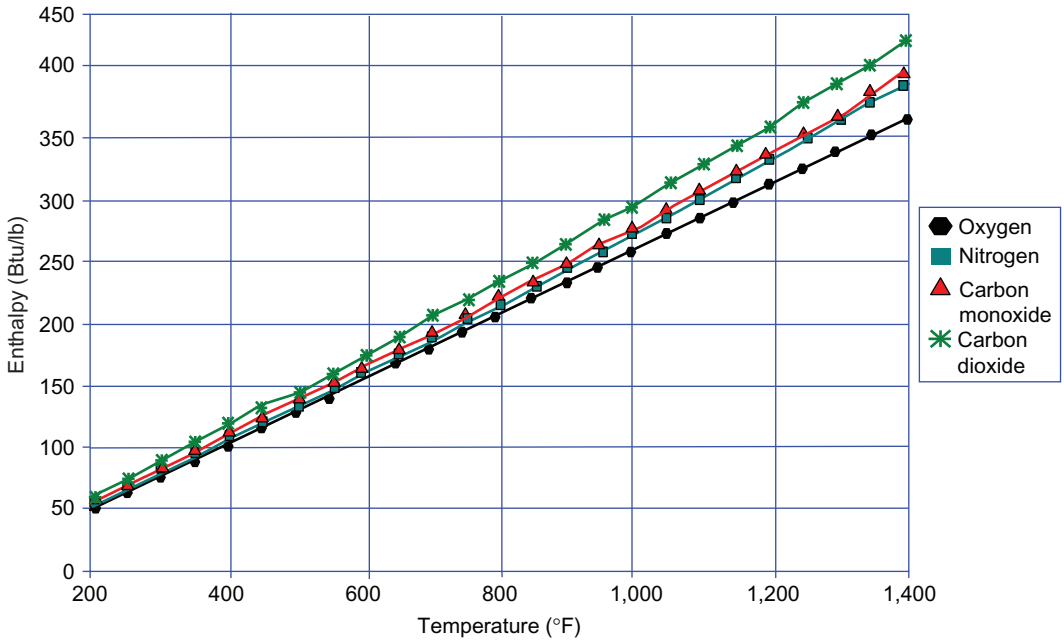


Figure 7.5: Enthalpies of FCC flue gas components.

Reactor Heat Balance

The hot regenerated catalyst supplies the bulk of the heat required to vaporize the liquid feed (and any recycle), to provide the overall endothermic heat of cracking, and to raise the temperature of dispersion steam and inert gases to the reactor temperature.

Heat In	Heat Out
Fresh feed	Reactor vapors
Recycle	Flue gas
Air	Losses
Steam	

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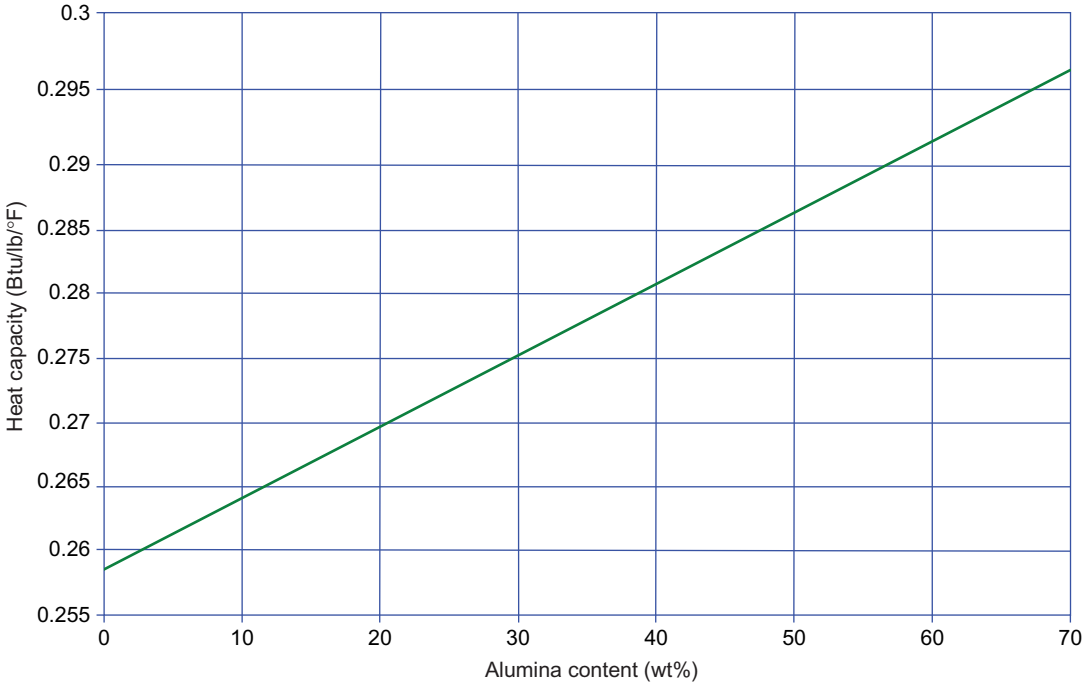


Figure 7.6: Heat capacity of the FCC catalyst as a function of the catalyst's alumina content.

The calculation of heat balance around the reactor is illustrated in Example 7.5. As shown, the unknown is the heat of reaction. It is calculated as the net heat from the heat balance divided by the feed flow in weight units. This approach to determining the heat of reaction is acceptable for unit monitoring. However, in designing a new cat cracker, a correlation is needed to calculate the heat of reaction. The heat of reaction is needed to specify other operating parameters, such as preheat temperature. Depending on conversion level, catalyst type, and feed quality, the heat of reaction can vary from 120 to 220 Btu/lb.

In the unit, the heat of reaction is a useful tool. It is first an indirect indication of heat balance accuracy. Trending the heat of reaction on a regular basis provides insight into reactions occurring in the riser and the effects of feedstock and catalyst changes.

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Example 7.5

Reactor heat balance

I. Heat into the reactor
   1. Heat with regenerator catalyst:
      $= 3.087 \times 10^6$ lb/h $\times$ 0.285 Btu/lb-°F $\times$ 1,309°F $= 1{,}151.5 \times 10^6$ Btu/h.
   2. Heat with the fresh feed:
      At a feed temperature of 594°F, API gravity = 25.2 and *K*-factor = 11.85, the feed liquid enthalpy is 405 Btu/lb (see Figure 7.7); therefore, heat content of the feed is = 658,914 lb/h $\times$ 400 Btu/lb $= 263.6 \times 10^6$ Btu/h.
   3. Heat with atomizing steam:
      From steam tables, enthalpy of 150-lb saturated steam = 1,176 Btu/lb; therefore, heat with steam = 10,000 lb/h $\times$ 1,176 Btu/lb $= 11.8 \times 10^6$ Btu/h.
   4. Heat of adsorption:
      The adsorption of coke on the catalyst is an exothermic process; the heat associated with this adsorption is assumed to be the same as desorption of coke in the regenerator, i.e. 35.3×10^6 Btu/h.
      Total heat in = 1,182.4 +266.9 +11.8 +35.3 $= 1{,}462.2 \times 10^6$ Btu/h.

II. Heat out of the reactor:
   1. Heat with spent catalyst = $3{,}087 \times 10^6$ lb/h $\times$ 0.285 Btu/lb-°F $\times$ 972°F
      $= 875.1 \times 10^6$ Btu/h.
   2. Heat required to vaporize feed:
      From Figure 7.8, enthalpy reactor vapors = 755 Btu/lb; therefore, heat content of the vaporized products = 658,814 lb/h $\times$ 778 Btu/lb $= 497.4 \times 10^6$ Btu/h.
   3. Heat content of steam:
      Enthalpy of steam at 972°F = 1,519 Btu/lb; therefore, heat content of steam = 10,000 lb/h $\times$ 1,519 Btu/lb $= 15.2 \times 10^6$ Btu/h.
   4. Heat loss to surroundings:
      Assume heat loss due to radiation and convection to be 2% of heat with the regenerated catalyst, i.e. $0.02 \times 299.1 \times 10^6 = 6.0 \times 10^6$ Btu/h.

III. Calculation of heat of reaction

Total heat out = total heat in
Total heat out = $875.1 \times 10^6 + 497.4 \times 10^6 + 15.2 \times 10^6 + 6.0 \times 10^6$ + overall heat of reaction = 1,373.7 $\times$ 106 Btu/h + heat of reaction
Total heat in = $1{,}462.2 \times 10^6$ Btu/h
Overall endothermic heat of reaction = 88.5×10^6 Btu/h or $\rightarrow$134.4 Btu/lb of feed.

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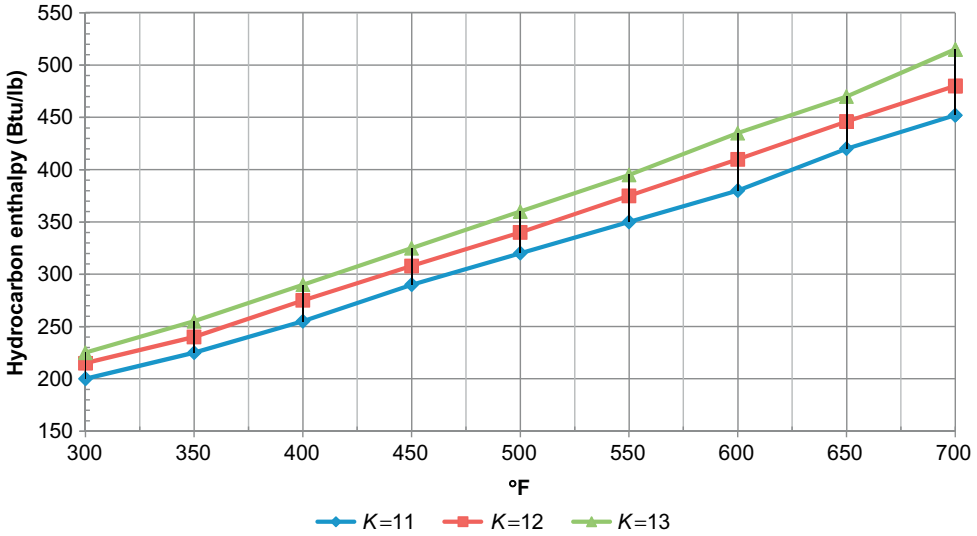


Figure 7.7: Hydrocarbon liquid enthalpies at various Watson *K*-factors (*based on API gravity = 25*).

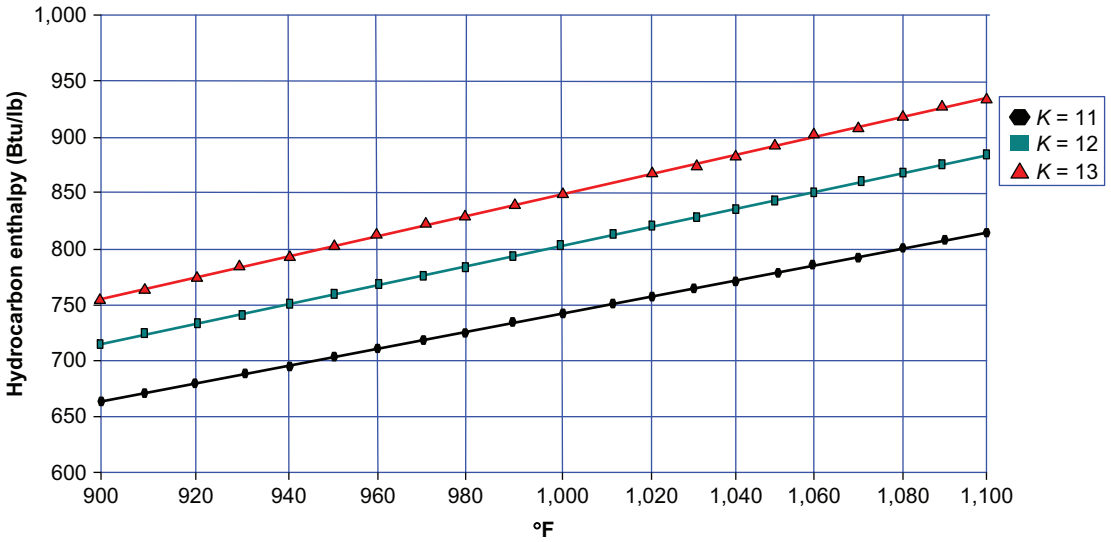


Figure 7.8: Hydrocarbon vapor enthalpies at various Watson *K*-factors.

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Analysis of Results

Once the material and heat balances are complete, a report must be written. It will first present the data. It will then discuss the factors affecting product quality and any abnormal results, and then the key findings and recommendations to improve unit operation.

In the previous examples, the feed characterizing correlations in Chapter 3 are used to determine composition of the feedstock. The results show that the feedstock is predominantly paraffinic, i.e. 61.6% paraffins, 19.9% naphthenes, and 18.5% aromatics. Paraffinic feedstocks normally yield the most gasoline with the least octane. This confirms the relatively high FCC gasoline yield and low octane observed in the test run. This is the kind of information that should be included in the report. Of course, the effects of other factors such as catalyst and operating parameters will also affect the yield structure and will be discussed.

The coke calculation showed the hydrogen content to be 9.9 wt%. As discussed in Chapter 1, every effort should be made to minimize the hydrogen content of the coke entering the regenerator. The hydrogen content of a well-stripped catalyst is in the range of 5−6 wt%. A 9.9 wt% hydrogen in coke indicates either poor stripper operation or erroneous flue gas analysis.

Pressure Balance

Pressure balance deals with the hydraulics of catalyst circulation in the reactor/regenerator circuit. The pressure balance starts with conducting a single-gauge pressure survey of the reactor−regenerator circuits. The following are the overall objectives:

- To ensure steady catalyst circulation is achieved
- To maximize catalyst circulation
- To maximize the available pressure drop at the slide valves
- To minimize the loads on the blower and the WGC.

A clear understanding of the pressure balance is extremely important in “squeezing” the most out of a unit. Incremental capacity can come from increased catalyst circulation or from altering the differential pressure between the reactor−regenerator to “free up” the WGC or air blower loads. One must know how to manipulate the pressure balance to identify the “true” constraints of the unit.

Using the drawing(s) of the reactor−regenerator, the unit engineer must be able to go through the pressure balance and determine whether it makes sense. He or she needs to calculate and estimate pressures, densities, pressure buildup in the standpipes, and so on. The potential for improvements can be substantial.

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Basic Fluidization Principles

A fluidized catalyst behaves like a liquid. Catalyst flow occurs in the direction of a lower pressure. The difference in pressure between any two points in a bed is equal to the static head of the bed between these points, multiplied by the fluidized catalyst density, but only if the catalyst is fluidized.

FCC catalyst can be made to flow like a liquid but only if the pressure force is transmitted through the catalyst particles and not the vessel wall. The catalyst must remain in a fluidized state as it makes a loop through the circuit.

To illustrate the application of the above principles, the role of each major component of the circuit is discussed in the following sections, followed by an actual case study. As a reference, Appendix 8 contains fluidization terms and definitions commonly used in the FCC.

Major Components of the Reactor–Regenerator Circuit

The major components of the reactor–regenerator circuit that either produce or consume pressure are as follows:

- Regenerator catalyst hopper
- Regenerated catalyst standpipe
- Regenerated catalyst slide (or plug) valve
- Riser
- Reactor–stripper
- Spent catalyst standpipe
- Spent catalyst slide (or plug) valve.

Regenerator Catalyst Hopper

In some FCC units, the regenerated catalyst flows through a hopper prior to entering the standpipe. The hopper is usually internal to the regenerator. The hopper is intended to provide sufficient residence time for the regenerated catalyst to be deaerated before entering the standpipe. This causes the catalyst entering the standpipe to have its maximum flowing density; the higher the catalyst flowing density, the greater the pressure buildup in the standpipe. In some FCC designs, the regenerated catalyst hopper is external with fluffing aeration to control the catalyst density entering the standpipe.

Regenerated Catalyst Standpipe

The standpipe's height provides the driving force for transferring the catalyst from the regenerator to the reactor. The elevation difference between the standpipe entrance and the slide valve is the source of this pressure buildup. For example, if the height difference is 30 ft (9.2 m) and the catalyst flowing density is 40 lb/ft^3 (641 kg/m^3), the pressure buildup is:

$$\text{Pressure gain} = 30 \text{ ft} \times \frac{40 \text{ lb}}{\text{ft}^3} \times \frac{1 \text{ ft}^2}{144 \text{ in.}^2} = 8.3 \text{ psi (57 kPa)} \qquad (7.2)$$

The key to obtaining maximum pressure gain is to keep the catalyst fluidized over the entire length of the standpipe. Longer standpipes will require external aeration. This aeration compensates for compression of the entrained gas as it travels down the standpipe. Aeration should be added evenly along the length of the standpipe. In shorter standpipes, sufficient flue gas is often carried down with the regenerated catalyst to keep it fluidized and supplemental aeration is unnecessary. Over-aeration leads to unstable catalyst flow and must be avoided.

Aside from proper aeration, the flowing catalyst must contain sufficient 0−40 μm fines, as well as minimum amount of 150 μm particles to avoid defluidization.

Regenerated Catalyst Slide Valve

The purpose of the regenerated catalyst slide valve is threefold: to regulate the flow of the regenerated catalyst to the riser, to maintain pressure head in the standpipe, and to protect the regenerator from a flow reversal. Associated with this control and protection is usually a 1−8 psi (7−55 kPa) pressure drop across the valve.

Riser

The hot regenerated catalyst is transported up the riser and into the reactor−stripper. The driving force to carry this mixture of catalyst and vapors comes from a higher pressure at the base of the riser and the low density of the catalyst/vapor mix. The large density difference between the fluidized catalyst on the regenerator side (approximately 40 lb/ft^3, or 640 kg/m^3) and the mixture of cracked hydrocarbon vapors and catalyst on the riser side (approximately 1 lb/ft^3, or 16 kg/m^3) is what that creates the catalyst circulation from the regenerated catalyst slide valve into the reactor housing. As for the pressure balance, this transported catalyst results in a pressure drop in the range of 5−9 psi (35−62 kPa). This pressure drop is due to the static head of the catalyst from downstream of the slide valve to the feed nozzles, the static head of the catalyst in the riser, and friction and acceleration losses from the catalyst/vapors within the riser and its termination device. In an existing riser, operating changes, such as higher catalyst circulation or lower vapor velocity, can affect the density of reaction mixture and increase the pressure drop. This will affect the slide valve differential pressure and operating percent opening.

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Reactor–Stripper

The catalyst bed in the reactor–stripper is important for three reasons:

1. To provide enough residence time for proper stripping of the entrained hydrocarbon vapors prior to entering the regenerator
2. To provide adequate static head for flow of the spent catalyst to the regenerator
3. To provide sufficient backpressure to prevent reversal of hot flue gas into the reactor system.

Assuming a stripper with a 20-ft (6 m) bed level and a catalyst density of 40 lb/ft^3 (640 kg/m^3), the static pressure is:

$$20 \text{ ft} \times \frac{40 \text{ lbs/ft}^3}{144 \text{ in.}^2/\text{ft}^2} = 5.5 \text{ psi (0.4 bar)} \tag{7.3}$$

Spent Catalyst Standpipe

From the bottom of the stripper, the spent catalyst flows into the spent catalyst standpipe. Sometimes the catalyst is partially defluidized in the stripper cone. To counter this, "dry" steam is usually added (through a distributor) to fluidize the catalyst prior to entering the standpipe. The loss of fluidization in the stripper cone can cause a buildup of dense-phase catalyst along the cone walls. This buildup can restrict catalyst flow into the standpipe, causing erratic flow and reducing pressure buildup in the standpipe.

Like the regenerated catalyst standpipe, the spent catalyst standpipe may require supplemental aeration to obtain optimum flow characteristics. "Dry" steam is the usual aeration medium.

Spent Catalyst Slide or Plug Valve

The spent catalyst slide valve is located at the base of the standpipe. It controls the stripper bed level and regulates the flow of spent catalyst into the regenerator. As with the regenerated catalyst slide valve, the catalyst level in the stripper generates pressure as long as it is fluidized.

In some of the earlier FCC units, spent catalyst is transported into the regenerator using 50–100% of the total air to the regenerator. The minimum carrier air velocity to the spent catalyst riser is usually in the range of 30 ft/s (9.1 m/s) to prevent catalyst slumping.

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Case Study

A survey of the reactor–regenerator circuit of a 50,000 bpd (331 m^3/h) cat cracker produced the following results (see Example 7.6; also see Figure 7.9 for a graphical representation of the preliminary results):

Reactor top pressure	=	19.0 psig/1.3 bar
Reactor catalyst dilute-phase bed level	=	25.0 ft/7.6 m
Reactor–stripper catalyst bed level	=	18.0 ft/5.5 m
Reactor–stripper catalyst density	=	40 lb/ft^3/640 kg/m^3
Spent catalyst standpipe elevation	=	14.4 ft/4.4 m
Pressure above the spent catalyst slide valve	=	26.1 psig/1.8 bar
Spent catalyst slide valve ΔP (at 55% opening)	=	4.0 psi/0.3 bar
Regenerator dilute-phase catalyst level	=	27.0 ft/8.2 m
Regenerator dense-phase catalyst bed level	=	15.0 ft/4.6 m
Catalyst density in the regenerator dense phase	=	30 lb/ft^3/480 kg/m^3
Regenerated catalyst standpipe elevation	=	30.0 ft/9.1 m
Pressure above the regenerated catalyst slide valve	=	30.5 psig/2.1 bar
Regenerated catalyst slide valve ΔP (at 30% opening)	=	5.5 psi/0.4 bar
Reactor–regenerator pressure ΔP	=	3.0 psi/0.2 bar

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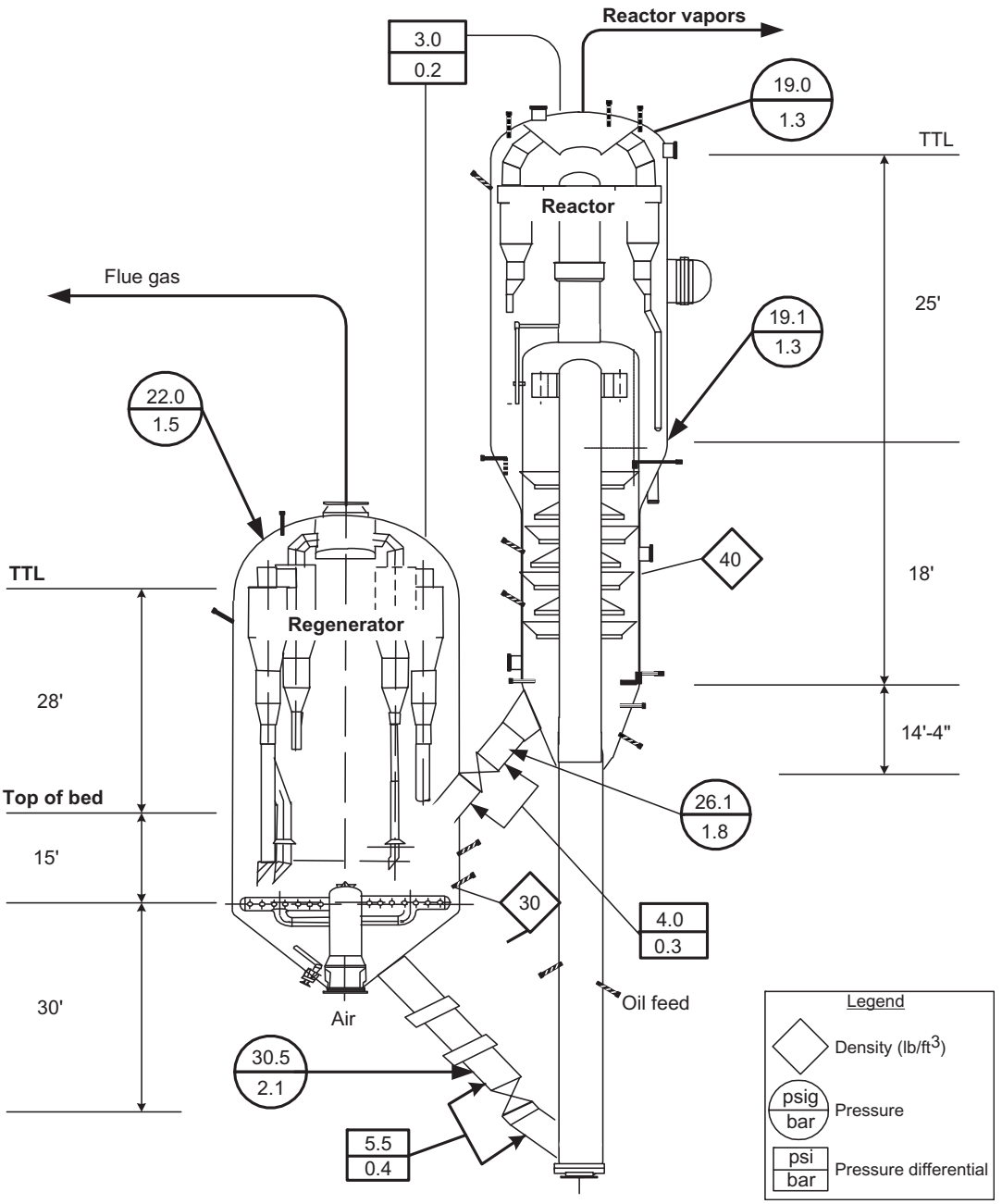


Figure 7.9: Preliminary findings of the pressure balance survey (*TTL = top tangent line*).

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Example 7.6

Survey of reactor–regenerator circuit

1. Starting with the reactor dilute pressure as the working point, the pressure head corresponding to 25 ft (7.6 m) of dilute catalyst fines is:
   $(25\ \text{ft}) \times (0.6\ \text{lb/ft}^3) \times (1\ \text{ft}^2/144\ \text{in.}^2) = 0.1\ \text{psig}\ (1.0\ \text{bar})$
2. Therefore, the pressure at the top of the stripper bed is:
   $19.0 + 0.1 = 19.1\ \text{psig}\ (1.3\ \text{bar})$
3. The static-pressure head in the stripper is:
   $(18\ \text{ft}) \times (40\ \text{lb/ft}^3) \times (1\ \text{ft}/144\ \text{in.}^2) = 5.0\ \text{psig}\ (0.3\ \text{bar})$
4. The pressure above the spent catalyst standpipe is:
   $19.1 + 5.0 = 24.1\ \text{psig}\ (1.7\ \text{bar})$
5. The pressure buildup in the spent catalyst standpipe is:
   $26.1 - 24.1 = 2\ \text{psi}\ (0.1\ \text{bar})$
6. The pressure below the spent catalyst slide valve is:
   $26.1 - 4.0 = 22.1\ \text{psig}\ (1.5\ \text{bar})$
7. The pressure head corresponding to 28 ft (8.5 m) of dilute catalyst fines in the regenerator is:
   $(28\ \text{ft}) \times (0.5\ \text{lb/ft}^3) \times (1\ \text{ft}^2/144\ \text{in.}^2) = 0.1\ \text{psig}\ (0.007\ \text{bar})$
8. The pressure in the regenerator dome is:
   $22.1 - 0.1 = 22.0\ \text{psig}\ (1.5\ \text{bar})$
9. The static pressure head in the regenerator is:
   $(15\ \text{ft}) \times (30\ \text{lb/ft}^3) \times (1\ \text{ft}^2/144\ \text{in.}^2) = 3.1\ \text{psig}\ (0.2\ \text{bar})$
10. The pressure above the regenerated catalyst standpipe is:
    $22.1 + 3.1 = 25.2\ \text{psig}\ (1.7\ \text{bar})$
11. The pressure buildup in the regenerated catalyst standpipe is:
    $30.5 - 25.2 = 5.3\ \text{psi}\ (0.4\ \text{bar})$
12. The pressure below the regenerated catalyst slide valve is:
    $30.5 - 5.5 = 25\ \text{psig}\ (1.7\ \text{bar})$
13. The pressure drop in the Wye section and riser is:
    $25 - 19 = 6\ \text{psi}\ (0.4\ \text{bar})$
14. The catalyst density in the spent catalyst standpipe is:
    $(2.0\ \text{lb/in.}^2) \times (144\ \text{in.}^2/\text{ft}^2)/(14.4\ \text{ft}) = 20\ \text{lb/ft}^3 = 320\ \text{kg/m}^3$
15. The catalyst density in the regenerated catalyst standpipe is:
    $(5.3\ \text{lb/in.}^2) \times (144\ \text{in.}^2/\text{ft}^2)/(30\ \text{ft}) = 25.4\ \text{lb/ft}^3 = 407\ \text{kg/m}^3$

Figure 7.10 shows the results of the pressure balance survey that is shown in Figure 7.9.

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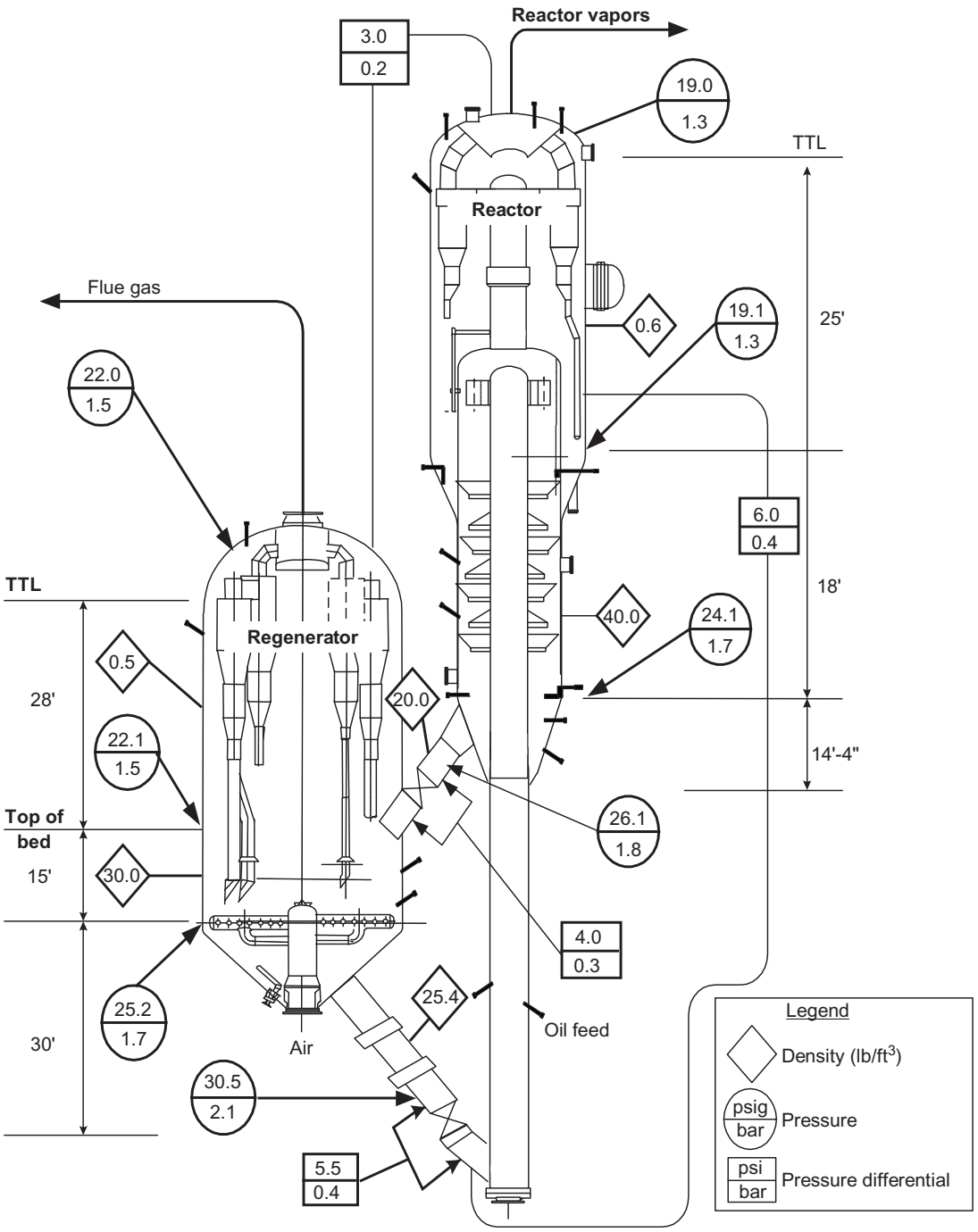


Figure 7.10: Results of the pressure balance survey showing standpipe-calculated densities.

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Analysis of the Findings

The pressure balance survey indicates that neither the spent nor the regenerated catalyst standpipe is generating "optimum" pressure head. This is evidenced by the low catalyst densities of 20 lb/ft^3 (320 kg/m^3) and 25.4 lb/ft^3 (407 kg/m^3), respectively. As indicated in Chapter 12, several factors can cause low-pressure buildup including "under" or "over" aeration of the standpipes. In a well-fluidized standpipe, the expected catalyst density is in the range of 35−45 lb/ft^3 (561−721 kg/m^3).

If the catalyst density in the spent catalyst standpipe were 40 lb/ft^3 (640 kg/m^3) instead of 20 lb/ft^3 (320 kg/m^3), the pressure buildup would have been 4.0 psi instead of 2.0 psi. The extra 2 psi (13.8 kPa) can be used to circulate more catalyst or to lower the reactor pressure.

In the regenerated catalyst standpipe, a 40 lb/ft^3 (640 kg/m^3) catalyst density versus a 25.4 lb/ft^3 (407 kg/m^3) density produces 3 psi (20.7 kPa) more pressure head, again allowing an increase in circulation or a reduction in the regenerator pressure (gaining more combustion air).

Summary

The only proper way to evaluate the performance of a cat cracker is by conducting a material and heat balance. One balance will tell where the unit is; a series of daily or weekly balances will tell where the unit is going. The heat and weight balances can be used to evaluate the previous changes or predict the result of future changes. Material and heat balances are the foundation for determining the effects of operating variables.

The material balance test run provides a standard and consistent approach for daily monitoring. It allows for accurate analysis of yields and trending of unit performance. The reactor effluent can be determined by direct sampling of the reactor overhead line or by conducting a unit test run.

The heat balance exercise provides a tool for in-depth analysis of the unit operation. Heat balance surveys determine catalyst circulation rate, delta coke, and heat of reaction. The procedures described in this chapter can be easily developed and programmed into a spreadsheet to calculate the balances on a routine basis.

The pressure balance provides an insight into the hydraulics of catalyst circulation. Performing pressure balance surveys will help the unit engineer identify "pinch points." It will also balance two common constraints: the air blower and the WGC.

Reference

[1] C.R. Hsieh, A.R. English, Two sampling techniques accurately evaluate fluid-cat-cracking products, Oil Gas J. 84(25) (1986) 38−43.

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CHAPTER 8

Products and Economics

The previous chapters have explained the operation of a cat cracker. However, the purpose of the FCC unit is to maximize the profitability of the refinery. All crude oils contain heavy gas oils and fuel oil components; unfortunately, the market for these products has disappeared. The cat cracker provides the added conversion capacity to minimize the production of these components, therefore helping the refinery survive.

The FCC unit improves the economics for the refinery, making it a viable entity. Over the years, refineries without cat crackers have been shut down because they have become unprofitable.

Understanding the economics of the FCC unit is as important as understanding its heat and pressure balances. The dynamics of FCC economics changes daily and seasonally. Market conditions and the availability/quality of crude oil have huge impacts on the FCC unit operating conditions and the resulting product slate. The 1990 Clean Air Act Amendment (CAAA) has imposed greater restrictions on quality standards for gasoline and diesel products, as well as on the emission of pollutants from the regenerator flue gas stream. The FCC is the major contributor to the gasoline and diesel pool and is significantly affected by these new regulations.

This chapter discusses the factors affecting the yields and qualities of FCC product streams. The section on FCC economics describes several options that can be used to maximize FCC performance and the refinery's profit margin.

FCC Products

The cat cracker converts less valuable gas oil feedstock to a more valuable product. A major objective of most FCC units is to maximize the conversion of gas oil to gasoline and LPG, though recently the trend has been in maximizing diesel production. The typical products produced from the cat cracker are:

- Dry gas (hydrogen, methane, ethane, ethylene)
- LPG (propane, propylene, isobutane, normal butane, butylenes)
- Gasoline

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- LCO
- HCO (in few FCC units)
- Decanted (or slurry) oil
- Combustion coke.

Dry Gas

Dry gas is defined as the C_2 and lighter gases that are produced in the FCC unit. Often the fuel gas stream leaving the sponge oil or secondary absorber tower is also referred to as "dry gas" despite its containing H_2S, inert gases, and C_3+ components. Once the gas is amine-treated for the removal of H_2S and other acid gases, it is usually blended into the refinery fuel gas system. Depending on the volume percent of hydrogen in the dry gas, some refiners will recover this hydrogen using processes such as cryogenics, pressure-swing absorption, or membrane separation. This recovered hydrogen is typically used in hydrotreating processes.

Dry gas is an undesirable by-product of the FCC unit; excessive yields load up the WGC, limiting the unit's feed rate and/or severity. The dry gas yield correlates with the feed quality, thermal cracking reactions, concentration of metals in the feed, and the amount of post-riser nonselective catalytic cracking reactions. The primary factors which contribute to the increase of dry gas production are as follows:

- Increase in the concentration of metals (nickel, copper, vanadium, and so on) on the catalyst
- Increase in reactor or regenerator temperatures
- Increase in the residence time of hydrocarbon vapors in the reactor
- Decrease in the performance of the feed nozzles (for the same unit conversion)
- Increase in the aromaticity of the feed.

When examining the chromatograph analysis of the sponge absorber off-gas, one must pay special attention to the concentrations of C_3+ components, as well as the amount of inert gases (N_2, CO_2, CO, O_2).

LPG

The overhead stream from the debutanizer or stabilizer tower is a mix of C_3's and C_4's, usually referred to as LPG. It is rich in propylene and butylenes. These light olefins play an important role in the manufacture of RFG. Depending on the refinery's configuration, the cat cracker's LPG is used in the following areas:

- *Chemical sale*, where the LPG is separated into C_3's and C_4's. The C_3's are sold as refinery or chemical grade propylene. The C_4 olefins are polymerized or alkylated.

- *Direct blending*, where the C_4's are blended into the refinery's gasoline pool to regulate vapor pressure and to enhance the octane number. However, new gasoline regulations require reduction of the vapor pressure, thus displacing a large volume of C_4's for alternative uses.
- *Alkylation*, where the olefins are reacted with isobutane to make a very desirable gasoline blending stock. Alkylate is an attractive blending component because it has no aromatics or sulfur, low vapor pressure, low end point, and high research and motor octane ratings.

The LPG yield and its olefinicity can be increased by:

- Changing to a catalyst which minimizes "hydrogen transfer" reactions
- Increasing unit conversion
- Decreasing residence time, particularly the amount of time product that the vapors spend in the reactor housing before entering the main column
- Adding ZSM-5 catalyst additive.

An FCC catalyst containing zeolite with a low hydrogen transfer rate reduces resaturation of the olefins in the riser. As stated in Chapter 6, primary cracking products in the riser are highly olefinic. Most of these olefins are in the gasoline boiling range; the rest appear in the LPG and LCO boiling range.

The LPG olefins do not crack further, but they can become saturated by hydrogen transfer. The gasoline and LCO-range olefins can be cracked again to form gasoline-range olefins and LPG olefins. The olefins in the gasoline and LCO range can also cyclize to form cycloparaffins. The cycloparaffins can react through H_2 transfer with olefins in the LPG and gasoline to produce aromatics and paraffins. Therefore, a catalyst which inhibits hydrogen transfer reactions will increase olefinicity of the LPG.

The conversion increase is accomplished by manipulating the following operating conditions:

- *Increasing the reactor temperature*: Increasing the reactor temperature beyond the peak gasoline yield results in overcracking of the gasoline and LCO fractions. The rate of production and olefinicity of the LPG will increase.
- *Increasing feed/catalyst mix zone temperature*: Conversion and LPG yield can be increased by injecting a portion of the feed, or naphtha, at an intermediate point in the riser (Figure 8.1). Splitting or segregating the feed results in a high mix-zone temperature, producing more LPG and more olefins. This practice is particularly useful where the reactor temperature is already maximized due to a metallurgy constraint.
- *Increasing catalyst to oil ratio*: The catalyst to oil ratio can be increased through several knobs including reducing the FCC feed preheat temperature and optimizing the stripping and dispersion steam rate, and by using a catalyst that deposits less coke on the catalyst.

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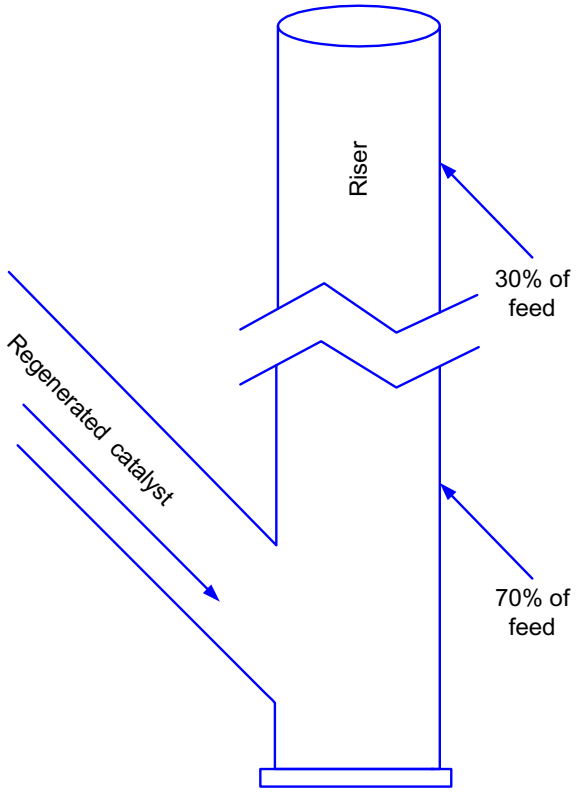


Figure 8.1: A typical feed segregation scheme.

Reduction of the catalyst/hydrocarbon time in the riser, coupled with the elimination of post-riser cracking, reduces the saturation of the "already-produced" olefins and allows the refiner to increase the reaction severity. These actions enhance the olefin yields and still operate within the WGC constraints. Elimination of post-riser residence time (direct connection of the reactor cyclones to the riser) or reduction of the temperature in the dilute phase virtually eliminates undesired thermal and nonselective cracking. This reduces dry gas and diolefin yields.

Adding ZSM-5 catalyst additive is another process available to the refiner to boost production of light olefins. ZSM-5 at a typical concentration of 0.5−3.0 wt% is used in a number of FCC units to increase the gasoline octane and light olefins. As part of the cracking of low-octane components in the gasoline, ZSM-5 also makes C_3, C_4, and C_5 olefins (see Figure 8.2). Paraffinic feedstocks respond the most to ZSM-5 catalyst additive.

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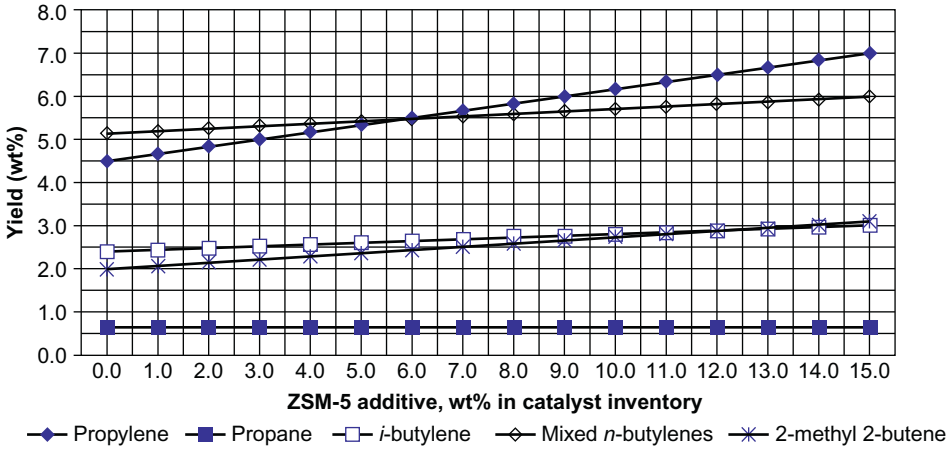


Figure 8.2: The effect of ZSM-5 on light-ends yield [1].

Gasoline

Traditionally, the FCC gasoline has always been the most valuable product of a cat cracker unit. FCC gasoline accounts for about 35 vol% of the total US gasoline pool. Historically, the FCC has been run for maximum gasoline yield with the highest octane.

Gasoline Yield

For a given feedstock, gasoline yield can be increased by:

- Increasing the catalyst to oil ratio by decreasing the feed preheat temperature
- Increasing catalyst activity by increasing fresh catalyst addition or fresh catalyst activity
- Increasing gasoline end point by reducing the main column top pumparound rate and/or overhead reflux rate
- Increasing reactor temperature (if the increase does not over-crack the already-produced gasoline)
- Lowering carbon on the regenerated catalyst.

Gasoline Quality

The key components affecting FCC gasoline quality are as follows:

- Octane
- Benzene
- Sulfur.

Octane

An octane number is a quantitative measure of a fuel mixture's resistance to "knocking." The octane number of a particular sample is measured against a standard blend of *n*-heptane,

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which has zero octane, and iso-octane, which has 100 octane. The percent of iso-octane that produces the same "knock" intensity as the sample is reported as the octane number.

Two octane numbers are routinely used to simulate engine performance: the RON simulates gasoline performance under low severity (at 600 rpm and 120°F (49°C) air temperature), whereas the *motor octane number* (MON) reflects more severe conditions (at 900 rpm and 300°F (149°C) air temperature). At the pump, road octane, which is the average of RON and MON, is reported.

Factors affecting gasoline octane are:

A. Operating conditions
   1. *Reactor temperature*: As a rule, an increase of 18°F (10°C) in the reactor temperature increases the RON by 1.0 and MON by 0.4. However, the MON contribution comes from the aromatic content of the heavy end. Therefore, at high severity, the MON response to the reactor temperature can be >0.4 per 18°F.
   2. *Gasoline end point*: The effect of gasoline end point on its octane number depends on the feedstock quality and severity of the operation. At low severity, lowering the end point of a paraffinic feedstock may not impact the octane number; however, reducing gasoline end point produced from a naphthenic or an aromatic feedstock will lower the octane.
   3. *Gasoline Reid vapor pressure (RVP)*: The RVP of the gasoline is controlled by adding C_4's, which increase octane. As a rule, the RON and MON gain 0.3 and 0.2 numbers for a 1.5 psi (10.3 kPa) increase in RVP.

B. Feed quality
   1. *API gravity*: The higher the API gravity, the more paraffins in the feed and the lower the octane (Figure 8.3).
   2. *K-factor*: The higher the *K*-factor, the lower the octane.
   3. *Aniline point*: Feeds with a higher aniline point are less aromatic and more paraffinic. The higher the aniline point, the lower the octane.
   4. *Sodium*: Additive sodium reduces unit conversion and lowers octane (Figure 8.4).

C. Catalyst
   1. *Rare earth*: Increasing the amount of rare earth oxide (REO) on the zeolite decreases the octane (Figure 8.5).
   2. *Unit cell size*: Decreasing the unit cell size increases octane (Figure 8.6).
   3. *Matrix activity*: Increasing the catalyst matrix activity increases the octane.
   4. *Coke on the regenerated catalyst*: Increasing the amount of coke on the regenerated catalyst lowers its activity and increases octane.

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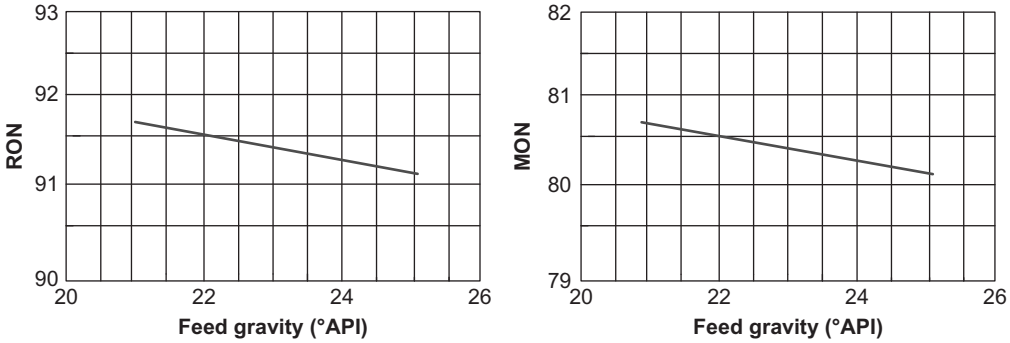


Figure 8.3: Feed gravity comparisons (MON and RON) [2].

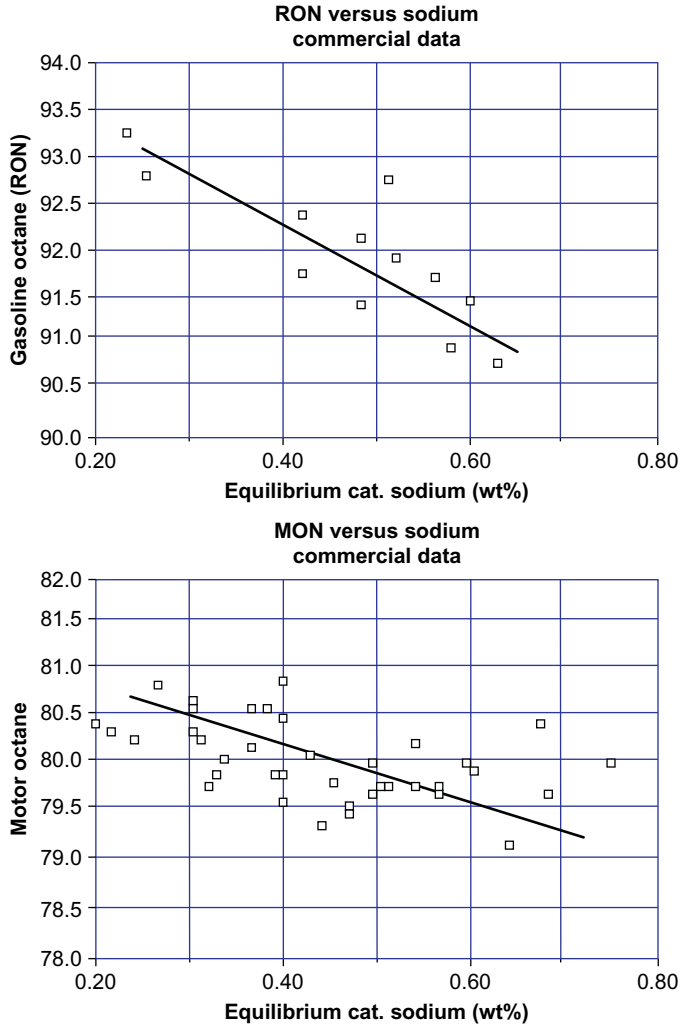


Figure 8.4: Effect of sodium on gasoline octane [3].

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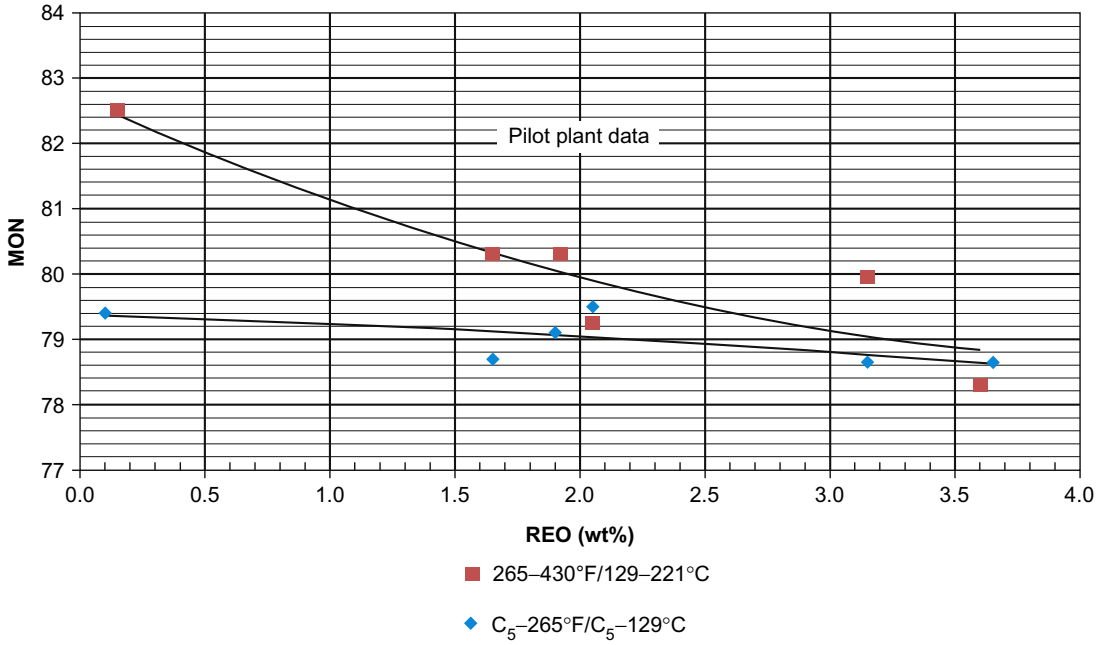


Figure 8.5: Effect of fresh REO on MON [4].

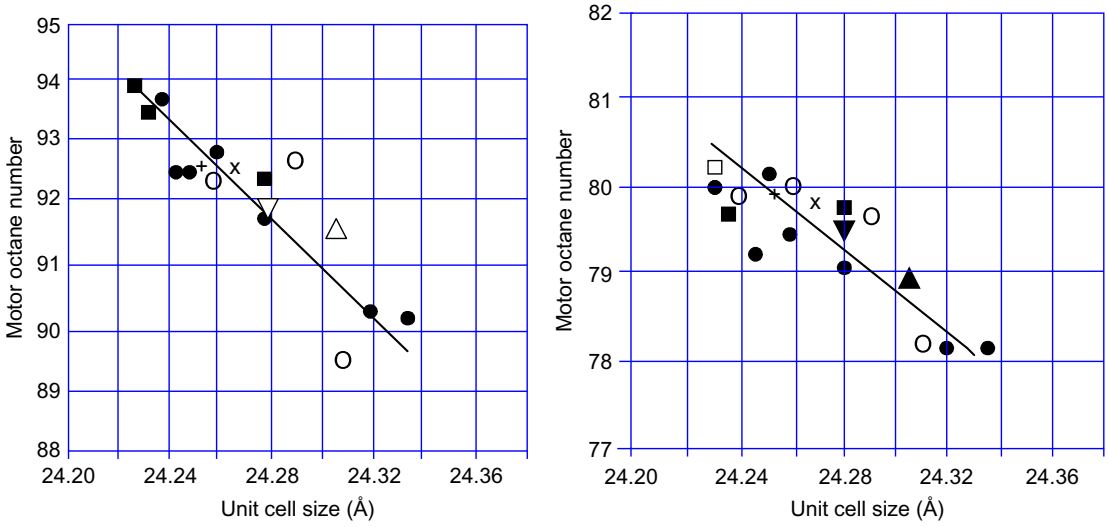


Figure 8.6: Effects of unit cell size on research and motor octane [5].

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Benzene

Most of the benzene in the gasoline pool comes from reformate. Reformate, the high-octane blending component from a reformer unit, comprises about 30 vol% of the gasoline pool. Depending on the reformer feedstock and severity, reformate contains 3−5 vol% benzene.

FCC gasoline contains 0.5−1.3 vol% benzene. Since it accounts for about 35 vol% of the gasoline pool, it is important to know what affects the cat cracker gasoline benzene levels. The benzene content in the FCC gasoline can be reduced by the following:

- Short contact time in the riser and in the reactor dilute phase
- Lower catalyst to oil ratio and lower reactor temperature
- A catalyst with less hydrogen transfer.

Sulfur

The major source of sulfur in the gasoline pool comes from FCC gasoline. Sulfur in FCC gasoline is a strong function of the feed sulfur content (Figure 8.7). Hydrotreating the FCC feedstock reduces sulfur in the feedstock and consequently in the gasoline (Figure 8.8). Other factors which can lower sulfur content are:

- Lower gasoline end point (Figure 8.9)
- Lower reactor temperature (Figure 8.10)
- Increased matrix activity of the catalyst
- Increase in the catalyst activity and hydrogen transfer properties
- Increase in catalyst to oil ratio (Figure 8.11)
- Increase in the use of main column overhead reflux rate instead of top pumparound to control the top temperature.

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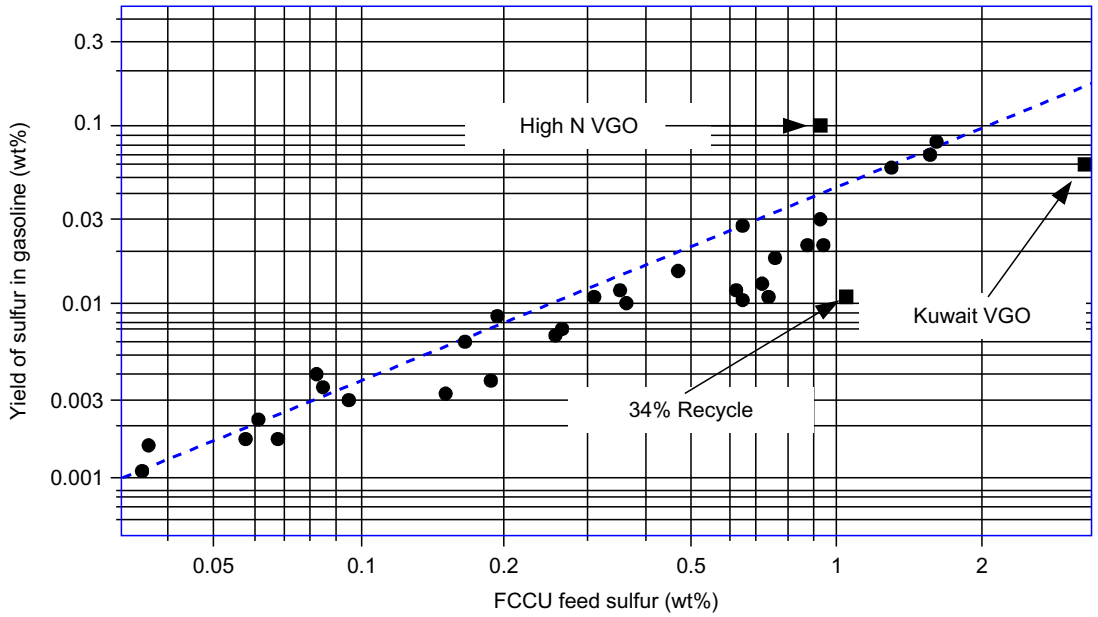


Figure 8.7: FCC gasoline sulfur yield [6] (*VGO = vacuum gas oil*).

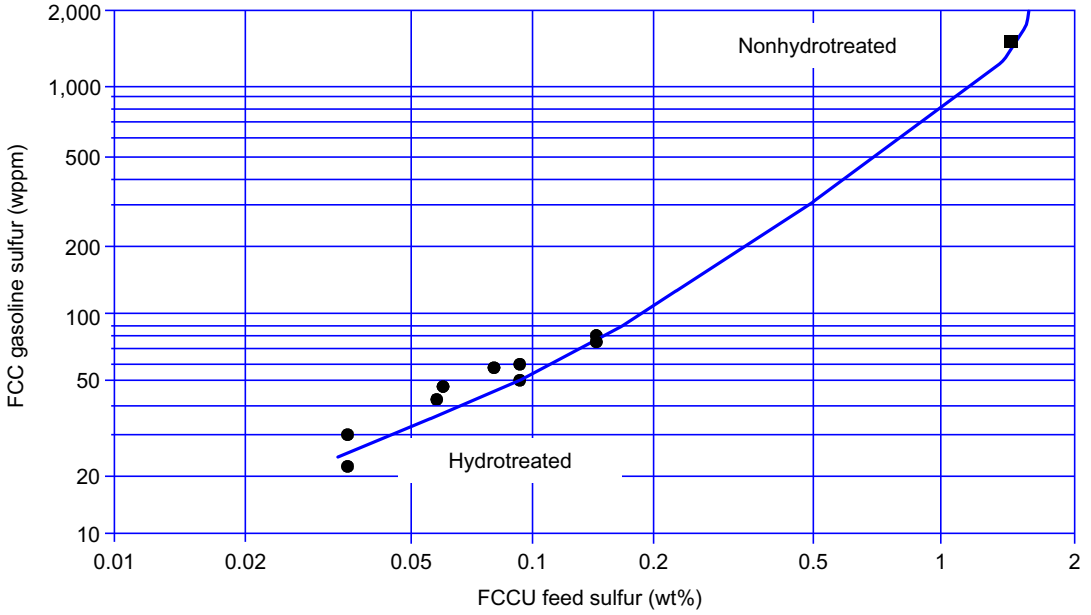


Figure 8.8: Hydrotreating reduces FCC gasoline sulfur [6].

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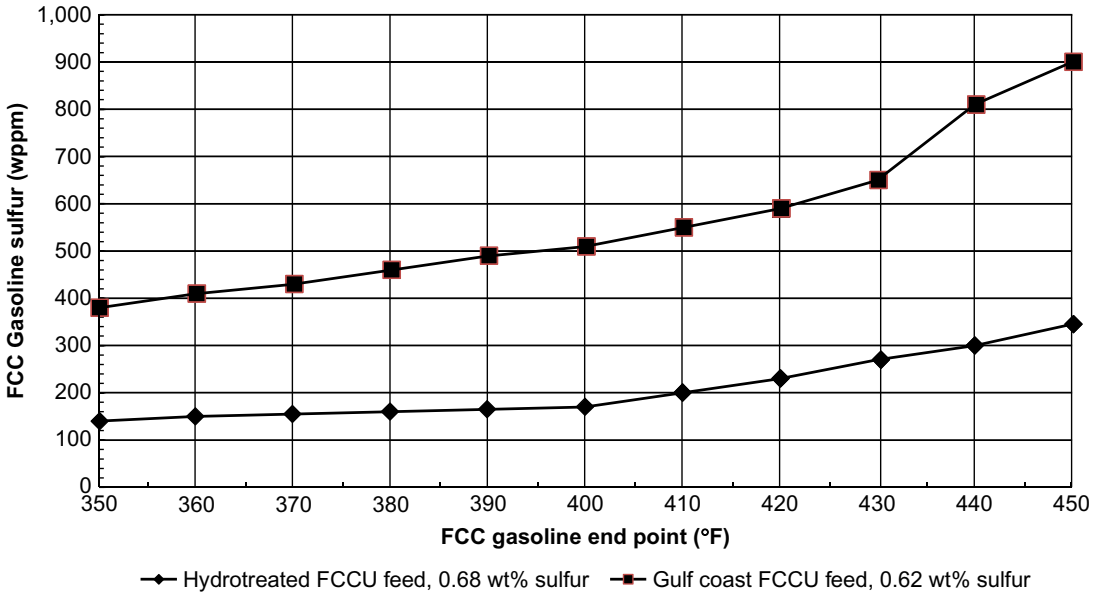


Figure 8.9: FCC gasoline sulfur increases with end point [6].

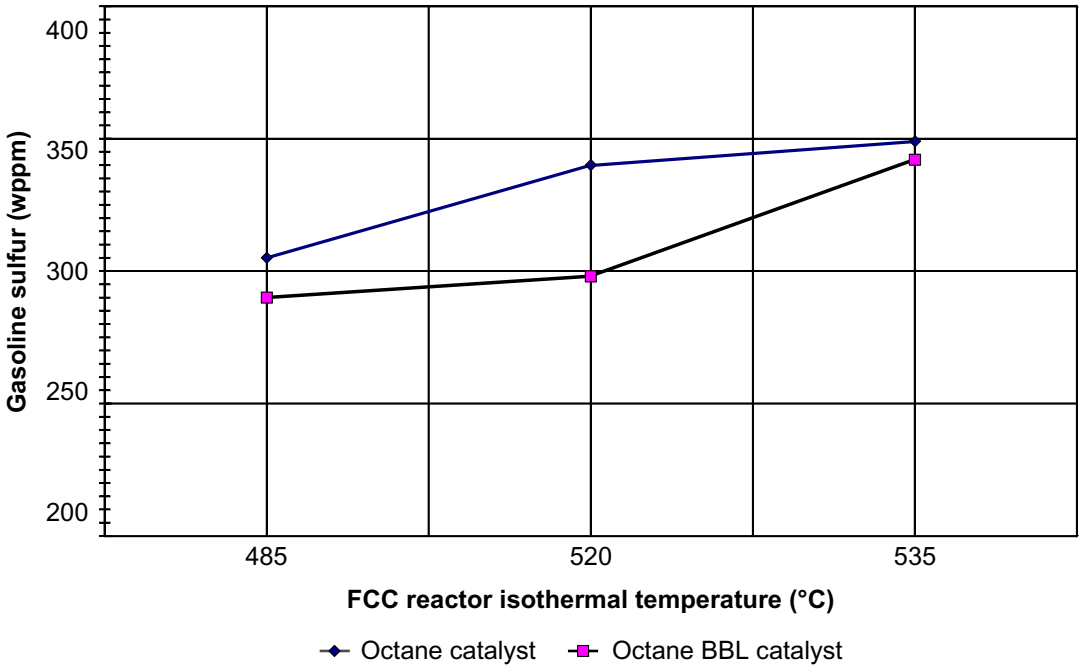


Figure 8.10: FCC gasoline sulfur increases with temperature [6].

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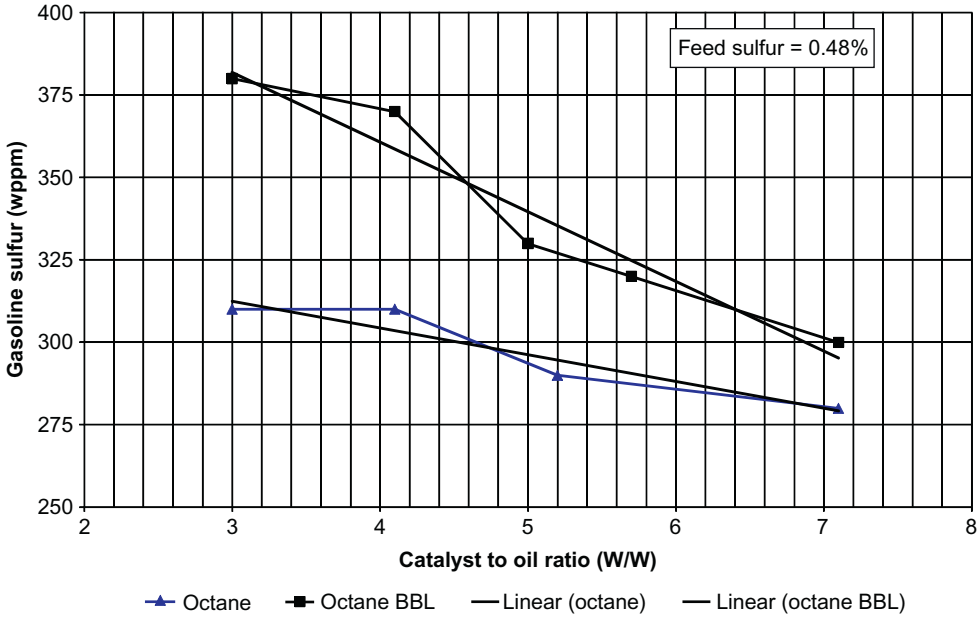


Figure 8.11: Increased catalyst to oil ratio decreases gasoline sulfur [6].

Light Cycle Oil

The emphasis on gasoline yield has sometimes overshadowed the importance of other FCC products, particularly LCO. LCO is widely used as a blending stock in heating oil and diesel fuel. Worldwide demand for diesel is expected to grow. This is particularly important during winter, when the price of LCO can be higher than gasoline. Under these circumstances, many refiners adjust the FCC operation to increase LCO yield at the expense of gasoline.

LCO Yield

The LCO yield is ~20 vol% of the FCC feedstock or about 3 million bpd. A refiner has several options to increase LCO yield. Since it is often desirable to maintain a maximum cracking severity while maximizing LCO yield, the simplest way to increase LCO yield is to reduce the gasoline end point. Gasoline end point is usually reduced by lowering the top temperature on the main column by increasing the top pumparound or the top reflux rate.

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The LCO distillation range is typically 430−670°F (221−354°C) ASTM D86. Undercutting the gasoline end point drops the heavy end of the gasoline fraction to be withdrawn with LCO. This affects only the apparent conversion and does not cause changes in the flow rate of other products. Reducing the gasoline end point usually increases the octane because of the lower octane components in the heavy end of gasoline.

A better method of increasing LCO yield is through better fractionation upstream. The removal of the fraction under 650°F (343°C) from the feed requires better stripping. The total refinery yield of diesel will increase when the light ends are fractionated from the feed (Table 8.1).

Some of the catalytic routes to maximize LCO yield are:

- Decrease in the reactor temperature
- Decrease in the catalyst to oil ratio
- Decrease in catalyst zeolite activity while increasing the matrix activity
- Increase in HCO recycle
- Use of bottoms upgrading catalyst additive.

Table 8.1: Effects of Feed Fractionation on Total Distillate Yield.

	Feedstock	
	"Raw" Gas Oil	"Fractionated" Gas Oil
Initial boiling point (°F/°C)	435/224	660/349
Final boiling point (°F/°C)	1,080/582	1,080/582
435°F/224°C to 660°F/349°C Content (wt%)	8	0
Conversion (wt%)	75.9	75.9
LCO (wt%)	15.4	14.0
Potential FCC LCO (wt%)	15.4	$(0.92 \times 14.0) = 12.9$
Total potential refinery distillate	15.4	$(12.9 + 8.0) = 20.9$

Source: Engelhard [7].

LCO Quality

The US Environmental Protection Agency (EPA) mandated 15 ppm as the allowable sulfur in the ultralow sulfur diesel (ULSD) for the on-road diesel pool. A minimum cetane number of 40 and a maximum aromatic concentration of 35% must also be met. By 2012, all off-road users, including railroad locomotives, must use ULSD specifications. The minimum cetane number in the European Union is 51.

Cetane

Like the octane number, the cetane number is a numerical indication of the ignition quality of a fuel. But the two numbers work backward. A gasoline engine is spark-ignited and an important fuel quality is to prevent premature ignition during the compression

stroke. A diesel engine is compression-ignited and it has to ignite when compressed. Unfortunately, components that increase octane will decrease cetane. For example, normal paraffinic hydrocarbons have a low octane number but a very high cetane number. Aromatics have a high octane number but a very low cetane number. The adjustments in the reactor yield mentioned above to improve LCO yield and quality will all lower gasoline yield and quality. To achieve the required cetane numbers, refiners may need to use cetane improvers such as the ones based on 2-ethyl nitrate (2-EHN).

Cetane number is measured in a single-cylinder laboratory engine (ASTM D613), but cetane index (CI) is more commonly used. Cetane index is a calculated value and correlates adequately with the cetane number. Two methods (ASTM D976 and ASTM D4737) are available to determine the cetane index. D4737 is an improvement over the D976 method. The difference is D976 uses two variables, density and distillation mid-boiling point, whereas D4737 uses two additional variables, 10% and 90% distillation. Most refiners use the ASTM equation (method D976-80) to calculate the cetane index. The equation uses 50% boiling point and API gravity (see Example 8.1).

Typical LCO is highly aromatic (50−75 wt%) and has a low cetane index (20−30). The cetane number and sulfur content determine the amount of LCO that can be blended into the diesel or heating oil pool.

Most (30−50 wt%) of the aromatics in the LCO are di- and triaromatic molecules. Hydrotreating the LCO can increase its cetane number. The degree of improvement depends on the severity of the hydrotreating. Mild hydrotreating (500−800 psig/3,500−5,500 kPa) can partially hydrogenate some of the di- and triaromatics and increase cetane by a number of 1−5. Severe hydrotreating conditions (>1,500 psig/10,300 kPa) can increase the cetane number above 40.

Other conditions that improve cetane are as follows:

- Undercutting the FCC gasoline
- Reducing the unit conversion
- Using an “octane” catalyst
- Processing paraffinic feedstock.

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Example 8.1

Cetane index equation

Method ASTM D976

$$CI_{976} = 65.01\ (\log T_{50})^2 + [0.192(^\circ\text{API}) \times \log T_{50}] + 0.16(^\circ\text{API})^2 - 0.0001809\ (T_{50})^2 - 420.34$$

or

where: $$CI_{976} = 454.74 - 1641.416D + 774D^2 - 0.554B_{50} + 97.803(\log B_{50})^2$$

T_{50} = mid-boiling temperature (°F), ASTM D86;
°API = API gravity at 60°F;
D = density at 15°C (g/ml) by test method ASTM D1298;
B_{50} = mid-boiling point (°C), ASTM D86.

Example:

T_{50} = 550°F;
°API = 19.0.

$$\begin{aligned} CI_{976} &= 65.01\ (\log 550)^2 + [0.192(19)(\log 550) + 0.16(19)^2 0.0001809(550)^2 - 420.34 \\ &= 65.01\ (2.74)^2 + [0.192(19)(2.74)] + 0.16(361) - 0.0001809(302,500) - 420.34 \\ &= 488.2 + 10.0 + 5.8 - 54.7 - 420.34 \\ CI_{976} &= 28.9 \end{aligned}$$

Method ASTM D4737

$$CI_{4737} = 45.2 + 0.0892T_{10N} + (0.131 + 0.901B)T_{50N} + (0.0523 + 0.420B)T_{90} + 0.00049(T^2{}_{10N} - T^2{}_{90N}) + 107B + 60B^2$$

where:

D = density at 15°C (g/ml) by test method ASTM D1298;
$B = (e^{(-3.5)(D-0.85)}) - 1$;
T_{10} = 10% distillation (°C), D86;
$T_{10N} = T_{10}$-215;
T_{50} = 50% distillation (°C), D86;
$T_{50N} = T_{50}$-260;
T_{90} = 90% distillation (°C), D86;
$D_{90N} = T_{90}$-310.

Heavy Cycle Oil and Decanted Oil

HCO is the sidecut stream from the main column that boils between the LCO and decanted oil (DO) product. HCO is often used as a pumparound stream to transfer heat to the fresh feed and/or to the debutanizer reboiler. If pulled as product, it is often processed in a hydrocracker or blended with the decanted oil.

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Decanted oil is the heaviest product from a cat cracker. It is also called slurry oil, clarified oil, and bottoms and FCC residue. Depending on the refinery location and market availability, DO is typically blended into No. 6 fuel, sold as a carbon black feedstock (CBFS) or even recycled to extinction.

Decanted oil is the lowest priced product and the goal is to reduce its yield. The DO's yield depends largely on the quality of the feedstock and the conversion level. Naphthenic and aromatic feedstocks tend to yield more bottoms than paraffinic feedstocks. If the conversion is in the low to mid-70s, increasing catalyst to oil ratio or using a catalyst with an active matrix can reduce slurry yield. Raising conversion reduces bottoms yield. If the conversion rate is in the 80s, there is little more to be done to reduce the bottoms yield. Other parameters that can reduce the DO product include higher fresh catalyst activity, effective feed atomization, and adequate residence time in the riser.

Decanted Oil Quality

Decanted oil properties vary greatly, depending on the feedstock quality and operating conditions.

Selling the decanted oil as carbon black feedstock often yields higher pricing than getting rid of it as cutter stock. To meet the CBFS specification, decanted oil must have a minimum Bureau of Mines Correlation Index (BMCI) of 120 and a low ash content (Table 8.2). Aromaticity and sulfur and ash contents are the three most important properties of CBFS.

Table 8.2: Typical Carbon Black Feedstock Specifications.

Property	Specification
Gravity (°API)	3.0, maximum
Asphaltenes (wt%)	5.0, maximum
Viscosity, SUS at 210°F (98.9°C)	80, maximum
Sulfur (wt%)	4.0, maximum
Ash (wt%)	0.05, maximum
Sodium (ppm)	15, maximum
Potassium (ppm)	2, maximum
Flash (°F)	200 (93.3°C), minimum
BMCI	120, minimum

$BMCI = (87{,}552/T) + [473.7 \times (141.5/131.6 + \text{API gravity})] - 456.8$
where:
T = mid-boiling point (°R).
For example:
T = 710°F (376.7°C) = 710°F +460 = 1,170°R;
API gravity = 1.0;
BMCI = 123.9.

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BMCI is a function of gravity and midpoint temperature. To make a BMCI of 120, the DO's API gravity should not exceed 2.0. The API gravity is a rough indication of aromaticity; the lower the gravity, the higher the aromaticity.

The ash content of the decanted oil product is affected by the reactor cyclone's performance and catalyst physical properties. To meet the CBFS' ash requirement (maximum of 0.05 wt%), DO product may need to be filtered for the removal of the catalyst fines.

Coke

In a "conventional gas oil" FCC unit, ~5 wt% of the fresh feed is deposited on the catalyst as coke. Coke formation is a necessary by-product of the FCC operation; more than 90% of the heat released from burning the coke in the regenerator supplies the heat for the cracking of the feed and heating up the combustion and carrier air entering the regenerator.

The structure of the coke and the chemistry of its formation are difficult to define. However, the coke in FCC comes from at least four sources, and they are as follows:

- *Catalytic coke* is a by-product of the cracking of FCC feed to lighter products. Its yield is a function of conversion, catalyst type, and hydrocarbon/catalyst residence time in the reactor.
- *Contaminant coke* is produced by catalytic activity of metals such as nickel and vanadium and by deactivation of the catalyst caused by organic nitrogen.
- *Feed residue coke* is the small portion of the (nonresidue) feed which is directly deposited on the catalyst. This coke comes from the very heavy fraction of the feed and its yield is predicted by the Conradson or Ramsbottom carbon tests.
- *Catalyst circulation coke* is a "hydrogen-rich" coke from the reactor−stripper. Efficiency of catalyst stripping and catalyst pore size distribution affect the amount of the hydrocarbons carried over into the regenerator.

A proposed equation [8] to express coke yield is:

$$\text{Coke yield (wt\%)} = g\,(Z_1, \ldots, Z_N) \times (C/O)^n \times (\text{WHSV})^{n-1} \times [e^{(\Delta_{EC}/RT_{RX})}] \qquad (8.1)$$

where:

$g(Z_1, \ldots, Z_N)$ = function of feed quality, hydrocarbon partial pressure, catalyst type, CRC, and so on;
$n = 0.65$;
C/O = cat to oil ratio;
WHSV = weight of hourly space velocity, weight of total feed per hour divided by weight of catalyst inventory in reaction zone (h^{-1})
Δ_{EC} = activation energy ~2,500 Btu/lb-mole (5,828 J/g-mole);
R = gas constant, 1.987 Btu/lb-mole-°R (8.314 J/g-mole-°K);
T_{RX} = reactor temperature (°R).

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The coke yield of a given cat cracker is essentially constant and mainly depends on the air blower capacity and/or availability of supplemental oxygen. The FCC produces enough coke to satisfy the heat balance. However, a more important term is delta coke. Delta coke is the difference between the coke on the spent catalyst and the coke on the regenerated catalyst. Delta coke is defined as:

$$\text{Delta coke} = \frac{\text{coke yield (wt\%)}}{\text{cat to oil ratio}} \tag{8.2}$$

At a given reactor temperature and constant CO_2/CO ratio, delta coke controls the regenerator temperature.

Reducing delta coke will lower the regenerator temperature. Many benefits are associated with a lower regenerator temperature. The resulting higher cat to oil ratio improves product selectivity and/or provides the flexibility to process heavier feeds.

Several factors influence delta coke, including quality of the FCC feedstock, design of the feed/catalyst injection system, riser design, operating conditions, and catalyst type. The following is a brief discussion of these factors:

- *Feedstock quality*: The quality of the FCC feedstock impacts the concentration of coke on the catalyst entering the regenerator. For example, a "heavier" feed containing a higher concentration of metals and organic nitrogen will directionally increase the delta coke as compared with a "lighter," impurity-free feedstock.
- *Feed/catalyst injection*: A well-designed feed nozzle injection system provides a rapid and uniform vaporization of the liquid feed. This will lower delta coke by minimizing noncatalytic coke deposition as well as reducing the deposits of heavy material on the catalyst.
- *Riser design*: A properly designed riser will help reduce delta coke by reducing the back-mixing of already "coked-up" catalyst with fresh feed. The back-mixing causes unwanted secondary reactions.
- *Cat to oil ratio*: An increase in the cat to oil ratio reduces delta coke by spreading out some coke-producing feed components over more catalyst particles and thus lowering the concentration of coke on each particle.
- *Reactor temperature*: An increase in the reactor temperature will also reduce delta coke by favoring cracking reactions over hydrogen transfer reactions. Hydrogen transfer reactions produce more coke than cracking reactions.
- *Catalyst activity*: An increase in catalyst activity will increase delta coke. As catalyst activity increases so does the number of adjacent sites, which increases the tendency for the hydrogen transfer reactions to occur. Hydrogen transfer reactions are bimolecular and require adjacent active sites.

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FCC Economics

The cat cracker's operational philosophy is dictated by the refinery economics. The economics of a refinery are divided into internal and external economics.

The internal economics depend largely on the cost of raw crude and the FCC unit's yields. The cost of crude can outweigh the benefits from the cat cracker yields. Refiners who operate their units by a kind of intuition may drive for more throughput, but this may not be the most profitable approach.

External economics are factors that are generally forced upon the refineries. Refiners prefer not to have their operations dictated by external economics. However, they may have to meet regulatory requirements such as those for regenerator flue gas emissions compliance and/or production of ultra-low sulfur diesel (ULSD).

To maximize the FCC unit's profitability, the unit must be operated against all its mechanical and operating constraints. Generally speaking, the incremental profit of increasing feed is more than the incremental profit from increasing conversion. The general target has historically been to maximize gasoline yield while maintaining the minimum octane that meets blending requirements. However, with the expected growth in middle distillate demand, the emphasis can shift from gasoline to diesel provided maximum bottoms upgrading is also achieved.

Because of the high cost of new units and the importance of the FCC to refinery profitability, improvements should be made to the existing units to maximize their performance. These performance indices are as follows:

- Improving product selectivity
- Enhancing operating flexibility
- Increasing unit capacity
- Improving unit reliability
- Reducing operating costs
- Meeting product specifications
- Reducing emissions.

Product selectivity simply means producing more liquid products and less "bad" coke and dry gas. Depending on the unit's objectives and constraints, below are some of the steps that directionally improve product selectivity:

- *Feed injection*: An improved feed injection system provides optimum atomization and distribution of the feed for rapid mixing and complete vaporization. The benefits of improved feed injection are reduced coke deposition, reduced dry gas yield, and improved gasoline yield.
- *Riser termination*: Good riser termination devices, such as closed cyclones, minimize the vapor and catalyst holdup time in the reactor vessel. This reduces unnecessary

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thermal cracking and nonselective catalytic recracking of the reactor product. The benefits are a reduction in dry gas and a subsequent improvement in conversion, gasoline octane, and flexibility for processing marginal feeds.

- *Reactor vapor quench*: LCO, naphtha, or other quench streams can be used to quench reactor vapors to minimize thermal cracking.
- *Reactor–stripper*: Operational and hardware changes to the stripper improve its performance by minimizing the amount of "soft coke" being sent to the regenerator. The main benefits are lower delta coke and more liquid products.
- *Air and spent catalyst distribution*: Modifications to the air and spent catalyst distributors permit uniform distribution of air and spent catalyst across the regenerator. Improvements are lower carbon on the catalyst, reduced afterburning, decline in NO_x emission, and less catalyst sintering. The benefits are a cleaner and higher activity catalyst, which results in more liquid products and less coke and gas.

Examples of increasing operating flexibility are as follows:

- *Processing residue or "purchased" feedstocks*: Sometimes, the option of processing supplemental feed or other components, such as atmospheric residue, vacuum residue, and lube oil extract, is a means of increasing the yields of higher value products and reducing the costs of raw material by purchasing less expensive feedstocks.
- *ZSM-5 additive*: Seasonal or regular use of ZSM-5 catalyst will center-crack the low-octane paraffin fraction of the FCC gasoline. The results are increases in propylene, butylene, and octane—all at the expense of FCC gasoline yield.
- *Catalyst cooler(s)*: Installing a catalyst cooler(s) is a way to control and vary regenerator heat removal and thus to allow processing of a poor quality feedstock to achieve increased product selectivity.
- *Feed segregation*: Split feed injection involves charging a portion of the same feed to a different point in the riser. This is another tool for increasing light olefins and boosting gasoline octane.

An example of increasing FCC unit capacity is oxygen enrichment.

- *Oxygen enrichment*: In a cat cracker, which is either air blower or regenerator velocity limited, enrichment of the regenerator air can increase the capacity or conversion, provided there is good air/catalyst distribution and that the extra oxygen does not just burn CO to CO_2.

In recent years, numerous mechanical improvements have been implemented to increase the run length and minimize maintenance work during turnarounds. Examples are as follows:

- *Expansion joints*: Improvement in bellows metallurgy to Alloy 800H or Alloy 625 has reduced the failures caused by stress corrosion cracking induced by polythionic acid.

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Additionally, placing fiber packing in the bellow-to-sleeve annulus, instead of purging with steam, has reduced bellows cracking. Reliability has also increased with the use of dual ply bellows.

- *Slide or plug valves*: Cast vibrating of the refractory lining and stem/guide modifications have minimized stress cracking and erosion.
- *Air distributors*: Improvements in the metallurgy, refractory lining of the outside branches, and better air nozzle design, combined with reducing L/D (length to diameter ratio) of the branch piping, have reduced thermal stresses, particularly during start-ups and upset conditions.
- *Cyclones*: Changes in the refractory anchor systems and materials, the hanger support system, longer L/D, and increasing the amount of welds in the anchor system have improved cyclone performance.

Summary

Improving FCC unit profitability requires operating the unit against as many constraints as possible. Additionally, selective modifications of the unit's components will increase reliability, flexibility, and product selectivity, and reduce emissions.

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CHAPTER 9

Effective Project Execution and Management

Since 1942, when the first FCC unit came onstream, numerous process and mechanical changes have been introduced. These changes improved the unit's reliability, allowed it to process heavier feedstocks, to operate at higher temperatures, and to shift the conversion to more valuable products.

But incorporating these changes in an existing unit is a major project, usually more complicated than building a new unit. The two critical components of a successful mechanical upgrade (or erection of a new unit) are effective project management and proper design standards.

This chapter addresses project management aspects of a revamp. It also provides design guidelines that can be used by a refiner in selecting the revamp components. The original driving force for a project is often a particular mechanical problem or a process bottleneck. The ultimate objective of a revamp should be a safe, reliable, and profitable operation.

Project Management

Aspects of an FCC Revamp

The modifications/upgrades to the reactor and regenerator circuit are made for a number of reasons: equipment failure, technology changes, and/or changes in processing conditions. The primary reasons for upgrading the unit are improving the unit's reliability, increasing the quantity and quality of valuable products, and enhancing operating flexibility.

The revamp (or erection of a new unit) requires successful execution of each phase of the project:

- Preproject
- Process design
- Detailed engineering

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- Preconstruction
- Construction
- Commissioning/start-up.

Preproject

In the preproject phase, a refiner must take many steps "in-house" before embarking upon a mechanical upgrade of an FCC unit. This is particularly true if the scope includes the use of new technology. The preproject activities include the following:

- Identifying the unit's mechanical and process constraints
- Identifying the unit's operational goals
- Optimizing the unit's current performance
- Obtaining a series of validated test runs
- Producing a "statement of requirement" or "revamp objectives" document
- Selecting an engineering contractor.

In many cases, a refiner decides to revamp a cat cracker and employ a new technology without first identifying the unit's mechanical and process limitations. Sometimes money is spent to relieve a constraint and the unit hits another constraint almost immediately. Failure to perform a proper constraint analysis of the existing operation can result in focusing on the wrong issues for the revamp. In addition, the revamp goals must match the refinery's overall objectives.

The refiner should identify economic opportunities internally before approaching a technology licensor. For example, what is the primary consideration: more conversion, higher throughput, or both? At times, a refiner may prefer to do the work internally, as opposed to hiring external resources, but all possible options should be explored.

It may often be more economical to purchase the desired product from another refiner than to produce it internally. The "marketplace" can be a less expensive source of incremental supply than the refiner's own in-house production capabilities.

Prior to a mechanical upgrade, the refiner must ensure that, given existing mechanical limitations, the unit's performance has reached its full potential with catalyst and operational changes. It is much easier to determine the effects of the mechanical upgrade with a well-operated unit. Use of more cost-effective changes could achieve the same return as expensive revamp options, when an optimized base case is determined.

Any project yield improvements should be based on conducting a series of operating test runs. The test runs should reflect "typical" operating modes. The results should be material/heat balanced. The test run should be performed shortly prior to the revamp. A comparison of the results, pre- and post-revamp, should reflect no major changes in the catalyst reformulation.

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The revamp objectives, constraints, and requirements must be clearly stated in a *statement of requirement* document transmitted to the engineering contractor. The document should be sufficiently detailed and require minimum interpretation so as to avoid oversights and unnecessary site visits.

Selection of a competent engineering contractor to perform process design and detail engineering is a key element in the overall success of a project. Important factors to consider when choosing a qualified contractor are as follows:

- Successful experience in FCC technology and revamps
- Related experience held by key members of the project team
- Current and projected workloads
- Biases and preferences as they relate to proven technologies and suppliers
- The strength and chemistry of project team members
- Range of services expected from the contractor, e.g. front-end engineering, detailed engineering, complete engineering procurement construction (EPC) through start-up
- Engineering rate, markup, and unit cost of a "change order."

Process Design

Few companies have their own technology for the predesign phase. For the purposes of this book, this phase will be referred to as *front-end engineering design* (FEED). FEED finalizes the process design basis so that the detailed engineering phase can commence. In most cases, FEED is performed by an engineering contractor, but sometimes it is prepared internally by the refiner. The FEED package must be sufficiently completed so that another engineering contractor can finish the detailed engineering with minimum rework.

In a revamp or construction of a new unit that involves a technology upgrade, the engineering contractor commonly supplies a set of product yield projections. Refiners normally use these yield predictions as the basis when conducting an economic evaluation and performance guarantee. It is essential that the refiner review these projects carefully to ensure that they agree with the theory and approach expressed by the licensor and that similar yield shifts have been observed by other refiners installing similar technologies. In other words, the refiner should independently check the validity of projected yield improvements.

During the FEED phase of the project, the engineering contractor can be asked to prepare two cost estimates. The initial cost estimate is usually prepared during the very early stages. The accuracy of this estimate is usually plus or minus 40−50%. This is a factored estimate of equipment and terms of reference. The second cost estimate is prepared at, or near, the completion of the FEED package. The accuracy of this cost estimate is normally plus or minus 20%. This estimate is usually the basis for obtaining funding for the detailed engineering stage.

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The format of the cost estimate is just as important as the content. The format can make a difference when proving whether or not the content is accurate. Therefore, the refiner should require that the contractor present cost estimates in a format that is easy to understand and analyze. In addition, the refiner's cost engineer should independently review the cost estimate to ensure its accuracy and applicability and also to determine the contingency amounts that the owner should maintain in his or her funding plans.

The FEED package typically consists of the following documents:

- Project scope of work and design basis
- PFDs
- Feedstock and product rates/properties
- Utility load data
- Operating philosophy, start-up and shutdown procedures
- List of equipment, materials of construction, and piping classes
- P&IDs, tie-in, and line list
- Instrument index, control valve, and flow element data sheets
- Electrical load, preliminary instrument, and electrical cable routing
- Preliminary plot plan and piping planning drawings
- Specifications and standards
- Cost estimate
- Project schedule.

Detailed Engineering

In the detailed engineering stage, the mechanical design of various components is finalized so that the equipment can be procured from the qualified vendors and the field contractor can install it. In preparing construction issue drawings, the designer should pay special attention to avoiding field interference and allowing sufficient clearance for safety, operability, and maintainability.

To ensure project-related safety, health, and environmental issues have been identified and resolved, the refiner should have in effect a process safety program that confirms the project complies with Occupational Safety and Health Administration (OSHA) requirements.

Procurement of materials in a timely fashion is a necessary part of detailed engineering. Successful procurement requires:

- Early involvement of the procurement team
- Identification of long-lead and critical items
- Identification of "approved" vendors
- Identification of appropriate specification standards
- Competitive bid evaluation based on quality, availability, and price

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- Establishment of a quality control program to cover fabrication inspection
- Establishment of an expediting system to avoid unnecessary delays.

Preconstruction

Activities performed in the preconstruction or preturnaround stage are essential to the success of the project. Some of the key activities are as follows:

- Finalizing the project strategy plan
- Determining required staffing
- Identifying lay-down needs and securing specific areas
- Performing the detailed constructability study
- Identifying additional resources such as special equipment or special skills
- Completing an overall execution schedule
- Reviewing the schedule to maximize preshutdown work
- Maximizing preshutdown tasks.

Construction

The guidelines for screening the general mechanical contractor and other associated subcontractors are similar to those for selection of an engineering contractor. The scope and complexity of the work will largely dictate the choice of the general contractor. Aside from availability and quality of skilled crafts, the contractor's safety record and the dedication of the frontline supervisor to the workers' safety should be an important factor in choosing a contractor.

Early selection of the general contractor is critical. The general contractor should be brought in at 30–40% engineering completion to review the drawings and interface with the engineering contractor. Additionally, early constructability meetings among the refiner, engineering contractor, and general mechanical contractor will prove valuable in avoiding delays and rework.

Pre-commissioning and Start-up

A successful start-up requires having in place a comprehensive plan that addresses all aspects of commissioning activities. Elements of such a plan include the following:

- Preparation of the operating manual and procedures to reflect changes associated with the revamp
- Preparation of training manuals for the operator and support groups
- Preparation of a field checklist to inspect critical items prior to start-up
- Development of a quality assurance/quality control (QA/QC) certification system to assure that the installation has complied with the agreed standards and specifications.

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Post-Project Review

Shortly after the start-up and before the general contractor leaves the site, a meeting should be held among key members of the project execution team to obtain and document everyone's feedback on what went right, what went wrong, and what could have been done better. A summary of the minutes of this "lessons learned" meeting should be sent to the participants and other relevant personnel.

Once the operation of the unit has "lined out," it is time to conduct a series of test runs to compare performance and economic benefits of the unit with what was projected as part of the original project justification. The results can also be used to determine if the unit's performance meets or exceeds the engineering contractor's performance guarantee.

Useful Tips for a Successful Project Execution

A successful project is defined as one that meets its stated objectives (safety, improved reliability, increased liquid yield, reduced maintenance costs, and so on) on or under budget and is completed on or ahead of schedule.

Some of the criteria that ensure a successful project are as follows:

- Plan carefully; this minimizes changes.
- Set the major reviews (PFDs, P&IDS, and so on) early, as opposed to waiting until the basic design is completed. This will minimize the project's cost by lessening rework.
- Assign dedicated refinery personnel to be stationed in the engineering contractor's office to coordinate project activities and act as a liaison between the refinery and the contractor.
- Make sure the key people from the operations, maintenance, and engineering departments are kept fully informed and that their comments are reflected early enough in the design phase to minimize costly field rework.
- Centralize all decision making to avoid project delays.

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CHAPTER 10

Refractory Lining Systems

The subject of refractory lining is quite extensive. Comprehensive discussion of this topic would require a dedicated book. The main objectives of this chapter are to provide readers with the following:

- An introduction to the different refractories employed in FCC units
- Examples of various refractory linings and associated anchors used in refractory systems
- Several installation techniques
- Guidelines for proper drying and curing refractory lining.

Refractories are construction materials designed to withstand aggressive service conditions at elevated temperatures. They are generally used as heat-resistant walls, coatings, or linings to protect units from oxidation, corrosion, erosion, and heat damage. The main types include castables, plastic refractories, ceramic fiber, and brick. Each type has advantages and disadvantages related to installation requirements, serviceability, cost, and convenience.

Understanding the refractory materials as well as the process's operating conditions is important in selecting the appropriate refractory lining system and to administer proper maintenance. Operating temperature, abrasive conditions, thermal shock, and hostile environments are generally the conditions that must be known and incorporated into the design and maintenance of refractory lining systems.

Materials/Manufacture

Cements

Cements are binders for castables and gunite mixes. Cement is a finely divided substance that is workable when first prepared. It becomes hard and stone-like as a result of a chemical reaction with water that produces crystallization of the cement. Cements are typically calcium silicate (Portland) or calcium aluminate (refractory) types and are produced in various compositions.

Fluid Catalytic Cracking Handbook.
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Aggregates

Aggregates, as applied to refractories, are ground mineral material, consisting of particles of various sizes. They are used with much finer sizes for making formed or monolithic bodies. The refractories industry utilizes numerous aggregates in the manufacture of castables and bricks.

Additives

Additives are materials added to a mix or blend that enhance specific properties of the installed refractory, such as installation characteristics of the mix.

Fiber

Fibrous refractory insulation is composed primarily of alumina and silica. Applicable forms include bulk, blanket, paper, module, vacuum-formed shapes, and rope.

Stainless Steel Fibers in Refractory

There are a variety of stainless steel fibers available for use in castables and plastic refractories. They are added to refractory linings to normalize shrinkage cracks and to improve the integrity of cracked refractory linings. The fiber addition evenly distributes the effect of shrinkage, which produces small cracks, instead of a small number of large cracks. When a lining experiences numerous thermal cycles, additional cracking occurs. The stainless steel fibers serve to reinforce the refractory section and bridge the crack which gives the lining greater stability and integrity.

Stainless steel fibers become ineffective above 1,500°F (815°C) because of oxidation. Once the fibers oxidize, they are no longer effective in providing stability. Oxidation can also contribute to deterioration of the refractory surface. The oxidized fibers experience a greater volume, which consequently causes the lining to fracture or rupture leading to loss of strength and reliability.

The melt extract stainless steel fibers are the most popular. These fibers are flexible and do not lead to plugging of hoses and gunite equipment, unlike the more rigid fibers. The slit sheet and wire fibers are more rigid and are not as friendly to the equipment, but once installed, appear to function well.

Types of Refractory

Bricks

Refractory bricks are prefired refractory, composed of an aggregate and a binder. Bricks have a matrix that is capable of withstanding hot loads and chemically abusive environments.

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Insulating Firebrick

Insulating firebricks (IFB) are lightweight bricks that provide excellent thermal conductivity. They have high porosity, which yields low thermal conductivity, but are much weaker than typical firebrick. These bricks are installed as working lining in furnaces but are used for backing up firebrick in high-temperature applications where chemical and physical integrities are important.

High Alumina Firebrick

High alumina firebrick is typically used in applications where high temperatures and harsh environments are damaging to conventional firebrick. Reaction furnaces in the sulfur recovery process utilize high temperatures to destroy ammonia and oxidize hydrogen sulfide. At elevated temperatures, the high alumina bricks are mechanically and chemically stable and provide long-term reliable linings.

Castables

Castable is a general term for refractory concretes composed of an aggregate and a binder. The aggregate usually accounts for 60–80% of the volume of the finished product and is generally a prefired mineral product. Broken bricks, calcined clay, bloated shale, and expanded volcanic ash are the most commonly used aggregate. Very expensive aggregates, such as silicon carbide and tabular alumina, are typically used only in special applications where severe service conditions preclude the more conventional types. The physical properties of the finished castable are the result of the combined effects of the aggregate and the binder. The aggregate type usually controls the density, strength, and upper temperature limit, while the binder has a significant effect on the strength. Together, the binder and the aggregate control properties such as thermal expansion, firing shrinkage, erosion resistance, and chemical resistance.

Most binders are of hydraulic type and use iron-containing calcium aluminate cements. There are also iron-free calcium aluminate cements that are used in applications where iron will interfere with the process reaction. The hydraulic cements work by reacting with water to form hydrated calcium aluminate phases that set into a rock-like mass.

Castables—Product Categories

Lightweight

Lightweight castables are designed to provide an efficient thermal barrier or lining. Furnaces or heaters are the most common applications for lightweight castable products. Lightweight castables for refinery applications are best defined as having densities in the

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range of 45–65 lb/ft^3 (720–1,040 kg/m^3). Compressive and flexural strengths are very low but are not likely to be the physical properties that govern its selection or use. Thermal conductivity is low, which provides for low heat flux (heat transfer) and ultimately low shell or casing temperatures. Porosity and permeability are high, which are the elements in low thermal conductivity.

Medium Weight

Medium weight castables have densities in the range of 65–90 lb/ft^3 (1,040–1,440 kg/m^3). These products have higher strengths and are used where thermal conductivity and strength are important. The medium weight products have greater integrity than lightweight products and are selected for applications where moderate mechanical abuse is apparent.

Moderate Density/Erosion Resistant

Moderate density/erosion-resistant products are a category initiated by Doug Hogue several years ago to describe products with a density range of 100–120 lb/ft^3 (1,602–1,920 kg/m^3) that exhibited good erosion resistance (<15 ml erosion loss).

General Purpose

General purpose castables are versatile products in the 125–140 lb/ft^3 (2,000–2,240 kg/m^3) range that exhibit moderate to good strength. They are typically rated for uses from 2,600°F to 3,000°F (1,426–1,650°C) and find applications where extreme services are not anticipated.

High Alumina

Castables are classified as high alumina when the alumina content exceeds 70%. In the refining industry, the need for high alumina is limited to specific processes where chemical stability is extremely important, such as hydrogen production and sulfur recovery (reaction furnaces).

Erosion Resistant

Erosion is common in FCC units. In areas where high velocity is coupled with relatively high concentrations of particulates, erosion-resistant products are required to provide reliable operating equipment. Erosion is the "wearing away" of a product or lining by the cutting action of entrained particles in a high-velocity stream. Refractories are used to protect metal components of process equipment, and when the refractory is worn away,

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erosion of the metal shell is rather quick. Erosion of the steel shell can cause emergency or unplanned turnarounds.

Extreme Erosion Resistant

Extreme erosion-resistant refractory is a category that distinguishes products for use in FCC unit applications. Riser lines, cyclones, and distributors are areas where extreme erosion is possible.

Low Cement

Low cement castables incorporate sintering aids into the castable mix that assist in the development of low-temperature physical properties. Lowering the cement content of a castable provides greater chemical resistance because the cement binder is prone to chemical deterioration or attack. Low cement castables have limited application in the refining industry because chemical resistance is not a major characteristic necessary for successful service. However, in some instances, low cement castables are acceptable choices as a lining material.

Mortar (Refractory)

Mortar is a finely ground preparation which becomes plastic and trowelable when mixed with water and is suitable for use in laying and bonding refractory bricks together. Mortars are produced in various compositions and are made to match the type of brick mortared or to the service conditions. A common binder for "air-setting" mortars is sodium and potassium silicates, and when used in very thin layers (<1-mm thick) provides excellent service to temperatures approaching 3,270°F (1,800°C). Heat-setting mortars are formulated with clay binders that develop strength during the first firing cycle. These mortars are capable of higher temperature service than the air-setting class. Phosphate binders are also used in mortars and are generally used when the phosphate bond is better suited for the operating environment.

Plastic Refractories/Ram Mixes

Plastic refractories are usually composed of a highly calcined aggregate, plasticizers, and binders. The term "plastic" is used because the material is workable, although very stiff, and is usually placed with a pneumatic hammer (rammer). Ram mixes are generally compositions similar to the plastic refractory but have significantly less water. These products are manufactured and placed in drums to preserve the product's working characteristics. Ram mixes are produced in granular form and require significant ramming

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energy to consolidate the material into a lining. These products have limited use in the refining industry.

Physical Properties

The key physical properties that are often used to assess refractory include the following:

- Bulk density
- Strength
- Permanent linear change
- Thermal conductivity
- Abrasion loss.

Other physical properties that are important in specific applications include:

- Thermal expansion coefficient
- Porosity and permeability.

Bulk Density

Bulk density is weight per unit volume (lb/ft^3, g/ml, kg/m^3). Density is a physical property that provides valuable information. It is measured using ASTM C134. In most conventional alumina silicate products, thermal conductivity is a function of density. Strength is not directly related to density; however, for specific products, density is useful in assessing other physical properties (i.e. if a product is low in density by 10−15%, other physical properties will show significant deficiencies).

Strength

Modulus of Rupture (psi, kg/cm^2)

Modulus of rupture (MOR) is like a three-point bend test. MOR measures the bond strength of the test specimen. For castables, it measures the bonding strength of the cement matrix. The particle size and packing of the aggregate system are factors in MOR, but the maturity of the cement bond contributes more to MOR values.

Cold Crushing Strength (psi, kg/cm^2)

Cold crushing strength (CCS) is a compressive test that measures the ability of a product to withstand a given load, normally measured at room temperature after firing to specific temperatures. It is measured by ASTM C133. Particle distribution and packing are very important in developing good CCS—and cement maturity, while important, does not affect this measurement as much as it does MOR. Products that develop good CCS are sometimes unacceptable because of other physical property deficiencies.

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Permanent Linear Change (Castables and Plastic Refractories) (%)

Permanent linear change (PLC) is known as shrinkage. This property is developed on the first firing of a castable or plastic refractory. It is measured by ASTM C113. Dimensional changes result from loss of moisture and mineralogical changes in the binder. Castables typically use cement as the binder, and hydration of the cement provides bonding of the aggregate system. Upon heating, the cement dehydrates, which causes changes in the mass, ultimately leading to a permanent dimensional change. In the refining industry, the operating temperatures of equipment are relatively high, and lightweight and medium-weight castables will rarely retain their installed dimensions. The result is cracking of the lining, and the magnitude of the cracks is a function of the amount of shrinkage in the product. The cracks in lightweight and medium-weight products will not close upon heating.

Thermal Conductivity (BTU-in./ft^2, h, °F, W/m^{2}K)

Thermal conductivity is a measure of heat transferred across a specific medium. In refractories, thermal conductivity is a function temperature and typically the thermal conductivity is higher at elevated temperatures.

In castable refractories, with cementitious bonds, thermal conductivity is also affected by the hydrated calcium aluminate cement. It is measured by ASTM C417 with equipment defined in ASTM C201. The first firing of a castable will remove all free moisture and will begin to dehydrate the hydrated cement. At moderate operating temperatures, the destruction of the hydrated cement is not complete, and the resulting thermal conductivity is higher than published by manufacturers. The American Petroleum Institute Task Group on Vessel Refractories conducted a study on thermal conductivity and determined that test methods showed significant discrepancies in measured thermal conductivity. Also ascending (heating) and descending (cooling) thermal conductivity curves varied significantly. The conclusion was that users should review the test method employed in developing data and utilize ascending thermal conductivity curves for applications in refining.

Erosion (Abrasion) (ml)

Erosion and abrasion are used synonymously in the refining industry. Erosion properties are generally associated with wear linings in FCC unit applications. Testing is performed in conjunction with ASTM C704; however, this test does not necessarily predict the absolute performance of the products in erosion service. The test is generally a quality control tool, but performance does generally follow erosion results.

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Anchors

Some of the key functions of anchoring for refractory systems include the following:

- They secure refractory against the shell and provide stability.
- They promote uniform cracking of thick refractory linings to minimize potential cracking.
- They help resist thermal and mechanical stresses inherent with thermal gradients.
- They are a vital component in enhancing erosion resistance of refractory lining.

Anchor Types

- Vee
- Longhorns
- Hex mesh grating.

Vee

Vee anchors are the primary anchor for monolithic refractory linings over 3-in. (75 mm) thick. The two most common Vee anchors are wavy Vee and double-hook Vee, footed anchors (Figures 10.1A and 10.1B).

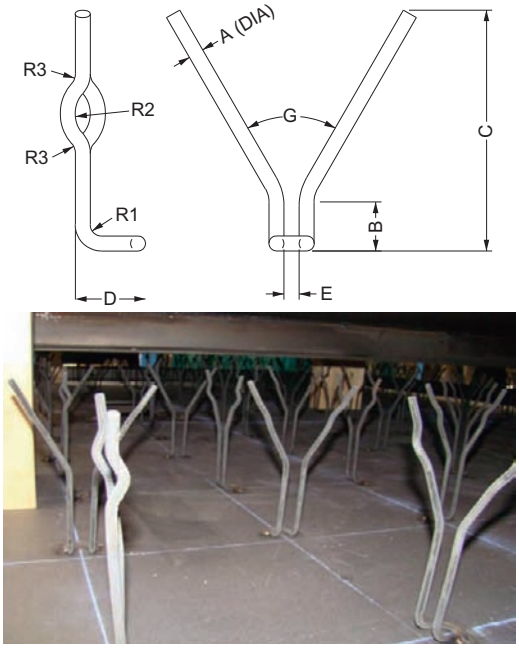


Figure 10.1A: Example of equal-length footed wavy Vee anchor (long). (*A = diameter; B = tyne extension; C = anchor height; D = foot length; E = foot bend radius; G = included angle of tyne; R1 = bend radius for tyne; R2 = inside bend radius for wave; R3 = outside bend radius for wave.*)

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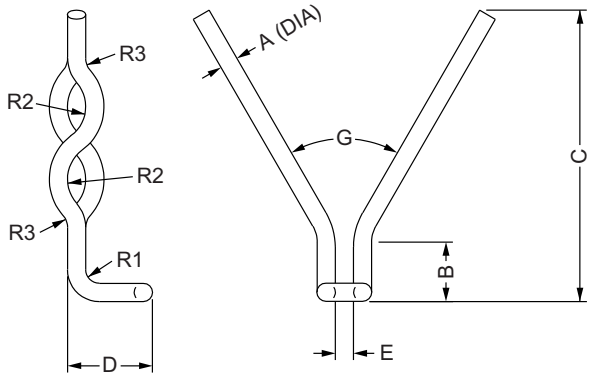


Figure 10.1B: Example of equal-length footed wavy Vee.

Longhorns

The longhorn anchor is suited for linings between 2- and 3-in. (50−75 mm) thick. The holding power of this anchor is not suitable for thick linings (Figure 10.2).

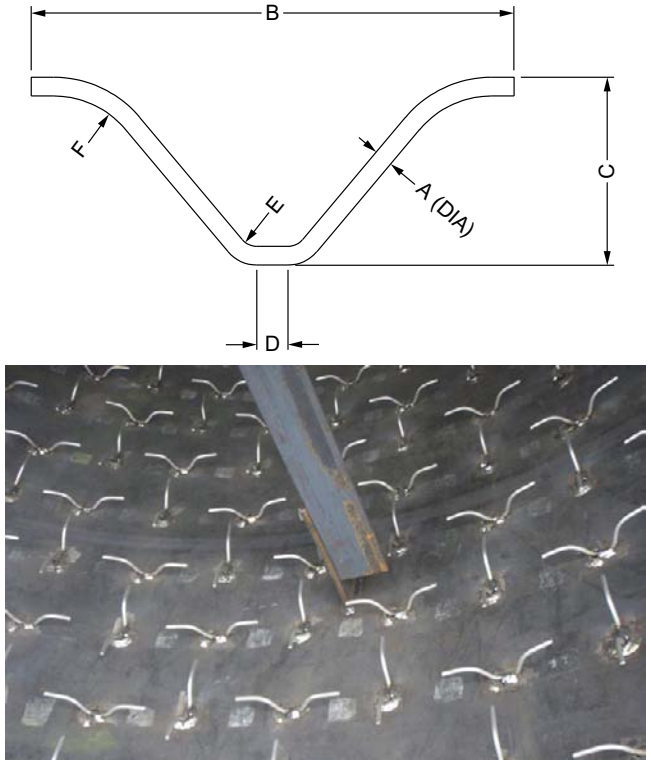


Figure 10.2: Example of longhorn anchor hex mesh grating. (*A = diameter; B = anchor width; C = anchor height; D = foot width; E = foot bend radius; F = bend radius of tyne tip*).

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Hex Mesh

Hex mesh is an arrangement of strands of metal to form hexagonal cells in a monolithic anchoring system. Hex mesh is typically used with thin 3/4 to 1 in. (19−25 mm) erosion-resistant lining such as cyclones, hot-wall risers, sugar scoops, and other hot-wall lining systems with severe erosion. The hex mesh anchoring system in conjunction with extreme erosion-resistant castable refractory is likely the best erosion-resistant system available. Hex mesh grating is difficult to work with and expensive; therefore, it is primarily used for new construction. Hex mesh grating is used very little for repairs because of the expensive installation cost for field applications such as turnarounds (Figure 10.3).

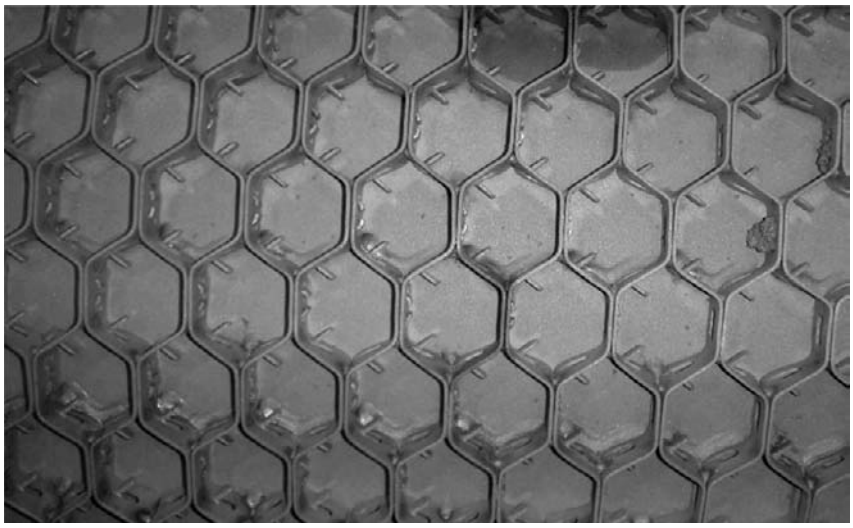


Figure 10.3: Example of hex steel.

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Independent Anchor Systems

Hex Cells

Hex cells are independent hexagonal anchors that are used to simulate the hex mesh grating system. The hex cell is popular because it is relatively inexpensive compared to hex mesh grating (Figures 10.4A and 10.4B).

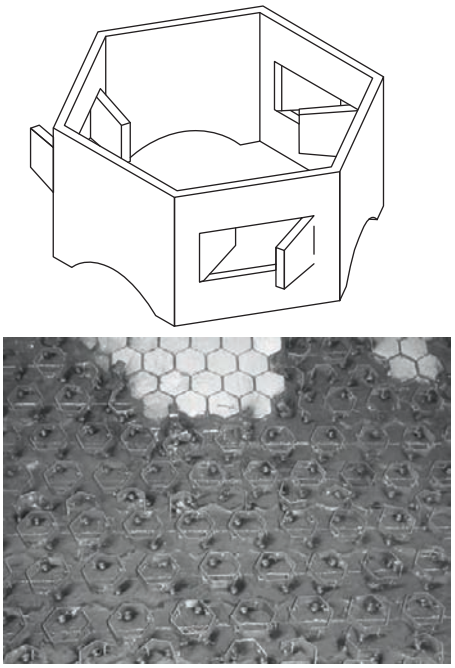


Figure 10.4A: Example of hex cell.



Figure 10.4B: Example of half hex cell layout.

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S-Bars

S-Bars are another independent anchoring system. The S-Bar is popular in repairing thin-layer erosion-resistant lining. It is effective and relatively inexpensive when compared to the hex mesh anchoring system. It also conforms easily to irregular geometrical shapes (Figure 10.5).

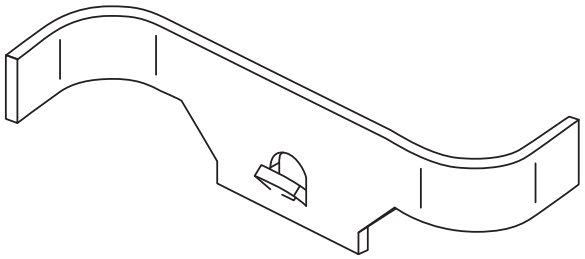


Figure 10.5: Example of S-Bar.

Curl Anchor®

Curl Anchors® are yet another independent anchoring system that provides greater holding power compared to the S-Bar. It is more expensive than the S-Bar in both material and installation costs but contributes more holding power (Figure 10.6).

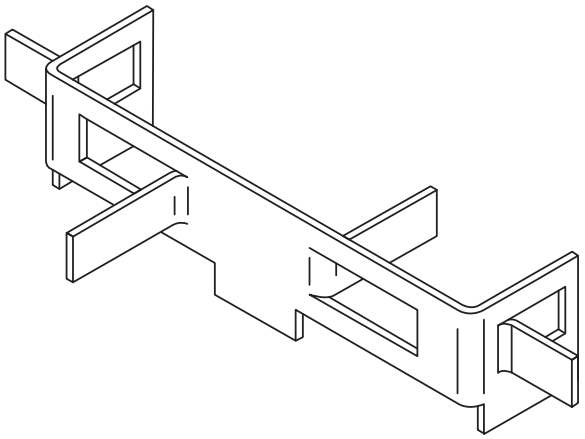


Figure 10.6: Example of Curl Anchor®.

K-Bars®

K-Bars® are an independent anchoring system developed primarily for stud welding applications. The anchor is expensive relative to the S-Bar, but the application cost is less because of the speed of stud welding (Figure 10.7).

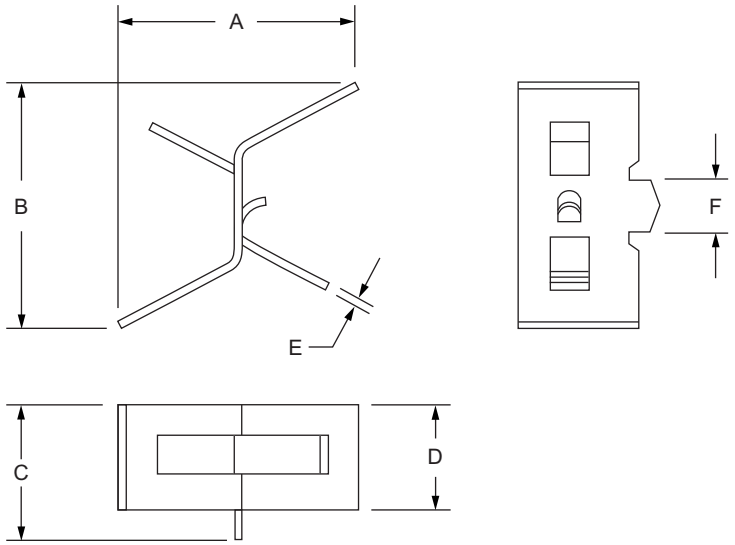


Figure 10.7: Example of K-Bars® (*A = anchor developed width; B = anchor developed length; C = anchor height; D = anchor bar height; E = material thickness (gauge); F = anchor foot width*).

Chain Link/Picket Fencing

Chain link and picket fencing are used primarily in insulating castable linings, such as duct and breaching, 2 in. (50 mm) or less. These anchoring systems are effective for thin linings where Vee-type anchors are ineffective (Figure 10.8).

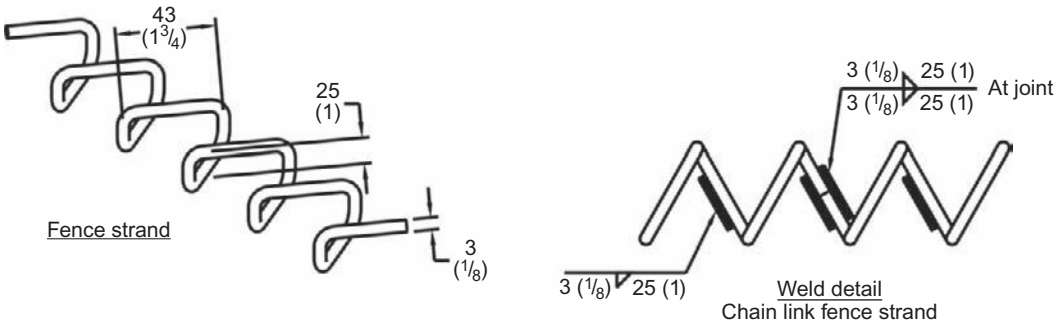


Figure 10.8: Example of chain link wire.

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Punch Tabs (Corner Tabs)

Punch tabs are used exclusively around corners associated with large nozzles such as manways, intersection of refractory lined pipe, outlet nozzles, and other linings where an abrupt change in direction is encountered (Figures 10.9A and 10.9B).

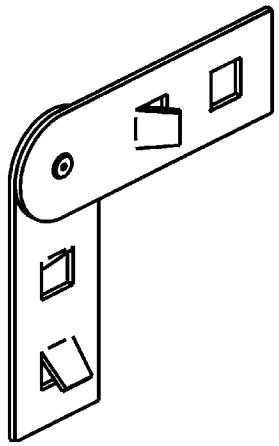


Figure 10.9A: Example of variable corner tab.

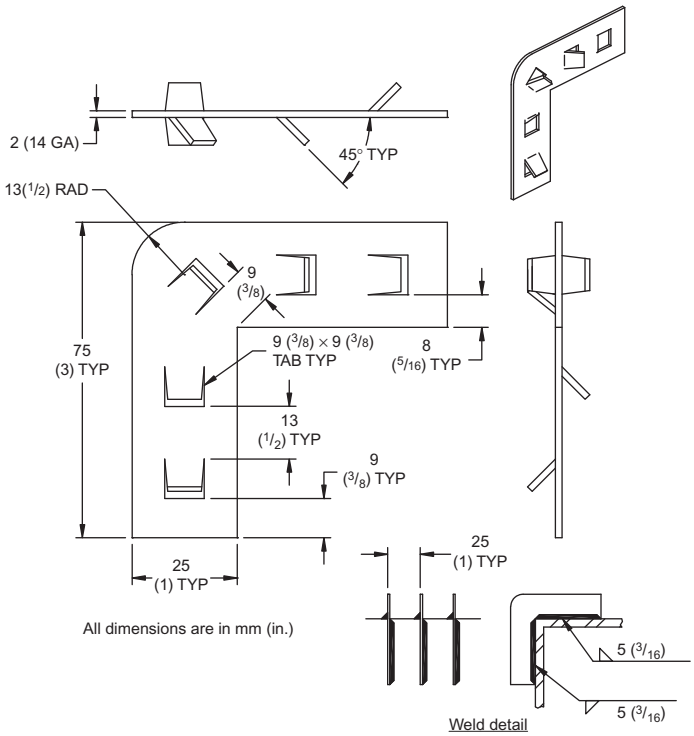


Figure 10.9B: Example of fixed corner tab (*GA = gauge; RAD = radius; TYP = typical*).

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Ring Tabs

Ring tabs are anchoring that fits small pipes/nozzles. This anchoring system is much more effective than other anchoring such as hex mesh, hex cells, and S-Bars (Figure 10.10).

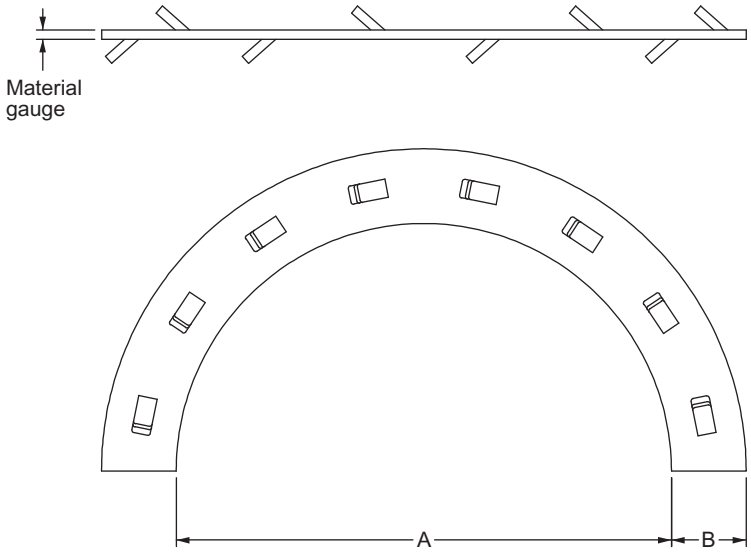


Figure 10.10: Example of ring tab (*A = ring tab diameter; B = ring tab height*).

Dual Layer Anchoring

Dual or two-layer linings should utilize anchoring for both layers of the lining. The back-up lining is typically anchored with Vee or Longhorn anchors, depending on thickness, and the hot-face lining is anchored with Vee anchors attached to stainless steel stud. The Vee anchor for the hot-face lining is fitted with a stainless steel nut (welded to the foot of the anchor), which in turn is secured to the stainless steel stud. The hot-face anchor is installed after the back-up lining is completed.

Anchor Patterns

Anchor patterns will vary depending on many criteria. Most companies will have guidelines for anchor spacing that utilizes experience as the main criteria for the various patterns.

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Designing Refractory Lining Systems

Designing refractory lining systems involves understanding the primary function of the lining. What is the lining's major function? Is it associated with temperature, erosion, environmental stability, structural stability, or chemical stability? It is very important to understand the process and how the refractory lining system functions relative to the process.

Elements of refractory design include:

- Lining thickness
- Choice of refractory
- Heat transfer
- Choice of anchoring.

Lining Thickness

Lining thickness is related to the function or purpose of the refractory lining. When the lining provides thermal protection, thickness is determined by the desired cold-face or shell temperature. When resisting erosion is the main purpose of the lining, lining thickness is based on the severity of the erosive medium and how long the lining must last.

Refractory Selection

The choice of refractory is vital to the success of refractory lining. Although physical properties are not a true indicator of refractory performance, when coupled with prior experience they will provide the necessary guidance in the selection process and improve the potential for designing a successful lining.

Heat Transfer

Heat transfer through a refractory lining is a function of the materials' thermal conductivity. Thermal conductivity of a refractory is generally reported by a manufacturer; however, the method of measuring thermal conductivity is very important. The test for thermal conductivity is dependent on the type of refractory and identified in ASTM Volume 15.01.

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Choice of Anchoring

Anchor selection is based on a variety of factors including:

- Lining thickness
- Service (e.g. coking, oxidizing, erosion, water)
- Lining type
- Insulating products
- Dense materials
- Thermal cycling
- Vibration
- External versus internal
- Temperature.

Anchor selection can directly influence lining reliability and stability along with potential hot-gas bypassing and hot-spot development. A thorough review of anchor requirements is prudent in all refractory lining systems.

Application Techniques

Castables/Gunning Mixes

- Gunite
- Wet gunning
- Casting
- Cast vibrating
- Ramming.

Gunite

Dry guniting is the most popular installation technique for castable applications in the refining industry. Dry guniting is the pneumatic placement of a castable where, after predamping the castable at the gun, the majority of the water requirements are added at the nozzle, as the refractory is gunited onto the lining surface. Guniting offers speed in refractory placement and provides flexibility, not available in casting where forming is difficult and expensive. Excellent linings are achievable with the guniting technique, but qualified personnel and a thorough quality control plan are vital to achieving the desired results. Dry guniting will have 18−20 variables and each can adversely affect lining quality.

Guniting of refractory monolithics has a large number of variables that influence the quality of the installed lining. While these variables can affect lining quality, the nozzleman's expertise, air pressure, and feed rate have instant and recognizable effects. An experienced nozzleman is aware of the importance of good gunning practices and of the flaws or imperfections that are

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common with gunning of refractory castables. Anchor shadowing is very common and reduces the effectiveness of the anchor because the anchor is not in contact with solid refractory. Shadowing of anchors is also a good indicator of the nozzleman's experience. When shadowing occurs, several factors such as water content and air pressure are not optimized. Water content and air pressure are the two very important properties because they affect density, strength, and homogeneity of the final lining. Low air pressure will result in low density, and other physical properties, such as strength and erosion resistance, are adversely affected. Inadequate water content also affects density but, more importantly, affects homogeneity, which is likely the most important aspect of gunited lining. Poorly consolidated and layered (laminated) linings are prone to premature failure. Thermal cycling of layered lining causes early failure of refractory lining, decreasing reliability, and increasing maintenance costs.

Wet Gunning

Wet gunning is an application technique that has changed significantly within the past 10 years. In wet gunning, the refractory castable is mixed with water to produce a pumpable product. The mixture is pumped through hoses and pipes to the application area where air is added to propel the mixture onto the wall. In most cases, an activator such as potassium silicate is added to provide "body" to permit the mixture to stay on the wall.

Casting

Casting is the oldest technique of installing refractory castables. Prior to the introduction of specialty castables which require more comprehensive installation techniques, such as cast vibrating, self-leveling, guniting, and wet guniting, castables were simply mixed to a "ball in hand" consistency, placed into a form, and gently vibrated with an internal vibrator to facilitate consolidation.

Cast Vibrating

Cast vibrating became popular in the mid- to late 1980s and is the greatest development in castable placement during the past 20 years. This technique of installing refractory is much more complex than other installation methods and requires considerable expertise and coordination. Forming is critical to the procedure and must be designed to withstand the force from the hydrostatic head of the castable and force produced by the vibrators. In parts such as elbows, curved pipe, and Wye sections, buoyancy must be considered. The buoyancy of a 165 lb/ft^3 (2,640 kg/m^3) castable is sufficient to "warp" or "bend" poorly supported or reinforced forms.

The cast vibration process appears simple enough. Form, vibrate, pour, and then strip the forms. As simple as it appears, the procedure will likely cause more trouble and lost revenue than any other installation technique, due to the cost of removing a cast-vibrated lining and performing a repair.

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Ramming

Ramming of certain castables in thin linings is more difficult and requires considerable experience. Castables pack differently than plastics and require a better understanding of placement characteristics. Since castables "set," any repairs resulting from poor installation will be more costly, time consuming, and complicated. A repair to plastic refractory linings prior to the thermal cure is simple because the lining is soft, easy to remove, and does not damage adjacent materials.

Plastic Refractory

- Ramming
- Gunite
- Hand packing.

Ramming

Ramming of plastic refractories has been a primary installation technique in the steel industry for many years. Ramming of both plastic refractories and some castables has gained popularity for refinery applications in the past 10−15 years. The installation of 9−13-in. (225−325 mm) thick walls in steel mill applications is significantly different to ramming 1−2-in. (25−50 mm) thick linings typical for refining applications. Walls over 4 in. (100 mm) thick will generally be rammed perpendicular to the hot face. Plastic refractory linings, <4 in. (100 mm) thick and typically 1−2 in. thick, will be rammed from the hot face of the lining.

In refineries, plastic refractories are used in thin, 1−2-in. (25−50 mm) lining predominately. All of these linings will be rammed from the hot face and the emphasis will be the consolidation of the plastic. Trimming of the plastic refractory lining is also important and requires significant experience to ensure that the lining materials remain tightly against the anchoring system. Pulling away of the plastic from the anchor can cause excessive abrasion loss in some instances. Ramming of plastic refractories offers advantages over other 1−2-in. (25−50 mm) thick lining materials. Speed is improved, but the main advantage is the quality of work.

The ease of installation and the absence of field preparation are important reasons for selecting plastic refractories; however, they must also provide the desired performance. Phosphate-bonded plastic refractories develop excellent abrasion resistance and moderate strength when heated properly. Abrasion losses (ASTM C704) of <5 ml are generally required for plastic refractories placed in FCC unit applications. Strength of these types of products can range from 5,000 to 10,000 psi (351.5 to 492.1 kg/cm^2); however, acceptance criteria are lower.

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Gunite

Guniting plastic refractory is common in the metals industry but has not provided advantages for the petroleum industry. Plastic refractory is granulated and pneumatically placed at very high pressures. In some instances, this application technique improves the speed of application which lowers overall cost, but large volume applications are necessary to profit from this technique.

Hand Packing

Hand packing is generally not a good application technique due to poor consolidation potential.

Quality Control Program

A comprehensive quality control plan is vital to obtaining a quality, reliable refractory lining system. In some instances, contractors have inherently adopted an informal quality control plan; however, this produces marginal success. Contractors that have well-defined quality control plans will have a much better understanding of refractory quality and can adapt to unusual situations during the installation of refractory linings.

The components of a quality control plan include written procedures, provisions for qualifying the crew members and procedures, production sampling, preshipment qualifications, and frequent monitoring by contractor personnel to ensure that a quality effort is demonstrated. The contractor will also demonstrate an understanding of pertinent specifications and standards and generally accepted installation practices.

The API Task Group on Vessel Refractories developed a comprehensive quality control program for installation of monolithic refractories related to the refining industry. The original document was RP 936 (recommended practice) but has recently been revised and is now API 936, which is a standard. Companies that do not prepare refractory specifications related to refractory quality control are urged to consider using this document.

Written Procedure

Prior to starting installation of refractory linings, approval for written installation procedure(s) shall be obtained from the company. Required elements of a written procedure include:

- Equipment requirements and back-up contingencies
- Mixing and handling methods
- Details of application
- Curing and drying procedures
- Material testing requirements
- Quality control program.

A good written procedure does not ensure a quality refractory installation; however, it establishes a common understanding of quality requirements and provides a basis

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for discussion when inconsistencies are observed by the company's designated inspector.

The written procedure also provides the owner an opportunity to dispute any procedure that is not consistent with perceived accepted practices. The ability to discuss and resolve procedural differences prior to beginning the work limits confusion during the installation and reduces the potential for unacceptable work.

Compliance Physical Property Data

The development of compliance data for physical properties of each refractory considered for a project or turnaround is critical to receiving quality refractory products. Agreement on preshipment acceptance/rejection requirements shall be obtained from the material manufacturer prior to purchase of any material. Manufacturer's data sheets are generally vague and rarely will the manufacturer agree to the values in the data sheet for preshipment qualifications. Therefore, an agreement is necessary to establish minimum standards for refractory materials. It is customary to set the preshipment requirements at or near 75% of the published values. However, a history of testing with a material is also helpful in determining what is proper for a material. In some instances, the manufacturer's data sheet clearly misrepresents the physical properties typical for a product. In these cases, historical data is helpful in developing minimum requirements more representative of the product.

Compliance data and preshipment testing do not ensure a quality job, but it is the first step towards achieving the desired results.

Preshipment Qualification Testing

Preshipment testing is customary in qualifying materials for a project or turnaround. Products are tested at a predetermined frequency and test results must meet with preshipment compliance requirements. If a material fails to meet the minimum requirements, it is rejected unless a second test is warranted.

Mock-ups and Crew Qualification

The contractor is responsible for furnishing qualified personnel for each refractory application anticipated for a project. Each applicator is given the opportunity to demonstrate his/her skill in each particular application technique. Inspection is required during the qualification process and certain minimum standards are used to qualify or reject an individual.

Production Sampling

Sampling during the installation of refractory linings is called production sampling. The purpose is to produce representative sampling of the installed lining. Sampling frequency is

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important and must be identified prior to commencing work. Sampling frequency is usually defined in the refractory or job-specific specifications.

Testing of Production Sampling

Testing of each production sample can be expensive and is not necessary; however, a testing scheme (number of samples to be tested) should be developed prior to commencing the project or turnaround to optimize testing and cost.

Mixing Log Sheets

Mixing log sheets are a means to monitor the activity of the installation crew. Proper use of mixing log sheets will allow the inspector to follow the application of work without constantly overseeing the refractory mixing process.

Inspection

Inspection of refractory lining installations is very important in validating the quality of the lining. Inspection after a lining is installed has little value, except for obvious imperfections due to incompetent installers. Effective inspection of refractory includes witnessing all aspects of the work including tear out, surface preparation, anchor layout, anchor welding, and refractory installation. It is impossible to witness the entire process; therefore, the inspector should witness key aspects of each or develop holds for the installer (being careful not to lengthen the total process).

Dryout of Refractory Linings

The purpose of drying refractory before placing it into service is to provide a stable lining that is unaltered or unaffected by conditions of start-up or operation. Dried refractory linings are less likely to be affected by rapid heating through poor or uncontrolled start-up of equipment.

Drying of refractory castables is designed to remove mechanical and chemical water from the refractory lining in a controlled manner. Mechanical water is defined as the water that is used to facilitate placement. Chemical water is defined as the water that combines chemically with the cement binder (hydration) to provide the desired physical properties of the product. Removal of water from the refractory occurs at different stages of temperatures in the drying procedure. Dehydration of the cement typically occurs between 400°F (204°C) and 1,200°F (650°C) and includes phase changes in the hydrated cement.

Removal of both types of water must be accomplished in a controlled manner. Excessive heating rates will cause development of steam in the refractory that may not dissipate through the refractory mass in a controlled manner. The result is explosive spalling, where steam pressure inside the refractory mass causes the material to rupture.

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Initial Heating of Refractory Linings

Refractory products such as castables containing cementitious binders require controlled drying. Uncontrolled or rapid drying can cause explosive spalling of the refractory and ultimately interruption in its service.

The objective of a dryout is to condition the refractory lining in a controlled manner and provide stability that is unavailable when water is present. Controlled drying provides the manageable release of moisture from the system and stabilizes the refractory. The ultimate goal is to thoroughly dry the refractory lining in a cost-effective manner.

Manufacturers of refractory castables issue general guidelines for drying castables that are typically very conservative. Drying of refractory castables is greatly influenced by the type and configuration of equipment containing the refractory. Straight pipe, such as ducting, risers, and standpipes, does not require the same considerations as elbows, strippers, and cyclones, which have hidden or shielded areas. The principles of drying the refractory remain the same for all lining; however, details of the dryout such as burner location, mass of drying medium, hold periods, and thermocouple placement require special considerations. Properly engineered refractory systems have these details identified.

Most specifications address initial heating of unfired refractory castables. The heating schedules are generally for shop-installed refractory linings dried in the shop, but are good guidelines for all dryouts because the principles apply to shop and field applications.

Always dry with air or other gaseous medium. *Never* allow a flame to contact unfired refractory. The heat flux associated with a flame is too great from unfired refractory and will generally always lead to explosive spalling.

Dryouts should be designed for each project or refractory application. It is highly recommended that qualified persons review the dryout plans and procedures prior to commencing a dryout activity.

Dryout of Refractory Linings During Start-up of Equipment

Drying of refractory lining upon start-up of equipment requires the same considerations as shop-dried linings. The difference in start-up is that limitations in the equipment will affect the dryout process. Therefore, adjustments in start-up are necessary to ensure that the refractory lining is not damaged during the start-up procedure.

In most cases, the equipment start-up procedure is sufficiently slow that very little change in start-up is necessary. However, when start-up procedures utilize fast heating rates, an adjustment is necessary to limit the potential for explosive spalling.

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A normal start-up heating curve should be developed that takes into consideration the normal start-up procedures. A process reactor is lined with 6 in. (150 mm) refractory, which is a moderate density/moderate erosion product that requires a slow heating rate. Normal start-up has a rapid heating rate from 250°F (121°C) to 550°F (288°C), which is a temperature range where explosive spalling is prevalent. The procedure would be altered by reducing the initial heating rate by a factor of two or doubling the time to achieve 550°F (288°C).

The most effective means of starting equipment containing significant amounts of unfired castable refractory is to adjust the normal start-up procedure. Manufacturers, consultants, and contractors will provide some guidance, but their advice is one-dimensional. They are usually not aware of the details of the process and have little to gain by offering less conservative schedules than that published. If one chooses to use the manufacturer's recommended schedule, significant changes in the process can be expected along with a substantial increase in overall start-up time.

Subsequent Heating of Refractory Lining Systems

Heating rates for previously fired refractory systems are governed primarily by the desire to maintain a reliable refractory lining system. Rapid heating and cooling causes undue stress in the refractory lining and the result is microcracking that will lead to mechanical spalling, loss of lining thickness, and an unreliable lining. Heating rates of 100°F (56°C) per hour are commonly recommended for all previously fired refractory linings, such as castables, plastic, and brick. Increased firing rates are not likely to cause immediate damage to a refractory lining, but it will reduce the service life of the refractory. Frequent occasions of rapid heating or cooling will reduce the life of a refractory castable, but occasional departure from the recommended rate is not likely to have a significant effect. Heating rates up to 200°F (111°C) per hour are acceptable because the effects are long-term.

Increased heating and cooling rates are sometimes justified by the potential gains available through increased availability of equipment. Therefore, it is important to realize that when process gains are available, increased rates are acceptable. The long-range consequences normally are significantly less than the process penalties inherent in slow start-ups. These situations should be reviewed carefully to ensure that apparent gains are greater than the risk.

Examples of Refractory Systems in FCC Units

Just about any equipment in the FCC reactor—regenerator circuits must employ refractory lining to protect against premature erosion, heat loss, and corrosion attack. These components include:

- Reactor and regenerator vessels
- Catalyst stripper vessel

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- Regenerated and spent catalyst standpipes
- Regenerated and spent catalyst slide or plug valves
- Wye or J-bend sections
- Riser and riser termination device
- Air and spent catalyst distribution systems
- Stripping steam and other steam distributors
- Reactor and regenerator cyclones
- Flue gas piping and pressure-control slide valves
- Orifice chamber
- Tertiary catalyst separation system
- Reactor vapor line.

The above components (except for the regenerator vessel) can be designed cold wall and/or hot wall. Cold-wall design often uses 4- or 5-in. (100/125 mm) thick internal refractory lining using carbon steel as the base material. Hot-wall design often employs 3/4- or 1-in. (20 or 25 mm) thick internal/external refractory lining to protect against excessive erosion of moving catalyst.

Table 10.1 shows the typical refractory type for the various equipment in the FCC unit.

Table 10.1: Example of FCC Unit Refractory Types for Equipment.

Location	Thickness (in.)	SS Fibers	Acceptable Types	Installation Method	Anchor Type
Regenerator shell/flue gas lines	4–5	Yes	Medium-weight insulating castable	Gunning	Wavy Vee
Reactor shell	As required	Yes	Medium-weight insulating castable	Gunning	Wavy Vee
Catalyst transfer lines	4	Yes	Moderate density/ moderate erosion	Cast vibrating or gunning	Wavy Vee
Hot-wall catalyst transfer lines	2	Yes	Extreme erosion-resistant refractory	Pneumatic ramming	2-in. hex cells
Cyclones/hot-wall risers/other thin-layer erosion-resistant lining	1	No	Extreme erosion-resistant refractory	Pneumatic ramming	1-in. full-depth hex metal
Air distributor	1	Yes	Extreme erosion-resistant refractory	Pneumatic ramming	Ring tabs
Flue gas lines	4–5	Yes	Density/moderate erosion castable	Cast vibrating	Wavy Vee
Riser/cold-wall and spent cat riser	5	Yes	Severe erosion-resistant castable	Cast vibrating	Wavy Vee
Refractory choke	NA	No	Crushed firebrick/ aggregate with jumbo firebrick cap layer	Placing	NA

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Summary

Refractory lining plays a critical role in the operational and mechanical reliability of a cat cracker. Understanding what goes into the design and application of various refractory systems will go a long way in achieving the expected benefits.

Acknowledgment

The bulk of material for this chapter was provided by Mr. Doug Hogue of Hogue Refractory Consulting Inc. (Tyler, TX) and I am grateful for his contribution. Once again, I would like to thank Doug Hogue for making this chapter possible.

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CHAPTER 11

Process and Mechanical Design Guidelines for FCC Equipment

Many aspects of past FCC developments have been the result of "trial and error." The present-day design standards are as much an art as they are science. Consequently, it is appropriate to review a few of the key developments over the past half-century that have influenced the current design philosophy of the FCC reactor–regenerator systems.

FCC Catalyst Quality

The early FCC catalysts were neither very active nor very selective; the product yield structure contained too much coke at the expense of gasoline and other valuable products. Regenerators operated in a partial combustion mode at a temperature range of around 1,100°F (590°C). The introduction of zeolite into FCC catalysts in the late 1960s brought about a significant improvement to the FCC process. The zeolite-based catalysts allowed major yield shifts toward a lighter liquids production.

Higher Temperature Operation

With the advances in catalyst technology, the need to process heavier feedstocks and the need to maximize the yield of desired products have resulted in operating the regenerator and reactor at higher temperatures. These higher operating temperatures have had deleterious effects on the mechanical components of the reactor/regenerator. The drawbacks of a higher temperature operation include greater concerns with thermal expansion of components, coupled with lower yield stresses of the steels, resulting in a lower load-carrying capacity of the steel.

Refractory Quality

Refractory lining systems were first developed primarily for use in the iron and steel industries. It was not until the refractory manufacturers began developing products

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specifically designed for FCC applications that the tremendous improvements in erosion and insulating properties were realized.

More Competitive Refining Industry

The run length of the early FCC units was very short; typically the unit was shut down every year or so for maintenance. The general approach in those early years was to make the necessary repairs and replace the damaged internal components. As the industry became more competitive, the focus became to increase the unit's run length, improving reliability, and maximizing the quantity and quality of desired products.

The evolution and improvements of the above-mentioned topics set the background for providing FCC design parameters. The following discussion presents the latest commercially proven processes and mechanical design recommendations for the FCC reactor–regenerator system components.

The presented design guidelines, though not universally agreed upon by every FCC "expert," can be useful to the refiner in ensuring that a mechanical upgrade of the FCC unit will be safe, reliable, and profitable.

The major components of the reactor–regenerator circuit in which process and mechanical design recommendations are provided are as follows:

- Feed injection system
- Riser and riser termination
- Spent catalyst stripper
- Standpipe system
- Air and spent catalyst distributors
- Reactor and regenerator cyclones
- Expansion joints
- Refractory.

Feed Injection System

Any mechanical revamp to improve the cat cracker's performance should always begin with installing an efficient feed injection and regenerated catalyst system. This is the single most important component of the FCC unit. An efficient feed injection and regenerated catalyst system reduces the slurry oil and dry gas production, while maximizing the total liquids production. A properly designed feed injection and regenerated catalyst system will also improve the unit's operational reliability by minimizing coke formation within the riser, reactor housing, reactor overhead vapor line, and main fractionator circuits.

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A properly designed feed injection and regenerated catalyst system should achieve the following objectives:

- Distribution of the feed throughout the cross section of the catalyst riser stream ensuring that all feed components are subjected to the same cracking severity
- Instantaneous and uniform atomization of the feed
- Minimization of "spent catalyst" recontacting with the fresh feed
- Injector nozzle production of properly sized oil droplets to penetrate into the catalyst stream through the cross-sectional area of the riser
- Minimization of erosion of the riser wall and attrition of the catalyst
- Size components to perform without plugging or causing erosion.

Process Design Considerations for Feed Nozzles

Table 11.1 shows the key process and mechanical design criteria used to specify high-efficiency feed injection nozzles. The mechanical design of any feed nozzle should be sufficiently robust and easily maintained (Figure 11.1). Its long-term mechanical reliability is critical in achieving the expected benefits of the upgrade. The following are a few of the mechanical problems which are often encountered:

- Erosion of the feed nozzle tip(s)
- Refractory erosion in the Wye section and the riser wall
- Blockage of the feed nozzles.

Table 11.1: Process and Mechanical Design Criteria for FCC Feed Nozzles.

Injectors	Multinozzles, <8,000 bpd per nozzle, located at the periphery of the riser and projected upward
Oil-side pressure drop	50–70 psi (3.5–4.9 kg/cm^2) at the design feed rate
Nozzle exit velocity	150–300 ft/sec (45–100 m/sec)
Dispersion media and rate	Steam, 1–3 wt% of feed rate for conventional gas oil; 4–7 wt% for residue feedstocks
Orientation and location	Radial; 4–5 riser diameters above the Wye work point
Feed nozzle type	Readily retractable
Insert material	304H stainless steel
Nozzle tip	Solid satellite or diffusion coating

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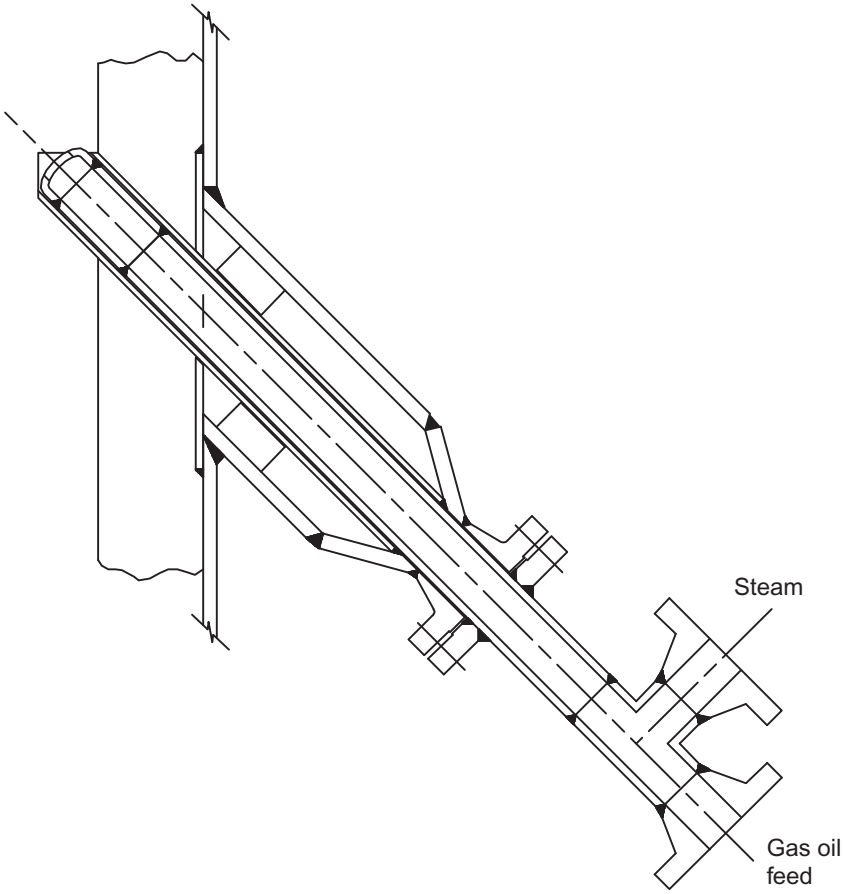


Figure 11.1: Typical feed nozzle installation.

Catalyst Lift Zone Design Considerations

In order to maximize the benefits of feed nozzles, the regenerated catalyst stream must be distributed evenly throughout the cross section of the riser. To achieve this, preacceleration of the catalyst to the feed zone is required. Steam or fuel gas is often used to lift the catalyst to the feed injection. In most designs that incorporate a "Wye" section for delivering the catalyst to the feed nozzles, a lift gas distributor is used, providing sufficient gas for delivery of "dense" catalyst to the feed nozzles. In other designs, the lift gas rate is several magnitudes greater with the intent of contacting the gas oil feed into a more "dilute" catalyst stream. In FCC units that use a "J-bend" (Figure 11.2A), steam is employed in lateral and vertical streams to ensure uniform contact of catalyst particles with the atomized gas oil feedstock. Figure 11.2B shows a schematic of a typical "Wye" section catalyst lift system.

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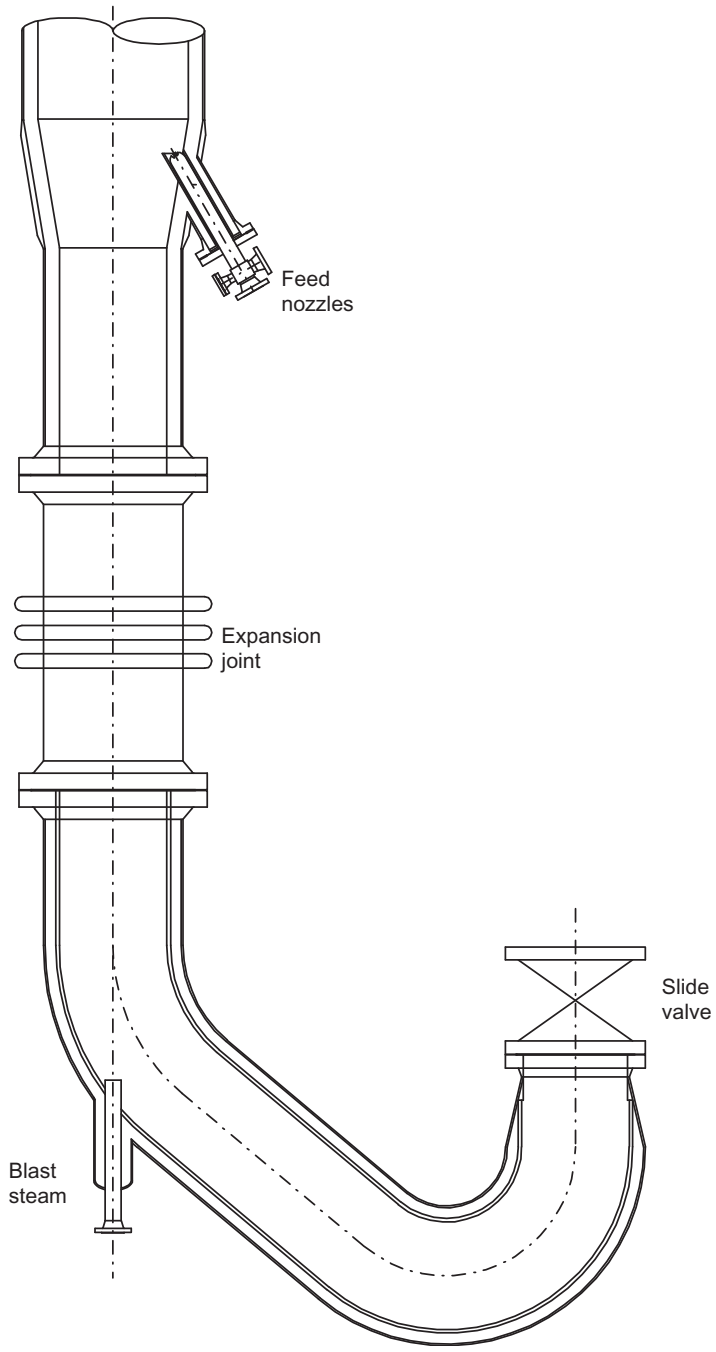


Figure 11.2A: Typical J-bend configuration.

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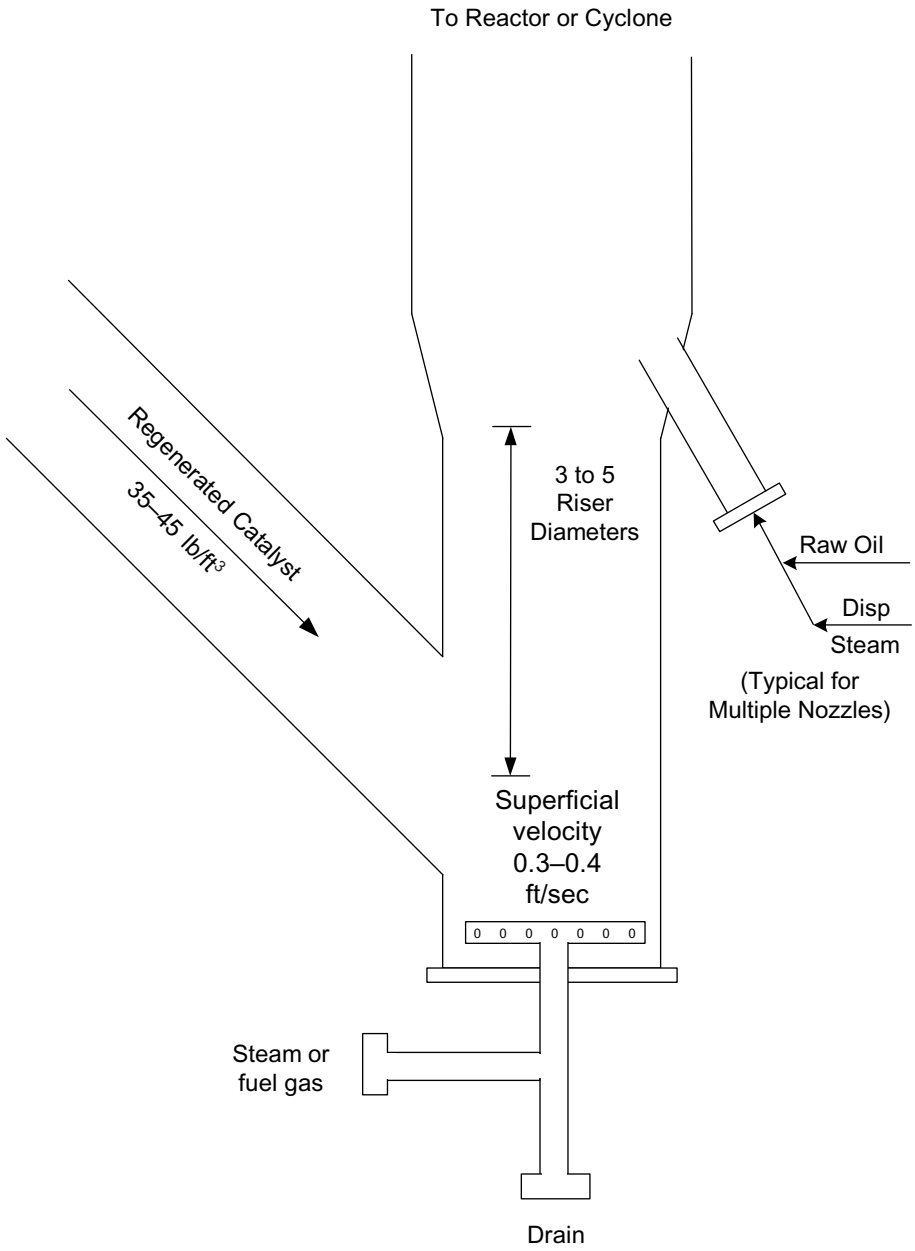


Figure 11.2B: Example of a typical "Wye" section catalyst lift system.

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Riser and Riser Termination

In most of today's FCC operations, the desired reactions take place within the riser. A number of refiners, in recent years, have modified their FCC units to eliminate, or severely reduce, postriser undesirable cracking and noncracking reactions. The quick separation of catalyst from the hydrocarbon vapors at the end of the riser is extremely important in increasing the yield of the desired products. The postriser reactions produce more dry gas and coke gasoline and distillate. Presently, there are several commercially proven riser disengaging systems offered by the FCC licensors that are designed to minimize postriser cracking of the hydrocarbon vapors.

Table 11.2 shows the process and mechanical design guidelines that can be used in designing a new riser.

Table 11.2: Process and Mechanical Design Guidelines for FCC Risers.

Hydrocarbon residence time	2–3 seconds based on the riser outlet conditions. Depending on the degree of catalyst back-mixing in the riser, the catalyst residence time is usually 1.5–2.5 times longer than the hydrocarbons
Vapor velocity	20 ft/sec (6 m/sec) minimum (without oil feed), 45–55 ft/sec (14–17 m/sec) at the design feed rate
Geometry	Vertical: to simulate plug flow and to minimize catalyst back-mixing
Termination	Riser-cyclone separator/device attached to another separation device to minimize recracking of hydrocarbon vapors and greater catalyst separation
Configuration	External or internal
Material	Carbon steel, "cold wall" as opposed to "hot wall" with 4–5 in. thick (10–12.5 cm) refractory lining

Spent Catalyst Stripper

A properly designed catalyst stripper minimizes the quantities of entrained and adsorbed hydrocarbons that are carried over to the regenerator. This reduction in carryover should be accomplished by the use of stripping steam. The major drawbacks for allowing the hydrogen-rich hydrocarbons into the regenerator are loss of liquid products and throughput, and reduction of catalyst activity.

The stripper performance is greatly influenced through proper design practices, but it is also very important to note that it is greatly influenced by the quality of feedstock, catalyst properties, and operating conditions. The key process parameters for designing the stripper are listed in Table 11.3 (also see Figure 11.3).

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Table 11.3: Reactor–Stripper Process and Mechanical Design Criteria.

Catalyst flux	600–900 lb/min/ft^2 (49–73 kg/sec/m^2)
Stripping steam rate	2–5 lb/1,000 lb of circulating catalyst
Stripping steam superficial velocity	0.5–0.75 ft/sec (0.15–0.25 m/sec)
Catalyst residence time	1–2 min
Steam quality	Dry steam
Steam distributor(s)	
Number of stages	One
Type	Pipe grid or concentric rings
Number of nozzles	Minimum of one nozzle per ft^2 of cross-sectional area of the stripper
Nozzles	
Orientation	Pointing downward
Exit velocity	100–150 ft/s (30–46 m/sec)
Pressure drop	Minimum of 2 psi (0.14 kg/cm^2) or 30% of the bed height
L/D	Minimum of 5, or long enough to expand "vena contracta"
Material of construction	
Stripper shell	Carbon steel, "cold wall" with 4 in. (10 cm) medium weight refractory lining
Distributors	Carbon steel, distributor externally lined with 1-in. (2.5 cm) thick erosion-resistant refractory
Baffles	Carbon steel or low chrome alloy
Nozzles	Carbon steel, schedule 160 minimum

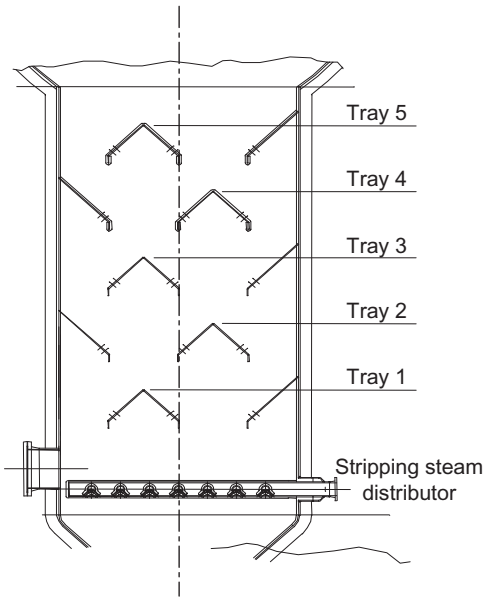


Figure 11.3: Schematic of a stripping steam distributor.

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Catalyst Flux

Catalyst flux is defined as catalyst circulation rate divided by the "full" cross-sectional area of the stripper. For efficient stripping, it is desirable to minimize the catalyst flux to reduce the carryover of hydrogen-rich hydrocarbons into the regenerator.

The stripping steam efficiency is proportionate to the stripping steam rate up to a certain point. Excess stripping steam overloads the reactor cyclones, main column, and the sour water treating system. Therefore, the stripping steam rate should be varied to determine the optimal feed rate. The optimal stripping steam rate usually corresponds to a value in which there would be no reduction in the regenerator bed and/or dilute-phase temperature.

The catalyst residence time in the stripper is determined by catalyst circulation rate and the amount of catalyst within the stripper. This amount usually corresponds to the quantity of the catalyst from the centerline of a "normal" bed level to the centerline of the lower stripping steam distributor. Increasing the catalyst residence time could improve the hydrocarbon stripping efficiency; however, it also increases the hydrothermal deactivation of the catalyst. In some cases, reducing the catalyst level can also enhance the hydrocarbon stripping efficiency.

It is important to note that, depending on the stripper operating pressure and temperature, a certain fraction of stripping steam is carried with the spent catalyst into the regenerator. Example 11.1 shows how to determine this amount.

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Example 11.1

Calculate the amount of entrained stripping steam into the regenerator from a reactor–stripper

Use the following conditions:

Catalyst skeletal density	=	150 lb/ft^3 (2,400 kg/m^3)
Catalyst flowing density	=	35 lb/ft^3 (560 kg/m^3)
Stripper operating pressure	=	25 psig (173 kPa)
Stripper operating temperature	=	980°F (525°C)
Catalyst circulation rate	=	40 short tons/min
	=	4,800,000 lb/h (2,200 mt/h)

Solution:

Volume of entrained steam = 1/35−1/150 = 0.0219 ft^3 of steam/lb of circulating catalyst (0.0014 m^3/kg)

$$\rho = \frac{M}{10.73} \times \frac{P + 14.7}{t + 460}$$

where:

ρ = gas or vapor density (lb/ft^3);
M = molecular weight;
P = pressure (pounds per square inch gauge);
t = temperature (°F).

$$\text{Steam density} = \frac{18}{10.73} \times \frac{25 + 14.7}{980 + 460} = 0.0462 \text{ lb of steam/ft}^3 \text{ of steam } (0.74 \text{ kg/m}^3)$$

Entrained steam

$$= (0.0219 \text{ ft}^3 \text{ of steam/lb of catalyst}) \times (0.0462 \text{ lb of steam/ft}^3 \text{ of steam}) \times 4,800,000 \text{ lb/h}$$
$$= 4,858 \text{ lb/h } (2,204 \text{ kg/h})$$

Standpipe System

The regenerated catalyst standpipe and reactor catalyst standpipe comprise the two standpipe systems used in FCC operations. The design of each standpipe is one of the most important factors in obtaining good catalyst circulation. The standpipe creates the necessary head pressure required to circulate the catalyst to the risers. The standpipe assembly is typically composed of three major components: the hopper, the standpipe, and a slide valve or a plug valve. The function and design for each component is described below.

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Hopper Design

A regenerated catalyst hopper (Figure 11.4) provides sufficient time for the initial deaeration of regenerated catalyst to flow into the standpipe. Proper catalyst deaeration should maximize the regenerated catalyst density while maintaining the catalyst in a "fluidized" state. Table 11.4 shows the key process parameters used in designing standpipe hoppers.

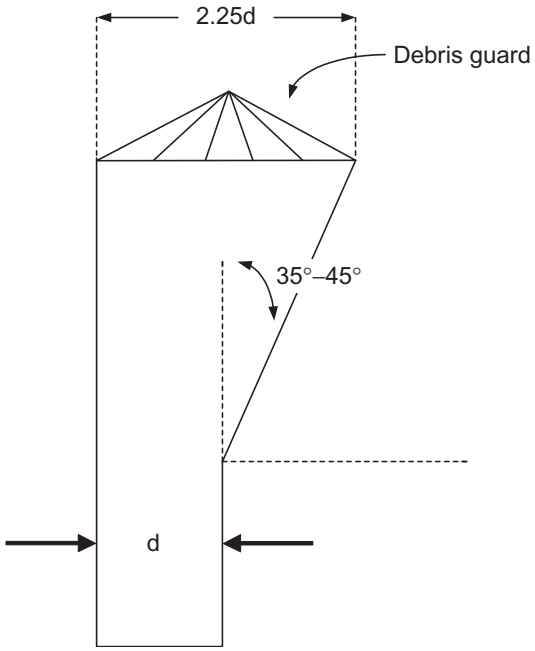


Figure 11.4: Schematic of a typical catalyst hopper.

Table 11.4: Process Design Considerations for Standpipe Hoppers.

Hopper entrance diameter	2.25 times the standpipe diameter
Angle of cone	35°–45° off the vertical
Desired regenerated catalyst density	40–45 lb/ft^3 (640–720 kg/m^3)
Catalyst velocity	0.5–1.0 ft/s (0.15–0.3 m/s)

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Standpipe

The standpipe provides the necessary head pressure required to achieve proper catalyst circulation. Standpipes are sized to operate in the fluidized region for a wide variation in catalyst flow rates. The maximum catalyst circulation rates are realized at higher head pressures. The higher head pressures can only be achieved when the catalyst is fluidized properly. Table 11.5 shows typical process and mechanical design criteria for the standpipe.

Slide Valve or Plug Valve

The slide valve or plug valve regulates the flow of catalyst between the regenerator and reactor. The slide valve or plug valve also provides a positive seal against a flow reversal of the hydrocarbons into the regenerator or hot flue gas into the reactor. Table 11.6 summarizes typical process and mechanical parameters for designing a slide valve.

Table 11.5: Process and Mechanical Design Criteria for Catalyst Standpipes.

Catalyst flux	150–300 lb/s/ft^2 (725–1,450 kg/s/m^2)
Catalyst velocity	2–6 ft/s (0.6–2 m/s), target for 4 ft/s (1.3 m/s)
Desired density	40–45 lb/ft^3 (650–800 kg/m^3)
Geometry	Vertical or sloped at maximum angle of 45° (off vertical)
Material	Carbon steel, "cold wall" with 5-in. (12 cm) thick heavy-weight, erosion-resistant refractory lining
Supplemental aeration	Every 5–8 ft (1.5–2.5 m) along the standpipe, use flow meters or rotameters to regulate aeration flow

Table 11.6: Process and Mechanical Design Guidelines for Slide Valves.

Operating pressure drop	Minimum 1.5 psi (10 kPa), maximum 10 psi (70 kPa)
% opening at design circulation	40–60%
Material	Shell: carbon steel with 4 to 5 in. (10–12 cm) thick heavy-weight, single-layer, cast-vibrated refractory with needles Internals: 304H stainless steel for temperature >1,200°F (650°C) and Grade H, 1½% chrome for <1,200°F Internal components exposed to catalyst should be refractory-lined for erosion resistance Sliding surfaces should be hard-faced, minimum thickness 1/8 in. (3 mm)
Bonnet design	Sloped bonnet (30° minimum) for self-draining of catalyst
Purge	Purgeless design of stuffing box. Guides: slotted, hard-surfaced, and supplied with purge connections (normally closed). Nitrogen is the preferred choice of purge gas
Actuator type	Electrohydraulic for fast response and accurate control
Actuator response time	A maximum of 3 s

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The formula to calculate the catalyst circulation rate through a slide valve is illustrated in Example 11.2.

Example 11.2

Illustrate the use of this equation:

$$W = A_p \times C_d \times 2{,}400 \times \sqrt{\Delta P \times \rho}$$

Determine the catalyst circulation rate from the following information:

Slide valve ΔP	=	5 psi (35 kPa)
Slide valve opening	=	40% corresponding to a port opening of 200 in.^{2} (1,290 cm^2)
Catalyst density	=	35 lb/ft^3 (560 kg/m^3)

Therefore:

$$W = 200 \times 0.85 \times 2{,}400 \times \sqrt{5 \times 35} = 5{,}397{,}333 \text{ lb/h } (2{,}444{,}992 \text{ kg/h})$$
$$= 45 \text{ short tons/min } (41 \text{ mt/min})$$

where:

W = catalyst circulation rate, lb/h (kg/h);
A_p = port or orifice opening, in.^{2} (m^2);
C_d = discharge coefficient = 0.85;
ΔP = valve pressure drop, psi (kPa);
ρ = density of catalyst in the standpipe, lb/ft^3 (kg/m^3).

Air and Spent Catalyst Distributor

The primary purpose of the regenerator is to produce a cleaned catalyst, while minimizing afterburn and NO_x formation, and reducing localized sintering of the catalyst. For efficient catalyst regeneration, it is very important that the air and the spent catalyst are evenly distributed. Although, in recent years, the design of air distributors has improved significantly, the same cannot be said for spent catalyst distributors. This is particularly true in the case of side-by-side FCC units. Most side-by-side units suffer from an uneven distribution of the spent catalyst.

A well-designed air distribution system has the following characteristics:

- Uniformly distributes the air across the regenerator cross section
- Mechanically designed to handle the wide range of operating conditions, including start-up, shutdown, normal operation, and upset conditions
- Provides reliability with minimal required maintenance.

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In several early designed FCC units, the spent catalyst from the catalyst stripper is carried into the regenerator using all the available air from the air blower(s). In virtually all the FCC units, combustion air is distributed across the regenerator through dedicated air distributors.

Flat pipe grid, *plate grid*, *dome*, *and ring* are the four dominant configurations of air distributors presently being used. The most common types are flat pipe grid and ring distributors. Overall, the pipe grid is preferred over an air ring design, primarily due to a more uniform coverage and a lower discharge velocity, which tends to minimize catalyst attrition. Additionally, the pipe grid maintains the same coverage of the regenerator cross-sectional area regardless of the air rate. Air rings obtain their coverage through jet penetration, and the coverage will be reduced at air rates less than design value due to lower velocity.

The three primary factors affecting the mechanical performance of the air distribution system are erosion, thermal expansion, and mechanical integrity of the supports. The distributor's design should reflect the erosive nature of high catalyst/air velocities, thermal expansion for the various operating conditions, and corresponding considerations of the supports to minimize thermal expansion loads. The process and mechanical design considerations of an air distributor are shown in Table 11.7 (see also Example 11.3 and Figure 11.5).

Table 11.7: Process and Mechanical Design Criteria for Air Distributors.

Recommended Type	Pipe Grid Distributor
Nozzle exit velocity	100–150 ft/s (30–45 m/s)
Pressure drop	1.5–2.0 psi (10–15 kPa) at design air rate; 10–30% of the bed static head at minimum air rate for downward-pointing nozzles
Material	304H stainless steel, externally lined with 1-in. (2.5 cm) thick erosion-resistant refractory
Branch pipe	*L*/*D* ratio of <10 to minimize the support requirement and vibration
Branch arm connection	Continuous pipe through the main header and slotted opening
Fittings	Forged fittings instead of miters for supporting the headers; the forged fittings minimize failures due to stress cracking
Nozzles	
Type and orientation	Dual diameter nozzles with orifice in the back of nozzle; downward at 45°
Length	Minimum of 4 in. (10 cm)
L/*D*	5/1 to 6/1
Location of first nozzles	8–12 in. (20–30 cm) from the edge of the slot in the branch arm

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Example 11.3

The pressure drop of the nozzle's orifice can be calculated from the equation:

$$\Delta P = \frac{\rho_o}{2 \times g_c \times 144} \times \left(\frac{V_o}{C_d}\right)^2$$

where:

V_o = velocity of air through the orifice (ft/s);
ρ_o = density of air (lb/ft^3);
g_c = gravitational constant (32.2 ft/s^2);
C_d = discharge coefficient = 0.85.

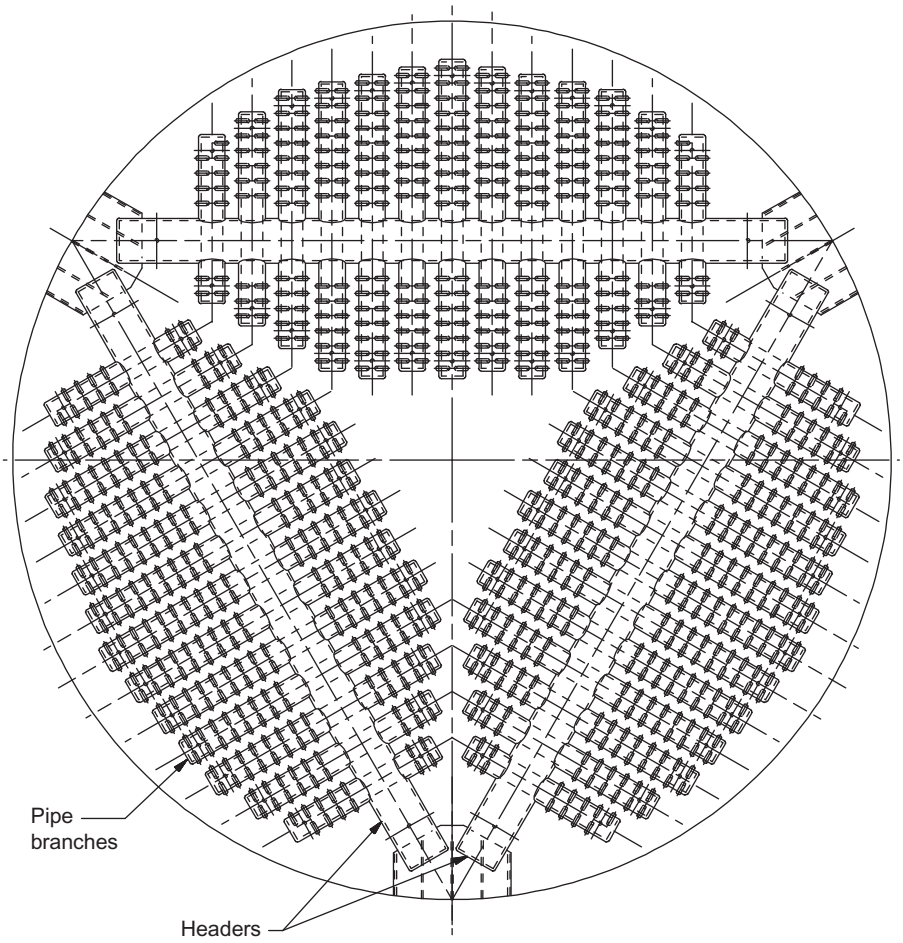


Figure 11.5: Typical layout of a pipe grid distributor. (*Courtesy of RMS Engineering, Inc.*)

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Reactor and Regenerator Cyclone Separators

A cyclone separator is an economical device for removing particulate solids from a fluid system. The induced centrifugal force (Figure 11.6) is tangentially imparted on the wall of the cyclone cylinder. This force, with the density difference between the fluid and solid, increases the relative settling velocity.

Cyclone separators are extremely important toward the successful operation of the cat cracker. Their performance impacts several FCC performance factors, including the additional cost of fresh catalyst makeup, extra turnaround maintenance costs, the allowable limits on emission of particulates, and the incremental energy recovery in the WGC, and hot gas expander.

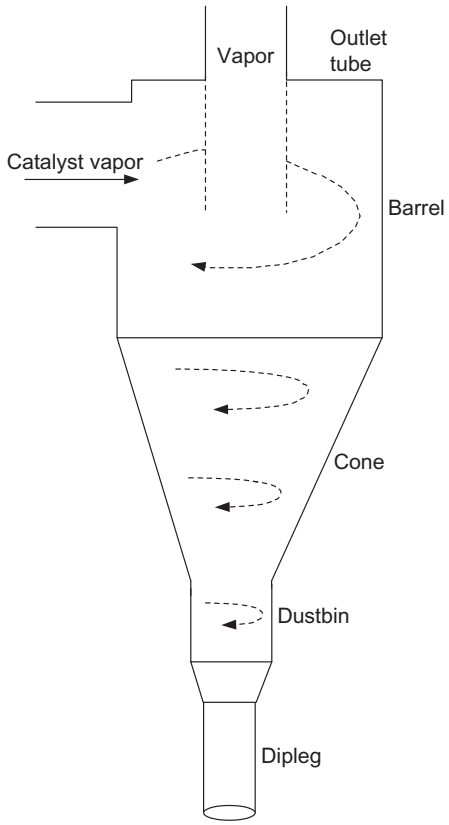


Figure 11.6: Schematic of a typical cyclone.

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Designing an "optimum" set of cyclones requires a balance between the desired collection efficiency, pressure drop, space limitations, and installation cost. The cyclone process and mechanical design recommendations are shown in Table 11.8.

Table 11.8: Process and Mechanical Design Guidelines for Reactor and Regenerator Cyclones.

Vapor Velocities at Design Feed Rate			
Cyclone Type		**Inlet ft/s (m/s)**	**Outlet ft/s (m/s)**
Reactor, single stage		60–65 (18–20)	100–110 (30–33)
Reactor or regenerator, primary or first stage		60–65 (18–20)	65–75 (20–23)
Reactor, secondary or second stage		65–70 (20–21)	100–110 (30–33)
Regenerator, secondary or second stage		65–70 (20–21)	90–120 (27–37)
Minimum cyclone velocity		25–35 (8–10)	
Dimensional Specifications			
Parameters	**Single Stage**	**Primary**	**Secondary**
L/*D*	5.0	3.5–4.5	4.5–5.5
Aspect ratio	2.3–2.5	2.3–2.5	2.3–2.5
Material			
Reactor cyclones	Carbon steel, chrome–moly alloy lined with 1-in. thick erosion-resistant refractory		
Regenerator cyclones	304H stainless steel, lined with 1-in. thick erosion-resistant refractory		
Regenerator plenum	Carbon steel, "cold wall" design to avoid high-temperature stress cracking		

Minimum overall collection efficiency = 99.9985%.
Rough cut or regenerator first-stage dipleg mass flux = 100–125 lb/ft^2/s (500–600 kg/m^2/s).
Penetration of the gas outlet tube into each cyclone should be at least 80% of the cyclone inlet duct height.
The projected vortex (see Figure 11.6) should be a minimum of 15 in. (40 cm) above the dust-bowl outlet.

Expansion Joint

Efforts should be made to eliminate the use of expansion joints in process piping; however, if needed, the expansion joints are used to mitigate the pipe stresses caused by large thermal movements. Table 11.9 lists the recommended mechanical design criteria for expansion joints.

Table 11.9: Mechanical Design Recommendation for Expansion Joints.

Shell's material	Carbon steel, "cold shell design," cast-vibrated 5-in. (12 cm) thick refractory lining
Bellow's material	Inconel 625
Purge requirement	Packed bellows, no purge
Configuration of bellows	Two-ply bellows with pop-out indicator for detecting leakage; each bellows should be capable of maintaining the full pressure
Packing material	Ceramic fiber blanket
Minimum bellows temperature	400°F (205°C) to minimize condensation and subsequent acid attack

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Summary

The process and mechanical design guidelines presented in this chapter can be used to ensure the equipment is designed correctly, in that it achieves process design objectives and maximum long-term reliability. In addition, these design criteria provide the process engineers with tools to optimize the performance of the cat cracker.

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CHAPTER 12

Troubleshooting

The cat cracker must operate reliably and efficiently. It must also operate safely and comply with federal, state, and local environmental requirements. A typical FCC unit circulates tons of catalyst per minute, processes various types of feedstock, and uses hundreds of control loops, any of which can make operation difficult. Proper troubleshooting will ensure that the unit operates at maximum reliability and efficiency, while complying with environmental concerns.

Troubleshooting deals with identifying and solving problems. Problems can be immediate or long term. They can be off-spec products, poor efficiency, equipment malfunction, or environmental excursion. Problems can be related to startup issues, instrumentation, loss of utilities, equipment wear, changes in the operating conditions, and operator errors.

This chapter outlines fundamental steps toward effective troubleshooting. It provides a practical and systematic approach to develop a solution. General guidelines are provided for identifying problems and determining a diagnosis. It is written with the unit process engineer in mind. No matter where the problem originates, he/she will be the point person for solving it.

Before beginning to troubleshoot, one must understand the unit's "normal" operating mode and be able to list several leading indicators to confirm the operating baseline of the unit. For example, what supporting evidences are there that the operation of the FCC unit is:

- Safe
- Clean (environmentally and meeting product specifications)
- Stable
- Operating within its maximum or minimum limits.

Once an abnormal situation occurs, effective troubleshooting starts by addressing the following questions:

- What is the "leading indicator" of an issue?
- What are some of the evidences that confirm this "abnormal issue"?
- What resources (e.g. DCS data/trends, lab data analyses, and outside operator's observance) are available to troubleshoot the abnormal situation?

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- What could be causing the problem (rank by importance, with 1 being most important)?
- Where or what would one look at to diagnose the problem?
- What corrective actions would one take to resolve this issue?
- Are there proactive actions that can be taken to prevent occurrences of this problem in the future?
- What would have been possible consequences of no or delayed response to the symptom/problem?

Long-term solutions can include improved operating procedures, scheduled training, preventative maintenance, and installation of new equipment or controls.

Several General Guidelines for Effective Troubleshooting

A successful troubleshooting assignment will require someone to:

- Be a good listener
- Know the "normal" operating parameters
- Gather historical background
- Evaluate "common" and "uncommon" causes of problems
- Examine goals and constraints to verify the applicability of the present operation.

Management, engineering, and operations departments perceive problems differently. Frequently, there is someone familiar with the operation that most likely knows the symptoms, and possibly can offer a solution to the problem, but for various reasons, people who are in a position to implement the solution may not have thought to ask that person. Typically, those closest to the problem are the unit operators and maintenance foremen, and they will offer the most valuable input. All four operating shifts need to be consulted. Do not draw any conclusions before gathering all applicable facts.

Examine similar problems that have occurred previously in the system to determine how they were diagnosed and solved. Review the operating and maintenance records. Compare the performance of the normally operating unit to the current problematic operation. Make sure that all the unit trends are current, including catalyst data, and the heat and weight balance data. Note any changes that might relate to the problem. Reliable historical data always helps to identify and diagnose problems.

Begin by listing all potential causes or combinations of causes, using a "brainstorming" approach. Then, systematically rule out each cause. Do not eliminate uncommon causes too quickly; if it were an easy problem someone would have already taken care of it. Additionally, ensure that the limits outlined by process and equipment documentation are consistent with the actual operation of the unit.

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Most FCC problems are due to changes in the feedstock, catalyst, operating variables, and/or mechanical equipment. As stated previously, the solution can take the form of improving yields, avoiding shutdowns or increasing unit reliability.

The majority of my troubleshooting assignments have been related to catalyst circulation issues, excessive catalyst loss, above average afterburning, premature coking, high CO/NO_x emission, and "abnormal" products quality/quantity.

Regarding catalyst circulation issues, it has been my experience that understanding the key physical properties of the FCC catalyst and unit's pressure will go long way in solving limitations and/or erratic catalyst circulation. Consequently, the next two sections contain fundamentals of physical properties, pressure balance, and catalyst circulation.

Key Aspects of FCC Catalyst Physical Properties

- FCC catalyst is composed of "microsphere" particles.
- The PSD ranges from 0.5 to 150 μm.
- The FCC catalyst's density is reported to be relative to water density.
- Water density is 62.4 lb/ft^3 (at 60°F) or 1 g/cm^3).
- The density of the "as shipped," fresh FCC catalyst is always less than water density.
- As shipped, the fresh catalyst's density typically ranges from 65% to 85% of water density (0.65−0.85 g/cm^3).
- The density of E-cat (spent) catalyst is also virtually less than water. In some instances, it can be slightly higher.
- A dense phase fluidized catalyst bed looks very much like a boiling liquid and shows "liquid-like" behavior. Fluidized solids will flow like a liquid from vessel to vessel. This is the basic concept for the operation of the FCC unit.
- For a catalyst to flow like water, the forces must be transmitted through catalyst particles and not to the vessel wall.
- Air, fuel gas, nitrogen, and steam are commonly used to help in the fluidization, or aeration, of the catalyst. However, they must be dry.
- The lowest superficial gas velocity in which the pressure drop across a fixed bed of catalyst equals the weight of the bed is referred to as incipient fluidization velocity or minimum fluidization velocity. Any slight increase in the gas velocity will cause incremental lifting or expansion of the catalyst bed. The velocity in which gas bubbles are first observed is known as "minimum bubbling velocity."
- The presence of fines in the PSD is helpful for fluidization. The fines act as a lubricant for the larger particles. These smaller particles move more easily in the gas.
- Deaeration is the loss of fluidity to a packed bed. The fines content, as well as the shape of the catalyst, affects the deaeration rate.

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- The ratio of minimum bubbling velocity to minimum fluidization velocity provides a useful tool to assess the fluidity of the FCC catalyst.
- The catalyst's PSD, its shape, and particle density play key roles in its ability to be fluidized.

Fundamentals of Catalyst Circulation

An FCC unit is a "pressure balance" operation, basically behaving similar to a water manometer. Differential pressure between the regenerator and reactor vessels is the driving force that allows for the fluidized catalyst to circulate between the regenerator and reactor vessels (see Figure 12.1 for a typical pressure balance). The slide or butterfly valve located in the regenerator flue gas line is used to regulate the differential pressure between the regenerator and reactor vessels. The reactor pressure is controlled by the WGC.

Fresh catalyst is added to make up for the catalyst losses from the reactor/regenerator vessels, as well as to compensate for the loss of catalyst activity. The catalyst inventory in the unit is controlled by periodic withdrawal of the excess catalyst from the regenerator vessel.

The catalyst level in the catalyst stripper vessel is controlled by a slide or plug valve located in the spent catalyst standpipe. In most FCC units, the cracking temperature is controlled by regulating the catalyst flow from the regenerator via slide or plug valves that are located in the regenerated catalyst standpipe. In Model IV and Flexicracker FCC units, the differential pressure between the reactor and regenerator is the primary control point for regulating catalyst circulation from the regenerator to the reactor.

In FCC regenerators that operate in *partial combustion mode* of catalyst regeneration, the combustion air rate is regulated to target a given concentration of carbon monoxide (CO) in the regenerator flue gas and/or a set level of CRC.

In FCC regenerators that operate in *full burn mode* of catalyst regeneration, an excess concentration of oxygen is maintained in the regenerator flue gas to ensure complete combustion of carbon monoxide (CO) to carbon dioxide (CO_2).

Catalyst "raw" level in the regenerator is determined by measuring the differential pressure between the pressure above the air distributor and the regenerator dilute/top pressure. There is often another pressure tap, about 5 ft (152 cm) above the air distributor that is used to measure catalyst flowing density.

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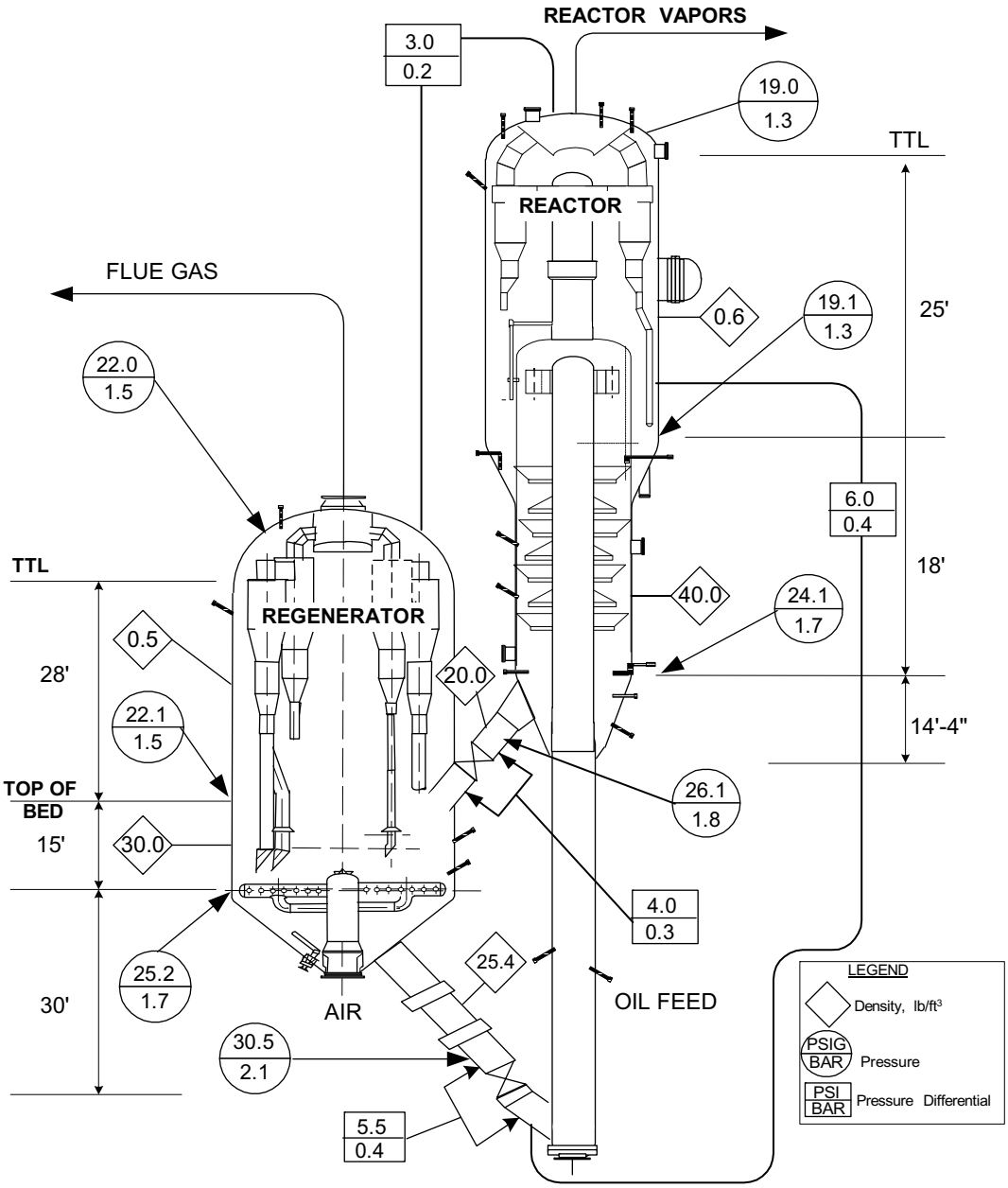


Figure 12.1: Typical FCC unit pressure balance.

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In the reactor/stripper, the "raw" catalyst level is determined by measuring the differential pressure from the catalyst stripper bottom versus the reactor top pressure. The actual catalyst level can be calculated by employing the catalyst density readings in the catalyst stripper.

Catalyst circulation rate is dependent on the following parameters:

- Fresh feed rate
- Use of naphtha, LCO, HCO, or slurry recycle to the riser
- Reactor temperature
- Feed temperature to the riser
- Reactor and regenerator pressures
- Regenerator dense bed temperature.

The regenerator dense bed temperature is dependent on the following:

- Feed quality
- Fresh catalyst addition rate and/or its activity
- Ambient condition and air blower discharge temperature
- Catalyst cooler duty and/or other removal schemes
- Performance efficiencies of feed nozzles and catalyst stripping
- Level of afterburning
- Concentration of CO in the regenerator flue gas.

The "ease" of catalyst circulation is largely influenced by the physical layout of the unit and fluidization properties of the catalyst. Some cat crackers circulate with ease regardless of the catalyst's physical properties. However, in other designs, the unit can experience circulation difficulties with minor changes in catalyst properties.

Things to remember with higher catalyst circulation rate:

- Pressure at the outlet of the regenerated catalyst slide valve goes up, mainly due to higher head pressure and greater friction loss across the J-bend/Wye-piece section, as well as across the riser. This will result in a lower ΔP across the regenerated catalyst slide valve (see also Example 12.1).
- The higher catalyst circulation rate directionally increases catalyst loss rates from the reactor/regenerator cyclones. This is largely from higher catalyst loading to the cyclones and a higher catalyst attrition rate.
- The performance efficiency of the catalyst stripper goes down due to a "faster flow rate" of catalyst through the stripper. This is particularly true, since most operators do not adjust the stripping steam rate with a higher catalyst circulation rate.
- The higher catalyst circulation rate drags more flue gas into the riser, which can tax the FCC vapor recovery section.
- Long term, the higher catalyst circulation rate adversely impacts the mechanical reliability of the FCC equipment.

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Despite the drawbacks noted above, the higher catalyst circulation rate and subsequent higher cat/oil ratio often deliver more liquid volume products from a given FCC feedstock and this often increases the profitability of FCCU operations.

Steady and smooth catalyst circulation increases confidence, as well as the "comfort zone" of the console operator, to optimize the performance of a cat cracker. For example, he or she will be able to:

- Increase feed to the unit
- Increase the stripping steam to reduce carry-under of soft coke and lower the regenerator temperature
- Reduce the feed preheat temperature to increase cat/oil ratio
- Increase the cracking temperature to produce more olefin feed and/or increase the gasoline octane
- Generate more steam from the catalyst cooler
- Operate at higher CO in the flue gas when operating in partial burn.

Consequently, having the flexibility to maximize the catalyst circulation rate is extremely critical in the long-term reliability and profitability of a given FCC unit.

Factors Hindering Catalyst Circulation

The key factors affecting the ability of FCC catalyst to flow smoothly in standpipes are as follows (see also Example 12.2):

- Condition of the catalyst before it enters the mouth of the standpipe. If the catalyst is not fluidized "correctly," it is difficult to keep it properly fluidized in the standpipe.
- Depending on the length/height of standpipe, supplemental fluidization may need to be used to compensate for compression of gas bubbles as it moves downward with the catalyst. The dryness and the amount of the supplemental flue gas, as well as spacing between the aeration taps, are extremely important. In addition, the reliability of measuring the aeration flow rate to each tap, or sets of taps, plays a key role in the success of the standpipe fluidization. Too much aeration can cause "bridging" of the catalyst flow, and not enough aeration can cause a "stick/slip flow" behavior of the catalyst.
- Catalyst PSD has a huge impact on the ease of catalyst circulation, especially in long standpipes and/or u-bends.

An average standpipe must produce 1 psig of head pressure per 4 ft of standpipe height (0.07 bar/1.2 m). This pressure gain should be uniform across the entire height of the standpipe. This gain in pressure corresponds to about 35 lb/ft^3 of catalyst flowing density (561 kg/m^3). There are standpipes in which the catalyst flowing density is in the 45 lb/ft^3 (721 kg/m^3) range.

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Example 12.1 Leading indicator

Regenerated Catalyst Slide Valve Opening Increase

Indicator: Regenerated catalyst slide valve opening has gradually increased from 40% to 60%

Evidences

Field verification:

- Slide valve ΔP
- Reactor–regenerator ΔP
- Riser temperature
- Regenerator dense bed temperature
- Feed rate.

Possible Causes

1. Pressure above the slide valve is less than typical:
   - Catalyst is not building enough pressure in the standpipe
   - Catalyst entering the standpipe is not properly fluidized
   - Not enough aeration along the standpipe
   - A foreign object restricting catalyst flow at the entrance to the standpipe
   - A foreign object has fallen into the slide valve.
2. Pressure below the slide valve is higher than normal:
   - Catalyst is not fully fluidized in the Wye-piece or J-bend section
   - Coke buildup around the feed nozzles
   - Coke in the reactor cyclones
   - Coke buildup in the reactor vapor line
   - Fouling of main column and/or overhead condensers.

Example 12.2 Leading indicator

Erratic Catalyst Circulation

Indicator: Erratic catalyst circulation

Evidences

- Low ΔP alarm coming in and out of fresh feed riser
- Fresh feed riser not holding set point
- Regenerator bed temperature is swinging.

Possible Causes

- Reactor–regenerator pressure balances are off
- Standpipe aeration is not right
- Air rate to the catalyst withdrawal well air rings is not adjusted
- Carbon on cat low or particle size is wrong
- Feed rate or gravity not stable.

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Catalyst Losses

Catalyst losses will have adverse effects on the unit operation, the environment, and operating costs. Catalyst losses appear as excessive catalyst carryover to the main fractionator or losses from the regenerator.

To troubleshoot excessive catalyst losses, one must identify whether the loss is from the reactor (see Example 12.3) or the regenerator (see Examples 12.4–12.6). In either case, the following general guidelines should be helpful in troubleshooting catalyst losses:

- Verify the catalyst bed levels in the stripper and regenerator vessels.
- Conduct a single-gauge pressure survey of the reactor–regenerator circuit. Using the results, determine the catalyst density profile and verify the back pressures to the various steam distributors are normal.
- Perform temperature scans to see areas of catalyst defluidization.
- Plot the physical properties of the equilibrium catalyst. The plotted properties will include PSD and ABD. The graph confirms any changes in catalyst properties.
- Have the lab analyze the "lost" catalyst for PSD. The analysis will provide clues as to the sources and causes of the losses.
- Compare the cyclone loading with the design. If the vapor velocity into the reactor cyclones is low, consider adding supplemental steam to the riser. If the mass flow rate is high, consider increasing the feed preheat temperature to reduce catalyst circulation.
- Confirm that the restriction orifices used for instrument purges are in proper working condition and that the restriction orifices are not missing.
- Consider switching to a harder catalyst. For a short-term solution, if the losses are from the reactor side, consider recycling slurry to the riser. If the catalyst losses are from the regenerator, consider recycling catalyst fines to the unit.
- Be prepared to "pressure bump" the reactor or regenerator vessel.

Example 12.3 Leading indicator

Catalyst Loss from Reactor

Indicator: High ash content—clarified oil (CLO)

Evidences	Possible Causes
• Sample shows high ash content.	• Reactor level is high • Plugged dipleg trickle valve • Hole in Dragon Head riser termination device (RTD) • Blast steam to riser was left on.

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Example 12.4 Leading indicator

Catalyst Loss from Regenerator

Indicator: Loss of catalyst from regenerator

Evidences

- Not gaining level in regenerator
- #1 bin at ESP was filling at a faster rate
- Increase in opacity
- Decrease in 0—40 μm fraction of E-cat
- Increase in 80 μm fraction of E-cat
- Increase in catalyst APS.

Possible Causes

- Holes in the cyclones
- Holes in the cyclone plenum
- Trickle valve flappers have fallen off
- Catalyst underneath trickle valves is not fluidized
- Catalyst is defluidized in the diplegs
- Dipleg diameter is too large
- Refractory lining hex-steel has fallen off and is restricting catalyst flow.

Example 12.5 Leading indicator

Catalyst Loss from Regenerator

Leading indicator: High flue gas opacity

Evidences

- DCS alarm.

Possible Causes

- ESP shutdown (transformer/rectifier (T/R) failure)
- CO boiler shutdown
- Loss of ammonia injection to ESP
- Instrument failure.

Example 12.6 Leading indicator

Loss of Electrostatic Precipitator (ESP)

Leading indicator: Cold temperature on ESP hopper

Evidences

- Heater not keeping hopper warm (DCS)
- No catalyst dropping out when opening hopper valve
- More arcing on hopper transformer/rectifier (T/R).

Possible Causes

- Catalyst bridging in hopper
- Hopper plugged
- Hopper heater failure.

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Coking/Fouling

Nearly every cat cracker experiences some degree of coking/fouling. Coke can be found on the reactor internal walls, reactor top head section, inside/outside of the reactor cyclones, reactor overhead vapor line, main fractionator bottom, and fouling of the slurry bottoms pumparound circuit. Coking and fouling always occur, but they become a problem when they impact throughput or cracking severity.

Troubleshooting Steps

The following are some of the steps that can be taken to minimize coking/fouling (see also Examples 12.7 and 12.8):

- *Avoid dead spots*. Coke grows wherever there is a cold spot in the system. Use "dry" dome steam to purge hydrocarbons from the stagnant area above the cyclones. Dead spots cause thermal cracking.
- *Minimize heat losses from the reactor plenum and the transfer line*. Heat loss will cause condensation of heavy components of the reaction products. Insulate as much of the system as possible; when insulating flanges, verify that the studs are adequate for the higher temperature.
- *Improve the feed/catalyst mixing system and maintain a high conversion.* A properly designed feed/catalyst injection system, combined with operating at a high conversion, will crack out high boiling feeds that otherwise could be the precursors for the formation of coke.
- *Ensure cracking temperature is high enough to vaporize/crack very high boiling fraction of the feedstock.*
- *Follow proper startup procedures*. Introduce feed to the riser only when the reactor system is adequately heated up. Local cold spots cause coke to build up in the reactor cyclones, the plenum chamber, or the vapor line.
- *Keep the tube velocity in the bottoms pumparound exchanger(s) >5 ft/s (1.5 m/s).* Putting the bundles in parallel for more heat recovery may lead to low velocity.
- *Hold the main column liquid bottoms temperature under 700°F (371°*C). For residue operation, this temperature should be <650°F (343°C). Use "pool quench" to control the main column bottoms temperature.
- *Minimize the bottoms level and residence time of the hot liquid.*
- *Ensure adequate liquid wash to shed trays or grid packing to minimize coking in the bottom of the main column.*
- *Utilize a continuous-cycle oil flush into the inlet of the bottoms exchanger*. This keeps the asphaltenes in solution and increases tube velocity.
- *Verify that no fresh feed is entering the main column*. Feed can enter the main column through emergency bypasses, through the feed surge tank vent line or safety relief valve.

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Example 12.7 Leading indicator

Coking and Fouling

Leading indicator: High reactor pressure alarm

Evidences	Possible Causes
• DCS trend	• Loss of main fractionator overhead cooling
• Feed rate had to be cut back	• Salting of the main fractionator trays or packing
• Blower surging.	• Coke deposition in the reactor vapor line
	• Coke deposition in the rough cut cyclone outlet tubes.

Example 12.8 Leading indicator

Coking and Fouling

Leading indicator: Main fractionator slurry pumps cavitations

Evidences	Possible Causes
• Low slurry pumparound rate	• Coke buildup in the main fractionator bottom
• High slurry pumparound return temperature	• Catalyst carryover from the reactor
• High bottoms temperature	• Bottoms temperature too high
• Reactor pressure climbing.	• Light components entrained with slurry oil.

Increase in Afterburn

The composition of coke on the spent catalyst is approximately 93% carbon, 7% hydrogen with traces of sulfur and organic nitrogen compounds. It is important that combustion of the coke (Table 12.1) occurs in the dense bed of catalyst. Without the catalyst bed to absorb this heat of combustion, the dilute phase and flue gas temperatures increase rapidly, largely from combustion of CO to CO_2. This phenomenon is called *afterburning*. It is critical that spent catalyst and combustion/lift air are being introduced into the regenerator as evenly as possible across the catalyst bed. It is also important to note that vertical mixing is much faster than lateral mixing.

The magnitude of afterburning in the regenerator largely depends on the operating conditions of the unit and the effectiveness of the contact between the combustion air and the spent catalyst. The geometry of the regenerator and the distribution of the spent

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catalyst also impact the level of afterburning (Example 12.9). Generally speaking, regenerators operating in partial combustion do not experience the same level of afterburning as compared with full-burn regenerators, due to the absence of oxygen in the dilute phase.

Table 12.1: Heat of Combustion.

			kCal/kg of C, H_2, or S	BTU/lb of C, H_2, or S
$C + ½O_2$	→	CO	2,200	3,968
$CO + ½O_2$	→	CO_2	5,600	10,100
$C + O_2$	→	CO_2	7,820	14,100
$H_2 + ½O_2$	→	H_2O	28,900	52,125
$S + xO$	→	SO_x	2,209	3,983

Example 12.9 Leading indicator

Increase in Afterburn—High Regenerator Cyclone Outlet Temperatures

Leading Indicator: Two out of six cyclone outlet temperatures are 50°F (28°C) higher

Evidences
- DCS
- Feed rate is cut back.

Possible Causes
- Broken air distributor arms
- Broken spent catalyst deflector/distributor
- Erratic catalyst flow from stripper
- Low regenerator bed level
- Low regenerator bed temperature.

Operating options to reduce afterburning include the following:

- Maximizing the feed preheat temperature
- Using HCO or slurry oil recycle
- Optimizing the use of CO combustion promoter
- Ensuring catalyst circulation from reactor is steady
- Ensuring catalyst stripping steam rate has been optimized
- Adjusting combustion air rates to each air distributor
- Changing the ratio of combustion air and carrier rates
- Increasing regenerator pressure
- Increasing the regenerator bed level, while ensuring it does not affect the catalyst loss rate
- Optimizing the flue gas excess oxygen.

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Hot Gas Expanders

Power recovery trains recover energy from the flue gas (see Figure 12.2 for a typical flue gas power recovery scheme). The FCC starts to resemble a large jet engine; air is compressed into a combustion zone and expanded across a turbine. Power recovery increases the efficiency of the unit but adds one more mechanical device to an already long list. Since they are too big to bypass, power trains need to be as reliable as the rest of the unit.

The main concerns in the design and operation of a power recovery system are catalyst fines and temperature. Catalyst fines will lead to serious blade wear, deposits, power loss, and rotor vibration. Deposit occurs mostly where flue gas velocities are at maximum levels, such as the blade outer diameter (see also Examples 12.10 and 12.11).

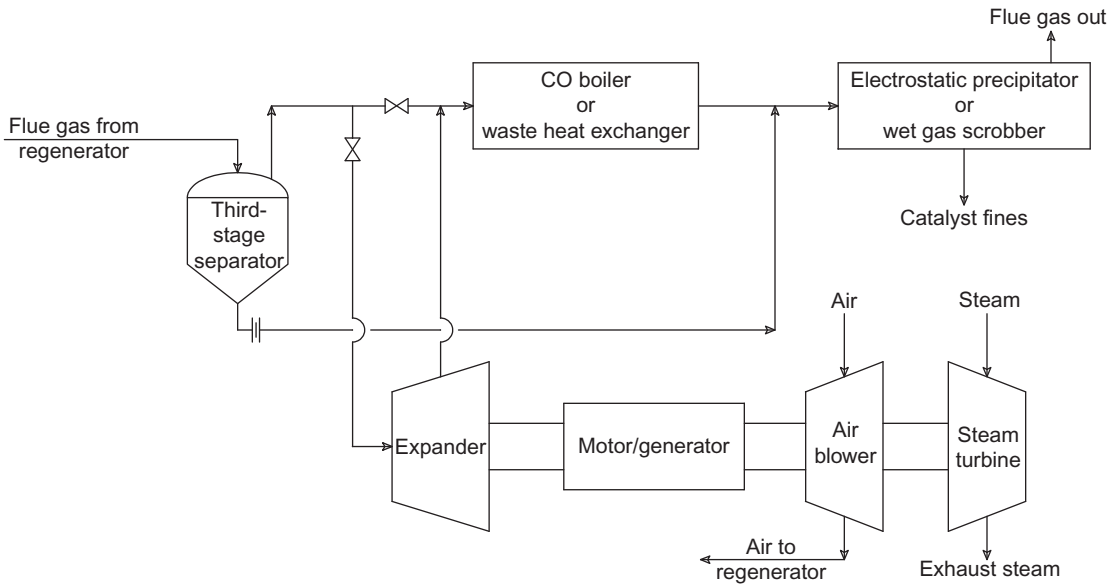


Figure 12.2: Typical flue gas recovery scheme.

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Example 12.10 Leading indicator

Hot Gas Expander

Leading indicator: Loss of horsepower

Evidences	Possible Causes
• More supplemental steam is needed	• Rotor blade erosion
• Suction butterfly valve is "more closed"	• Critical flow nozzle damaged
• Expander outlet temperature has increased.	• Bypass valve is 100% open.

Troubleshooting Steps

1. Regular monitoring of rotor blade conditions by visual inspection, photographs, and/or video recording. A port is usually installed for this.
2. Continuous monitoring of rotor casing vibration, bearing temperatures, and the expander inlet/outlet temperatures. Problems can be either instantaneous or slow growing. Instantaneous problems occur during startup, upset, and shutdown, and are easy to note. Slow-growing problems can creep up and are almost invisible, while everything is running well. Compare the readings month-to-month to spot trends.
3. Continuous monitoring of the third-stage separator performance. If catalyst is showing up downstream, consider using more than the "standard" 3% flue gas underflow. The blowcase needs more attention than it usually gets.
4. Online cleaning—injecting of walnut hulls into the inlet of the expander weekly.
5. Thermal shocking—reduce feed in 20% increments, while maintaining maximum air rate to the regenerator. Cool the expander inlet temperature to around 1,000°F (540°C) and hold for at least 1 h. This is not a procedure that the expander vendor supports, but it is practiced by many refiners.

Example 12.11 Leading indicator

Hot Gas Expander

Leading indicator: Expander vibration has increased

Evidences	Possible Causes
• DCS trend	• Catalyst buildup on the shroud
• Field verification	• Disk failure from intergranular sulfidation attack
• Higher stack opacity	• Third-stage separator not working properly
• Higher catalyst loss from regenerator	• Soft catalyst
• Increase in fresh catalyst usage.	• High concentration of sodium, vanadium, magnesium, iron, or calcium on the catalyst
	• Catalyst being attritted prematurely.

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Flow Reversal

A stable pressure differential must be maintained across the slide valves. The direction of catalyst flow must always be from the regenerator to the reactor and from the reactor–stripper back to the regenerator. A negative differential pressure across the regenerated catalyst slide valve can allow fresh feed and oil-soaked catalyst to backflow from the riser into the regenerator. This flow reversal can result in uncontrolled burning in the regenerator and potentially damage the regenerator internals due to the extreme high temperature, costing a refiner several million dollars in production loss and maintenance expense.

Similarly, a negative pressure differential across the spent catalyst slide valve can allow hot flue gas to backflow to the reactor and the main fractionator, severely damaging the mechanical integrity of these vessels.

Some of the main causes of loss of pressure differential across the slide valves are as follows:

- Loss of the main air blower (MAB) or the WGC
- Loss of the catalyst cooler
- Presence of water in the feed
- High catalyst circulation rates, resulting in excessive slide valve opening and low differential
- Loss of regenerator or reactor–stripper bed levels
- Failure of the reactor temperature controller and reactor–stripper level controller
- Bypass open around a shutdown valve.

Reversal Prevention Philosophy

The FCC process is very complex and many scenarios can upset operations. If the upset condition is not corrected or controlled, each scenario could lead to a flow reversal. Table 12.2 contains a cause/effect shutdown matrix indicating scenarios in which a shutdown (reversal) could take place. In most cases, a unit shutdown is not necessary if adequate warning (low alarms before low/low shutdowns) is provided. The operating staff must be trained to respond to those warnings.

The shutdown system will have adequate interlocks to prevent inadvertent trips. The system must include “two-out-of-three voting” (2oo3) or backup instruments. The operators must trust the system for it to stay in service.

Slide valves will have an independent low differential pressure override controller to prevent the reactor temperature controller from opening the slide valves to the point where low differential pressure could allow feedback to the regenerator.

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Table 12.2: A Cause-and-Effect Shutdown Matrix.

Cause ↓ / Effect →	Close Riser Regenerated Catalyst Slide Valve	Open Riser Emergency Steam Valve	Close Feed to Riser	Close Slurry Recycle Valve	Close HCO Recycle Valve	Close Spent Catalyst Slide Valve	Open Regenerator Emergency Steam Valve	Alarm Only
Regenerated catalyst slide valve low ΔP								X
Spent catalyst slide valve low ΔP								X
Air blower low/ low air flow	X	X	X	X	X	X	X	
Riser low/low feed flow rate	X	X	X	X	X	X	X	
Low reactor temperature								X
Reactor vessel high catalyst level								X
Manual shutdown	X	X	X	X	X	X	X	

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Example 12.12 Common scenarios/leading indicators

Leading Indicators	Confirming Evidence	Probable Causes
Loss of charge (instrument freeze up)	• Increase in heater temperature • Regenerator bed temperature increase • Reactor top temperature increase • Too much compressor suction pressure.	• Loss of charge pump • Water in charge • Instrument failure (freeze up).
Feed preheater control valve went open to 100%	• DCS feedback • Verification of control valve position • Feed pump operation • Feed preheater pressure increase.	• Water in feed.
Loss of MAB (main air blower)	• Unit gets quiet • Riser slumps.	• Steam issues—wet steam • Lube oil system for MAB • Loss of oil pressure • Vacuum issues.
Started losing vacuum on blower	• Loss of vacuum (DCS).	• Heavy rain • Steam pressure drop • Loss of sealing steam • Vacuum leak on pump • Hot well level • Surface condenser pump failure.
Riser temperature falls below 900°F (482°C)	• Low temperature DCS alarm • Regenerator slide valve wants to open • ΔP dropping on regenerator slide valve • No automatic feed diversion.	• Bad riser temperature indicator (TI) • Reduced catalyst circulation (or none) • No catalyst cracking • Feed oil going in with no catalyst.
Regenerator temperature increase of 6°F (3.3°C)	• Compare other regenerator TI's • Regenerator overhead temperature is up • Slide valve position has decreased • Catalyst circulation has decreased	• Poorer feedstock • O_2 controller backed off from partial to full combustion • High feed preheat temperature • Too much fresh catalyst addition.

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Example 12.12 (Continued)

Leading Indicators	Confirming Evidence	Probable Causes
	• Conversion has decreased.	
Regenerator dilute phase temperature increase of 40°F (22.3°C)	• Regenerator temperature profile • MAB speed • Air ring position • Flue gas analyzers (O_2 and CO) • Regenerator operating temperature.	• Air/catalyst maldistribution • High air rate • Possible broken air ring • Transition between burns • Mechanical failure • Change in feed quality • MAB flow has decreased.
Carbon on catalyst is going up from 0.1 to 0.3 wt%	• Lab data—visual inspection of catalyst • Reactor—stripper operations are poor • Regenerator flue gas analyzer has changed.	• Enriched oxygen feed has decreased • Poor hydrocarbon stripping in reactor—stripper • Too much Sox additive.
Regenerator slide valve opening increased from 40% to 60%	• Riser temperature lowered • Decrease in feed temperature • Field-verify valve opening %.	• Feed preheater tripped • Emergency steam flow control valve (FCV) failed to open • Catalyst bridged above slide valve in standpipe.
Spent catalyst slide valve opening increased from 30% to 60%	• Reactor bed level • Reactor pressure taps • Valve position indicator • Pressure change.	• Reactor level high due to bridging • Plugged taps in regenerator • Trash in unit.
Flue gas slide valve position increased from 35% to 65%	• ΔP across slide valve has dropped • Field-verify position of valve • Regenerator pressure increase.	• Catalyst restrictions • Orifice chamber malfunction.
High CO boiler firebox temperature	• Low dense bed temperature • High CO carryover • High supplemental fuel gas flow.	• Lost air to regenerator (compressor) • Lost instrumentation on fuel gas • Poor unit conversion.
CO boiler firebox temperature increase of 30°F (16.7°C)	• Increase in steam production • Increase in flue gas temperature from CO boiler outlet	• Lower API feed quality • Lower oxygen from MAB • Not enough stripping steam • Catalyst addition—issues, losses • Fuel gas quality

(*Continued*)

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Example 12.12 (Continued)

Leading Indicators	Confirming Evidence	Probable Causes
	• Increase in CO level in regenerator • Flue gas slide valve has increased opening • Feed quality.	• Drop in feed temperature.
Poor unit conversion	• Lab data • Change in hydrocarbon cuts on fractionator side • Change in carbon on regenerated catalyst (CRC).	• Too low combustion air rates • Charge makeup changed • Improper reflux rates.
Rise in CLO gravity from −4 to 0°API	• Lab analysis • CLO flow increases • LCO and HCO flow decreases • Main fractionator level increases.	• Main fractionator temperature control problem • Feed temperature, conversion, catalyst activity • Feed quality decrease • Slurry exchangers have uneven flow.
CLO gravity went to 0 or positive API	• Lab results • Main fractionator level rising • Temperature on main fractionator.	• CLO make is too great • Uncracked feed to main fractionator • Feed composition • Main fractionator bottom temperature too low • Riser temperature low.
High decant oil make rate	• Decant oil flow rate is high • APC system misses target rate • Mass balance indications • Main fractionator bottoms level is high/low temperature • Decant oil API gravity is high • Pumparound flow is high.	• Riser temperature is low • Feed preheat temperature is high • Main fractionator pressure is high • Feed composition has changed (worse) • Catalyst activity is down • Feed drum is relieving to the main fractionator.
CLO gravity increases from −4 to +2°API	• CLO rate increases • Fractionator bottoms level increases	• Main fractionator bottoms X-ray level control malfunction • LCO purge to pump

(*Continued*)

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Example 12.12 (Continued)

Leading Indicators	Confirming Evidence	Probable Causes
	• Heavy gas oil (HGO) cutter rate increases.	• Feed to main fractionator fails.
Main fractionator loss of level	• Level indicators (DCS and outside) • No pumparounds • Main fractionator high temperature • Main fractionator ΔP lower.	• Pump out is open • Started with no level • Hot reactor overhead to main fractionator with no pumparounds • Operator experiences level low.
Loss of flow through slurry exchangers	• Decrease flow rates (U factors, DCS) • Low flow to debutanizer reboiler.	• Catalyst carryover • Polymer buildup.
Dry gas yield increase of 20%	• Compressor amp load increases (DCS) • Reactor temperature increases • Regenerator pressure increases • Dry gas scrubber ΔP increases.	• Feed changes (lower API gravity), aniline point decreases, higher metals content • Regenerator dense bed temperature increased • Catalyst flow rate increased.
Dry gas yield increases from 10% to 15%	• Lab analysis—check C_3's • Absorber flow • WGC • Absorber temperature profile.	• Increased reactor outlet temperature • High regenerator temperature • Amount of dispersion steam • Riser outlet temperature (ROT).
WGC is at its capacity limit	• High first-stage deviation • High off-gas make rate • Poor unit conversion.	• High metals concentration on catalyst • Not enough gasoline condensing in main column overhead receiver • Hydrogen dumping from gasoline sulfur removal unit to cold receiver.
Loss of first-stage WGC	• High pressure in first-stage KO drum • Main fractionator pressure up • Reactor pressure up • Slide valve ΔP low • Regenerator pressure up	• Lube oil pump trip • First-stage suction KO drum level high • First-stage compressor vibration trip • Loss of power to Bentley Nevada shutdown system.

(*Continued*)

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Example 12.12 (Continued)

Leading Indicators	Confirming Evidence	Probable Causes
	• Second-stage compressor trip.	
Debutanizer bottoms temperature decreases by 30°F (16.7°C)	• HCO flow/temperature to debutanizer reboiler • HCO to debutanizer reboiler control valve position • Debutanizer temperature profile • HCO pumparound system • Main fractionator temperature profile • Debutanizer analyzers ΔP.	• Loss of HCO pump • Control valve failure (HCO to debutanizer reboiler) • Main fractionator upset—loss of slurry pump resulting in loss of HCO tray level • Debutanizer tower mechanical issue • Rapid feed increase to debutanizer • Debutanizer reflux rate increase • Water in feed to debutanizer.
Debutanizer bottoms temperature falls 60°F (33.3°C)	• Tower level went up • Tower top temperature went down • Level in overhead drum went down • RVP in gasoline went up.	• Loss of 600# steam • Loss of HCO • Control valve problems • HCO pump problems.
High pressure in debutanizer tower during startup	• Tower bottoms temperature cold on debutanizer and stripper • Absorber pressure high • High C_2's on analyzer (absorber stripping tower).	• Absorber stripping tower cold • No heat medium flow • Absorber stripping tower pressure high.
"Fly wheeling" of H_2S stripper (deethanizer)	• Increase of feed to stripper • High ΔP across the stripper • High liquid level in the high pressure separator.	• High pressure receiver is too cold • Not enough reboiling.

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Summary

This chapter emphasizes that effective and timely troubleshooting largely depend on being extremely familiar with "normal" conditions as they relate to the feedstock quality, catalyst properties, operating conditions, reactor yields, pressure balance, and equipment performance parameters. This chapter also provides examples of common problems, symptoms, and probable causes that one may encounter in troubleshooting FCC units. In addition, a systematic approach is outlined to provide solutions and corrective action. The suggested solutions are necessarily generic but apply to a wide variety of units.

In closing, the remaining pages contain examples of actual events as described by FCC operators during my customized training classes. These case studies can be used as a guide to troubleshoot similar events.

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CHAPTER 13

Optimization and Debottlenecking

Troubleshooting, optimization, and debottlenecking are three steps in a continuous process. There is some overlap and gray area among them.

Troubleshooting refers to the solution of short-term problems. The assignment is usually initiated by operations or maintenance. The solution usually involves something that can be done online. Troubleshooting was discussed in Chapter 12.

Optimization refers to maximizing feed rate and/or conversion with the existing equipment, while reaching as many constraints as possible. It can be the response to changes in the feed quality, ambient conditions, or the market demands. It is not discussed separately here but is the incentive for most debottlenecking projects.

Debottlenecking often refers to hardware changes, small or large. It is directed at the bottlenecks identified during optimization. It includes projects that cannot be completed online, such as installing new internals in a vessel. Debottlenecking is the main focus of this chapter.

Introduction

Most FCC units are big profit makers. Therefore, they are operated to several constraints. Optimization is the effort to locate and overcome these constraints. The profitability of an FCC operation is maximized when the unit is "pushed" simultaneously against multiple constraints. Optimization means finding the constraint or combination of constraints that cost the refinery lost opportunities and arriving at the right fix.

A properly configured APC system could allow for online, continuous optimal unit operation and push the FCC operations to multiple constraints simultaneously.

The main purpose of optimization is to increase the refinery's profit margin. In the FCC, this usually means:

- Raising or reducing the feed rate
- Increasing or reducing the fresh catalyst addition rate

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- Increasing or decreasing the fresh catalyst surface area, rare earth and/or its activity
- Use of purchased E-cat to reduce catalyst impurities
- Processing lower quality feedstock
- Increasing or decreasing feed preheat temperature
- Adjusting the cracking temperature
- Minimizing excess flue gas oxygen (full burn units)
- Increasing or reducing CO concentration of flue gas (partial burn units)
- Lowering or increasing CRC (often in partial burn regenerator)
- Lowering or in some cases increasing the regenerator bed temperature
- Increasing or decreasing the amount of various steams flowing into the reactor section
- Minimizing the reactor pressure
- Reducing or increasing catalyst bed levels in the reactor and regenerator vessels
- Using recycle streams to the riser when limited by fresh feed rate
- Using proper catalyst additives
- Adjusting WGC suction and discharge pressures
- Adjusting the main fractionator top and bottom temperatures
- Adjusting the regenerated and spent catalyst slide/plug valve differential pressures.

As with troubleshooting, a proper optimization exercise must consider the effects of feedstock, catalyst, operating conditions, mechanical hardware, environmental issues, and the ability of the refinery to handle the additional feed/product rates and quality.

Approach to Optimization

Optimization requires a comprehensive test run to determine "where you are." Elements of a test run include:

- Overall and component material balance
- Reactor/regenerator heat balance
- Hydrogen balance
- Sulfur balance
- Reactor/regenerator pressure survey
- Utility balance
- Evaluation of the interaction among feed quality, catalyst properties, and operating conditions
- Main fractionator and gas plant modeling.

If the object of optimization is to run heavier feeds, multiple test runs may be needed with heavy feed added in stages.

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The next step is to identify the incremental value of:

- Fresh feed rate
- Each FCC product
- Octane and cetane numbers
- Other product quality issues (sulfur, slurry ash level, etc.).

With this information, the constraints on operation can be identified and the value of addressing them can be evaluated.

Improving FCC Profitability Through Proven Technologies

Once the performance of the FCC unit is optimized through using new catalyst and operating practices, the unit's profitability can be further improved by installing proven hardware technologies. The purpose of these technology upgrades is to enhance product selectivity and unit reliability. Since the 1980s, mechanical upgrade of FCC units has proceeded at a fast pace. New feed/catalyst injection systems and elimination of post riser reactions have been the forefront of these mechanical upgrades.

Apparent Operating Constraints

The unit operating philosophy and its apparent operating limits often dictate unit constraints. For example, limitations on the main column bottoms temperature, the flue gas excess oxygen, and the slide valve ΔP often constrain the unit feed rate and/or conversion. Unfortunately, some of these limits may no longer be applicable and should be reexamined. Some of them may have resulted from one bad experience and should not have become part of the operating procedure.

Debottlenecking

The remainder of this chapter contains suggested ways of addressing constraints in the following areas of the FCC unit:

- Feed/preheat section
- Reactor−regenerator section
- Main fractionator and gas plant.

Included are discussions regarding the feed/catalyst system, instrumentation, and off-site. It should be noted that a change in one system usually affects others.

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Feed Circuit Hydraulics

Figure 1.11 shows a typical feed preheat configuration. A hydraulic limitation usually manifests itself when increasing fresh feed rate and/or installing high-efficiency feed injection nozzles.

Typical Feed Preheat Section

The hydraulic pinch points in the feed preheat system are identified with a single-gauge pressure survey. The bottlenecks are often related to:

- Feed pumps
- Fresh feed control valve
- Piping
- Preheat exchangers
- Preheat furnace
- Feed nozzles.

The feed pump will be rerated for the new conditions. With higher viscosity and higher gravity, the pump driver may need work. If the system is not adequate, heavier feed can be piped through a separate circuit in parallel with the existing circuit, preferably on flow ratio control.

If the pump is the bottleneck, before changing it, consider:

- Installing a larger impeller
- (Turbine) increasing turbine speed. Evaluate the steam level and consider adding an exhaust condenser
- (Motor) changing to a variable speed drive (VSD). VSDs make startup easier and most can support 10% overspeed
- Changing the driver
- Adding pumps in parallel
- Adding a booster pump downstream.

As shown in Example 13.1, increasing the pump impeller size from 13 to 13.5 in. (33 to 34.3 cm) increases the flow by 3.8%, discharge pressure by 7.8%, and horsepower by 12%. Increasing the turbine speed from 3,300 to 3,400 rpm increases the flow by 3%, the discharge pressure by 6.1%, and the horsepower by 9.4%.

New internals in the control valve or a larger control valve can be the cheapest option if no piping needs to be changed.

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If the pressure drop in the feed piping is excessive, consider increasing the line size or installing a parallel line. Check the existing flange ratings if any changes are made in the pump or piping, or if the temperature is changed significantly.

If diluent is being added to the feed, evaluate the optimum point for minimum pressure drop and maximum heat recovery.

The preheat furnace can be a bottleneck. The first consideration is that it may not be needed in the new operation. With the increase in the FCC rate, the pressure drop will increase. Consider:

- Using the furnace bypass
- Verifying the position of the inlet balancing valves. When balancing a heater, operators tend to pinch the valves. At least one of the valves should be wide open
- Decoking the heater. Consider hydraulic cleaning
- Increasing the number of tube passes. Changing from a two-pass to a four-pass arrangement can reduce the pressure drop by over 75%. See Example 13.2
- Adding diluents downstream.

Example 13.1

Q_1, h_1, bhp_1, d_1, n_1 = Initial capacity, head, brake horsepower, diameter, and speed
Q_2, h_2, bhp_2, d_2, n_2 = New capacity, head, brake horsepower, diameter, and speed

Diameter Change Only	Speed Change Only	Diameter and Speed Change
$Q_2 = Q_1(d_2/d_1)$	$Q_2 = Q_1(n_2/n_1)$	$Q_2 = Q_1(d_2/d_1 \times n_2/n_1)$
$h_2 = h_1(d_2/d_1)^2$	$h_2 = h_1(n_2/n_1)^2$	$h_2 = h_1(d_2/d_1 \times n_2/n_1)^2$
$\text{bhp}_2 = \text{bhp}_1(d_2/d_1)^3$	$\text{bhp}_2 = \text{bhp}_1(n_2/n_1)^3$	$\text{bhp}_2 = \text{bhp}_1(d_2/d_1 \times n_2/n_1)^3$

where:

$d_1 = 13$ in.;
$d_2 = 13.5$ in.;
$n_1 = 3{,}300$ rpm;
$n_2 = 3{,}400$ rpm.

Flow increase
3.8% (impeller only)
3.0% (speed only)
7% (impeller and speed)

Head increase
7.8% (impeller only)
6.1% (speed only)
14.5% (impeller and speed)

Horsepower increase
12.0% (impeller only)
9.4% (speed only)
22.5% (impeller and speed)

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Example 13.2

Changing piping in furnace from two-pass to four-pass

Case I: Two-pass furnace

50,000 bpd total charge (25,000 bpd to each pass)
API gravity of feed = 25
Furnace outlet temperature = 500°F
Furnace tube diameter (ID) = 4.5 in.

$$\Delta P_{100} = 0.0216 \times \frac{f \times \rho \times Q^2}{d^5}$$

where:

ΔP_{100} = pressure drop (psi) per 100 ft of pipe;
f = friction factor = 0.017;
ρ = flowing density = 47.4 lb/ft^3;
Q = actual flow rate = 867.8 GPM;
d = tube inside diameter = 4.5 in.;
ΔP_{100} = 7.0 psi.

Assuming a total 700 ft of equivalent pipe in the furnace, the total pressure drop is 49 psi.

Case II: Switching to four-pass

ΔP_{100} = 1.8 psi.

Assuming a total 500 ft of equivalent pipe in the furnace, the total pressure drop is 9.0 psi.

Savings in pressure drop = 49.0 − 9.0 = 40.0 psi, or an 81.6% reduction.

Reactor/Regenerator Structure

This section addresses the following:

- Mechanical limitations
- Riser termination device
- Feed and catalyst injection system
- Spent catalyst stripper
- Slide valves
- Regeneration.

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Mechanical Limitations

Mechanical limitations include the design temperature and pressure of the reactor and the regenerator.

Debottlenecking the Reactor Pressure/Temperature

The FCC reactor pressure is usually controlled at the suction of the WGC. The reactor pressure is the WGC suction pressure plus the pressure drop through the main fractionator system, reactor vapor line, and reactor cyclones.

Reactor temperature is usually controlled directly by adjusting the slide valve openings or changing the pressure differential between the reactor and generator. Mechanical design conditions of the reactor systems can limit operating at more severe conditions. To debottleneck these limitations:

- The reactor vessel can be rerated based on actual metal thickness and corrosion history at the new operating temperature.
- An external cyclone can be used to unload the vessel.
- Internal lining can be added.
- A reactor quench system can be used.
- Split feed injection can be considered.
- The riser and the reactor can be replaced with a cold-wall design.

Debottlenecking the Regenerator Pressure/Temperature

The regenerator is already a cold-wall vessel; rerating is not often practical. High regenerator temperature requires typically installing either catalyst coolers, operating in partial combustion, or injecting a quench stream into the riser.

Riser Termination Device

Post-riser hydrocarbon residence time leads to thermal cracking and nonselective catalytic reactions. These reactions lead to degradation of valuable products, producing dry gas and coke at the expense of gasoline and LPG. Improvements in FCC catalyst have eliminated any incentive for these reactions.

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Thermal reactions are a function of time and temperature; yields are proportional to the following equation:

$$k = \mathrm{A}e^{-E/RT} \tag{13.1}$$

where:

k = rate per time
A = frequency factor
e = 2.718
E = activation energy
R = gas constant rate
T = temperature

Figure 13.1 shows the typical effects of vapor residence time and temperature on dilute phase cracking. For example, at 5 s residence time, the dry gas yield increases 8% when the reactor temperature increases from 960°F (516°C) to 980°F (527°C). Increasing the residence time to 10 s increases the dry gas yield another 8%.

Since the mid-1980s, FCC technology licensors and several oil companies have employed a number of riser termination devices to reduce nonselective post-riser cracking reactions. Two general approaches have been used to reduce post-riser cracking. The most widely used approach is direct connection of the cyclones to the riser and on to the reactor vapor line. The second approach is quenching the reactor vapors downstream of the riser cyclones (rough-cut cyclones).

Riser termination devices separate the catalyst and the oil vapor immediately at the end of the riser. The cyclone vapor usually discharges directly to the second-stage cyclones

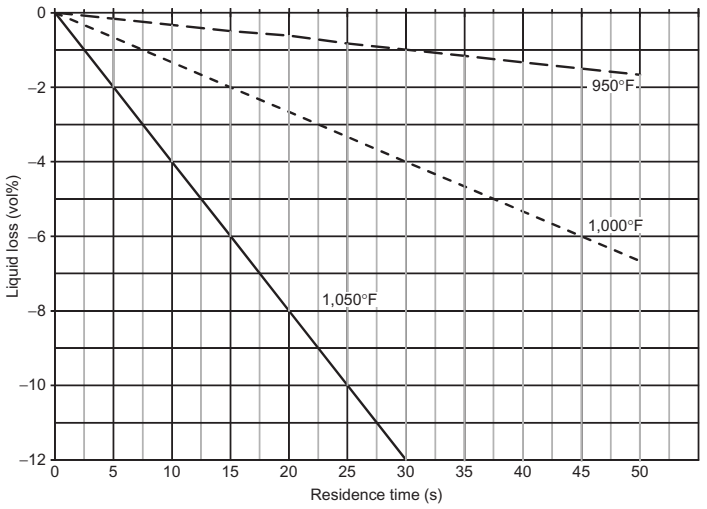


Figure 13.1: Liquid loss from thermal cracking.

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and then to the reactor vapor line. The catalyst is directly discharged into the stripper. The "reactor" is simply a vessel for holding the cyclones. Technologies are offered by:

- UOP
- KBR
- The Shaw Group
- CB&I Lummus.

UOP VSS System

UOP's current riser termination device offering is the vortex separation system (VSS), as shown in Figure 13.2. VSS is for FCC units having an internal riser and a similar design (vortex disengaging system (VDS)) is for external risers. The catalyst−vapor mixture travels up the riser through the chamber and exits through several arms. These arms generate a centrifugal flow pattern that separates the catalyst from the vapor inside the chamber. The catalyst accumulates in a dense phase at the base of the chamber, where it is "prestripped" prior to flowing into the reactor stripper. The stripped hydrocarbon vapors are fully contained in the chamber and exit with the rest of the riser effluent vapors to the secondary cyclones.

The reactor vapors leave the VSS through an outlet pipe. Secondary cyclones are directly connected to this outlet pipe through an expansion joint. The VSS outlet pipe contains several vent pipes through which the reactor dome steam and a portion of the stripping steam/hydrocarbon vapors leave the reactor.

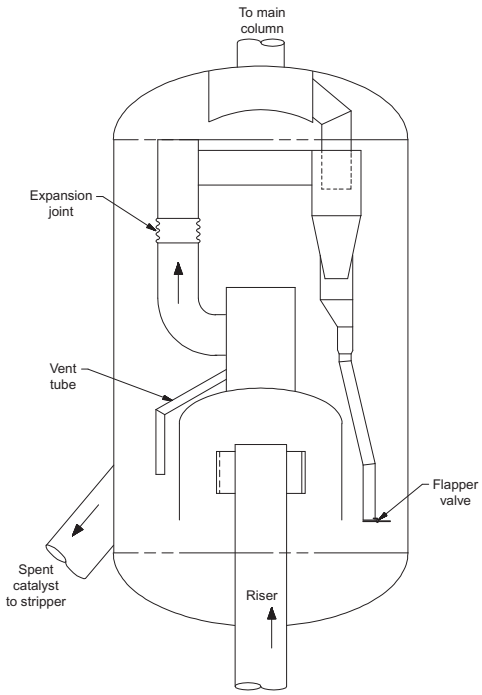


Figure 13.2: UOP vortex separation system (VSS).

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KBR Closed Cyclone Offerings

KBR licenses two riser termination technologies that were originally developed by Mobil Oil and Exxon Oil Research & Engineering.

In the Mobil Oil design, the riser cyclones are hard-piped to the riser. The diplegs of both the riser cyclone and the upper reactor cyclone are often sealed with catalyst. This minimizes the carry-under of reactor vapors into the reactor housing and maximizes the collection efficiency of the riser cyclones. No trickle or flapper valves are used on the riser cyclone diplegs. The riser cyclone diplegs terminate with a splash plate (Figure 13.3). The upper reactor cyclone diplegs use conventional trickle valves. Sealing the upper reactor cyclone diplegs with about 3 ft (0.9 m) of catalyst provides insurance in case the trickle valves become stuck open and also enhances the trickle valve reliability. In this design, the riser cyclones operate at a positive pressure and sealing the diplegs is expected to minimize carry-under of reactor vapors into the reactor housing.

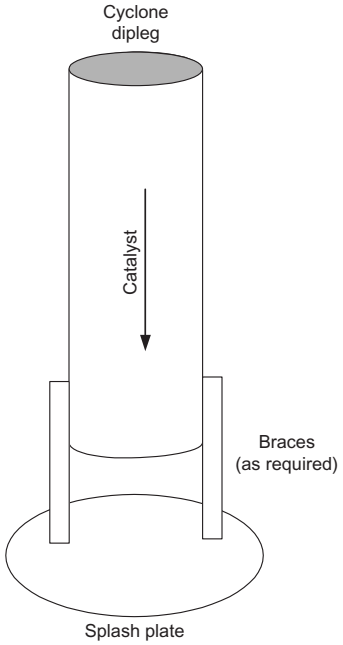


Figure 13.3: Typical splash plate.

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The catalyst must be fluidized to provide an effective seal for the diplegs. Fluidization is critical; without it, the diplegs cannot discharge the catalyst, and the diplegs can plug and massive carryover to the main fractionator can occur. To ensure this uniform fluidization, this system uses an additional steam distributor. In this design, each set of riser and upper reactor cyclones is connected via the use of a "slip joint" conduit. The stripper steam and hydrocarbons as well as dome steam exit the reactor housing by entering through this conduit, as shown in Figure 13.4.

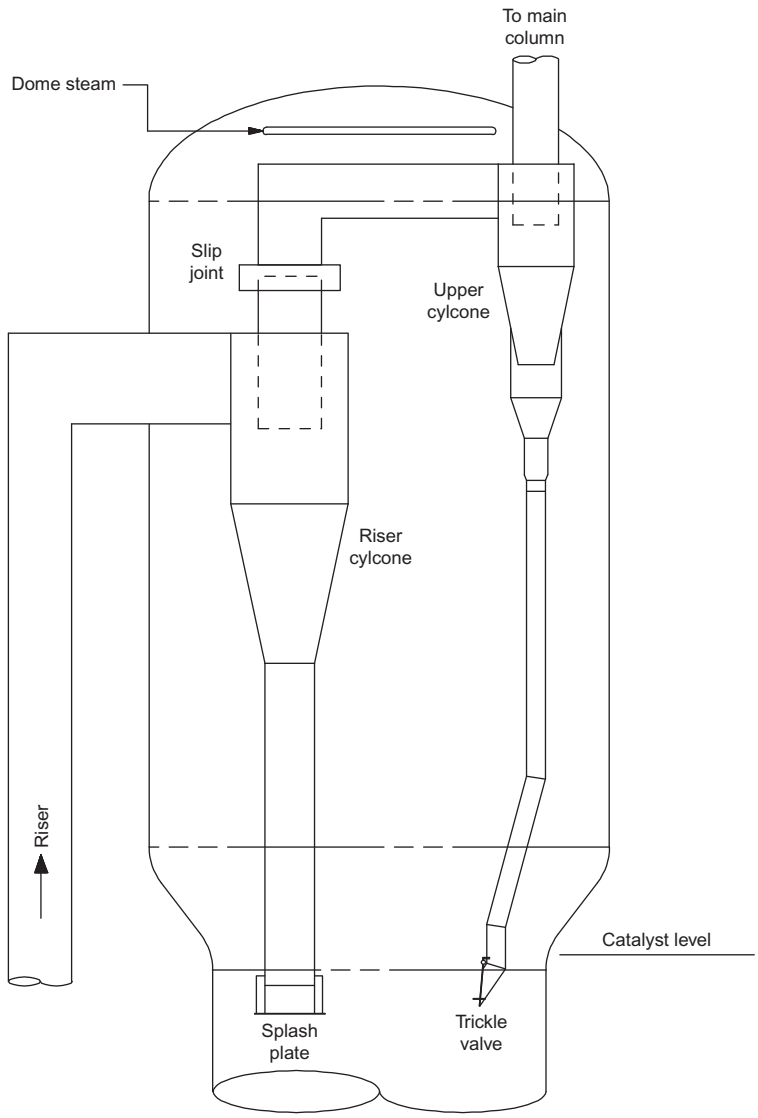


Figure 13.4: KBR closed cyclone system (using Mobil Oil technology).

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In the Exxon Research & Engineering configuration, the riser cyclones are not hard-piped to the riser. However, the outlets of the riser cyclones are directly connected to the inlet of the upper cyclones. In this configuration (Figure 13.5), both the first-stage and second-stage cyclones are being operated "under vacuum" and consequently minimal carry-under of reactor vapors is expected from the first-stage cyclone diplegs. For this reason, the first-stage trickle valves are not often covered with catalyst.

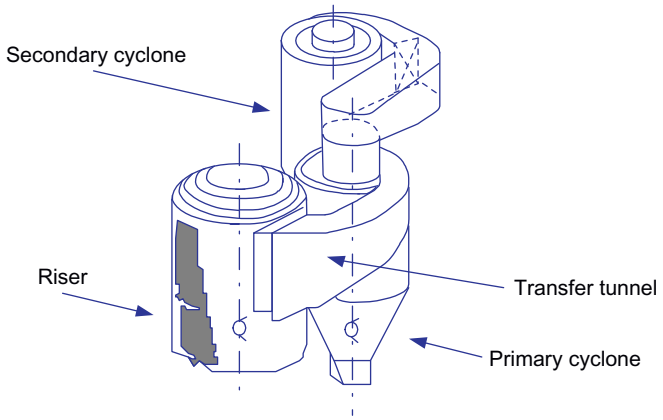


Figure 13.5: Exxon Research & Engineering configuration in KBR closed coupled cyclone.

The Shaw Group

The Shaw Group offers both "a reactor quench system" and "a closed cyclone system" to minimize post-riser reactions. In the reactor quench setup, LCO is injected at the outlets of the riser primary separation devices (Figure 13.6). The primary separation devices could be "rough-cut cyclones," or their truncated cyclones referred to as an LD^2 (linear disengaging device). The LD^2 is intended to separate catalyst from reactor vapors quicker than conventional cyclones. LCO flow rate is adjusted to reduce the temperature of reactor vapors to <950°F (510°C).

The riser separation system (RSS) often has four segments: two separation chambers with diplegs and two stripping chambers, to allow the gas to exit the device with direct connection to the four cyclones above (Figure 13.7). Gas and catalyst come up the riser and enter the separator at the top of the RSS curved surface. Catalyst is thrown into the outside wall inside the RSS and enters the two diplegs. Gas makes a "U turn" of 180° to enter the gas outlet window that communicates to the adjacent stripping chambers. Within the stripping chambers, the gas from the separation chambers enters vertically upward by way of the windows and is joined by the stripping steam and gas from below. These two chambers are not submerged in the stripper bed and thereby allow for the stripping gas to enter the chamber. The combined gas then flows to the gas outlet collector, which is located centrally, above the riser end cap. The gas outlet tube is connected to the reactor cyclones that are then connected to a plenum and the reactor overhead line. Mechanically, an expansion joint is provided in the vapor line to the cyclones to allow for thermal expansion.

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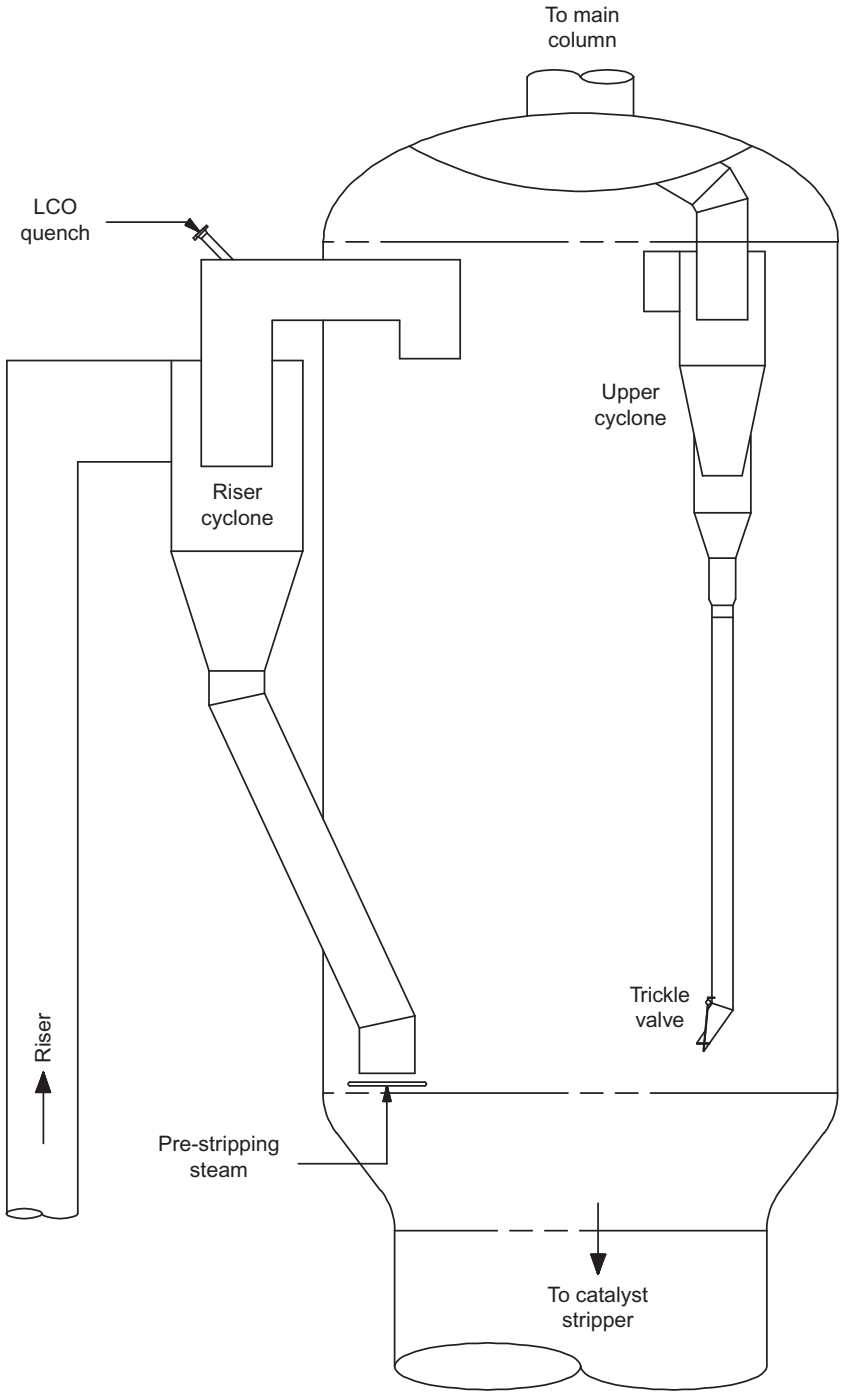


Figure 13.6: The Shaw Group external cyclone with LCO quench.

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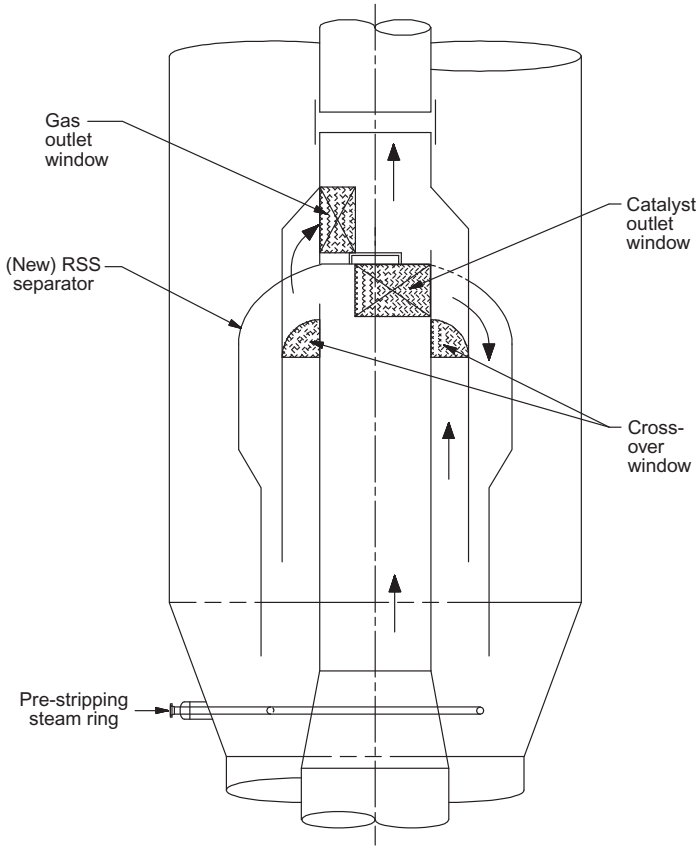


Figure 13.7: Example of a Shaw Group RSS.

CB&I Lummus' Direct Coupled Cyclones (DCC) Features

The CB&I Lummus riser termination device design consists of a two-stage reactor cyclone system (Figure 13.8). The riser cyclones (the first stage) are hard-piped to the riser. Attached to the end of each riser cyclone dipleg is a "conventional" trickle valve as shown in Figure 13.9. Each trickle valve has a small opening to prevent catalyst defluidization. At the vapor outlet of the first-stage cyclones, an opening allows entry of stripping steam/vapors and reactor dome steam. This opening is sized to allow the second-stage cyclones to be operated at a negative pressure relevant to the reactor housing pressure.

Attached to the end of the upper reactor cyclone diplegs are horizontal, counterweighted flapper valves (Figure 13.10). These valves provide a tight seal between discharging catalyst and upflowing vapors in the reactor housing.

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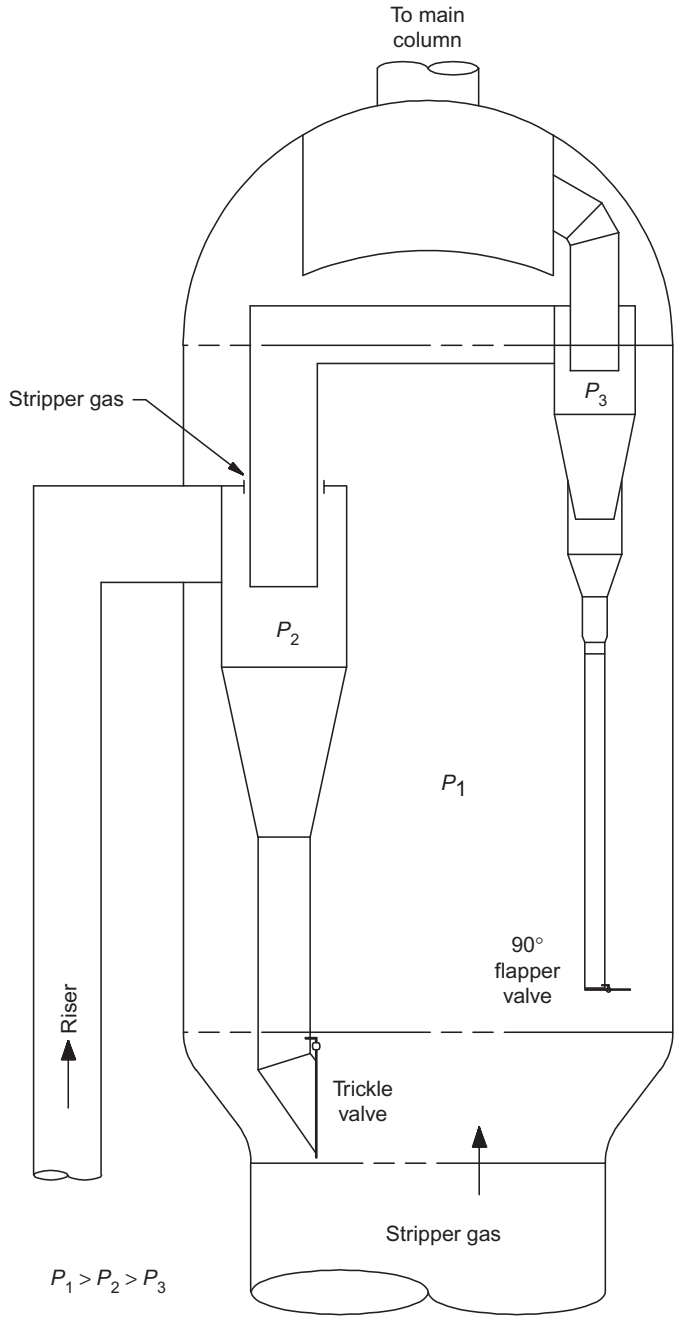


Figure 13.8: CB&I Lummus direct coupled cyclone design.

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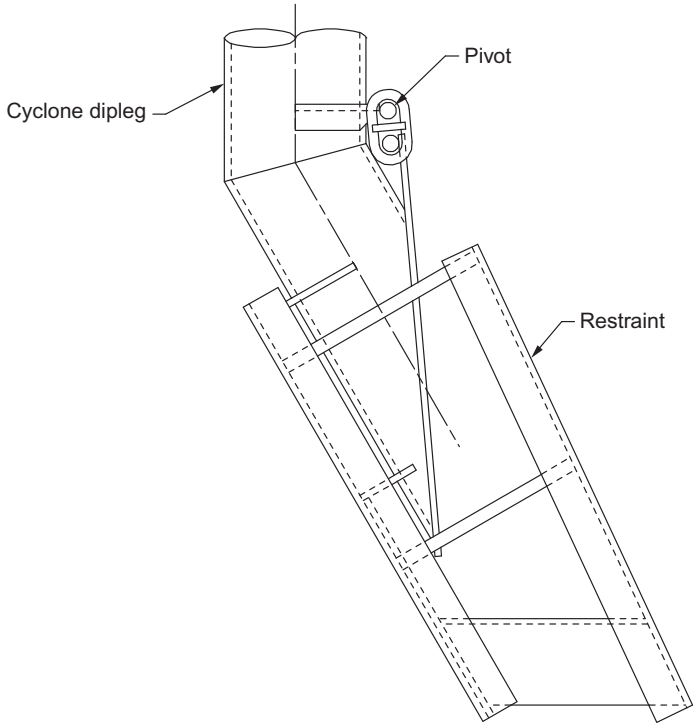


Figure 13.9: Typical trickle valve.

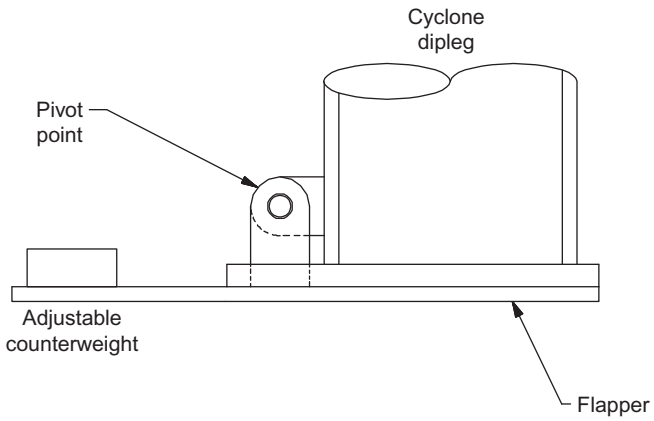


Figure 13.10: Counterweighted flapper valve.

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Feed Nozzles

Important features of a feed injection system include:

- Fine atomization of feed
- High-velocity coverage of riser cross-section
- Intimate mixing of catalyst and oil
- Rapid heat transfer from catalyst to oil
- Instantaneous vaporization of feed
- Minimizing catalyst back-mixing
- Maximizing catalytic reactions while minimizing thermal reactions.

A good feed injection system will produce:

- Small droplet size
- Efficient mixing of oil and catalyst
- Complete riser coverage.

The feed injection system has come a long way. The early designs were open pipes with no consideration for feed vaporization or catalyst/vapor mixing. Currently, FCC technology licensors offer their own version of feed injection systems. Figure 13.11 is a typical modern feed nozzle. In general, these nozzles incorporate some of the following design features:

- Steam is used to disperse and atomize the gas oil/residue feed.
- The spray pattern of the oil/steam leaving the nozzle tips tends to be flat (fan spray).
- The assembly includes multiple nozzles in a radial pattern.
- The nozzles are designed for a "medium" oil-side pressure drop, generally in the order of 50 psi (3.45 bar).

Some of the general criteria for choosing feed injection technology include:

- Total installed cost
- Dispersion steam and/or lift steam/gas requirements, including flow rate, temperature, and pressure
- Oil and steam pressure requirements
- Proven track record of operational reliability.

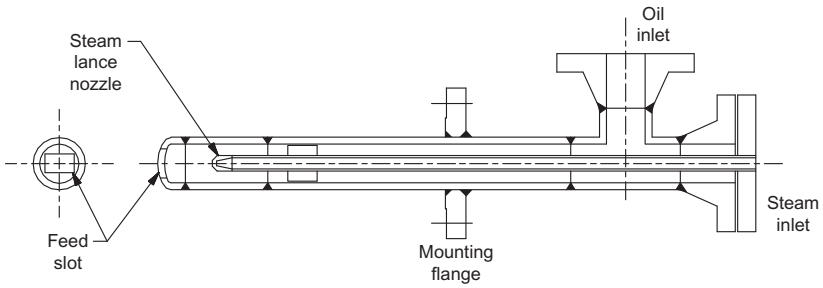


Figure 13.11: Typical modern feed nozzle (The Shaw Group feed nozzle design).

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The choice of the feed injection system should be based on the vendor's experience in similar units with similar feeds and on his yield projection and/or performance guarantee. However, it may be difficult to substantiate the guarantee when other changes are being made in the unit.

Spent Catalyst Stripper

Spent catalyst from the reactor/cyclones discharges into the stripper. Stripping steam displaces hydrocarbon vapors entrained with the catalyst and removes volatile hydrocarbons from the catalyst.

As part of optimizing the unit, the stripping steam rate should be adjusted up and down by 5%. The regenerator temperature and/or CO_2/CO ratio will be the main indicator of insufficient stripping. The test ends when there is no significant response in the regenerator temperature.

In the past several years, more attention has been given to improving the mechanical performance of the reactor stripper. Proprietary stripper designs are being offered by the FCC technology licensors in attempts to improve the catalyst/steam contact. The use of shed trays, disk/donut and grid packing has been successful. Proper design of the stripping steam distributor is very important in achieving uniform steam distribution and long-term reliability.

Air and Spent Catalyst Distribution System

Historically, combustion of coke in the regenerator has not received the same attention as upgrading the feed injection system and/or riser termination device. This is largely due to the absence of an apparent economic incentive. The thinking is that as long as the catalyst is cleaned (fully or semi), it would be difficult to justify upgrade of the air/spent catalyst distribution.

In recent years, because of stricter flue gas environmental regulations, particularly CO and NO_x emissions, more and more refiners have shown interest in improving the mixing efficiency of air and spent catalyst.

The coke burning efficiency is measured by:

- CRC and its uniform color
- CO concentration in the flue gas
- Level of afterburning
- NO_x concentration in the flue gas

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- Efficiency of SO_2-removal additive
- Stack opacity
- Catalyst loss rate
- Pressure buildup in the standpipe.

A properly designed air/spent catalyst distribution system (see Figures 1.16B, C, and 1.17) will:

- Lower coke on the catalyst
- Reduce CO concentration in the flue gas
- Lower NO_x emission
- Reduce afterburning, thus provide more air for combustion
- Improve efficiency of SO_2-reducing additive
- Minimize catalyst attrition, thus lowering the stack opacity and catalyst loss rate
- Improve pressure buildup of catalyst in the regenerated catalyst standpipe.

The above benefits become more prominent when a refiner is processing deep hydrotreated feedstock into the FCC unit, in which the regenerator bed temperature will be approximately 1,200°F (649°C), taxing the combustion efficiency.

Debottlenecking Catalyst Circulation

Any attempt to increase the unit feed rate and/or severity will generally require greater catalyst circulation rate. The unit pressure balance and the catalyst circulation limitations were covered in the section on troubleshooting (Chapter 12).

The following should be considered when debottlenecking:

- Differential pressure alarm/shutdown
- Increasing slide valve size
- Standpipes
- Catalyst selection.

Differential Pressure Alarm/Shutdown

Differential pressure shutdowns are a critical part of the unit's safety system. No attempt to lower the setting on the shutdown should be made without careful consideration. On the other hand, pressure is lost across the slide valves and costs money.

Multiple independent differential pressure alarm/shutdown switches can be installed with "two-out-of-three voting." This can satisfy the safety requirement, increase comfort factor, and gain valuable pressure drop.

Radial feed nozzles also minimize the possibility of a reversal. New valve actuators can operate more quickly and more reliably, also increasing the safety factor.

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The test run may indicate that the slide valve is open too far. Most operators prefer to keep the valve in the 40−60% range. They get nervous if the valves are open more than this. A larger valve or a larger port can be installed in the existing valve.

Standpipes

If the unit pressure balance indicates that either the pressure gain in the standpipes is inadequate or the ΔP across the slide valves is erratic, standpipe aeration and instrumentation should be examined. Redesigning the aeration systems or replacing the standpipes can gain valuable pressure head. Proper instrumentation can include independent aeration flow to each tap, flow indicators/controllers on each, and differential pressure indicators between the taps.

Beyond the standpipes, the available ΔP across the valve is affected by the pressure drop in other circuits. For the regenerated catalyst slide valve, downstream pressure is affected by:

- Feed injection system
- Riser
- Reactor cyclones
- Reactor vapor line
- Main fractionator and overhead system.

The regenerated catalyst slide valve upstream pressure is increased by:

- Increasing the regenerator bed level
- Increasing the regenerator pressure
- Increasing the 0−40 μm content of the circulating catalyst.

Debottlenecking Combustion Air

Many FCC units are constrained by the air blower, particularly during the summer months. Air blowers are commonly designed to deliver a given volume of air. However, the heat balance demands a given weight of air (oxygen). Therefore, the amount (by weight) of air pumped by an air blower decreases with:

- Increasing air blower inlet temperature
- Increasing ambient relative humidity
- Decreasing suction pressure.

Several low-cost items that can be implemented to increase the flow of air/oxygen into the regenerator are:

- Ensuring the air blower suction filters are clean
- Ensuring the pressure drop in the suction piping is not excessive

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- Ensuring the pressure drop in the air blower discharge piping system, particularly across the check valve and air preheater, is not excessive.

To deliver more air:

- Consider lowering the regenerator pressure.
- Consider lowering the regenerator catalyst bed level.
- Evaluate the trade-off between the air blower capacity and WGC capacity. Spare horsepower at one can be used to unload the other.
- Consider cooling the inlet air through the use of a chiller or suction water spray.
- Consider the use of portable air blowers during the hottest months.
- Consider oxygen injection.
- Consider a bypass around the air heater.

Other more capital-intensive modifications include installing a dedicated air blower or a booster air compressor for the spent catalyst riser. The spent catalyst riser often requires a higher back-pressure to deliver the catalyst into the regenerator than the main air blower. Therefore, less total combustion air would be available if one common blower is used to transfer spent catalyst and provide combustion air to the air distributors. The main air blower can also be upgraded to provide added capacity. This includes reducing seal clearance, increasing flow passing area, and increasing wheel tip diameter. The original equipment manufacturer (OEM) can be contacted for feasibility of this upgrade.

Regeneration

Regenerator designs have changed since most units were built. If the unit test run indicates high CRC, or if the catalyst will benefit from a lower CRC, the regenerator internals should be reviewed. If the data indicates wide temperature differences across the bed or afterburning, or if the unit has had some excursions, it needs to be examined.

The regenerator review will include spent catalyst distribution, air distribution, and cyclones. If the test run with heavy feed indicates a temperature limitation, catalyst coolers, partial combustion, or riser quench should be considered.

Flue Gas System

The FCC is usually constrained by environmental permits. If the unit undergoes significant expansion, it may lose "grandfather" protection. The environmental limits include the amount of coke burned in the regenerator and emission rates of particulates, CO, SO_x, and NO_x. Increasing the feed rate or running heavier crude can increase all of these emissions. The various options to comply with emissions of these pollutants are discussed in Chapter 14.

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FCC Catalyst

The FCC catalyst's physical and chemical properties can dictate desired feed quality, feed rate, and cracking severity. Chemical properties, such as rare earth and UCS, affect the unit heat balance and WGC loading. Physical properties, such as PSD and density, can limit catalyst circulation and flue gas emissions.

Consider reformulating the catalyst; custom formulations are routine. For example, increasing rare earth content can reduce the wet gas rate. Unfortunately, for today's exuberant rare earth surcharge, just about every refiner is reducing the rare earth concentration of the catalyst.

Unfortunately, FCC catalyst is often selected for its low price and properties rather than its ability to flow. But if it does not flow, it is not going to work well. Catalyst physical properties should be compared with those of catalysts that have circulated well. The use of various catalyst additives, such as ZSM-5, should always be employed to take advantage of market changes.

Debottlenecking Main Fractionator and Gas Plant

Debottlenecking usually results in more feed and/or higher cracking severity. Main fractionator, gas plant, and treating units must be able to recover the incremental products and treat them accordingly.

The main fractionator can be limited by several factors including:

- Heat removal limitations
- Tray flooding
- Fouling and coking.

Heat removal can be limited by several factors including:

- Fixed reboiling duties in the gas plant
- Lack of heat exchanger in the pumparound circuits
- Jet or liquid flooding in one or more sections of the main fractionator
- High bottoms temperature leading to fouling or high LCO end point
- Overhead condensing capacity.

Moving heat up the tower improves fractionation by increasing the vapor–liquid traffic. This is often limited by flooding constraints and excessive temperature in the bottom.

One way to maximize the LCO end point is to control the main fractionator bottoms temperature independently of the bottoms pumparound. Bottoms quench ("pool quench") involves taking a slipstream from the slurry pumparound directly back to the bottom of the tower, bypassing the wash section (Figure 13.12). This controls the bottoms temperature

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independently of the pumparound system. Slurry is kept below coking temperature, usually about 690°F (366°C), while increasing the main column flash zone temperature. This will maximize the LCO end point and still protect the tower.

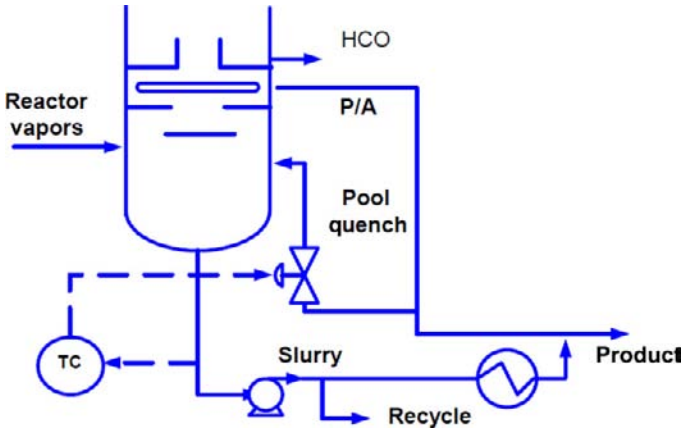


Figure 13.12: Pool quench to main column bottoms.

If the main fractionator bottoms temperature is limited, for example to 690°F (366°C), adding a "pool quench" can provide an additional 150 bpd of LCO product recovery. Assuming there are no penalties for the bottoms product quality and available cooling capacity in the upper section of the fractionator, this incremental LCO yield could be worth $1,500+ per day.

If flooding occurs in the main fractionator, increasing the bottoms pumparound rate reduces vapor loading, but it can have a negative effect on fractionation.

Normally, the economic incentive is to maximize the fresh feed rate and/or conversion, sacrificing the bottoms cut point and rate. Increasing conversion by 1.5% (through increasing the riser top temperature by 10°F (5.5°C)) provides an incremental profit, although 145 bpd of LCO is lost to bottoms.

Either high-capacity packing and/or high-efficiency, high-capacity trays can be installed. Trays in the bottoms wash section can be replaced with grid or packing. The packing has greater capacity at lower pressure drop.

The typical "packed" column has several packed sections, each consisting of a support plate, a hold-down support plate, and a liquid distributor.

In a packed column, liquid and vapor flow countercurrently and separation between the liquid and vapor phases takes place continuously. In contrast, in a column with trays, separation occurs stage-wise. In a packed column, vapor does not bubble through the liquid as in the columns with trays. Because of this and the absence of the vapor flow orifices, packed columns

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operate at a much lower pressure drop. In addition, because liquid and vapor contact in a packed column is less agitated than in a trayed column, packed columns are less likely to foam.

Satisfactory operation must be between the upper and lower limits for both liquid and vapor flow rates. At liquid rates below 0.5 GPM/ft^2 (20.4 liters/min/m^2) of packing cross section, liquid does not distribute uniformly enough to ensure thorough wetting. At liquid rates between 25 and 70 GPM/ft^2 (1,018−2,853 liters/min/m^2) of packing, the column is considered liquid-loaded and becomes very sensitive to additional liquid or vapor flow.

An adequate vapor rate produces a pressure drop greater than 0.1 in. (0.3 cm) of liquid per foot of packing. Flooding occurs when the pressure drop exceeds 1.3−2.5 in. (3.3−6.4 cm) of liquid per foot of packing. At high vapor rates, the liquid cannot flow down the column.

The liquid distributor is the most important internal structure of a packed column. The distributor strongly influences packing efficiency. It must spread the liquid uniformly, resist plugging/fouling, provide free space for gas flow, and allow operating flexibility.

Packed columns can flood prematurely. Some of the reasons include:

- Fouling (caused by precipitation, lodgment of loose material and debris), damaged packing
- Foaming
- Improper feed introduction
- Restricted liquid outlet.

In addition to changing to packing or high-efficiency trays, the tower can be unloaded by:

- Removing more heat from the pumparound returns, either by generating steam or adding coolers. This can decouple the fractionator from the reboilers in the gas concentration unit
- Reviewing the LCO product system. If some or all of the LCO is being hydrotreated, that portion can bypass the stripper if it is direct-fed to the other unit through pressure vessels. Stripping is difficult to justify and sends wet feed to the unit
- Changing the control system so stripping steam flow is proportional to LCO stripper product
- Reviewing the overhead water wash: most overhead condensers are washed continually to minimize fouling. Since multiple bundles are common, solenoids and a PLC can be used to wash one bundle at a time, say for 10 min each. This can lower the pressure drop and increase the available cooling with minimal impact
- Advanced instrumentation can be used
- If the rich oil is being returned from the secondary absorber, consider different processing.

Debottlenecking the Wet Gas Compressor (WGC)

A portion of liquid from the overhead receiver is often refluxed back to the tower; the remainder is pumped on to the gas plant. The vapor from the receiver goes to the wet gas

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compressor. The pressure for the reactor/main fractionator system is usually controlled at the compressor suction.

Improving overhead cooling will increase the wet gas compressor capacity. Excessive pressure drop or limited cooling in the overhead system prematurely limits the wet gas compressor capacity. Some of the reasons include:

- Inadequate condensing/cooling surface area
- Uneven distribution of hydrocarbon vapors and/or cooling water
- Corrosion and salt deposition
- Water coolers tend to be elevated, limiting water flow rate; consider adding a booster pump at grade
- Water outlet temperature above 125°F (51.6°C) can cause rapid fouling
- Isolation valves that "chew up" pressure drop.

In most cases, the wet gas compressor should always run at its capacity limit, especially if the reactor pressure can be lowered. Increasing the available pressure/flow to the machine often improves the FCCU's performance. There are several low-cost options to increase the compressor capacity, including the following:

- Install a large diameter main fractionator overhead vapor line, or parallel line, if the pressure drop across this line is more than 0.5 psi (0.034 bar).
- Upgrade the overhead air condensing/cooling if the pressure drop is more than 3.0 psi (0.21 bar).
- Install a properly designed online solvent or water wash, to minimize blade fouling on both the compressor and turbine.
- Ensure the spillback valves are not open.
- Consider removing external streams: if gas comes from another unit or vents from a column in the gas concentration unit, consider routing it to the interstage rather than the suction. The refinery needs to evaluate if external streams are worth recovering or whether they can be routed elsewhere.
- Ensure the suction valve is properly sized to minimize its pressure drop.
- Install an advanced surge control system.
- Verify that the flow rates of corrosion inhibitor and antifoulant are adequate for the new operating conditions.

Improving Performance of Absorber and Stripper Columns

The objective of the primary absorber/stripping towers is to maximize recovery of C_3 and heavier components while rejecting C_2 and lighter to fuel. C_3 is first absorbed and then C_2 and lighter components are stripped. Although maximizing C_3-C_4 recovery for alkylate feed is very profitable, lower recoveries are often accepted to maximize the FCC conversion and/or feed rate.

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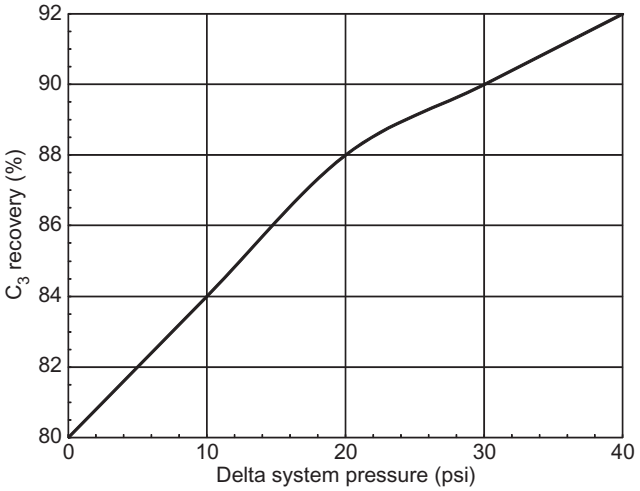


Figure 13.13: C_3 recovery versus system pressure.

Propane/propylene recovery can be enhanced by:

- *Increasing the gas plant pressure*. A 10 psi (0.69 bar) increase in absorber pressure increases C_3 recovery by 2% (Figure 13.13). However, this can reduce the wet gas compressor capacity. Fractionation efficiency decreases as the column pressure increases.
- *Reducing the operating temperature*. Consider adding an intercooler on the absorber. Minimize lean oil temperature. Consider the use of chiller. Each 10°F (5.5°C) reduction in lean oil temperature will increase C_3's recovery by about 0.8% (Figure 13.14).
- *Increasing lean oil rate*. This rate is often limited by the debutanizer hydraulic and reboiling/cooling capacity. A 50% increase in lean oil/off-gas ratio increases C_3's recovery by about 2%.
- *Removing water from the lean oil*. Installation of water draws and/or a coalescer can improve recovery. Water can become trapped in the tower and cause poor tray efficiencies, foaming, and premature flooding.
- *Minimizing over-stripping*. Over-stripping can start a flywheeling effect with the absorber. A 10% cut in stripping rate can increase C_3's recovery by 0.8% (see Figure 13.15).

Debottlenecking Debutanizer Operation

As the gasoline Reid vapor pressure (RVP) is reduced, the operation of the debutanizer becomes more critical. The allowable vapor pressure in gasoline makes it difficult to prevent

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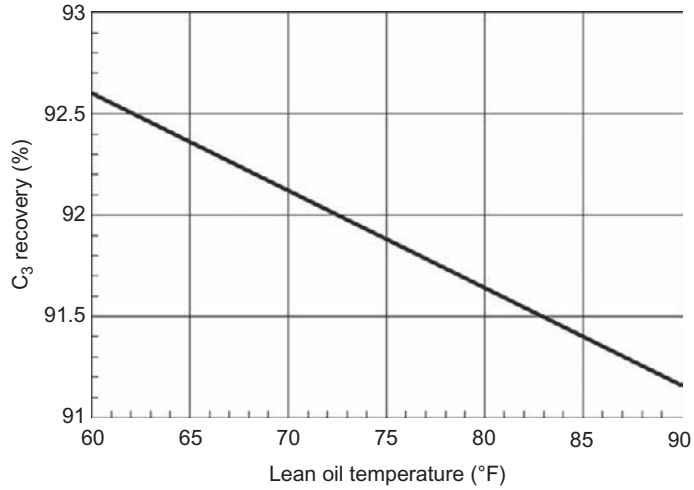


Figure 13.14: C_3 recovery versus lean oil, °F.

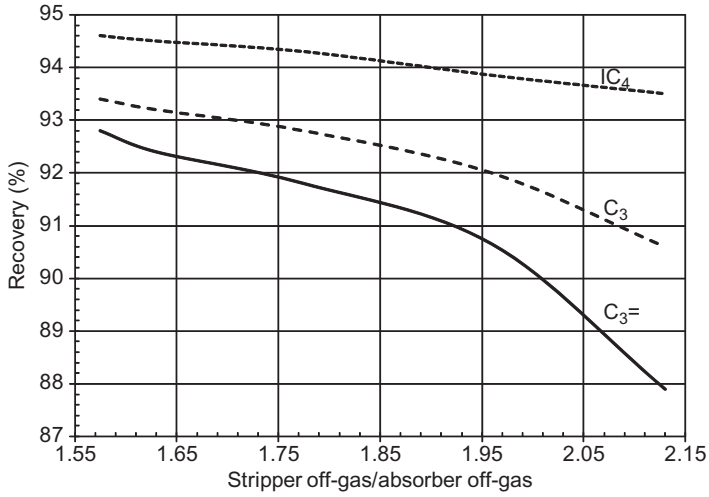


Figure 13.15: Light ends recovery versus stripper/absorber off-gas ratio.

heavy ends in the alkylation feed. This can limit the production of gasoline without sacrificing alkylation. This limitation is often from insufficient overhead cooling and reboiling:

- Optimum debutanizer feed preheat temperature can optimize column loading. Increasing preheat temperature reduces reboiler duty and loading in the stripping section of the tower. Decreasing preheat temperature decreases overhead condensing duty and loading in the rectifying section. Adding an exchanger on the stripper bottoms can make this a controllable variable.

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- ΔP indicators should be installed on both the top section and the bottom section.
- Optimize the operating pressure to balance reboiling, condensing, and loading. Consider floating pressure control. With tightening vapor pressure specifications, the debutanizer is an excellent candidate for this type of control. Floating pressure will unload the tower and give better separation.
- If slurry pumparound is the heat medium, consider HCO pumparound to minimize fouling.
- Revamp the tower internals with high-capacity trays or packing.
- If the receiver vent is in continuous service, route it back to the wet gas compressor interstage drum rather than to the suction. Consider adding a chiller on the vent gas.

Instrumentation

Additional analyzers should be considered. Temperature and pressure are no longer adequate to control distillation columns to tight specifications. Consider chromatographs on the overhead streams. One chromatograph with multiple sample streams can be adequate for most services. Ensure that qualified service is available locally.

If the unit does not have a DCS, a debottlenecking project is the right time to justify it. If it does have a DCS, this is the time to justify advanced control projects.

- A DCS will give better control of the unit and stay closer to constraints. Operating closer to constraints is what optimization and debottlenecking are all about.
- A DCS has trending and reporting ability. Data can be dumped to a spreadsheet program and variables plotted against one another.
- A DCS is a valuable troubleshooting tool.
- A DCS with a host computer allows moving on to advanced control and multivariable control. The unit is sensitive to day/night temperature swings and the multivariable control can track ambient changes.

Many case histories are available on changing over to a DCS while the unit is operating or during a unit turnaround.

Utilities/Off-sites

Tankage/Blending

Significant debottlenecking in the FCC will affect the tank farm and blending system. One must ensure the storage tanks can handle the increased product yields and changes in the quality. The blending department needs maximum warning about changes in gasoline components.

Steam/Boiler Feed Water

Adding, for example, a catalyst cooler may back a boiler down, or it may require more boiler feed water and a home for the steam. New feed nozzles may require more steam.

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Retrofitting the riser termination device will often require more steam during unit-ups and outages. One must check the availability of the steam system to deliver the required steam on demand. A cogeneration unit can be an attractive option.

Sour Water/Amine/Sulfur Plant

Running heavier crude to the FCC will convert more of the sulfur in the refinery crude to H_2S. Therefore, sour water stripping and sulfur plant capacity need to be checked.

Relief System

Increasing the wet gas compressor capacity and increasing duties through the gas plant can impact the flare system.

Fuel System

Processing heavier feedstock will make more fuel gas and adversely affects the fuel gas composition. One must verify that, for example, increased hydrogen content will not impact any heaters. Depending on the header design, it could be a problem if all goes to the same branch of the header.

Summary

Cat cracking has been, and will continue to be, a big "money maker" for the refining industry. It is unlikely that any new cat crackers will be built (especially in the United States) in the near future. Therefore, emphasis will be placed on finding ways to improve the operational reliability and profitability of the existing FCCs.

Performance of an FCC unit is often maximized when the unit is operated against multiple constraints simultaneously. It is essential that the specified constraints allow for minimum "comfort zones." An operator-friendly advanced control program, coupled with proper selection of catalyst formulation, would allow optimizing the performance of the unit on a daily basis.

This chapter provides many no-to-low cost recommendations that, once implemented, can provide cost-effective added value to the operation of the FCC unit. Examples of such items include tips on debottlenecking the air blower, wet gas compressor, and catalyst circulation. Also included in this chapter are discussions on the latest technologies regarding the feed injection system, riser termination devices, catalyst stripping, and air/spent catalyst distribution. Prior to implementing any new technologies, it is critical that the objectives

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and the limitations of the unit are clearly defined to ensure the expected benefits of the new technology are realized.

The selected technology must match the mechanical limitations of a given cat cracker. All the technologies that were discussed in this chapter have been commercially proven; therefore, the choice must include the total installed costs, as well as the projected benefits to the refinery.

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CHAPTER 14

Emissions

FCC has the flexibility to process various feedstock qualities. FCC feedstock properties directly or indirectly impact the operation of the regenerator. The feed quality and its feed rate affect the combustion/carrier air rate and any supplemental oxygen flow rate to the regenerator for achieving "stable" catalyst regeneration. The changes in the air rate impact the catalyst loss rate from the regenerator, as well as the amount of other pollutants. This chapter discusses options available to a refiner to regulate and to control the discharge of these pollutants to the atmosphere to levels that meet and/or exceed the regulatory requirements. It should be noted that the mode of catalyst regeneration (full or partial combustion) will greatly influence the selection of "right" technologies to comply with the environmental standards.

Combustion of coke in the FCC regenerator produces several atmospheric pollutants that need to be controlled. These potential pollutants include carbon monoxide (CO), sulfur oxides (SO_2/SO_3), nitrogen oxides (NO_x), nickel compounds (Ni), particulate matter (PM), as well as opacity.

In the United States, there are presently three major different regulatory requirements that affect the FCC unit flue gas emission controls (some local districts also have regulations). These are:

1. Continuing application of New Source Performance Standards (NSPS)
2. Implementing Maximum Achievable Control Technology (MACT II)
3. Implementing the EPA enforcement actions and Consent Decrees.

Each of the above regulatory requirements impacts the selection of the emission control technology for a given refinery.

New Source Performance Standards

NSPS for FCC units were established for the control of particulate matter, carbon monoxide, and sulfur dioxide emissions. These standards apply to FCC units constructed

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after January 17, 1984, as well as existing units that trigger their applicability with either of the following occurrences:

- Major FCC modifications (reconstruction), wherein cumulative investments over a 2-year period exceed 50% of the fixed capital cost of the facility replacement
- Changes in equipment or operation, which increase the rate to the atmosphere of any pollutant to which a standard applies.

NSPS does not set explicit limits on NO_x emissions from FCC regenerators. However, site- and situation-specific NO_x limits may be established at the time the FCC unit is permitted or modified.

Maximum Achievable Control Technology (MACT II)

The EPA's National Emission Standards for Hazardous Air Pollutants (NESHAP) for catalytic cracking units, catalytic reforming units, and sulfur recovery units became effective on April 11, 2002. The existing affected units had to be in compliance by April 11, 2005. This rule is also known as Refinery MACT II.

In regard to FCC units, the MACT II metals emission limitations provide refiners four options to comply with Hazardous Air Pollutants (HAP) not subject to NSPS for PM in 40 CFR 60.102 (Table 14.1). For organic HAP requirements, carbon monoxide emissions (CO is surrogate for organic hydrocarbon emissions) must not exceed 500 ppmv (dry basis).

The MACT II particulate matter and carbon monoxide limits will be the same as the current NSPS requirements, but will apply to the FCC units that were previously grandfathered with respect to NSPS.

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Table 14.1: Metal HAP Emission Limits for Catalytic Cracking Units.

Table 1 to Subpart UUU of Part 63. As stated in Section 63.1564(a) (1), you shall meet each emission limitation in the following table that applies to you.
For each new or existing catalytic cracking unit, you shall meet the following emission limits for each regenerator vent.

1. **Subject to NSPS for PM in 40 CFR 60.102.**
   PM emissions must not exceed 1.0 kilogram (kg) per 1,000 kg (1.0 lb/1,000 lb) of coke burn-off in the catalyst regenerator; if the discharged gases pass through an incinerator or waste heat boiler in which you burn auxiliary or in supplemental liquid or solid fossil fuel, the incremental rate of PM emissions must not exceed 43.0 grams per gigajoule (g/GJ) or 0.10 pounds per million British thermal units (lb/million Btu) of heat input attributable to the liquid or solid fossil fuel; and the opacity of emissions must not exceed 30%, except for one 6-min average opacity reading in any 1-h period.
2. **Option 1: NSPS requirements not subject to the NSPS for PM in 40 CFR 60.102.**
   PM emissions must not exceed 1.0 kg/1,000 kg (1.0 lb/1,000 lb) of coke burn-off in the catalyst regenerator; if the discharged gases pass through an incinerator or waste heat boiler in which you burn auxiliary or supplemental liquid or solid fossil fuel, the incremental rate of PM must not exceed 43.0 g/GJ (0.10 lb/million Btu) of heat input attributable to the liquid or solid fossil fuel; and the opacity of emissions must not exceed 30%, except for one 6-min average opacity reading in any 1-h period.
3. **Option 2: PM limit not subject to the NSPS for PM in 40 CFR 60.102.**
   PM emissions must not exceed 1.0 kg/1,000 kg (1.0 lb/1,000 lb) of coke burn-off in the catalyst regenerator.
4. **Option 3: Ni lb/h not subject to the NSPS for PM in 40 CFR 60.102.**
   Nickel (Ni) emissions must not exceed 13,000 milligrams per hour (mg/h) (0.029 lb/h).
5. **Option 4: Ni lb/h 1,000 lb coke burn-off not subject to the NSPS for PM in 40 CFR 60.102.**
   Nickel (Ni) emissions must not exceed 1.0 mg/kg (0.001 lb/1,000 lb) of coke burn-off in the catalyst regenerator.

EPA Consent Decrees

In 2001, the EPA began entering into binding consent decrees with several refiners to significantly reduce the amount of SO_2 and NO_x emissions from FCC units. The limits of 25 ppm for SO_2 and 20 ppm for NO_x are considered achievable.

Control Options

The following sections discuss each pollutant in detail and practical options to control and minimize their emissions to atmosphere.

CO Emission

Catalyst leaving the reactor stripper typically contains 0.5−1.3 wt% coke. This coke has about 7% hydrogen, 93% carbon, with traces of organic sulfur and nitrogen compounds. A typical

bubbling bed regenerator design has two zones: a rather high-density (25−40 lb/ft^3, 400−641 kg/m^3) fluidized bed, commonly referred to as the dense bed, and a dilute phase zone often known as freeboard region. Combustion products from burning coke and some entrained catalyst are constantly conveyed out of the dense bed into the freeboard region. The entrained catalyst returns to the dense bed via cyclone diplegs. The flue gas velocity has a significant impact on the amount of catalyst being entrained in the dilute phase region.

The burning of carbon in the regenerator can be in either partial or full combustion. In partial combustion, air rate to the regenerator is controlled either to achieve a certain concentration of CO in the regenerator flue gas or to maintain a desired regenerator bed temperature while controlling a "respectable" level of CRC. The final concentration of CO is achieved through operation of CO boiler(s). In full combustion, often the employment of a CO promoter additive and maintaining excess oxygen in the flue gas are used to ensure CO emission of $<$500 ppm.

In full combustion, many factors affect the CO level in the regenerator flue gas. These include feed quality, catalyst properties, operating conditions, and effectiveness of the air and spent catalyst distribution systems. Regenerator dense bed temperature, regenerator catalyst bed level, catalyst/flue gas residence time in the regenerator, flue gas excess oxygen, and the amount/type of CO promoter are examples of operating parameters that can affect CO emission. Directionally, the CO in the flue gas can be reduced by a higher regenerator bed temperature, higher feed preheat temperature, longer catalyst/flue gas residence time in the regenerator, higher regenerator catalyst bed level, greater concentration of coke on the spent catalyst, and higher flue gas excess oxygen. A "heavier" FCC feedstock and an active fresh catalyst will increase the regenerator bed temperature and thus promote the combustion of CO to CO_2.

The evenness of the air/spent catalyst mixing is extremely critical in ensuring CO compliance, especially with the deep hydrotreated FCC feedstock. There is often a trade-off between CO and NO_x levels. Higher CO concentration often lowers the NO_x and vice versa.

For units operating in partial combustion, the concentration of CO in the CO boiler stack depends on the design of CO boiler, firebox temperature, concentration of incoming CO, stack excess oxygen, residence time of flue gas in the CO boiler, and mechanical design of the CO boiler.

SO_x Emission

Approximately 5−12% of the FCC feed sulfur is converted in the riser and embedded with the coke on catalyst. The factors affecting concentration of this coke-laden sulfur depend on the FCC feed sulfur concentration, type of sulfur species, and reactor−regenerator operating conditions. Combustion of this sulfur-laden coke produces more than 90% SO_2, with the remainder being largely SO_3.

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Depending on the required amount/concentration of SO_2 in the flue gas, refiners often employ catalyst additive or flue gas scrubbing. If the overall objectives are to reduce sulfur in the FCC products (gasoline and LCO) as well as enhancing the quality of the FCC feed, deep hydrotreating of the gas oil feed will also reduce SO_2 emission significantly. In this scenario, the SO_2 emission of <25 ppm can be achieved solely with deep hydrotreating and/or with addition of SO_2-reducing catalyst.

SO_2-Reducing Additive

In FCC units in which the concentration of the SO_2 in the regenerator flue gas is <750 ppm, it is usually cost-effective to use SO_2-reducing catalyst additive to meet the SO_2 emission requirements. The additive is injected separately into the regenerator. The three key ingredients of these additives are magnesium oxide (40–60%), cerium oxide (12–16%), and vanadium oxide (2–5%). In the regenerator, cerium oxide promotes reaction of SO_2 to SO_3. Magnesium captures SO_3 in the regenerator (oxidizing atmosphere) and releases sulfur as H_2S in the reactor (reducing atmosphere). A reliable online SO_2 analyzer will ensure that a sufficient quantity of additive is injected. Operating conditions of the regenerator, especially partial versus full combustion and excess oxygen level, will greatly influence the additive's effectiveness. Also critical to pickup efficiency of the additive is the effectiveness of air/spent catalyst distribution in the regenerator. The FCC units that use the SO_2-reducing additive often limit to 10% of total addition of the fresh catalyst + additive.

Flue Gas Scrubbing

The wet flue gas scrubbing process is rather simple, forgiving, and commercially proven despite being rather expensive both in initial investment and its operating costs. Nevertheless, it is extremely effective in removing both SO_2/SO_3 and particulate matter.

Wet gas scrubbing systems are devices that use a liquid (generally water and caustic) to remove particulate and gaseous pollutants. All designs attempt to provide good liquid-to-flue gas contact to achieve high removal efficiency (>95%). Wet gas scrubbers saturate the flue gas stream, thereby creating a water vapor plume, as well as a waste water stream blowdown that needs to be treated prior to its discharge. Wet gas scrubbing is extremely effective in neutralizing the SO_2, while removing SO_3 and catalyst particles.

About 95% of flue gas scrubbers in the FCC application are nonregenerative designs. The majority of the nonregenerative units use sodium hydroxide (caustic) solution to neutralize SO_2. Other alkaline agents such as soda ash, magnesium hydroxide, calcium carbonate (limestone), or calcium oxide (lime) can also be used. There are also several FCC flue gas scrubbers that use once-through seawater to remove SO_2 and SO_3 by absorption with bicarbonate in the seawater.

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The regenerative systems use an alkaline reagent solution, or proprietary amine solution, to capture SO_2. The reagent captures the SO_2 and is then regenerated in a separate process unit, which produces fresh reagent and an SO_2-rich off-gas. The SO_2-rich stream can be processed in either a sulfuric acid plant or the refinery's sulfur recovery unit. It should be noted that the installed cost of the regenerative system can be easily more than twice the nonregenerative design.

The two major FCC flue gas scrubbing technology providers are Belco Technologies Corporation (a DuPont Company) (Figure 14.1) and Hamon Research—Cottrell (HRC). HRC is the licensor of the ExxonMobil wet flue gas scrubbing system (Figure 14.2).

Some of the key parameters impacting the design and performance of the wet flue gas scrubbers include the following:

- Inlet particulate mass rate (normal condition, upset condition, and end of run)
- PSD (particle size distribution) of incoming catalyst particles
- Inlet temperature
- Reagent selection
- Available pressure at the scrubber inlet
- Pressure rating of the system upstream of the scrubber, such as an existing CO boiler and its ability to withstand additional back pressures imposed by the scrubber
- Concentration of inlet SO_2 and SO_3
- Flue gas composition
- Choice and sources of the makeup water
- Desired SO_2/SO_3 and particulate removal efficiencies
- Required utilities
- Purge treatment system design.

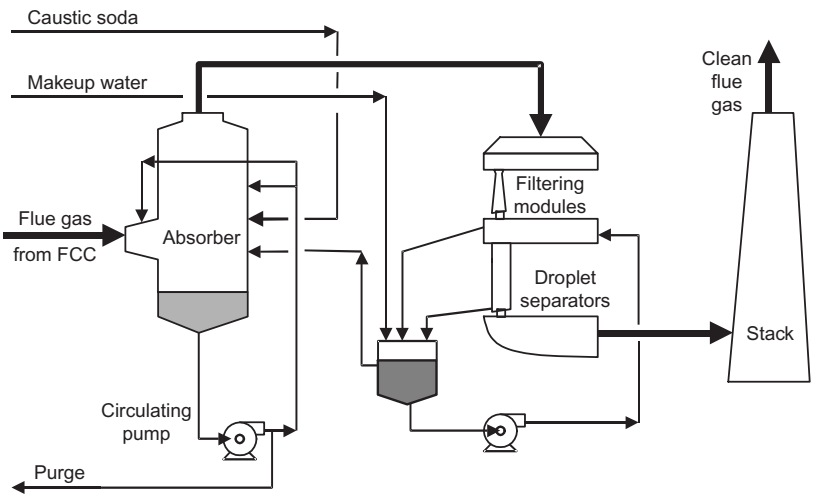


Figure 14.1: Schematic of the "BELCO EDV® wet gas scrubbing system."

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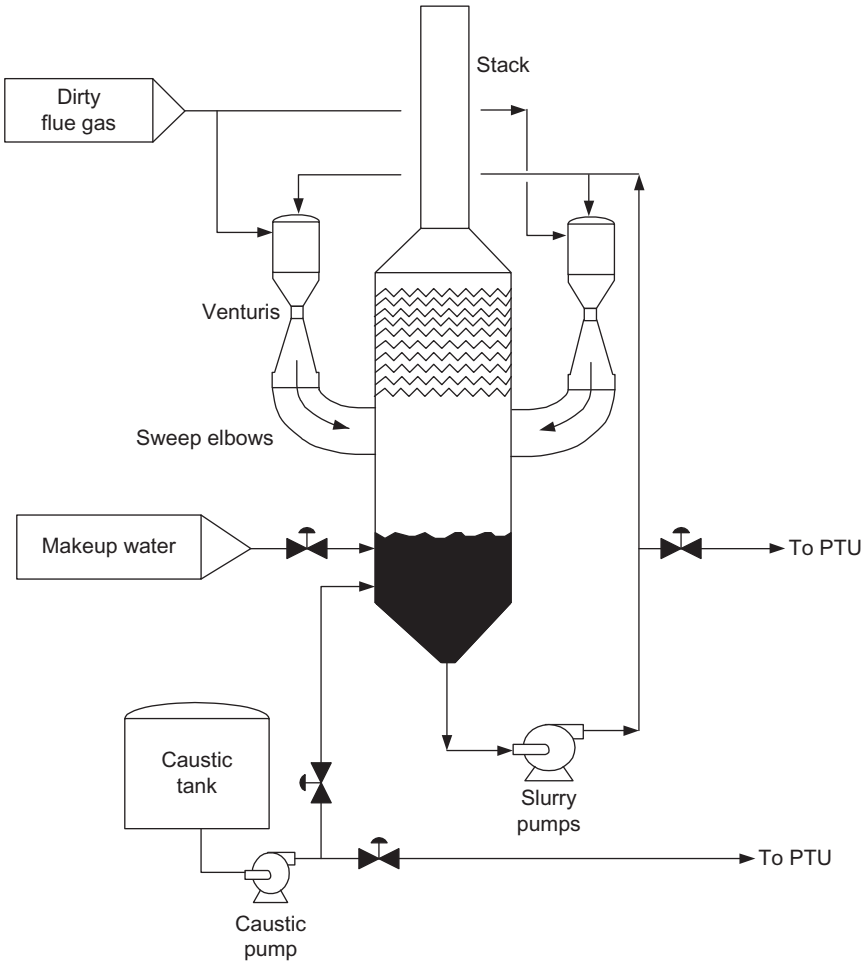


Figure 14.2: Schematic of HRC's ExxonMobil design of wet gas scrubber (*PTU = purge treatment unit*).

Particulate Matter

Particulate emission limits are often expressed in units of milligrams per normal cubic meter (mg/Nm^3) of the flue gas. EPA's unit of measurement is pounds of particulate matter per 1,000 pounds of coke burned. Depending on the mode of catalyst regeneration and the CO_2/CO ratio, 1 pound of particulate per 1,000 pounds of coke burned is about 95−125 mg/Nm^3.

The concentration of FCC catalyst leaving the regenerator cyclones is usually in the range of 0.08−0.15 grains of catalyst per actual ft^3 (gr/acf) of flue gas. The compliance requirements for the amount of particulates (catalyst and noncatalyst particles) being emitted to atmosphere is often expressed as function of the amount of coke being burned in

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the regenerator. The requirement for particulate emission varies among the refiners and regulating authorities. The most common criteria is 1 pound of particulate emission per 1,000 pounds of coke burn. In some instances, this requirement is 0.5 pound of particulate per 1,000 pound of coke burn or less.

About 90% of FCC units employ some types of tertiary separation devices in the regenerator flue gas system to remove residual particles. Some of the most common options practiced are:

- Third-stage/fourth-stage cyclone systems
- Wet flue gas scrubbing
- Dry electrostatic precipitator.

Third-Stage/Fourth-Stage Separator

The third-stage separator (TSS) can consist of several "conventional" large diameter cyclones that are being offered by the traditional cyclone vendors such Buell, Emtrol, and Van Tongeren. The TSS can be combined with an underflow catalyst filtering system. There are also TSS designs/technologies that use "smaller" cyclones which are being offered by companies such as KBR, Shell Global Solutions (SGS), and UOP. These offerings claim to achieve <1 pound of particulates per 1,000 pounds of coke burn-off. However, I do not have experience with any of these designs that offer a sustainable performance efficiency of achieving 0.5 lb/1,000 lb or less. Therefore, the commercially proven technologies to achieve <0.5 lb/1,000 lb particulate emissions are the use of flue gas scrubbing, ESP, or pulse-jet filtration such as the Pall GSS (gas solid separation) filter.

Some of the factors that affect performance of the TSS unit are:

- PSD (particle size distribution) of inlet catalyst
- Number and configuration of cyclones
- Uniform distribution of flue gas
- Cyclone velocities
- Design of the critical flow nozzle
- Design of fourth-stage and/or catalyst recovery hopper.

Dry Electrostatic Precipitator

The ESP employs high-voltage electrodes to impart a negative charge to the catalyst particles entrained within the flue gas (Figure 14.3). These negatively charged particles are then attracted to a grounded collecting surface (collecting plates), which is positively charged. The particles deposit on the collecting plates. At periodic intervals, the plates are "rapped," causing the particles to fall into the hoppers. The negatively charged rigid discharge electrodes are centered between the collecting surfaces and supported from high-voltage insulators.

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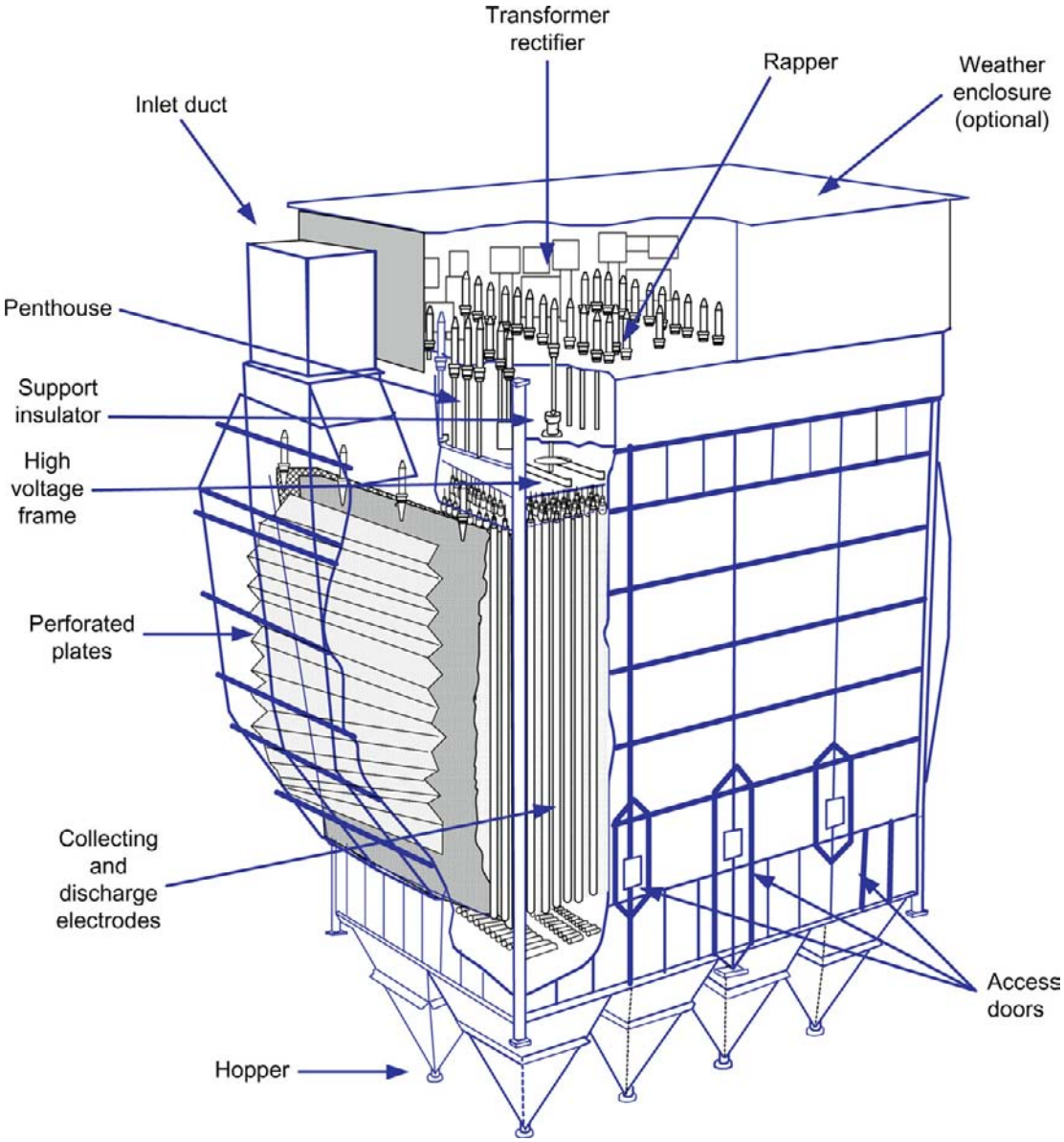


Figure 14.3: Typical Electrostatic Precipitator.

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Particle resistivity, the ability to accept a charge, plays a key role in the collection efficiency of the ESP. If a particle is resistive to receiving an adequate charge, the particle resistivity needs to be modified or the ESP treatment time needs to be increased. Some of the key factors that would directionally lower the catalyst's resistivity are:

- Higher inlet temperature
- Higher concentration of metals on the catalyst
- Higher rare earth concentration in the catalyst
- Higher carbon on the catalyst
- Ammonia injection
- Moisture content.

The design and performance of an ESP also depends on:

- Inlet catalyst loading
- Superficial flue gas velocity inside the ESP
- Catalyst particle size distribution
- Number of gas passages per chamber
- Collecting electrode spacing
- Total treatment length
- Treatment time
- Discharge electrode type, quantity, and spacing
- Electrical sectionalization (number of fields in series)
- Hopper volume, heater capacity, and level detection.

Sintered Metal Pulse-Jet Filtration

Another option to comply with particulate matter emission ($PM_{2.5}$ and PM_{10} limits) is to employ barrier filters (such as Pall Corporation's PSS® cylinders) using sintered stainless steel or silicon carbide filter elements.

The filter medium provides a surface on which a cake of particles forms. This particle layer will continue to build until a predetermined pressure drop. This pressure drop is a function of cake thickness and compressibility. A reverse flow of clean gas (blowback) is then introduced to dislodge the filter cake. The dislodged solids are purged from the filter system, where they may be returned directly to the process for reuse or removed from the process stream and dispatched to a collection unit.

These high-temperature filter systems can operate up to 1,472°F (800°C) using iron aluminide composite alloy, although other alloys (such as the 300 series sintered stainless steel PSS® filter elements) are used at lower operating temperatures. These filter systems employ online blowback cleaning with plant air (Figure 14.4).

These filters can be installed in the place of a TSS. They can also be installed on the TSS underflow flue stream which is typically 3−6% of the total flue gas flow (Figure 14.5).

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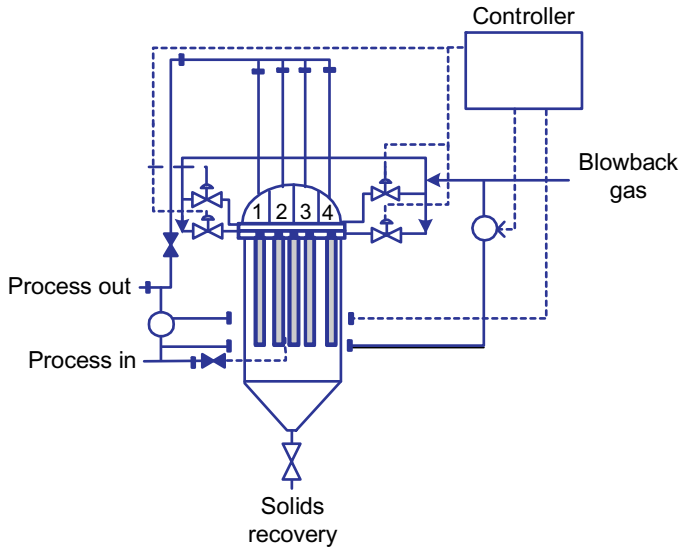


Figure 14.4: Typical PSS® blowback filter configuration (*courtesy of Pall Corporation*).

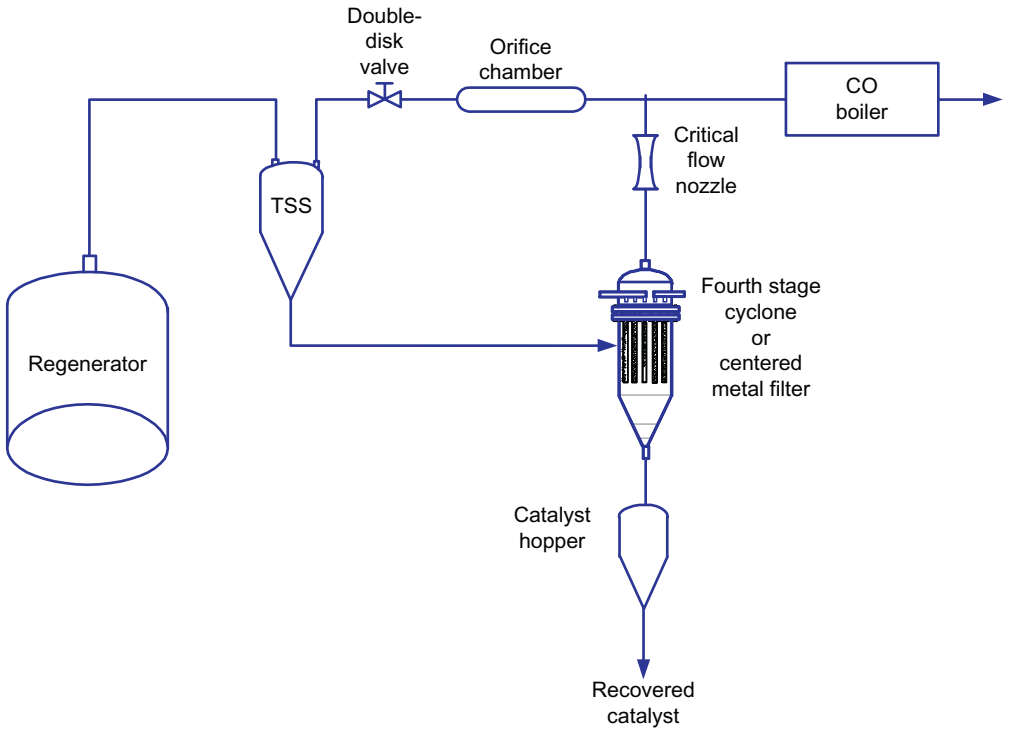


Figure 14.5: Example of filter installed in place of a fourth-stage cyclone.

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NO_x

NO_x, by definition, is NO and NO_2. In the FCC regenerator operating in full combustion, over 90% of NO_x is formed as NO with the remainder as NO_2 and N_2O. The two main ways that NO_x can be formed are thermally and chemically. Thermal NO_x is formed from fixation of nitrogen in the combustion air ($N_2 + O_2 \rightarrow 2NO$). The rate of formation of thermal NO_x is a function of temperature (>1,500°F or 815°C), oxygen concentration, and residence time. Depending on the FCC unit regenerator design, catalyst stripper performance, and regenerator bed temperature, a fraction of the NO_x in the regenerator flue gas can be thermally produced.

Chemical or fuel NO_x is produced from combustion of nitrogen compounds in the FCC regenerator operating in full combustion. Approximately 50% of feed nitrogen is converted and deposited as coke on the spent catalyst entering the regenerator. In full combustion mode of catalyst regeneration, about 95% of these nitrogen compounds are directly or indirectly converted to elemental nitrogen (N_2) with the remaining 5% becoming nitrogen oxides such as NO. In partial mode of catalyst regeneration, due to the absence of excess oxygen, the NO formation is minimal. Instead, the regenerator flue gas contains intermediate nitrogen compounds such as ammonia and hydrogen cyanide.

Feedstock Quality

Feedstock quality, operating conditions, and mechanical hardware impact concentration of NO_x in the FCC flue gas stack.

FCC feedstock quality impacts NO_x emission both directly and indirectly. For example, deep hydrotreating of the FCC feedstock will reduce the NO_x emission by removing the organic nitrogen compounds in the feedstock. Gas oil feedstock with a higher percentage of coker gas oil or residue tends to produce a greater amount of NO_x, especially since they adversely impact the performance of catalyst stripping and/or catalyst regeneration.

Operating Conditions

Adjusting some of the FCC operating conditions/practices can marginally reduce NO_x emission. These parameters include reducing excess oxygen in the flue gas, lowering the regenerator bed temperature, and eliminating/minimizing the platinum-based CO promoter. Through these adjustments, one can lower the NO_x.

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Catalyst Additives

The catalyst additives are solid catalyst particles that can be used to reduce NO_x emission in full burn catalyst regeneration. Their effectiveness can vary from no reduction up to 50% reduction. The mechanical design of the regenerator/internals and the FCC feedstock quality are the key parameters influencing the performance efficiency of these additives.

The most effective NO_x additives use copper as the reducing element. Copper can increase the FCC gas yields by about 10%. The hydrogen fraction of the absorber off-gas can be easily doubled with the use of these additives. The regenerator afterburning and the CO emission can also increase. In addition, the effectiveness of an SO_2-reducing additive can be adversely affected by the use of these NO_x-reducing additives.

On the positive side, the trial of these additives (only in full burn regenerators) does not require any capital expenditure. Their performance can be determined rather quickly, usually in less than 60 days. In addition, there is a limit on the additive cost (kick-out factor). This factor is \$10,000 per ton of NO_x removal, or 1.8 pounds of NO_x removal per pound of additive used.

Mechanical Hardware

Since NO_x is produced in the regenerator, one would expect that modifying how the spent catalyst and combustion air mix should reduce unnecessary NO_x generation.

It is my experience that the concurrent intimate mixing of the spent catalyst and combustion/lift air produces a greater amount of NO_x than if the spent catalyst and air were being mixed in a countercurrent approach.

Selective Catalytic Reduction

Selective catalytic reduction (SCR) is a proven process that can lower the NO_x to $<$20 ppm. A typical SCR unit uses a solid catalyst, containing vanadium/tungsten oxides coated on a titanium substrate. The catalyst system can be of honeycomb, metal plate, or corrugated design. Ammonia is used as part of neutralizing NO, according to the following chemistry:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \tag{14.1}$$

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \tag{14.2}$$

The "ideal" flue gas operating temperature is usually between 550°F and 750°F (288°C and 399°C). The process often requires a minimum of 1% excess oxygen in the flue gas for the reaction to proceed to completion. The proper design of the ammonia injection system is critical for complete mixing in the flue gas steam.

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The following factors affect the effectiveness of the SCR process:

- Integration of the SCR unit into the existing flue gas system can have a noticeable impact on the overall project costs
- Residence time required for SCR reaction to occur
- Control of allowable ammonia slip
- Concentration of SO_2/SO_3 in the flue gas can cause catalyst fouling
- Premature plugging of the catalyst bed with very small FCC catalyst particles.

The advantages of SCR are very high NO_x removal (as much as 97%) with less ammonia slip (<10 ppm). Disadvantages include safety concerns with storage and handling of ammonia, high capital costs, high operating conditions, and a higher flue gas pressure drop, especially if the catalyst bed gradually gets plugged. Additional disadvantages are requirements of a large plot space and the potential for sulfur to precipitate as ammonium bisulfate.

Selective Noncatalytic Reduction

The selective noncatalytic reduction (SNCR) process can be used to reduce NO_x emission. Ammonia (NH_3), or 50% urea solution, $CO(NH_2)_2$, is injected into the hot flue gas, using air or steam as a carrier gas. There are two commercial SNCR processes in the marketplace:

1. NO_xOUT® process from Fuel Tech Inc., which uses a 50% urea solution
2. Thermal DeNOX™ from EMRE, which uses ammonia and hydrogen.

The NO_xOUT process, using urea solution, is licensed by Fuel Tech Inc. The operating temperature "window" is from 1,800°F to 2,000°F (982°C and 1,093°C). The process typically achieves 20−60% NO_x reduction.

The following items affect the performance of the NO_xOUT® process:

1. Temperature
2. Boiler design
3. Residence time within the temperature window
4. Flue gas velocity/direction
5. Baseline NO_x concentration.

At very high furnace temperatures, the performance is decreased by competing reactions that either consume the urea solution or lead to NO_x formation. Compressed air is often used as the carrier gas for atomizing the urea solution. Ammonia slip can be excessive if the urea distribution is not optimum.

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When urea is used, it first decomposes to ammonia. The overall reaction is:

$$CO(NH_2)_2 + 2NO + \frac{1}{2}O_2 \rightarrow 2N_2 + CO_2 + 2H_2O \quad (14.3)$$

This reaction favors good mixing and adequate residence time. SNCR tends to work best in the temperature range of 1,800−2,000°F (982−1,093°C). Therefore, this process can be applicable for FCC units that employ CO boilers and/or a fired furnace in their flue gas system.

The thermal DeNOX™ process uses ammonia, as well as hydrogen gas, as an additive to allow the NO_x reduction to proceed at operating temperatures in the range of 1,250−1,350°F (677−732°C).

The overall chemistry of the reaction is:

$$NO + NH_3 + \frac{1}{2}O_2 + 2H_2O + \frac{1}{2}H_2 \rightarrow N_2 + 4H_2O \quad (14.4)$$

The NO_x removal efficiency is expected to be in the range of 20−40%. However, with the use of hydrogen gas as a reducing agent, the removal efficiency is *claimed* to approach approximately 70%. The mixing efficiency of ammonia, the flue gas temperature, the flue gas excess oxygen content, the flue gas residence time, and ammonia slip influence the removal efficiency of this process.

LoTOx™ Technology

LoTOx™ Technology is available for refinery applications from Belco Technologies Corporation (a DuPont Company) under license from Linde Industrial Gases (formerly BOC Gases). The LoTOx™ System is an oxidation process in which ozone (O_3) is injected into the flue gas line to oxidize insoluble NO_x (NO and NO_2) into water-soluble compounds such as N_2O_5. These reactions must occur at temperatures <300°F (<149°C). These oxides then react with the water content of the flue gas to form nitric acid. In a typical caustic-soda-based flue gas scrubber, nitric acid is scrubbed and converted to sodium nitrate.

The process chemistry involves the following:

$$\begin{aligned} NO + O_3 &\rightarrow NO_2 + O_2 \\ 2NO_2 + O_3 &\rightarrow N_2O_5 + O_2 \\ N_2O_5 + H_2O &\rightarrow 2HNO_3 \end{aligned} \quad (14.5)$$

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The operating costs associated with the LoTOx™ system are largely derived from electrical power, oxygen, and cooling water from the ozone generator. These costs are nearly directly proportional to the level of NO_x treated. The system is proven to deliver <10 ppmvd of NO_x at the system outlet and/or $>95\%$ removal efficiency, irrespective of flue gas changes or load swings.

The advantages of the LoTOx™ Technology are that the system has very low flue gas pressure drop, it does not convert SO_2 to SO_3, and it operates at the flue gas saturation temperature (i.e. wet scrubber operating temperature). Capital costs associated with the LoTOx™ Technology are similar to those of an SCR unit, though the annual operating costs of LoTOx™ Technology are higher than SCR. In addition, a cost-effective source of oxygen is essential in employing LoTOx™ Technology.

Summary

Compliance with the emission of the pollutants from the FCC unit regenerator flue gas is here to stay. There are numerous options available to a refiner to meet these requirements. However, before embarking on the treatment option, one must optimize the ongoing performance of the cat cracker operationally and ensuring uniform air/catalyst distribution across the regenerator.

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CHAPTER 15

Residue and Deep Hydrotreated Feedstock Processing

FCC is an amazing process. Its flexibility to meet future energy and environmental demands is unparallelled.

With high crude oil prices, more and more refiners are either retrofitting their FCC units to process residue or installing residue cat crackers (Resid FCC/RFCC) instead of conventional gas oil cracking. This is particularly true in countries in the Far East, Middle East, and Africa.

On the opposite side, there are refiners with FCC feed that is considered "too good" in quality, which can adversely affect catalyst regeneration and product recoveries.

The focus of this chapter is to discuss residue cracking and to offer insight into successful processing of residue feedstock to achieve long-term operational and mechanical reliability.

Also included in this chapter are steps that can be taken for successful processing of "deep" hydrotreated feedstock into an FCC unit.

Residue Cracking

An RFCC is distinguished from a conventional gas oil FCC in the quality of the feedstock. The common definition of residue is the fraction of the feed that boils above 1,050°F (565°C) and concarbon residue levels greater than 0.5 wt%. The residue content of RFCC feeds typically ranges from 1.0 to 6.0 wt%. Aside from its residue concentration, the residue feed often has the following elevated concentration of contaminants:

- Organic nitrogen
- Organic metals (vanadium, nickel, iron, sodium, and calcium).

Fluid Catalytic Cracking Handbook.
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Table 15.1 shows typical properties of residue feed to an RFCC unit. Table 15.2 contains properties of E-cat (circulating catalyst) corresponding to these feedstock properties.

Not all residue contents have similar molecular structures. However, on average, about 50% microcarbon residue is deposited on the catalyst as coke. For example, if 5 wt% of the gas oil feed is converted to coke in conventional gas oil cracking, processing residue feedstock having 4% concarbon residue (with typical impurities) results in 7% coke yield.

Cat cracking is a heat rejection process, meaning that the heat from combustion of hard/soft coke in the regenerator must provide enough heat to:

- Vaporize the feedstock from its preheat temperature
- Increase feed temperature to its final cracking temperature
- Compensate for an overall endothermic heat of reaction
- Heat up the combustion/carrier air rates from air blower discharge temperature to flue gas temperature
- Heat up various steam streams to the riser/reactor
- Heat up any recycle stream entering the riser to the cracking temperature
- Compensate for the heat losses from the reactor−regenerator components.

In residue cracking, the amount of heat/energy produced in the regenerator often exceeds the above demands. Consequently, this extra heat must be removed to control the regenerator bed temperature to a reasonable level, preferably <1,350°F (730°C).

The regenerator dense bed temperature is the consequence of having good and bad hard/soft coke on the catalyst entering the regenerator. The "bad" coke comes from:

- Subpar catalyst and gas oil mixing in the feed injection zone
- Insufficient residue atomization
- Inadequate response to the feed impurities
- Inadequate residence time in the riser
- Unfit riser termination device
- Subpar catalyst stripping.

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Table 15.1: Typical FCC Unit Combined Feed Properties.

Refinery	A	B	C	D
Mode of regeneration	Partial	Full/partial	Partial	Partial
Catalyst cooling	Yes	No*	No	Yes
API gravity	18.3	19.4	22.6	20.4
Distillation	D1160, °F	SIMDIS, °F	SIMDIS, °F	SIMDIS, °F
IBP	563	450	390	425
5%	675	622	525	561
10%	721	674	582	622
30%	859	776	714	765
50%	991	850	787	886
70%		936	872	1,031
90%		1,112	1,046	1,215
95%		1,234	1,168	1,310
EP		1,400	1,411	1,390
Watson *K*-factor	11.78	11.71	11.76	12.10
Hydrogen content, wt%	12.02	12.0	12.46	12.55
Molecular weight	468	423	375	534.3
Sulfur, wt%	2.14	1.05	0.65	0.35
Organic nitrogen, ppm				
Basic	622	610	438	766
Total	1,569	1,674	1,692	2,380
Residue, wt%	7.5	3.2	1.2	5.0
Nickel, ppm	16.4	3.7	4.1	10.4
Vanadium, ppm	14.1	5.9	7.5	1.6
Sodium, ppm	1.4	0.5	0.7	1.2
Iron, ppm	6.9		19.0	5.2
Calcium, ppm			2.8	32

*Unstabilized naphtha is used.

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Table 15.2: Typical Equilibrium (E-cat) Data.

Refinery		A	B	C	D
Catalyst addition rate	lb/bbl	0.68	0.39	0.72	0.82
Catalyst addition rate	kg/MT	2.1	1.2	2.5	2.5
Activity	wt%	68.0	78.0	67.6	69.2
Alumina (Al_2O_3)	wt%	47.6	43.4	59.1	54.0
Rare earth (RE)	wt%	2.9	3.5	1.33	1.84
Coke factor	wt/wt	1.34	1.2	2.3	1.1
Gas factor	vol.	3.84	1.9	3.0	1.4
Total surface area (SA)	m^2/g	134	173	106	116
Matrix surface area (MSA)	m^2/g	33	38	67	57
Zeolite surface area (ZSA)	m^2/g	101	135	39	59
Zeolite/matrix (Z/M) ratio	wt/wt	3.1	3.9	0.58	1.0
Average bulk density (ABD)	g/ml	0.85	0.85	0.82	0.86
Pore volume (PV)	ml/g	0.36	0.37	0.33	0.33
Sodium (Na)	wt%	0.28	0.26	0.33	0.42
Nickel (Ni)	ppm	5,940	270	2,310	4,900
Vanadium (V)	ppm	5,830	1,027	4,000	1,215
Iron (Fe)	wt%	0.62	0.53	0.99	0.51
Copper (Cu)	ppm	18	–	37	22
Calcium oxide (CaO)	wt%	0.19	0.08	0.20	1.13
Coke on catalyst (CRC)	wt%	0.07	0.09	0.31	0.1
Antimony (Sb)	ppm	576	14.20	600	1,450
Antimony/nickel ratio	wt/wt	0.10	0.05	0.26	0.30
Particle size distribution					
0–20 μm	wt%	0.0	3.48	0	0
0–40 μm	wt%	2.0	16.84	2.5	3.7
0–80 μm	wt%	40	66.9	32	51
Average particle size (APS)	μm	88	67.9	107	79

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Things to Consider When Processing Residue

- The true final boiling point of residue feedstock can be easily >1,800°F (980°C) and its molecular weight could be more than 500.
- For proper feed atomization, the feed nozzles must be designed to process a dispersion steam rate equivalent to a minimum 5.0 wt% of the fresh feed rate.
- There should be adequate ΔP across the oil-side of the feed nozzles with a minimum ΔP of 50 psi (3.5 bars).
- The CRC should be targeted to be <0.15 wt%.
- The antimony solution injection system must be designed properly to provide maximum nickel passivation.
- Proper fresh catalyst formulation is critical. A catalyst with active matrix and accessibility to the active sites is preferred.
- The regenerated catalyst must uniformly contact the feed to atomize the residue feedstock.
- The riser residence time (based on riser outlet conditions) must be at least 2.5 s to ensure cracking of large/heavy molecules.
- The cracking temperature must be at least 980°F (527°C) to ensure cracking of large/heavy molecules.
- The riser termination device and reactor cyclones must be robust to avoid premature coke deposition.
- The catalyst residence time in the stripper must be in the range of 1.5 min to help with bed cracking of the soft coke. The stripping steam rate should be at least 3 lb of steam per 1,000 lb of catalyst circulation rate (3 kg/1,000 kg).

Available Design Options to Process Residue

A conventional FCC unit can process residue depending on:

- Concentration of residue and its impurities
- Desired feed rate and conversion level
- Catalyst handling constraints
- Partial or full burn regeneration
- Existing and/or planned flue gas emission controls
- Maximum regenerator operating temperatures
- Available air blower and WGC capacities.

Depending on the concentrations of concarbon and other impurities, the regenerator bed temperature will go up noticeably when processing residue feedstock. Ideally, it is best if the regenerator bed temperature can be kept to <1,325°F (718°C) in order to minimize

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catalyst deactivation and to reduce premature thermal cracking reactions in the riser. This can be accomplished by:

- Minimizing the feed preheat temperature
- Operating the regenerator in partial combustion mode if a CO boiler is already in place
- Injecting naphtha into the feedstock to reduce its viscosity and, more importantly, to remove heat from the regenerator
- Injecting steam into the regenerator dilute phase
- Injecting sour water into the fresh feed
- Installing dense phase catalyst coolers.

The concentration of metals, especially the ratio of vanadium to nickel, plays a key role in the amount of fresh catalyst and/or purchased E-cat that is needed to achieve reasonable catalyst activity. The deleterious effects of nickel poisoning can be minimized by injecting antimony solution into the feed. However, there are really no cost-effective treatments for having high levels of vanadium, iron, sodium, and calcium.

FCC catalyst will lose its zeolite and matrix activities largely from:

- High regenerator bed temperature
- Subpar catalyst stripping
- Above average levels of vanadium, sodium, iron, and calcium.

There are two approaches used by refiners to achieve reasonable catalyst activity when processing residue feedstock. The first approach is using all fresh catalyst. The typical fresh catalyst addition rate is in the range of 0.5−1.0 lb of catalyst per barrel of feed (1−3 kg/MT). The second approach is to use a blend of fresh catalyst and purchased E-cat to flush out the high metal concentrations. The optimum choice depends on:

- Availability of steady and good-quality purchased E-cat
- Catalyst handling facilities
- Desired feed rate and conversion levels
- Total catalyst costs versus the expected savings.

RFCC Technology Offerings

In the United States, no new FCC or RFCC units have been installed for some time. Consequently, the refiners that process residue in their FCC units accomplish this task through:

- Installing dense phase catalyst cooling
- Operating in partial combustion mode of catalyst regeneration

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- Controlling the regenerator operating temperature near 1,400°F (760°C) in full combustion, with no external heat removal
- Injecting steam into the regenerator dilute phase and/or injecting sour water into the feed.

Outside the United States, the two common technologies used to process residue feedstock are:

1. Shaw Axens RFCC
2. UOP RFCC.

Both technologies employ two-stage catalyst regeneration largely to minimize premature catalyst deactivation from vanadium poisoning.

Shaw Axens RFCC Units

The key features of Shaw Axens RFCC units (Figure 15.1) are as follows:

- The spent catalyst from catalyst stripper is distributed into the R1 regenerator via a "bathtub" distributor.
- The R1 regenerator operates in partial burn mode with the R2 regenerator in full combustion mode.
- The catalyst from the R1 regenerator is lifted into the R2 regenerator with the use of a plug valve and lift line.
- The partially regenerated catalyst is fully regenerated in the R2 regenerator.
- Combustion air to both R1 and R2 regenerators, as well as the lift air, is often delivered by one axial air blower.
- The R1 regenerator contains several pairs of internal cyclones.
- The cyclones in the R2 regenerator can be either external or internal.
- Regenerated catalyst is withdrawn from the R2 regenerator through an external withdrawal well hopper.
- The R1 and R2 pressures are controlled separately.
- Dense phase catalyst cooling can be installed to remove heat from the regenerator.
- Unstabilized naphtha can be recycled to the riser, using dedicated nozzles, to remove heat from the R2 regenerator.

UOP RFCC Units

The UOP two-stage RFCC unit (Figure 15.2) has the following key features:

- An above average elevated feed injection system that will use steam and fuel gas in order to preaccelerate the regenerated catalyst prior to feed injection. The intent is to passivate the active metals before feed/catalyst contact.

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- Spent catalyst from catalyst stripper enters the first-stage regenerator (upper regenerator) via a "ski-jump" catalyst deflector.
- Approximately 70% of the total combustion air is consumed in the first-stage regenerator with the remaining 30% in the second-stage (lower) regenerator.
- Flue gas from the second-stage regenerator travels up into the first-stage regenerator through vent tubes located on the second-stage bottom head.
- The combined flue gas exits the first-stage regenerator after flowing through several second-stage cyclone systems.
- The first-stage regenerator operates in partial combustion with a typical CO_2/CO ratio of 3.0.
- A recirculating catalyst standpipe/slide valve is used to transfer catalyst from the first-stage to the second-stage regenerator.
- Back-mix catalyst coolers can be used to remove heat from the first-stage regenerator.
- The regenerated catalyst leaves the second-stage regenerator via a sloped standpipe.

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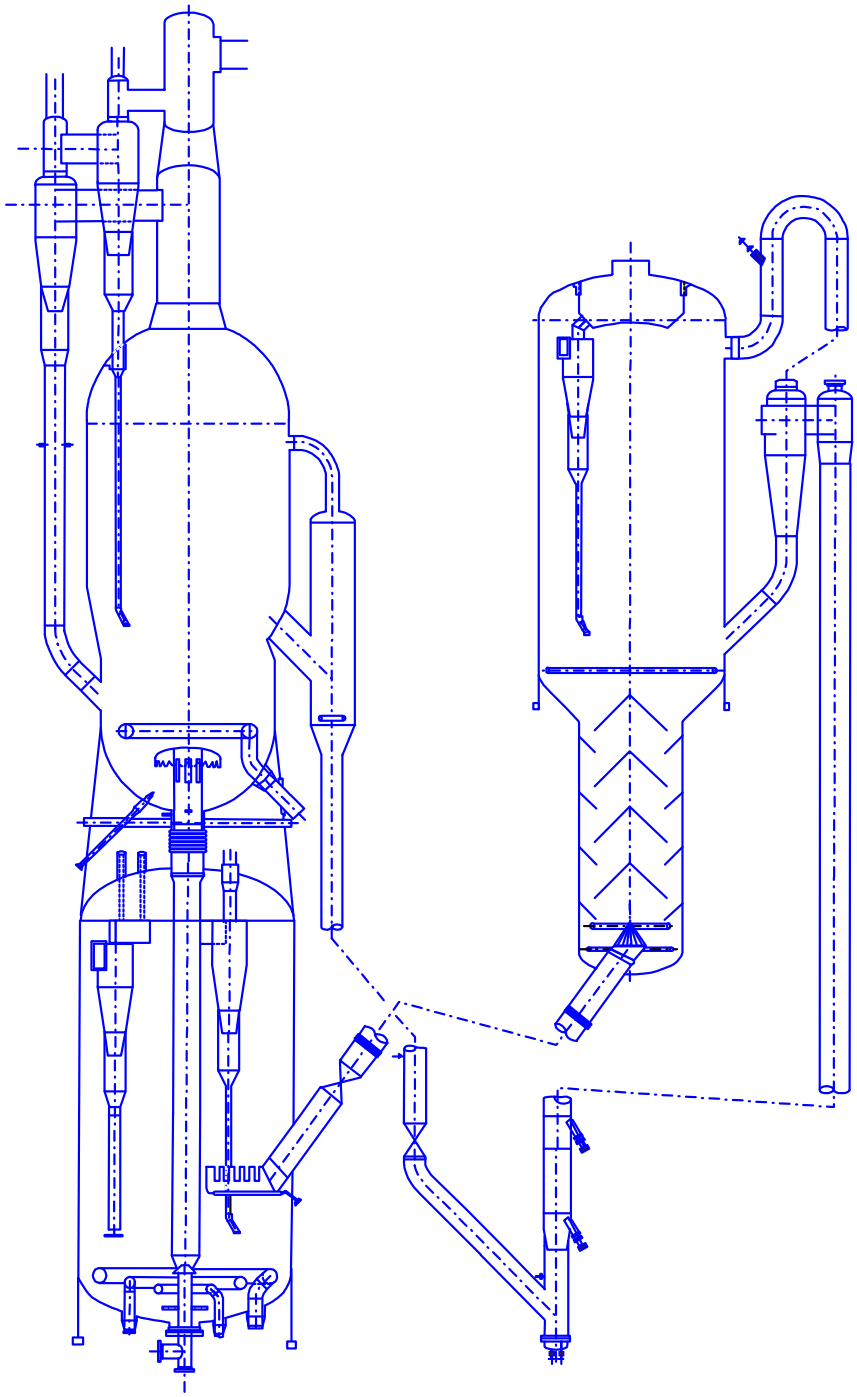


Figure 15.1: Example of Shaw Axens RFCC.

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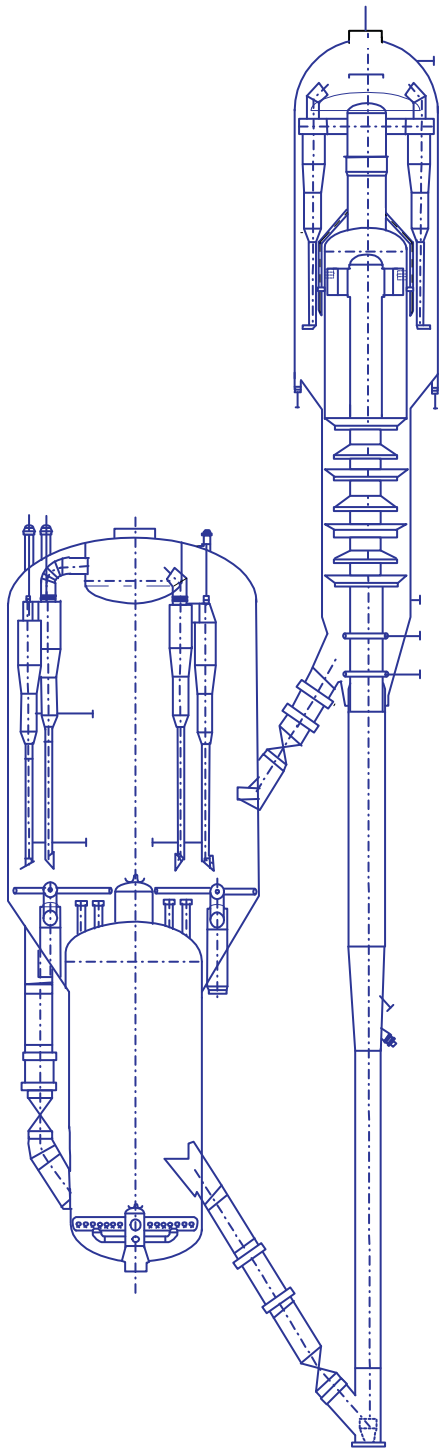


Figure 15.2: Example of UOP RFCC.

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Operational and Mechanical Reliability

Processing residue in the FCC unit is as not as forgiving as conventional gas oil cracking. The most common reasons for not achieving the desired run length and premature unit outages are:

- Coking
- Excessive catalyst losses
- High-temperature excursions.

Coking can occur around the feed nozzle injectors, inside the riser, reactor housing, inside/outside the reactor cyclones, reactor vapor line, main fractionator bottom, and around the spent catalyst slide valve. Inefficient feed atomization, inadequate cracking temperature, not long enough riser residence time, insufficient catalyst activity, and introducing the feed too early are the main reasons. Coking in the reactor top section can be minimized by injecting dry and hot dome steam.

Any coke formation inside the reactor cyclones can result in significant catalyst losses, which often requires immediate unit shutdown. The reactor cyclones must be designed to ensure adequate catalyst scouring to minimize accumulation of coke in the cyclone dustbowls and diplegs.

Since the fresh catalyst addition rate is several times greater than "conventional" gas oil cracking, the corresponding catalyst losses will also be higher. Therefore, it is critical that the physical properties of the fresh catalyst and/or purchased E-cat do not contribute to excessive catalyst losses.

Maintaining a stable regenerator temperature profile is extremely important for achieving long-term regenerator cyclone integrity. Consequently, provisions must be made to avoid frequent temperature swings due to changes in the feed quality and/or heat removal devices. Keeping the bed temperature "reasonable" will go a long way in ensuring the mechanical reliability of the reactor–regenerator equipment.

Operational Impacts of Residue Feedstocks

The combination of higher concarbon residue and other impurities would have the following effects on the unit operations:

- Frequent catalyst loading and unloading. Often the limitation with cooling of the regenerated catalyst limits the catalyst withdrawal rate and subsequently the addition rate.

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- The logistics and disposal costs of the withdrawal catalyst will be challenging.
- The greater catalyst addition rate increases catalyst losses from the reactor and regenerator cyclones. This could lead to unacceptable ash concentration in the slurry oil product and/or greater catalyst concentration in the flue gas scrubber purge water, or in the ESP hoppers.
- The dry gas or absorber off-gas yield is at least 50% more than the gas oil cracking. Consequently, this taxes the Wet Gas Compressor capacity and adversely impacts the C_3/C_4 recoveries.
- The fresh catalyst's stability is critical, considering the regenerator temperature and concentration of metals. Rare earth exchanged catalysts provide this stability. However, with the high prices of rare earth, the compromise can have adverse effects on the reactor yields.
- Greater levels of nitrogen and sulfur in the residue feed would challenge and increase compliance costs associated with emissions of NO_x and SO_x.
- The main fractionator bottom temperature must often kept to be <650°F (345°C) to avoid premature fouling.

Processing "Deep" Hydrotreated Feedstock

Sulfur reduction of diesel and gasoline fuels has been one of the most impressive changes in the refining industry. To meet the new sulfur concentrations in gasoline and diesel fuels, several refiners have elected to "deep" hydrotreat/mild hydrocrack FCC feedstock, while maximizing diesel fuel production. As shown in Table 15.3, the resulting FCC feedstock has a very high hydrogen content and no impurities.

Table 15.3: Typical Deep Hydrotreated Feed Properties.

API Gravity	30.5
Distillation (wt%)	D2887 SIMDIS, °F
IBP	576
5%	658
10%	691
30%	761
50%	812
70%	874
90%	966
95%	1,010
EP	1,111
Watson *K*-factors (calculated)	12.45
Hydrogen content, wt% (calculated)	14.00
Molecular weight (calculated)	410.3
Sulfur, wt%	0.0081
Organic nitrogen, ppm	7
Aniline point, °F	226
Refractive index (at 70°C)	1.4614
Carbon residue, wt%	0.01

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Unfortunately, with the significant decline in coke precursors, the delta coke (concentration of coke on the spent catalyst) is quite low, resulting in a rather low regenerator bed temperature. This is because the heat produced in the regenerator is not enough for cracking the gas oil and heating of the combustion air in the regenerator.

This rather low regenerator temperature, $<$1,250°F (677°C), often results in excessive afterburning and can exceed the permitted CO emission concentration. This is particularly true with inadequate flue gas/catalyst residence time in the regenerator and/or uneven air/catalyst distribution.

The deep hydrotreated feedstock does not produce very much slurry oil product. Consequently, it affects the heat balance across the main fractionator tower. There will not be enough heat in the lower/middle section of the tower. Additionally, with a very low slurry oil yield, the residence time of the main fractionator bottom liquid can go up significantly. This can lead to premature coke formation, especially if the main fractionator bottom temperature is not adjusted.

To achieve stable catalyst regeneration as well as main fractionator operations, options to consider are as follows:

- Increasing feed preheat temperature in the range of 600−700°F (315−370°C)
- Ensuring there is plenty of zeolite and matrix activity in the fresh catalyst
- Using an effective CO promoter
- Installing dedicated slurry or HCO recycle nozzles in the riser
- Ensuring the spent catalyst and combustion air is mixed uniformly
- Retrofitting the main fractionator internals to match the revised reactor yields
- Recycling slurry oil product to extinction.

Summary

Processing residue feedstock into the FCC or RFCC units provides challenges that must be addressed during the design of a new unit, or in the case of an existing unit, need to be completely evaluated. Optimum feed/catalyst injection system, proper choice of catalyst formulation/addition rate, and adequate heat removal from the regenerator dense bed are extremely critical to the long-term success of residue cracking. The cracking temperature must be high enough and the regenerator bed temperature needs to be cool enough to crack the large molecules to minimize catalyst deactivation, to prevent premature coking, and to deliver maximum liquid products.

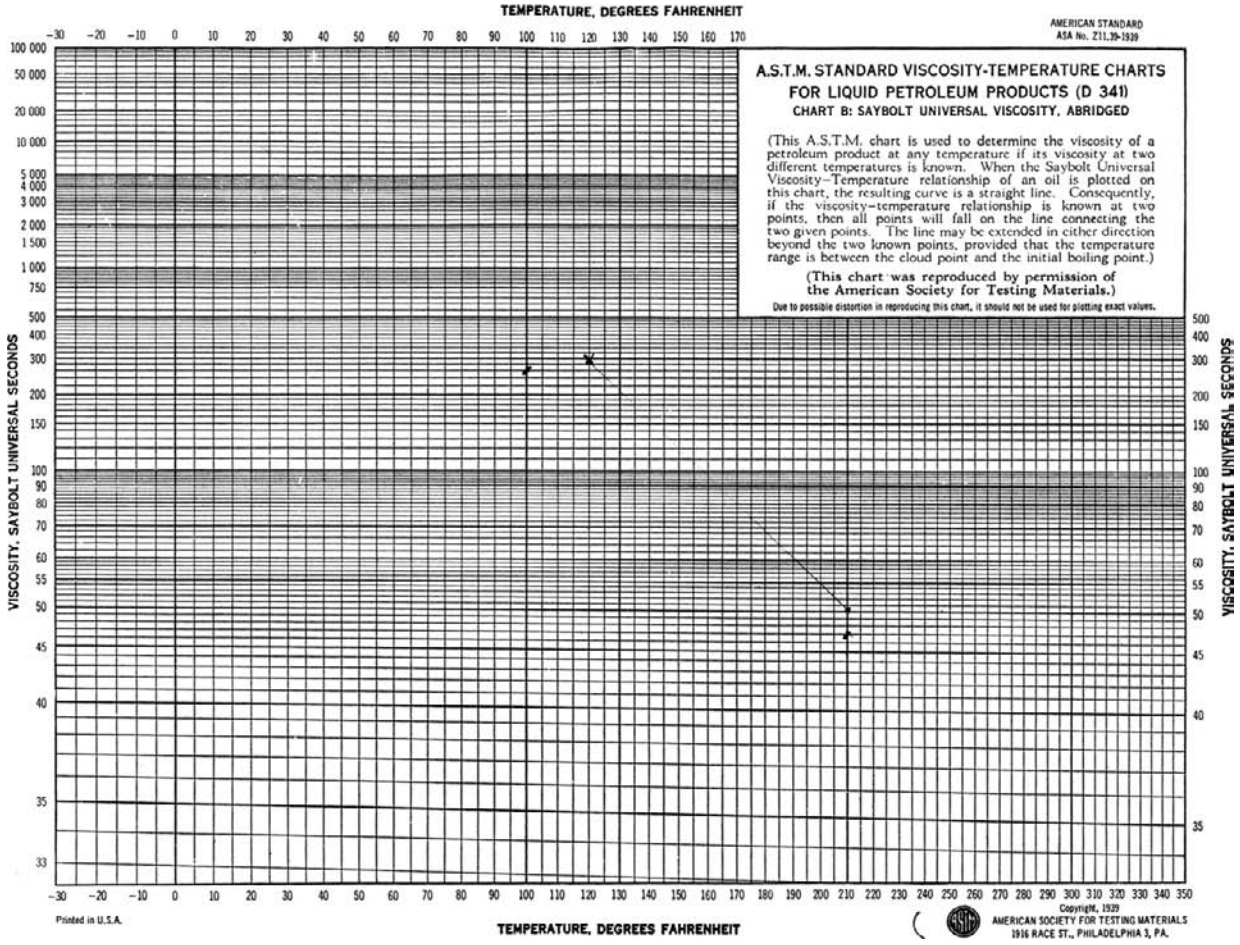
When processing deep hydrotreated feedstock, having stable catalyst regeneration is a must. Above-average feed preheat and above-average catalyst activity coupled with uniform air/catalyst distribution would be needed to control CO emissions while minimizing premature afterburning.

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Temperature Variation of Liquid Viscosity



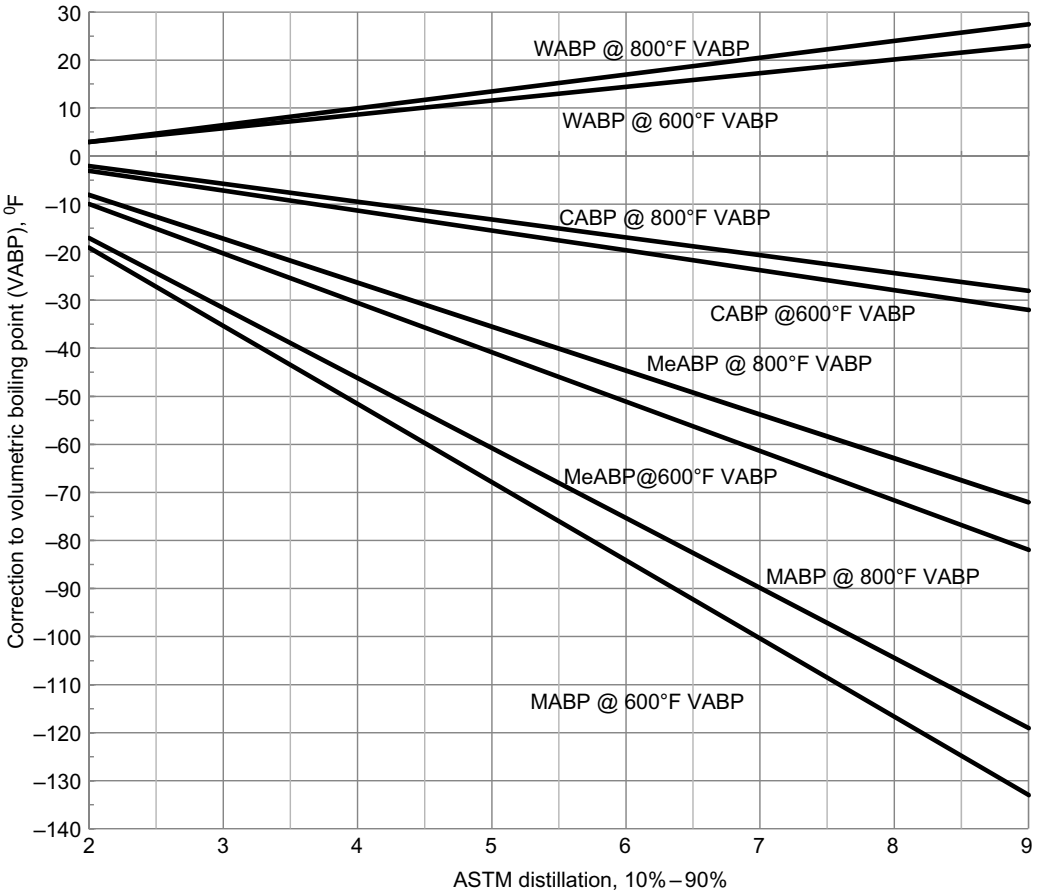
Referenced in Example 3.3.

Source: U.S. Department of Commerce, adapted from ASTM D-341-09, Chart 1 Kinematic Viscosity High Range. (Kinematic viscosity range, 0.3—20,000,000 cSt. Temperature range, −70°C to 370°C.)

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APPENDIX 2

Correction to Volumetric Average Boiling Point



CABP = cubic average boiling point; MABP = molal average boiling point; MeABP = mean average boiling point; WABP = weighted average boiling point.

Also found in Chapter 3 in text and Example 3.1.

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APPENDIX 3

TOTAL Correlations

Aromatic Carbon Content

$$C_A = -814.136 + 635.192 \times RI_{(20)} - 129.266 \times SG + 0.013 \times MW - 0.34 \times S - 6.872 \times \ln(V)$$

Hydrogen Content

$$H_2 = 52.825 - 14.26 \times RI_{(20)} - 21.329 \times SG - 0.0024 \times MW - 0.052 \times S + 0.757 \times \ln(V)$$

Molecular Weight

$$MW = 7.8312 \times 10^{-3} \times SG^{-0.09768} \times (AP, {}^\circ C)^{0.1238} \times (VABP, {}^\circ C)^{1.6971}$$

Refractive Index at 20°C (68°F)

$$RI_{(20)} = 1 + 0.8447 \times SG^{1.2056} \times (VABP, {}^\circ C + 273.16)^{-0.0557} \times MW^{-0.0044}$$

Refractive Index at 60°C (140°F)

$$RI_{(60)} = 1 + 0.8156 \times SG^{1.2392} \times (VABP, {}^\circ C + 273.16)^{-0.0576} \times MW^{-0.0007}$$

Referenced in Chapter 3.

Source: H. Dhulesia, New correlations predict FCC feed characterizing parameters, Oil Gas J. 84(2) (1986) 51–54.

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APPENDIX 4

n–d–M Correlations

$\nu = 2.51 \times (\mathrm{RI}_{(20)} - 1.4750) - (D_{20} - 0.8510)$

$\omega = (D_{20} - 0.8510) - 1.11 \times (\mathrm{RI}_{(20)} - 1.4750)$

If ν is positive: $\%C_A = 430 \times \nu + \frac{3{,}660}{\mathrm{MW}}$

If ν is negative: $\%C_A = 670 \times \nu + \frac{3{,}660}{\mathrm{MW}}$

If ω is positive: $\%C_R = 820 \times \omega - 3 \times S + \frac{10{,}000}{\mathrm{MW}}$

If ω is negative: $\%C_R = 1{,}440 \times \omega - 3 \times S + \frac{10{,}600}{\mathrm{MW}}$

$\%C_N = \%C_R - \%C_A$

$\%C_P = 100 - \%C_R$

Average Number of Aromatic Rings per Molecule (R_A)

$R_A = 0.44 + 0.055 \times M \times \nu$ if ν is positive

$R_A = 0.44 + 0.080 \times M \times \nu$ if ν is negative

Average Total Number of Rings per Molecule (R_T)

$R_T = 1.33 + 0.146 \times M \times (\omega - 0.005 \times S)$ if ω is positive

$R_T = 1.33 + 0.180 \times M \times (\omega - 0.005 \times S)$ if ω is negative

Average Number of Naphthene Rings per Molecule (R_N)

$R_N = R_T - R_A$

Referenced in Example 3.3.

Source: ASTM Standard D3238-80. Copyright ASTM. Used with permission.

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APPENDIX 5

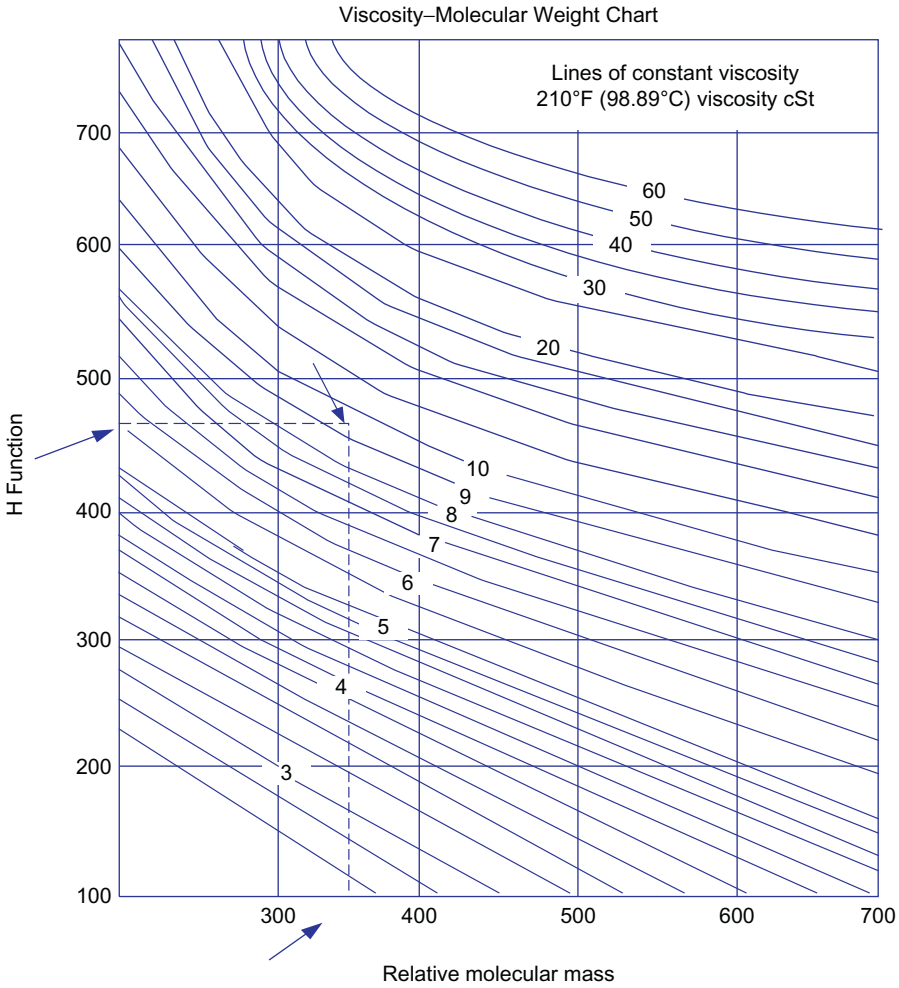
Estimation of Molecular Weight of Petroleum Oils from Viscosity Measurements

Kinematic Viscosity (mm^2/s) at 37.8°C	Tabulation of H Function (Partial) from D2502 Table 1									
	H									
	0	1	2	3	4	5	6	7	8	9
40	334	336	339	341	343	345	347	349	352	354
50	355	357	359	361	363	364	366	368	369	371
60	372	374	375	377	378	380	381	382	384	385
70	386	387	388	390	391	392	393	394	395	397
80	398	399	400	401	402	403	404	405	406	407
90	408	409	410	410	411	412	413	414	415	415
100	416	417	418	419	420	420	421	422	423	423
110	424	425	425	426	427	428	428	429	430	430
120	431	432	432	433	433	434	435	435	436	437
130	437	438	438	439	439	440	441	441	442	442
140	443	443	444	444	445	446	446	447	447	448
150	448	449	449	450	450	450	451	451	452	452
160	453	453	454	454	455	455	456	456	456	457
170	457	458	458	459	459	460	460	460	461	461
180	461	462	462	463	463	463	464	464	465	465
190	465	466	466	466	467	467	468	468	468	469

Referenced in Example 3.3.

Source: ASTM Standard D2502. Copyright ASTM. Used with permission.

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Source: ASTM Standard D2502. Copyright ASTM. Used with permission.

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APPENDIX 6

Kinematic Viscosity to Saybolt Universal Viscosity

Kinematic Viscosity (cSt)	Equivalent Saybolt Universal Viscosity (SUS)	
	At 100°F	At 210°F
1.81	32.0	32.2
2.71	35.0	35.2
4.26	40.0	40.3
7.27	50.0	50.3
10.33	60.0	60.4
13.08	70.0	70.5
15.66	80.0	80.5
18.12	90.0	90.6
20.55	100.1	100.8
43.0	200.0	201.0
64.6	300.0	301.0
86.2	400.0	402.0
108.0	500.0	503.0
129.4	600.0	603.0
139.8	648.0	652.0
151.0	700.0	
172.6	800.0	
194.2	900.0	
215.8	1,000.0	

Referenced in Example 3.3.

Extracted from ASTM Method D-2161-87. Copyright ASTM. Used with permission.

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APPENDIX 7

API Correlations

Mol Fraction of Paraffins (X_P)

$$X_P = a + b\,(Ri) + c\,(VGC)$$

Mol Fraction of Naphthenes (X_N)

$$X_N = d + e\,(Ri) + f\,(VGC)$$

Mol Fraction of Aromatics (X_A)

$$X_A = g + h\,(Ri) + i\,(VGC)$$

Constants	Heavy Fractions $200 < MW < 600$
$a =$	2.5737
$b =$	1.0133
$c =$	−3.573
$d =$	2.464
$e =$	−3.6701
$f =$	1.96312
$g =$	−4.0377
$h =$	2.6568
$i =$	1.60988

$R_i =$	refractivity intercept
VGC =	viscosity gravity constant

$$R_i = RI_{(20)} - \frac{d}{2}$$

where:

$RI_{(20)}$ = refractive index at 20°C
d = density at 20°C

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Viscosity gravity constant (VGC)

$$\mathrm{VGC} = \frac{\mathrm{SG} - 0.24 - 0.022 \times \log(v_{210} - 35.5)}{0.755}$$

where:

V_{210} = Saybolt Universal Viscosity at 210°F in seconds

Refractive index at 20°C (68°F)

$$RI_{(20)} = \left(\frac{1 + 2 \times I}{1 - I}\right)^{1/2}$$

$$I = A \times \exp\left(B \times \mathrm{MeABP} + C \times \mathrm{SG} + D \times \mathrm{MeABP} \times \mathrm{SG}\right) \times \mathrm{MeABP}^{E} \times \mathrm{SG}^{F}$$

Constants
$A = 2.341 \times 10^{-2}$
$B = 6.464 \times 10^{-4}$
$C = 5.144$
$D = -3.289 \times 10^{-4}$
$E = -0.407$
$F = -3.333$

$$\mathrm{MW} = a \times \exp\left(b \times \mathrm{MeABP} + c \times \mathrm{SG} + d \times \mathrm{MeABP} \times \mathrm{SG}\right) \times \mathrm{MeABP}^{E} \times \mathrm{SG}^{F}$$

Constants
$a = 20.486$
$b = 1.165 \times 10^{-4}$
$c = -7.787$
$d = 1.1582 \times 10^{-3}$
$e = 1.26807$
$f = 4.98308$

Referenced in Example 3.4.

Source: M.R. Riazi, T.E. Daubert, Prediction of the composition of petroleum fractions, Ind. Eng. Chem. Process Des. Dev. 19(2) (1982) 289–294.

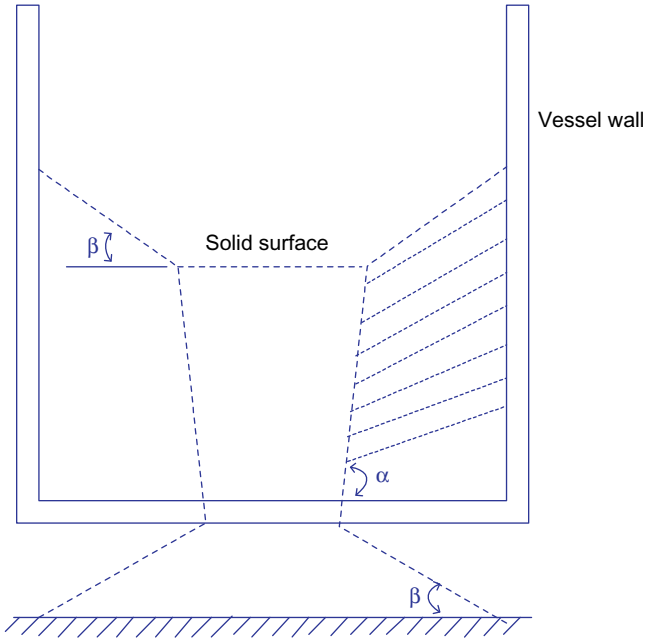
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APPENDIX 8

Definitions of Fluidization Terms

Aeration: Any supplemental gas (air, steam, nitrogen, etc.) that increases fluidity of the catalyst.

Angle of Internal Friction α: Angle of internal friction, or angle of shear, is the angle of solid against solid. It is the angle at which a catalyst will flow on itself in the nonfluidized state. For an FCC catalyst, this is about 70°.



Angle of Repose β: The angle that the slope of a poured catalyst will make with the horizontal. For an FCC catalyst, this is typically 30°.

Apparent Bulk Density (ABD): The density of the catalyst at which it is shipped, either in bulk volume or bags. It is density of the catalyst at minimum fluidization velocity.

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Bed Density (ρ_b): The average density of a fluidized bed of solid particles and gas. Bed density is mainly a function of gas velocity and, to a lesser extent, the temperature.

Minimum Bubbling Velocity (Umb): The velocity at which discrete bubbles begin to form. Typical minimum bubbling velocity for an FCC catalyst is 0.03 ft/s (0.9 cm/s).

Minimum Fluidization Velocity (Umf): The lowest velocity at which the full weight of catalyst is supported by the fluidization gas. It is the minimum gas velocity at which a packed bed of solid particles will begin to expand and behave as a fluid. For an FCC catalyst, the minimum fluidization velocity is about 0.02 ft/s (0.6 cm/s).

Particle Density (ρ_p): The actual density of the solid particles, taking into account any volume due to voids (pores) within the structure of the solid particles. Particle density is calculated as follows:

$$\rho_p = \frac{\text{Skeletal density}}{(\text{Skeletal density} \times \text{PV}) + 1}$$

Pore Volume (PV): The volume of pores or voids in the catalyst particles.

Ratio of Minimum Bubbling Velocity to Minimum Fluidization Velocity (Umb/Umf): This ratio can be calculated as follows:

$$\frac{\text{Umb}}{\text{Umf}} = \frac{2,300 \times {\rho_g}^{0.126} \times \mu^{0.523} \times \exp(0.716 \times F)}{{d_p}^{0.8} \times g^{0.934} \times (\rho_p - \rho_g)^{0.934}}$$

where:

ρ_g = gas density (kg/m^3);
μ = gas viscosity (kg/m/s);
F = fraction of fines less than 45 μm;
d_p = mean particle size;
ρ_p = particle density (kg/m^3);
g = gravitational constant = 9.81 m/s^2.

The higher the ratio, the easier it is to fluidize the catalyst.

Skeletal Density (SD): The actual density of the pure solid materials that make up the individual catalyst particles. For an FCC catalyst, the skeletal density can be calculated as follows:

$$\text{SD} = \frac{100}{\left(\frac{\text{Al}}{3.4} + \frac{\text{Si}}{2.1}\right)}$$

where:

Al = alumina content of the catalyst (wt%);
Si = silica content of the catalyst (wt%).

Slip Factor: The ratio of vapor velocity to catalyst velocity.

Stick Slip Flow: The continuous sudden stoppage and resumption of catalyst flow in a standpipe. This is usually caused by under-aeration.

Superficial Velocity: The velocity of the gas through the vessel or pipe without any solids present. It is the volumetric flow rate of fluidization gas divided by the cross-sectional area.

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APPENDIX 9

Conversion of ASTM 50% Point to TBP 50% Point Temperature

The following equation can be used to convert an ASTM D86 50% temperature to a TBP 50% temperature:

$$\text{TBP (50)} = 0.87180 \times \text{ASTM D86 (50)}^{1.0258}$$

where:

TBP (50) = true boiling point distillation temperature at 50 vol% distilled (°F);

ASTM D86 (50) = observed ASTM D86 distillation temperature at 50 vol% distilled (°F).

Example:

Given ASTM D86 (50) = 547°F, determine TBP 50% temperature:

$$\text{TBP (50)} = 0.87180 \times (547)^{1.0258}$$

$$\text{TBP (50)} = 0.87180 \times 644$$

$$\text{TBP (50)} = 561^{\circ}\text{F}$$

Source: T.E. Daubert, Petroleum fraction distillation inter-conversions, Hydrocarbon Process. 73(8) (1994) 75–78.

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APPENDIX 10

Determination of TBP Cut Points from ASTM D86

The difference between adjacent TBP can be determined by the following equation:

$Y_i = A\ X\ \frac{B}{i}$

Where:

Y_i = difference in TBP distillation between two cut points (°F);

X_i = observed difference in ASTM D-86 distillation between two cut points (°F);

A, B = constants varying for cut points ranges, shown in the following table:

I	Cut Point Range (%)	A	B
1	100–90	0.11798	1.6606
2	90–70	3.0419	0.75497
3	70–50	2.5282	0.820072
4	50–30	3.0305	0.80076
5	30–10	4.9004	0.71644
6	10–0	7.4012	0.60244

$\text{TBP}\ (0) = \text{TBP}\ (50) - Y_4 - Y_5 - Y_6$

$\text{TBP}\ (10) = \text{TBP}\ (50) - Y_4 - Y_5$

$\text{TBP}\ (30) = \text{TBP}\ (50) - Y_4$

$\text{TBP}\ (70) = \text{TBP}\ (50) + Y_3$

$\text{TBP}\ (90) = \text{TBP}\ (50) + Y_3 + Y_2$

$\text{TBP}\ (100) = \text{TBP}\ (50) + Y_3 + Y_2 + Y_1$

Source: T.E. Daubert, Petroleum fraction distillation inter-conversions, Hydrocarbon Process. 73(8) (1994) 75–78.

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APPENDIX 11

Nominal Pipe Sizes

Nominal Pipe Size	OD	ID		Schedule Designations			Wall Thickness		Weight	
Inch mm	Inch mm	Inch	mm	ASME			Inch	mm	lb/ft	kg/m
1/8	**0.405**	**0.335**	8.52	5			**0.035**	0.889	**0.138**	0.205
6	10.3	**0.307**	7.81	10		10S	**0.049**	1.245	**0.190**	0.283
		0.291	7.40	30			**0.057**	1.448	**0.212**	0.316
		0.269	6.85	STD	40	40S	**0.068**	1.727	**0.257**	0.382
		0.215	5.47	XS	80	80S	**0.095**	2.413	**0.315**	0.468
1/4	**0.540**	**0.442**	11.21	5			**0.049**	1.245	**0.257**	0.382
8	13.7	**0.408**	10.35	10		10S	**0.066**	1.676	**0.330**	0.491
		0.394	9.99	30			**0.073**	1.854	**0.364**	0.542
		0.364	9.23	STD	40	40S	**0.088**	2.235	**0.425**	0.632
		0.302	7.65	XS	80	80S	**0.119**	3.023	**0.535**	0.796
3/8	**0.675**	**0.577**	14.61	5			**0.049**	1.245	**0.328**	0.487
10	17.1	**0.545**	13.80	10		10S	**0.065**	1.651	**0.420**	0.625
		0.529	13.39	30			**0.073**	1.854	**0.470**	0.699
		0.493	12.48	STD	40	40S	**0.091**	2.311	**0.568**	0.845
		0.423	10.70	XS	80	80S	**0.126**	3.200	**0.739**	1.099
1/2	**0.840**	**0.710**	18.00	5		5S	**0.065**	1.651	**0.538**	0.801
15	21.3	**0.674**	17.08	10		10S	**0.083**	2.108	**0.671**	0.998
		0.650	16.47	30			**0.095**	2.413	**0.757**	1.126
		0.622	15.76	STD	40	40S	**0.109**	2.769	**0.851**	1.266
		0.546	13.83	XS	80	80S	**0.147**	3.734	**1.088**	1.619
		0.466	11.80	160			**0.187**	4.750	**1.309**	1.948
		0.252	6.36	XXS			**0.294**	7.468	**1.714**	2.550
3/4	**1.050**	**0.920**	23.40	5		5S	**0.065**	1.651	**0.684**	1.017
20	26.7	**0.884**	22.48	10		10S	**0.083**	2.108	**0.857**	1.276
		0.860	21.87	30			**0.095**	2.413	**0.970**	1.443
		0.824	20.96	STD	40	40S	**0.113**	2.870	**1.131**	1.683
		0.742	18.88	XS	80	80S	**0.154**	3.912	**1.474**	2.193
		0.612	15.57	160			**0.219**	5.563	**1.944**	2.893
		0.434	11.05	XXS			**0.308**	7.823	**2.441**	3.632
1	**1.315**	**1.185**	30.10	5		5S	**0.065**	1.651	**0.868**	1.291
26	33.4	**1.097**	27.86	10		10S	**0.109**	2.769	**1.404**	2.089
		1.087	27.61	30			**0.114**	2.896	**1.464**	2.178
		1.049	26.64	STD	40	40S	**0.133**	3.378	**1.679**	2.498
		0.957	24.31	XS	80	80S	**0.179**	4.547	**2.172**	3.232
		0.815	20.70	160			**0.250**	6.350	**2.844**	4.232

(*Continued*)

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Nominal Pipe Size	OD	ID		Schedule Designations			Wall Thickness		Weight	
Inch mm	Inch mm	Inch	mm	ASME			Inch	mm	lb/ft	kg/m
		0.599	15.21	XXS			**0.358**	9.093	**3.659**	5.445
1-1/4	**1.660**	**1.530**	38.90	5		5S	**0.065**	1.651	**1.107**	1.647
32	42.2	**1.442**	36.66	10		10S	**0.109**	2.769	**1.806**	2.687
		1.426	36.26	30			**0.117**	2.972	**1.930**	2.872
		1.380	35.09	STD	40	40S	**0.140**	3.556	**2.273**	3.382
		1.278	32.50	XS	80	80S	**0.191**	4.851	**2.997**	4.460
		1.160	29.50	160			**0.250**	6.350	**3.765**	5.602
		0.896	22.79	XXS			**0.382**	9.703	**5.214**	7.758
1-1/2	**1.900**	**1.770**	45.00	5		5S	**0.065**	1.651	**1.274**	1.896
40	48.3	**1.682**	42.76	10		10S	**0.109**	2.769	**2.085**	3.102
		1.650	41.95	30			**0.125**	3.175	**2.372**	3.529
		1.610	40.93	STD	40	40S	**0.145**	3.683	**2.718**	4.044
		1.500	38.14	XS	80	80S	**0.200**	5.080	**3.631**	5.403
		1.338	34.03	160			**0.281**	7.137	**4.859**	7.230
		1.100	27.98	XXS			**0.400**	10.160	**6.408**	9.535
2	**2.375**	**2.245**	57.00	5		5S	**0.065**	1.651	**1.604**	2.387
50	60.3	**2.209**	56.08				**0.083**	2.108	**2.030**	3.021
		2.157	54.76	10		10S	**0.109**	2.769	**2.638**	3.925
		2.125	53.95	30			**0.125**	3.175	**3.000**	4.464
		2.093	53.14				**0.141**	3.581	**3.360**	5.000
		2.067	52.48	STD	40	40S	**0.154**	3.912	**3.652**	5.434
		2.031	51.56				**0.172**	4.369	**4.050**	6.026
		1.999	50.75				**0.188**	4.775	**4.390**	6.532
		1.939	49.23	XS	80	80S	**0.218**	5.537	**5.022**	7.473
		1.875	47.60				**0.250**	6.350	**5.670**	8.437
		1.687	42.82	160			**0.344**	8.738	**7.462**	11.103
		1.503	38.15	XXS			**0.436**	11.074	**9.029**	13.435
2-1/2	**2.875**	**2.709**	68.78	5		5S	**0.083**	2.108	**2.475**	3.683
73.0	73	**2.635**	66.90	10		10S	**0.120**	3.048	**3.531**	5.254
		2.499	63.45	30			**0.188**	4.775	**5.400**	8.035
		2.469	62.69	STD	40	40S	**0.203**	5.156	**5.793**	8.620
		2.323	58.98	XS	80	80S	**0.276**	7.010	**7.661**	11.400
		2.125	53.95	160			**0.375**	9.525	**10.010**	14.895
		1.771	44.96	XXS			**0.552**	14.021	**13.690**	20.371
3	**3.500**	**3.334**	84.68	5		5S	**0.083**	2.108	**3.029**	4.507
80	88.9	**3.260**	82.80	10		10S	**0.120**	3.048	**4.332**	6.446
		3.124	79.35				**0.188**	4.775	**6.656**	9.904
		3.068	77.93	STD	40	40S	**0.216**	5.486	**7.576**	11.273
		2.900	73.66	XS	80	80S	**0.300**	7.620	**10.250**	15.252
		2.624	66.65	160			**0.438**	11.125	**14.320**	21.308
		2.300	58.42	XXS			**0.600**	15.240	**18.580**	27.647
3-1/2	**4.000**	**3.834**	97.38	5		5S	**0.083**	2.108	**3.472**	5.166
90	101.6	**3.760**	95.50	10		10S	**0.120**	3.048	**4.973**	7.400
		3.624	92.05	30			**0.188**	4.775	**7.661**	11.400
		3.548	90.12	STD	40	40S	**0.226**	5.740	**9.109**	13.554
		3.364	85.45	XS	80	80S	**0.318**	8.077	**12.500**	18.600
		2.728	69.29	XXS			**0.636**	16.154	**22.850**	34.001

(*Continued*)

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Nominal Pipe Size	OD	ID		Schedule Designations			Wall Thickness		Weight	
Inch mm	Inch mm	Inch	mm	ASME			Inch	mm	lb/ft	kg/m
4	**4.500**	**4.334**	110.08	5		5S	**0.083**	2.108	**3.915**	5.826
100	114.3	**4.260**	108.20	10		10S	**0.120**	3.048	**5.613**	8.352
		4.188	106.38				**0.156**	3.962	**7.237**	10.769
		4.124	104.75	30			**0.188**	4.775	**8.658**	12.883
		4.026	102.26	STD	40	40S	**0.237**	6.020	**10.790**	16.056
		3.938	100.03	60			**0.281**	7.137	**12.660**	18.838
		3.826	97.18	XS	80	80S	**0.337**	8.560	**14.980**	22.290
		3.626	92.10	120			**0.437**	11.100	**19.000**	28.272
		3.438	87.33	160			**0.531**	13.487	**22.510**	33.495
		3.152	80.06	XXS			**0.674**	17.120	**27.540**	40.980
4-1/2	**5.000**	**4.506**	114.45	STD	40	40S	**0.247**	6.274	**12.530**	18.645
115	127	**4.290**	108.97	XS	80	80S	**0.355**	9.017	**17.610**	26.204
		3.580	90.93	XXS			**0.710**	18.034	**32.430**	48.256
5	**5.563**	**5.345**	135.76	5		5S	**0.109**	2.769	**6.349**	9.447
125	141.3	**5.295**	134.49	10		10S	**0.134**	3.404	**7.770**	11.562
		5.047	128.19	STD	40	40S	**0.258**	6.553	**14.620**	21.755
		4.813	122.25	XS	80	80S	**0.375**	9.525	**20.780**	30.921
		4.563	115.90	120			**0.500**	12.700	**27.040**	40.236
		4.313	109.55	160			**0.625**	15.875	**32.960**	49.044
		4.063	103.20	XXS			**0.750**	19.050	**38.550**	57.362
6	**6.625**	**6.407**	162.76	5		5S	**0.109**	2.769	**7.585**	11.286
150	168.3	**6.357**	161.49	10		10S	**0.134**	3.404	**9.289**	13.822
		6.249	158.75				**0.188**	4.775	**12.920**	19.225
		6.065	154.08	STD	40	40S	**0.280**	7.112	**18.970**	28.227
		5.761	146.35	XS	80	80S	**0.432**	10.973	**28.570**	42.512
		5.501	139.75	120			**0.562**	14.275	**36.390**	54.148
		5.187	131.77	160			**0.719**	18.263	**45.350**	67.481
		4.897	124.41	XXS			**0.864**	21.946	**53.160**	79.102
7	**7.625**	**7.023**	178.41	STD	40		**0.301**	7.645	**23.570**	35.072
175	193.7	**6.625**	168.30	XS	80		**0.500**	12.700	**38.050**	56.618
		5.875	149.25	XXS			**0.875**	22.225	**63.080**	93.863
8	**8.625**	**8.407**	213.56			5S	**0.109**	2.769	**9.914**	14.752
200	219.1	**8.329**	211.58	10		10S	**0.148**	3.759	**13.400**	19.939
		8.125	206.40	20			**0.250**	6.350	**22.350**	33.257
		8.071	205.03	30			**0.277**	7.036	**24.700**	36.754
		7.981	202.74	STD	40	40S	**0.322**	8.179	**28.550**	42.482
		7.813	198.48	60			**0.406**	10.312	**35.640**	53.032
		7.625	193.70	XS	80	80S	**0.500**	12.700	**43.390**	64.564
		7.439	188.98	100			**0.593**	15.062	**50.950**	75.814
		7.189	182.63	120			**0.718**	18.237	**60.710**	90.336
		7.001	177.85	140			**0.812**	20.625	**67.760**	100.827
		6.875	174.65	XXS			**0.875**	22.225	**72.420**	107.761
		6.813	173.08	160			**0.906**	23.012	**74.690**	111.139
9	**9.625**	**8.941**	227.13	STD	40		**0.342**	8.687	**33.90**	50.443
225	244.5	**8.625**	219.10	XS	80		**0.500**	12.700	**48.72**	72.495
		7.875	200.05	XXS			**0.875**	22.225	**81.77**	121.674

ASME = American Society of Mechanical Engineers; OD = outside diameter; ID = inside diameter.

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APPENDIX 12

Conversion Factors

1 atmosphere (atm)	=	14.696 lb (force)/in.^{2} (absolute)
1 atmosphere (atm)	=	1.013×10^5 Newton/square meter (N/m^2)
1 atmosphere (atm)	=	1.013 bar
1 bar	=	10^5 pascal
1 barrel (bbl), 42 US gal	=	0.159 cubic meter (m^3)
1 barrel/day	=	6.625×10^{-3} m^3/h
1 Btu	=	1,055 joule (J)
1 Btu	=	252.0 calories (cal)
1 Btu/h	=	3.93×10^{-4} horsepower (hp)
1 Btu/h	=	0.252 kcal/h
1 Btu/h	=	0.29307 W
1 Btu/lb	=	0.556 calorie/gram (cal/g)
1 Btu/lb	=	2.326 joules/gram (J/g)
1 Btu/lb °F	=	4.186 joules/gram °C
1 Btu/lb	=	1.0 calorie/gram °C
1 Btu/h-ft^2	=	4.882 kg-cal/h-m^2 °C
degree Fahrenheit (°F)	=	$1.8 \times$ °C +32
degree Kelvin (°K)	=	°C +273
degree Rankine (°R)	=	460 + °F
1 foot (ft or ′)	=	12 inches (in. or ″)
1 foot (ft or ′)	=	0.3048 meter (m)
1 gallon (gal), US	=	3.785 × liters
1 gallon (gal), US	=	3.785×10^{-3} cubic meter (m^3)
gas constant (°R)	=	10.73 (psia) × (ft^3)/(lb-mole) × (°R)
gas constant (°R)	=	8,314 N/m^2 × m^3/kg-mole × °K
1 horsepower (hp)	=	746 watts (W)
1 inch (in. or ″)	=	2.54 centimeters (cm)
1 inch (in. or ″)	=	0.0254 meter (m)
1 pound (lb), weight	=	453.6 grams (g)

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1 lb/ft^{2}s	=	4.8761 kg/m^{2}s
1 lb/ft^3	=	0.016 gram/cubic centimeter (g/cm^3)
1 lb/ft^3	=	0.016 gram/milliliter (g/ml)
1 lb/ft^3	=	16.018 kilogram/cubic meter (kg/m^3)
1 lb/gal (US)	=	0.1198 g/cm^3
1 lb (force)/in.^{2} (psi)	=	0.0689 bars
1 lb (force)/in.^{2} (psi)	=	0.0680 atmospheres (atm)
1 lb (force)/in.^{2} (psi)	=	0.0703 kg/cm^2
1 mile	=	1.61 kilometers
1 ton (short)	=	2,000 pounds (lbs)
1 ton (short)	=	907.2 kilograms
1 ton (metric)	=	1,000.00 kilograms
1 ton (long)	=	1,016.0 kilograms
1 ton (long)	=	2,240 lbs

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Glossary

Absorption is the disappearance of one substance into another so that the absorbed substance loses its identifying characteristics, while the absorbing substance retains most of its original physical aspects. Absorption is used in refining to selectively remove specific components from process streams.

Acid Treatment is a process in which unfinished petroleum products such as gasoline, kerosene, and lubricating oil stocks are treated with sulfuric acid to improve color, odor, and other properties.

Adsorption is the adhesion of the molecules of gases or liquids to the surface of solid materials.

Advance Process Control (APC) is a mechanism which manipulates regulatory controls toward more optimum unit operation.

Aeration is a general term used for any gas used to fluidize FCC catalyst.

Afterburn is the combustion of carbon monoxide (CO) to carbon dioxide (CO_2) in the dilute phase or in the cyclones of the regenerator.

Alkylation is one of the refining processes in which light olefin molecules are reacted with isobutane (in the presence of either sulfuric or hydrofluoric acid) to produce a "desirable" gasoline component called alkylate.

American Society of Testing and Materials (ASTM) is the organization that develops analytical tests and procedures to facilitate commerce.

Aniline Point is the minimum temperature for complete miscibility of equal volumes of aniline and the hydrocarbon sample. In cat cracking, aniline solution is used to determine aromaticity of FCC feedstocks. Aromaticity increases with reducing aniline point.

Antimony is a metal, in either hydrocarbon or aqueous solution, commonly injected into the fresh feed to passivate nickel.

API Gravity (American Petroleum Institute gravity) is an "artificial" scale of liquid gravity defined by: (141.5/SG) −131.5. The scale was developed for water = 10. The main advantage of using API gravity is that it magnifies small changes in liquid density.

Apparent Bulk Density (ABD) is the density of catalyst as measured, "loosely compacted" in a specified container.

Aromatics are organic compounds with one or more benzene rings.

Asphaltenes are asphalt compounds soluble in carbon disulfide but insoluble in paraffin naphthas.

Average Particle Size (APS) is the weighted average diameter of a catalyst.

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Back-Mixing is the phenomenon by which the catalyst travels more slowly up the riser than the hydrocarbon vapors.

Benzene is an unsaturated, six-carbon ring, basic aromatic compound.

Basic Nitrogen is the organic nitrogen compounds in the FCC feed that react with the catalyst acid sites, thereby reducing the catalyst's activity and selectivity.

Beta-Scission is splitting of the C—C bond two bonds away from the positively charged carbon atom.

Binder is the material used in the FCC catalyst to bind the matrix and zeolite components into a single homogeneous particle.

California Air Resources Board (CARB) is a state agency which regulates and sets standards for air quality and emissions of various pollutants.

Carbenium Ion is a positively charged ($R-CH_2^+$) ion that is formed from a positive charge to an olefin and/or by removing a hydrogen and two electrons from a paraffin molecule.

Carbocation is a generic term for a positively charged carbon ion. Carbocations are further subdivided into carbenium and carbonium ions.

Carbon Black Feedstock (CBFS) is used in the FCC to represent slurry oil product that can be sold as feedstock to produce Carbon Black.

Carbonium Ion is a positively charged (CH_5^+) ion which is formed by adding a hydrogen ion (H^+) to paraffin.

Cat/Oil Ratio is the weight ratio of regenerated catalyst to the fresh feed in the riser feed injection zone.

Catalyst Activity is the conversion of feed (gas oils) to gasoline, lighter products, and coke in the MAT (Microactivity Test) laboratory.

Catalyst Cooler is a heat exchanger that removes heat from the regenerator through steam generation.

Catalytic Cracking is the process of breaking up heavier hydrocarbon molecules into lighter hydrocarbon fractions by use of heat and catalysts.

Cetane Number is a numerical indication of a fuel's (kerosene, diesel, heating oil) ignition quality. Cetane number is measured in a single cylinder engine, whereas cetane index is a calculated value.

Coke is a hydrogen-deficient residue left on the catalyst as a by-product of catalytic reactions.

Coke Factor is coke-forming characteristics of the equilibrium catalyst relative to coke-forming characteristics of a standard catalyst at the same conversion.

Coke (Carbon) on Regenerated Catalyst (CRC) is the level of residual carbon remaining on the catalyst when the catalyst exits the regenerator.

Coke Yield is the amount of coke the unit produces to stay in heat balance, usually expressed as percent of feed.

Cold Crushing Strength (CCS) is a compressive test that measures the ability of a product to withstand a given load, normally measured at room temperature after firing to specific temperatures.

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Conradson Carbon, or Concarbon is a standard test to determine the level of carbon residue present in a heavy oil feed.

Conventional Gasoline is a non-RFG gasoline that meets exhaust benzene, sulfur, olefins, and T90 specifications.

Conversion is often defined as the percentage of fresh feed cracked to gasoline, lighter products, and coke. Raw conversion is calculated by subtracting the volume or weight percent of the FCC products (based on fresh feed) heavier than gasoline from 100, or:

$$\text{Conversion} = 100 - (\text{LCO} + \text{HCO} + \text{DO}) \text{ vol\% or wt\%}$$

Converter is referred to as the reactor–regenerator section of the FCC unit.

Cracking is the breaking up of heavy molecular weight hydrocarbons into lighter hydrocarbon molecules, through the application of heat and pressure, with or without the use of catalysts.

Cyclone is a centrifugal separator which collects and removes particulates from gases.

D-86 is a common ASTM test method that measures the boiling point of "light" liquid hydrocarbons at various volume percent fractions. The sample is distilled at atmospheric pressure, provided its final boiling point (end point) is less than 750°F (399°C).

D1160 is an ASTM method that measures the boiling point of "heavy" liquid hydrocarbons at various volume percent fractions. The sample is distilled under vacuum (results are converted to atmospheric pressure). The application of D1160 is limited to a maximum final boiling point of about 1,000°F (538°C).

Debottlenecking often refers to employing hardware changes to improve FCC unit performance.

Decanted Oil (DO), Slurry, Clarified Oil, or Bottoms is the heaviest and often the lowest priced liquid product from a cat cracker.

Delta Coke is the difference between the coke content of the spent catalyst and the coke content of the regenerated catalyst. Numerical value of delta coke is calculated from:

$$\text{Delta coke} = \text{coke yield (wt\%/catalyst to oil ratio)}$$

Dense Phase is the region where the bulk of the fluidized catalyst is maintained.

Desalting is the removal of mineral salts (mostly chlorides, e.g. magnesium chloride and sodium chloride) from crude oil.

Dilute Phase is the region above the dense phase which has a substantially lower catalyst concentration.

Dipleg is the part of a cyclone separator that provides a barometric seal between the cyclone inlet and the cyclone solid outlet.

Disengager is a term used for the reactor housing. Since virtually all the desired cracking reactions take place in the riser, the traditional reactor is no longer a reactor but rather a vessel to hold cyclones and separate catalyst from vapors.

Distributive Control System (DCS) is a digital control system that has a distributive architecture where different control functions are implemented in specialized controllers.

Dry Gas is often referred as the C_2 and lighter gases (hydrogen, methane, ethane, and ethylene) produced in the FCC unit.

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Dynamic Activity is an indication of conversion per unit coke using data from the MAT laboratory.

Equilibrium Catalyst (E-cat) is the regenerated catalyst circulating from the reactor to the regenerator.

Exhaust Benzene is the amount of benzene toxins released. Exhaust benzene is a function of aromatics and benzene.

Expansion Joint is a mechanical assembly designed to eliminate large thermal stresses in the piping.

Faujasite is a naturally occurring mineral, having a specific crystalline, alumina−silicate structure, used in the manufacturing of the FCC catalyst. Zeolite faujasite is a synthetic form of the mineral.

Filler is the inactive component of the FCC catalyst.

Flapper Valve, Trickle Valve, or Check Valve is often attached to the end of a cyclone dipleg to minimize gas leakage up the dipleg and also catalyst losses during the unit start-up.

Flue Gas in FCC process refers to combustion products exiting the regenerator. The typical "wet" flue gas stream leaving a full-burn regenerator has about 73% N_2, 16% CO_2, 10% steam, and 1% oxygen with traces of CO, SO_2, and nitrogen oxides.

Free Radical is an uncharged molecule formed in the initial step of thermal cracking. Free radicals are very reactive and short-lived.

Full (or Complete) Combustion refers to the FCC regenerators in which the coke on the catalyst is combusted to CO_2 with traces of CO gas leaving the regenerator.

Gas Oil is the middle-distillate petroleum fraction, with a boiling range of about 350−750°F (177−399°C), and usually includes diesel fuel, kerosene, heating oil, and light fuel oil.

Gas Factor is the hydrogen and lighter gas-producing (C_1−C_4) characteristics of the equilibrium catalyst, relative to the hydrogen and lighter gas producing characteristics of some standard catalyst at the same conversion.

Gasoline is a blend of naphthas and other refinery products with sufficiently high octane and other desirable characteristics to be suitable for use as fuel in internal combustion engines.

Hard Coke is Reza's definition of coke deposited on the catalyst in the cracking process. This coke does include any hydrocarbon molecules that do not get fully vaporized/cracked and/or volatile hydrocarbon molecules that are stripped.

Heat Balance is where the heat produced in the regenerator matches the demand for cracking FCC feedstock to the desired cracking temperature, as well as heating up the blower air to the flue gas temperature while maintaining an "acceptable" regenerator temperature.

Heat of Cracking is the amount of energy required to convert FCC feed to the desired products.

Heavy Cycle Oil (HCO) is a stream that is lighter than slurry oil and heavier than LCO products. It is mostly used as a pumparound stream for removal of heat from the main fractionator tower.

High Pressure Liquid Chromatography (HPLC) is a very useful lab technique (unfortunately not readily available) that can be used to determine core and noncore aromatic rings in the FCC feedstock, as well as the fraction of saturates.

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Hydrocracking is a refining process that uses high operating pressure 1,500−3,000 psig (105−210 bar), rather high temperatures 650−800°F (345−425°C), and fixed catalyst bed reactors to convert gas oil feed and LCO into lower boiling products (naphtha, distillate, and LPG).

Hydrogen Transfer is the secondary reaction that converts olefins (predominantly iso-olefins) into paraffins, while extracting hydrogen from larger, more hydrogen-deficient molecules.

Hydrotreating is a refinery process that uses hydrogen in a fixed catalyst reactor to remove sulfur, organic nitrogen and, depending on the operating pressure, saturates multiring aromatic molecules.

Inert Gases in the FCC unit are referred to as the flue gas mixture (N_2, CO, CO_2, O_2) that is dragged/entrained with the regenerated catalyst entering the riser. They end up leaving the unit with the secondary absorber off-gas.

Inhibitor is an additive used to prevent, or retard, undesirable changes in the quality of the product, or in the condition of the equipment in which the product is used.

Isooctane is a hydrocarbon molecule (2,2,4-trimethylpentane) with excellent antiknock characteristics, on which the octane number of 100 is based.

Kaoline is a clay filler typically incorporated into FCC catalysts, as part of the manufacturing process, to balance catalyst activity.

***K*-Factor** is an index designed to balance density and boiling point such that it relates solely to the hydrogen content of the hydrocarbon.

Liquefied Petroleum Gas (LPG) consists of light hydrocarbons (propane, propylene, butane, and butylenes) that are vapors at ambient conditions and are liquid at moderate pressures.

Matrix is a substrate in which the zeolite is embedded in the cracking catalyst. Matrix is often used as a term for the active, nonzeolitic component of the FCC catalyst.

Maximum Achievable Control Technology (MACT II) is the regulations for air emissions as set under Title III of the 1990 Clean Air Act Amendments by the Environmental Protection Agency for burning hazardous waste.

Mean Average Boiling Point (MeABP) is a pseudo boiling point of FCC feedstock that is calculated from the distillation curve's volumetric average boiling point from other feedstock properties.

Microactivity Test (MAT) is a small, packed-bed catalytic cracking test that measures activity and selectivity of a feedstock-catalyst combination.

Mix Zone Temperature is the theoretical equilibrium temperature between the regenerated catalyst and the uncracked vaporized feed at the bottom of the riser.

Modulus of Rupture (MOR) measures refractory bending or tensile strength. For castables, it measures the bonding strength of the cement matrix.

Molecular Sieve is a term applied to zeolite. Zeolite exhibits shape selectivity and hydrocarbon absorptions.

Motor Octane Number (MON) is a quantitative measure of a fuel to "knocking," simulating the fuel's performance under severe operating conditions (at 900 rpm and at 300°F (149°C)).

National Emission Standards for Hazardous Air Pollutants (NESHAP) are the EPA's emission standards for catalytic cracking units, catalytic reforming units, and sulfur recovery units, which

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became effective on April 11, 2002. The existing affected units had to be in compliance by April 11, 2005. This rule is also known as Refinery MACT II.

n−d−M is an ASTM method that estimates the chemical composition of a liquid stream.

New Source Performance Standards (NSPS) for FCC units were established for the control of particulate matter, carbon monoxide, and sulfur dioxide emissions.

Octane Barrel Yield as used in the FCC, is defined as (RON + MON)/2, times the gasoline yield.

Octane Number is a number [(RON + MON)/2] indicating the relative antiknock characteristics of gasoline.

Olefins are a family of unsaturated hydrocarbons with one carbon−carbon double bond and the general formula C_nH_{2n}.

Optimization refers to maximizing feed rate and/or conversion with the existing equipment, while reaching as many constraints as possible.

Oxygenate is an oxygen-containing hydrocarbon. The term is used for oxygen-containing molecules blended into gasoline to improve its combustion characteristics.

Paraffins are a family of saturated aliphatic hydrocarbons (alkanes) with the general formula C_nH_{2n+2}.

Partial Combustion refers to FCC units in which burning of coke in the regenerator is controlled to achieve a desired level of CO in the regenerator flue gas.

Particle Density is the actual density of solid particles, taking into account volume due to any voids (pores) within the structure of the solid particles.

Particle Size Distribution (PSD) is the particle size fractions of the FCC catalyst expressed as percent through a given sized hole.

Permanent Linear Change (PLC) is a test method that covers the determination of the permanent linear change of refractory brick when heated under prescribed conditions, to determine any potential shrinking.

Plenum is a means of collecting gases from multiple sets of cyclones before they are exhausted from the unit.

Polynuclear Aromatics (PNA) are any of numerous complex hydrocarbon compounds consisting of three or more benzene rings in a compact molecular arrangement.

Pore Diameter is an estimate of the average pore size of the catalyst.

Pore Volume is the open space in the FCC catalyst, generally measured by mercury, nitrogen, or water. Mercury is used to measure large pores, nitrogen measures small pores, and water is used for both.

Preheater is an exchanger, or heater, used to heat hydrocarbons before they are fed to a unit.

Pressure Balance deals with the hydraulics of catalyst circulation in the reactor/regenerator circuit.

Pressure Differential Indicating Controller (PDIC) is used to regulate and control pressure differences across the slide valves and between the reactor−regenerator vessels.

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Pyrophoric Iron Sulfide is a substance typically formed inside tanks and processing units by the corrosive interaction of sulfur compounds in the hydrocarbons and the iron and steel in the equipment. On exposure to air (oxygen) it ignites spontaneously.

Quench Oil is oil injected into a product leaving a cracking or reforming heater or reactor to lower the temperature and stop the cracking process.

Ramsbottom similar to Conradson Carbon, is a quantitative indication of the carbon residue of a sample.

Rare Earth is a generic name used for the 14 metallic elements of the lanthanide series used in the manufacturing of FCC catalyst to improve stability, activity, and gasoline selectivity of the zeolite.

Reactor or Riser Outlet Temperature (ROT) is often used to regulate the catalyst circulation rate from the regenerator to the reactor.

Reformulated Gasoline (RFG) is the gasoline sold in some ozone nonattainment metropolitan areas designed to reduce ozone and other air pollutants.

Refractive Index (RI) similar to aniline point, is a quantitative indication of a sample's aromaticity.

Refractory is a cement-like material used to stand abrasion and erosion.

Reid Vapor Pressure (RVP) is gasoline vapor pressure at 100°F (38°C).

Research Octane Number (RON) is a quantitative measure of a fuel to "knocking," simulating the fuel's performance under low engine severity (at 600 rpm and 120°F (49°C)).

Resid refers to a process, such as resid cat cracking, that upgrades residual oil.

Residue is the residual material from the processing of raw crude (e.g. vacuum *residue* and not vacuum resid).

Riser is a vertical "pipe" where virtually all FCC reactions take place.

Riser Termination Device (RTD) is any mechanical device connected to the end of the riser to separate the bulk of incoming catalyst.

Saybolt Furol Viscosimeter (SFV) is an instrument for measuring viscosity of very thick fluids, for example heavy oils.

Selectivity is the ratio of yield to conversion for the "desired" products.

Silica Oxide to Alumina Oxide Ratio (SAR) is used to describe the framework composition of zeolite.

Skeletal Density is the actual density of the pure solid materials that make up individual particles.

Slide Valve or Plug Valve is a valve used to regulate the flow of catalyst between reactor and regenerator.

Slip Factor is the ratio of catalyst residence time to the hydrocarbon vapor residence time in the riser.

Soda Y Zeolite is a "crystallized" form of Y-faujasite before any ion exchanges occur.

Soft Coke is Reza's term used to describe volatile hydrocarbon with the spent catalyst, any portion of the unvaporized/uncracked FCC feedstock, as well as the torch oil that is used in the regenerator.

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Sonic Velocity In dry air, the speed of sound is 1,126 ft/s (343 m/s) or 768 m/h (1,236 km/h).

Sour Gas is a natural gas that contains corrosive, sulfur-bearing compounds such as hydrogen sulfide and mercaptans.

Specific Gravity is the ratio of the density (mass of a unit volume) of a substance to the density (mass of the same unit volume) of a reference substance (i.e. water for liquids or air for gases).

Spent Catalyst is the coke-laden catalyst in the stripper.

Standpipe is a means of conveying the catalyst between reactor and regenerator.

Stick-Slip Flow is erratic circulation caused when the catalyst packs and bridges across the standpipe.

Straight-Run Gasoline is gasoline produced by the primary distillation of crude oil. It contains no cracked, polymerized, alkylated, reformed, or visbroken stock.

Stress Corrosion Cracking (SCC) is the unexpected sudden failure of normally ductile metals subjected to a tensile stress in a corrosive environment, especially at an elevated temperature in the case of metals.

Superficial Velocity is simply the velocity of a fluid in a vessel in the absence of any internal equipment (e.g. cyclones).

Sweetening is processes that either remove obnoxious sulfur compounds (primarily hydrogen sulfide, mercaptans, and thiophenes) from petroleum fractions or streams, or convert them, as in the case of mercaptans, to odorless disulfides, to improve odor, color, and oxidation stability.

Thermal Conductivity is a measure of heat transferred across a specific medium.

Thermal Cracking is the breaking up of heavy oil molecules into lighter fractions by the use of high temperature without the aid of catalysts.

Third Stage Separator (TSS) is a cyclonic collection device, or system installed following the two stages of cyclones within the FCC regenerator in the gas outlet line. Its function is to capture catalyst escaping from the regenerator to protect downstream equipment and/or reduce particulate emissions to the atmosphere.

Transport Disengaging Height (TDH) is the zone required for particles with terminal velocities less than the gas velocity to fall back to the bubbling bed.

True Boiling Point (TBP) is the distillation separation which has characteristics of 15 different theoretical plates at 5 to 1 reflux ratio.

Turnaround (TAR) is a planned complete shutdown of an entire process or section of a refinery, or of an entire refinery to perform major maintenance, overhaul, and repair operations and to inspect, test, and replace process materials and equipment.

Ultralow Sulfur Diesel (ULSD) is diesel fuel with a maximum sulfur content of 15 ppm.

Ultrastable Y (USY) is a hydrothermally treated Y-faujasite, which has a unit cell size at or below 24.50 Å and exhibits superior hydrothermal stability over Soda Y faujasite.

Unit Cell Size (UCS) is an indirect measure of active sites and SAR in the zeolite.

UOP formerly Universal Oil Products.

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Vortex Disengaging System (VDS) is a riser termination device design offered by UOP for FCC units with external risers.

Vortex Separation System (VSS) is a riser termination device design offered by UOP for FCC units with internal/central risers.

Wet Gas is a gas containing a relatively high proportion of hydrocarbons that are recoverable as liquids.

Wet Gas Compressor (WGC) compresses the wet gas or vapors from the main fractionator overhead drum. The WGC is typically a two-stage intercooled centrifugal machine.

Zeolite is a synthetic crystalline alumina−silicate material used in the manufacturing of FCC catalyst.

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