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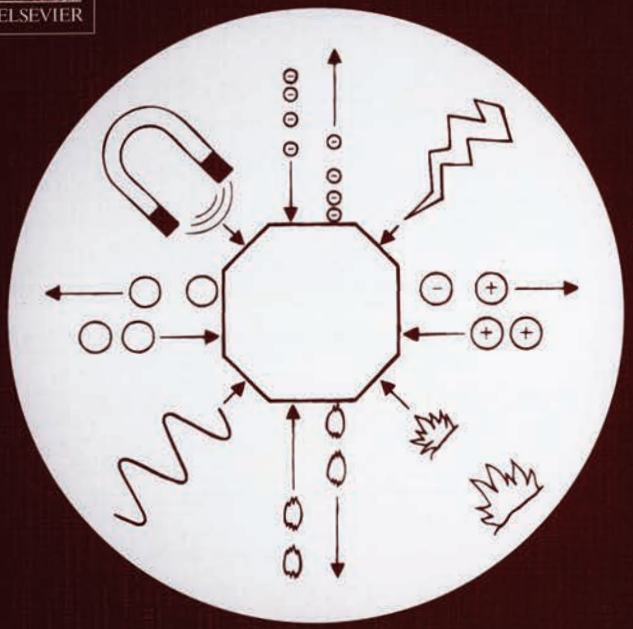
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FISCHER-TROPSCH TECHNOLOGY

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A.P. Steynberg
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FOREWORD

Fischer-Tropsch technology is unique in many ways. Discovered early in the last century along with many other bulk chemical technologies, its development has been hampered by the lack of a continuous market pull. Interest in Fischer-Tropsch technology as a source of alternate fuels has been in spurts, driven by wars, political situations and peaks in the price and availability of crude oil. There have been surges of interest in the thirties and during the Second World War, in the fifties, as a result of the oil crisis of the seventies and now again in the last seven years or so. It is just possible that the present interest in Fischer-Tropsch technology is sustainable and will result in the establishment of a GTL industry. The signs are good.

There is a solid realization that the gas reserves exist and that they are largely in areas where the normal pipeline and power uses are not feasible. There are several nations and geographical areas with the right mix of gas reserves, local infrastructure and intent to add to their existing portfolios. The qualities of Fischer-Tropsch products are excellent and their environmental properties are being recognized as very valuable in the ongoing drive towards cleaner fuels and engines. The perceptions of supply/demand balance and pricing of crude oil are beginning to create an economic incentive for the conversions of gas to liquid fuels. And, above all, technology improvements reported by many of the major players have resulted in large and unprecedented reductions in the cost of the technology. All of these positive factors combined lead one to an expectation that Fischer-Tropsch technology will at last take its place as a significant factor in the global energy scene.

While the beginnings of Fischer-Tropsch were in the search for ways to turn coal into a liquid transport fuel, from the above it is now likely that its future is as a means of monetizing natural gas. Gas to Liquids technology, or GTL as it is referred to, is a complex integrated set of technologies with Fischer-Tropsch at its heart. While conversion of both coal and natural gas to liquids has been practiced in numerous locations over the whole history of the technology, today the only commercial operations are in South Africa (both coal and natural gas) and in Malaysia. The operations provide the springboard from which large modern GTL plants can be built and operated. While large plants, which benefit from economy of scale, are usually studied and are considered to be most likely to be viable, the use of GTL in niche applications for recovery of associated gas should not be forgotten.

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For GTL technology to be converted from a curiosity into a modern industry, it has to be practiced by several players in multiple plants in several geographical areas. The GTL fuels and indeed the chemical co-products need to be marketed globally. The extent of the challenge involved should not be underestimated. To achieve commercial success GTL plants need to be built at a scale that has not been done before. In many cases, technologies practiced at a size of a few hundred barrels per day need to be scaled up by a factor of 100 or more and then incorporated into complexes costing billons of dollars. The plants will be located in remote locations often with unique difficulties. Of the many organizations preparing to enter this field only one or two have any commercial experience with the technology. The risks are indeed daunting. They are particularly so for multiple gas based units and products not often handled in the past. Small mistakes, omissions and oversights during design can very quickly lead to lengthy and extremely costly delays.

The construction by Sasol and its partner in Qatar of the 34,000 barrel per day Oryx GTL plant is a first step down the road. The approval of this project and its financing by consortia of international banks has clearly demonstrated to the world that GTL is real. This is confirmed by the large number of announcements of even larger projects mostly in the Middle East. There is every reason to believe that the technology patented by two German scientists, Frans Fischer and Hans Tropsch so many years ago is now well on the road to be the basis for a new global industry.

Given the interest in GTL, I believe that this book is extremely well timed. Its contents will be valuable to large numbers of engineers and scientists from the major GTL players through to the engineering contractors and equipment suppliers involved in the industry. Many of the chapters will give valuable background to newcomers to the industry and will reinforce the knowledge of the experienced. A blend of technical history book, academic review and reference, practical design manual and record of commercial reality, it will be welcomed by all technical people in the field.

The book contains a summary and review of a large amount of published material supplemented by the authors' extensive experience and know-how. Sasol related background has clearly dominated the book but, with over 50 years of practical CTL, GTL and Fischer-Tropsch experience this is not surprising. Indeed a Fischer-Tropsch reference without Sasol would not be complete. The many co-authors are all well known in the industry and bring together a collective experience that will be hard to beat.

In conclusion I would like to express my hope that Fischer-Tropsch will find its place in the global energy world and that this book will play its part in helping reach this goal.

John Marriott – July 2004

PREFACE

Remote natural gas has traditionally been used to supply energy markets through Liquefied Natural Gas (LNG), and sometimes to produce chemical products e.g. methanol. The last few years have seen a marked increase in the interest for the application of Fischer-Tropsch (FT) technology for the conversion of natural gas into easily transportable liquid hydrocarbon products. Several commercial scale plants have been announced and some are in advanced stages of design or even construction.

The successful commercial application of FT technology requires a very broad range of expertise. This demands a cooperative effort. Perhaps this is why companies that are active in the field stress the need for teamwork. Although some of the major oil companies may be capable of putting FT facilities in place using mainly in-house technology, it is expected that the most cost effective plants will require cooperation between several technology providers.

As an example of this approach Sasol™ and ChevronTexaco have formed the Sasol Chevron global alliance in order to apply FT technology to the conversion of remotely located natural gas to liquid products. This is expected to place the Gas-to-Liquids (GTL) industry on a footing similar to the LNG industry and involves massive capital expenditure measured in billions of US dollars ($US X 10^9). The prime example of a major oil company using mainly in-house technology for their GTL projects is Shell.

In the case of Sasol Chevron, the ChevronTexaco partner is well versed with natural gas utilization and the recovery of value from the associated condensate and natural gas liquids (NGL's, i.e. C_3+ hydrocarbons). The alliance uses technology from Haldor-Topsøe to produce synthesis gas from the lean natural gas. The synthesis gas preparation requires oxygen prepared in large scale air separation units (ASU's). The ASU's are provided by a number of American and European companies that bid on a competitive basis for the supply of these units. The ASU is the single most expensive unit in the GTL complex. Sasol provides the FT technology and the primary liquid products are upgraded using ChevronTexaco hydroprocessing technology. ChevronTexaco has a well established global network for the marketing of the fuel and lubricant products while Sasol has a significant global presence in the marketing of relevant commodity chemicals.

For the Sasol Chevron projects, a diverse team at the Foster Wheeler office in Reading, England does the feasibility studies and the Front End Engineering and Design (FEED) and prepares bid packages to enable large engineering and construction firms to bid for the engineering, procurement and construction (EPC). Currently detailed engineering and procurement is being done in Rome, Italy by Technip-Coflexip for the ORYX GTL Limited plant in

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Qatar (a joint venture between Sasol and Qatar Petroleum). Sasol initiated this project prior to the formation of Sasol Chevron.

Sasol uses Stone & Webster in Cambridge, USA to assist with the engineering for the FT unit. The design of the FT unit is based on technology that was developed and demonstrated in Sasolburg, South Africa, where the Sasol corporate R&D facilities are located. Sasol also has an alliance with IHI from Japan for the supply of the FT reactor vessels. Currently, the only vessel fabricators capable of delivering these large vessels on a competitive basis are all based in Japan and Korea. Based on Sasol's commercial experience with large and complex plants using FT technology, Sasol takes overall technical responsibility as the single point licensor in addition to licensing the FT unit.

Two significant questions may be posed:

- How did FT technology develop to the point where it is set to form the basis for a significant new industry in the 21st century?
- What scope is there for the further development and application of this technology?

If these questions are of interest then this book should provide some useful insight.

This book has two primary aims: firstly, it is a comprehensive work documenting the state of the art for FT technology. It will be of use to people active in advancing and implementing this technology. There are comprehensive references to patents and previous publications. (A useful website for the location of additional historical publications relating to FT technology may be found at http://www.fischer-tropsch.org).

Secondly, this book is suitable for use as a reference book for courses in the fields of chemistry and chemical engineering. The book provides an explanation of the basic principles and terminology that are required to understand the application of FT technology. Known and proposed applications for the technology are described.

The intended audience is therefore researchers active in the development of FT technology, engineers involved in the implementation of this technology and students in the fields of chemistry and chemical engineering.

Existing text books and reference works dealing with the theory and application of FT technology are now somewhat dated. No single source exists that covers past, present and future applications starting with an explanation of the basic principles. This is the first publication that allows students to understand both theory and application for modern FT technology. The book is also useful as a contemporary reference work for those wishing to study the history of the application of FT synthesis. It can be used to locate previously

reported research work and to understand the context and significance of the cited research. The text identifies the aspects of the technology that are proprietary and describes those aspects that can be considered to be open art. The emphasis is on explanation of principles, limits and the reasons for compromise in this technology field.

As with other endeavours relating to FT technology, this book is the result of a cooperative effort. Although it is the result of a Sasol initiative, the intention is to serve the interests of the rapidly expanding industries based on the use of FT technology. An attempt was made to involve the world's leading academic authorities and industry experts.

On the subject of synthesis gas generation from natural gas there was no need to look further than Haldor-Topsøe who are at the forefront of technology developments in this field and have previously produced many excellent publications. Their contribution to Chapter 4 is greatly appreciated. In the case of the coal gasification route to synthesis gas it was decided to use in-house experts from Sasol since Sasol is the world's largest producer of synthesis gas from coal. My thanks go to Dr Martin Keyser and Retha Coertzen for their contributions.

Nobody is better suited to bridge the gap between academic endeavour and industrial application than Professor Mark Dry from the University of Cape Town and formerly the head of Fischer-Tropsch research at Sasol. Professor Dry assisted with the editing of all parts of this book and provided a great deal of guidance in determining the content of the book. Mark Dry is the sole author for Chapter 3 dealing with the chemical principles that need to be understood for FT applications and Chapter 7 dealing with FT catalysts.

Professor Hans Schultz, a world renowned FT researcher from the University of Karlsruhe, also provided guidance on the appropriate ordering of the material. Professors Michael Claeys and Eric van Steen both now at the University of Cape Town had previously worked closely with Hans Schultz and were recommended by him to contribute a chapter dealing with the understanding of FT chemistry at a fundamental level. The result is Chapter 8.

My main contribution is to be found in Chapter 2 dealing with the FT reactors with which I have had a 24 year love affair. I am also very grateful to Professor Krishna from the University of Amsterdam, The Netherlands, for reviewing the material on FT reactors in Chapter 2. Excellent research is done on fluidization technology in the Netherlands and there is good cooperation in this field between a number of Dutch and German universities. Professor Krishna has published extensively and is especially well known for his work on slurry bubble column reactor systems. Thanks to Dr Berthold Breman who heads the Sasol Technology Process Development group based at Twente University in the Netherlands for the material dealing with fixed bed reactors.

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This Process Development group was founded recently by Dr Ben Jager (now retired) who was also responsible for establishing the Process Development group in Sasolburg in which I worked for most of my career.

Important contributions particularly in Chapter 2 were also made by Professor Burtron Davis from the University of Kentucky. He is at the forefront of research in the field of FT catalysis, particularly for iron based catalysts used in low temperature FT reactors and is also particularly knowledgeable on the history of FT technology. He is well versed in all research and technology development activities in the USA that relate to FT technology. Professor Davis also reviewed Chapters 1, 2, 3, 5, 7 and the gasification material in Chapter 4.

Dr Marco Frank from the Twente group and Dr Jannie Scholtz (FT Technology Manager at Sasol) provided some valuable insights into the thermodynamic constraints for FT applications that are discussed in Chapter 5.

Chapter 6 was produced primarily by in-house experts at Sasol. Arno de Klerk provided the material dealing with the upgrading of products from the Synthol process (i.e. high temperature FT, HTFT) while Luis Dancuart was mainly responsible for the section dealing with the low temperature FT (LTFT) products. Dr Rob de Haan provided some sections dealing with hydroprocessing catalysts. The contribution from Dr Jerome Meyer and Richard Moore from ChevronTexaco, after reviewing all the material relating to hydroprocessing, is also gratefully acknowledged.

Given that this book is the result of part time contributions from people employed to do other things it has taken some time to reach completion. There is no doubt still room for improvement. Some areas such as those dealing with FT catalysts and FT products could benefit from more in depth publications that will hopefully follow this book.

Many other Sasol employees provided some assistance with this book. In particular I would like to thank Dr Anton Vosloo and Dr Jannie Scholtz for reviewing all the material; Ed Koper who was a constant source of support (moral and financial) and Caleb Hattingh for helping with some of the illustrations and equations.

Finally I would like to thank my employer, Sasol Technology, for allowing me to spend company time on the production of this book, Sasol Chevron for their financial support and to my family for accepting my neglect while working on this project.

André P. Steynberg
Sasolburg, May 2004

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Chapter 4

Synthesis gas production for FT synthesis

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1. INTRODUCTION

The technology used to prepare the synthesis gas used for Fischer-Tropsch synthesis can be separated into two main categories, gasification and reforming. The use of these terms is not unambiguous, see Section 3.1. Gasification is the term normally used to describe processes for conversion of solid or heavy liquid feedstock to synthesis gas, while reforming is used for conversion of gaseous or light liquid feedstock to synthesis gas. Some technologies, particularly high temperature partial oxidation, can be used for a whole range of feeds and the literature may then refer to 'gasification' to include methane reforming. In a recent text book on the topic of gasification by Higman and van der Burgt [1], the term 'gasification' includes what is classified here as adiabatic oxidative reforming. The reader is advised to consult this book [1] for both more detailed description of gasification technologies and a broader description of applications that do not involve Fischer-Tropsch (FT) synthesis.

Future FT synthesis units may include the co-production of electrical power, so an understanding of the issues relating to power generation is also relevant to the application of FT technology. Even without power export, FT technology applications require large scale power generation for in-house use.

The most common feeds used to prepare synthesis gas for FT synthesis are coal, which is rich in carbon, and natural gas, which is rich in methane. The term 'carbonaceous' feed is commonly used and this implies any carbon containing feed material. Other feedstock examples are coal bed methane, heavy oils, bitumen and petroleum coke (petcoke). In general, the feed will become more

desirable as the hydrogen content increases. The reasons for this are explained in Chapter 5.

It is usually better to convert carbonaceous liquids directly to refined products, for example by some type of hydroprocessing technology, rather than by conversion via synthesis gas. Gaseous hydrocarbons are already valuable products if they can be piped to nearby consumers. Only remotely located gas is considered for large-scale conversion to liquid fuels. However, smaller scale applications for the production of high value chemicals are common wherever natural gas is found. Coal conversion is more expensive than natural gas conversion but may be worthwhile if the coal price is low enough and if both electricity and higher value hydrocarbon products are co-produced with liquid fuels on a large scale.

2. SYNTHESIS GAS PREPARATION VIA REFORMING

2.1 Introduction

The synthesis gas preparation section is an important part of the entire GTL complex. It is the most expensive of the three process sections (synthesis gas preparation, FT synthesis, and product work-up), and it is responsible for the largest part of the energy conversion in the plant. The design of the synthesis gas preparation unit is, therefore, critical for the economics of a GTL project. However, as explained in Chapter 5, the design of the synthesis gas section depends critically on factors outside the section itself, ultimately of course on the feedstock characteristics and the desired product slate. The product slate will determine the choice of type of FT synthesis (HTFT, LTFT, iron or cobalt-based catalyst, type of synthesis reactor, etc.) and the operating conditions in the chosen synthesis unit, and this will in turn determine the desired characteristics of the synthesis gas. The feedstock characteristics will then, together with the desired product gas, dictate the choice of synthesis gas technology to be applied. When the feedstock is natural gas or similar, the choice will be between various forms of reforming and gasification technologies and combinations thereof.

Without going into details it is noted that with respect to desirable synthesis gas characteristics, mainly two situations exist:

A. The FT synthesis catalyst has, in addition to its activity for the FT synthesis reaction, also activity for the shift reaction. CO_2 is thus a reactant, and the desired synthesis gas composition is similar to that of methanol synthesis gas. It may be characterised by the so-called stoichiometric number (SN) or module $M = (H_2 - CO_2)/(CO + CO_2)$ or by the so-called Ribblett ratio $R = H_2/(2CO + 3CO_2)$. For stoichiometric gas for production of hydrocarbon products with H/C = 2.0 (or of methanol), $M = 2R = 2.0$.

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B. The FT synthesis catalyst has no activity for the shift reaction. CO_2 is essentially inert, and the synthesis gas composition is best characterised by the H_2/CO ratio, which should ideally be somewhere between 2.0 and 2.2 depending on the overall H/C ratio in the product. However, the H_2/CO ratio actually required depends on catalyst characteristics and may differ from the ideal value.

In both situations, the ideal synthesis gas has a low content of inerts, mainly CH_4 and N_2, and a high CO/CO_2 ratio. Some claim that a high content of inerts, e.g. N_2 from synthesis gas preparation processes using air, is beneficial, since it assists in controlling the temperatures in the FT synthesis reactors. However, this argument is false. By proper design of the synthesis reactors, satisfactory temperature control can be achieved without dilution with inerts. Furthermore, a high content of inerts in the synthesis gas excludes internal and external recycle of tail gas, and this leads to undue restrictions in the optimisation of overall process schemes, especially when energy export from the GTL complex is undesirable.

In order to identify the optimum overall layout of the synthesis gas section, extensive integration studies involving intimate knowledge about synthesis gas technology and technology for FT synthesis and product work-up are required. The result of such studies will in most cases be that the synthesis gas section will have to process not only fresh feedstock, but also considerable amounts of gas recycled within the complex, with properties which are determined by the design of the other sections of the plant. This means that changes in e.g. operating parameters in one section will have an influence on the conditions for design of other sections, and this of course significantly complicates the studies.

It is not the purpose of the following sections to discuss the specific integrated solutions, which may result from studies for specific situations. This will be discussed in Chapter 5. Rather, this chapter will present technologies for conversion of natural gas to synthesis gas by various forms of reforming. Furthermore, the possible process schemes obtainable by combinations of the technologies will be described.

The technologies to be discussed are:

- Final feed gas purification
- Adiabatic prereforming
- Fired tubular and heat exchange steam reforming
- Adiabatic, oxidative reforming
- Other technologies such as CPO (Catalytic Partial Oxidation) and CMR (Ceramic Membrane Reforming).

An impressive amount of literature is available on the various types reforming. Examples discussing several different technologies and containing further references may be found in [2 – 9].

2.2 Feedstock purification

2.2.1 Feed gas characteristics and purification requirements

The feedstock for a GTL facility may be natural gas or associated gas. In both cases the primary feedstock may be treated in gas treating units to remove and recover higher hydrocarbons (NGL or LPG) and, when relevant, by gas sweetening to reduce high concentrations of CO_2 and/or S compounds. Gas treating technology is considered to be outside the scope of this section. Typically, the normal, treated feed will be lean with a high CH_4 content. However, the upstream treating units may fail, and it will in most cases be necessary to design the synthesis gas preparation unit in such a way that it can absorb significant changes in feed composition without adverse effects in downstream units.

Typical feed gas specifications are shown in Table 1.

Table 1
Typical feed gas specifications

	Natural Gas		Associated Gas	
	Lean	Heavy	Lean	Heavy
N_2, vol%	3.97	3.66	0.83	0.79
CO_2, vol%	-	-	1.61	1.50
CH_4, vol%	95.70	87.86	89.64	84.84
C_2H_6, vol%	0.33	5.26	7.27	6.64
C_{3+}, vol%	-	3.22	0.65	6.23
Max. total S, vol ppm	20	20	4	4
Hydrogen sulphide, vol ppm (typical)	4	4	3	3
COS, vol ppm (typical)	2	2	n.a.	n.a.
Mercaptans, vol ppm (typical)	14	14	1	1

The most important impurities to be considered in the feedstock purification unit are H_2S and other S compounds, since these compounds are poisons for downstream catalysts, both in the synthesis gas preparation section and in the FT synthesis section. In most actual cases details about type and concentration of individual S compounds will not be available or, if they are given, they will often be unreliable and prone to variations over time. However, it must be expected that organic S compounds such as COS, mercaptans, and also heavier compounds such as sulphides, di-sulphides and thiophenes may be present in low concentrations - perhaps too low to allow detection, but still high enough to be harmful to catalysts.

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Other impurities, e.g. solids, moisture, and certain trace components such as Hg may be present in the raw feedstock. Removal of such impurities is considered part of gas treating. N_2 and CO_2 are often present in minor quantity. N_2 will generally be an inert with no detrimental effects other than the resulting dilution of the synthesis gas. Trace amounts of N compounds such as NH_3 and HCN may be formed in the reactors in the synthesis gas preparation section and may have to be removed from the synthesis gas before it is passed to the FT synthesis section. The effects of a content of CO_2 are significant and must be taken into account as described in the following paragraphs. Halogens such as organic Cl compounds or HCl are generally not present in typical feeds to GTL plants. If they are present they must be removed to a very low level since they may otherwise cause problems (catalyst poisoning and corrosion) in downstream units. Oxygenates may also be present in the feed, e.g. methanol added to the natural gas to avoid hydrate formation. Oxygenates may also be present in recycle gases originating from other sections of the plant.

There is no absolute value for the acceptable concentration of S compounds in the purified gas. However, for certain types of downstream catalysts, both in the synthesis gas preparation section and in the FT synthesis section, very low concentrations, preferably single digit ppb, are necessary to ensure acceptable lifetime. It may be noted that it is not a trivial task to determine S concentrations at these levels. First of all sampling is difficult, because most surfaces may adsorb and later desorb S compounds depending on the gas phase concentrations. Special materials and procedures are required to obtain a representative sample of the gas. Surveys of available analytical methods for analysis of total S concentration and concentration of individual S compounds in gases may be found in [10, 11]. With the methods described, the detection limit is about 10 ppb for individual S compounds and down to 2 ppb for total S content.

The main problem in final gas purification is thus to remove essentially all S compounds - type and concentration uncertain and variable – from the feed to a concentration in the purified synthesis gas that is preferably below the detection limit, using standard analysis equipment, of a few ppb.

2.2.2 Principles of gas desulphurisation

The typical process concept for desulphurisation of natural gas and similar feedstock is a two-step process based on hydrogenation of organic S compounds (and Cl compounds if they are present) and subsequent adsorption/absorption of H_2S (and HCl). This process concept has been used industrially for decades and is well documented in the literature, see e.g. [12 – 14]. A typical layout for desulphurisation of gas with a relatively high S concentration is shown in Fig. 1.

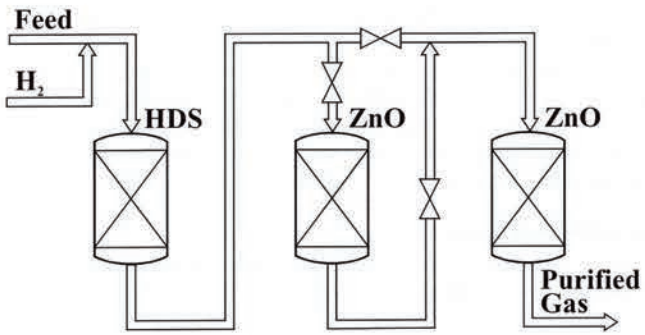


Figure 1 Typical process flow diagram for desulphurisation of natural gas

The feedstock is mixed with a small amount of hydrogen or hydrogen-rich gas, preheated to 350-400°C, and passed to a first reactor containing a hydrogenation catalyst, typically based on cobalt and molybdenum (CoMo) or nickel and molybdenum (NiMo). After the hydrogenation reactor the gas passes to two S absorbers in series, both typically containing zinc oxide (ZnO), which absorbs the H_2S formed in the hydrogenation reactor. In special cases, e.g. when the feed contains high concentrations of CO_2 and very low concentrations of S compounds, a special absorption material may be required downstream the ZnO. If organic Cl compounds are present in the feed, HCl will be formed in the hydrogenator. The HCl can react with ZnO and form $ZnCl_2$. At normal operating conditions in the S absorber, $ZnCl_2$ will sublimate and deposit on downstream catalysts or heat transfer surfaces. Therefore, HCl should be removed by a special absorbent, normally an activated alumina, placed in a vessel between the hydrogenator and the first S absorber.

Variations of the process concept shown in Fig. 1 may be used. In the simplest case, only one vessel is used with a top layer of hydrogenation catalyst and a bottom layer of ZnO. In other cases, the hydrogenation reactor is followed by only one S absorber. In special cases, a last layer of an absorption material with high chemisorption capacity may be installed in the bottom of the last S absorber or in a separate vessel after the last S absorber. In the layout shown in Fig. 1, valves and piping are installed so that the first S absorber can be isolated for change of ZnO as needed while the plant is running. In an alternative layout with two S absorbers, valves and piping are installed so that the vessel with fresh ZnO will always be the last of the two absorbers ('Swing operation'). This arrangement is not well-suited for cases with stringent requirements for purification, since some sulphur will always be absorbed on piping etc. upstream

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the absorber, and part of this sulphur will, after a 'swing', be passed to downstream catalysts.

Other processes such as cold absorption of S compounds on iron oxide or molecular sieves have been used to desulphurise natural gas before processing in e.g. ammonia and hydrogen plants, see e.g. [15, 16]. However, these processes can not provide the very high purity required in GTL applications; they will not be considered in the following text.

2.2.3 Reactions in the hydrogenator

The conversion of organic S-compounds over the hydrogenation catalyst depends on hydrogenolysis (addition of hydrogen over the S-C bond) by reactions such as:

$$R\text{-}SH + H_2 = RH + H_2S \quad (1)$$
$$R\text{-}S\text{-}R_1 + 2H_2 = RH + R_1H + H_2S \quad (2)$$
$$R\text{-}S\text{-}S\text{-}R_1 + 3H_2 = RH + R_1H + 2H_2S \quad (3)$$
$$C_4H_8S \text{ (tetrahydrothiophene)} + 2H_2 = C_4H_{10} + H_2S \quad (4)$$
$$C_4H_4S \text{ (thiophene)} + 4H_2 = C_4H_{10} + H_2S \quad (5)$$
$$R\text{-}Cl + H_2 = RH + HCl \quad (6)$$

All these reactions have very large equilibrium constants in the temperature range relevant for desulphurisation reactors, see [13]. This means that full conversion is achievable for all types of organic S compounds, if sufficient H_2 is present. If no or too little H_2 is present, the S compounds may react by thermal decomposition forming olefins and H_2S. For some compounds this may happen at temperatures prevailing in the preheaters upstream the hydrogenation reactor. This is undesirable, and H_2 should therefore preferably be added before preheating. It may be added that the same tendency can be seen for dehydrogenation of hydrocarbons. As an example, Fig. 2 shows the equilibrium concentration of butene in n-butane as function of temperature with and without the presence of H_2. It is seen that significant concentrations of olefins may be formed at high temperature in H_2-free gas.

The hydrogenolysis reactions are generally first order with respect to the S compound and between zero and first order with respect to H_2 [13] The reaction rate differs significantly for the different types of S compounds with sulphides ($R\text{-}S\text{-}R_1$) and thiophenes being the most difficult to convert followed by di-sulphides and mercaptans.

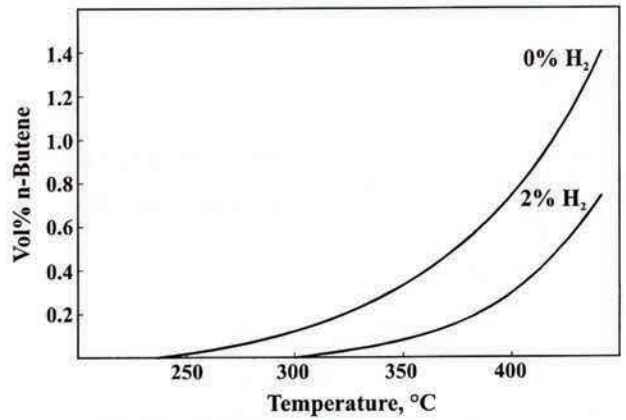


Figure 2 Equilibrium concentration of butene in n-butane at 30 bar g

Oxygenates such as methanol may react with H_2S in the hydrogenator to form organic S-compounds such as mercaptans and sulphides:

$$CH_3OH + H_2S = CH_3SH + H_2O \quad (7)$$
$$2CH_3SH = (CH_3)_2S + H_2S \quad (8)$$

If the temperature is too low, the rate of conversion of the organic S compounds may be too low, and some mercaptans or sulphides may pass unconverted through the hydrogenator. At sufficiently high temperature, practically complete conversion to H_2S (and COS) will be ensured.

Carbon oxides and carbonyl sulphide (COS) interact with H_2 and steam according to the following reactions:

$$COS + H_2O = CO_2 + H_2S \quad (9)$$
$$CO + H_2O = CO_2 + H_2 \quad (10)$$

Both these reactions will generally be at equilibrium after the hydrogenator. The equilibrium constants are shown in Fig 3.

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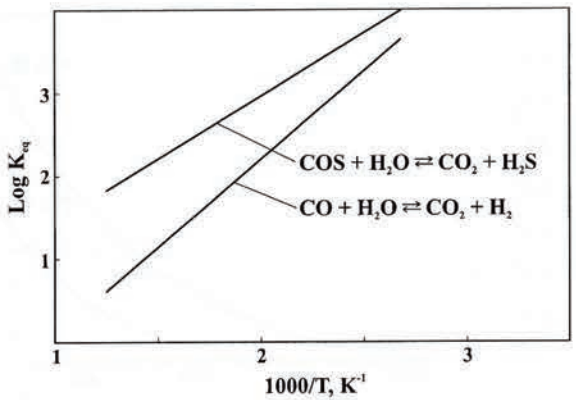


Figure 3 Equilibrium constants for COS hydrolysis and the shift reaction

In total a potentially rather complicated situation exists. However, as indicated above it may be expected that all the reactions (1) – (10) are active in the hydrogenator and reach a close approach to equilibrium. Calculations show that if this is the case, then the concentration of organic S compounds other than COS will be below 1 ppb at all temperatures below about 450°C. The equilibrium concentration of COS may be quite high, especially at high temperature and high CO_2 concentration.

2.2.4 Hydrogenation catalysts

The catalysts used for hydrogenolysis of the organic S compounds are based on either cobalt molybdate (CoMo) or nickel molybdate (NiMo). The catalysts are prepared by impregnation on high surface area carriers, usually alumina. The catalysts supplied by leading catalyst suppliers such as Haldor Topsøe, Südchemie and Johnson Matthey are all of this type, although differences obviously exist in formulation and shape.

The active phase in the operating catalyst is the so-called Co-Mo-S or Ni-Mo-S phases. The Co-Mo-S phase - and the corresponding Ni-Mo-S phase - is not a well-defined compound. Rather "it should be regarded as a family of structures with a wide range of Co concentrations, ranging from pure MoS_2 up to essentially full coverage of the MoS_2 edges by Co" (cited from p. 32 in [17], an authoritative review of hydrotreating catalysts and catalysis).

The hydrogenation catalysts are manufactured and supplied normally in the oxide state and must be converted to the sulphided state to gain full activity. This sulphidation will normally take place by exposing the catalyst as delivered

to the normal operating conditions in the plant, i.e. the sulphur for the sulphidation is supplied by the feed and at the concentration at which it is available.

The degree of sulphiding and thereby the catalyst activity depends on the amount of sulphur present in the feedstock used for sulphiding and during normal operation. At high concentrations of sulphur in the feedstock, the sulphiding is rapid and complete and the activity is at a high and constant level. When the sulphur concentration in the natural gas is low, the amount of the active Co-Mo-S phase in the catalyst will decrease and the catalyst activity is likewise lower. The sulphidation will also take a long time, in extreme cases several months. In such cases the sulphidation may be accelerated and enhanced by addition of an easily decomposed S-compound (usually di-methyl-di-sulphide, DMDS) to the feed until full sulphidation has been achieved.

If the S content in the feed is constant and low, the stable S concentration in the catalyst and thus the activity will be low. The reduced activity is normally not a problem as long as the low sulphur content in the feedstock is constant. However, if the organic sulphur content suddenly increases, the catalyst may not convert these compounds sufficiently for a short period (days) due to insufficient activity. After a few days of operation at high S concentration the hydrogenation catalyst will be fully sulphided and the slip of organic sulphur goes down. In cases where such variations are foreseen, problems may be avoided by addition of a sulphur compound e.g. DMDS to the feed in periods with very low S concentration.

2.2.5 Reactions in the sulphur absorber

After the hydrogenation reactor the gas will, as explained above, mainly contain S in the form of H_2S. Any Cl will be present as HCl. If CO_2 is present in the hydrocarbon feed, significant amounts (several hundred ppb) of COS may also be present. Other S compounds may be present only in low ppb concentrations in the product gas from a well functioning hydrogenator.

In the absorption vessel, H_2S reacts with ZnO according to:

$$ZnO + H_2S = ZnS + H_2O \qquad (11)$$

The equilibrium constant for this reaction is shown in Fig.4.

In addition to the bulk phase reaction with H_2S the ZnO also has some activity for reaction (9), COS hydrolysis, and for reaction (10), the shift reaction. Absorption of H_2S will cause the COS hydrolysis (9) to proceed to full conversion, and COS will thus be completely removed by ZnO operating at the proper temperature. Finally, a certain capacity for chemisorption of H_2S must be taken into account when considering the performance of ZnO in the absorption vessel.

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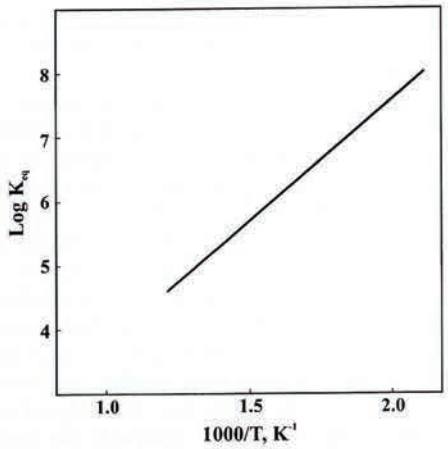


Figure 4 Equilibrium constant for reaction (11)

If the feedstock contains carbon dioxide, the reverse of the shift reaction (10) will cause the steam content in the gas to increase considerably. The increased steam content will have an impact on the equilibrium for absorption of H_2S on the ZnO, reaction (11). Fig. 5 shows, as an example, the equilibrium content of H_2S as function of temperature over ZnO at a CO_2 content in the feedstock of 5% and varying H_2 concentration.

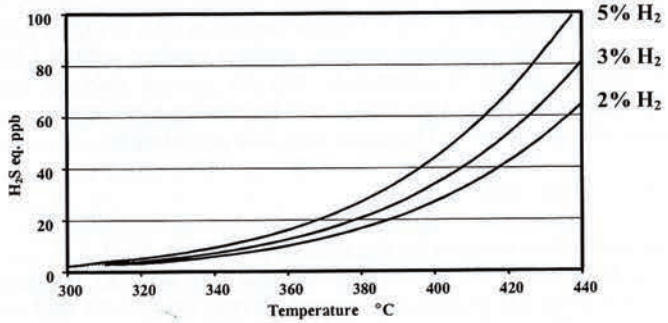


Figure 5 Equilibrium H_2S, 5% CO_2 in natural gas

Fig. 6 shows, for the case with 3% H_2 in the feed, the concentrations of CO, CO_2 and H_2 in the equilibrated gas. It is seen that significant amounts of CO may be formed. The possible formation of carbon in downstream equipment due to this presence of CO must be taken into account in the design, see [18].

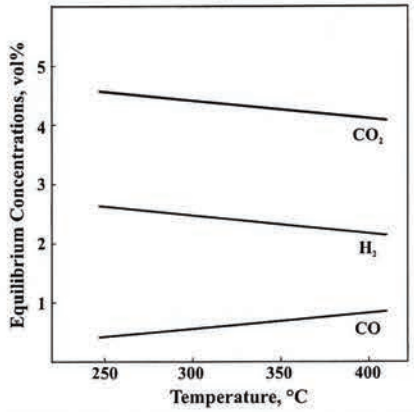


Figure 6 Equilibrium concentrations of CO, CO_2, and H_2; 3% H_2 and 5% CO_2 in the feed

From the above it is obvious that there are two ways to reduce the equilibrium level of hydrogen sulphide and CO over ZnO in cases where CO_2 is present in the feed:

- By reducing the temperature in the HDS section
- By reducing the H_2 recycle

It is noted that the temperature has a greater impact on the equilibrium sulphur content on ZnO than the amount of hydrogen recycle.

However, as previously discussed, both the hydrogen recycle and the temperature play a vital role with regard to the performance of the HDS section. If the hydrogen recycle is reduced, the reaction rate on the hydrogenation catalyst is decreased, and there is a risk that organic sulphur starts to leak. If the temperature is decreased, the hydrogenation reaction rate is again reduced, and the sulphur absorption efficiency of the ZnO becomes lower. Furthermore, the risk for leakage of organic S compounds from the hydrogenator increases at low temperature, and the ability of ZnO to absorb these compounds decreases with decreasing temperature.

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The sulphur uptake in a zinc oxide reactor ideally consists of various zones as illustrated in the Fig. 7.

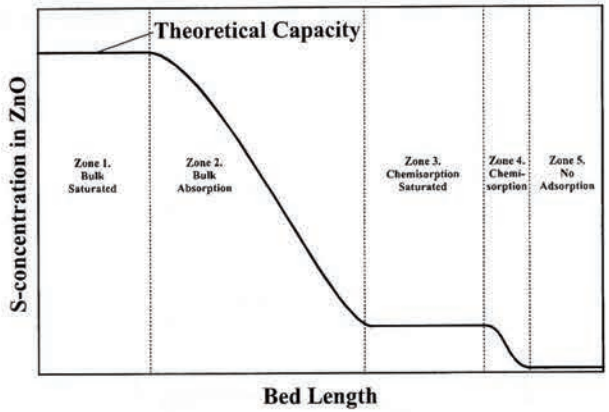


Figure 7 Ideal sulphur profile in a zinc oxide bed

Fig. 7 shows the situation at one particular time. The fronts will gradually move through the ZnO bed towards the outlet, and eventually breakthrough will occur.

Five distinct zones may be identified:

- **Zone 1:** Bulk saturated. The zinc oxide in this zone is fully saturated with sulphur. The gas phase concentration is constant and equal to the feed gas concentration.
- **Zone 2:** The bulk absorption front. The zinc oxide has capacity for absorbing the sulphur. The sulphur is transported through the catalyst pellets by means of solid diffusion and pore diffusion until full saturation is achieved. The gas phase concentration drops to the bulk equilibrium level as determined by reaction (10) and (11), as described above.
- **Zone 3:** Chemisorption saturated. The surface of the zinc oxide is covered with sulphur. The gas phase concentration is constant at the bulk equilibrium level.
- **Zone 4:** The chemisorption front. In cases with low concentration of H_2S and high concentration of CO_2, zone 4, the chemisorption front will develop. The H_2S, which escapes zone 2 due to equilibrium according to reaction (11), will be chemisorbed on the fresh catalyst. The gas phase concentration drops to a very low level. In theory, H_2S and COS are removed to sub ppb levels.
- **Zone 5:** Fresh ZnO. No reactions occur.

If the H_2S concentration in the feed is 'high', and when CO_2 is absent or present in low concentration only, the bulk absorption front will move faster than the chemisorption front, which will then not be visible. There will be only one absorption front, and the gas phase concentration will drop directly from the inlet concentration to the outlet concentration which will in the ideal case correspond to the unmeasurably low chemisorption equilibrium. In such cases the bulk absorption determines the design of the absorption vessel, and the ideal absorption material has the highest possible absorption capacity per volume.

However, in cases where low (single digit ppm or lower) concentrations of H_2S (+ COS) and high CO_2 concentrations (several vol% are not uncommon in natural gas) are present in the feed, calculations may show that the chemisorption front moves faster than the bulk absorption front at normal operating conditions and with normal quality ZnO absorption material. In such cases the operating temperature may be reduced to the lowest acceptable level (to decrease the equilibrium concentration of H_2S according to reaction (11)), and a ZnO with highest possible chemisorption capacity (highest possible surface area per volume) may be selected. If this is not enough, a special absorption material with high chemisorption capacity, e.g. based on Cu, may be installed downstream the ZnO to ensure efficient removal of H_2S.

H_2S appears to absorb on ZnO according to a 'core-shell-model' or 'shrinking-core-model', see e.g. [19]. However, new research, (see e.g. Ref. [20]), as well as industrial feedback indicates that this simple model can not adequately describe all situations. Deviations from expected profiles are sometimes seen, especially at low S concentration and high CO_2 concentration in the feed.

The shrinking-core-model assumes that H_2S (and COS) is absorbed as soon as it meets a clean ZnO surface, and that it is subsequently removed from the surface by solid state diffusion. This means that a partly saturated particle will consist of a 'shell' of ZnS surrounding a 'core' of ZnO. ZnS has a higher molar volume than ZnO, and the conversion of ZnO to ZnS (reaction (11)) will therefore cause an expansion of the solid phase. If the initial porosity of the unconverted ZnO is too low, the volume expansion may lead to closure of the pores so that the unconverted 'core' becomes inaccessible, and full conversion in zone 1 becomes impossible.

2.2.6 S Absorption materials

As mentioned in the preceding paragraphs ZnO is the universal S absorption material in modern desulphurisation units. Leading catalyst suppliers such as Haldor Topsøe, Südchemie, and Johnson Matthey each have their own products with specific properties. ZnO will normally be supplied in the form of extruded cylindrical pellets consisting of almost 100% pure ZnO. In order to ensure highest possible absorption capacity per volume installed absorption

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material, the highest possible bulk density is normally desired. However, as mentioned above, a certain porosity is required to ensure proper functioning of the material, and this limits the achievable bulk density.

In certain situations it may be desirable to optimize not the bulk absorption capacity, but the chemisorption capacity. In such cases the bulk density and consequently the S-content at full saturation will be lower. It may also, in certain applications, be advantageous to add promoters to the ZnO, e.g. alumina to enhance the ability to absorb COS directly (see e.g. [21]) or Cu or similar metals to increase the chemisorption capacity and/or to add hydrogenation activity to the material.

2.3 Steam reforming

Steam reforming of hydrocarbons is the dominating process for the manufacture of hydrogen especially for refineries. The typical feedstock ranges from natural gas and LPG to liquid fuels including naphtha and in some cases kerosene. Steam reforming is often used in combinations with various oxygen or air-blown partial oxidation processes for production of synthesis gas for ammonia, methanol and various petrochemical products. In recent years steam reforming is also seen as an option for converting the primary feed into a gas suitable for a fuel cell. In this case, the choice of the steam reforming technology depends on the type of fuel cell.

Steam reforming by itself is not the preferred technology for production of synthesis gas for the large-scale GTL applications. Large-scale steam reformers have a poor economy of scale compared to processes based on partial oxidation and air separation. Furthermore, large heat input is required and steam reforming produce gases with an H_2/CO ratio well above the desired value of about 2. Processes based on adiabatic oxidative reforming are therefore in general preferred for the Syngas Generation Unit (SGU) in a GTL plant.

In spite of the above steam reforming plays a role in optimised GTL plants. The steam reforming reactions also take place in adiabatic oxidative reforming reactors. Stand-alone steam reformers may also be used in an optimised GTL plant in the form of adiabatic prereforming or heat exchange reforming. The latter may also in some cases be used for revamp of existing facilities to boost the capacity. Finally, tubular reforming provides a means for pure hydrogen production for example for the hydrodesulphurisation or hydrocracking units in an optimised GTL facility or for adjustments of the composition of hydrogen lean synthesis gas produced by partial oxidation.

Steam reforming is carried out in several different types of reactors in a GTL facility. Each of these is optimised for a specific application. The main types of reactors include:

- Adiabatic prereformers
- Tubular or primary steam reformers
- Various types of heat exchange reformers

The fundamentals of the steam reforming reactions are described in the following Section 2.3.1. This is followed by a description of the characteristics of the above mentioned three types of reactors in Section 2.3.2-4. In Section 2.3.5 the catalysts used in the reactors are described along with the reaction mechanisms and the typical reasons for catalyst deactivation.

2.3.1 The reactions

Steam reforming converts hydrocarbons into hydrogen and carbon oxides. The key reactions involved are given in Table 2 along with the enthalpy of reaction and an expression for the equilibrium constants.

Table 2
Key reactions in steam reforming

Reaction	Std. Enthalpy of Reaction ($-\Delta H^\circ_{298}$, kJ/mol)	Equilibrium Constant $\ln K_p = A + B/T$ *)	
		A	B
1. $CH_4 + H_2O \rightleftarrows CO + 3H_2$	-206	30.420	-27,106
2. $CH_4 + CO_2 \rightleftarrows 2CO + 2H_2$	-247	34.218	-31,266
3. $CO + H_2O \rightleftarrows CO_2 + H_2$	41	-3.798	4160
4. $C_nH_m + nH_2O \rightarrow nCO + (n + \frac{m}{2})H_2$	-1175**)		

*) Standard state: 298K and 1 bar; **) For n-C_7H_{16}

Reaction (1) in Table 2 is the steam reforming of methane. The reaction results in gas expansion, and high temperature and low pressure are needed to give high equilibrium conversions. The conversion of methane at various process conditions is depicted in Fig. 8. High values of the steam-to-methane ratio in the feed are required to give high conversions especially at elevated pressure.

Steam can be partially substituted by carbon dioxide to perform CO_2 reforming (reaction (2) in Table 2). This reduces the H_2/CO ratio in the product gas, which in some cases may be more economical, especially if a source of low-cost carbon dioxide is available. Steam (and CO_2) reforming is always accompanied by the water gas shift reaction (reaction (3) in Table 2) which is generally fast and may be considered in equilibrium at most conditions.

The methane steam reforming reaction is strongly endothermic as illustrated by the high negative value of the standard enthalpy of reaction. The

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heat required to convert a 1:2 mixture of methane and steam from 600°C to equilibrium at 900°C is 214 kJ/mole CH_4 at 30 bar.

Reaction (4) in Table 2 is the steam reforming of higher hydrocarbons (hydrocarbons with two or more carbon atoms). This is also a highly endothermic reaction, which may be considered irreversible at all conditions of practical interest.

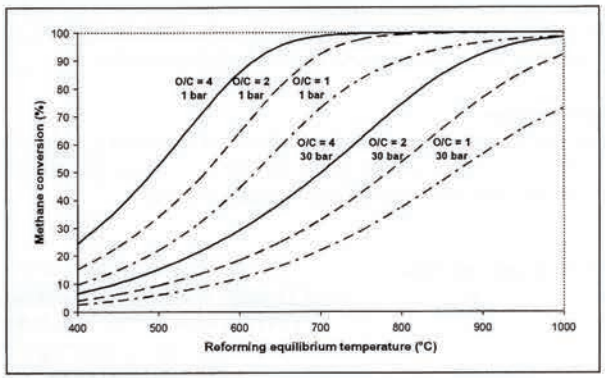


Figure 8 Steam reforming and methane conversion (O/C: ratio of steam to methane in the feed gas).

2.3.2 Adiabatic prereforming

Adiabatic prereforming has during the last 20 years become an integrated step in modern synthesis gas production. Adiabatic gasification of naphtha was already known during the first part of the 1960's for production of town gas and substitute natural gas, see [22-24]. These applications are mainly of historical interest. Today adiabatic prereforming is used widely in the chemical process industry. Adiabatic prereforming is well established in the ammonia and methanol industries, for hydrogen production in refineries, and for the production of synthesis gas for a variety of other chemicals [22].

The adiabatic prereformer converts higher hydrocarbons in the feedstock into a mixture of methane, steam, carbon oxides and hydrogen according to the reactions in Table 2.

All higher hydrocarbons are quantitatively converted by reaction (4) assuming sufficient catalyst activity [22]. This is accompanied by the equilibration of the exothermic shift (3) and methanation (the reverse of methane steam reforming (1)) reactions.

2.3.2.1 Reactor characteristics and operating conditions

The operating conditions in an adiabatic prereformer depend on the type of feedstock and the application. The typical inlet temperature is between 350°C and 550°C. The selection of the operating conditions is in many cases dictated by the limits of carbon formation on the catalyst. For a given feedstock and pressure, the adiabatic prereformer must be operated within a certain temperature window. The formation of a whisker type of carbon will occur above the upper temperature limit. Operation below the lower temperature limit may result either in a polymeric type of carbon formation (gum) or lack of sufficient catalyst activity. The formation of carbon on the catalyst is further discussed in Sections 2.3.2.2 and 2.3.5.3.

The overall prereforming process is often exothermic for heavy feedstock such as naphtha. In Fig. 9 the temperature profile for a prereformer with naphtha feed in a hydrogen plant is shown. For lighter feedstock such as LPG and natural gas the overall reaction may be endothermic, thermoneutral, or exothermic [22, 25]. In Fig. 10 the temperature profile with natural gas feed at high steam-to-carbon (H_2O/C) ratio in an ammonia plant is illustrated.

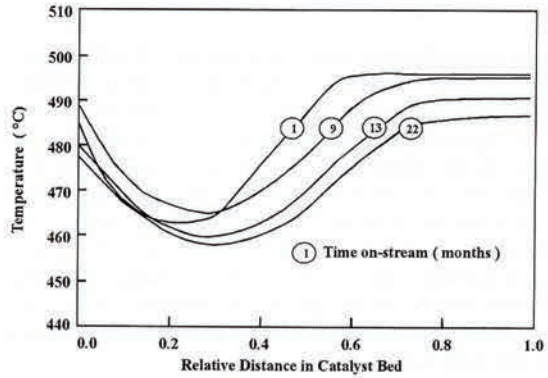


Figure 9 Temperature profile of an adiabatic prereformer with naphtha feed [22]. H_2O/C=3.5. P=26 bars. The movement of the temperature profile with time is due to catalyst poisoning by sulphur (see Section 2.3.5.2).

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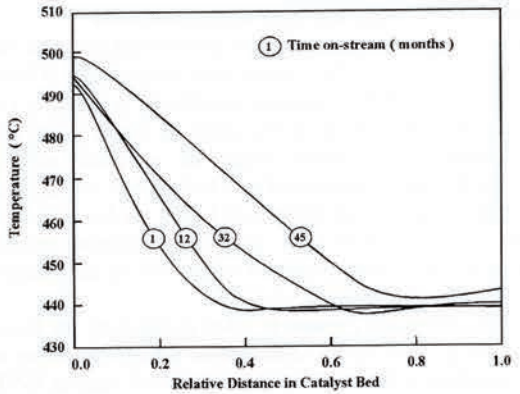


Figure 10 Temperature profile of an adiabatic prereformer with natural gas feed in a 1600 MTPD ammonia plant [22]. H_2O/C=2.8 P=35 bars. The movement of the temperature profile with time is due to catalyst poisoning by sulphur (see Section 2.3.5.2).

The reactor is an adiabatic vessel with specially designed catalysts typically based on nickel. The low operating temperature requires a catalyst with high surface area to obtain sufficient activity and resistance to poisoning especially by sulphur. The optimal shape of the catalyst particle depends on the specific application and on the plant capacity. In many cases catalyst particles of a cylindrical shape in a size of 3-5 mm are used [22]. This particle provides a large surface area for access of the gas into the pore system. The pressure drop over the prereformer is often low (<0.4 bars) for small or medium-scale plants even with such particles giving low void. For large-scale plants, a shape-optimised catalyst will be an advantage and particles in the form of rings or large cylinders with axial holes are usually the preferred choice for minimum pressure drop and high activity [22].

Deactivation of the prereformer catalyst may take place during operation. The cause is typically sulphur but sintering and other poisons may also play a role as discussed in Section 2.3.5. The deactivation of the catalyst can be observed as a progressive movement of the temperature profile as illustrated in Fig. 9 and Fig. 10. The resistance to deactivation is an important aspect in the design of adiabatic prereformers.

The assessment of the performance of an adiabatic prereformer during operation is used to determine the actual rate of deactivation and the optimal time for changing the catalyst [25]. This can be done by monitoring a number of

parameters. It is important to follow the content of higher hydrocarbons as an increase in concentration may indicate loss of activity. The approach to equilibrium of the methane steam reforming reaction at the reactor exit is also a parameter, which can be used to monitor the performance. The approach to equilibrium is expressed by a temperature difference defined as:

$$T_R = T(\text{exit catalyst}) - T(Q_R),\ Q_R = \frac{P_{CO}P_{H_2}^3}{P_{CH_4}P_{H_2O}} \qquad (5)$$

in which $T(Q_R)$ is the equilibrium temperature corresponding to an equilibrium constant equal to the reaction quotient Q_R.

The approach to equilibrium and the content of higher hydrocarbons in the prereformer exit are generally close to zero and constant throughout the operation period of the prereformer. In many cases a graphical deactivation plot is used to assess the performance of the prereformer [25]. The deactivation plot shows the length of the reaction front as a function of operation time. The method is illustrated in Fig. 11.

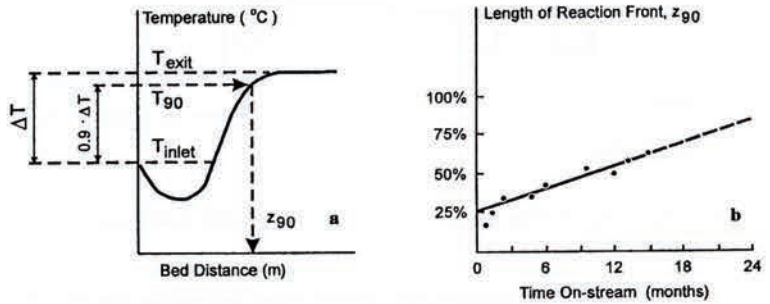


Figure 11 Graphical deactivation plot for performance prediction [25].
a) Estimation of length of reaction front, z_{90} from temperature profile.
b) Deactivation plot.

The temperature difference between the outlet and the inlet is calculated. The axial position (z_{90}) at which 90% of the temperature difference has been obtained is plotted versus time. A steep slope indicates a high rate of deactivation. The inverse slope of the deactivation plot is known as the resistance number defined as the amount of feed required to deactivate 1 g of catalyst. A large resistance number indicates slow deactivation.

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2.3.2.2 Adiabatic prereformers in GTL applications

Adiabatic prereforming is a key element in an optimised design of the synthesis gas generation unit (SGU) in a GTL plant. In Fig. 12 the typical installation of an adiabatic prereformer in an SGU based on autothermal reforming in a GTL plant is illustrated [26]. The natural gas is mixed with steam and a minor amount of hydrogen. The resultant mixture is fed to the adiabatic prereformer after desulphurisation and preheating to the desired reactor inlet temperature. The effluent from the prereforming step is further preheated, mixed with a CO_2-rich gas and fed to the autothermal reformer [26].

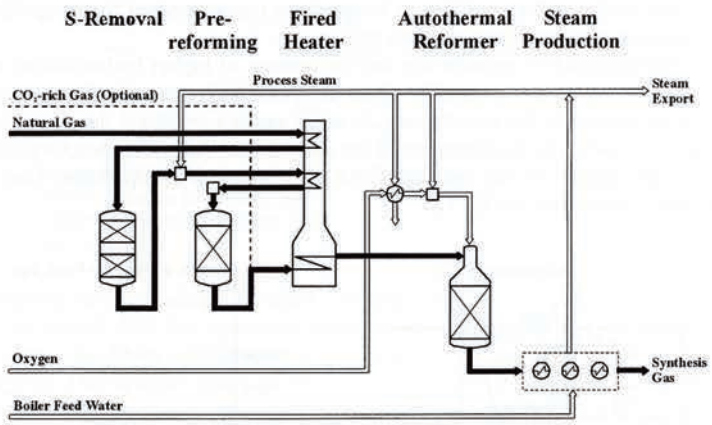


Figure 12 Typical layout of the syngas generation unit with adiabatic prereformer in a GTL plant [26].

The removal of the higher hydrocarbons from the natural gas in a GTL plant has several advantages. A higher feed temperature to the autothermal reformer can be applied without the risk of thermal cracking in the preheater coil. A higher feed temperature reduces the oxygen consumption in a GTL plant (per unit of Fischer-Tropsch product) and improves the carbon efficiency. A temperature profile for an adiabatic prereformer operating at low H_2O/C ratio is given in Fig. 13 [26].

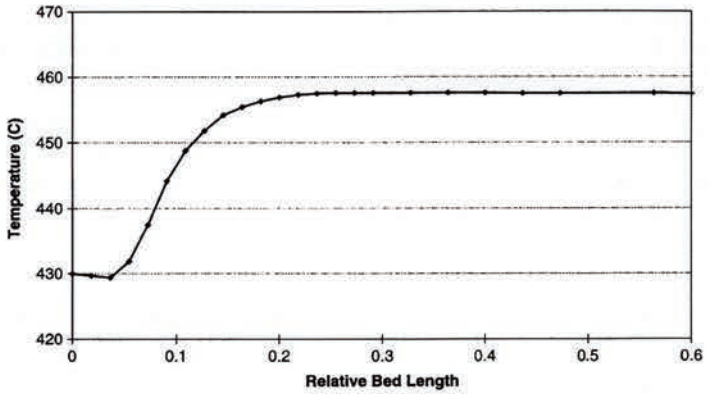


Figure 13 Temperature profile in adiabatic prereformer during pilot plant operation. $H_2O/C = 0.4$ [26].

A GTL plant is operated at a low H_2O/C ratio for optimal process economics. Operation at low H_2O/C ratio involves the risk of formation of carbon on the catalyst in the prereformer. Carbon may form either from methane or higher hydrocarbons as illustrated below:

$$CH_4 \leftrightarrow C + 2H_2 \quad (6)$$

$$C_nH_m \rightarrow nC + \tfrac{1}{2}mH_2 \quad (7)$$

The selection of the catalyst and the operating conditions of an adiabatic prereformer in a GTL plant are often dictated by the limits of the above reactions. The limits of reaction (6) may in principle be determined from thermodynamics. Carbon will form if the gas shows affinity for carbon formation after establishment of chemical equilibrium of the methane steam reforming and shift reactions [22]. The risk of carbon formation by reaction (6) is most pronounced in the reaction zone where the temperature is highest. In the evaluation of the potential for carbon formation the correct equilibrium constant should be used as described in Section 2.3.5.3.

Carbon formation from higher hydrocarbons is an irreversible reaction that can only take place in the first part of the reactor with the highest concentration of C_{2+} compounds. Carbon may form even if thermodynamics predict no affinity at equilibrium. The criterion for carbon formation can be described as a kinetic competition between the carbon forming and steam reforming reactions. A thorough kinetic analysis, both with fresh catalyst, and towards end-of-run at

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each point in the reactor, is required to accurately evaluate this criterion. In general the limits for carbon formation from reaction (6) are approached with reduced ratio of steam to higher hydrocarbons and with increased temperature [22, 27].

The knowledge of the carbon limits is imperative for optimal design. Examples of pilot plant experiments at low pressure performed to gather information about these limits are given in Table 3. Post-test analysis indicated that the carbon formation could be ascribed to reactions (5) and (6) [22].

Table 3
Adiabatic prereforming at low H_2O/C ratio [22]

Experiment	A	B	C	D
H_2O/C	0.40	0.25	0.13	0.25
Inlet temperature, °C	455	395	400	430
Pressure, Mpa	0.8	1.0	1.0	0.9
Carbon formation	No	No	Yes	Minor

2.3.2.3 Modelling of adiabatic prereformers

The use of mathematical models is an invaluable tool in the design and optimisation of adiabatic prereformers. The chemical conversion versus time can be determined by combining reaction kinetics, pore diffusion, pressure drop, and effects of catalyst deactivation and poisoning [22].

No radial concentration gradient exists in a prereformer due to its adiabatic nature. A one-dimensional axial model is thus sufficient to simulate the temperature and concentration profile. Simulation of (pre)reformers may be carried out by heterogeneous and pseudo-homogeneous models, see sec. 2.3.3.2. The heterogeneous model is based on intrinsic kinetics. This model takes into account the pore diffusion inside the catalyst particle and the transport restrictions across the film on the external surface. Accurate representations of the conditions inside the catalyst particle may be obtained. However, these models are mostly used for development of novel catalysts and catalytic systems and for detailed investigations of deactivation phenomena [22]. For design purposes, pseudo-homogenous models are often used.

The prereformers often operate in the diffusion-controlled regime, which validates the use of pseudo-homogenous models. The pseudo-homogeneous model does not take into account the difference in temperature and concentration between the catalyst particle and the bulk gas phase. The transport restrictions are implicitly taken into account by the use of effective reaction rate expressions.

The pseudo-homogeneous model may be expressed as given below (for one reaction, [22]):

$$-u_s \frac{dC}{dZ} = r_v \tag{8}$$

$$u_s p_g c_p \frac{dT}{dz} = (-\Delta H) r_v \tag{9}$$

$$-\frac{dp}{dz} = \frac{2 f p_g U_s^2}{g d_{p,v}} \tag{10}$$

The parameters of significance for the model equations (8-10) are:

u_s = superficial velocity
r_v = effective reaction rate, volume basis
p_g = gas density
c_p = heat capacity
ΔH = heat of reaction
f = friction factor
g = acceleration of gravity
$d_{p,v}$ = equivalent particle diameter
P = pressure
T= temperature
C: molar concentration
Z: axial distance

In Fig. 14 [22] calculated and experimental temperature and conversion profiles are given for a pilot plant experiment at low H_2O/C ratio. The good agreement illustrates the validity of the use of pseudo-homogeneous models. The simulation of the concentration and temperature profiles may be coupled with detailed models for catalyst deactivation and carbon formation.

The conversion profile in an adiabatic prereformer is largely determined by the kinetics of the steam reforming of the higher hydrocarbons [22]. The rate of reaction can typically be represented by a power law kinetic expression. An example for steam reforming of ethane is given in the following [27]:

$$r = 2.2 \times 10^5 \exp(-9100/T)\, p_{C_2H_6}^{0.54} p_{H_2O}^{-0.33} p_{H_2}^{0.2} \tag{11}$$

The numerical value of the reaction order with respect to steam decreases with increasing temperature. For heavier components than ethane the reaction order with respect to hydrocarbon may decrease [27]. The reaction orders may depend considerably on the type of catalyst.

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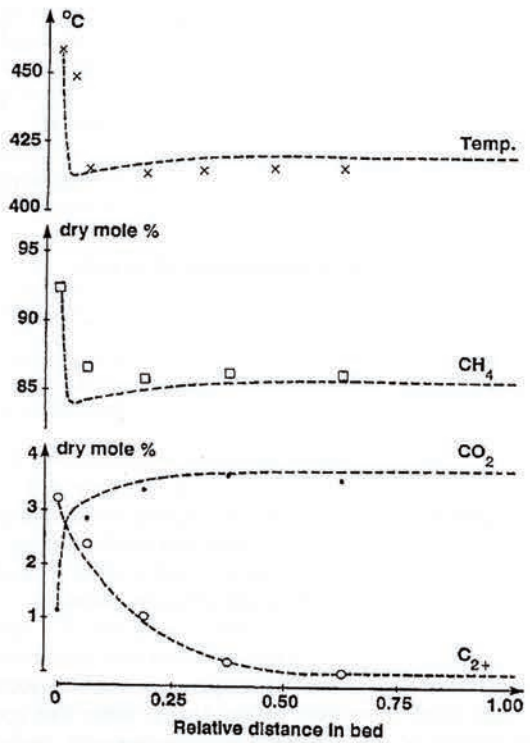


Figure 14 Temperature and conversion profiles for prereforming of natural gas, H_2O/C ratio = 0.40, P = 8 bar. Measured data: x - temperature; □ - CH_4 concentration, • - CO2 concentration; o - C_{2+} concentration. Calculated profiles are shown as dashed lines. [22].

2.3.3 Design of steam reformers

Steam reforming is, in industrial practice, mainly carried out in reactors referred to as steam reformers, which are essentially fired heaters with catalyst-filled tubes placed in the radiant part of the heater. The process may also be carried out in reactors referred to as heat exchange reformers. These are essentially heat exchangers with catalyst-filled tubes. Heat exchange reformer design is discussed in Section 2.3.4. Abundant literature is available on steam reforming and design of steam reformers. Examples are [4, 27–34]. Reference to older literature may be found in [3].

Steam reforming is a mature process [27]. The first industrial steam reformer was installed at Baton Rouge in Louisiana, USA, by Standard Oil of New Jersey and commissioned in 1930. Six years later a steam reformer was commissioned at ICI, Billingham, UK. During the fifties, metallurgical developments made it possible to design reformers for operation at elevated pressures. This improved the energy efficiency of the overall process, because higher pressure facilitates the heat recovery and results in savings in compression energy in ammonia and methanol plants. In 1962, two tubular reformers operating at around 15 atm and using "high molecular weight hydrocarbone" as feed were commissioned by ICI. Less than five years later, a Topsøe reformer was operating at 40 atm.

Already at this time, the basic types of reformers (see below) had been developed and industrialised [28], and all later developments have, in spite of major improvements in performance and cost, not basically changed the designs.

The tubular reformer is an energy converter [27], since most of the energy input for many processes is added via the reformer with the hydrocarbon feed and the fuel (often the same hydrocarbon). The energy is transferred into hot, steam-containing synthesis gas, and hot flue gas. The synthesis gas is subsequently processed further and converted into products by mainly exothermic reactions, releasing more heat. The latent heat of the process streams and of the flue gas must be recovered to achieve high energy efficiency, and this requires tight integration of the reformer with other parts of the process.

2.3.3.1 Mechanical design

The main elements in the design of a steam reformer furnace are:

- Tube and burner arrangement
- Inlet and outlet systems
- Tube design
- Burner characteristics

Tube and Burner Arrangement

Tubes and burners shall ideally be arranged in the furnace box in such a way that adjustment and control of temperature and heat flux along the tube length can be obtained.

Reformers are designed with a variety of tube and burner arrangements. Basically there are four types of reformers as illustrated in Fig. 15 [4, 27, 29, 30]:

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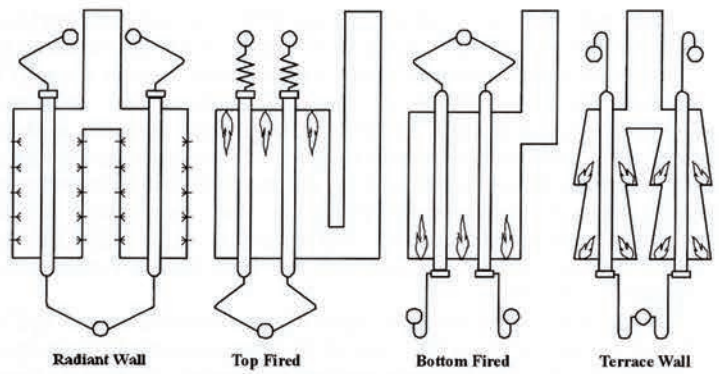


Figure 15 Tube and burner arrangements [4]

The radiant wall or **side fired** reformer contains tubes mounted in a single row along the centreline of the furnace. In larger installations, two such furnaces are erected side by side with common inlet and outlet systems and with common fuel supply, flue gas duct, and waste heat section. Burners are mounted in several levels in the furnace walls, and the flames are directed backwards towards the walls. The tubes are heated by radiation from the furnace walls and the flue gas and to a minor extent by convection. The flue gas leaves the furnace at the top so that the flow of process gas and flue gas is counter-current. The most important supplier of reforming technology based on the side fired design is Haldor Topsøe [3, 4, 27-34]. A cross section of a typical side fired reformer for CO production (high outlet temperature), (Topsøe design) is shown in Fig. 16 [4].

The **top fired** reformer features of a furnace box with several rows of tubes. Burners are mounted in the furnace ceiling between the tube rows and between the tubes and the furnace wall. From the burners, long flames are directed downwards, and the tubes are heated by radiation from the flames and the hot flue gas and by convection. The flue gas leaves the furnace box at the bottom, so that the flow of process gas and flue gas is co-current. The top fired reformer design is used by e.g. Howe Baker [35,36], KBR [28], Lurgi [37,38], Technip/KTI [39], and Uhde [40].

A photo of a large reformer (for H_2 production) is shown in Fig. 17 [34].

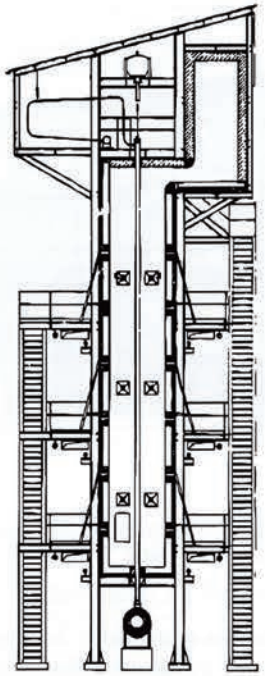


Figure 16 Cross section of side fired reformer

The **bottom fired** type has easy access to the burners and gives an almost constant heat flux profile along the length of the tube. Since the tubes are hot in the bottom a substantial margin is required on the tube design temperature limiting the outlet temperature. The bottom fired design is today considered outdated. It was used in the past by e.g. Exxon and Chemico, and it may still be seen in small-scale plants from e.g. Caloric [41].

The **terrace wall fired** type reformer is a modification of the bottom fired type, having slightly lower tube wall temperatures. Problems can arise at the 'pinch point' in the middle of the furnace where the tubes are subject to both radiation from the burners and to enhanced convection from the flue gas. The terrace wall fired design is used by Foster Wheeler [42].

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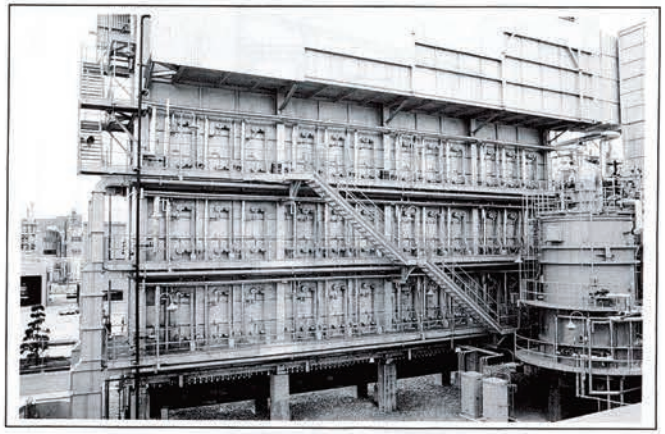


Figure 17 Photo of Topsøe Reformer [34]

Inlet and Outlet Systems

Inlet and outlet system shall be designed to allow thermal expansion of the hot parts without any risk of excessive stresses.

Gas Inlet

The feed gas to the reformer is normally distributed to the individual reformer tubes from an inlet header through so-called 'pigtails'. The design will depend on the type of tube support and on the temperature of the feed gas. Typical designs are shown in Fig. 18 [4, 29].

For reformers designed for traditional inlet temperatures the inlet hairpin is connected to the top of the reformer tube. The hairpin is designed to absorb the thermal expansion of the catalyst tube and the thermal expansion of the inlet header. Due to the flexibility of the hairpin it can easily be swung aside to give free access to the catalyst tubes for loading or unloading of the catalyst.

In cases where preheat of the gas inlet temperature is high, the inlet hairpin may be connected to the side of the reformer tube. By means of insulation inside the top of the reformer tube this design will bring down the temperature of the flange assembly to a level where tightness can be ensured. This type of reformer will normally have conditions for the reformer tubes where spring support arrangements are needed in order to avoid bending of tubes.

Gas Outlet

The gas outlet system should in all cases be flexible enough to withstand the thermal expansion and contraction during start-up and shutdown as well as

during normal operation. The outlet system connecting the catalyst tubes to the manifolds is critical in most reformer designs. A considerable number of failures in manifolds/pigtails have been reported, and therefore a thorough analysis of stress in these areas is important.

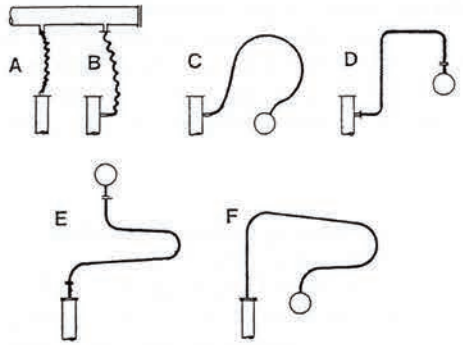


Figure 18 Typical design of gas inlet systems

Two main types of outlet systems are illustrated in Fig. 19 [4, 29].

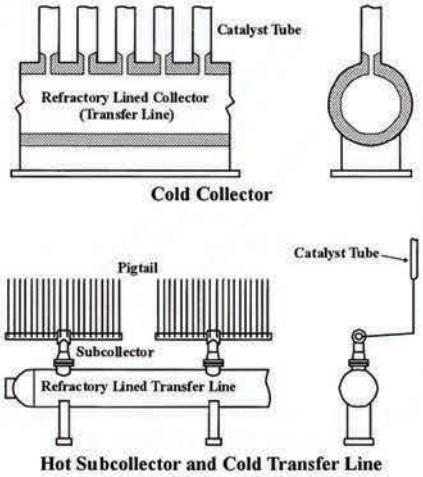


Figure 19 Typical designs of gas outlet systems [4]

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In the **cold collector** system the reformed gas is introduced direct from the individual tubes to the transfer line which is located outside the furnace. In this system, special devices are required for connecting the hot parts to the cold collector. Different versions of this concept are used by Haldor Topsøe [4], Lurgi [37, 38], and Uhde [40].

In the **subcollector** system, groups of catalyst tubes are connected through pigtails or hairpins to hot subcollectors, and the subcollectors are joined to the main collector. In relatively small reformers, the pigtails may be connected direct to the transfer line. The pigtails are designed to relax thermal stress. This concept is dominating in reformers designed for 'low' outlet temperatures (below about 900°C).

Tube Design

A steam reformer may contain up to about 1000 high alloy steel tubes filled with catalyst. The outer diameter is typically 100 - 180 mm, the tube wall thickness is 8 - 20 mm, and the heated length may be 10 - 14 m. The traditional materials used for reformer tubes were HK 40 (25 Cr 20 Ni) or IN 519 (24 Cr 24 Ni Nb) [29, 43, 44]. However, the demand for better creep rupture properties led to the development of new alloys with greater strength. The development in the strength of reformer tube materials is illustrated in Fig. 20 [44].

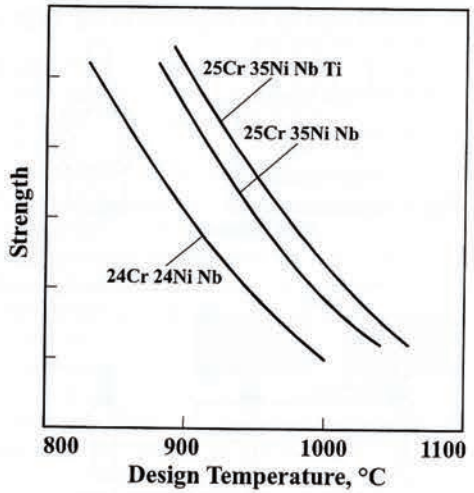


Figure 20 Creep rupture strength for different reformer tube materials [44]

Today, the preferred tube materials are the so-called 'microalloys', typically 25 Cr 35 Ni Nb Ti [43]. The other types of materials will only be used in cases where the strength of the microalloys cannot be used fully, as there is a lower limit for the wall thickness of the tubes.

Reformer tubes are normally designed according to the 'remaining life assessment' technique, API-530 [45], for an average lifetime before creep rupture of 100,000 hours. The main parameters in the design are the design pressure; the design temperature and the creep rupture strength of the material used. However, the determination of these parameters can be ambiguous, and each reforming technology licensor applies in-house procedures to determine the parameters and to introduce necessary design margins.

The calculation of the design temperature is demanding since it requires detailed understanding of the heat transfer. This includes heat transfer to the individual tube by radiation from the furnace internals including furnace walls and neighbouring tubes as well as heat transfer by convection from gas to tube wall, by conduction through the tube wall, and by convection from the inner tube wall to the catalyst and the reacting gas. Secondly, an understanding of reaction kinetics, catalyst ageing, and heat and mass transfer (radial and axial) in the catalyst bed, etc. is required. The interplay between catalyst, reacting gas and reformer tube is also essential for the prediction of the limits for carbon formation.

Burner Characteristics

Reformer burners are a speciality product supplied by a few companies only. For descriptions, reference is made to [46-49]. Originally, burner developments were mainly directed towards control of the radiation heat transfer by control of flame shape and combustion intensity. Lately, environmental issues (NO_x control) have become a major concern, and this has to some extent changed the combustion characteristics. CFD modelling of the furnace side including correct simulation of the combustion is important in the analysis of the effect of this development on reformer design and performance.

2.3.3.2 Modelling of the reformer

Simulation of Furnace Chamber

Tubular steam reforming is a complex interaction of heat transfer and coupled chemical reactions [27]. The heat released by the burners is transferred via radiation and convection to the reformer tubes. The heat passes through the tube walls by conduction and is transferred to the catalyst bed by convection and radiation. At the same time, a network of chemical reactions creates temperature and concentration gradients in the radial direction of the tube and around and within the porous catalyst particles.

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An ideal model should be able to simulate the reformer performance on the basis of the individual burner duties, the feed stream characteristics, the properties of the catalyst and the reformer geometry.

Early simulations of the process gas side in tubular reformers were generally uncoupled from the furnace box by assuming an outer tube wall temperature profile or a heat flux profile. These profiles were established or checked by feedback from measurements in industrial plants and monotube pilot plants. It should be pointed out, however, that measurements of tube wall temperatures are difficult [50]. Pyrometric methods involve complex corrections because of reflections from furnace walls and flames. The correction is largest at the coldest position of the tube at the reformer inlet, where reaction conditions at the same time are most complex. Thermocouples welded into the tube wall give more exact information but their life may be limited. Shadowing effects in the tube row cause another uncertainty. The extent of this distortion increases with decreasing tube pitch.

Tube Side

One-dimensional pseudo-homogeneous models are adequate for studying reformers at non-critical conditions and for simulation of the over-all performance. They are, however, insufficient for reformers operating close to carbon limits. For such cases a more detailed analysis of the local phenomena in the reformer is required.

Radial temperature and concentration profiles are included in two-dimensional pseudo-homogeneous models, whereas the gradients in and around the catalyst pellets are neglected.

Such models are generally plug flow reactor models with detailed kinetic schemes considering 2D axi-symmetric radial temperature and concentration gradients within the tube. Heat transfer is calculated as an effective radial conductivity within the bed and a film heat transfer coefficient at the tube wall. The main parameters are the reaction kinetics and parameters in the heat transfer and the pressure drop equations. Such data are proprietary parameters, and generally quite difficult and costly to establish. However, it must be remembered that the usefulness of even the most sophisticated models is not better than the accuracy by which the relevant parameters are known.

Haldor Topsøe's proprietary, in-house process model is described in Refs. [30, 51]. The parameters in this model were determined by experiments in a full-size monotube reformer PDU (Fig. 21) [4, 51] and validated against a large amount of industrial data.



Figure 21 Tubular reformer Process Demonstration Unit (PDU) [4]

An application of this model is shown in Fig. 22 [51], which shows a comparison between calculated and measured axial catalyst bed temperatures at measured outer tube wall temperatures.

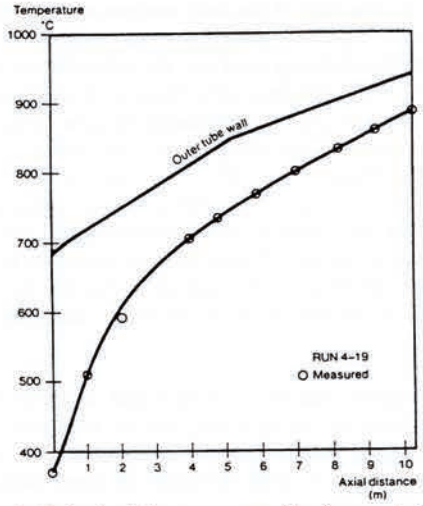


Figure 22 Measured and calculated axial temperature profiles from run in PDU [51]

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The data are from an experiment carried out on the monotube PDU at a low steam to carbon ratio of 1.18 but also with a low average heat flux of 50,500 kcal/m^2/h on the inner tube surface. It is seen that there is a good agreement with the measured temperature data. Similar agreement has been obtained in simulations of a large number of data sets, and the mathematical model is therefore used in the design of both heat exchange type reformers and tubular reformers, without further adjustments of the parameters.

Reaction Kinetics

The properties of steam reforming catalysts and fundamental aspects of their behavior in the reactor (reaction mechanism and mechanism of carbon formation and S poisoning) are discussed in Section 2.3.5. Detailed discussions of the reaction kinetics of the reforming reactions may be found in [27, 33]. In the following text only some main points are highlighted.

The activity of a reforming catalyst depends mainly on the nickel surface area. The nickel crystals will sinter quickly at high temperature. This may be partly prevented by a stable micropore system because the nickel particles may hardly grow larger than the pore diameter of the support.

The activated chemisorption of methane is usually considered to be the rate-determining step in steam reforming. Likewise, there is general agreement on first order kinetics with respect to methane, but the impact of steam and hydrogen on the rate is complex. The kinetics depends on the temperature range and the catalyst composition. The rate of the shift reaction is much faster and it can be assumed to be at equilibrium in all positions of the reformer.

For normal steam reforming catalysts, the utilization of the activity, i.e. the effectiveness factor, is far less than 10% because of transport restrictions. The mass transport restrictions are related mainly to pore diffusion, whereas heat transfer restrictions are located in the gas film. The strong endothermic reaction results in a temperature drop of ca. 5-10°C over the gas film. This means that the activity is roughly proportional to the external surface area, and that there is in the normal case a surplus of activity in the reformer tube. The surplus of activity can be used in more advanced reformer designs with only thin layers of active catalyst material e.g. for honeycomb catalysts having low pressure drop or even in designs with the catalyst supported directly on the heat transfer surfaces.

Physical Properties

The catalyst support material must be stable under the process conditions and under the conditions prevailing during start-up and shutdown of the plant. In particular, the conditions during upsets may become critical. Degradation of catalyst may cause partial or total blockage of some tubes, resulting in the development of 'hot spots', 'hot bands' or totally hot tubes. Carbon formation may cause similar problems.

The catalyst particle size and shape should be optimized to achieve maximum activity and maximum heat transfer while minimizing the pressure drop. The high mass velocities in steam reforming plants (40,000 – 70,000 kg $m^{-2}h^{-1}$) necessitate a relatively large catalyst particle size to ensure a low pressure drop across the catalyst bed; but the particle size is limited by the requirement for effective packing. The pressure drop depends strongly on the void fraction of the packed bed and decreases with particle size.

Also, the particle size has a certain impact on the heat transfer coefficient. The optimum choice is a catalyst pellet with high void fraction and high external surface area. Fig. 23 shows an optimized catalyst shape, the 7-hole catalyst.



Figure 23 Steam reforming catalyst. Topsøe R-67 R-7H.

To summarize, the effective catalyst activity is a complicated function of the particle size and shape and the operating conditions. A high intrinsic catalyst activity is still important to control tube wall temperatures, in particular in those parts of the reformer having a high heat flux.

Heat Flux and Activity

The acceptable maximum heat flux in reformer tubes is dictated by mechanical and metallurgical constraints rather than by the catalyst activity. Present catalysts could work at average heat fluxes twice the present maximum if the heat flux profile could be controlled [34]. However, deactivation of the catalyst or unsuitable flux profile may result in overheating of tubes.

Most commercial catalysts have a surplus of catalyst activity. This means that apart from the inlet of the reformer tube, the gas composition is, at all positions in the tube, not far from equilibrium at the average catalyst temperature. In other words, the slope of the temperature profile is the 'driving force' for the reaction, and the reaction proceeds as fast as the required heat can be supplied through the tube wall.

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The slope may become very high in the upper part of top fired reformers or in the bottom of bottom fired or terrace wall fired reformers, or if the catalyst looses activity, e.g. by poisoning or aging. In such cases the reaction rate may not be able to follow the rate of heat input, and the temperatures of the gas and the tube wall and also the approach to equilibrium will increase.

It is evident from the above that lack of catalyst activity will cause high temperatures both in the gas and in the tube material. The advantage of high catalyst activity (and the disadvantage of an unsuitable flux profile) is illustrated in Fig. 24 [30] which shows calculated tube wall temperatures in a top fired reformer for various relative catalyst activities in the upper half of the reformer tube. It is seen that loss of activity in the upper part of the tube may lead to significant overheating of the tube.

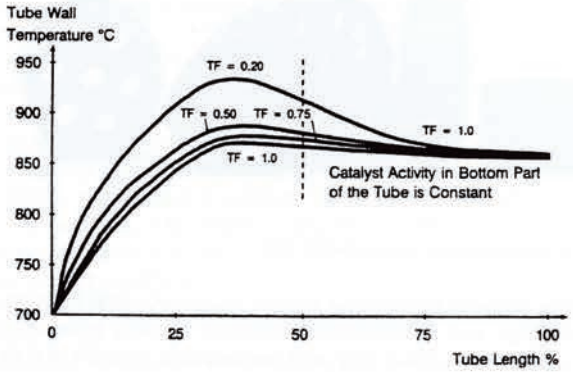


Figure 24 Tube wall temperatures in top fired reformer at various catalyst activity levels (TF) in the upper 50% of the tube.

Modelling by CFD

CFD (Computational Fluid Dynamics) is becoming a preferred tool for modelling and simulation of steam reformers. Results obtained by simulation of top fired furnaces have been reported in e.g. [53, 54] and, of a terrace fired furnace in [55] and of a side fired furnace in [56].

It is emphasised that these descriptions at best show status in 2002. Developments in CFD modelling are rapid, and more comprehensive and accurate models are being elaborated.

At Haldor Topsøe numerous experiments have been performed on a full size PDU. Some of the experiments have been performed in order to provide data for the verification of computational models, including a CFD model. The

PDU contains a single full size catalyst-filled tube located in the centre of the furnace. The furnace has 5 burner rows.

Qualitatively the behaviour of the PDU resembles that of industrial reformers. However, the temperature distribution in the furnace is more homogeneous in the PDU than in industrial reformers. This is due to the smaller number of tubes per unit volume. Furthermore, there are no shadowing effects due to the presence of other tubes.

Fig. 25 compares the calculated outer tube wall temperature to the measured temperature in one run in the PDU. The outer tube wall temperature agrees well with the measured temperature. The small deviation (less than 10 degrees) is well within the measurement accuracy.

Fig. 26 shows for the same run the outer tube wall heat flux calculated by the CFD model and the in-house process model. It is seen that the furnace model accurately predicts the transferred duty, but that the predicted heat flux profiles deviate slightly.

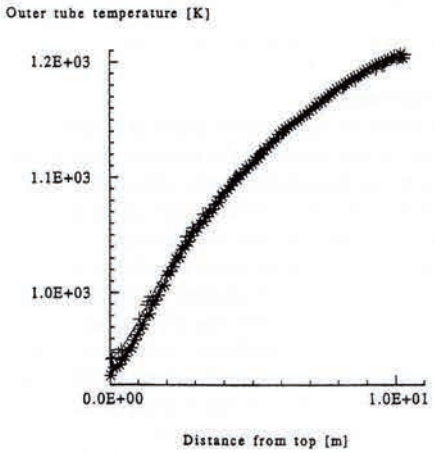


Figure 25 Calculated and measured outer tube wall temperature Measured Outer Tube Wall Temperature [56]

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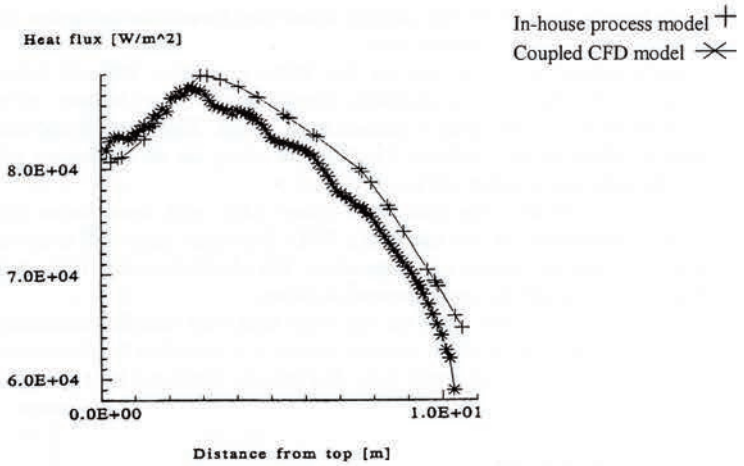


Figure 26 Heat flux calculated by CFD and by in-house process model [56]

2.3.4 Design of heat exchange reformers

Basically, a heat exchange reformer is a steam reformer where the heat required for the reaction is supplied predominantly by convective heat exchange. The heat can be supplied from a flue gas or a process gas - or in principle by any other available hot gas. In the following, the various types of heat exchange reformers are discussed on the basis of source of heat and mechanical concept.

When the heat and mass balance on the process (catalyst) side only is considered, there is no difference between heat exchange reforming and fired tubular reforming, where the heat transfer is predominantly by radiation. This means that all process schemes using heat exchange reforming will have alternatives where the function of the heat exchange reformer is performed in a fired reformer. The process schemes differ 'only', in the amount of latent heat in flue gas and/or process gas and in the way this heat is utilised.

Models for design and simulation of heat exchange reformers are combinations of models for steam reformer catalyst tubes (as described in Section 2.3.3.2) and models for convective heat transfer (as used in design and simulation of normal gas/gas heat exchangers).

2.3.4.1 Types of heat exchange reformers

Three different concepts for heat exchange reformer design have been commercialised by various companies. The three concepts are illustrated in Fig. 27.

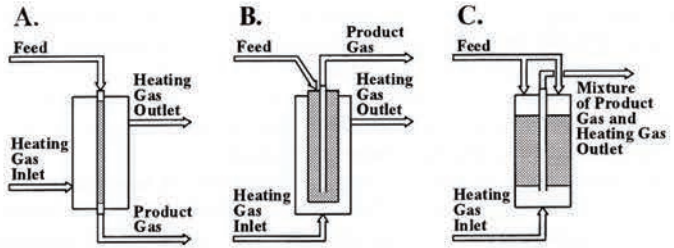


Figure 27 A: Concept with 'straight-through' tubes;
B: Concept with bayonet tubes;
C: Concept with mixing of heating gas and product gas before heat exchange.

Type A and B in Fig. 27 can be used with all types of heating gas, whereas type C can only be used when the desired product gas is a mixture of the heating gas and the product gas from the catalyst in the heat exchange reformer.

Flue Gas Heated Heat Exchange Reformers

These heat exchange reformers are stand-alone reformers, and their function is similar to normal fired reformers. Two designs by Haldor Topsøe A/S, HER [57, 58] and HTCR [59, 60] are examples of this category. As seen in Fig. 28, the HER consists of a number of concentric cylinder shells around a centrally placed burner, while the HTCR as shown in Fig. 29 features a bundle of bayonet tubes and a burner in a separate chamber.

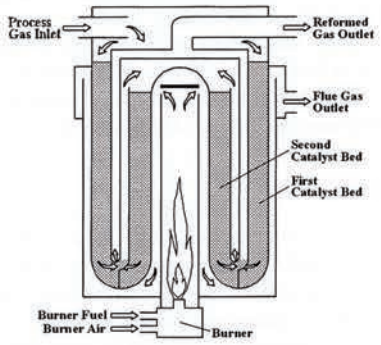


Figure 28 Topsøe Heat Exchange Reformer (HER) [57]

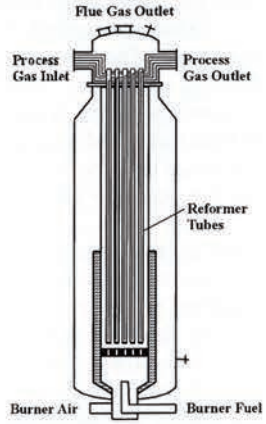


Figure 29 Topsøe Convection Reformer (HTCR) [59]

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Also others, e.g. KTI [61] have developed heat exchange reformers with bayonet tubes. (It may be argued that reformer concepts with bayonet tubes are partly gas heated reformers (see below) since the process gas is cooled by heat exchange with the catalyst bed, thus providing part of the heat required for the reforming reaction. However, bayonet tubes and similar concepts are in this context only considered as special reformer tube designs).

BP is promoting a so-called 'Compact Reformer' in co-operation with Kvaerner [62]. It is according to the definition above somewhat doubtful whether this is actually a Heat Exchange Reformer. One piece of equipment contains a reformer feed heating/flue gas cooling heat exchanger, a combustion chamber, and a synthesis gas cooling/air and fuel heating heat exchanger. In the combustion chamber, reformer tubes are embedded in "a sea of flames", apparently created by controlled injection of preheated fuel into preheated combustion air. Flame impingement on tubes is mentioned as taking place by design.

Chiyoda have developed a reformer design based on regenerative burners developed by NFK, the so-called HICOT technology [63]. Although this design is not strictly speaking a heat exchange reforming unit, it competes for the same market as heat exchange reformers.

The potential application for large scale GTL and methanol production of the above described types of heat exchange reformers may be doubtful because stand alone steam reforming seems unsuitable for such applications.

Heat Exchange Reformers Heated by Process Gas

Reformers heated by process gas are normally called Gas Heated Reformers. They may be classified in two types depending on the process concept, see Fig. 27. One type, which may be referred to as GHR or 'Two-in, two-out' (both type A and B in Fig. 27 are of this type), can in principle be used in both series and parallel arrangements. (See below under Process Concepts). The other type (type C in Fig. 27), which may be called GHHER or 'Two-in, one-out', can only be used in the parallel arrangement.

GHR or 'two-in, two-out'

Synetix (now Johnson Matthey) have commercialised two types of heat exchange reformers. The first, referred to as GHR, uses bayonet tubes. It was used in the so-called Leading Concept Ammonia (LCA) process, where the GHR is used in combination with an air-blown secondary reformer. Two NH_3 plants based on this concept were started at Severnside in England in 1988 [64], and a copy of one of the Severnside ammonia plants has later been built for Mississippi Chemicals in Yazoo City, USA. The GHR design has later been used in combination with an O_2-blown secondary reformer in the so-called

Leading Concept Methanol (LCM) process, which was used in a 200 MTPD Methanol Research Plant for BHP in Australia, started in 1994.

Synetix have commercialised a second generation heat exchange reformer called Advanced Gas-Heated Reformer (AGHR) [65]. This new design replaced the original GHR design in the methanol research plant in Australia in 1998. The AGHR uses 'straight-through' tubes with two tube sheets and with a special sliding seal on each tube at the hot end.

Toyo claim in a paper describing a process for large-scale production of DME [66] that they have commercialised technologies for autothermal reforming and heat exchange reforming, and a sketch is shown of a so-called TAF-X Reactor. No details are given of the commercial experience. The reactor is a 'two-in, two-out type' heat exchange reformer with two tube sheets at the top and a floating head at the bottom. There are bellows shown at the top of each tube and at the bottom between the floating head and the outlet flange.

GIAP, the State Institute for Nitrogen Industry of the former Soviet Union, developed a gas heated reformer design called the TANDEM reformer [67]. The design was implemented in an ammonia plant based on O_2-blown autothermal reforming of natural gas in Grodno, Belarus. The TANDEM reactor is a "two-in, two-out" design, and the process concept in Grodno was a 'two-step reforming with GHR', see Section 2.3.4.2.

GHHER or 'two-in, one-out'

In a GHHER, the heating gas and the reformed gas from the catalyst bed in the heat exchange reformer are mixed in the equipment and leave through one exit after having supplied heat to the reforming reaction. The principle is illustrated in Fig. 27C. Haldor Topsøe's GHHER [68], is of this type. The GHHER technology has been successfully demonstrated in a large industrial installation in co-operation with Sasol in South Africa, where it has operated at demanding conditions in parallel with an O_2-blown autothermal reformer [68].

Air Products are promoting the 'Enhanced Heat Transfer Reformer' (EHTR) [69]. The concept is promoted in co-operation with Technip/KTI and seems to be what KTI has earlier referred to as 'post-reforming'. The EHTR has been commercialised as revamp of a H_2 plant, operating in combination with the existing fired tubular reformer.

M. W. Kellogg (now KBR) has commercialised the Kellogg Reformer Exchanger System (KRES) technology. KRES is based on a 'two-in, one-out' heat exchange reformer design operating in combination with an air or O_2-blown autothermal reformer. It has been used for revamp of ammonia plants. The KRES reactor has a bundle of open ended catalyst tubes and baffles on the shell side. Reactor design, process concept, and operating experience have been described in some detail in e.g. Ref. [70]. The possible application in production of MeOH syngas is discussed in Ref. [71].

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Uhde have developed and commercialised a so-called Combined Autothermal Reformer (CAR [72]). The first - and only - industrial size application, a demonstration facility in Chemco s.p. Strazske in Czechoslavia, was started in 1990. CAR is a combination of a 'two-in, one-out' type heat exchange reformer with a POX reactor.

2.3.4.2 Process concepts

Heat exchange reformers heated by process gas are of course always installed in combination with another reformer, which may be a fired tubular reformer or an air or O_2-blown secondary or autothermal reformer. Evidently, a significant number of possible combinations exist. If there is more than one feedstock, as e.g. in GTL plants, where recycled tail gas from the synthesis may be used as additional feed to adjust the gas composition, the number of possible process concepts increases further. The use of a prereformer may also be considered, also increasing the number of possible process concepts. In the following, an attempt is made to describe systematically the possible combinations of heat exchange reformers with either a fired tubular reformer or a secondary or autothermal reformer. Only cases with one feed are considered. This feed will most often be natural gas. The cases may be divided into two main types, series and parallel arrangements.

Series Arrangements

In series arrangements, all the process feed gas passes through first a heat exchange reformer and then through a second reformer, and the product gas from the second reformer supplies heat to the heat exchange reformer. The second reformer in the series arrangement may be a fired tubular reformer (Fig. 30). This process concept has been referred to as 'Gas Heated Prereforming'.

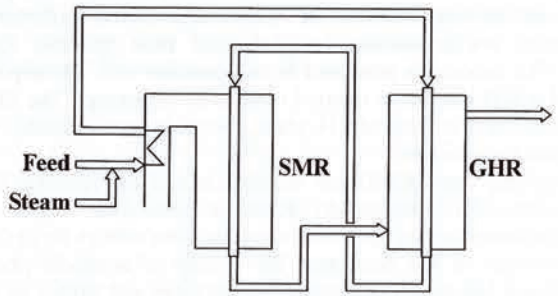


Figure 30 'Gas Heated Prereforming': Fired tubular reforming (SMR) and Gas Heated Reformer (GHR) in series arrangement

Alternatively, the second reformer may be an air or O_2-blown secondary reformer (Fig. 31). This concept, which is often referred to as GHR, is equivalent to two-step reforming and could be called 'two-step reforming with GHR'. (In two-step reforming, a fired tubular reformer is operated in a similar way in series with an air-fired secondary reformer for production of NH_3 synthesis gas or with an O_2-blown secondary reformer for production of synthesis gas for methanol or FT synthesis).

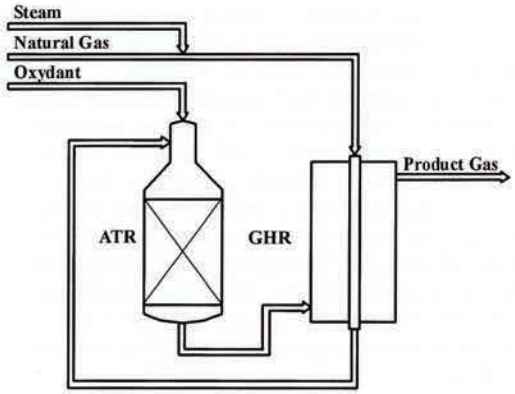


Figure 31 'Two-step reforming with GHR': Autothermal reformer (ATR) and Gas Heated Reformer (GHR) in series arrangement.

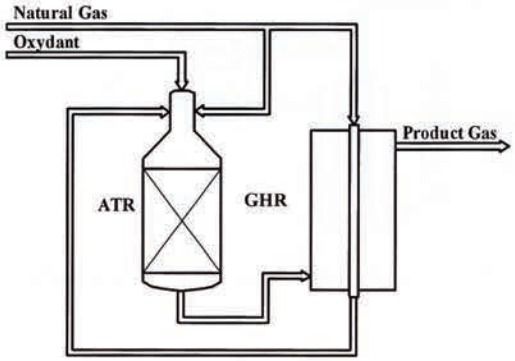


Figure 32 'Combined Reforming with GHR':
Autothermal reformer (ATR) and Gas Heated Reformer (GHR) in series arrangement with partial by-pass of feed over the GHR.

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There is an alternative where only part of the feed passes through the GHR, while the rest is bypassed direct to the secondary reformer (Fig. 32). This could be called 'Combined Reforming with GHR'.

The operating conditions (e.g. S/C ratio) may in these concepts be limited by the steam reforming in the GHR, whereas the final gas composition will be determined by the exit conditions from the secondary reforming.

Parallel Arrangements

For obvious reasons, the 'two-in, one-out' concept can only be used in parallel arrangements, i.e. process arrangements, where the feed gas is split into two streams. One goes direct to a conventional reformer, while the other goes to a gas heated reformer heated by the outlet gas from the conventional reformer or by the mixed outlet gases from the two reformers. In parallel arrangements, either the GHR or 'two-in, two-out' design or the GHHER or 'two-in, one-out' design can be used. With a GHR, it is in principle possible to produce two different product gases, whereas the GHHER for obvious reasons allows only production of one product gas, the mixture of product gases from the two reformers. The heat exchange reformer may be coupled with a tubular reformer or with an air or O_2-blown autothermal reformer. Operating conditions (S/C ratio) in the two reformers may be different; final gas composition is determined by the exit conditions from the two reforming catalyst beds. The four possible schemes are shown in Fig. 33-36.

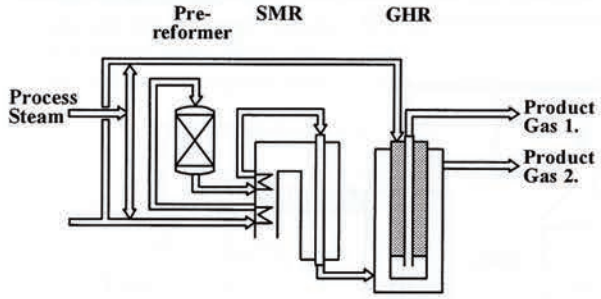


Figure 33 Tubular reformer (SMR) and Gas Heated Reformer ('Two-in, two-out', GHR) in parallel arrangement

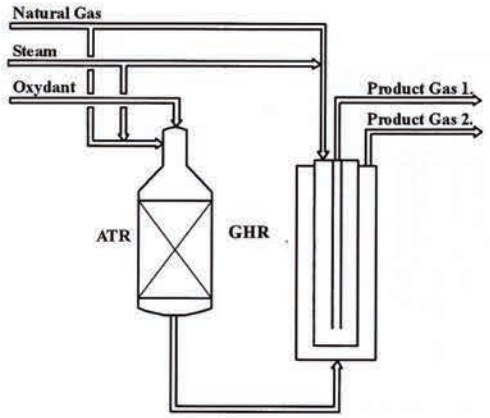


Figure 34 Autothermal reformer (ATR) and Gas Heated Reformer ('Two-in, two-out', GHR) in parallel arrangement

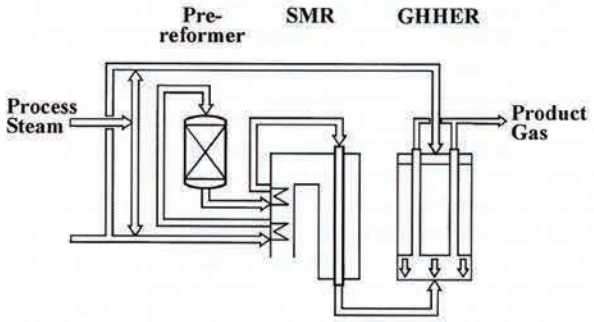


Figure 35 Tubular Reformer (SMR) and Gas Heated Reformer ('two-in, one-out', GHHER) in parallel arrangement

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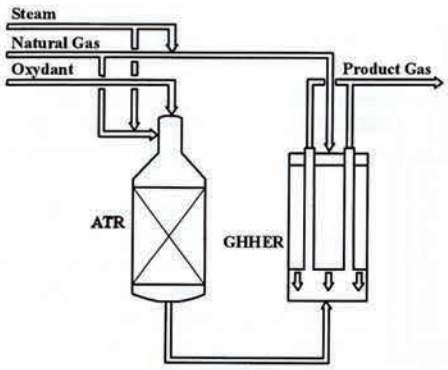


Figure 36 Autothermal Reformer (ATR) and Gas Heated Reformer ('two-in, one-out', GHHER) in parallel arrangement

2.3.4.3 Metal dusting

In all process concepts using heat exchangers heated by process gas, the problem of avoiding metal dusting corrosion on the heat transfer surfaces is a challenge. Metal dusting is a carburisation phenomenon, which may occur on metal surfaces at specific conditions, especially characterised by temperatures in the range 400 – 800°C and contact with a gas with high carbon activity. Metal dusting is well known in the process industry, but unfortunately it is not (yet) completely understood. It results in loss of material, in some cases as 'metal dust', a mixture of metal, carbides, and/or carbon. In severe cases the material wastage can be very fast, leading to catastrophic failure of equipment.

Very significant efforts have been undertaken, especially in recent years, in order to clarify the mechanism and causes of metal dusting and to identify means to cope with the challenge. Reviews of the status of knowledge with comprehensive literature surveys are given in Refs. [73] and [74].

On alloys protected by oxide layers, e.g. stainless steels and Ni-based alloys, metal dusting involves breakdown of the protective oxide layer, transfer of carbon into the base alloy, formation of internal carbides, and disintegration of the matrix. The metal particles generated by the disintegration of the Fe- or Fe-Ni-matrix act as catalysts for carbon formation resulting in coke growing from the corrosion pit [75]. The mechanism on Fe and Fe-Ni-based alloys seems to be different causing different visual appearance of the corroded metal and different types of corrosion products. Full understanding and agreement concerning the mechanism and the kinetics of the attack has not been achieved [74, 75]. The role of gas composition, temperature, and pressure is understood in some detail, but the knowledge is not sufficiently detailed to allow reliable

prediction of the risk of metal dusting on different alloys at different conditions and of the progress of possible attack. Studies of metal dusting are therefore empirical, and experimental work is difficult because of the demanding conditions required, and because significant time lag is sometimes seen before an attack takes place. Also the surface condition of the metal and its history may have an influence on the susceptibility for attack. Efforts to improve the understanding are ongoing, see Refs. [73, 74] and for more recent studies see Refs. [76-78].

Metal dusting can be prevented by addition of sulphur to the process gas [74], by proper choice of construction materials [79], or by application of protective coatings [80], especially by Al_2O_3 by so-called alonising [81] or aluminising [82]. Equipment can be designed to avoid 'dangerous' temperatures, special surface treatments including pre-treatment with air or steam at high temperature may be advantageous, while other treatments such as traditional pickling should if possible be avoided. But in spite of these possibilities, metal dusting will remain a challenge in the design of processes and equipment until the ultimate materials or protection methods are developed, and a complete understanding of the phenomena is acquired.

2.3.5 Steam reforming catalysts

The optimal steam reforming catalyst depends to some extent on the application. In an adiabatic prereformer a high activity and a high surface area are desirable to increase the resistance to deactivation and poisoning. The activity is not as important in primary reformers and heat exchange reformers as the reactor design and volume is typically determined by heat transfer and mechanical criteria. In these cases the catalyst activity is normally much higher than needed. Instead the catalysts are designed for maximum heat transfer and minimum pressure drop. However, in all cases the catalyst should ensure equilibrium conversion throughout its lifetime and sufficient resistance to carbon formation and poisoning.

In the following text the typical properties and types of steam reforming catalysts are described. This is followed by sections on sulphur poisoning and carbon formation. Finally, in Section 2.3.5.4 various fundamental aspects and mechanisms of steam reforming catalysis are outlined.

2.3.5.1 The steam reforming catalysts

Most steam reforming catalysts are based on nickel as the active material. Cobalt and noble metals also catalyse the steam reforming reaction but are generally too expensive to find widespread use, although both Ruthenium and Rhodium have higher activity per metal area than nickel [27, 83]. A number of different carriers including alumina, magnesium-aluminium spinel, and zirconia are employed. In Fig. 37 a steam reforming catalyst is shown on a nano-scale.

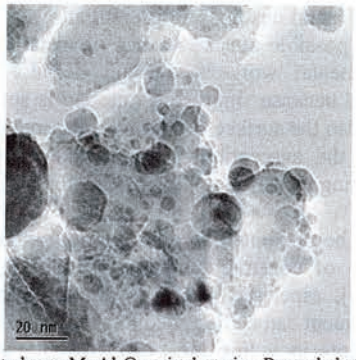


Figure 37 Nickel supported on a $MgAl_2O_4$ spinel carrier. Recorded at 550°C and 7 mbar of hydrogen using the *insitu* electron microscope at Haldor Topsøe A/S.

The intrinsic activity of the catalyst is proportional to its nickel surface area. The catalyst consists of a huge number of small nickel particles on the ceramic carrier. The active surface area may be calculated from Eq. (1) when the average nickel particle diameter, d_{Ni} and the Ni-loading X_{Ni} (g/m_3) are known:

$$A_{Ni}(m^2g^{-1}) = \frac{6800X_{Ni}}{d_{Ni}(\text{Å})} \quad (1)$$

Eq. (1) applies to spherical nickel particles. A_{Ni} is the nickel surface area in m^2g^{-1}.

The catalyst should be optimized for the given application as mentioned above. A key criterion for designing a catalyst for a heated reformer is to maximize the heat transfer at low pressure drop. A high heat transfer coefficient may reduce the tube wall temperature and thereby minimize the required wall thickness. The high heat transfer is not needed for a prereformer catalyst due to the adiabatic nature of this reactor. In all cases the catalyst should be optimized for low pressure drop and high strength.

2.3.5.2 Deactivation by sintering and poisoning

Catalysts in a reforming reactor may lose activity for a number of reasons. In all cases the design of the reactor must be made to take into account the effect of progressive deactivation during the catalysts lifetime.

Sintering is loss of surface area of the active species of the catalyst. The mechanism for sintering is migration and coalescence of nickel particles on the carrier surface [84]. Sintering is a complex process influenced by several parameters including chemical environment, catalyst structure and composition,

and support morphology. Factors that enhance sintering include high temperature and high steam partial pressure [84].

Steam reforming catalysts are susceptible to sulphur poisoning. At steam reforming conditions, all sulphur compounds are converted into hydrogen sulphide, which is chemisorbed on the nickel surface:

$$H_2S + Ni_{surface} \rightleftarrows Ni_{surface}\text{-}S + H_2 \quad (2)$$

Sulphur forms a well-defined structure with a S:Ni stoichiometry of approximately 0.5 corresponding to a sulphur uptake of 440 mg S per m^2 of Ni surface. The maximum sulphur uptake on a reformer catalyst is proportional to the nickel surface area and inversely proportional to the extent of sintering. Formation of nickel sulphide only takes place at much higher sulphur levels than normally experienced in a reformer.

The fraction of the nickel surface area covered with sulphur at equilibrium (the sulphur coverage, θ_s) depends on temperature and the P_{H2S}/P_{H2} ratio [22, 27, 30, 85]:

$$\theta_s = 1.45\text{-}9.53\cdot10^{-5}\cdot T + 4.17\cdot10^{-5}\cdot T\cdot\ln P_{H2S}/P_{H2} \quad (3)$$

This expression is not valid for θ_s close to zero and close to one.

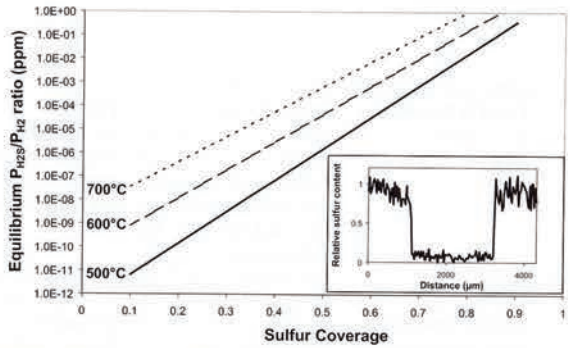


Figure 38 Equilibrium P_{H2S}/P_{H2} ratio as a function of the sulphur coverage. The inserted figure gives the sulphur profile in a strongly sulphur poisoned catalyst pellet

In Fig. 38, P_{H2S}/P_{H2} the ratio at equilibrium is plotted as a function of the sulphur coverage for three different temperatures. The equilibrium partial pressure

of H_2S is extremely low at the lower temperature. This means that any sulphur in the feed will be quantitatively withheld in an adiabatic prereformer, thus protecting downstream catalysts against sulphur poisoning.

The poisoning by sulphur takes place as shell poisoning due to pore diffusion restrictions as indicated in the insert of Fig. 38. The average coverage of the particle will be much lower than in the shell and it may take years before the chemisorption front has moved to the centre of the particle [22].

Sulphur is a severe poison for any reforming catalyst [86]. The intrinsic activity of a catalyst decreases rapidly with the sulphur coverage as expressed below:

$$R_{sp}(\theta_s) = R^{o}_{sp} \cdot (1 - \theta_s)^3 \qquad (4)$$

Where $R_{sp}(\theta_s)$ and R^{o}_{sp} are the specific reaction rates for sulphur poisoned and sulphur free catalyst, respectively.

Other poisons include silica and alkali metals. Silica may substantially reduce the activity of the catalyst by acting as a pore mouth poison [25]. The alkali metals reduce the reaction rates in some cases by orders of magnitude.

2.3.5.3 Carbon formation

Steam reforming involves the risk of carbon formation. Three types of carbon are in general considered in steam reforming reactors as shown in Table 4 and Fig. 39 (see also Section 2.3.2.2).

Table 4
Overview of the routes to carbon formation in a reformer

	Critical Parameters	Characteristics	Effects
Whisker carbon	Low H_2O/C Low H_2O/C_nH_m High T	Dissociation of hydrocarbons at the nickel surface and formation of a carbon whisker at the backside of the nickel crystal.	No immediate deactivation but mechanical disintegration of the catalyst and increased ΔP
Pyrolytic carbon	High T Low activity (sulphur poisoning) High partial pressure of C_nH_m	Non-catalytic cracking of higher hydrocarbons to form carbon on catalyst and tube	Carbon formation in tube and on catalyst. Formation of "hot bands" and increased ΔP
Encapsulating carbon	Low T Heavy feed Low H_2O/C Low H_2O/C_nH_m	Encapsulating of the nickel particles by a CH_x film	Deactivation of the catalyst.

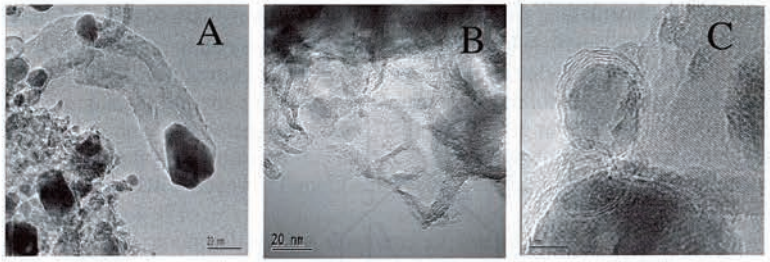


Figure 39 Electron microscopy pictures of whisker carbon (a), pyrolytic carbon on a ceramic carrier b), and encapsulating carbon (c). C_nH_m: Higher hydrocarbons (hydrocarbons with two or more carbon atoms)

Whisker carbon is the most destructive form of carbon formed in steam reforming over nickel catalysts. It may be formed from higher hydrocarbons or from methane in equilibrated gas if the overall H_2O/C ratio is too low as described in Section 2.3.2.2. Carbon whiskers grow by the reaction of hydrocarbons at one side of the nickel particle and nucleation of carbon as a whisker on the other side of the nickel particle as shown schematically in Fig. 40.

The carbon whisker has a higher energy than graphite [87]. This means that operation at conditions at which thermodynamics predict formation of graphite may be feasible without carbon formation of the catalyst. The carbon limit also depends upon the crystal size of the nickel particle. Smaller nickel crystals are more resistant towards carbon formation as demonstrated by the data in Fig. 41.

The temperature of the onset of whisker carbon formation was approximately 100°C higher for the catalyst with small nickel crystals (around 7 nm) than for that with large crystals (around 100 nm).

Pyrolytic carbon results from the exposure of higher hydrocarbons to high temperatures. Reddish zones known as 'hot bands' on the walls of tubular reformers are in many cases the result of pyrolytic carbon formed by cracking of higher hydrocarbons often if the catalyst in the top part is deactivated due to sulphur poisoning. The temperature of the tubes at the point of carbon formation increases because pyrolytic carbon thermally isolates the tubes and encapsulates the catalyst pellets resulting in no activity and no consumption of the supplied heat.

Encapsulating carbon (gum) may be formed in reforming of heavy feeds with a high content of aromatic compounds. The rate of gum formation is enhanced by low temperatures and high final boiling point of the hydrocarbon

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mixture. Encapsulating carbon is a thin CH_x film, which covers the nickel particles and leads to deactivation of the catalyst bed.

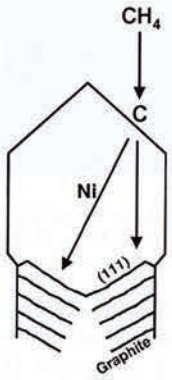


Figure 40 Schematic illustration of the process by which carbon whiskers are formed at the nickel particle during steam reforming.

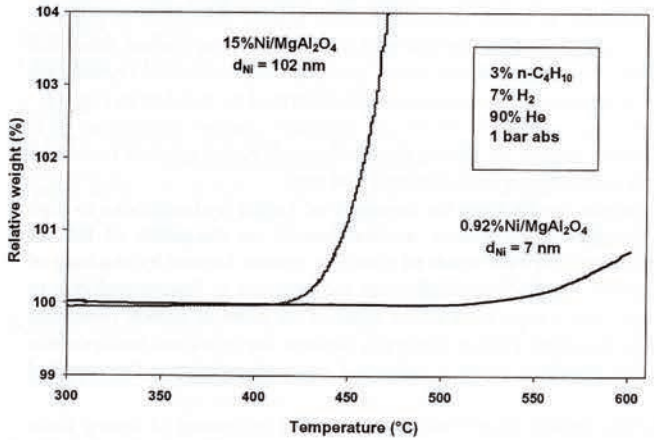


Figure 41 Relative weight increase as a function of the temperature for two catalysts with different nickel crystal size but the same nickel surface area and reforming activity

2.3.5.4 Fundamental aspects of the steam reforming reaction

Fundamental understanding of the reforming process is very important as a guide and as inspiration for new directions in catalyst developments. For example, insight into the mechanism of carbon prevention by promotor addition may lead to new and better promoters. In the following text, a consistent picture of the reforming reaction at the atomic level is given. The description has emerged from DFT (Density Functional Theory) calculations and *insitu* electron microscopy [88-90].

The full potential energy diagrams of the reforming reaction on two different nickel surfaces, Ni(111) and Ni(211) were calculated, and the structures involved in the first four reaction steps for both surfaces are shown in Figs. 42 and 43.

The energetics of the full reforming reaction are shown in Fig. 44. This figure shows the energies of the intermediates on the nickel surface and activation barriers separating the intermediates along the reaction path. Steps are much more reactive than the close packed surface. However, all intermediates are also much more strongly bound at steps than on terraces resulting in more free active sites at terraces. There are therefore (at least) two different reaction channels, one with a low activation barrier, which is associated with steps, and another associated with terraces.

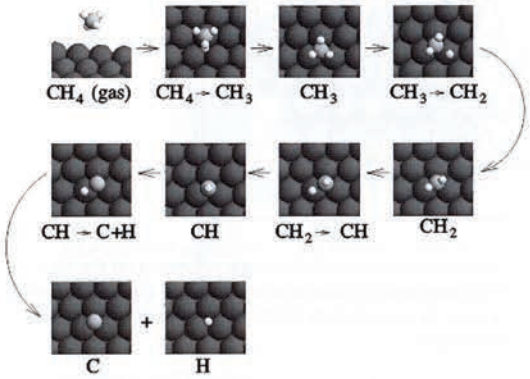


Figure 42 Calculated structures of intermediates and transition states for all elementary processes in the transformation of methane into adsorbed carbon and hydrogen on a Ni(111) surface [89].

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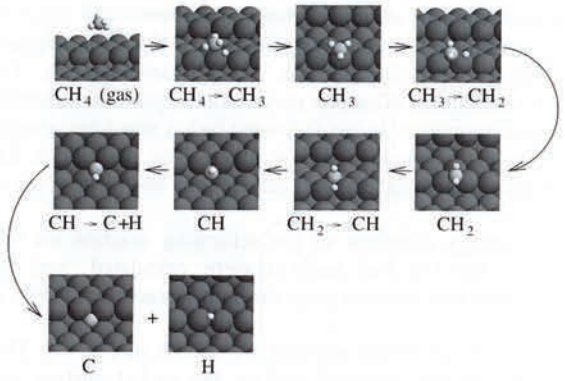


Figure 43 Calculated structures of intermediates and transition states for all elementary processes in the methane activation reactions on the step sites of a Ni(211) surface [89].

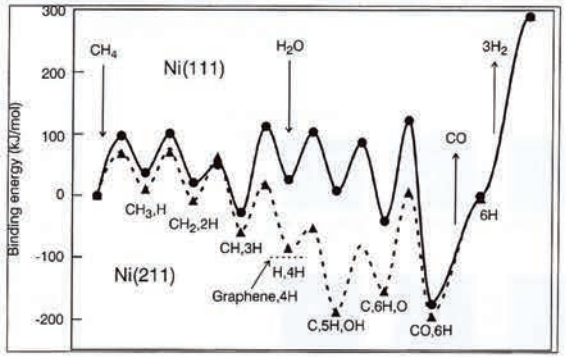


Figure 44 Calculated energies along the reaction path for steam reforming on the Ni(111) and Ni(211) surfaces. The corresponding structures are shown in Figs. 42 and 43. All energies are given relative to a situation in which all reactants are in the gas phase far from the clean surface [89].

It is clear from Fig. 44 that adsorbed atomic carbon is much more stable at the steps than at the terraces. Consequently, steps are better nucleation sites for carbon than terraces. When carbon atoms cover step sites, a graphene layer

(single graphite layer) can grow from the step, as illustrated in Fig. 45. In Fig. 44, the energy of a graphene layer on a Ni(111) surface is included as a dashed line. Because this line is below the energy of the most stable form of adsorbed carbon on the surface (at the step), there is a driving force for graphene formation. After a graphene island is nucleated, the growth may continue by transport of carbon atoms to the island. The graphene may eventually cover the whole crystallite. New layers may nucleate at the step by pushing the already formed layer(s) further out. It is therefore assumed that carbon formation is initiated by formation of graphene islands on a nickel surface.

Recently, carbon formation on a supported nickel catalyst was observed by *insitu* electron microscopy. Fig. 46 shows the initial formation of carbon; the formation of the first graphene layers and how the nickel particle is pushed away from the carrier surface. There is an extra small energy gain associated with the formation of graphite-like layers associated with the weak interlayer interaction.

The carbon atoms are so much more stable at a step than on the flat (111) surface that it is energetically advantageous to form new steps as observed in Fig. 46. New nucleation sites can therefore be formed spontaneously during the steam reforming process, and the system has the freedom to rearrange the nickel particles to best form graphene layers.

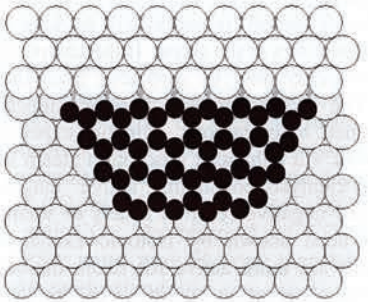


Figure 45 Illustration of a graphene island nucleated from a step on a Ni(111) surface.

These arguments suggest that the availability of step sites is important both for a high turnover rate and for graphite formation. This raises the question of where promoters such as potassium are located on the surface during the catalytic reaction. DFT calculations show potassium was most stable as -K-O-K-O- rows along the steps. Thus, the major carbon-preventing effect of this promoter may be to block the steps and hence remove the nucleation sites for graphite formation. Addition of the promoters should decrease the activity of the catalyst and the decrease should be determined by the promoter coverage at the steps.

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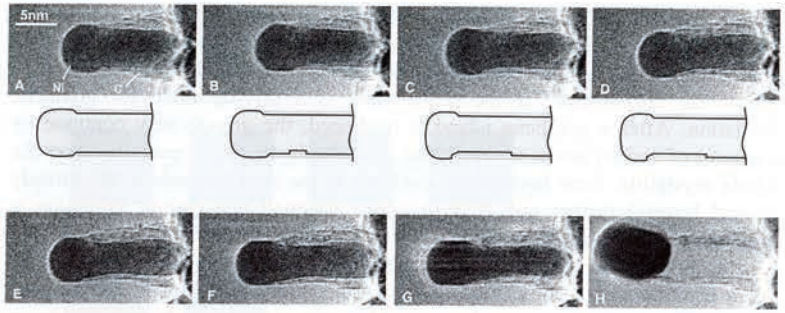


Figure 46 Image sequence of the initial carbon formation on a $Ni/MgAl_2O_4$ catalyst. Drawings are included to guide the eye in locating the positions of mono-atomic Ni step edges at the C-Ni interface. The images are acquired in situ with CH_4:H_2 = 1:1 at a total pressure of 2.1mbar with the sample heated to 536°C.

The promoters need not cover all step sites to prevent nucleation of carbon, because a graphene island of a finite size is needed for it to be stable. The addition of less than an almost complete step coverage will lead to a fraction of the steps being completely covered while the rest are free and open for synthesis. The inhibition of carbon formation will work as long as the promoter is present in sufficient quantities at the steps. If the chemical potential of carbon is high enough, the promoter may be displaced from the step and graphite formation will start. The promotion will therefore appear as a shift in the tolerance towards higher hydrocarbons. Kinetic experiments indicate that promoters may also work via enhanced absorption steam and spill over to the active metal surface on catalysts containing "active" magnesia and alkali [27]. This was reflected in the negative reaction orders of steam obtained for these catalysts. It has also been shown by isotopic exchange experiments that magnesia-based catalysts are more active for steam dissociation than alumina supported catalysts. This observation possibly explains the huge difference in the resistance towards carbon formation between these two supports [89].

2.4 Adiabatic oxidative reforming

In adiabatic oxidative reforming the heat for the reforming reactions is supplied by internal combustion. This is in contrast to fired tubular reforming (Section 2.3.3) and heat exchange reforming (Section 2.3.4), where the heat is supplied by heat exchange from an external source. Initially it may be worth

considering: 'What are the benefits of using adiabatic oxidative reforming rather than steam reforming processes such as fired tubular reforming?'

The product gas from a reforming process may be referred to as raw synthesis gas. It consists of a mixture of H_2, CO, CO_2, H_2O, and CH_4 at equilibrium with respect to the steam methane reforming reaction and the carbon monoxide shift reaction. It will further contain any inerts such as N_2 and Ar, which have been introduced to the process.

In steam reforming, where the hydrocarbon feed is reacted with steam alone, the composition of the raw synthesis gas is governed by the steam reforming reaction and the shift reaction only. When an oxidant is used to supply heat for the reforming reactions by internal combustion, additional reactions are introduced, see Section 2.5. The overall reaction is adiabatic, meaning that there is no exchange of heat with the surroundings except a very limited heat loss, and the composition of the raw synthesis gas can be predicted by a heat and mass balance over the reactor. It should be noted that the combustion reactions are all irreversible. At the conditions applied (high temperature and addition of an under-stoichiometric amount of oxidant), all oxygen will be consumed, because this is the limiting reactant.

The raw synthesis gas is often characterised by the ratio between H_2 and carbon oxides, specifically by the so-called stoichiometric number (SN) or 'module' $M = (H_2 - CO_2)/(CO + CO_2)$ or by the Ribblett Ratio $R = H_2/(2CO + 3 CO_2)$, see Section 2.1.

With CH_4 as the reactant, steam reforming alone will produce a gas with a module of 3.0 (or a Ribblett Ratio of 1.5). This makes it possible, by full recycle of CO_2 from the raw synthesis gas back to the steam reformer, to produce hydrogen and carbon monoxide in a ratio of 3. This concept is often used in so-called HYCO plants, where both H_2 and CO are products [91].]. Alternatively, CO may be converted to CO_2 utilising the water gas shift reaction, producing a 4 to 1 mixture of H_2 and CO_2. By removal of CO_2 (and other undesired components in e.g. a PSA unit), pure H_2 may then be produced. This is the dominating process in H_2 production [60].

Adiabatic oxidative reforming will produce raw synthesis gas with different composition. Fig. 47 [92] shows as an illustration the values of the module M and the H_2/CO ratios, which can be obtained by autothermal reforming of CH_4 using O_2 as the oxidant.

It is seen that the use of an oxidant has brought the gas composition closer to desired values, which are a value of M close to 2.0 for methanol, DME and high temperature FT synthesis, and a H_2/CO ratio close to 2.0 for low temperature FT synthesis with Co catalyst. Means for final adjustment of the synthesis gas composition will be described in the following text:

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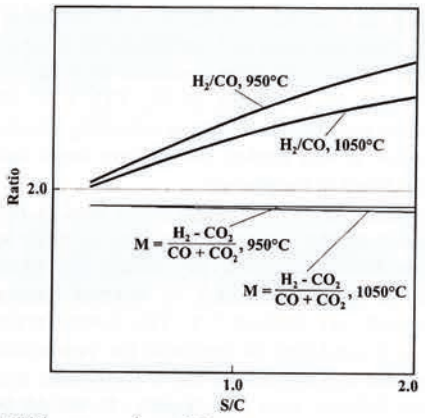


Figure 47 M and H_2/CO in raw gas from ATR

There are of course also other advantages (and disadvantages) related to the use of an oxidant as additional reactant in reforming reactions. The main advantages are related to economics of scale – much larger single stream units are possible with adiabatic oxidative reforming than with steam reforming – and to size of equipment – adiabatic oxidative reformers are very compact units compared to fired reformers. Furthermore, reformer tube materials limit the outlet temperature from fired reformers to a maximum of about 950°C, while the adiabatic oxidative reforming processes easily exceed 1000°C. This makes higher conversion of the feed possible, even at low steam to carbon ratio.

The main disadvantage of adiabatic oxidative reforming, especially with O_2 as oxidant, is that it requires an oxygen source. Oxygen plants are expensive, and the associated investments constitute a major part of the total investments in a synthesis gas generation unit. However, the advantages usually outweigh this disadvantage, especially for the very large capacities required for FT synthesis units and for modern 'mega'-methanol plants.

2.4.1 Process concepts

The process concepts for adiabatic oxidative reforming may be split into three categories considering the type of chemical reactions taking place in the reactor:

- homogeneous reactions
- heterogeneous reactions
- combination of homogeneous and heterogeneous reaction

Furthermore, oxidative adiabatic reforming processes may be characterised by the type of feed. If the feed comes directly from a desulphurisation unit or from a prereformer, and the reactions are carried out homogeneously without the aid of a reforming catalyst, then the oxidative adiabatic reformer is referred to as a gasification or partial oxidation unit. If the reactions are carried out heterogeneously on one or several catalysts, they are referred to as catalytic partial oxidation (CPO). If they are initiated by homogeneous reactions, e.g. in a burner, and completed by heterogeneous catalysis, then the reactor is called an autothermal reformer (ATR). If the feed has been partly reformed in a fired tubular reformer, the ATR reactor is most often called a secondary reformer. Secondary reformers are almost always based on a combination of homogeneous reactions (combustion) followed by catalytic conversion.

Finally, the processes based on adiabatic oxidative reforming may be characterised according to type of oxidant. Here, the split is between processes based on the use of air or enriched air in one group and the use of oxygen in another group.

There is also the possibility to integrate the process layouts with a heat exchange reformer, where the heat of the gas leaving the adiabatic oxidative reformer is used to perform reforming of the feed for the oxidative reformer or of a separate feed stream. Such process schemes are described in Section 2.3.4.2.

Descriptions given of the various process concepts and their principal characteristics and applications are given in the following. A survey is shown in Table 5.

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Table 5
Survey of process concepts and characteristics

	Secondary Reformer (Air)	Secondary Reformer (O_2)	Autothermal Reformer (O_2)	Autothermal Reformer (Air)	PDU (O_2)	PDU (Air)
Burner/Mixer Type	Burner	Burner	Burner	Burner	Mixer	Mixer
Hydrocarbon Feed	Process gas	Process gas [1]	Natural gas [2]	Natural gas	NG/diesel	NG/diesel
CH_4 content, dry mole%	10-15	10-40	85-100 [3]	85-100 [3]	85-100 [3*]	85-100 [3*]
C_nH_m content, dry mole%	None	None	1-10 [3]	1-10 [3]	1-10 [3*]	1-10 [3*]
Oxidant Feed	Air	Oxygen/steam	Oxygen/steam	Air	Oxygen/ Enriched air	Air
Process Gas Temp. °C	770-830	750-810	350-650	350-650	<200	<AIT [4]
H_2O/C ratio, mole/mole	2.5-3.6	1.5-2.5	0.4-3.5	2-4	0-2	<2.0 [5]
Feed Ratio Gas/oxidant, mole/mole	3-4	7-12	1-3	0.5-1.0	1-4	1-5
Flame Temp. °C						
Peak	~2000	~2500	2500-3500	2200-2500	-	-
Adiabatic [6]	~1200	1200-1500	1300-2100	1200-1500	-	-
Catalyst Temp. °C						
Exit	970-1020	950-1020	850-1100	1000-1100	750-1300	750-1200
Typical products	Ammonia synthesis gas	Methanol synthesis gas Hydrogen	Hydrogen/ Carbon monoxide Syngas for FT synt.		Syngas for FT synt.	Fuel Cells Syngas for FT synt.

1) Partly converted process gas from primary reformer
2) Naphtha and LPG feed can also be converted directly in an autothermal reformer
3) For natural gas. In case of naphtha and LPG feed, approx 100% C_nH_m and no methane contents
3*) For natural gas. In case of diesel, 100% and no methane contents
4) Preheat depends on the auto-ignition temperature of the fuel
5) High H_2O/C ratios quench the reactions
6) For the reaction: $CH_4 + 3/2O_2 \rightarrow CO + 2H_2O + Q$. Higher hydrocarbons react by similar reaction scheme.

2.4.1.1 Processes based on homogeneous reactions. gasification or partial oxidation (POX)

Production of the synthesis gas based on homogeneous reactions alone is referred to as gasification or partial oxidation (POX). The oxidant and the hydrocarbon feedstock is mixed in a reactor, where they are allowed to react homogeneously at very high temperatures typically 1300-1400°C. The resulting gas is quenched or cooled by steam production, and carbonaceous by-products like soot are removed by washing. This formation of carbonaceous by-products has an influence on the carbon efficiency.

As mentioned in Section 2.1, gasification is a versatile process which can convert a wide range of feedstocks to synthesis gas. Especially the entrained flow gasification technologies have been adapted to operation on liquid or gaseous feed. Both Shell and Texaco have supplied technology for natural gas conversion by gasification for decades, and lately Lurgi is also promoting a multi-purpose gasification process (MPG) which is available in a version adapted for operation on natural gas feed. The information available in the open literature about these technologies is scarce. However, some information can be found as follows: The Shell process: Refs. [93-95]; The Texaco process: Refs. [96-98]; The Lurgi process: Refs. [99,100].

When operating on gas, the gasifiers will most often be in the boiler mode, where the product gas from the gasifier is cooled by steam production in a boiler, which is specially designed to tolerate the aggressive process conditions and the presence of soot. The exit temperature from the gasifier is high, typically 1300-1400°C, to minimise soot formation and ensure close to complete conversion of the feedstock.

Typical operating conditions for a gas gasification unit are shown in Table 6. The feedstock is assumed to be light natural gas; the product gas is in equilibrium with respect to the steam reforming reaction, but equilibrated with respect to the shift reaction at a lower temperature, about 1125°C - the reaction runs homogeneously backwards at the highest temperatures in the cooling unit. The H_2/CO ratio in the product gas is slightly below 2.0; lower values can be achieved by recycle of CO_2, while steam additions (beyond small amounts added for burner cooling) can not be tolerated due to increased soot formation. In GTL applications tail gas (CO_2-rich) may be recycled to the gasifier to improve carbon yield. If this is done, the gas production in the POX unit must be supplemented by gas production in a steam reformer as in the Shell Middle Distillate Synthesis process [93-95]. In the Shell Bintulu GTL plant, each gasifier has a capacity corresponding to about 3000 b/d FT products. However, Shell claim that the gasification units may be scaled up to about 8000 b/d for new projects [95]. Similar capacities are quoted for the Lurgi MPG process.

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Table 6
Typical operating conditions for a POX unit operating on natural gas feedstock

Oxygen/NG Ratio, mol/mol	0.55 – 0.65
H_2O/C Ratio, mol/mol	0 – 0.15
Exit Pressure, kg/cm^{2}g	25 – 40 [1]
Exit Temperature, °C	1300 – 1400
Exit Gas Characteristics	
H_2/CO Ratio	1.6 – 1.9
CO_2/CO Ratio	0.05 – 0.1
CH_4 Content, mol%	0.1

[1] Higher pressure is feasible, but probably not relevant for GTL.

2.4.1.2 Processes based on heterogeneous reactions.
catalytic partial oxidation (CPO)

The production of synthesis gas based only on heterogeneous catalytic reactions is normally referred to as CPO (catalytic partial oxidation). The oxidant and the hydrocarbon feedstock are premixed in a mixer before the feed enters the catalytic bed. The catalyst bed consisted, in older designs, of an ignition catalyst followed by a reforming catalyst. In some modern versions, only one catalyst is employed, and ultra short residence time is used. The risk of auto-ignition limits the preheat temperature, which results in a higher consumption of oxidant. The process is reported to be able to handle a wide range of feedstocks including heavy aromatic-containing hydrocarbons like diesel. However, for GTL applications the feed will of course be natural gas.

CPO with air as oxidant has been promoted for GTL applications by Syntroleum [101]. However, as for other adiabatic oxidative reforming processes, the use of air has also in this case severe disadvantages, and the process has not been used in practice. Conoco is developing a process apparently based on CPO with oxygen as the oxidant [102, 103]. The process has been developed to the demonstration stage, but only scarce information has been made available in the open literature. CPO is further described in Section 2.6.1.

2.4.1.3 Processes based on combined homogeneous and heterogeneous reactions.
autothermal reforming (ATR) and secondary reforming

Processes in which the reactions are initiated homogeneously, e.g. in a burner, and completed heterogeneously in a catalyst bed are called autothermal reforming (ATR) or secondary reforming.

ATR

In ATR, the feed goes directly from desulphurisation or from a prereformer to the adiabatic oxidative reformer. ATR is used mainly with O_2 as oxidant,

although it has in the past been used with air or enriched air for production of NH_3 synthesis gas [3]. (In order to make a stoichiometric NH_3 synthesis gas (H_2/N_2 = 3.0) by ATR with enriched air, 30 – 40 vol% O_2 is required in the oxidant).

As shown in Fig. 47, it is not possible to produce synthesis gas for production of methanol, DME or FT synthesis directly by autothermal reforming of pure feed. It is necessary either to adjust the composition of the gas by removal of carbon oxides or by addition of H_2 (for methanol synthesis gas and similar) or by addition of carbon-rich gas (for low temperature FT synthesis). The carbon-rich gas may be recovered or imported CO_2 or carbon-rich tail gas from the synthesis. However, the advantages of ATR are such that it has, especially after development of processes operating at steam to carbon ratios below 1.0, become the preferred route to synthesis gas for these syntheses, especially for very large capacities [8, 26, 104-106].

Two concepts for large-scale production of methanol with synthesis gas production by ATR are shown in Fig. 48 and 49 [104].

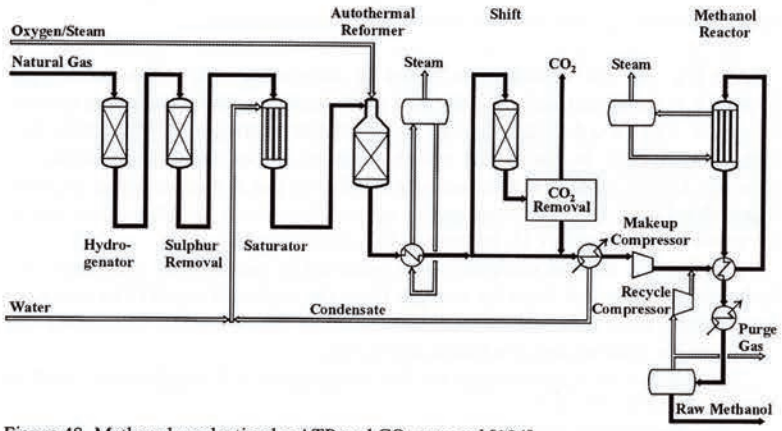


Figure 48 Methanol production by ATR and CO_2 removal [104].

The two process concepts differ mainly in the way the composition of the raw synthesis gas is adjusted in order to match the requirements of the methanol synthesis. As mentioned above and shown in Fig. 47, the raw synthesis gas from an ATR is lean in H_2. Typical values of the module M are 1.7-1.8, whereas a value slightly above 2.0 is preferred for methanol (and HTFT) synthesis.

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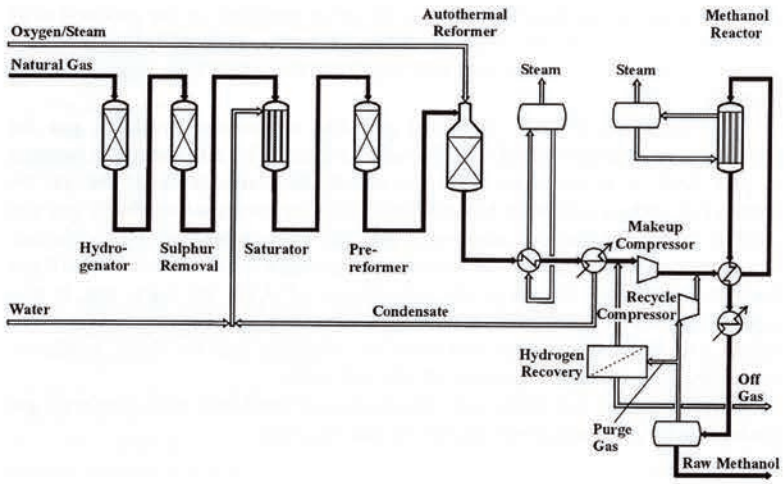


Figure 49 Methanol production by ATR and H_2 recovery and recycle [104]

In Fig. 48, the module is adjusted by removal of CO_2. The natural gas feedstock is desulphurised and saturated with steam to a steam to carbon ratio of 0.6 – 1.0. The mixed feed is passed to a prereformer and, after preheating to a high temperature, to the ATR, which operates at an outlet temperature of typically 1050°C and an outlet pressure of 30 – 40 bar g. Higher outlet pressure is possible [106], but not advantageous at very low steam to carbon ratio due to the resulting increase in CH_4 leakage in the synthesis gas.

In Fig. 49, the gas composition is adjusted by addition of hydrogen. The hydrogen is recovered from the tail gas from the methanol (or HTFT) synthesis loop. Apart from this the process scheme and the operating conditions are similar to the scheme and conditions in Fig. 48.

Production of synthesis gas for low temperature FT synthesis by ATR is illustrated in Fig. 50 [26].

This process has after careful analysis of alternatives been chosen by Sasol and others as the most economically attractive process for this purpose. As a consequence it will be employed in the large GTL units under realisation in Qatar and Nigeria and in future GTL plants considered by Sasol and their partners [107].

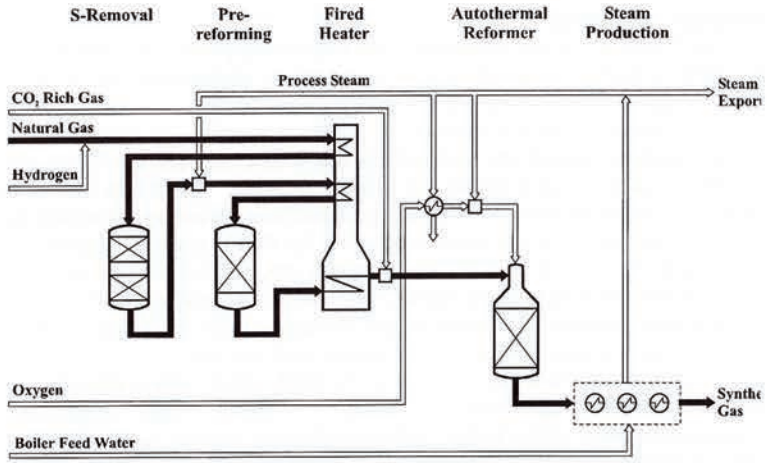


Figure 50 Typical process flow diagram for synthesis gas production for GTL

The process scheme is quite simple. The natural gas feedstock is desulphurised, and process steam is added to a steam to carbon ratio of 0.6. The mixture of feed and steam is passed to a prereformer and further, after mixing with carbon rich tail gas from the FT synthesis and preheating, to the ATR. Here it reacts with O_2 to form a synthesis gas with the desired composition. Heat is recovered from the synthesis gas by production of high pressure steam, and the gas is cooled for removal of H_2O, before it is passed without compression to the synthesis section.

Although simple in principle, the process offers significant challenges. One is the size of equipment, piping, valves, etc. For production of 34,000 bbl/d of FT products, about 1.5 million Nm^3/h of synthesis gas will be produced in just two ATR reactors. For future projects, even larger reactors are contemplated. Another challenge is the risk for metal dusting corrosion in downstream equipment, see Section 2.3.4.3.

Design of the ATR reactor and the mixer burner is treated in Section 2.5.

ATR may, as fired tubular reforming, be combined with heat exchange reformers in a number of process schemes. Such schemes are described in Section 2.3.4.2.

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Secondary reforming

Air-blown secondary reforming is the dominating process for manufacture of synthesis gas for NH_3 production from natural gas and naphtha [3]. A typical process scheme is shown in Fig. 51 [108].

The process concept is used by all important suppliers of technology for NH_3 production. Natural gas is desulphurised, mixed with process steam, and passed to a fired tubular reformer, the 'primary reformer'. The product gas from the primary reformer is reacted with air in the secondary reformer to produce the raw synthesis gas, which is processed further by shift conversion, removal of CO_2, and methanation to give the final synthesis gas, a 3 to 1 mixture of H_2 and N_2 with small amounts of inerts, mainly CH_4 and Ar. The amount of air added to the secondary reformer is adjusted to give the correct ratio of H_2 and N_2 in the synthesis gas. Variations of the process scheme exist, see [3].

The secondary reformer is a refractory lined vessel with a mixer/burner (normally a multi-nozzle design), a combustion chamber, where homogeneous reactions take place, and a bed of Ni-based reforming catalyst, where the shift- and reforming reaction are equilibrated by heterogeneous reaction on the catalyst.

In a modern NH_3 plant, the steam to carbon ratio at the inlet of the primary reformer is in the range 2.5 – 3.5, the pressure at the outlet of the secondary reformer is 25 – 35 bar g, and the outlet temperatures from the primary and secondary reformers are 750-850°C and 950 – 1050°C, respectively.

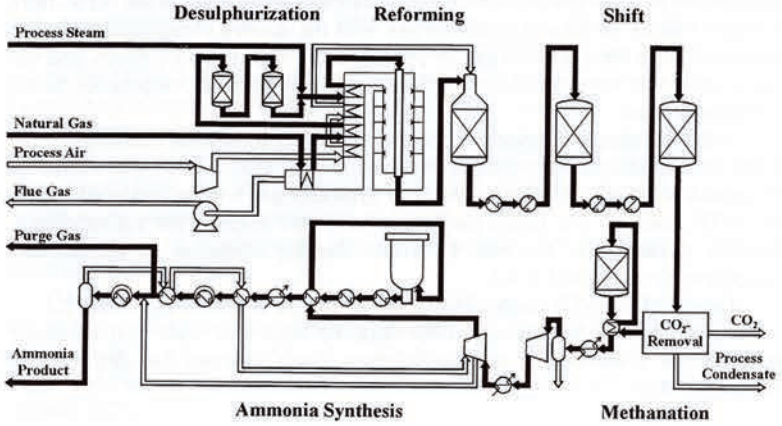


Figure 51 Complete ammonia plant [108]

Use of enriched air as oxidant in the secondary reformer has been suggested as a revamp option [109] in combination with a fired reformer.

Combinations with heat exchange reformers are used in Johnson Matthey's LCA process and in KBR's KRES process. These processes are described in Section 2.3.4.2. Both concepts with air and enriched air are described.

When N_2 is an undesired constituent in the synthesis gas, O_2 is may be used as the oxidant in the secondary reformer. This is the case in production of synthesis gas for methanol, dimethylether (DME), and high temperature FT synthesis.

A process scheme used by Haldor Topsøe for production of methanol synthesis gas by so-called 'two-step reforming', using prereforming, fired tubular reforming, and O_2-blown secondary reforming is illustrated in Fig. 52 [104]. This process scheme was used in a large methanol plant in Norway [110]. The natural gas feed is desulphurised, and process steam is added in a saturator. The mixture of feed and steam is passed to a prereformer, a primary reformer, and an O_2-blown secondary reformer. The steam to carbon ratio at the inlet to the prereformer is 1.5 – 2.0, the outlet pressure from the secondary reformer is about 35 bar g, and the outlet temperatures from the three reformers are about 450°C, 750 – 800°C, and 1000 – 1050°C, respectively.

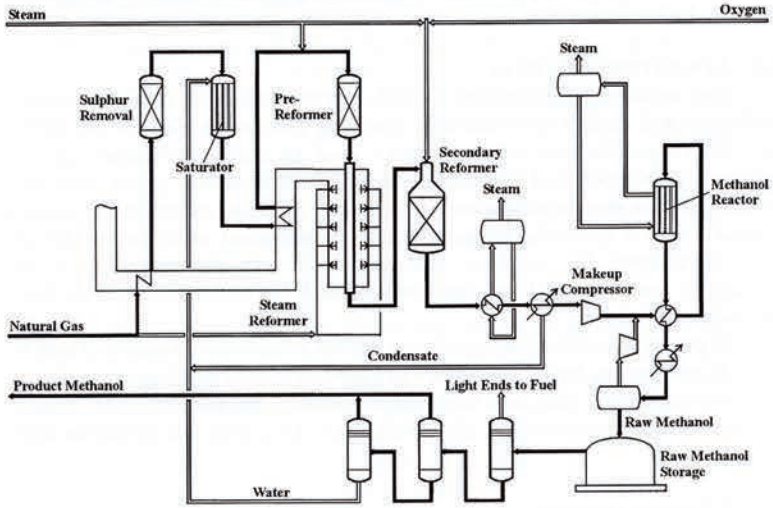


Figure 52 Methanol production by two-step reforming [104].

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The design of the secondary reformer is very similar to the design used in air-blown processes. However, the operating conditions in the secondary reformer are more severe than in the air fired concept, and multi-nozzle burner design can not be used. Instead, a design similar to the design of burners for autothermal reformers (see Section 2.5) is used.

In a variation of the concept, the natural gas feed is split into two parts. One is added to the primary reformer, whereas the other part is sent directly to the secondary reformer. This concept, originally suggested by Foster Wheeler, is normally referred to as 'combined reforming'. It is mainly used by Lurgi [111] in their process for production of methanol synthesis gas. It has also been used in the high temperature FT synthesis plant owned and operated by PetroSA (Mossgas) [112].

The advantage of using O_2 instead of air as oxidant is obvious. The presence of N_2 as an inert in the final synthesis gas is avoided. Use of air as oxidant has been suggested in production of synthesis gas for methanol [113] and FT synthesis [92,114]. However, this is not economically feasible [115], since the presence of large amounts of N_2 – about 50 vol% in the dry synthesis gas – makes recycle concepts in the synthesis gas impossible leading to low overall efficiency. Furthermore, compression of the large amounts of air required consumes more power than required for production and compression of O_2 in O_2-blown concepts.

2.5 Autothermal reforming

The autothermal reforming (ATR) process has been used to produce hydrogen- and carbon monoxide-rich synthesis gas for decades. In the 1950's and 1960's autothermal reformers were used to produce synthesis gas for ammonia production and methanol [116, 117]. In ammonia plants, hydrogen production was maximised by operating at high steam to carbon ratios ranging from 2.5 to 3.5 on molar basis, while in the methanol units carbon dioxide removal adjusted the synthesis gas composition. In the early 1990's, the technology was improved and operation at much lower steam to carbon ratios was achieved [118].

In production of CO-rich synthesis gas for production of pure CO and H_2 and CO mixtures as feed for methanol or Fischer Tropsch synthesis, operation at low steam to carbon ratio feed ratios are beneficial. Operation at H_2O/C ratio of 0.6 has been demonstrated in pilot scale [118, 132, 155] and industrial scale [119].

2.5.1 Chemical reactions

ATR is a combined combustion and catalytic process carried out in an adiabatic reactor. A mixture of natural gas and steam is partially converted by

pressurized combustion at fuel-rich conditions and the final conversion of hydrocarbons into an equilibrated synthesis gas is made over a fixed catalyst bed. The overall chemical reactions taking place in the ATR reactor can be described by the below reactions:

Combustion	$CH_4 + {}^3/_2\, O_2 \rightarrow CO + 2\, H_2O$	$-\Delta H^0_{298} = +519$ kJ/mole (1)
Reforming	$CH_4 + H_2O \rightleftarrows CO + 3\, H_2$	$-\Delta H^0_{298} = -206$ kJ/mole (2)
Shift	$CO + H_2O \rightleftarrows CO_2 + H_2$	$-\Delta H^0_{298} = +41$ kJ/mole (3)

The ATR reactor is described in section 2.5.2. It can be divided into three zones;

- Combustion zone
- Thermal zone
- Catalytic zone

The ***combustion zone*** is a turbulent diffusion flame, where hydrocarbon molecules and oxygen are gradually mixed and combusted. The combustion reactions are exothermic and very fast, and from a global point of view it can be assumed progressing as 'mixed is burnt'. Combustion in an ATR is sub-stoichiometric with an overall oxygen to hydrocarbon ratio of 0.55 to 0.6, but when simplified as a one-step model the flame zone can be described as a single reaction (1) of CH_4 to CO and H_2O with an O_2/CH_4 ratio of 1.5. Although simplified in a single reaction (1) above, combustion of hydrocarbons consists of a large number of homogenous radical reactions. Combustion chemistry is described in more details in Section 2.5.1.1. The local stoichiometry in the flame zone will vary from very fuel-lean to very fuel-rich. The core of the flame will have parts that are close to stoichiometric, and therefore the centre of the flame will be very hot as the adiabatic flame temperature for the stoichiometric mixture exceeds 3000°C.

In the ***thermal zone*** above the catalyst bed, further conversion occurs by homogeneous gas-phase-reactions. These reactions are slower reactions like CO oxidation and pyrolysis reactions involving higher hydrocarbons. The main overall reactions in the thermal zone are the homogeneous gas-phase steam methane reforming (2) and shift reaction (3). Reactions between N_2 and hydrocarbon radicals, which may form by-products like HCN and NH_3 are also proceeding in the thermal zone. The N-chemistry in relation to sub-stoichiometric combustion is described in Section 2.5.1.4.

In the ***catalytic zone*** the final conversion of hydrocarbons takes place through heterogeneous catalytic reactions including steam methane reforming

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(2) and shift reaction (3). The catalytic zone is described in more detail in Sections 2.5.2.3 and 2.5.2.4.

Fuel-rich combustion in partial oxidation processes involves the risk of incomplete combustion. Methane combustion at fuel-rich conditions is mainly proceeding through reaction steps with C_2-radicals as intermediates, which may react to soot precursors like poly-aromatic hydrocarbons (PAH) and further to soot particles [120]. ATR operation is soot-free at normal circumstances, and this is achieved through a careful burner design, by addition of small amounts of steam and finally by catalytic conversion of soot precursors, and therefore the exit gas contains no other hydrocarbons than methane. Soot formation chemistry is described in Section 3. Soot formation is unwanted and. It would reduce the carbon efficiency of the process, and soot particles would need to be removed from the synthesis gas.

2.5.1.1 Combustion chemistry

The gas phase combustion reactions between hydrocarbons (i.e. methane) and oxygen proceeds through radical reactions. The reaction mechanism consists of a large number of species (molecules and radicals) and reactions. Even for a simple hydrocarbon like methane a precise description includes several hundred reactions. The combustion chemistry of the lighter aliphatic hydrocarbons present in natural gas has been studied intensively during the recent years [120, 121]. Fig. 53 shows the simplified reaction path for high temperature methane combustion.

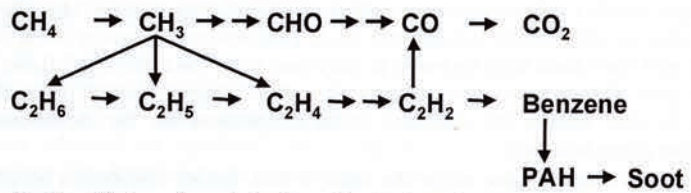


Figure 53 Simplified reaction path for C_1 and C_2 chemistry CH_4 combustion [118].

The combustion chemistry is controlled by radicals; the primary radicals are the hydrogen radical (H), the hydroxyl radical (OH) and the oxygen radical (O). A large number of hydrocarbon radicals exist as well, some of them are included in Fig. 53 (CH_3, C_2H_5, and CHO). The hydrocarbon radicals are generally produced as combustion intermediates primarily by reaction between a molecular hydrocarbon and a radical, but it may also be formed from a hydrocarbon molecule alone. Examples of these types of reactions are given below by the reaction between methane and the hydroxyl radical (4), and the

reaction between ethane and a third body molecule (M) (5) forming methyl radicals:

$$CH_4 + OH \rightarrow CH_3 + H_2O \quad (4)$$
$$C_2H_6 + M \rightarrow CH_3 + CH_3 + M \quad (5)$$

In combustion of hydrocarbons, the C_1 chemistry is the basis for the reactions leading to oxidation to CO and CO_2, while the C_2 chemistry leads to formation of unsaturated hydrocarbons, aromatics and soot precursors. Even in a methane flame with methane as the only hydrocarbon source, ethane, ethylene and acetylene will be formed especially in the fuel rich parts of the flame.

The chemistry of hydrocarbon combustion can be modelled as a large number of elementary reactions described in detailed kinetic models. This will be further described in Section 2.5.3.2.

2.5.1.2 Ignition

The establishment of a flame, normally referred to as ignition, is a special part of the radical combustion chemistry. The ignition reactions involve chain branching and chain termination reactions. At T>1000 K the radicals H, O, OH become responsible for the chain branching reactions. Once the ignition is established the propagation reactions proceed by radical attacks on the fuel [122, 123].

The ignition is often controlled by two competing reactions involving the oxygen molecule leading either to radical branching (ignition) or radical termination. The branching reaction is:

$$O_2 + H \rightarrow OH + O \quad (6)$$

At lower temperature, this reaction may lead to formation of the peroxide radical instead:

$$O_2 + H (+ M) \rightarrow HO_2 (+ M) \quad (7)$$

The peroxide radical is less reactive than other radicals meaning that it has lower rates when reacting with hydrocarbons, and it will lead to radical termination through reactions with another hydrogen radical:

$$HO_2 + H \rightarrow H_2 + O_2 \quad (8)$$

The net reaction of (7) and (8) is a recombination of two hydrogen radicals to form a hydrogen molecule, (i.e. radical termination), while (6) reaction leads

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to radical branching. Furthermore, the oxygen radical is very reactive and is likely to react in a new branching reaction:

$$H_2 + O \rightarrow OH + H \qquad (9)$$

Once the flame is ignited, the process condition for the ATR process with temperatures in the combustion chamber above the auto-ignition temperature of the process gas ensures the flame stability.

To understand more about ignition behaviour the general overview given by Westbrook [123] is recommended.

Although the ATR process is a non-sooting technology, there is a potential for soot formation in the combustion chamber at abnormal operating conditions and during start-up transients. To avoid soot formation, it is necessary to have detailed knowledge of the mechanisms for soot formation and limits for on-set of soot formation.

Soot may be formed as a by-product in all combustion processes involving hydrocarbons [124-126]. One of the best known flames is that of a candlelight with the yellowish flame. The yellowish flame is due to soot formation in the fuel rich part of the diffusion flame. Close to the wick, the colour of the flame is a darker bluish. This is where the fuel oxidation is initiated, but with insufficient air to allow for complete combustion. Therefore, pyrolysis reactions are allowed to occur resulting in fuel decomposition and formation of aromatic species subsequently leading to soot particles. In candlelights, the soot is oxidised as air is mixed with the fuel rich gas leaving the overall flame non-sooting. However, if the wick becomes large allowing more fuel to evaporate or if the flame is interacting with other flows e.g. crosswind, the temperature in the diffusion layer may drop, quenching the soot particles oxidation and leaving a black plume of soot.

In methane combustion, reaction steps involved in formation of hydrocarbon radicals, aromatic species and formation of soot particles are schematically illustrated in Fig. 54 [126, 127]. Once aromatic species are formed, there is a potential for growth of the aromatic structure forming poly-aromatic hydrocarbons (PAH), and subsequently PAH clusters will lead to inception of soot particles.

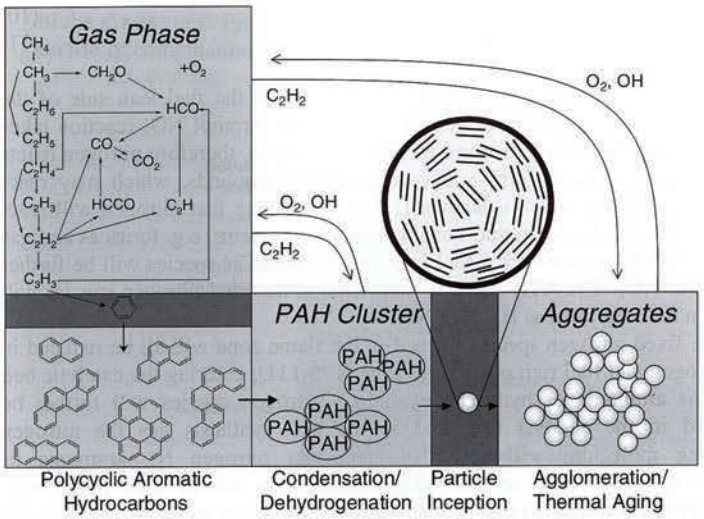


Figure 54 Schematic representation of reaction steps involved in the soot formation in methane combustion, taken from [128].

Oxidation of PAH and soot particles are competing reactions to soot particle formation. Although soot is formed in the flame, it may have time to be oxidised making the overall flame non-sooting as observed in most candlelights. Limitations in the reaction pathway to soot are illustrated in Fig. 54 as dark zone; Benzene formation and particle inceptions. The first step is the formation of the initial aromatic species allowing the PAH chemistry to initiate. The second step is the inception of the initial soot particle. While the gas phase chemistry leading to the formation of the aromatic species is well understood [124-127], the chemistry leading to formation of PAH clusters and soot particle inception cannot presently be described in detail [128].

2.5.1.3 N-chemistry

The feed streams for an ATR also contain some inerts; the inerts are primarily argon from the air separation unit and nitrogen from the hydrocarbon source. Nitrogen is not completely inert in combustion processes. Two reaction mechanisms can break the nitrogen-nitrogen bond in the nitrogen molecule forming nitrogen oxides and hydrogen cyanide. The dominant mechanisms are the thermal NO_x and the prompt NO_x reactions, respectively, and main reaction steps are given below as reaction (10) and (11).

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$$N_2 + O = NO + N \quad (10)$$
$$N_2 + CH_i = H_iCN + N \quad (11)$$

While the thermal NO_x reaction takes place on the fuel lean side of the flame at elevated temperatures (above 1200°C), the prompt NO_x reaction takes place in fuel rich areas. In the prompt NO_x mechanism, therefore nitrogen reacts with a hydrocarbon to form amines or cyano compounds, which may react further to NO_x. The index i denotes 1, 2 or 3 meaning that nitrogen will react with all C_1 fuel radicals. In traditional combustion systems, e.g. furnaces and gas turbines, which operate with a fuel lean flame, the H_iCN species will be further oxidized to NO_x. The ATR flame is fuel rich and the fired nitrogen species will remain in reduced form as H_iCN or NH_i.

The fixed nitrogen species formed in the flame zone will all be reduced in the hydrogen and fuel rich post flame zone [129-131], entering the catalytic bed mainly as ammonia or hydrogen cyanide. Nitrogen species will further be converted in the catalyst bed, and in the exit synthesis gas the nitrogen containing molecules will be either molecular nitrogen N_2, ammonia or hydrogen cyanide. The concentration of the latter two will be in the ppm range. The concentration will depend on the amount of nitrogen in the natural gas and in the oxygen. In air-blown processes more ammonia and hydrogen cyanide will be formed than in oxygen-blown processes.

2.5.2 ATR process and reactor design

The ATR reactor design consists of a burner, a combustion chamber, a fixed catalyst bed section, a refractory lining, and a reactor pressure shell as illustrated in Fig. 55. The key elements of the ATR technology are the burner and the catalyst:

- The *burner* provides proper mixing of the feed streams, and the fuel-rich combustion is taking place as a turbulent diffusion flame. Intensive mixing is essential in order to avoid soot formation.
- The *catalyst* equilibrates the synthesis gas and destroys soot precursors. The catalyst particle size and shape is optimized to achieve high activity and low pressure drop in order to obtain a compact reactor design.

A careful design of the process burner and combustion chamber is required in order to avoid excessive temperatures and formation of soot particles. Further, the detail design and construction of the whole ATR reactor including refractory and catalyst bed is of utmost importance for ensuring safe design and operation

of the syngas unit. Predictions and design are facilitated by reactor models based on use of computational fluid dynamics (CFD) and on chemical kinetics.

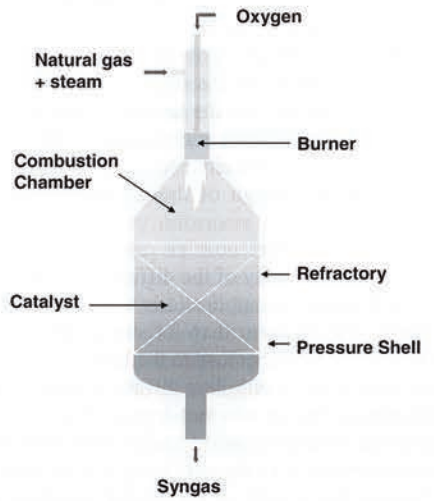


Figure 55 Illustration of an ATR reactor [taken from 132].

2.5.2.1 The ATR burner and combustion chamber

The ATR process burner is a key element of the technology. The burner provides the mixing between the hydrocarbon feed and the oxidant in a turbulent diffusion flame. The flame core may exceed 3000°C. It is essential to minimise heat transfer by thermal radiation or hot gas recirculation to the burner parts.

In the design of the burner and the combustion chamber the following reaction-engineering aspects must be considered in order to ensure optimal reactor performance, safe operation and satisfactory equipment lifetime:

- Effective mixing at the burner nozzles
- Low-metal temperature of the burner
- Soot-free combustion
- Homogeneous gas and temperature distribution at the catalyst bed entrance
- Protection of the refractory from the hot flame core.

Recirculation of the reacted gas from the thermal zone to the burner can protect the refractory and the burner from the hot flame core and gases from the

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combustion zone. An efficient external re-circulation will enhance the position of the flame core along the centreline of the combustion chamber and protect the refractory from the hot flame core [134]. The temperature of the gas circulating along the walls and into the catalyst bed is reduced to the range 1100-1400°C by the endothermic reactions proceeding in the thermal zone.

An optimised re-circulation will also provide a homogeneous distribution of gas and temperature at the entrance to the catalyst bed. Inhomogeneity will result in larger distance to equilibrium, and the methane concentration in the exit gas is increased. The more even the distribution of gas to the catalyst bed, the better the utilization of the catalyst activity. An even flow and temperature distribution is obtained by proper design of the geometry of the combustion chamber.

The flow velocities in the burner nozzles can be selected within large ranges. Highly turbulent mixing intensity of the diffusion flame is obtained with high velocities in the nozzle gaps. For applications with oxygen or enriched air as oxidant, the flame speed will be faster than for similar air flames [133]. The position of an oxygen flame will be very close to the burner nozzles especially at highly turbulent mixing intensities. A turbulent diffusion flame is in steady-state seen over a certain time period, but an inherent feature of the turbulent flame is that the flame is dynamic and changes position within short time frames.

A process burner concept, the CTS burner [134], was developed in 1991 by Haldor Topsøe. CTS burners have been in successful operation since 1992 in both ATR reactors and oxygen-blown secondary reformers for production of a variety of products ranging from methanol, hydrogen, and ammonia to pure CO and Fischer-Tropsch products. A new and optimized version of the CTS burner has been developed with special focus on operation at low S/C-ratios with high flame temperatures. The flow patterns and mechanical design of the burner nozzles have been optimized by use of tools like CFD (computational fluid dynamics), stress-analysis with Finite Element Analysis (FEA) and real-environment testing in pilot scale and in full size demonstrations.

Burners in secondary reformers and autothermal reformers operation are exposed to high operating temperatures. Industrial operation has from time to time faced problems ranging from burner wear without serious process implications to severe failure. However, safe operation and long burner lifetime has been obtained by proper design of the burner [134, 156], whereby severe consequences to equipment and production loss have been avoided. And example of a severe failure of an oxygen-blown secondary reformer refractory and reactor shell following a burner related incident is described by Mossgas [135]. Burners for high temperature reformers can be designed with a focus on mechanical and thermal integrity in combination with the combustion chamber

design [134]. CFD (Computational Fluid Dynamics) can be used to predict the flow pattern and avoid unwanted behaviour.

2.5.2.2 Vessel and refractory

The reactor vessel is lined on the inside with refractory. The refractory insulates the steel wall of the pressure vessel from the high temperature reaction environment. The refractory is commonly constructed of several layers with different materials and insulation properties. Efficient refractory design ensures that reasonable low mechanical temperature design temperatures can be applied for the pressure shell. Typically the temperature of the reactor wall is reduced to 100-200°C at normal operation.

In air-blown secondary reformers it is common practise today to use a design with two refractory layers. In older designs a design with only one layer was applied, but such a design was sensitive to cracks in the refractory layers, which resulted in gas flow and transfer of heat to the shell and thereby in hot spots on the pressure shell [136]. In oxygen-blown secondary reformers and ATR reactors the operating conditions are more severe including a higher operating temperature in the combustion zone. In ATR reactors, a refractory design with three layers of refractory is commonly used today. The inner layer has high thermal resistance and stability and is typically a high density alumina brick layer. The installation of the refractory lining is important and involves skilled craftsmen.

Transport of hot gasses from the high temperature combustion chamber and the catalyst bed through the refractory layers to the reactor wall is not happening with a good refractory design and installation. But it is a potential risk and may lead to increased temperatures at the reactor walls, which could develop into so-called 'hot spots'", where the design temperature of the vessel is approached or exceeded. The risk of gas bypass through the refractory is especially high in the combustion chamber where the temperature is highest, and at the catalyst bed where the catalyst bed creates a pressure drop which may force the gas through weak zones of the refractory.

The outside of the reactor vessel is either non-insulated and exposed to the atmosphere or covered in a water jacket. In non-insulated designs a thermal sensitive paint is applied on the reactor surface. Such paint allows visual monitoring and inspections for colour changes indication increased temperature in case of hot spot development. With a water jacket it is more difficult to detect hot spots, but this can be done to a certain degree by monitoring the increased evaporation rate from the water jacket.

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2.5.2.3 Catalyst bed

The hydrocarbons are only partly converted in the combustion chamber, and the gas leaving the combustion chamber contains a significant amount of methane and traces of other hydrocarbons. In the catalytic zone the final conversion of methane and other hydrocarbons takes place. The reactions are heterogeneous steam reforming reactions (see Section 2.5.1) over the fixed catalyst bed. The methane steam reforming reaction is endothermic, and the temperature will decrease from typically 1200-1300°C at the inlet to the catalyst bed to approx 1000°C at the exit of the catalyst bed. The catalyst bed operates adiabatically with only a small heat loss to the surroundings. The gas composition is ideally in total equilibrium when the catalyst has sufficient activity. But the gas distribution to the catalyst bed and especially the temperature and homogeneity of the inlet gas composition will affect the average product gas composition.

A layer of protecting tiles is often placed on top of the catalyst bed to protect it from the very intense turbulent flow in the combustion chamber. The radiation from the flame and the circulation velocities in the combustion chamber require that the tiles have a high thermal stability and can resist the thermal shocks during start-up and trips.

The requirements for the catalyst include;

- high thermal stability
- sufficient activity to reach equilibrium
- low pressure drop to avoid bypass of gas through the refractory

The preferred catalyst for autothermal reforming is a nickel based reforming catalyst. The catalyst is exposed to high operating temperatures and the nickel metal is subject to a high degree of sintering resulting in a low intrinsic catalyst activity.

It is also a requirement for the support for the nickel catalysts that it has a high thermal stability to achieve sufficient strength at the high operating temperatures. In ATR and secondary reformers carriers of both alumina (α-Al_2O_3) and magnesium alumina spinel ($MgAl_2O_4$) are used. Spinel has higher melting point and in general higher thermal strength and stability than the alumina based catalysts.

The shape of the catalyst pellet is an important design parameter for the catalyst bed. The pressure drop should be kept low in order to reduce the risk of bypass around the catalyst bed through the refractory. Bypass would have the consequence that flow through the refractory layers transports heat into the refractory layers, which could increase temperature on the pressure shell and result in an increased risk of local hot spots., see section 2.5.2.2. A shape optimised catalyst e.g. seven-axial holes with low pressure drop should be

selected [134]. In shape optimization, a pellet shape with high catalyst pellet activity can be selected. The optimal loading of the catalytic fixed bed may consist of several layers of different types of catalysts.

2.5.2.4 Catalyst deactivation in ATR operation

Generally an ATR catalyst is robust with a high thermal stability and not prone to deactivation. However, some deactivation may occur, mainly due to:

- sintering
- sulphur poisoning
- fouling by ruby deposition leading to ΔP increase

Sintering proceeds as in all steam reforming catalysts, see Section 2.3.5.2. However, the activity of the catalyst in ATR service is rapidly reduced due to the high operating temperatures, and after this initial sintering only minor further deactivation is expected due to sintering.

The main poison for the catalyst in ATR operation is sulphur. Sulphur is a well-known poison on the nickel based steam reforming catalyst, as described in Section 2.3.5.2. Sulphur originates from impurities in ppb levels in the feed streams that remains in the hydrocarbon feed stream after feed purification or in the process steam. The sulphur is adsorbed on the nickel surface as nickel sulphide and thereby deactivates the catalyst [28].

The adsorption is described by sulphur adsorption isotherm (cfr. eqs (2) and (3) in Section 2.3.5.2). The sulphur coverage at lower temperatures is close to 90-100%. However, only a partial coverage of the nickel surface is found at the elevated catalyst temperatures of the ATR. At 1000°C the sulphur coverage can be calculated to approx 30%, when the inlet gas to the catalyst bed contains a low sulphur concentration. Thus, desulphurization is normally not necessary for a stand alone ATR unit. In GTL plants sulphur is removed upstream of the ATR in order to protect the prereforming catalyst and this then also protects the downstream FT synthesis catalyst.

In high temperature ATR and secondary reformers, it is common to observe a deposition of white and pink crystals on the catalyst outer pellet surface. The crystals are mixtures of alumina and chromium-alumina spinel. The latter is also known as the ruby with a purple colour. Ruby formation is not a poisoning as such, but it reduces run time between shutdowns, because pressure drop over the catalyst increases and may increase the risk of formation of hot spots on the reactor wall. Ruby formation and deposition are well known to industry, but the knowledge about the mechanism of ruby formation is very empirical. A case history is described in Ref. [137] supported by some more theoretical viewpoints. The primary process leading to fouling seems to be

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transport of 'rubies' from the refractory and deposition in the catalytic bed. The 'ruby' formation is caused by case story describes the "ruby formation" as evaporation of aluminium species, probably AlOOH, from the high-alumina bricks in the refractory. When the gas is cooled in the catalytic bed because of the reforming reaction, AlOOH will condense and together with impurities of chromium and iron deposit as rubies. The chromium and the iron come from construction materials upstream of the combustion chamber and the ATR reactor. Often ruby deposition is seen in a narrow section in the upper part of the catalyst bed. In such cases, only 'skimming' of the layer with rubies may be sufficient to solve pressure drop problems.

2.5.3 Modelling

Modelling of an ATR reactor may be done in several steps with focus on the different reactions zones and different levels of details.
The modelling approaches described in the following sections include:

- Computational Fluid Dynamics (CFD)
- Chemical kinetic modeling
- Combined models (chemical kinetics and flow)
- Catalytic fixed-bed modeling.

The combustion in the ATR combustion chamber is a complex interaction of combustion chemistry and fluid dynamics. Complete modelling of this combustion process includes detailed modelling of the gas phase radical reactions, flow equations (e.g. Navier Stokes), radiation and turbulence models, all implemented into CFD. However, due to the complexity of such models and the fact that the turbulent flow and the chemical reactions have different time scales, the mathematical problems are so complex that even with supercomputer access, long computing times are required. Therefore, work has been carried out on de-coupled models, where the variations in the flow pattern are solved separately from the chemistry.

2.5.3.1 Computational fluid dynamics

Computational fluid dynamics (CFD) is a powerful tool in design and performance prediction of the ATR burner and combustion chamber. CFD is used to calculate the flow pattern of the ATR combustion chamber and of the flame [134, 138].

Computational Fluid Dynamics (CFD) software is a general purpose fluid flow simulation software which makes it possible to analyse turbulent and laminar flow problems in arbitrary complex geometries. Use of CFD simulation software is widespread today for design of advanced apparatus like diesel

engines, gas turbines and slurry bed reactors. All applications are characterized by interaction between complex flow fields and chemical reaction. Various software packages are available among which Fluent, CFX-5 from ANSYS CFX and STAR-CD from CD Adapco Group are the most common.

The first step in each CFD calculation is division of the reaction space into a three-dimensional grid. Each grid cell is a discrete computational cell in which the equations for fluid flow and chemical reaction are solved. A typical grid may contain from 10.000 to 100.000 cells. The next steps are selection of models for thermodynamic properties, chemical reaction kinetics, turbulence, and thermal radiation, as well as definition of boundary conditions.

The chemical models implemented into CFD are usually relative simple, often only a few chemical reactions in order to maintain reasonable calculation times and at the same time describe the chemical conversion in sufficient details. For combustion processes such chemical models is a compromise as the combustion proceeds through numerous radical reactions as described in Section 2.5.1.1. In some applications, the 'mixed-is-burnt' approximation is an acceptable approach in order to de-couple the fluid flow from the chemical reaction in the flame, as most of the combustion reactions are very fast. But in order to describe thermal expansion and slower reactions the use of more detailed chemical models is advantageous.

The choice of a turbulence model is essential, and in some cases the simple k-ε model is too simple an approach, so it is necessary to include a higher order turbulence model, like a Reynolds stress model [138, 139].

Besides the fluid flow pattern and temperature distribution in the combustion chamber, the CFD simulation also gives information about the temperature on the burner nozzle parts and on the refractory surfaces.

An example of a CFD simulation results for an ATR burner and combustion chamber is shown in Fig. 56. The simulation is made with CFX-4 [140] using a 2D model assuming rotational symmetry in the combustion chamber. The calculation shows that a flow pattern in the combustion chamber with a centrally positioned flame is obtained. A good re-circulation is obtained, which keeps the refractory cool, provides sufficient cooling of burner parts, and ensures a homogeneous composition and flow at the inlet to the catalytic bed [134].

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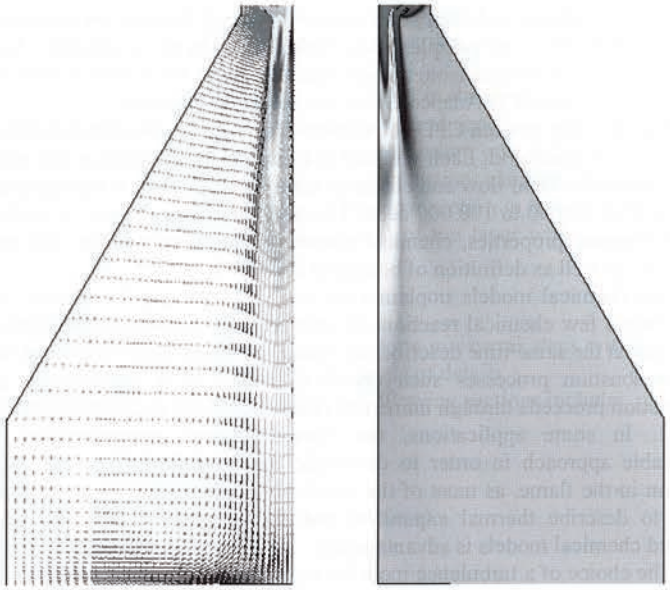


Figure 56 Example of CFD modelling results for the combustion chamber in an ATR reactor. The left part show velocity vectors and the right part show temperatures. [134]

2.5.3.2 Chemical kinetic modelling

Chemical kinetic modelling is based on a detailed kinetic gas phase model in a simplified reactor, either a plug flow reactor or a perfectly stirred reactor. It is solved using e.g. CHEMKIN II [141].

Reaction schemes with the combustion chemistry of methane and ethane are presently well described for ambient pressure and at stoichiometric conditions. Detailed kinetic models describing the chemistry based on elementary reactions are available in the literature and some can be downloaded from the Internet [121]. However, to adopt a model, it should carefully be considered what needs to be simulated and how the selected model can be verified for reaction conditions corresponding to those to be modelled. Since most of the present kinetic models have been developed based on ambient pressure conditions, adoption for high-pressure conditions, as is the case for an ATR reactor, should be done with caution.

Detailed chemical kinetic simulations with the CHEMKIN II software package [141] can be used for the simulation of the combustion chamber of the ATR reactor. Reaction path analyses [142] can be used to deduce reaction mechanisms and preferred reaction channels. Pathways in soot formation in methane oxidation at fuel-rich conditions were studied at atmospheric pressure [142], and a channel producing benzene was identified. The mechanism describes that benzene subsequently reacts to phenanthrene and pyrene, which could lead to inception of soot particles.

The chemistry and flow interaction in the combustion chamber of an ATR reactor introduce a lot of complexities regarding modelling. Detailed kinetic models have been developed to describe the combustion of hydrocarbons [120, 121]. However, most detailed kinetic models have focussed primarily on fuel lean combustion at ambient pressure. This is far from the conditions in the combustion chamber of an ATR reactor, where the pressure is much above atmospheric and the overall chemistry very fuel rich. Nevertheless, the detailed kinetic models have been adopted for this purpose and used to model the conversion in the combustion chamber with surprisingly good results [132] as further described below.

Ignition may be modelled using detailed kinetic models as well, but the combustion models described above are typically optimised for higher temperatures and may not provide reliable results for auto-ignition calculations. However, there are more appropriate models available e.g. from studies of spark engine knocking [143, 144], although these studies are made for air as oxidant. Modelling of the ignition has the purpose to predict the necessary temperature at start-up for the feeds to auto-ignite. Normally, the start-up conditions are characterized by lower temperature and possibly also lower pressure than normal operation, and they are therefore more critical with respect to flame ignition and stability.

2.5.3.3 Combined modelling of flow and chemistry

The complex interaction between fluid flow and chemistry in the turbulent diffusion flame of the ATR combustion chamber makes it difficult to apply the simplified models in both the detailed chemical kinetic simulations (detailed chemistry, simple reactor geometry) and the CFD simulation (complex reactor geometry, detailed fluid flow and simplified chemistry). Two solutions have been suggested. A reactor network consisting of plug-flow reactors and perfectly stirred reactors has been developed [132] as a means of including more detailed information about fluid flow into the detailed chemical kinetic simulations. The model has been further developed into CFD post processing tool [128, 148], in which detailed chemistry for the combustion reactions and for the PAH and soot chemistry is calculated in all cells of the CFD-grid.

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A reactor flow network model consisting of a combination of plug flow reactors and perfectly stirred reactors was defined [145] using information from the CFD simulation about flow pattern and residence time in the ATR reactor at given conditions. Such a model has been tested with two different detailed kinetic models and compared with experimental measurements of the gas composition in the combustion chamber at the ATR process demonstration unit. The GRI-Mechanism, Version 2.11 (279 reactions with 49 species) [146], has been compared with a mechanism developed by Miller and co-workers (301 reactions with 65 species) [147]. Both consist of reactions including H, C, O, N and Ar species up to C_2 hydrocarbons, but in the mechanism by Miller and co-workers, the selected reactions and species leading to formation of benzene have also been included. Each kinetic model is used together with the reactor model to describe the chemistry in the combustion chamber and to predict the composition of the gas entering the catalyst bed. The calculations have been performed with the CHEMKIN-II software packages [141]. The results of the experimental measurements and modelling taken from [132] are listed in Table 7.

Table 7
Comparison between experimental measured concentrations and chemical kinetic modelling results for an ATR combustion chamber [132]

	H_2	H_2O	CO	CO_2	CH_4	C_2H_6	C_2H_4	C_2H_2	N_2
Experimental	48.8	16.0	24.9	3.51	6.46	0.0151	0.0672	0.0168	0.190
Calculated:									
GRI-MECH Ver. 2.11	48.7	16.1	24.9	3.46	6.62	0.0025	0.0137	0.0020	0.190
Miller and co-workers	48.7	16.1	24.9	3.47	6.61	0.0027	0.0148	0.0025	0.190

This type of modelling can provide detailed information about the chemistry occurring in the combustion chamber, but it is at the expense of loss of information about the complicated flow pattern and the influence of turbulence on the chemistry especially in the flame.

In order to keep the detailed kinetic models and get further details of the flow in the combustion chamber, a chemical kinetic post-processor for CFD calculations has been suggested [128, 148]. In this case the grid structure used to solve the CFD modelling is adapted as a reactor network consisting of perfectly or partially stirred reactors. The turbulence intensity may be included in the post processor and the reaction rates can therefore be determined either by turbulence or by the finite reaction rates calculated by the detailed kinetic model. This will especially improve the modelling of the turbulent diffusion flame, where turbulent mixing is controlling the reaction between hydrocarbon feed and oxidant.

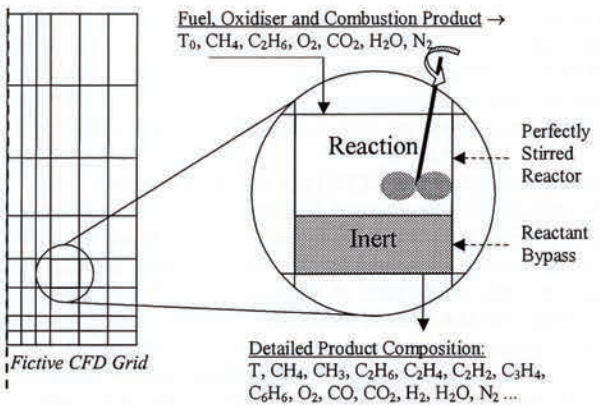


Figure 57 Schematic illustration of the partially stirred reactor approach used to model individual cells in the detailed chemical kinetic post-processing of the post-processing procedure taken from [148].

2.5.3.4 Fixed bed simulation of the catalytic bed

Modelling of the catalyst bed of the ATR reactor is in itself a challenge. Simulation of the catalyst bed includes radial distribution of gas and temperature, gas diffusion in the gas film and catalyst pore system, heterogeneous catalytic reactions, and pressure drop. The catalyst bed is simulated by fixed bed reactor models using input from the CFD simulation with respect to the gas and temperature distribution profiles into the fixed bed. Although the pressure drop is the simplest part, it may nevertheless be the most important, since a catalyst with too high pressure drop will result in gas bypass through the refractory leading to hot-spots on the pressure shell.

Fixed-bed reactor models are divided into two groups: pseudo-homogeneous and heterogeneous models [149]. The catalyst in an ATR is exposed to very high temperatures and thus a high degree of sintering. The catalyst performance is controlled by a combination of both film diffusion and pore diffusion, and relatively successful simulations were achieved with both a heterogeneous model [150] and with a pseudo-homogeneous model [151]. A key parameter in determining the necessary catalyst volume is the gas distribution at the entrance to the catalyst layer. In air blown secondary reformers, it is well-known that burners of poor design and damaged burners may cause an increased average methane leakage from the catalyst bed. This is a result of inefficient mixing in the combustion chamber leading to uneven flow and temperature distribution at the entrance to the catalyst bed [134]. Even with an optimal burner design, some gradients in temperature and concentrations are

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observed along the radius of the reactor as a result of the mixing efficiency. Variations in the O/C and H/C atomic ratios along the inlet to the catalyst bed will result in different adiabatic equilibrium states at the exit of the catalyst bed, which may be seen as an increased overall approach to equilibrium which is caused more by mixing and gas distribution than by catalyst activity.

2.5.4 Autothermal reforming (ATR) in GTL applications

In the mid-1990s, Autothermal Reforming (ATR) was identified as being an attractive process for conversion of natural gas to liquid fuels (GTL) [152]. ATR has been selected as synthesis gas technology for a number of large-scale GTL plants for the production of synthetic fuels by Fischer-Tropsch (FT) synthesis (30-35,000 bbl/d liquid products) [153, 154]. The preferred lay-out of the syngas production section is a combination of adiabatic prereforming and ATR, see fig. 50. The lay-out results in large flexibility for variations in natural gas and in FT recycle-gas composition as well as reduced oxygen consumption per unit synthesis gas produced. Operation at low steam-to-carbon ratio (H_2O/C) is one of the key parameters to achieve good economic performance for GTL applications.

The H_2O/C ratio of the autothermal reforming process was previously in the high range 1.5 – 2.5 [118]. ATR operating at low H_2O/C ratios was developed by Haldor Topsøe through the 1990's [92, 118, 132, 155]. The breakthrough for the use of ATR technology for application in Fischer-Tropsch process flow schemes has been enabled by soot-free operation at low H_2O/C ratios, of 0.6 and below, and by the development of new burners ensuring safe operation and high on-stream factors [134]. Application of ATR technology in mega-size plants involves aspects such as scale-up of equipment design, maximum size of equipment and capacity for single-line plants. In GTL applications, a synthesis gas with H_2/CO ratio $\cong 2.0$ is often needed. ATR can produce this gas by recycling a gas rich in carbon oxides from the FT synthesis unit for H_2/CO adjustment. The recycle gas with FT applications is rarely pure CO_2 but rather contains CO and small amounts of hydrocarbons of various types, e.g. paraffins and olefins.

Operation at low H_2O/C ratios challenges the limitations of the technology; soot formation must be avoided, and the process burner must have a sufficient lifetime without excessive burner wear and degradation at the high operating temperatures.

2.5.4.1 Industrial operation at low H_2O/C ratio

ATR operation at low H_2O/C around 0.6 has become the state-of-the-art synthesis gas technology for Fischer-Tropsch applications. An industrial unit based on ATR technology for production of CO-rich synthesis gas has been in operation in Europe at H_2O/C=0.6 since 2002. Two units with a combined production of synthesis gas of 430.000 Nm^3/hr (H_2+CO) will start at Sasolburg, South Africa, in 2004. The synthesis gas will be used for production of chemicals and waxes by FT synthesis (see Chapter 5, section 3.1). Large dedicated GTL plants will start up in 2005 in Qatar and in Nigeria in 2007 (107). These plants will both feature 2 synthesis gas units based on ATR at S/C=0.6 with a combined production of about 1.5 million Nm^3/hr synthesis gas.

The first operation at industrial scale was a demonstration test in an ATR unit operating with approx. 20,000 Nm3/hr hydrocarbon feed gas [119]. This unit is one of 16 autothermal reformers owned and operated by Sasol at their site in Secunda, South Africa. These reforming units were originally revamped in 1997 to use burner technology from Haldor Topsøe [156]. One of the units was modified specifically for the demonstration run at H_2O/C ratio of 0.6 in stead of the normal high ratio of 1.5 - 2.0. During the demonstration run which lasted 5 weeks, satisfactory and stable operation at the low H_2O/C ratio was demonstrated without soot formation. The demonstration test pushed the limits for application of the ATR technology.

2.5.4.2 Development and demonstration at PDU-scale

The ATR process for operation at low H_2O/C ratios was developed through the 1990's. Operating parameters were studied in a process demonstration unit (PDU) [118, 155] built at the pilot plant facilities of Haldor Topsoe, Inc., Houston, Texas in 1990 (Fig,. 58). The process demonstration unit was built using the same design principles as industrial units. The layout of the PDU-unit is shown schematically in Fig. 59.

The ATR plant is operated with natural gas feed at a capacity corresponding to typically 100 - 150 Nm^3/hr and produces synthesis gas (CO + H_2) in the range from 250 to 450 Nm^3/hr. The feed streams consist of natural gas, steam, pure oxygen (O_2 > 99.5%), hydrogen and, optionally, carbon dioxide and liquid hydrocarbons. At normal operating conditions, no soot formation is taking place, but when testing operating conditions close to and beyond the limit for onset of soot formation, minor amounts of soot can be formed and captured in the condensate. The condensate is investigated through both gravimetric and spectrophotometric methods.

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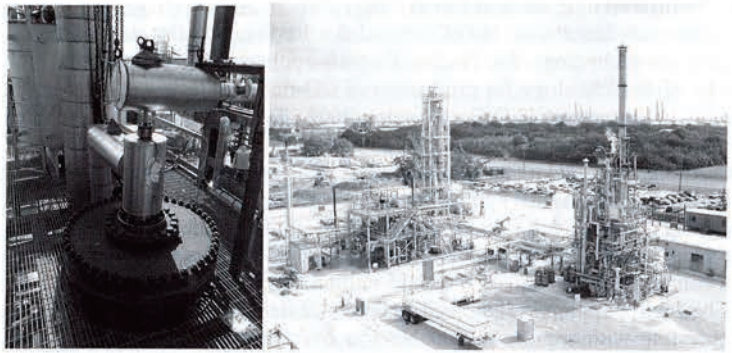


Figure 58 ATR Process Demonstration Unit, Houston, Texas [132]

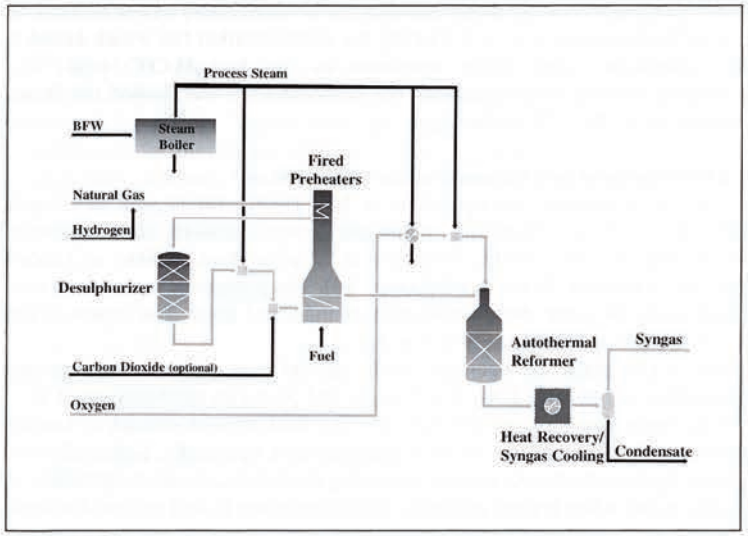


Figure 59 Process layout of ATR Process Demonstration Unit

Soot-free operation and satisfactory burner performance was demonstrated at a H_2O/C ratio of 0.6 in the early 1990's [118]. Similar results at H_2O/C ratios down to 0.2 were obtained in later demonstrations [155], see Section 2.5.4.3.

2.5.4.3 ATR process performance tests related to GTL applications

Numerous tests with varying operating parameters were performed in the ATR PDU in order to establish safe design background at the very low H_2O/C ratio of 0.6 and below. This included the influence of variations in H_2O/C ratio, temperatures, and pressure as well as the effect of feed composition such as content of higher hydrocarbons, CO_2, and H_2 on the limits for soot-free operation.

Limits for soot formation were studied intensively in a pilot-scale the ATR PDU reactor representing real-environment operation. Various operating conditions were tested, and the limits for onset of formation of soot particles in the exit condensate were identified. Tests included prereformed natural gas, variations in feed gas composition with different levels of C_{2+} in natural gas, and variations in recycle gas composition, e.g. CO_2 and hydrocarbons. Tests with prereformed natural gas showed a larger margin to the onset of soot formation than with a natural gas containing higher hydrocarbons at similar operating conditions. Even though the prereformed natural gas implies an improvement with regards to the risk of soot formation in the ATR, it is still prone to form soot at certain operating conditions, which made it necessary to establish the limits and extend the models to include a wider range of feedstocks [157].

Explorative tests as well as tests of longer duration with steam-to-carbon ratios in the range of 0.2-0.6 are described in Ref. [155]. The tests were made with the purpose of reducing the H_2O/C ratio as much as possible without reaching the range of soot formation. Results from various pilot programs are shown in Fig. 60 [118, 155] and Table 8.

All data represent operating conditions without soot formation, but they do not represent the limits of the technology. The ATR can produce synthesis gas within a wide range of H_2/CO-ratio, when the H_2O/C ratio, CO_2-recycle and exit temperatures are optimized.

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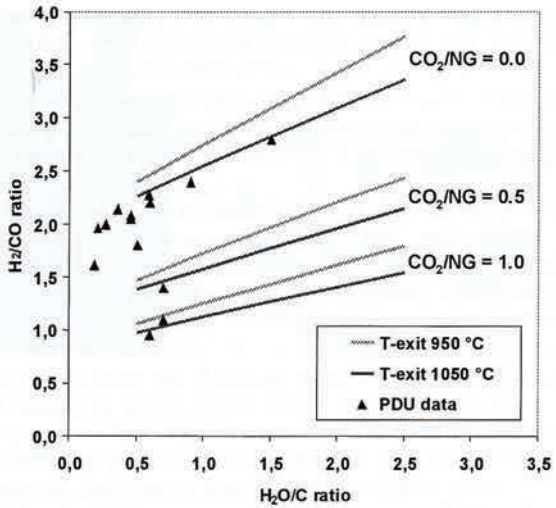


Figure 60 Syngas equilibrium; experimental data from soot-free ATR-operation [155]

Table 8 ATR PDU Runs [118, 155].
ATR pilot plant demonstration runs

TEST		A	B	C	D	E
Feed Ratios[1]	*(mole/mole)*					
H_2O/C		0,59	0,21	0.51	0.60	0.36
CO_2/C		0,01	0,01	0.19	0.01	0.01
O_2/C [2]		0,62	0,59	0.62	0.58	0.57
Product Gas						
Temperature	(°C)	1065	1065	1025	1020	1022
Pressure	(bar)	24,5	24,5	27.5	28.5	28.5
H_2/CO	(mole/mole)	2,24	1,96	1.80	2.30	2.15
CO/CO_2	(mole/mole)	5,05	9,93	4.44	4.54	6.78
CH_4-leakage	(dry mole %)	0,48	1,15	0.92	1.22	1.66

Notes:
1) Mole per mole of hydrocarbon C-atoms
2) The O_2/C-ratio is approximately 5% higher than truly adiabatic reactors with same exit temperature.

2.6 Other technologies

Most or all of the technologies described in the previous section are in commercial use today for production of synthesis gas. However, substantial efforts to develop new technologies are undertaken due to the fact that the most capital intensive part of a GTL plant is the Syngas Generation Unit (SGU). The

focus of many of these developments is to reduce or eliminate the use of oxygen and/or reduce the size of the primary reactor in the SGU. In the following text the production of synthesis gas by Catalytic Partial Oxidation (CPO) and Oxygen Membrane Reforming (OMR) will be briefly described.

2.6.1 Catalytic Partial Oxidation

The principle of CPO is illustrated in Fig. 61. The hydrocarbon feed and the oxidant are mixed in an inlet zone upstream the catalyst bed. In the catalytic section, the mixture reacts by heterogeneous reactions (partial and total combustion along with the methane steam reforming and shift reactions). The catalyst is normally based on noble metals and the space velocity is in many cases very high. Catalysts in the form of pellets, monoliths, and foams have been used to perform the reaction.

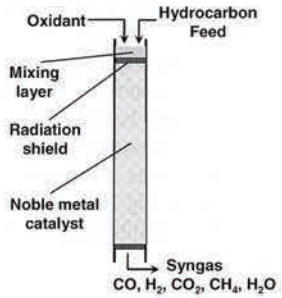


Figure 61 CPO Principle

The methane steam reforming and shift reactions are typically at or close to equilibrium at the reactor exit. It has been claimed [158] that methane reacts by partial oxidation according to reaction (1) below and that methane conversions above those corresponding to thermodynamic equilibrium of the methane steam reforming reaction can be obtained.

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad (1)$$

However, in practice the products of reaction (1) will further oxidise and fundamental studies have shown that partial oxidation is only kinetically favoured at temperatures above 900°C [159]. Gas compositions indicating higher conversions than thermodynamic equilibrium most likely reflect the temperature of the catalyst [160].

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CPO differs from ATR especially by the fact that no burner is used. Instead all the chemical reactions take place in the catalytic zone. Total combustion takes place to some extent in the first part of the catalyst layers making the catalyst very hot in this region. Laboratory measurements have indicated that this temperature may be higher than 1100°C [161]. In order to avoid overheating of the gas upstream of the catalyst a thermal shield is often employed as indicated in Fig. 1. It should be noted that the gas temperature remains comparatively low as compared to the catalyst surface temperature in the inlet zone [161].

CPO has been investigated extensively for many years. Before 1992 most studies were carried out at moderate or low space velocities at a residence time of 1s or above [161]. However, during the later years CPO has been carried out at least in the laboratory at very short contact times between 0.1 and 10 ms in some cases without preheating the feedstock and with no steam addition. Additional information regarding research, mainly of a fundamental nature, can be found for example in a series of papers by L.D. Schmidt and co-workers [159, 162-166].

Both air and oxygen may in principle be used as oxidant in a CPO reactor. An example of the use of oxygen in a CPO reactor in the laboratory is given in Fig. 62, illustrating that stable conversion may be obtained at elevated pressure. Experiments with CPO and air as oxidant have been conducted at the Topsøe pilot plant in Houston, Texas. Selected results at various pressures with and without steam in the feed are presented in Fig. 63. In all cases, the methane conversion corresponds closely to the equilibrium of the methane steam reforming reaction.

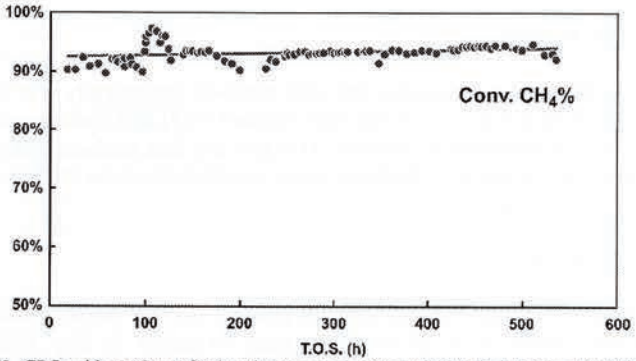


Figure 62 CPO with methane feed and oxygen as oxidant [161]. P=1.5 Mpa. H_2O/CH_4=0.26; CO_2/CH_4=0.11;O_2/CH_4=0.56

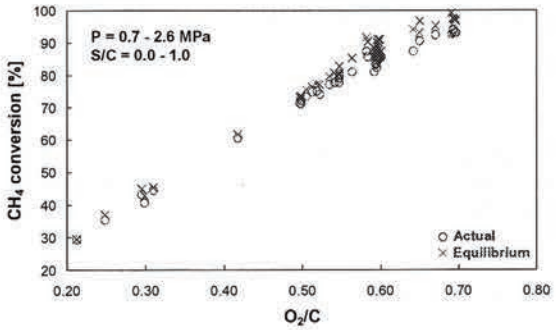


Figure 63 Methane conversion in CPO pilot plant experiments with air as oxidant [167]

Table 9
Auto-ignition temperatures for natural gas in air [168]

Pressure (bar)	Auto-ignition Temp., (°C)
1	465
4	313
20	267
40	259

Table 10
Relative oxygen and natural gas consumption for CPO- and ATR-based GTL front-ends for production of hydrogen and carbon monoxide [26]

Reactor	S/C ratio	Hydrocarbon feed temperature, reactor inlet (°C)	Oxygen consumption (relative)	Natural gas consumption (relative)
ATR	0.6	650	100	100
CPO	0.6	200	121	109
ATR	0.3	650	97	102
CPO	0.3	200	114	109

An adiabatic pre-reformer is located upstream the ATR. CO_2 is introduced before the partial oxidation reactor at 200 °C in an amount to give H_2/CO=2.00.
Pressure: 25 bar abs. Oxygen temperature: 200 °C. Exit temperature: 1050 °C.

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The presence of a flammable mixture in the inlet zone upstream the catalyst may in some cases make use of CPO at high inlet temperatures difficult especially at elevated pressures. In Table 9 the auto-ignition temperature is given for natural gas in air as a function of pressure. The auto-ignition temperatures are lower with oxygen as oxidant. For safety reasons, the inlet feed temperatures of the hydrocarbon feedstock and oxidant must be kept low. This increases the oxygen consumption as shown in Table 10. Higher oxygen consumption increases the ASU investment and the level of inerts in the synthesis gas.

2.6.2 Oxygen Membrane Reforming

The principle of Oxygen Membrane Reforming (OMR) is indicated in Fig. 64.

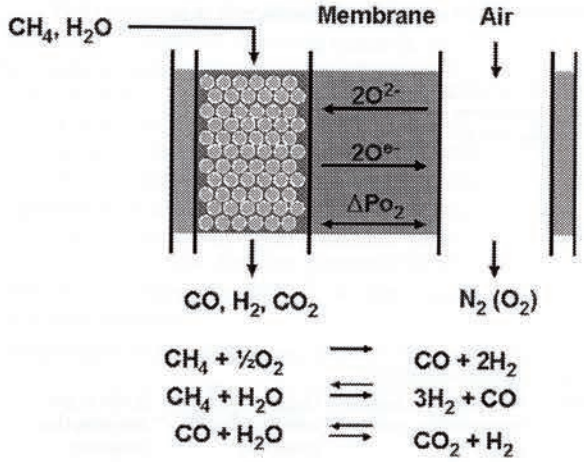


Figure 64 Principle of oxygen membrane reforming

Very significant efforts are undertaken to develop OMR, see e.g. [169] for a recent overview. Air is introduced at one side of a membrane through which oxygen in the form of ions is transported selectively to the other side of the ceramic membrane. At the other side of the membrane the oxygen reacts with the hydrocarbon feedstock to produce synthesis gas. The concept simultaneously avoids the capital cost of the Air Separation Unit and a high content of inert nitrogen in the synthesis gas. The catalyst on the synthesis side of the membrane may be in the form of pellets or directly attached to the membrane itself.

The membrane itself is made out of a ceramic material often in the form of a perovskite or a brownmillerite. The driving force across the membrane is proportional to the logarithm of the ratio of the partial pressures of oxygen on the two sides. Hence, in principle air may be introduced at ambient pressure to supply oxygen to the other side at elevated pressure because the oxygen partial pressure on the process side is extremely low. The temperature should probably be above 750-800°C for sufficient oxygen flux.

The membrane material must enable a high flux probably in the range of more than 10 Nm^3 O_2/m^2 hr. The membrane should also withstand reducing gas on one side and air on the other. Various types of composite membranes have been proposed and research is also undertaken to place a thin membrane on a stronger porous support.

A key challenge in the development of OMR is the absolute pressure difference across the membrane. It may render the process non-economical if air must be compressed to ensure similar pressures on the two sides of the membrane. It sets great demands on the mechanical integrity of the membrane if ambient pressure air is used. In any case the process may be best suited for small or medium scale applications as the scaling factor of the membrane unit will be close to unity.

3. SYNTHESIS GAS PREPARATION VIA GASIFICATION

3.1 Introduction

Gasification involves the reaction of a source of carbon, possibly associated with hydrogen, with a source of hydrogen (usually steam) and/or oxygen to yield a gas containing hydrogen, carbon monoxide, carbon dioxide and methane. Proportions of these component gases depend on the ratio of the reactants used and on the reaction conditions [170]. It is a versatile process which can be used to convert a variety of solid or liquid carbonaceous feedstocks into synthesis gas (syngas).

Once the feedstock has been converted to a gaseous state, undesirable substances such as sulphur compounds and entrained solid particles may be removed from the gas by a range of techniques.

Coal gasification yields a wide variety of useful products for residential, utility and industrial markets [171]. Clean syngas, essentially a mixture of carbon monoxide (CO) and hydrogen (H_2), can be converted into gaseous fuels, liquid fuels, chemicals, electric power or a combination of these products.

The first companies to convert coal to combustible gas through pyrolysis were chartered in 1912, while the first true gasifier, a Lurgi moving bed gasifier, was in operation by 1887. During the 1930's, the first commercial coal gasification plants were constructed, followed by town gas applications in the

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1940's. In the 1950's, chemical process industries started applying gasification for hydrogen production. Sasol is now by far the largest single user of gasification technology. Sasol's first coal gasification plant was commissioned in 1954. Studies to generate electric power in a more efficient manner in an Integrated Gasification Combined Cycle (IGCC) followed in the 1970's, and are still being actively pursued. At present, there is about 11 GW of gasification capacity in operation around the world in the chemicals industry or synthetic transport fuels production [170] and a little over 40 GW total syngas production capacity [1]. Gasification can be said to be a commercially proven, mature technology, and furthermore, proven in combination with various downstream technologies [170].

Users of gasification technologies are seldom willing to experiment with new equipment, preferring proven technology [172], since gasification often forms a vital link in extensive flow schemes and involves rather extreme reaction conditions. Selecting proven gasification technology minimises the risk associated with the high capital investment cost for new installations. Therefore most of the current research, development and demonstration efforts are aimed towards technical and economic improvements for established technologies [171]. Improvements in efficiency, reliability and capital and operating cost of gasification are all means to the same end – cheap and 'clean' coal conversion processes.

There is a growing realisation that the world will be dependent on fossil fuels for the foreseeable future to meet ever-increasing energy requirements. Dwindling supplies and rising prices of other fossil fuels like oil and gas are increasing the attractiveness of the vast remaining coal reserves. A higher energy demand in several countries has resulted in a re-focus on indigenous coal resources and available technologies for the conversion of coal into useful products [173]. At the same time increasing environmental pressure is challenging increased coal utilisation. As gasification is the cleanest coal technology available, there is a strong drive for its further growth.

3.2 Possible applications for gasification processes

There are many possible uses for coal. Gasification is a prominent coal conversion technology, yielding the most diverse group of products (see Fig. 1). Besides coal, a wide variety of other, usually low value, carbonaceous feedstocks can be gasified to produce fuels and chemicals. These feedstocks include renewable energy sources e.g. biomass, wastes e.g. paper pulp and municipal solid wastes (MSW) and refinery by-products e.g. petcoke and vacuum residues.

Synthesis gas production through gasification was growing at a rate of about 10% per annum in 1983 [174]. From about 1985 to 1995 there was a

period of constant capacity before the growth in capacity resumed [171]. In the USA, the September 11-events in 2001 and the more recent political conflict with Iraq brought about a renewed urgency concerning energy security and independence. In this regard, the utilisation of the abundant coal resources in places such as China, India, South Africa, Australia and the USA through clean technologies gives new impetus to the interest in gasification technology. Many of the coal-fired power stations in the USA and elsewhere are over thirty years old and operating with typical efficiencies of 30-35%. Replacement with cleaner and more efficient gasification based power generation at efficiencies of about 46% would extremely beneficial to the environment.

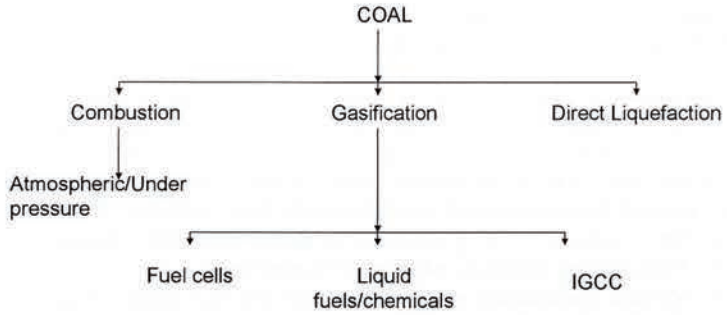


Figure 65 Different options for coal conversion and power generation. [175]

After gas cooling and purification, pure synthesis gas is then ready for conversion into the numerous possible end products. The product range depends on the hydrogen to carbon ratio of the clean synthesis gas. Products include, among others, methanol, acetic acid, oxo-chemicals, liquid fuels and chemicals via the Fischer-Tropsch process and electric power [176]. The synthesis gas can also be converted into synthetic natural gas (SNG) for use in town gas and heating fuel applications.

3.3 Integrated Gasification Combined Cycle (IGCC)

The combustion of coal to generate power is the historical backbone of the electric utility industry. This is due to the availability, low price and security of supply of coal compared to other fuels, and the relative simplicity of the combustion process. Tightening environmental requirements result in substantial increases in both capital and operating cost for conventional coal-fired combustion plants, while adversely affecting plant efficiency and reliability. A

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combination of gasification with a combined cycle is the only coal-based technology that can approach the environmental performance of natural gas-fired systems [177].

The IGCC plant design essentially involves two stages of combustion with gas cleaning between the two stages [178]. A number of variations of IGCC plant designs exist, primarily due to differences in the selected gasifier technology [179] and subsequent raw gas cleaning methods. Integration of gasification and combined cycle facilities is achieved mainly through the plant steam system. IGCC technology has been proven for a variety of fuels, particularly heavy oils, heavy oil residues, petcokes, and bituminous coals [180].

The first stage of the IGCC system employs gasifiers where partial oxidation of a solid or liquid fuel occurs to produce a combustible gas. The produced gas is then cleaned to remove particulates, sulphur compounds and other undesirables, before being fed to a gas turbine combustor to complete the combustion. The combustion turbine is normally followed by a turbine driven by steam generated from the hot tail gas of the combustion turbine [181].

IGCC systems can achieve high thermal efficiencies, which correspond to lower CO_2 production. Low emissions of acid rain precursors (NO_x and SO_x) are achieved [181]. The IGCC process offers several additional advantages over conventional coal-based power generation technology, including [182]:

- Decreased coal consumption due to increased generating efficiency
- Reduced land area and cooling water requirements
- Modular construction which allows economic increments of capacity to match load growth
- Potential for design standardisation due to modular construction, which should reduce required engineering effort, construction time and delays due to permitting complications for future plants
- Greater fuel flexibility.

It is generally accepted that IGCC is clean and efficient. Regrettably, it is also expensive and not entirely commercially proven. There are, however, clear factors favouring the selection of IGCC for future applications [177]:

- An absence of cheap natural gas, and not enough proven (local) gas reserves
- Tight emission limits
- Higher coal prices, demanding high efficiency
- The opportunity for co-gasification of wastes and biomass.

High capital and operating costs remain the greatest challenge to IGCC implementation. Even though IGCC is at least 10 to 12% more efficient than a

conventional coal-fired power plant [182], the capital cost may be about 20% more than for a pulverised coal combustion (PCC) boiler plant [183]. At present, operational costs are considerably more for IGCC than for PCC boiler plants, with operating costs for IGCC estimated at $ 7.00 - $ 9.00/MWh compared to $ 3.00 - $ 5.00/MWh for a conventional PCC plant. Other hindering factors, which have to be addressed, can be summarised as follows [184]:

- Concerns regarding long-term reliability and operability
- Uncertain long term operating and maintenance costs
- Few deeply capitalized and credit worthy technology suppliers
- Few qualified and experienced operators
- Uncertainties regarding competitive economics
- Money lenders are strongly disposed to highly demonstrated technologies
- Environmental and utility regulators are more comfortable with demonstrated technologies
- Poor availability [177]
- Poor operational flexibility [177].

Apart from the barriers listed above, another major reason why IGCC has yet to impact significantly on the power generation landscape is that most of the recent coal-fired capacity development occurred in countries such as India and China, where there is a particularly strong emphasis on reliability and cost, both still challenges to IGCC [177]. However, with the developed world once again moving towards coal utilisation, IGCC technology has now reached the commercialisation stage in the USA and EU with a number of plants already in operation [185]. Coal-based IGCC plants that are or were in operation up to the year 2000 are listed in Table 1.

Although IGCC technology was originally conceived as a clean method of using coal for electricity production, it has been proposed as a solution to the growing problem of surplus heavy fuel oil. For example, the ISAB (Industria Siciliana Asfalti e Bitumi) complex in Sicily, which started up in 1998, is one of the largest IGCC installations in the world, and produces hydrogen and electric power through gasification of high-sulphur heavy liquid residues from an adjacent refinery [186]. The complex, which uses Texaco gasifiers, can produce 540 MW.

Serious operational problems have been encountered at various IGCC installations. One of the most crucial problems is that gas turbines are not always able to meet the demands set by the IGCC plant. A number of failures have been reported in hot gas cleanup systems, e.g. breakage of ceramic candle filters and stress corrosion cracking in heat exchangers [181]. Availability has proven to be a major challenge, but is improving with greater operating experience. For example, Shell reported an availability of 86%, including 4%

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planned outages, at the Pernis refinery in the Netherlands in 2001 [172]; an installation that was retrofitted for IGCC, commissioned in 1997 and runs on heavy residues.

Table 1
Commercial IGCC plants across the world [181, 187]

PROJECT	CAPACITY	OPERATION	REMARKS
Coolwater Plant, Barstow,California, USA	125 MW	Operated 1984-88	Texaco Gasifier (1000TPD)
Plaquemine Plant, Louisiana,USA	160 MW	In operation since April,1987	Dow (Destec) Gasifier (2200TPD)
Demkolec Buggenum Plant, Netherlands	253 MW	Started operation in 1993.	Shell Gasifier – Initial problems encountered in Gas Clean-up System. Now operating with good availability.
PSI Energy, Wabash River Plant, USA	262 MW	Commissioned November,1995	Destec Gasifier
Tampa Electric Polk Power Plant, USA	260 MW	Commissioned Sep. 1996	Texaco Gasifier
Sierra Pacific Pinon Pine Plant, USA	100 MW	Commissioned 1998	KRW Gasifier
ELCOGAS, Puertollano, Spain	335 MW	Commissioned 1998	Prenflow, Krupp Uhde gasifier commissioned in 1998
Schwarze Pumpe, Germany	40 MW	Commissioned September,1996	Noell KRC, 7 fixed bed gasifiers. Power/methanol production.

A key development area is the integration of emission control systems for simplification and cost reduction. The concept of integrated environmental control has several dimensions [179]: (1) interactions between control methods for air, water and solid waste emissions, so that a reduction in one type of discharge does not unduly increase others, (2) the integrated use of pre-combustion, combustion and post-combustion emission control methods, and (3) the development of new processes for combined pollutant removal in lieu of separate processes for individual pollutants.

Texaco was once the world leader in IGCC gasification technology but ChevronTexaco sold this business recently (2004) to General Electric (GE). GE is the leading supplier of gas turbines to the power industry. Several installations use Texaco gasification technology for IGCC, but only one plant uses coal as feedstock, the Tampa Electric plant in the USA, which co-feeds coal and petroleum coke.

Although the integration of systems complicates plant operation and control, IGCC technology has matured to the point where it is cleaner and more energy efficient than conventional combustion/steam station power generation plants. Further efficiency improvements are envisaged with more research and better integration. Studies are in progress to investigate the combination of IGCC technology with Fischer-Tropsch synthesis for the combined production of liquid hydrocarbons and electricity (see Chapter 5).

3.4 Characteristics of coal important for gasification

Coal is a polymeric substance with no repeating monomers [171]. It can be defined as a macromolecular gel and the concepts and techniques of polymer science may be applied in the study of coal. The main constituents of coal are hydrocarbon chains, mineral matter and moisture, while other components, e.g. halogens, are present in small concentrations.

The composition and structure of coal influences the applications that a specific coal is suitable for. Coals are classified by rank, i.e. according to the degree of metamorphism in the series from lignite to anthracite [171]. Time and pressure gradually transform the initial biomass from lignite to sub-bituminous coal to bituminous coal and then to anthracite. For gasification, coal of three ranks are used; sub-bituminous, bituminous and lignite [188]. Lignite is also called brown coal, particularly in Europe and Australia. Also important for gasification are the coal caking properties, water content and the ash properties.

Chemical and physical properties of coal show a large variation from source to source. Because these properties relate directly to gasifier behaviour, detailed analyses of coal are essential to predict gasification performance when a specific coal source or mixtures of coal sources are to be gasified.

Some of the tests that are usually conducted on coal sources to determine suitability for gasification purposes include the following:

- Proximate and ultimate analysis
- CO_2 gasification reactivity
- Particle size distribution
- Thermal fragmentation
- Caking properties
- Ash melting properties and ash viscosity
- Ash composition

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Other analyses that may also be relevant include mechanical fragmentation, Fischer Assay to determine tar production, total sulphur content, determination of the heating value of the coal, maceral composition and rank. The importance of the different analyses depends on the specific gasifier technology. For example, a Fischer Assay is more important in a fixed bed gasifier where tars and oils are produced as by-products, while ash viscosity is important in a slagging gasifier since ash will be extracted in a liquid state.

ASTM or ISO standards exist for most of the typical analyses done to classify a specific feedstock. Additionally, gasification technology suppliers generally have a suite of in-house developed feedstock characterisation techniques to ensure the compatibility of a particular feedstock with their gasifiers. Most of that information, however, is not available in the open literature.

The starting point for an understanding of the composition of the coal is the proximate and ultimate analysis. The proximate analysis determines the moisture, volatile matter, fixed carbon and ash in the coal. The methods for performing these analyses have been standardized by all the major standards institutions (e.g. ASTM, ISO, DIN, BS, and others). The standards differ in some details so it is important to specify the method used.

For the ultimate analysis the percentage of carbon, hydrogen, oxygen, sulphur and nitrogen are determined for the hydrocarbonaceous part of the coal (i.e. excluding non-volatile the mineral matter and water). Higman and van der Burgt [1] may be consulted for guidance on the significance of the various standard coal analyses.

3.5 Gasification chemistry

Gasification is the conversion of coal or other solid or liquid carbonaceous feedstock (hereafter, only coal will be mentioned for simplification) to a combustible gas via pyrolysis and heterogeneous reactions [183]. The conversion is usually accomplished by partial combustion of coal in an air/steam or oxygen/steam mixture [189].

Upon entering the gasification vessel, coal undergoes several transitions as it moves through different temperature zones in the moving bed gasifier:

- Drying, to evaporate moisture
- Devolatilisation, or pyrolysis, producing gas, vaporised tars and oils and solid char residue
- Gasification, or partial oxidation of the solid char and pyrolysis tars and gases
- Combustion

The mineral matter remaining from coal then exits the gasifier as ash.

For the moving bed type gasifiers, the different stages listed above occur in distinct zones. For other types of gasifiers no separate zones can be identified e.g. entrained flow gasifiers which operate at constant high temperatures and fluidized bed gasifiers which are well-mixed.

Upon initial exposure to heat in the gasifier, coal loses its surface moisture. Since the drying process consumes energy, the feed moisture content has an influence on the thermal efficiency of the gasification process.

Pyrolysis can be defined as the "decomposition of organic substances by heat" [190]. These decomposition reactions commence at 350 to 400°C, depending on the coal properties, most specifically the rank of the coal [191]. Pyrolysis is a complex process, involving cracking, hydrogenation and free radical reaction mechanisms. As a host of feedstock and process parameters have an influence on the pyrolysis reactions, it is problematic to predict the eventual yield and composition of the pyrolysis products and difficult to fully understand all the process steps.

Pyrolysis products are destroyed in most types of gasifiers, but not in the Sasol-Lurgi fixed bed dry bottom gasifier, where tars, pitches and phenols are valuable co-products from gasification. It is widely recognised that the initial pyrolysis step in coal conversion processes has a noteworthy effect on the yield and distribution of end products and emissions.

A few examples of pyrolysis reactions follow [192]:

$$Ar\,CH_2CH_2CH_2Ar \rightarrow ArCH_2CH_2\bullet + \bullet CH_2Ar \quad (1)$$

$$ArCH_2CH_2\bullet + \bullet Ar \rightarrow \begin{cases} ArCH_2CH_3 + HAr \\ ArAr + CH_2{=}CH_2 \end{cases} \quad (2)$$

$$ArCOOH \rightarrow ArH + CO_2 \quad (3)$$

where Ar represents an aromatic ring compound.

After drying and pyrolysis, gasification (or reduction) and combustion (or oxidation) reactions occur in the gasifier, with the exothermic combustion reactions supplying energy to the endothermic gasification reactions. The gasification process takes place in a variety of parallel and/or consecutive reactions. Presented in simplest form, the process can be regarded as the reaction of carbon with the gasifying agent [170].

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In an oxygen and steam fed gasifier the reactions can essentially be summarised as [170, 184, 193]:

$C + H_2O \rightarrow CO + H_2$ $\Delta H = 119$ kJ/mol ...(4) , steam/carbon reaction and
$C + \frac{1}{2} O_2 \rightarrow CO$ $\Delta H = -123$ kJ/mol ...(5) , partial oxidation.

In addition to partial oxidation, total combustion can also occur. Partial combustion predominates at high temperatures, while total combustion predominates at lower temperatures [194].

Water-gas shift (WGS) and methanation reactions proceed to near chemical equilibrium in the case of most gasifiers:

$CO + H_2O \rightarrow CO_2 + H_2$ $\Delta H = -40$ kJ/mol ... (6), WGS and
$CO + 3H_2 \rightarrow CH_4 + 2\,H_2O$ $\Delta H = -206$ kJ/mol ...(7), methanation.

The WGS reaction can be used to manipulate the H_2/CO ratio of the final syngas to a certain extent.

Methane formation is favoured at high pressures (> 70 bar) and low temperatures (760-920°C) [175]. Methane content is usually higher than equilibrium would predict because methane is also formed during devolatilisation.

The rates and degree of conversion for the various reactions involved in gasification are functions of temperature, pressure and the nature of the coal being gasified. At higher operating temperatures, the conversion of carbon to CO and hydrogen increases, while the production of methane, water and CO_2 decreases [188].

Overall carbon conversion cannot be predicted from thermodynamic principles, as this is often dictated by slow reaction kinetics and diffusion limitations, which is a function of the specific feedstock properties (e.g. ash content, rank, maceral composition, etc).

Sulphur in the feedstock reacts to produce hydrogen sulphide, carbonyl sulphide, and smaller amounts of other sulphur compounds, while nitrogen in the feedstock is converted to ammonia, hydrogen cyanide, other nitrogen compounds and molecular nitrogen. The presence of coal-derived nitrogen in the product gas is one reason why it is not essential to use ultra pure oxygen for for coal gasification. The percentage of the nitrogen in the coal that is converted into nitrogen molecules in the synthesis gas will depend on the type of nitrogen compoundsin the coal. It is widely accepted that SO_x and NO_x compounds do not exit the gasifier, except perhaps in trace amounts in lower temperature gasifiers, because a reducing atmosphere exists in the vessel. As a result sulphur and nitrogen is reduced to H_2S, NH_3 etc. [170].

3.6 Classification of gasifiers

A wide variety of gasifier technologies exist. More than a 100 different gasification technologies can be found in the literature. These technologies are in various stages of development, ranging from laboratory to commercial scale.

Gasifier designs differ primarily in the type of reactor bed selected for coal gasification, which is directly related to the method of contact between the solid and gas phases during gasification [195]. Most gasifier technologies can be classified into one of the following three generic groups according to the type of gasifier bed used [174]:

- Fixed bed or moving bed, also known as 'descending bed' gasifiers [196], of which the Sasol-Lurgi gasifier is a prominent example. Coal flows counter-current with the steam and oxidant and the highest temperatures are reached towards the bottom of the gasifier.
- Fluidized bed gasifiers, such as the Kellogg-Rust-Westinghouse (KRW) gasifier. The coal, steam and oxidant are well-mixed, leading to a more uniform temperature distribution in the gasifier.
- Entrained flow gasifiers, like the Texaco and Shell gasifiers. Entrained flow gasifiers are plug flow reactors in which the coal and reactants move co-currently through the reactor. These gasifiers essentially operate using a flame with high and uniform temperatures throughout.

Other gasifier types have been developed based on e.g. rotary kilns, molten baths or in-situ (underground) gasification, but there are no gasifiers of these types near to commercial application [191].

Gasifiers are also classified according to how carbonaceous material, steam and the oxidising agent are injected in relation to each other, e.g. counter-current or co-current.

Another, more theoretical method classifies gasifiers according to their operating temperatures as either high-temperature or low-temperature gasifiers [188]. Low-temperature gasifiers are thermally more efficient, produce more methane and also produce tars. These processes have low throughput. High-temperature processes avoid tar production and have higher throughput. However to avoid low thermal efficiencies it is necessary to recover energy in a downstream boiler and/or power turbines, increasing operational complexity. Gasifiers operating at lower temperatures release the mineral content of the feedstock as an ash, whilst those operating at higher temperatures produce a molten slag which can be water-quenched to produce a hard glassy slag that is generally non-leachable [170].

It is important to note that there is not one particular gasification technology which will be the most economic and practical selection in every instance. Rather, the optimum technology selection is dependent on the specific

process application. The selection of a gasification process cannot be done without considering the supporting processes, as each gasification technology has its own unique set of characteristics which have separate challenges such as gas cleanup, by-product disposal, etc. [188]. Some of the important factors that have to be taken into account when selecting a gasification technology include the following [197, 198]:

- Feedstock characteristics
- Quality requirements for clean gas
- Quality of waste products
- Operating characteristics
- Site-specific conditions
- Environmental legislation

Of the above factors, feedstock, i.e. coal, may be the least flexible factor for economical, geographical and political reasons and it is usually necessary to select the gasification technology according to the feedstock that has to be processed [191]. Some of the important operating parameters and characteristics, to illustrate the differences between types of gasifiers, are included in Table 2.

The composition and maximum outlet temperature of the syngas which is produced by the gasifier will depend on the feedstock utilized, the steam to oxygen ratio and the temperature and pressure at which the gasifier is operated, all directly related to the type of gasifier selected [170]. Important characteristics of the raw gas include the methane and ammonia content, whether there are tars and oils present (which influence the gas cooling and cleaning sections), and most importantly, the H_2/CO ratio obtained.

Gasifier design determines the vessel's ability to handle a particular feedstock. For instance, a very high ash coal cannot be processed in a slagging gasifier, as the energy required to slag the ash would be excessive, impacting negatively on the economy of the process, while caking coal cannot be processed in a moving bed type gasifier. Some gasifiers can handle feedstock in liquid form better than others.

Other factors that influence the choice of gasifier include the ability to cope with a specific size particle, e.g. moving bed gasifiers cannot handle fine coal well, as well as the steam and oxidant requirements.

Table 2
Operating parameters for generic types of gasifiers [199, 200]

	FIXED BED	FLUIDIZED BED	ENTRAINED BED
Preferred feedstock	Lignite, reactive bituminous coal, wastes	Lignite, bituminous coal, cokes, biomass, wastes	Lignite, reactive bituminous coal, petcokes
Coal feed size (mm)	6 – 75	< 6	< 0.1
Ash content	No limit, for slagging type < 25% preferred	No limitation	< 25% preferred
Exit gas temperature (°C)	420 – 650	920 – 1050	±1200
Ash conditions	Dry/slagging	Dry/agglomerating	Slagging
Key distinguishing characteristic [192]	Hydrocarbon liquids in the raw gas	Large char recycle	Large amount of sensible heat energy in the hot raw gas
Key technical issue[192]	Utilisation of coal fines and hydrocarbon liquids	Increased carbon conversion	Raw gas cooling
Well-known technology supplier	Sasol-Lurgi	Kellogg Rust Westinghouse (KRW)	Texaco

Common gasifying agents used in industrial gasifiers include a mixture of steam and air or oxygen, with the amount of oxygen being generally one-fifth to one-third the amount theoretically required for complete combustion [191]. The choice between air and oxygen as the oxidant depends on several factors, including the reactivity of the feedstock, the type of gasifier used and the application(s) the produced gas will be used for. Oxygen-blown gasification delivers syngas with a heating value of 10 to 16 MJ/kg, or about one fourth the heating value of natural gas, compared to a heating value of less than 5 MJ/kg for air blown gasification [197], since the syngas is then diluted with nitrogen [175]. The nitrogen from the air also results in greater volumes of gas to be treated downstream.

Depending on the gasification application three types of syngas, with different calorific values, can be produced [191]:

- Low heating value gas, with a calorific value (CV) of 3.8 – 7.6 MJ/m^3. The applications include fuel gas for gas turbines and smelting and reduction of iron ore. It cannot be used as a natural gas replacement or for chemical synthesis due to its high nitrogen content, since this type of gas is obtained from certain air-blown gasifiers.
- Medium heating value gas, with a CV of 10.5 – 16 MJ/m^3. The usage of this type of gas includes fuel gas for gas turbines, a replacement for natural

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gas and for chemical synthesis. Depending on the H_2/CO ratio, this type of gas can be used in Fischer-Tropsch synthesis, methanation, methanol and ammonia production and H_2 production for refinery, fuel cell and other applications.

- High heating value gas with a calorific value of more than 21 MJ/m^3. This type of gas is mostly used as a substitute for natural gas.

The average compositions of the exit gas for some gasifiers are reported in Table 3.

Table 3
Typical gasifier raw gas outlet gas compositions (dry basis).

	Sasol-Lurgi dry bottom (fixed bed) [196]	KRW (fluidized bed) [196]	Texaco (entrained flow) [201]
H_2	38-41	31	26-36
CO	21-26	44	31-47
CO_2	26-29	18	6-16
CH_4	8-10	6	<0.3
H_2/CO ratio	1.7-2.0	0.7	0.7-0.9
Heating value (MJ/Nm^3)	12 - 14	10 – 12	10 - 11

Selection of the method of cooling the hot raw gas depends on the composition of this gas (e.g. is there tars and oils present or not) and the intended application. Cooling can either be done by direct contact with the cooling medium (quench) or via an indirect cooling method [191, 202, 203]. While the quench approach is somewhat less efficient, it is also less expensive and more suitable for feeds with a high metal content. The indirect, or heat-exchange approach offers higher overall efficiency but requires a greater capital investment, and there is a higher risk involved [186].

With direct cooling, the hot raw gas is quenched with liquid or cooled recycle gas. The direct liquid-quench method is often used, especially in systems where entrained particles must be removed from the raw gas before further processing. The water quench approach is especially suitable where the hydrogen content of the syngas needs to be increased by the shift reaction, for example when modifying the syngas for ammonia production. Some synthesis gas shifting to increase hydrogen content may also be needed for methanol and HTFT synthesis. For these intermediate H_2/CO ratio requirements, a combination of quench and waste-heat boiler cooling is possible [204].

If a water quench is used in power generation applications then energy efficiency can be improved by operating the gasifier at high pressure and

recovering energy from the water vapour when it passes through an expansion turbine together with the solids free syngas. Texaco and others have proposed the use of a quench IGCC design in which the gasification is conducted at a higher pressure of about 70 bar [205]. Additional power can then be generated by expansion of the clean fuel gas to about 20 bar followed by gas reheat and firing in a gas turbine. The gas cooling by an expander can also be used to provide much of the refrigeration demand of a physical absorption desulphurization system [206].

Syngas expansion is being used in two of the heavy oil IGCC plants at Falconera and Priolo in Italy. This approach is especially suitable for the integration of IGCC power generation with FT synthesis. In this case expansion down to about 30 bar would be followed by further clean-up and then FT synthesis to provide FT tail gas to a gas turbine at 20 bar. The steam produced by the FT reactor cooling system is integrated into the IGCC steam system. This approach is discussed in more detail in Chapter 5.

For the Lurgi moving bed dry bottom gasifier design, as well as for the direct quench version of the Texaco gasifier, raw gas is quenched with recycled aqueous liquor (also known as 'gas liquor'), resulting in the condensation of oils and tars and removal of particulate matter. Thereafter, the liquor is separated into aqueous and hydrocarbon fractions for further treatment. Quenched raw gas is subsequently passed through a waste heat boiler for further cooling, but only low quality steam can be generated as most of the sensible heat is lost during the quench, thus giving lower thermal efficiencies.

For indirect cooling, a high temperature syngas cooler is used [191]. High pressure steam is produced from the recovery of sensible heat. The oxygen-blown high temperature coal gasification processes with indirect cooling have significant steam raising capability in the raw gas cooling section. This allows for the development of clean fuel gas plants with combined steam turbine power generation which efficiently produce large quantities of electrical power [203].

High temperature gasifiers may use dry coal feed systems or coal-water slurry feed systems. Dry-coal fed gasifiers have the advantage over coal-water slurry fed gasifiers that they can operate with a minimal amount of steam and avoid the oxygen combustion required to provide the energy needed for the latent heat to vaporize the water. This implies in practice that they have a 20 – 25% lower oxygen consumption than coal-water fed gasifiers. However, steam generation facilities need high quality boiler feed water while the water quality is a minor issue for coal-water slurries.

The big advantage of coal-water slurry fed gasifiers is the more elegant method of pressurizing the coal. Lock hoppers as used in dry-coal fed gasifiers are costly and bulky equipment with complex valve systems that have to provide a gas-tight block in a dusty atmosphere [1]. Pumping a coal-water slurry is not a

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simple matter either, but it is definitely less complex. The practical pressure limit for dry-pulverized coal lock hoppers is about 50 bar, wheras for coal water slurry pumps the pressure could, in principle, be as high as 200 bar [1]. Typical commercial operating pressures for high pressure slurry fed gasifiers are between 60 and 100 bar.

In order to compensate for virtually all drawbacks of using water slurry the slurry can be preheated [1]. This provides the following advantages:

- The water has to be heated less in the reactor, and the heat of evaporation becomes lower at higher temperatures.
- Atomization becomes better with hotter liquid containing feedstocks, increasing the accessibility of the coal for gaseous reactants, especially when the feedstock slurry is preheated such that the carrier flashes upon introduction into the gasifier. Also, the reduction in surface tension of the carrier liquid at higher temperature enhances atomization.
- More reactor space becomes available for the gasification per se, which will increase the carbon conversion.
- The oxygen consumption will decrease and the cold gas efficiency will increase.
- The water will expand resulting in lower water requirement to maintain good slurry conditions.

If the water is heated close to its critical point then the above effects will be most pronounced and the heat of evaporation is then minimal. Furthemore, the coal in the slurry is also preheated to above 300°C, a feature that is not possible using dry-coal feeding because the coal particles will become sticky.

With a suitable preheat system, the efficiency of a slurry fed IGCC system is almost equal to that of a dry-coal fed system (49 versus 50%) [1].

A brief overview of the three generic gasification technologies will be presented in the next three sections.

3.6.1 Fixed bed gasifiers

Fixed bed gasifiers, have been in use since the beginning of the gasification industry. Somewhat confusingly, these gasifiers are sometimes also referred to as moving bed gasifiers. The coal moves downwards through the gasifier but the various zones within the gasifier are 'fixed' in location. These gasifiers have maintained a strong position in the broad range of reactor types used for coal gasification [189].

Carbonaceous feedstock enters the gasifier at the top periodically during operation, resulting in an essentially full gasifier at all times during normal operation. As coal has to enter the gasifier during operation, a coal lock hopper

is used to feed the coal or other carbonaceous material into the pressurised gasification reactor, after being pressurised itself [185, 201].

The feedstock is consumed as it moves downward through the bed and ash is removed at the bottom. A rotating grate with ash lock is employed for dry ash removal systems, which is absent in the case of slagging fixed bed gasifiers. This grate also serves as agent distributor.

To remove entrained solid particles and condense heavy hydrocarbons (tars and oils) in the hot raw gas leaving the gasifier at the top, a wash cooler is attached to the gasifier, where the gas is scrubbed with recycled gas liquor (water produced when raw gas is cooled). A large amount of the sensible heat in the raw gas is degraded by the scrubbing step which substantially decreases the temperature of the scrubbed gas entering the downstream heat recovery systems.

Fixed bed gasifiers are suitable for solid feedstocks, usually in the form of coarse coal particles. Coarse particles ensure good bed permeability and help to avoid excessive pressure drop and channel burning, both of which can lead to unstable gas outlet temperatures and gas composition. As coarse coal particles are required, this greatly simplifies feedstock preparation steps leading to reduced gasification cost.

Run-of-mine (ROM) coal is typically screened at about 6 mm, resulting in a fine coal fraction which can be routed to steam plants or pulverised coal combustion units for electricity generation. The only additional coal preparation required in some instances is the proper blending of multiple coal sources, or the homogenisation of single or multiple sources, which have highly varying properties, to ensure stable gasifier operation.

Pressure drop and entrained solids can limit gas throughput in certain circumstances. While feedstock particle size distribution (PSD) can be managed correctly to ensure stable gasifier operation [183], mechanical and thermal fragmentation during gasification could make it difficult to control the PSD at all times during the process. These fragmentation phenomena are determined by the feedstock characteristics, and high moisture content in coal has been shown to be largely responsible for particle size reduction due to thermal fragmentation when coal is exposed to the high gasifier temperatures [207, 208].

Co-current fixed bed gasifiers have not been able to succeed commercially yet, although the concept has been widely studied. Commercial fixed bed gasifiers are all counter-current. Coal flows counter-current to the steam and oxidant feed. Cold coal comes into contact with hot ascending product gases. As the coal moves downward under gravity in the reactor, it passes through several zones which are defined according to the reactions and temperatures occurring at different heights in the fuel bed [209]. These are the drying, devolatilisation, reduction and combustion zones. These zones are somewhat better defined than is the case in other gasification technologies. The distinct

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temperature zones aid the overall conversion of coal to gas [195]. In the reduction zone mainly endothermic reactions occur and in the combustion zone exothermic oxidation reactions take place to supply energy to the endothermic gasification reactions.

The 'cold gas efficiency' of a gasifier is defined as the chemical energy from the coal that is contained in the raw gas exiting the gasifier. Fixed bed gasifiers have high cold gas efficiencies. This is due to the heat exchange achieved in the counter-current operation which allows the gas and solid product streams to exit at relatively low temperatures, with the minimum of energy contained as sensible heat in the product gases [171]. Other advantages of the fixed bed type gasifier include high heating value syngas due to its high methane content and low oxygen consumption [175].

Tars and oils, formed in the pyrolysis zone at the top of the gasifier, exit the vessel with the raw gas. Due to the presence of these compounds in the raw gas, gas cleanup is more complex than for gasifiers in which condensable hydrocarbons are destroyed during the gasification process. To avoid deposition of these substances in downstream equipment, the raw gas must be quenched with water or gas liquor, resulting in reduced raw gas heating values. However, these tars and oils can be utilised as feedstocks for the production valuable products like coke and creosotes for wood preservation.

The biggest challenge for fixed bed gasifiers is their limited ability to handle fine coal, necessitating the disposal of the portion of the run-of-mine coal that is too fine to be used for feed.

A shortcoming is the strong possibility of excessive coal segregation inside the fixed bed gasification vessel, aggravated by broad particle size distributions. Segregation can lead to difficulty in maintaining uniform gas flow through the coal bed [195], which in turn will lead to unstable gasifier operation. This complexity makes scale-up to very large units difficult, so that smaller units will be duplicated rather than risking scale-up, even though larger units would provide better economic performance. Multiple units result in high maintenance cost, but are advantageous in that very high plant availability can be achieved, so that the downstream plant does not suffer due to loss of syngas production, a phenomenon which generally occurs in plants with a few large gasifiers.

Another disadvantage of fixed bed gasification is the relatively high steam consumption. A large excess of steam is injected into the gasifier to reduce the bottom temperature, protecting the vulnerable mechanical ash grate from extreme temperatures [171, 189]. This results in lower overall efficiency, but the water-gas shift reaction is pushed towards higher hydrogen production, so that syngas with an H_2/CO ratio directly acceptable for all Fischer-Tropsch processes is produced. For large scale applications such as the Sasol plants in South

Africa, separate steam generation plants are required to supply most of the high-pressure steam demand.

There are only three commercial fixed bed gasification processes [191]. Two of these were originally developed by Lurgi, these being the Sasol-Lurgi fixed bed dry bottom gasifier (dry ash gasifier) and the British Gas Lurgi (BGL) slagging gasifier. The other fixed bed gasifier, also a dry ash gasifier, was developed by BHEL (Bharat Heavy Electricals Ltd).

For the dry ash versions, temperatures at the bottom of the bed are controlled below the ash fusion temperature to allow coal ash to be removed as a solid. As a result of the low operating temperatures that must be maintained, these gasifiers are suited to reactive coals like lignites [191]. For the BGL, bottom temperatures are high enough to allow the ash to melt and to be removed as a molten slag.

There are currently 152 Lurgi dry bottom gasifiers operational throughout the world, most notably 97 which are operated by Sasol in South Africa, producing syngas which is converted to Fischer-Tropsch liquids (fuels and chemicals). Another significant installation is at the North Dakota Gasification Company in the USA, where 14 gasifiers are used to produce synthetic natural gas (SNG).

For IGCC applications, there are presently three installations which gasify their feedstock in fixed bed gasifiers. These are at Schwarze Pumpe, where 8 fixed bed gasifiers are used, one of which is a BGL slagging gasifier; in Scotland at the FIFE Energy plant where 1 BGL slagging gasifier is in operation [184] and in the Czech Republic, where 26 Lurgi dry bottom gasifiers have been in use since 1996 to produce electricity and steam. In Luenen, Germany, 5 Lurgi dry bottom gasifiers were in operation from 1972 to 1977, but the plant was decommissioned because it was not economical.

The two main types of fixed bed gasifiers, these being the Sasol-Lurgi dry bottom gasifier and the BGL slagging gasifier will be described in more detail in the following two sections.

3.6.1.1 Sasol-Lurgi fixed bed dry bottom gasifier

The Sasol-Lurgi fixed bed dry bottom gasifier was originally developed and marketed by Lurgi. In South Africa, 97 of these gasifiers are operated by Sasol. In 2002 the Sasol-Lurgi joint venture was established to further develop and market the fixed bed dry bottom gasification technology, with Sasol and Lurgi each holding a 50% share in the new company.

The Sasol-Lurgi gasifier is a pressurised fixed bed gasifier, and a schematic drawing is shown in Fig. 2.

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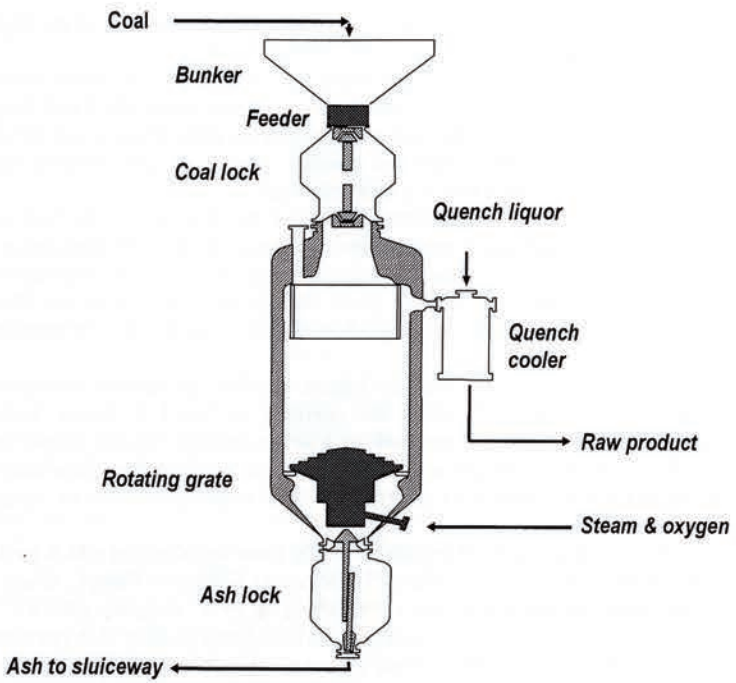


Figure 66 Sasol-Lurgi fixed bed dry bottom gasifier [191]

Lump coal, sized to a typical particle size distribution of 6 mm to 75 mm, is fed into the top of the gasifier through a lock hopper. The hopper is filled, sealed and pressurised and the coal is then released in the reactor. The process is continuous, so that the gasifier is almost filled with coal at all times. Steam and oxygen enter at the bottom and react with the coal as the gases move up through the bed.

Due to the counter-current mode of operation, hot ash exchanges heat with cold incoming agent (steam and oxygen), while hot raw gas exchanges heat with cold incoming coal at the top. As a result, the ash and raw gas leave the gasifier at relatively low temperatures compared to other types of gasifiers, which improves the thermal efficiency and lowers the steam consumption. The Sasol-Lurgi dry ash gasifier consumes the lowest amount of oxygen per unit coal feed due to the high thermal efficiency. A water jacket cools the gasifier vessel and part of the steam for gasifier consumption is generated in the jacket.

A typical temperature profile for a Lurgi dry bottom gasifier is presented in Fig. 3. It can be seen that the temperature of the agent (steam/oxygen mixture) and the hot ash is around 300 °C, but can vary depending on the position of the ash bed, which is determined by the rate of ash extraction. The agent inlet temperature can be used to control the ash temperature. The raw gas outlet temperature is typically in the region of 500-600 °C, and depends on process parameters as well as coal properties (e.g. moisture content).

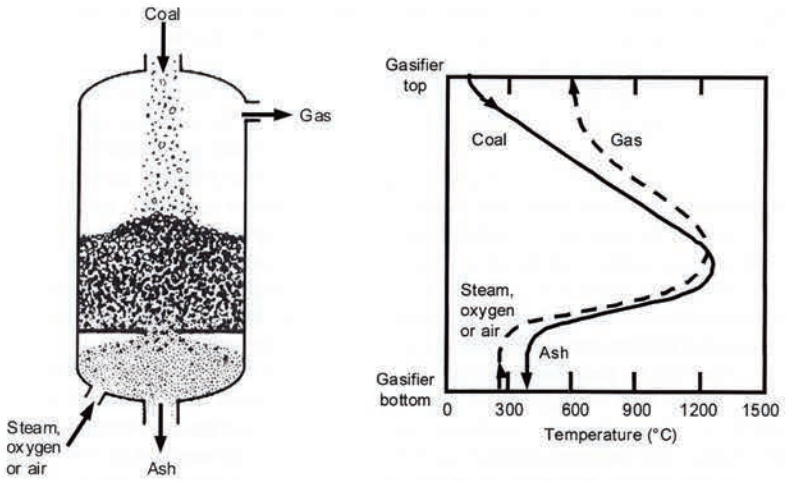


Figure 67 Lurgi dry bottom gasifier and typical temperature profile [174]

The cold gas efficiency of these gasifiers is typically about 80%, and can rise to 89% if liquid hydrocarbon products are included in the calculation.

Ash is removed at the bottom of the gasifier by a rotating grate and lock hopper. Coal with high ash content can be gasified without severe losses in thermal efficiency, as the ash is not extracted in a molten state. The Sasol-Lurgi gasifiers have been shown to be capable of handling coal with an ash content as low as 6% to as high as 35% [173]. However, it is important to maintain the ash content as constant as possible in order to achieve stable gasifier operation, especially at high load conditions.

The H_2/CO ratio of the syngas produced is in the range of 1.70 to 2.0, which makes it suitable for methanol synthesis and for Fischer-Tropsch synthesis (see Chapter 3) without the need for water-gas shift conversion to adjust the ratio.

By-products like tars, pitches, oils and chemicals like ammonia are present in the exiting raw gas, and the raw gas is quenched to separate these products from the syngas. Approximately 85% of the tar is condensed in the crude gas quench, and the remainder is condensed as oils and naphtha in downstream gas purification units [195]. The treatment of these by-products is an added cost to the technology, and is regarded as a disadvantage in instances where no market exists for the by-products. These by-products can be recycled to the gasifiers and converted to additional synthesis gas. However, with very large scale applications such as the Sasol plants, large enough quantities of by-products are produce to achieve good economics of scale for the upgrading of the by-products to valuable products. Examples from the Sasol operations include the production of high quality anode coke from pitch, as well as creosotes, phenols and other valuable aromatic compounds from the tars. If the syngas is converted to transportation fuels, the aromatic by-products from the gasification process can be used as octane enhancers, since synthetic fuels contain substantially lower amounts of aromatics than crude oil derived fuels.

At the Secunda petrochemical complex, Sasol operates the largest coal to synthesis gas conversion process in the world. Low-grade sub-bituminous coal with relatively high ash content is upgraded through gasification and gas cleaning to purified synthesis gas, which is used as feed to a Fischer-Tropsch conversion process for the production of fuels and chemicals.

The first 10 fixed bed dry bottom gasifiers which were installed by Sasol in 1954, had a coal throughput of approximately 28 tons/h and produced about 23500 m^3_n/h of dry raw synthesis gas [173]. Two scaled-up versions were developed. The original design was first scaled up to a throughput of 54 tons/h of coal (producing 45500 m^3_n/h of dry raw gas). Most of the fixed bed gasifiers in operation today are of this type, with Sasol operating 83 of these gasifiers. A further scale-up to 75 tons/h of coal followed (producing 63000 m^3_n/h of dry raw gas), and one of these gasifiers is commercially operated by Sasol. The further optimisation of the Sasol-Lurgi gasification process is ongoing, and it is believed that further gains is throughput, efficiency and utility consumption are achievable [175]. In 2003 approximately 52 million tons of coal was mined by Sasol's coal mining division, of which about 40 million tons was consumed by two Sasol synthetic fuels plants at Secunda. About 6 million tons was consumed by Sasol's smaller chemical producing plant at Sasolburg, and about 3 million tons was exported. Approximately 70% of the total coal consumption is for gasification to synthesis gas by Sasol-Lurgi fixed bed dry bottom gasifiers, while the remaining 30%, a finer coal fraction not suitable for gasification, is combusted to produce steam and electric power required by the process. The total pure synthesis gas production from Sasol's 97 fixed bed dry bottom gasifiers is approximately 3.6×10^6 m^3_n/h.

In addition to coal, Lurgi gasifiers can handle a variety of different feedstocks, e.g. at Schwarze Pumpe seven Lurgi fixed bed gasifiers are employed to treat solid wastes, such as plastics, sewage sludge, rubber, contaminated wood, paint residues and household wastes [210]. However, a feedstock preparation step such as briquetting or pelletising may be required to ensure the desired feedstock particle size for optimum gasifier operation.

3.6.1.2 British Gas Lurgi (BGL) slagging gasifier

The BGL gasifier is a dry feed pressurised fixed bed slagging gasifier. It was developed by British Gas, London and Lurgi for the gasification of coals and cokes, and is primarily a methane and fuel gas producer [188]. It is the only gasifier in which gasification of large particles and vitrification of inorganic matter can be carried out under pressure in the same reactor [210]. The BGL can handle up to 40 tons per hour of coal feedstock.

The gasifier is provided with a motor-driven coal distributor/mixer to stir and evenly distribute the incoming coal mixture (coarse coal, fines, briquettes and flux). Oxygen and steam are introduced to the gasifier vessel through sidewall-mounted tuyeres at the elevation where combustion and slag formation occur (at the bottom of the vessel).

The coal mixture descends through several reaction zones, similar to that of the Sasol-Lurgi fixed bed dry bottom gasifier. Below the gasification zone, any remaining carbon is oxidised and the mineral matter in the coal is liquefied, forming slag. The slag is withdrawn through a slag tap at the bottom of the gasifier, quenched with water and removed by a lock hopper.

The crude gas exiting the gasifier contains tars and oils from the carbonisation zone in the gasifier. The gas is scrubbed with recycled gas liquor to remove the condensable hydrocarbons. These are then separated by gravity from the liquor. The tar and oil by-products, as well as any solids which are entrained from the gasifier, can be recycled to the top of the gasifier, or re-injected trough the tuyeres at the bottom of the gasifier. A limited amount of coal fines can also be fed through the tuyeres. The cold gas efficiency of the BGL is about 88% [173] and It has a nominal dry gas capacity of 21 000 to 24 000 Nm^3/hr, depending on the degree of tar-oil recycle.

High ash content, combined with a high ash melting point, will result in addition of a fluxing agent, so that the BGL could be costly to operate. The tapping temperature (1400°C) is lower than for most entrained flow gasifiers, and for some feedstocks, high amounts of fluxing agent have to be added to comply with this operating limit. The optimum slag viscosity for a BGL is approximately < 5 Pa.s, in comparison to < 15 Pa.s in entrained flow gasifiers [191].

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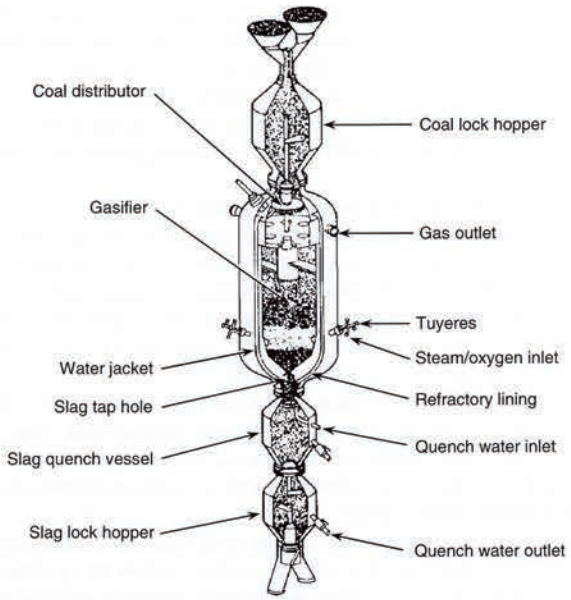


Figure 68 BGL gasifier [174, see also 177]

3.6.2 Fluidized bed gasifiers

Fluidized bed gasification with oxygen and steam was first done in a gasifier developed by Winkler [171]. These gasifiers are completely mixed, partially cocurrent reactors.

A fluidized bed gasifier consists of a vertical, cylindrical, refractory-lined vessel with cyclones above the fluidized bed that separate entrained solids from the outlet gas; bottom ash cooling and if required, dry fly ash removal and a wet gas scrubbing system [199].

Solid, crushed dry fuels are used as feed. Reactive coals like lignites and brown coals are favoured as feedstock, as the relatively low operating temperatures make it difficult to maintain high carbon conversion without very high solid recycle rates.

It is usually not desirable to have coal particles agglomerating, as it causes uneven fluidisation in dry ash fluidized bed gasifiers. Therefore, it is necessary to process coals that have a higher ash fusion temperature than the operating temperature of the gasifier. Mineral matter is a major constituent of the bed and therefore coal ash characteristics can have a large impact on the operation of the

gasifier [191]. Highly varying ash characteristics are problematic, and the feedstock should be well-mixed to maintain the same characteristics as far as possible. Coals with a low swelling index are also preferable to avoid agglomeration.

The presence of pyrite and sodium silicates formed during gasification is believed to be among the factors that cause agglomeration in fluidised bed systems. Therefore, very careful control of the gasifier operating temperature is required when processing coals with high alkali content. However, from an environmental point of view, fluidized bed gasifiers are tolerant to coals with high sulphur content as up to 90% of sulphur in the coal feed can be retained by adding a sorbent, like calcium oxide.

Dry coal particles of less than 6 mm are introduced at the bottom of the gasifier and then fluidised using oxidant and steam [174]. Heat exchange between the cool steam/oxidant feed and the hot ash discharged increases the thermal efficiency. Upon entering the gasifier, the solids undergo rapid heating. Coal particles are suspended in the gas flow and feed particles are mixed with particles already undergoing gasification reactions [191], so that no clear reaction zones can be distinguished. Because the coal is well-mixed with steam and oxidant more uniform and moderate temperature distributions are achieved than for other types of gasifiers. Unreacted entrained particles are recovered by cyclones for recycle to the vessel. The recycle of solids efficiently transfers heat to the bed material.

Residence time for the solids is typically in the order of 10 to 100 seconds. Ash can be discharged in dry form or as agglomerated particles, as for the KRW gasifier [191].

Fluidized bed gasifiers are usually operated at near atmospheric pressure, and therefore well suited for smaller capacities (approximately 20 tons per hour of coal) [200]. If the gasifier is operated at elevated pressures, higher gasifier capacities can be achieved. Operating temperatures are relatively low at around 1000°C. At the bottom of the gasifier, where oxidising conditions prevail, the temperatures must be lower than the ash fusion temperature of the coal, unless the gasifier has an agglomerating ash removal system.

No pyrolysis by-products are produced, as they are combusted to provide energy for endothermic gasification reactions. The raw gas exiting the vessel is essentially free of hydrocarbons heavier than methane.

Fluidized bed gasifiers use a moderate amount of steam and oxygen during gasification. Due to relatively low operating temperatures, there is little thermal stress on the equipment. A typical temperature profile for a fluidized bed gasifier is presented in Fig. 5.

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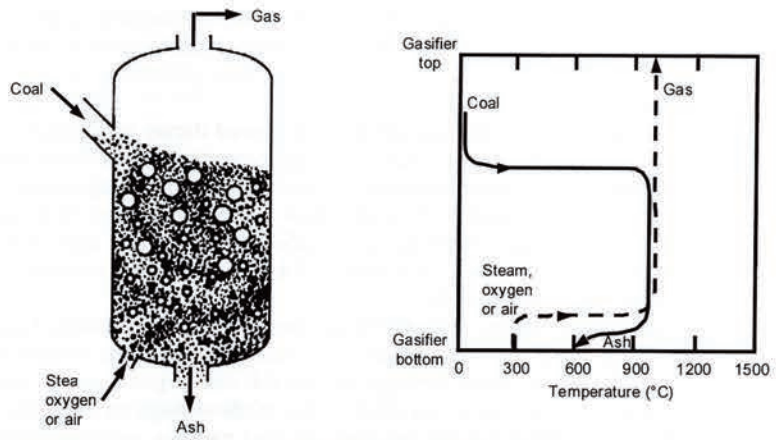


Figure 69 Fluidized bed gasifier and typical temperature profile [174].

At present, 21 fluidised bed gasifiers are operational, most notably 8 GTI U-GAS gasifiers in China, applied to produce fuel- and town gas.

The two main contenders for fluidized bed gasifier technology are the High Temperature Winkler (HTW) and the Kellogg Rust Westinghouse (KRW) gasifiers. KRW is now known as KRW Energy Systems. These technologies have not been applied extensively on commercial scale due to various reasons, including low capacity throughput, high operating cost, low carbon conversion, large char recycle and ash agglomeration problems. From a recent survey conducted by the Gasification Technologies Council it is evident that fluidized bed technology is not a major contender for future applications [178].

Perhaps the most promising fluidized bed technology is the transport gasifier developed by Kellogg, Brown and Root Inc., which is currently being tested at the Power Systems Development Facility in Wilsonville, AL [203]. This type of gasifier, as well as the HTW and KRW gasifiers will be discussed in more detail in the following sections.

3.6.2.1 KRW fluidized bed gasifier

Coal, via a lock hopper, and oxidant (air) enter the gasifier at the bottom of the vessel via a burner, ensuring thorough mixing of coal and oxidant.

Upon entering the vessel, coal releases volatile matter almost instantaneously. The volatiles burn rapidly and supply heat to the endothermic gasification reactions. The resultant gas forms large bubbles that rise up the

centre of the gasifier, causing char and sorbent (if added) in the bed to move down the sides of the reactor and back into the central jet [199].

The gasifier bed is maintained in a fluidized form by injecting controlled amounts of steam, air and recycled gas through nozzles in the combustion zone. Steam reacts with the char in the bed, converting it to fuel gas. If a sorbent like limestone was added to the coal upon feeding, the calcined form (CaO) now reacts with H_2S released from the coal during gasification to form CaS, removing a portion of the sulphur gases from the raw gas before it exits the vessel.

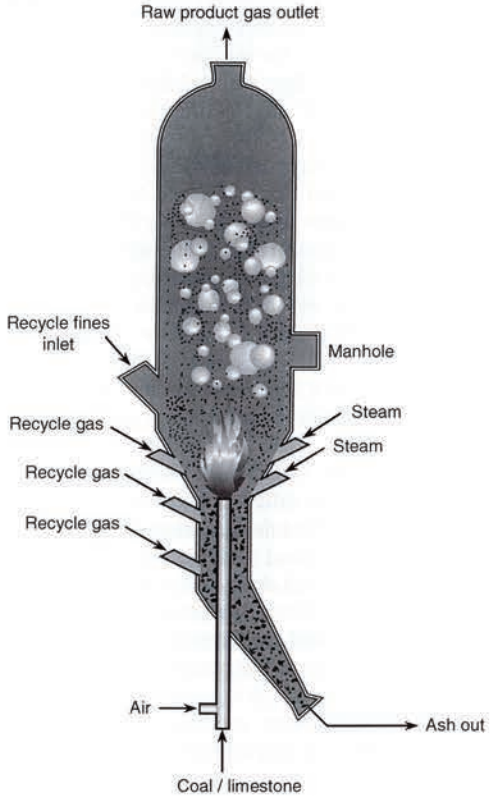


Figure 70 KRW gasifier [192]

To remove ash, particles are recycled through the flame of the burner at the bottom of the gasifier, where low-melting mineral matter partially melts, causing particles to agglomerate [199]. The ash agglomerating zone, which is hotter than the main fluidized bed, makes the process distinctly different and more complex than conventional fluidized bed gasifiers such as the HTW (High Temperature Winkler) [174], where dry ash removal is done. The agglomeration allows for the efficient recycle of even small particles in the feed. The velocity of gases in the reactor is selected to maintain most of the particles in the bed and smaller agglomerated particles return to the bed for further reaction.

Some of the finer particles are carried out of the gasifier, but are recaptured in a high efficiency cyclone and returned to the conical section of the gasifier. Eventually most of the smaller particles agglomerate as they become richer in ash and gravitate to the bottom of the gasifier. Since the ash and spent sorbent particles are substantially denser than the coal feed, they settle to the bottom of the gasifier where they are cooled and classified by a counter-flowing stream of recycled gas.

The DOE and its predecessor agencies have supported development of KRW Energy Systems' fluidized bed gasifier technology since 1972 when the design of a process development unit was first initiated under a contract with Westinghouse Electric Corporation [192]. This unit was completed in 1975 at Westinghouse's Waltz Mill Facility in Pennsylvania. The addition of limestone and dolomite to the gasifier for in-bed sulphur removal was successfully demonstrated during the 1980's. During this same period, numerous coal types were tested as feedstock to the KRW gasifier. Sasol in South Africa collaborated with Westinghouse to construct a demonstration unit in South Africa, but due to economic and other considerations the project was aborted.

3.6.2.2 The High Temperature Winkler (HTW) gasifier

The HTW process is a modified version of the Winkler fluidized bed gasification process, which was first developed in the 1920's.

The HTW is a refractory-lined fluidized bed gasifier with water jacket [174, 180]. Feed coal is crushed and dried before it is pneumatically conveyed to feed bins. Coal in the receiving bin is then dropped via a gravity pipe into the fluidised bed of ash, semi-coke and coal particles [190].

The gasifier is fluidized from the bottom with either air or oxygen and steam. These reactants are injected at two levels in the fluidized bed to maximise carbon conversion [177] and reduce methane and other hydrocarbon yields [174]. The gasifier is operated at 750 to 800 °C [174]. Operating pressure can vary from 1 to 3 MPa, depending on the use of the syngas produced [191].

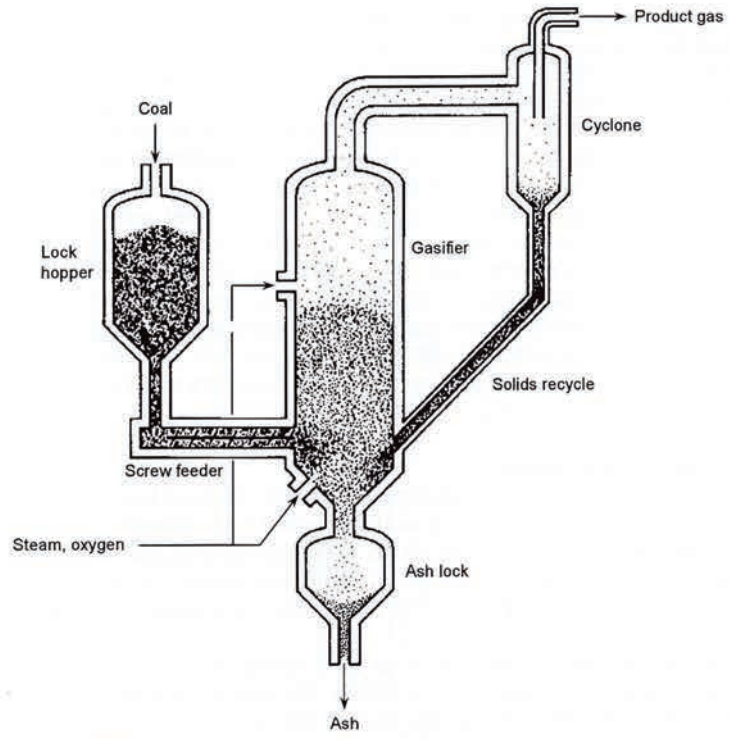


Figure 71 HTW gasifier [174, see also 177]

A portion of ash and char is entrained in the reactor effluent. The raw gas passes through a cyclone to remove particulates and is then cooled [191]. Solids that are recovered in this way are recycled to the gasifier and dry ash is removed at the bottom of the gasifier via a discharge screw.

The choice of feedstock is restricted to high reactivity feedstocks like reactive coals, chars derived from lignite carbonisation, peat and wood. Other feedstock requirements are an ash melting point of above 1200°C and non-caking tendencies, as the formation of agglomerates would disrupt the uniformity of the fluidized bed.

The cold gas efficiency (chemical energy from the coal that is contained in the raw gas exiting the gasifier) of the HTW is approximately 82%, and if the energy content of steam generated during gas cooling is added to the fuel gas

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energy content, and the energy for coal drying and steam feed to the gasifier is deducted, the efficiency increases to 85%.

The HTW gasifier was first developed by Rheibraun in Germany to gasify lignites for the production of a reducing gas for iron ore [191], and was a natural outflow from the low temperature process previously used. It was successfully applied for the synthesis of methanol from lignites at Berrenrath in Germany between 1986 and 1997. It was shut down at the end of 1997, because the process was no longer economically viable. Another plant utilising HTW gasification technology has been operating in Finland from 1988, producing ammonia from peat. A plant to study HTW technology with the aim of utilising it for IGCC in future plants was constructed at Wesseling in Germany in 1989. This 140 t coal/day plant provided operational data required to design a potential 300 MW power plant (KoBra), but the plant was never built. There is, however, an ongoing project to replace 26 Lurgi moving bed gasifiers at Vresova (Czech Republic) with two HTW units.

3.6.2.3 The transport gasifier

The transport reactor is an advanced circulating fluidised bed reactor that can function as a combustor or as a gasifier. Ground coal, sorbent (for sulphur capture), air and recycled solids are mixed in the mixing zone and injected into the reactor. Small particles, together with multiple passes of the coal/char through the gasification zone result in high carbon conversion at reasonable temperatures.

Gas with entrained solids moves up from the mixing zone into the riser, and from there into the disengager (see Fig. 8). The disengager removes a major portion of the solids from the gas by gravity separation. The separated solids flow downward through the aerated vertical standpipe. The gas stream then flows to the primary cyclone where additional particles are removed from the gas stream. These solids flow downward through a dipleg into the standpipe. The solids flow from the standpipe through the J-leg back into the mixing zone.

Gasification in the transport reactor is conducted at temperatures of 870°C to 1000°C and at a pressure of up to 17 bar(g).

The design is capable of very high throughputs and could lead to economically attractive IGCC fluidised bed designs. Further development and research is taking place at the Power Systems Development Facility (PSDF), which is specifically focused on reducing capital cost and increasing efficiency of an IGCC plant [178]. The transport reactor was designed to allow for scale-up of fluidised bed gasification technology to commercial applications, and a 99.9% combustion efficiency, 99% sulphur removal, very low particulate emissions (below 1 ppm) and reliable system operation are among its successes.

In September 1999 the transport reactor was converted to gasification mode. Its viability as a gasifier was confirmed by the results that included: (1) production of synthesis gas with a heating value high enough to fire a combustion turbine, (2) stable operation and pressure drop in the HTHP filter, (3) stable operation of the transport reactor, and (4) control of oxygen content during start-ups and process upsets.

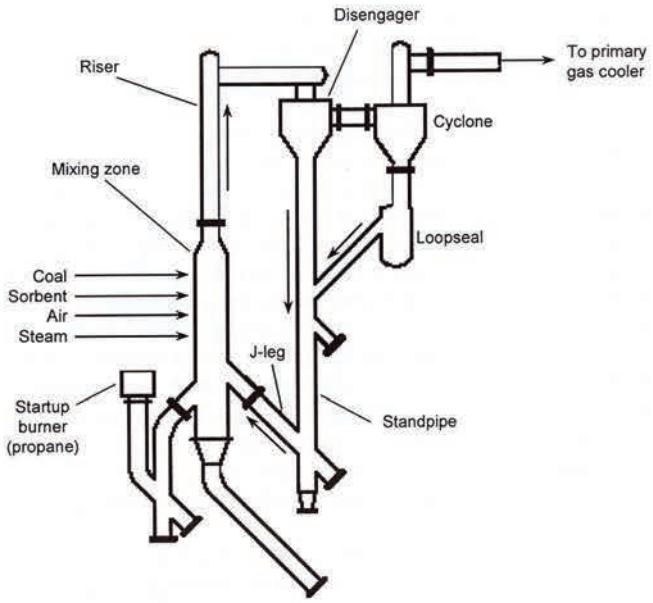


Figure 72 Transport reactor [191]

3.6.3 Entrained flow gasifiers

The entrained flow type of gasifier is the most widely used design [170]. These gasifiers are co-current, plug flow reactors. Finely ground feed, in the case of solids, or liquid feed is introduced into the gasifier along with the oxidant and steam or liquid water as moderator. Coal and gases flow co-currently at high speed. As a result, very short gas residence times are

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experienced, and the coal has to be pulverised to ensure high carbon conversion. All entrained flow gasifiers are of the ash slagging type.

A strong driver for the application of this technology is the wide range of feedstocks that can be accommodated [191]; including organic wastes, refinery by-products, solids and liquids, as well as fine coal, making this type of gasifier the most versatile. Entrained flow gasifiers operate at high temperatures (above ash slagging temperatures) to ensure high carbon conversion and syngas free of tars and phenols [191]. The fact that no hydrocarbons are produced which require clean-up and processing, makes it a desirable technology for many applications [174]. Texaco has marketed its entrained gasification technology very successfully as add-ons to existing refineries so that heavy liquid and solid by-products can be processed. The synthesis gas can be applied elsewhere in the refinery for clean heating fuel or to supplement the hydrogen demand, and there are also applications where electric power is generated from the synthesis gas.

Entrained flow gasifiers can accept almost any type of coal as long as the coal can be pulverised to very fine particles. However, there are certain feed requirements linked to each type of entrained gasifier design, e.g. a minimum ash content is required for gasifiers with slag self-coating walls [174]. High ash coals are usually not economical to gasify in this type of reactor, as the energy required to slag the ash could raise the oxygen consumption to unacceptable levels. If sulphur and halogens are present in considerable quantities, the cooling, cleaning and ash tapping equipment may have to be constructed from specialised materials. Other coal requirements, which varies slightly depending on the gasifier design, are an ash fusion temperature of below 1400°C, a slag viscosity of < 15 Pa.s at 1400°C, little or no flux requirement (< 3 wt%), a critical temperature viscosity and a SiO_2/Al_2O_3 ratio of about 2, which minimises limestone addition and avoids slag crystallisation at tapping temperatures [191].

Control of the fuel/oxidant ratio is more critical in entrained flow gasifiers as they have a smaller heat capacity and no inventory of process feedstock. Therefore, operating entrained flow gasifiers at varied load can prove difficult [191].

No reaction zones can be distinguished in the entrained flow gasifier. Gasification reactions typically occur at temperatures in excess of 1200°C. The high operating temperatures ensure high carbon conversion. Bed temperatures are above the ash fusion temperature, and hence the ash forms a slag. The raw gas usually exits the vessel above 1000°C [174].

The high operating temperatures have an impact on burners and refractory life and require the use of expensive materials of construction [191]. In Fig. 9, a typical temperature profile for an entrained flow gasifier is shown.

The outlet gas from the gasifier is free of hydrocarbons heavier than methane. Methane production is low due to the unfavourable thermodynamic equilibrium for methane formation at high temperatures. Likewise, the production of CO in preference to CO_2 is favourable due to the effects of low steam addition and high operating temperature on the water-gas shift equilibrium. A large amount of sensible heat is present in the raw gas leaving the gasifier.

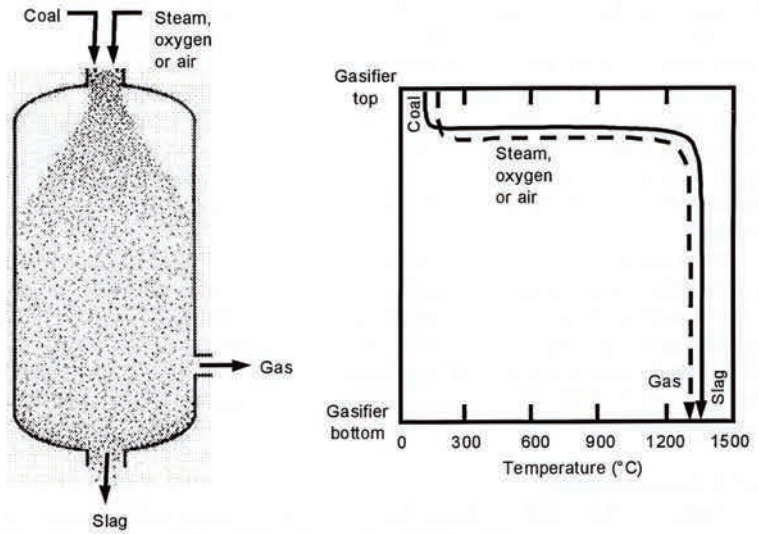


Figure 73 Entrained flow gasifier and typical temperature profile [174].

To maintain high thermal efficiency, the sensible heat has to be recovered from the raw gas, which is complicated by the possibility of molten ash deposition on heat transfer surfaces [195]. To limit the impact of molten ash, sophisticated high temperature heat exchangers have to be used to cool the syngas below the ash softening temperature in order to avoid fouling and control corrosion problems [191].

The entrained flow gasifier offers many advantages. These include the ability to handle a wide variety of coals, the elimination of tar and oil formation (not necessarily positive in all scenarios) and water-condensate and solid residue which can be easily disposed of [171].

One of the main disadvantages arises from the low inventory of coal in suspension. Due to cocurrent flow, the temperature drops from the inlet to the

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outlet while the carbon content and reactivity decreases. It is thus difficult to obtain high carbon conversion, as a very large reactor would be required to compensate for long residence times. To keep the reactor volume within bounds, high temperatures are used to speed up the reaction rates, and a certain amount of unconverted coal is acceptable [195].

Some operational difficulties are experienced with entrained flow gasifiers. These include material limitations regarding high operating temperatures, limited refractory life and difficult slag control. Gasification of coal with high ash content can be problematic, since the ash has to be melted and therefore high ash content feedstock impacts negatively on the thermal efficiency and oxidant requirement. High ash fusion feedstock could be problematic, and a suitable flux may be required to achieve ash melting at acceptable temperatures in order to protect gasifier linings. Operation at atmospheric pressure is also a handicap with some of the entrained flow gasification technologies, as the produced syngas has to be pressurised for most applications. However, most of the entrained flow gasification technologies have been adapted to operate under pressure.

Most commercial gasifiers in the world are entrained flow gasifiers. There are more than 240 entrained flow gasifiers operational in the world, and 50 more in the planning phase. Of the operational gasifiers, more than 50% of the gasifiers are Texaco gasifiers and 36% are Shell gasifiers. It is also the type of gasifier most favoured for IGCC applications at present, specifically Texaco gasifiers, which is the most popular in these installations (used in 7 IGCC projects up to 2001) [174].

3.6.3.1 Texaco gasifier

Texaco is the world's leading licensor of gasification technologies. The first gasification plant utilising Texaco gasification technology was commissioned in 1956, and used oil as feedstock. The first coal-based gasification plant of this nature was started up in 1978. There are currently 72 commercial facilities that employ Texaco gasification technology, of which 60 are operating and 12 are under construction or in the engineering phase. A total of 125 gasifiers are installed in these facilities [176], with a combined nominal capacity of 154 200 000 m3n/day. The technology is currently owned and marketed by ChevronTexaco after the merge between the Texaco and Chevron companies.

The Texaco gasifier is a cylindrical pressure vessel. The upper gasification section is refractory-lined, while the lower part extends into a water reservoir in the case of the direct quench type. The reservoir acts as a slag quencher and has a restricted orifice through which slag from the gasification section exits with the raw gas [188].

These gasifiers are single-stage, downward firing units. The oxidant can be pure oxygen, air or oxygen-enriched air [201], and enters the vessel via a specially designed burner. If solids like coke or coal are used as feedstocks, it is introduced as a pumpable slurry in water. A solid concentration in the range of 60-70% is preferred.

Slurryability is an important coal property to take into account. As the water requirement for producing a pumpable slurry increases, oxygen demand of the gasifier increase due to the larger quantity of water that has to be evaporated, leading to lower thermal efficiencies and poor operating economics [174]. Slurryability and grindability are interrelated as size distribution affects the slurry properties of the coal and the conversion in the gasifier, i.e. if a coarse grind size distribution is used, a high solid concentration slurry can be produced but the larger coal particles will not gasify as well as the smaller particles [191].

The Texaco gasifier is operated at temperatures of 1260°C to 1430°C and 41 bar is a typical operating pressure [188]. Coal residence time is a few seconds, and the ash is removed as a molten slag, which is inert and can be safely disposed of by landfilling. Due to the gasification conditions, the raw gas is rich in hydrogen and carbon monoxide, with a higher concentration of CO than H_2. The hydrogen content of the produced gas can be increased by further processing through a shift converter, if required.

Entrained flow slagging gasifiers have a relatively high oxygen requirement due to high operating temperatures and oxygen consumption for Texaco gasifiers is even higher than that for other entrained flow gasifiers which operate with a dry feed, due to the energy required to vaporise water in the slurry feed [174]. However, since the coal is injected as a coal-water slurry, no additional steam is required, unless the temperature in the reactor is above the desirable temperature, in which case a moderator, usually steam, is injected to control the temperature [188].

One of the disadvantages of the Texaco gasifier is a limited ability to economically handle low-rank coals because of the water/slurry feed system, high temperature operation which can lead to high maintenance costs and high-temperature gas cooling equipment that has to be utilised. The wet feeding system does however offer the advantage of being safe due to the elimination of dust and the associated explosion hazard [201]. Also, the water need not be processed to the high purity required for steam-fed gasifiers.

The operating temperature (1260°C-1430°C) of the gasifiers has to be high enough for the coal mineral matter to melt and flow freely down to the bottom of the gasifier. The ASTM ash fusion temperature method is used to determine the minimum gasifier operating temperature for successful tapping operation [191]. A maximum of 12% ash (on a weight basis) is recommended for coals to be processed in a Texaco gasifier.

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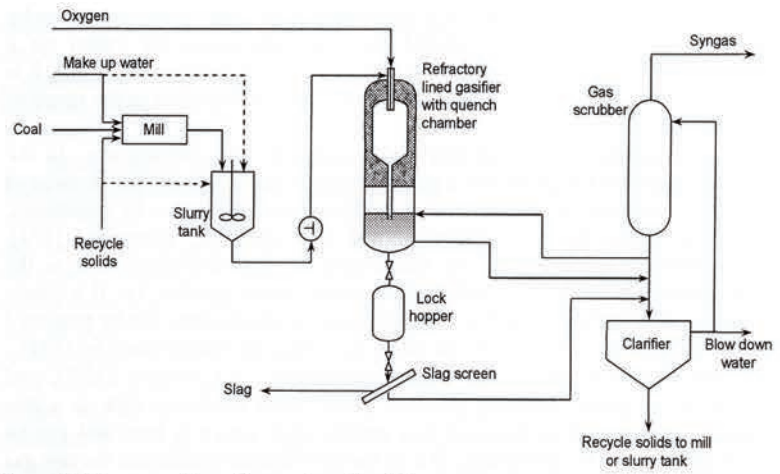


Figure 74 Texaco gasifier with quench cooling[1]

The Texaco gasifier has a typical cold gas efficiency of 77%, with the quench cooling approach that is usually used to minimize the capital cost and increase gasifier availability. If high-pressure is steam generated during cooling of the raw gas then the efficiency can be as high as 95% [174].

To cool the syngas, a direct or indirect cooling method can be employed. In the quench (direct) variant, raw gas from the gasifier is shock-cooled with water (see Fig. 10). Crude syngas leaves the bottom of the gasifier through a quench tube, which is submerged in a pool of water. In passing through the water, crude gas is cooled to the saturation temperature of the water and is cleaned of slag and soot particles. The cooled, saturated syngas then exits the vessel through a duct on the side wall for further cooling and cleaning or direct use [177]. Most Texaco gasifiers currently in operation use the quench variant. The major advantage is that it is cheaper and more reliable, but it is less thermally efficient.

In the full heat recovery (indirect) variant, the raw gas leaves the gasifier section and is cooled in a radiant syngas cooler from 1400°C to approximately 700°C. The recovered heat is used to generate high-pressure steam. Molten slag flows down the cooler and is quenched in a bath at the bottom, from where it is removed through lock hoppers. The partly-cooled syngas leaves the bottom of the gasifier and is then cooled further in convective coolers before being cleaned for use in the downstream application [177].

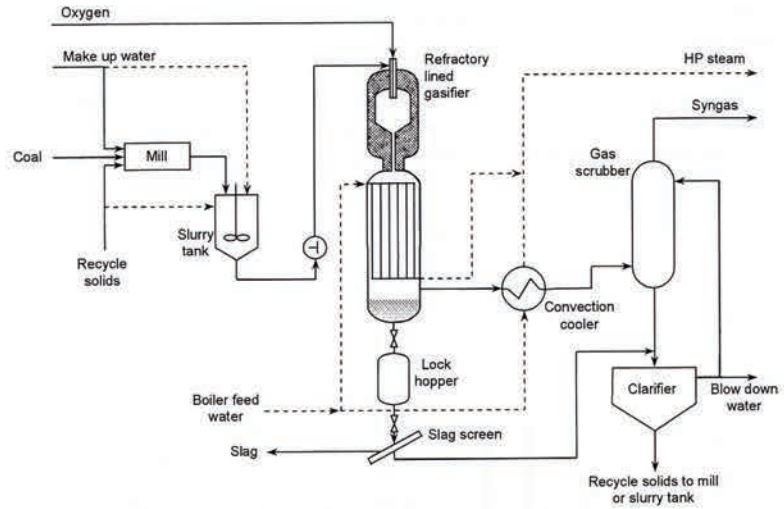


Figure 75 Texaco gasifier with radiant cooling [1].

3.6.3.2 Shell gasifier

The Shell gasifier is a dry feed pressurised entrained slagging gasifier [199]. Feed coal is pulverised and dried with the same type of equipment used for conventional pulverised coal boilers. The coal is then pressurised in lock hoppers and fed into the gasifier with a transport gas by dense-phase conveying. The oxidant is preheated to minimize oxygen consumption and mixed with steam as moderator prior to feeding to the burner. The coal reacts with oxygen at temperatures in excess of 1370°C to produce principally hydrogen and carbon monoxide with very little CO_2. Operation at elevated temperatures eliminates the production of hydrocarbon gases and liquids. The high temperature gasification process converts the ash into molten slag, which runs down the refractory-lined wall of the gasifier into a water bath, where it solidifies and is moved through a lock hopper as a slurry [174]. Some of the molten slag collects on the cooled walls of the gasifier to form a solidified protective coating. The raw gas leaving the gasifier at 1600°C contains small quantities of unburned carbon and about half of the molten ash. To make the ash less sticky, preventing it from fouling surfaces, the hot gas leaving the reactor is partially cooled by quenching with cooled recycle product gas to approximately 900°C. Further cooling takes place in the waste heat recovery unit, which consists of radiant, superheating,

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convection, and economising sections where high pressure superheated steam is generated before particle removal.

Cooled syngas is filtered through ceramic filters. About 50% of the cooled syngas is then recycled to the top of the gasifier to act as quenching medium for the exiting gas. The remainder is washed to remove halides and ammonia and then passed on for desulphurisation [177].

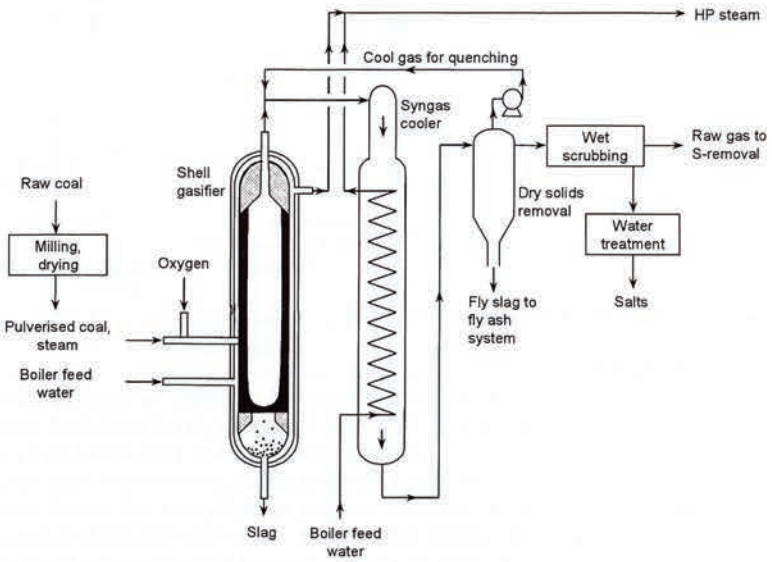


Figure 76 Shell gasifier [218, 219]

Shell claims that this type of gasifier has high flexibility in terms of coal rank and ash, sulphur and moisture content [191]. Any coal that can be milled to the right size and pneumatically transported can be gasified in the Shell entrained flow gasifier, although some adjustments are necessary in the case of specific coals. For example, bituminous coals require steam injection and oxygen/coal (dry, ash free) ratios from 0.85 to 1.05 for producing a syngas with an H_2/CO ratio of 0.4 to 0.45 and 1-2.5% CO_2. Sub-bituminous coals on the other hand do not require steam injection and can be operated with oxygen/coal ratios of between 0.8 and 0.9.

The ash content of a coal has an impact on the performance of the gasifier in terms of efficiency, as slag forms part of the insulation of the wall of the

gasifier and so prevents excessive heat loss during gasification [191]. An ash content of more than 8% but lower than 15% is recommended, as increased ash content increases the overall cost of the operating system. However, coals with an ash content of up to 40% can be processed. The ash content can also have an impact on the performance of the slag tap and the slag handling system. Elements like Cl, F, Pb, K, Na and P need to be taken into account as they vaporise during gasification and then condense in the syngas cooling systems, sticking to ash particles and causing fouling.

Large variations in the coal sulphur content have the largest impact on the gasification process, followed by variation in ash content and moisture content [191].

The Shell gasifier has a cold gas efficiency of 80%, which is higher than that of the Texaco entrained flow gasifier due to reduced oxygen consumption and lower CO_2 generation. If the energy content of the high pressure steam generation in the gasifier jacket and the gas coolers is added to that of the fuel gas and if the energy for coal drying and steam feed to the gasifier is deducted, the actual efficiency would increase to 94% [174].

IGCC using the Shell gasification technology has been demonstrated over the last few years at the Buggenum facility in the Netherlands. The single Shell gasifier has a throughput of approximately 23 kg/s coal [211], which translates to 2070 tons/day of coal. The plant is currently owned by Nuon, which is the largest electric power supplier in the Netherlands. Trials are under way to co-feed renewable energy sources such as agricultural waste and chicken litter [212].

3.6.3.3 Lurgi Multi-purpose gasifier (MPG)

The MPG developed from a well-proven partial oxidation technology that was acquired by Lurgi to offer all production and treating processes for gas production from a single source [213]. The MPG was developed from Lurgi's fixed bed coal gasification technology and a demonstration unit has been in operation at Schwarze Pumpe since 1968. The MPG can process an extreme variety of hydrocarbon-containing feeds ranging from natural gas, coal tars and oils, heavy refinery residues, asphalts, etc. It is even possible to feed several streams of non-mixable substances simultaneously.

The feed enters the refractory-lined vessel through a top-mounted robust burner, which is able to process fluids of high viscosity, emulsions and slurries containing particles of several mm in diameter [211]. Oxygen is mixed with steam before being fed to the burner. The steam acts as temperature moderator. The process is non-catalytic and is carried out at temperatures of 1200°C to 1450°C and pressures of 30 to 75 bar.

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Depending on the feed composition, the oxidant and the actual gasification temperature, the raw syngas contains H_2, CO, CO_2, etc. in various concentrations. The H_2/CO ratio of the obtained syngas is in the range of 0.5 to 0.8. Typical characteristics of the raw gas exiting the MPG, compared to the Sasol-Lurgi dry bottom fixed bed gasifier, are listed in the table below.

Table 4
Comparison of raw gas composition and temperature for the Sasol-Lurgi gasifier and Lurgi MPG [211]

		Sasol-Lurgi gasifier	**MPG**
H_2	% vol.	39	41
CO	% vol.	18	53
CO_2	% vol.	31	4
CH_4	% vol.	11	0.15
N_2 + Ar	% vol.	1	1.85
Raw gas temp.	°C	300 - 600	1200 / 220
H_2 / CO		2.2	0.77

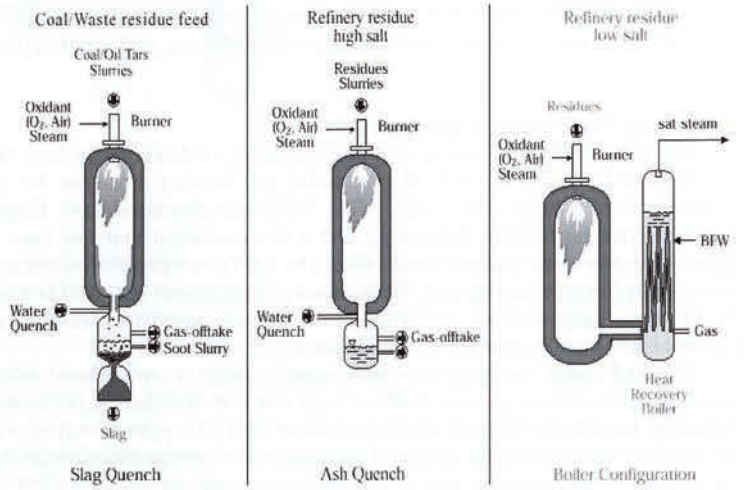


Figure 77 Different modes of operation for a MPG [211]

Soot and ash are removed from the raw syngas by means of wash water [213]. The resulting slurry is routed to a treatment step. After separation from the solid particles, the greater part of this water is recycled to the washing units.
To provide maximum feedstock and product flexibility, two variants for the syngas cooling section are offered for the MPG. The MPG gas cooling can either be a quench configuration or boiler configuration. Application of a waste heat boiler utilizes a major portion of waste heat to generate high-pressure steam. However, if the feedstock contains high levels of precipitation-prone contaminants which could block boiler tubes of the waste heat boiler, the quench mode is preferred. This option offers highest flexibility at lowest investment cost traded off against lower energy efficiency.

3.6.3.4 E-Gas two-stage gasifier

The E-Gas Technology, formerly Destec, process is an entrained flow, two-stage oxygen-blown gasifier. Coal is slurried, which is a more elegant way of pressuring coal than lock-hoppering [1], combined with pure oxygen, and injected into the first stage of the gasifier.

Two-stage gasification involves a first high-temperature slagging stage to which only part of the reactants are fed and a second non-slagging stage where the hot gas from the first stage drives the endothermic reactions. Unreacted carbon and dry ash which exits the second stage with the raw gas is removed from the gaseous stream and recycled to the first stage, so that almost all ash is removed as a slag. The two-stage gasifier has a higher thermal efficiency than single-stage gasifiers as the sensible heat in the raw gas is reduced and has a lower oxygen requirement than single-stage gasifiers. However, for a two-stage slurry-feed gasifier, such as the E-Gas gasifier, the disadvantage of a higher steam consumption, which is the case for dry-feed two-stage gasifiers, is not applicable, since the amount of steam is dictated by the coal:water ratio in the slurry, which is not affected by the staging arrangement.

In the case of the E-Gas gasifier, coal slurry undergoes partial oxidation at temperatures high enough to bring the coal ash above melting point in the first stage. Fluid ash falls through a tap hole at the bottom of the first stage into a water quench, forming an inert vitreous slag. The hot gas flows to the second stage, where additional coal slurry is injected.

The E-Gas gasifier is the only two-stage process with an operating commercial-scale demonstration plant, at the Wabash River site in Indiana, which was started up in 1996. Until 2000, sub-bituminous coal-water slurry was injected into the hot gases from the first stage. Particulate matter (char) was removed from the exiting gas in a particulate-removal unit featuring metal candle filters, after which it was injected with oxygen and/or steam into the first slagging stage, operating at a temperature of approximately 1400°C. The result

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was that, although sub-bituminous coal is used, the slagging part of the gasifier saw a feed upgraded by a dry char stream that required relatively little oxygen to be gasified.

Until the year 2000, 2550 tpd of coal was processed at the Wabash complex. Thereafter, the feedstock was switched to petcoke, and currently, 2000 tpd of petcoke is processed, with a 262 MWe net output. In fact, the E-Gas gasifier offers the highest petcoke throughput possibility of any gasifier at 2700 t per vessel per day [214].

The Wabash River Coal Gasification Repowering project, an IGCC complex, is claimed to be the cleanest coal-fired power plant in the world, operating at emissions well below its 1993 permit. The E-Gas technology has been operated in this IGCC application for over 15 years, and provides a highly efficient, environmentally superior and competitive based-load power alternative. IGCC achieves low SO_x and NO_x emissions, near zero particulate emissions and more than 90% of mercury in the feedstock can be removed. Coal ash from the E-gas process is an inert saleable construction material.

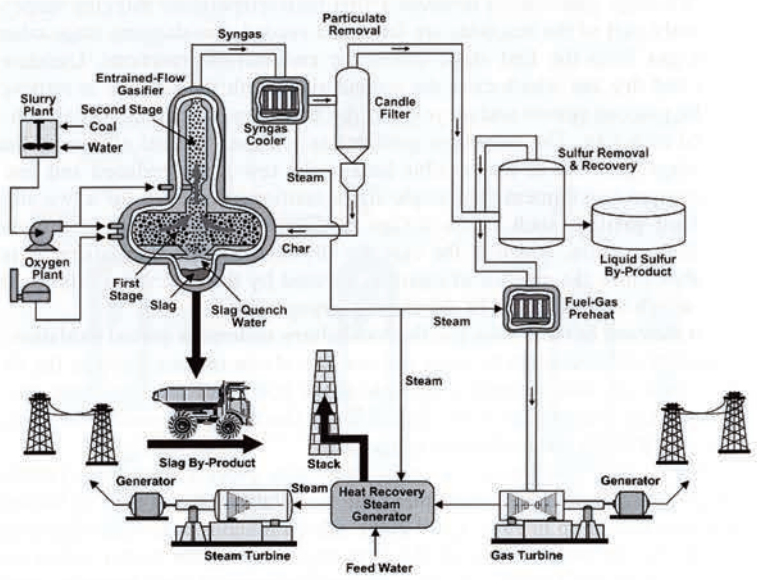


Figure 78 Wabash River Coal Gasification Repowering plant [215]

Numerous problems were experienced during the first years of operation. These included (1) ash deposition on the walls of the second stage of the gasifier and downstream piping, (2) particulate breakthrough in the hot gas filter system, (3) chloride and metals poisoning of the COS catalyst, (4) cracking problems with the gas turbine combustion liners and tube leaks in the heat recovery steam generator. However, these problems were all solved by the fourth year of operation.

The Wabash plant has been used to test certain improvements to the E-Gas gasification technology and integration into IGCC. ConocoPhillips claims that the technology will have a reduced capital cost, improved availability, GT-ASU integration and cyclone/hot gas filter hybrid system for gas cleaning from particulates to offer in future. The immediate future for E-Gas Technology appears to lie with applications where low-cost feedstocks can be used and co-production options are desired, e.g. the co-production of steam, fuels/chemicals and electricity [215].

The Wabash River Coal Gasification plant was owned by Dynegy at the beginning of the re-powering project. At the end of demonstration in December 1999, Global Energy Inc. purchased Dynegy's gasification assets and technology, and marketed the technology under the name E-Gas Technology. ConocoPhillips purchased the E-Gas technology in 2003, since the gasification technology was identified as a means to solve potential disposal problems of wastes from coking operations, and to meet refinery hydrogen needs. E-Gas Technology is a proven clean and efficient commercial process for converting coal or petroleum coke into a hydrogen-rich syngas, ideally suited for refining, power and chemicals applications.

ConocoPhillips was formed in 2002 with the merger of Conono Inc. and Phillips Petroleum Company. ConocoPhillips is the world's number one petcoke producer and also licenses coker technology [216].

3.7 Combinations of Sasol-Lurgi and entrained flow gasifiers

Sasol-Lurgi dry bottom fixed bed gasifiers have several advantages:

- The H_2/CO ratio of the syngas produced is in the range of 1.70 to 2.0, which makes it ideally suited to applications for high temperature Fischer-Tropsch (HTFT) synthesis without the need for water-gas shift conversion to adjust the H_2/CO ratio.
- High ash coals can be used as feedstock without major economic implications.
- The proven reliability and availability of these units is extremely high. As several smaller units are used, maintenance is easy and can be done without much impact on the process, by taking one unit off-line at a time.
- Low oxygen consumption and low capital cost for suitable applications.

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A strong driver for the application of entrained flow gasifiers is that a wide range of feedstocks can be processed, including organic wastes and refinery by-products. Also, most types of coal can be gasified in entrained flow gasifiers. However, each type of entrained flow gasifier has certain requirements of its feed, depending on the design. There is a minimum ash content required for gasifiers with slag self-coating walls, which have to be covered by slag to function and minimise heat loss through the wall [217]. A maximum ash content is usually also fixed for each type of entrained flow gasifier, as the tolerance to ash content depends on economic and technical factors.

The outlet gas from the gasifier is free of any hydrocarbons heavier than methane, which is present in very low concentrations due to the unfavourable thermodynamic equilibrium for methane formation at high temperatures. Likewise, the production of CO over CO_2 is favoured due to the effects of low steam addition and high operating temperature on the water-gas shift equilibrium. A large amount of sensible heat leaves the gasifier in the raw gas, but it can be recovered in a waste heat boiler with the generation of high-pressure steam. However, this heat recovery is relatively expensive.

To address the challenges related to entrained flow gasifiers and Sasol-Lurgi gasifiers, combinations can be considered. Entrained flow gasifiers could be used to treat tars, oils, aqueous by-products, fine coal, and even other problematic material not specifically related to Sasol-Lurgi gasification such as refinery residues and chemical waste streams. Entrained flow gasifiers could even be used to partially reform methane, reducing or eliminating the separate reformer capacity often required in schemes employing Sasol-Lurgi gasifiers.

In some instances, syngas with a relatively low H_2/CO ratio is required, e.g. for low temperature FT synthesis (LTFT) using iron catalyst. The Sasol-Lurgi fixed bed dry bottom gasifier can usually only be operated within a very narrow H_2/CO band. The gas from an MPG or entrained flow gasification unit could be used to manipulate the H_2/CO ratio of syngas to obtain the optimum composition for the downstream synthesis process.

In summary, employing entrained flow gasifiers together with with Sasol-Lurgi fixed bed dry bottom gasifiers would have the following advantages:

- Simpler flow scheme, since tar and phenosolvan (aqueous product) work-up can be simplified or eliminated.
- The possibility to produce the maximum amount of synthesis gas from coal, as all black products will be converted to syngas as well.
- Better flexibility in terms of feedstock, as Sasol-Lurgi gasification offers the opportunity to process high-ash coals, while entrained flow gasifiers offer the opportunity to process fine coal and hydrocarbon and aqueous wastes.
- Better flexibility in terms of products, as the syngas can be manipulated to suit the downstream synthesis processes.

3.8 Particulate removal

Before the raw syngas from a gasifier can be fed to an expansion turbine, gas turbine or condensing heat exchanger it is necessary to remove entrained solids. Currently this requires a cooling step immediately after the gasifier. This may be a significant source of energy degradation and compares unfavourably with gas reforming that does not require this solids removal step.

In most existing plants the solids are washed out with water in venture scrubbers or wash towers. This scrubbing takes place below the dewpoint of the gas so that the finest solid particles can act as nuclei for condensation, thus ensuring that all solids are removed efficiently [1].

ChevronTexaco and others have proposed the use of a quench IGCC design in which the gasification is conducted at higher pressure of about 70 bar [1]. Additional power can then be generated by expansion of the clean syngas fuel to about 20 bar followed by reheat and firing in the gas turbine. Fuel gas expansion is being used in two of the heavy oil IGCC plants at Falconara and Priolo in Italy.

A significant development has been the use of dry solids removal at gas temperatures up to 500 °C using ceramic candle filters [1].

Dry particulate removal must take place at a temperature that is sufficiently low that alkali compounds can be removed as solids so that they do not form corrosive alkali (hydro-) sulphates. This temperature is about 500 °C, which represents an upper bound for the particulate removal [1]. The lower bound is governed by the ammonium chloride sublimation temperature and lies at about 280 – 300 °C [1]. Within this allowable range of 280 - 500 °C it is preferable to remain close to the upper limit when feeding the syngas to a gas turbine to ensure the highest possible efficiency if this gas is to be fed to a turbine.

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