archive.org

DECLARATION OF MINA CHING

1. I am a Records Request Processor at the Internet Archive. I make this declaration of my own personal knowledge.

2. The Internet Archive is a website that provides access to a digital library of Internet sites and other cultural artifacts in digital form. Like a paper library, we provide free access to researchers, historians, scholars, and the general public. The Internet Archive has partnered with and receives support from various institutions, including the Library of Congress.

3. The Internet Archive has created a service known as the Wayback Machine. The Wayback Machine makes it possible to browse more than 450 billion pages stored in the Internet Archive's web archive. Visitors to the Wayback Machine can search archives by URL (i.e., a website address). If archived records for a URL are available, the visitor will be presented with a display of available dates. The visitor may select one of those dates, and begin browsing an archived version of the Web. Links on archived files in the Wayback Machine point to other archived files (whether HTML pages or other file types), if any are found for the URL indicated by a given link. For instance, the Wayback Machine is designed such that when a visitor clicks on a hyperlink on an archived page that points to another URL, the visitor will be served the archived file found for the hyperlink's URL with the closest available date to the initial file containing the hyperlink.

4. The archived data made viewable and browseable by the Wayback Machine is obtained by use of web archiving software that automatically stores copies of files available via the Internet, each file preserved as it existed at a particular point in time.

5. The Internet Archive assigns a URL on its site to the archived files in the format http://web.archive.org/web/[Year in yyyy][Month in mm][Day in dd][Time code in hh:mm:ss]/[Archived URL] aka an "extended URL". Thus, the extended URL http://web.archive.org/web/19970126045828/http://www.archive.org/ would be the URL for the record of the Internet Archive home page HTML file (http://www.archive.org/) archived on January 26, 1997 at 4:58 a.m. and 28 seconds (1997/01/26 at 04:58:28). The date indicated by an extended URL applies to a preserved instance of a file for a given URL, but not necessarily to any other files linked therein. Thus, in the case of a page constituted by a primary HTML file and other separate files (e.g., files with images, audio, multimedia, design elements, or other embedded content) linked within that primary HTML file, the primary HTML file and the other files will each have their own respective extended URLs and may not have been archived on the same dates.

INTERNET ARCHIVE

archive.org

6. Attached hereto as Exhibit B are true and accurate copies of the Internet Archive's records of the archived files for the URLs and the dates specified in the attached coversheet of each file.

7. I declare under penalty of perjury under the laws of the United States of America that the foregoing is true and correct.

DATE: April 05, 2025

Mina Ching

Mina Ching

EXHIBIT B

https://web.archive.org/web/20090711142105/http://www.ecn.nl/docs/library/report/2009/e09011.pdf

Energy conservation potential of the nitrogen fertiliser industry

P. Lako

ECN-E--09-011 March 2009

Acknowledgement

This study presents an analysis of the potential for energy conservation the 'resource-intensive' Nitrogen (N) fertiliser industry. The author wishes to express his gratitude for comments and additional information provided by Mr. R. Coster of VKP (Vereniging van Kunstmest Producenten), Mr. J. van Damme of Yara (Sluiskil), Mr. H. Duisters of DSM Agro (Geleen), and Mr. W. Wetzels (ECN Policy Studies). The contents of the study, however, remain the responsibility of the author. The project is registered at ECN under project number 7.7731.

Abstract

This study mainly focuses on the energy efficiency potential of the N fertiliser industry (ammonia and urea production, etc), with special attention for the Netherlands. The time horizon is 2020. First, the potential for energy efficiency improvement in the industry in general is discussed. Then, the Dutch N fertiliser industry is analysed in that respect. In order to put the results in perspective, the efficiency potentials are compared with an 'ICARUS-4' study from 2000. This results in a view of energy efficiency and capacity increase realised and remaining options for efficiency improvement in plants belonging to the Dutch N fertiliser industry.

Topsoe, Inc. – EX1020
Page 6 of 54

Contents

List of tables 4

List of figures 4

Summary 5

1. Introduction 7

2. Cross-cutting technologies for industrial energy conservation 9
   - 2.1 Introduction 9
   - 2.2 U.S. petrochemical industry 11
     - 2.2.1 Current separation processes 11
     - 2.2.2 Medium-term conservation potential 11
   - 2.3 U.S. chemical industry 12
     - 2.3.1 Low-energy separation potential USA 13

3. Energy conservation potential in the Dutch N fertiliser industry 17
   - 3.1 Introduction 17
   - 3.2 Ammonia 17
   - 3.3 Nitric Acid 25
   - 3.4 Urea 28
   - 3.5 N fertiliser industry in general 30
   - 3.6 Roundup and comparison to efficiency potential of ICARUS-4 31

4. Conclusions and recommendations 35

Acronyms and abbreviations 37

References 38

Internet sources 42

Appendix A Energy conservation potential of the U.S. chemical industry 43

Topsoe, Inc. – EX1020
Page 7 of 54

List of tables

Table 2.1 *Industrial mass transfer separation processses* 9
Table 2.2 *Industrial applications with potential for alternative low-energy separation technologies* 10
Table 2.3 *Potential of low-energy separation in the U.S. petroleum refining industry 2001* 12
Table 2.4 *Potential of low-energy separation in the U.S. chemical industry 2001* 13
Table 3.1 *Global production and production capacity of Ammonia (2002-2003)* 17
Table 3.2 *World nitrogen fertiliser supply and demand balance 2005/06 through 2009/10* 19
Table 3.3 *World Ammonia production capacity and balance 2005-2011* 19
Table 3.4 *Net efficiency (estimate) of Ammonia plants in the Netherlands (2005)* 21
Table 3.5 *Energy use of state-of-the-art Ammonia plants with credit for steam or utilities* 22
Table 3.6 *Potential energy saved by reduced separation energy for three Ammonia plants* 23
Table 3.7 *Investment cost of Ammonia(Urea) plants for a range of plant capacities* 23
Table 3.8 *Global production and production capacity of Urea (2002)* 29
Table 3.9 *Energy efficiency Ammonia and Urea plants in Europe c.q. Netherlands 2002* 29
Table 3.10 *Total energy requirement for Ammonia & Urea in the Netherlands (2002/2005)* 30
Table 3.11 *Energy efficiency potential Ammonia and Urea production in the Netherlands* 31
Table 3.12 *Energy conservation with regard to electricity in the Dutch fertiliser industry* 33
Table 3.13 *Energy conservation with regard to Ammonia production in the Netherlands* 33

Table A.1 *Energy & exergy analysis of 25 chemical technologies U.S. chemical industry* 44
Table A.2 *Production (2002), energy use & conservation potential U.S. chemical industry* 45

List of figures

Figure S.1 *Production capacity of Ammonia plants in the Netherlands* 5
Figure S.2 *Energy requirement of BAT Ammonia plants 1968-2005* 6

Figure 3.1 *Ammonia production in different world regions, 2003-2006* 18
Figure 3.2 *World nitrogen fertiliser nutrient consumption, in crop years [Mt NH_3-N]* 18
Figure 3.3 *Worldwide Ammonia production capacity* 19
Figure 3.4 *Forecast of fertiliser demand in the EU-25, 2005-2015* 20
Figure 3.5 *Production and production capacity of Ammonia plants in the Netherlands* 20
Figure 3.6 *Net energy efficiency of 66 Ammonia plants cf. benchmark of PSI [GJ/t NH_3]* 21
Figure 3.7 *Energy requirement of BAT Ammonia plants 1968-2005* 24
Figure 3.8 *Industrial gas prices ($/GJ) in various countries and world regions* 25
Figure 3.9 *Monthly prices of Ammonia ($/ton, Gulf) and of natural gas ($/MBtu) in the USA* 25
Figure 3.10 *Flow diagram of Nitric Acid and Ammonium Nitrate production* 26
Figure 3.11 *Applications of Nitric Acid* 26
Figure 3.12 *Net energy export of Nitric Acid plants [GJ/t HNO_3-N]* 27
Figure 3.13 *Production of Ammonia plants in the Netherlands [1000 t NH_3/year]* 32

Summary

This study mainly focuses on the energy efficiency potential of the N fertiliser industry, with special attention for the Netherlands. The time horizon is 2020. Trends observed and the energy efficiency potentials may be used for models employed by ECN Policy Studies, albeit with precaution as energy efficiency potentials prove to be difficult to quantify.

The Dutch N fertiliser industry is largely based on ammonia plants in Geleen (DSM Agro) and Sluiskil (Yara). From 1996, several important changes occurred in ammonia production:

- In 1996, one of the three ammonia plants of Yara was 'revamped', thereby increasing the production capacity by approx. 35%. Around 2005, the two most modern plants were also 'upgraded', increasing production capacity by approximately 15%. The additional production capacity resulting from the two operations amounts to about 800 t NH_3/day.
- In 1997, DSM executed a revamp, including some small creep projects, of its twin units at Geleen, increasing the combined capacity by 10% at a total cost of NLG 100 mln (approximately € 45 million). The additional production resulting from the revamp etc. amounts to about 300 t NH_3/day.
- In 2000, the Kemira plant with a production capacity of 1,500 t NH_3/day was closed.

Figure S.1 shows the combined effect of these refurbishments and closure of the Kemira plant.

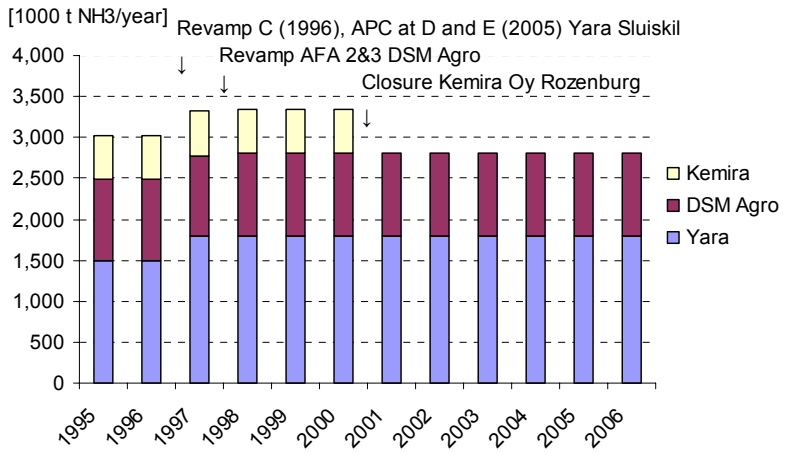

Figure S.1 *Production capacity of Ammonia plants in the Netherlands*
Note: Revamp of Yara's unit C (1996) and Automatic Process Control in 2005 has been taken as one step.

Ammonia plants in the Netherlands - three in Sluiskil (Yara) and two in Geleen (DSM Agro) - have an estimated energy use for feedstock and utilities (steam and electricity) of approximately 31 GJ/t NH_3. Dutch plants are energy efficient in comparison to plants in other countries of the world (Figure 5.2).

Topsoe, Inc. – EX1020
Page 9 of 54

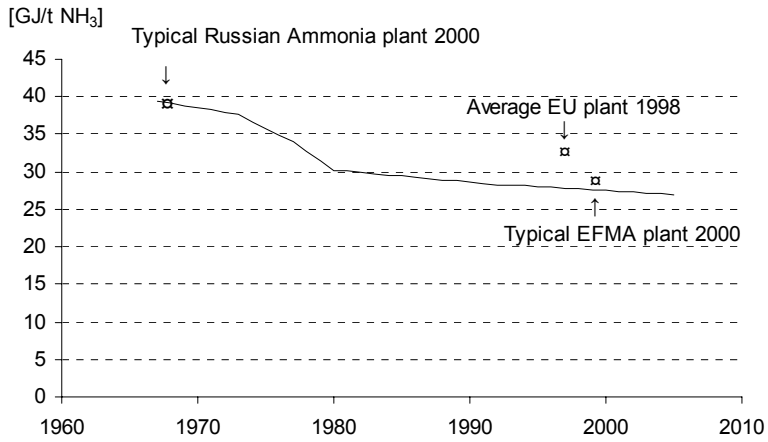

Figure S.2 *Energy requirement of BAT Ammonia plants 1968-2005*
Note: In 2000, energy use of Russian plants corresponded to the state-of-the-art of 1968 (~40 GJ/t NH_3).

This result may be attributable to continuous energy efficiency improvement at the Ammonia plants in Geleen - installation of a purge gas converter and simultaneous solution swap to aMDEA - and Sluiskil - solution swap to aMDEA, installation of Automatic Process Control. Recently, a benchmark study for 66 Ammonia plants by Plant Surveys International (PSI) for IFA showed that the average net energy efficiency was 36.9 GJ/t NH_3, and that of the 10 best-in-class plants approximately 30 GJ/t NH_3. Yara's D and E plants (Sluiskil) with a capacity of 1,750 t NH_3/d and 2,000 t NH_3/d, respectively, are in the first quartile of the corresponding class of the benchmark. This ranking appears to be confirmed by the fact that Ammonia plants that have been revamped exhibit a net energy efficiency of at best 7.1 Gcal/t $NH_3 \approx$ 29.7 GJ/t NH_3.

A significant energy efficiency improvement might be the application of new, more easily regenerable sorbents, membranes, etc. instead of the current CO_2 separation by aMDEA. If this type of technology would be applied at three relatively modern ammonia plants in the Netherlands, the energy conserved could amount to 1 PJ/year. However, the pay-out-time is too long (approximately 7 years) to warrant economical feasibility. Another option is application of pervaporation for Urea production. This could save approximately 0.3 PJ/year, and the pay-out time could be shorter than 7 years (in case of membranes etc. for Ammonia production).

With regard to Nitric Acid (NA), PDC - assisted by DSM Agro and Yara - has developed an energy benchmark system. The calculation method is based on an exergy model. In 2004, a benchmark with 83 Nitric Acid plants worldwide was executed. The best plant had an energy efficiency of -1.83 GJ/t HNO_3 (energy export) and the most inefficient one had an energy efficiency of +3.8 GJ/t NHO_3 (energy import). Only 43% of the plants had net energy export.

For Dutch Ammonia and Nitric Acid plants, it seems that 'There are no easy reductions in energy consumption, or low hanging fruit…' as an industrial expert noted. An exception may be pervaporation for Urea production. Economically viable energy savings in the N fertiliser industry may amount to 0.5 PJ/year or more, including 0.3 PJ/year from pervaporation for Urea plants.

1. Introduction

This study may provide a background on energy efficiency improvement in the Nitrogen (N) fertiliser industry. In 2001, the Utrecht Centre for Energy Research (UCE) published an in-depth study of the energy conservation potential of the Dutch industry in order to update their so-called ICARUS-4 database. That study was financed by the Ministry of Economic Affairs and the Ministry of Housing, Spatial Planning and Environment in the Netherlands. An 'resource-intensive' industrial (sub-)sectors covered by the study of UCE, notably the N fertiliser industry (Nieuwlaar, 2001) is revisited in the present study.

For the development of medium-term (2020) scenario studies of the energy system of the Netherlands, ECN Policy Studies makes use of a number of models including energy conservation potentials based on the ICARUS-4 study. Since the publication of the ICARUS-4 study, profound changes have occurred in the conditions governing the Dutch energy economy, viz.:

- Introduction of carbon trading in January 2005: the European Emission Trading Scheme (EU ETS).
- A steep increase of oil and gas prices, culminating in a temporary maximum oil price of approximately $78 per barrel in 2006 and up to maximum of approx. $145 per barrel in 2008.
- An increased attention for energy conservation and renewable energy - next to other options like advanced coal and nuclear power - in order to combat climate change, reduce the dependence on imported oil and gas, and reduce the cost of energy for the economy.

It is beyond the scope of this study to evaluate the complete ICARUS-4 study dating from 2000. Also, the effect of the changes signalled above cannot be evaluated in the framework of the present study. First, the study focuses on two generic energy conservation studies for the U.S. industry, viz. a study of the U.S. 'Energy Efficiency and Renewable Energy' (EERE, Department of Energy) performed in 2005 (EERE, 2005) and the so-called 'Chemical Bandwidth Study' of JVP International (JVP, 2004), in order to formulate some conclusions with regard to the medium and long-term industrial energy conservation potential, more specifically for the chemical, petrochemical, and pulp and paper industry. These studies give ample information on the potential of so-called 'cross-cutting' energy conservation technologies. These are technologies that apply to a number of (resource-intensive) industries. One example of a cross-cutting technology is the use of membranes and other low-energy separation technologies. These technologies are in the stage of R&D or just entering the demonstration stage. Therefore, they may have an impact on the energy use in particular industrial sectors in the period 2008-2020.

As models used for scenario studies for the Netherlands generally focus on energy conservation options on the medium term - not options that need another 10 to 15 years before deployment - the present study focuses on technologies that may enter the market between 2010 and 2015 at the latest. Also, technologies need to have a reasonable energy efficiency potential in the Dutch industry. Therefore, there are a few criteria that determine whether a technology is prospective in terms of potential and cost and whether it fits in the timeframe used in this study (2020), a timeframe in which climate policies will become more and more effective on the EU level.

Chapter 2 presents an overview of the energy conservation potential offered by technologies that may be called 'cross-cutting' energy conservation technologies and that conform to the abovementioned criteria of broad applicability, medium-term potential, and cost-effectiveness. This Chapter addresses the applicability in sectors of the U.S. industry, as the studies referenced focus on the U.S. industry. Energy efficiency potentials for the USA cannot be applied without further investigation to the Dutch energy economy, as some (chemical) industries in the USA are much less energy-efficient than corresponding industry in the Netherlands.

Topsoe, Inc. – EX1020
Page 11 of 54

Chapters 3 focuses on the energy efficiency potential in the Dutch N fertiliser industry - production of, e.g., Ammonia and Urea - and ends with an overview and discussion of the potential that is described by (Nieuwlaar, 2001). Chapter 4 presents conclusions and recommendations.

Topsoe, Inc. – EX1020
Page 12 of 54

2. Cross-cutting technologies for industrial energy conservation

2.1 Introduction

This Chapter presents cross-cutting technologies with potential for energy conservation in the U.S. industry based on two generic energy conservation studies for the U.S. energy economy, viz. a study of the U.S. 'Energy Efficiency and Renewable Energy' (EERE, Department of Energy) performed in 2005 (EERE, 2005) and the so-called 'Chemical Bandwidth Study' of JVP International (JVP, 2004). These studies are used because they describe technologies across a number of industries and consistently assess their potential, taking into account the growth or stabilisation in industrial sub-sectors and thus the factors favouring or limiting their deployment.

(EERE, 2005) gives an overview of cross-cutting technologies in the U.S. industry (Table 2.2). Although there are significant differences between individual refineries and forest products factories (in the Netherlands called 'pulp and paper industry'), each of these industries relies basically on one process flow scheme. New energy efficiency improvement technologies in these industries can therefore be applied generally across the entire industry. The U.S. chemical industry has over 70,000 process flow schemes, and new technologies seldom apply across multiple categories of chemicals. Therefore, in (EERE, 2005), evaluations were carried out on those few large-volume processes that dominate the energy consumption in the U.S. chemicals industry. Therefore, it is worthwhile to focus on technologies that are cross-cutting, such as low-energy separation processes as exhibited in Table 2.1 (Choate et al., 2005).

Table 2.1 *Industrial mass transfer separation processses*

	Material's primary role	Energy intensity	Technical status	Share of separation energy use [%]
Distillation	Structural member	High	Established	}
Evaporation[a]	Structural member	High	Established	} 80
Drying	Structural member	High	Established	}
Absorption	Separation agent	Medium	Established	
Adsorption	Separation agent	Medium	Established	
Pervaporation	Separation agent	Low	Novel	
Membrane	Separation agent	Low	Emerging	
Crystallisation	Structural member	Low	Established	
Physical	Structural member	Very low	Established	

a As exhibited in Table 2.2, Choate et al. (2005) indicate that evaporation is an existing technology used for the production of Caustic soda, Phosphoric Acid, and black liquor.

Source: Choate et al., 2005.

Membranes and other low-energy separation technologies offer a substantial potential for energy efficiency improvement in energy-intensive industries that are heavily dependent on separation processes. Membranes appear to have all the characteristics of a 'disruptive technology', one that could bring about huge reductions in energy intensity in large-scale separations (Internet Source 1). The potential of new, energy-efficient separation processes and the like is summarised for the U.S. petrochemical industry in § 2.2 and for the U.S. chemical industry in § 2.3. Appendix B presents a brief overview of the energy conservation potential of the U.S. chemical industry.

Topsoe, Inc. – EX1020
Page 13 of 54

Table 2.2 *Industrial applications with potential for alternative low-energy separation technologies*

	Distillation	Evaporation	Membranes	Extraction	Adsorption & Ion exchange	Absorption	Filtration	Gas treatment based on air-fuelled furnaces [a]	Hybrid systems	Untreated waste
Petroleum industry	*					Δ				
Gas recovery			Δ							
Hydrogen recovery			Δ							**
Chemical industry	*		Δ	Δ		Δ			Δ	
Phenol/Cumene	*		Δ	Δ	Δ				Δ	
Ethylene	*			Δ				*	Δ	
Methanol	*		Δ						Δ	
Styrene/Ethylbenzene			Δ	Δ	Δ					
Ammonia			Δ			*				
Caustic soda	*	*	Δ							
Nitrogen/Oxygen			Δ						Δ	
Phosphoric Acid		*	Δ	Δ						
Lime			Δ					*		
Sodium carbonate			Δ					*		
Forest products industry										
Black liquor concentration		*	Δ				Δ		Δ	

Notes: a Generated from air-fuelled furnaces to be replaced by oxygen-fuelled furnaces with pre-treated oxygen-enriched feed.
* Existing technology.
** Petroleum flare gas.
Δ Energy-saving alternative technology.

Note: According to (VKP, 2007), absorption is state-of-the art in Ammonia production. Therefore, an * has been added in the corresponding column.

Source: EERE, 2005.

2.2 U.S. petrochemical industry

2.2.1 Current separation processes

(EERE, 2005) shows that the petroleum refining industry - shortly 'refineries' - is a large energy consumer, accounting for 10% of the U.S. industrial/manufacturing energy use. Refineries produce various fuels, e.g., gasoline, kerosene, distillate and residual oil, Liquefied Petroleum Gas (LPG, see Appendix A for acronyms and abbreviations), and coke, as well as non-fuel products like petrochemicals, asphalt, road oil, lubricants, solvents, and wax. Bulk petrochemicals (ethylene, propylene, benzene, and others) are used to manufacture chemicals and plastics.

Refinery operations fall into four major categories: separation, cracking, reforming, and blending of hydrocarbons. How the main processes are used varies considerably from refinery to refinery, as well as within an individual refinery, depending on the product range that is desired. In the following, a number of options are presented to reduce the energy consumption of the petroleum refining industry by low-energy separation processes. The major separation processes are:

- Atmospheric distillation.
- Vacuum distillation.
- De-asphalting of oil.
- Sulphur removal.
- Gas recovery.

2.2.2 Medium-term conservation potential

Improved gas recovery

Petroleum refining is one of the most energy-intensive manufacturing industries in industrialised countries. It is also a complex industry involving numerous reaction and separation operations. The separation operations - atmospheric and vacuum distillation, solvent de-asphalting, desulphurisation, and gas recovery - account for almost one-third of the total energy consumed in the process.

On the one hand, refineries are a mature industry, and in general there seem to be few opportunities for major energy savings from the introduction of alternate separation technologies within the current process. On the other hand, in the gas recovery unit operation more energy-efficient separation technologies have potential in the medium term. In the USA, the annual production of refinery gases is estimated at 20 Mt (EERE, 2005). The separation energy used (57 PJ/yr in the USA) could be reduced by 20% or 10.5 PJ/yr through membranes or absorbents (Table 2.3).

Increased hydrogen recovery

Another medium-term option is increased hydrogen (H_2) recovery from petroleum flare gas. New membranes could permit H_2 to remain compressed at high pressure. Compressed H_2 may be used to process fuels or to drive fuel cells. Current membranes usually operate under continuous steady-state conditions with three streams. The feed stream - a high-pressure gas mixture - passes along one side of the membrane. The permeate stream passing the membrane generally exists of, e.g., H_2, whereas the retentate stream consists of heavier molecules like hydrocarbons and CO_2. A pressure difference across the membrane drives the permeation process.

(Internet Sources 2 and 3) show that a family of rubbery materials based on cross-linked poly(ethylene-oxide) have potential for overcoming problems of extensive pre-treatment. The materials are strongly solubility selective for the removal of CO_2 from natural gas, and also for CO_2 in CO_2/H_2 mixtures that are typical for petroleum flare gas (Turk, 2001; Dorgan, 2003).

Topsoe, Inc. – EX1020
Page 15 of 54

Membranes could become available that could separate H_2 and CO_2 better than previous membranes as they are much more permeable to H_2 than to CO_2. Membrane developers estimate that dedicated membranes could save 3 PJ/yr of H_2 from petroleum flare gas in the USA (Table 2.3).

Table 2.3 *Potential of low-energy separation in the U.S. petroleum refining industry 2001*

Process	Annual production	Final energy (process energy) [a]	Separation energy	Energy savings potential [PJ/yr]	
	[Mt/yr]	[PJ/yr]	[PJ/yr]	Medium term	Long term
Atmospheric/vacuum distillations	888	749	749		150
Cracking, reforming, LubeOil, Asphalt and Viscosity Breaking	1,006	733	733	10.5	145
Gas recovery	20	57	57	11.5	
Hydrogen recovery				3	
Subtotal [b]	1,914	1,539	1,539	25	295
Total (medium term + long term)				320	
Percent studied (EERE, 2005) [c]	94%	49%	100%		

a In (EERE, 2005) final energy is denoted as 'process energy', a term not commonly used for final energy.
b The medium-term potential pertains to de-asphalting of oil, gas recovery, and hydrogen recovery.
c Processes covered by the industry analysis are represented by the row Subtotal. In case of the refineries, the fraction analysed represents 94% of the annual production (by weight) and 49% of the process energy.
Source: EERE, 2005.

De-asphalting of oil

A third medium-term option is the use of hybrid systems of pervaporation - membrane-distillation hybrid system - or distillation-adsorption hybrid processes[1] for de-asphalting of oil. The potential energy saving is high. Such hybrid systems, when applied in U.S. refineries, could reduce the separation energy for de-asphalting of oil by 33%, from 32 PJ/yr to about 10.5 PJ/yr.

Medium-term conservation potential (until 2020) seems to be available in gas recovery, hydrogen recovery, and de-asphalting of oil. In addition, in the long term (>2020), membranes could potentially save approximately 20% of the energy currently used in distillation separation, viz. for:

- Atmospheric and vacuum distillations (749 PJ/yr).
- Cracking, reforming, LubeOil, Asphalt and Viscosity Breaking (733 PJ/yr).

For the USA, the additional long-term potential of low-energy separation processes in refineries would amount to 20% of approximately 1,480 PJ/yr, or 295 PJ/yr (Table 2.3). The total medium- and long-term potential amounts to 320 PJ/yr, or about 20% of the separation energy.

2.3 U.S. chemical industry

The chemical industry is a conglomerate of organic and inorganic industries, accounting for 23% of manufacturing energy use in the USA. §2.3.2 focuses on separation processes for:

- Ethane/Ethylene, Propane/Propylene and Styrene/Ethylbenzene.
- Dehydration and sour-water stripping.
- Ammonia and Urea.
- Caustic soda, Phosphoric Acid, lime and sodium carbonate.
- Methanol and MTBE.
- Phenol/Cumene.
- Nitrogen/Oxygen.

[1] The distillation-adsorption hybrid process involves a rough separation with distillation followed by polishing with adsorption.

Topsoe, Inc. – EX1020
Page 16 of 54

2.3.1 Low-energy separation potential USA

Summary

Table 2.4 shows the low-energy separation potential of the chemical industry (EERE, 2005). The medium-term potential is 175 PJ/yr, or about 20% of the separation energy. The total potential is approximately 250 PJ/yr, which is of the same order of magnitude as for refining (§ 2.2).

Table 2.4 *Potential of low-energy separation in the U.S. chemical industry 2001*

Process	Annual production	Final energy (process energy) [a]	Separation energy	Energy efficiency potential [PJ/yr]	
	[Mt/yr]	[PJ/yr]	[PJ/yr]	Medium term	Long term
Ethylene/Methane etc.	23.6	528	127	58	
(Ethylene/Ethane) [b]	(N/A)	(N/A)	(19)	(6)	
Propane/Propylene [c]	*N/A*	*N/A*	*41*	*14*	
Styrene/Ethylbenzene	5.0	211	42	12	
Natural gas Dehydration [c]	*N/A*	*N/A*	*38*	*13*	
Inorganic Acid Dehydration [c]	*N/A*	*N/A*	*16*	*5*	
Acetic Acid Dehydration [c]	*N/A*	*N/A*	*9*	*3*	
Sour-water stripping [c]	*N/A*	*N/A*	*19*	*6*	
Ammonia	13.2	211	53	16	66
Urea [b]	*7.2*	*N/A*	*6*	*2*	
Caustic soda	11.3	422	211	4	
Phosphoric Acid	10.9	211	53	6	
Lime	18.6	106	1	0	3
Sodium carbonate	10.4	95	21	0	1
Methanol	3.2	53	11	2	1
MTBE [c]	*N/A*	*N/A*	*6*	*2*	
Phenol/Cumene	2.3	53	32	9	
Nitrogen/Oxygen	30.8	50	50	24	
Subtotal [c]	129	1,938	600 (*755*) [c]	~ 130 (*175*) [c]	~70
Total (medium term + long term)	1,090	3,185	1,275	~ 200 (*245*)	
Percent studied in (EERE, 2005) [d]	12%	61%	47% (*59%*) [c]		

a In (EERE, 2005) final energy is denoted as 'process energy', a term not commonly used for final energy.
b Pervaporation for ethane/ethylene separation saves much less energy than the process on top of the list.
c The separation options in italics have not been analysed in depth in (EERE, 2005).
d The fraction studied in (EERE, 2005) is 12% of the production by weight, 61% of the process energy, and 47% of the separation energy. Including the separation options in italics increases the percentage from 47% to 59%.
Sources: EERE, 2005; USGS, 2004.

Ethane/Ethylene, Propane/Propylene and Styrene/Ethylbenzene

The primary separation technology used in ethylene production is cryogenic distillation. The separation consumes only 22% of the total energy input to the system. Of this amount of energy, virtually all is consumed in running the compressor that provides refrigeration for the cooler and the cryogenic distillation. About 27% of the total energy input is consumed in reaction operations and another 22% in the heat of reaction. The remaining 29% is consumed in the conversion of energy to other forms. This conversion involves first the production of steam which is used to provide heat to several of the process steps, but a major fraction is consumed in the generation of mechanical work which in turn is used to provide refrigeration for the condenser and the cryogenic distillation column.

Use of membranes for methane (CH_4) separation and the application of liquid extraction, membrane, or adsorbents to reduce or eliminate the cryogenic distillation operation are estimated to have the potential to save 58 PJ/yr in the USA. Alternatively, the use of pervaporation - membrane-distillation hybrid system - in the separation of ethane would have a potential of sav-

Topsoe, Inc. – EX1020
Page 17 of 54

ing 6 PJ/yr. Also, in the U.S. chemicals industry, an energy efficiency improvement could be achieved of 33% or 14 PJ/yr in case of separation of propane and propylene by pervaporation.

Like crude oil refining, styrene/ethylbenzene production contains numerous distillation operations. Nearly 60% of the total energy input is consumed in reaction operations and 20% in separation operations. Distillation currently accounts for more than 90% of the energy used in the separation process. Liquid/liquid extraction utilising high-selectivity extractants could potentially be developed for use instead of the benzene and ethylbenzene recycle columns. Membrane separation technology could also be used in the final purification step for styrene. It is estimated that a potential saving of 30% could be achieved in each of these operations resulting in the U.S. chemical industry in a net saving of about 12 PJ/yr.

Dehydration and sour water stripping

Pervaporation - membrane-distillation hybrid systems - could be developed and applied for dehydration of natural gas, inorganic acid, and acetic acid, with potential savings of 13 PJ/yr, 5 PJ/yr, and 3 PJ/yr, respectively (based on an assumed energy saving of 33%). Also, pervaporation could be applied to sour-water stripping, incurring an energy saving of 6 PJ/yr in the USA.

Ammonia and Urea

Natural gas is the most common feedstock in Ammonia production via steam reforming (JVP, 2004). The synthesis CO_2 gas separator is the largest source of exergy losses (hot exit CO_2 stream, exchanger cooling of MEA). The next largest source of energy loss is ammonia synthesis, occurring in the high-pressure syngas compressor, syngas reactor, and cooling and refrigeration units. Much of the low-quality energy is due to low temperature levels. In preheating and reforming, large internal exergy losses occur in the secondary reformer and waste heat boiler downstream of the reformer. These losses occur due to large temperature gradient-driven heat transfer operations. Considerable waste heat recovery is already used. There is little incentive for R&D as the market for ammonia is not growing very fast and producers are under severe economic pressure. A fair amount of energy recovery is already practised in the global ammonia and urea industry. Improved CO_2 removal is one potential area for reducing energy losses.

The conventional steam reforming process involves a single separation operation, i.e. the removal of CO_2 produced from the use of natural gas feed to the reformer as a source of hydrogen. The single step consumes 25% of the total energy input to the process. Currently, CO_2 removal is accomplished using aqueous amine solutions (e.g., Activated Methyl Di-Ethanolamine, aMDEA[2]) or physical solvents like glycol di-methyl-ethers (Selexol). New, more easily regenerable sorbents, membranes, or ionic liquids could potentially save 30% of the separation energy. The energy efficiency potential of the U.S. fertiliser industry is estimated at 16 PJ/yr[3]. This is very ambitious, but an energy efficiency potential of this order of magnitude might be available in U.S. Ammonia plants that are less efficient than European plants (VKP, 2007).

Following bulk CO_2 removal, traces of CO and CO_2 are catalytically reacted with H_2 to avoid poisoning the ammonia synthesis catalyst. There is significant potential for improvement by:

- Development of a highly efficient means to produce H_2 as feed to the process.
- Development of an ammonia synthesis catalyst that would be resistant to poisoning by CO_2, thus eliminating the CO_2 removal unit and methanation operations entirely. For the USA, this would save 66 PJ/yr. It involves a saving in process energy in addition to separation energy use. However, the CO_2 removal section has developed into a very efficient process step, using energy-efficient aMDEA solvent or physical absorbents. Furthermore often pure CO_2 is needed for other uses like Urea production (VKP, 2007), thereby making it also necessary to have a CO_2 removal step in the ammonia plant This option is deemed to be 'long-term',

[2] The MEA (Mono EthanolAmine) process is characterised by relatively high energy consumption for regeneration. Therefore, the MEA process is not regarded as a BAT (Best Available Technique) process (EFMA, 2000a).

[3] Alternatively, pervaporation could be used to save a much lower amount of energy, viz. 2 PJ/yr in the USA.

Topsoe, Inc. – EX1020
Page 18 of 54

viz. beyond 2020.

Besides the medium- and long-term energy savings achievable in Ammonia production, pervaporation is estimated to save 33% of the separation energy, or 2 PJ/yr in Urea production.

Caustic soda
Caustic soda production contains numerous separation operations including electrolysis, evaporation, and settling. In total these operations comprise over 40% of the energy input to the plant. The production of steam and electricity accounts for another 35% and the heat of reaction consumes nearly 18%. In the separation operations the multiple-effect evaporator associated with re-crystallisation and recycling of NaCl consumes over 18% of the energy feed to the plant and the final evaporator consumes 6%. The final evaporation step may lend itself to the application of membranes or crystallisation to pre-concentrate the NaOH solution prior to final vaporisation resulting in potential savings in the U.S. chemical industry of the order of 4 PJ/yr (2%).

Phosphoric Acid
More than 60% of the total energy input to the Phosphoric Acid production using the dehydrate process is consumed in the grinding of the phosphate containing rock. Just over 30% of the energy is used in separation. This is split roughly into one-third filter operations to remove the insoluble gypsum and two-thirds to concentrate the phosphoric acid by steam-driven water evaporation. Roughly five tons of gypsum is generated for each ton of the acid produced.

Improved filter material and the development of membrane, extraction, and/or crystallisation process for pre-concentration water removal could save ~20% of energy consumed in the filtration and evaporation operations, which is equivalent to 6 PJ/yr in the USA.

Lime and sodium carbonate
Analysis of the lime and sodium carbonate processes did not reveal significant opportunities for energy savings in the separation operations, representing 1% and 16%, respectively, of the total energy input to the processes. However, O_2 enrichment of the air to the kiln was considered to reduce the mass of N_2 heated and released to the stack. It is estimated that membranes to enrich the O_2 by reducing the mass of N_2 by 50% could save 170 kJ/kg of lime or about 3 PJ/yr. The savings in the sodium carbonate industry are estimated at 1 PJ/yr. However, O_2 enrichment for furnaces would generate insufficient net energy savings presumed that the energy consumption for N_2/O_2 separation would be reduced by merely 50%. Substantially more energy-efficient N_2/O_2 separations (presented below at 'nitrogen/oxygen') would be needed for significant net energy savings in the lime industry and - to a lesser extent - the sodium carbonate industry. Therefore, this is a long-term option.

Methanol
Methanol is generally produced from natural gas. Two-thirds of the separation energy is used by the final distillation to remove water from the methanol. It is estimated that liquid/liquid extraction or a hybrid pervaporation process could reduce this energy consumption by 25% or 2 PJ/yr (in the USA).

The other major energy consumer is the reformer furnace. O_2 enrichment of the air fed to the furnace will reduce the mass of N_2 heated and released to the stack. Just like for O_2 enrichment for furnaces in the lime and sodium carbonate industries, substantially more energy-efficient N_2/O_2 separations are needed for significant energy savings of 1 PJ/yr and are therefore 'long term'.

MTBE
MTBE (methyl tertiary-butyl ether) is produced from methanol and isobutylene. As a gasoline additive (oxygenate), it may profit from low-energy separation processes like pervaporation

Topsoe, Inc. – EX1020
Page 19 of 54

(membrane-distillation hybrid system) developed for, e.g., dehydration of natural gas, inorganic acid, Acetic Acid, etc. Application of pervaporation to the manufacture of MTBE would incur a potential energy saving of 2 PJ/yr in the U.S. chemical industry.

Phenol/cumene

Phenol/cumene is produced by one of two processes. The UOP gas phase reaction process is the dominant manufacturing process in the industry and is the reference technology. The separation operations associated with phenol/cumene production are almost exclusively distillation and consume over 60% of the energy fed to the plant. The application of membranes, new extractants/sorbents could significantly reduce the energy consumed in the repeated vaporisation of the components as required by distillation. Estimated energy savings of 30% in each of the four largest distillation operations would incur savings of nearly 9 PJ/yr. This is a conservative estimate and does not include potential associated reduction in the energy consumed in the boiler to produce steam for the distillation columns (constituting ~30% of the total energy input).

Nitrogen/Oxygen

Separation of O_2 and N_2 through membranes would offer significant energy savings. The compressor in the cryogenic process consumes 91% of the energy fed to the process. It is estimated that the application of alternate technology such as membranes could reduce the overall energy consumption by 50%, or 24 PJ/yr. Membranes for separation of O_2 and N_2 appear to offer potential on the medium term only if O_2 is needed today. In case of O_2 enriched air for lime and sodium carbonate (kilns), and reformer furnaces at methanol plants, substantially more energy-efficient N_2/O_2 separations would be needed, which is clearly a long-term prospect.

Topsoe, Inc. – EX1020
Page 20 of 54

3. Energy conservation potential in the Dutch N fertiliser industry

3.1 Introduction

This chapter highlights the energy efficiency potential of the (N) fertiliser industry in the Netherlands, based on §2.3.1 and on additional information with regard to Ammonia production. §3.2 addresses the energy conservation potential for Ammonia, §3.3 for Nitric Acid, and §3.4 for Urea production. §3.5 is a synthesis of the preceding paragraphs for the Dutch N fertiliser industry. Finally, §3.6 gives a roundup of the energy efficiency potential in Ammonia and Urea plants and a comparison to the energy efficiency potential estimated by (Nieuwlaar, 2001).

3.2 Ammonia

In 2002, global Ammonia production was 108 Mt NH_3-N (as contained N) and in 2007 it amounted to 125 Mt NH_3-N (USGS, 2008; Sukumaran Nair, 2006), as exhibited in Table 3.1. The latter figure of 125 Mt NH_3-N is equivalent to approx. 152 Mt NH_3 (Internet Source 4).

Table 3.1 *Global production and production capacity of Ammonia (2002-2003)*

Country	Capacity 2002	Production 2002		Production 2007	
	[Mt N]	[Mt N]	[%]	[Mt N]	[%]
China	30.000	30.100	27.9	39.500	31.6
India	11.500	9.830	9.1	9.200	7.4
Russia	10.900	8.600	8.0	11.000	8.8
USA	13.700	10.100	9.4	8.300	6.6
Indonesia	4.670	4.200	3.9	4.400	3.5
Ukraine	4.090	3.700	3.4	4.200	3.4
Canada	4.520	3.590	3.3	3.700	3.0
Trinidad	3.260	3.300	3.1	5.200	4.2
Others	48.360	34.580	32.0	39.500	31.6
Total	131.000	108.000	100.0	125.000	100.0

Sources: Sukumaran Nair, 2006; USGS, 2008.

Figure 3.1 presents global Ammonia production data from the International Fertilizer industry Association, IFA, which regularly publishes studies and statistics on fertilisers (IFA, 2008). In the last few years, Ammonia production increased by 4%/year on average. A few regions exhibited relatively high growth rates, *inter alia* Oceania 13% and West Asia (M. East) 10%/year.

Topsoe, Inc. – EX1020
Page 21 of 54

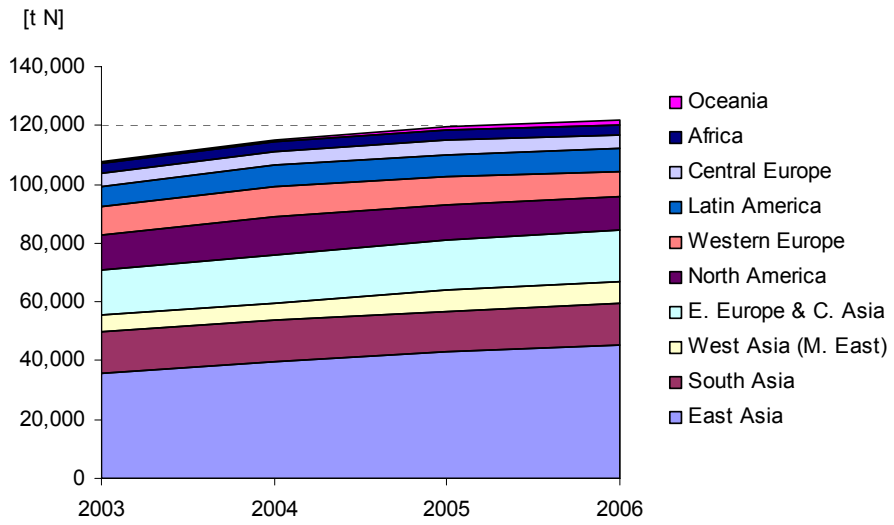

Figure 3.1 *Ammonia production in different world regions, 2003-2006*
Source: IFA, 2008.

Figure 3.2 shows the consumption of nitrogen fertiliser in the world. Clearly, consumption of N fertiliser in Asia is on the rise, whereas consumption in other regions is stable or declining.

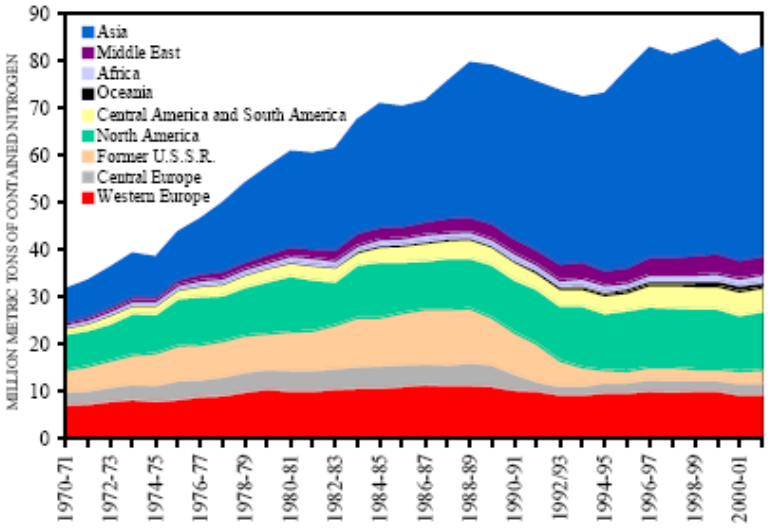

Figure 3.2 *World nitrogen fertiliser nutrient consumption, in crop years [Mt NH_3-N]*
Source: USGS, 2004.

According to (FAO, 2005), the growth of demand for nitrogen fertiliser (currently approx. 1%/a) will not be curtailed by the growth in supply capacity (2.2 %/a) until 2009/10 (Table 3.2).

Table 3.2 *World nitrogen fertiliser supply and demand balance 2005/06 through 2009/10*

	N fertiliser supply, demand and surplus [Mt N]				
(Season)	2005/06	2006/07	2007/08	2008/09	2009/10
Maximum supply	96.5	100.0	103.6	106.0	107.7
Total demand	90.7	92.0	93.2	94.3	95.5
Balance (+ = surplus)	+ 5.8	+ 8.0	+ 10.4	+ 11.7	+ 12.2

Source: FAO, 2005.

The relation between supply and demand for Ammonia is shown in Table 3.3, based on the demand and the supply capability projected by (IFA, 2005a), and capacity data of (USGS, 2004).

Table 3.3 *World Ammonia production capacity and balance 2005-2011*

	N fertiliser demand, capacity, and supply capability [Mt N]			
	2005	2007	2009	2011[a]
Demand	98.1	100.7	103.6	107.2
Production capacity (nameplate)	135.8			
Supply capability of ammonia[b]	119.9	122.7	134.6	
Of which available for fertilisers	99.5	106.7	111.0	
Nitrogen balance (+ = surplus)	+ 1.4	+ 6.0	+ 7.4	

a According to (IFA, 2007), nitrogen nutrient demand will grow by a compounded 7.3% from 2007 to 2011.
b Figures in this row denote maximum supply of Ammonia, accounting for non-availability (maintenance).
Sources: IFA, 2007; IFA, 2005a; IFA, 2005b; USGS, 2004.

According to (IFA, 2007), the consumption of nitrogen nutrients until 2011 will increase by an overall 7.3%, which equals an annual growth rate of 1.8%. Total nitrogen nutrient consumption is forecast at 107.2 Mt N in 2011, compared to 99.8 Mt N in 2007. Urea will take the bulk of the growth in demand. The N supply/demand balance - although tight in the short term - will expand into a surplus situation in subsequent years. In terms of cumulative growth of demand over supply (total capability of Ammonia), supply is forecast to grow by 2.5 %/year. A surplus is expected for the period 2006-2009 if all announced Ammonia plants are completed in time.

The largest manufacturer of Ammonia plants in the world, KBR[4], expects global production capacity to grow to nearly 190 Mt NH_3 (~156 Mt N) in 2010 (Gosnell, 2005), see Figure 3.3.

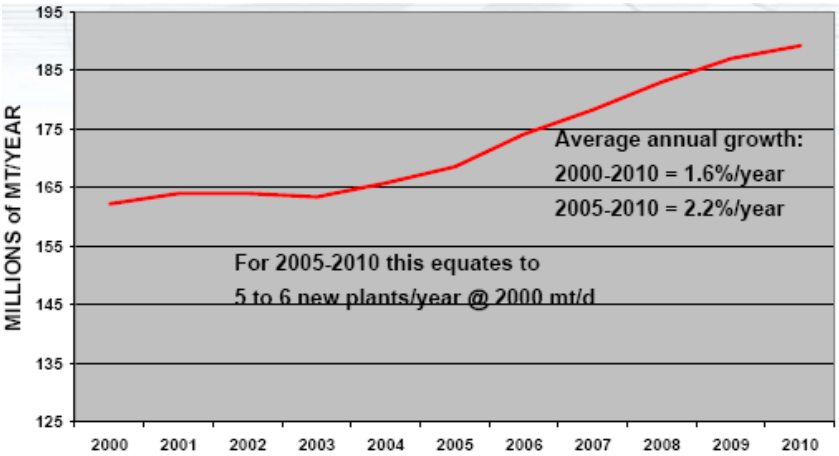

Figure 3.3 *Worldwide Ammonia production capacity*

[4] In 1992, M.W. Kellogg and Ocelot Ammonia Company started Ammonia production using a new ruthenium catalyst deposited on an active carbon support: Kellogg Advanced Ammonia Process, 'KAAP'. KBR - merger of Kellogg and Braun & Root (1999) - accounts for more than 50% of the world's ammonia capacity added since 1965.

Topsoe, Inc. – EX1020
Page 23 of 54

According to the European Fertilizer Manufacturers' Association, EFMA, the demand for N-fertiliser in the EU-25 will increase by about 2.5% in the period 2006-2016 (Figure 3.4). Most of the EU-15 will see a decreasing demand, except Denmark, Austria and Sweden for which slight increases in N-fertiliser consumption are projected - due to particularly bad situations in these countries. In the EU-10, on the other hand, consumption of all nutrients will increase.

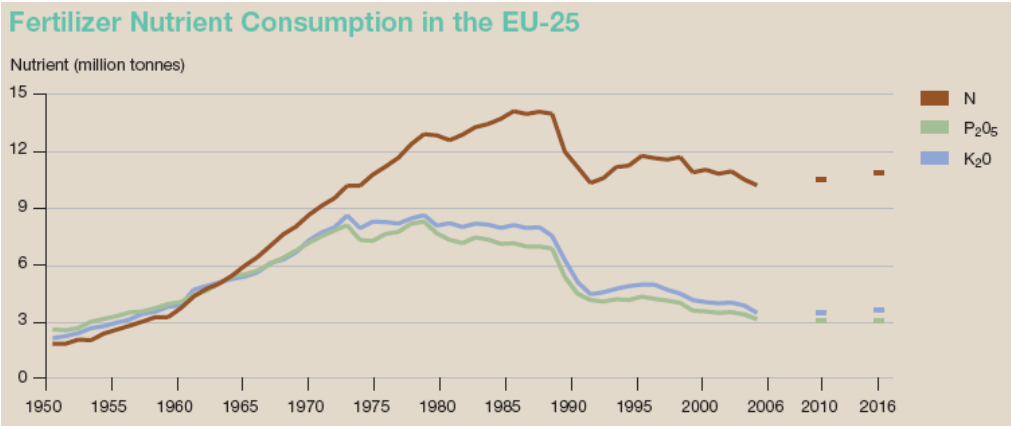

Figure 3.4 *Forecast of fertiliser demand in the EU-25, 2005-2015*
Note: Forecast of EFMA (European Fertilizer Manufacturers' Association).
Source: EFMA, 2006.

Until 1991, Ammonia production in the Netherlands increased approximately at the same rate as worldwide. Then, it declined, whereas production in, e.g., the Middle East (based on stranded gas) increased significantly. Until 1992, Ammonia production in the Netherlands had a share of around 3%, but then it declined steadily to approx. 1.5% (USGS, 2008; Internet Sources 5-6).

Figure 3.5 shows production and capacity data of Ammonia production in the Netherlands. In the period 1992-2005, production declined sharply from 2.588 to 1.800 Mt N - due to closing of two ammonia plants - which corresponds to a capacity utilisation of 90% considering the simultaneous decline in capacity. The Ammonia industry is capable of plant availabilities in the range of 91-92%, according to (Gosnell, 2005).

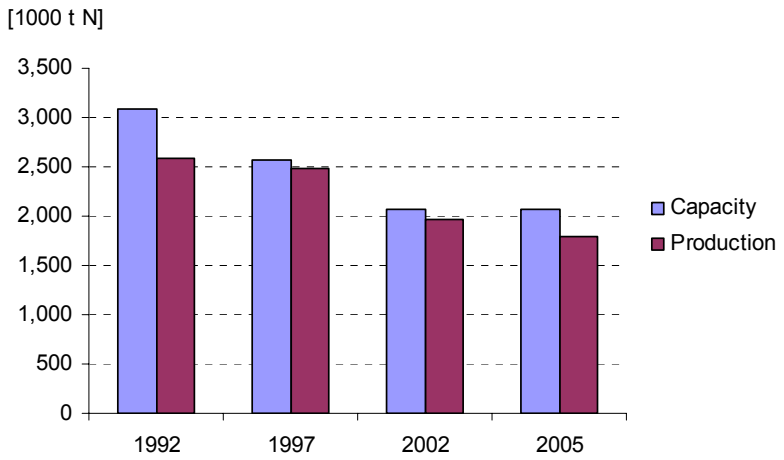

Figure 3.5 *Production and production capacity of Ammonia plants in the Netherlands*
Source: USGS, 2008; Internet Sources 6-7.

In 1996/1997, the combined capacity of units AFA-2 and AFA-3 at Geleen increased by 100 t NH_3/d, by installation of a purge gas converter (Roos et al., 2000). Table 3.4 shows data and estimates for the Ammonia plants in the Netherlands (2005). The average energy efficiency of the Ammonia plants is tentatively estimated at 30.8-31.0 GJ/t NH_3, which is explicated in the following. The capacity of 2,304 kt N/year (equivalent to 6,567 t NH_3/d) is based on (VKP, 2007).

Table 3.4 *Net efficiency (estimate) of Ammonia plants in the Netherlands (2005)*

Company/Site	Code/year built	Licence	Capacity [t NH_3/d]	Capacity [t N/d]	Capacity [kt N/year]	Efficiency [GJ/t NH_3]	References
DSM Agro/ Geleen	AFA-2/ 1971	Bechtel	1,500[a]	1,234	412		Roos et al, 2000; Verduijn and De Wit, 2001; VKP, 2007;
	AFA-3/ 1983	Kellogg	1,500[a]	1,234	412		
	Revamp/ 1997	Haldor Topsøe					
	Subtotal		3,000[a]	2,468	824	~ 31.7	
Yara[b] (formerly Hydro Agri) / Sluiskil	C/ 1973	Braun	1,231	1,012	321		Boot, 1994; Internet Source 7; VKP, 2007
	D/ 1984	Braun	1,750	1,439	535	~ 30.5	
	E/ 1988	Braun	2,004	1,648	625	~ 30.0	
	Subtotal		4,985[c]	4,100	1,480	~ 30.5	
Total			7,985	6,567	2,304	30.8-31.0	

a Simultaneous with the revamp in 1997, which included installation of a purge gas converter and some small creep projects, which increased the combined capacity of AFA-2 and AFA-3 by 100 kt NH_3/year, a solution swap to activated Methyl Di-Ethanol Amine (aMDEA™) was implemented (VKP, 2007).

b Yara and IPCOS deployed APC (Automatic Process Control) systems on the plants D and E at Sluiskil. Benefits generated are about 0.5 to 2% for the combined optimisation objectives (Internet Source 7). Recently, Yara retrofitted plant C with a low-temperature methanation catalyst (VKP, 2007).

c According to (VKP, 2007), the total production capacity of Yara Sluiskil is approx. 4,985 t NH_3/d or 1.75 Mt/a.

Since the introduction in the 1960s of large single-train Ammonia plants, based on centrifugal compressors, manufacturing capacities have increased from 600 to 1,800 metric tonne per day (mtpd) and more, and the energy efficiency decreased from 40 to 30 GJ/t NH_3 (Verduijn and de Wit, 2001). Some process licensors claim, that the net energy use of a new Ammonia plant is 27.6 GJ/t NH_3, an improvement of 30% compared to one designed around 1970. Figure 3.6 presents results of a benchmark study for 66 Ammonia plants by Plant Surveys International (PSI) for IFA (Williams and Al-Ansari, 2007).

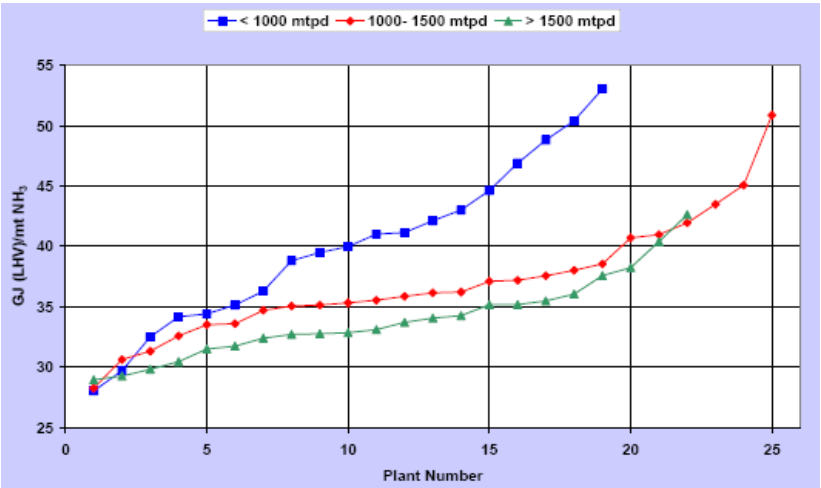

Figure 3.6 *Net energy efficiency of 66 Ammonia plants cf. benchmark of PSI [GJ/t NH_3]*
Source: Williams and Al-Ansari, 2007.

The average net energy efficiency was 36.9 GJ/t NH_3, and that of the 10 best-in-class plants approximately 30 GJ/t NH_3 (Williams and Al-Ansari, 2007; Sukalac, 2005).

Yara's D and E plants (Sluiskil) with a capacity of 1,750 t NH_3/d, and approx. 2,000 t NH_3/d, respectively, are in the first quartile of the corresponding class of the benchmark (green 'triangles' in Figure 3.6). This ranking appears to be confirmed by the fact that Ammonia plants that have been revamped exhibit a net energy efficiency of at best 7.1 Gcal/t NH_3 ≈ 29.7 GJ/t NH_3, according to (Nielsen, 2007a).

The net energy efficiency in BAT - Best Available Technique - reforming processes ranges from 28 to 31 GJ/t NH_3 (Balken, 2007). When using process waste heat in a gas heated reformer, the process itself will not produce enough steam to drive all the compressors. Part of the power demand may be imported, whereby the energy use may be reduced to the practical minimum of 27 GJ/t NH_3 (EFMA, 2000a). Around 1998, the reference was 28.3 GJ/t NH_3 (Kongshaug, 1998). Advanced processes - KBR's KAAP*plus*™, Uhde's Dual Pressure[5], and Haldor Topsøe's Leading Concept - show efficiencies of 27.5 to 29 GJ per tonne of NH_3 (Table 3.5).

Table 3.5 *Energy use of state-of-the-art Ammonia plants with credit for steam or utilities*

Company	BAT 1998	Lurgi	Haldor Topsøe	ICI	KBR	ICI	KBR
Process	Autothermal reforming?	MEGAMMONIA[R]	Low Energy Ammonia	Leading Concept	KAAP*plus*™		Dual Pressure
Size of plant [mtpd]		Up to 4,000	650-2,050	450	Up to 1,850	230-1,350	500-3,300
Plants worldwide		-	60	N/A	>200	3	14
Feed [GJ/t NH_3]	25.0						
Fuel [GJ/t NH_3]	5.6						
Steam [GJ/t NH_3]	-2.5						
Electricity [GJ/t NH_3]	0.2						
Energy use [GJ/t NH_3]	28.3	29.5	27.6-28.8	31.1	27.9[a]	29.3	27.6-30.1[b]
[Gcal/t NH_3]	6.76		6.6-6.89	7.2	6.673[a]	7.0	6.6-7.2[b]

a Based on an Ammonia/Urea plant in China with a capacity of 450,000 t/a of ammonia (Yexin, 2004).

b A net efficiency of 7.1-7.2 Gcal/t NH_3 ≈ 29.7-30.1 GJ/t NH_3, in the Middle East corresponds to 6.95-7.05 Gcal/t NH_3 ≈ 29.1-29.5 GJ/ t NH_3 in Western Europe with approx. 10°C lower cooling water temperatures (Humphrys, 2005; Nielsen, 2007a).

Sources: Nielsen, 2007a; Balken, 2007; Lippmann and Frisse, 2004; Yexin, 2004; Okuzumi et al., 2001; Christensen, 2001; Humphrys, 2005; Uhde, 2006; Kongshaug, 1998; DoE, 2005; Internet Sources 8-9.

The typical range of heat consumption in a chemical absorption process is 30-60 MJ/kmol CO_2 or 1.34-2.67 MJ/Nm^3 CO_2 (EFMA, 2000a). The heat consumption of aMDEA™ is 40 kJ/mol and of Selexol 10 kJ/mol CO_2 (Verduijn and de Wit, 2001). Energy use, *including primary energy related to electricity*, of UOP's 'Benfield hybrid LoHeat process' (physical absorption) is 865 kcal or 3.62 MJ/Nm^3 CO_2 (Furukawa and Bartoo, 1997). As new, more easily regenerable sorbents, membranes, etc. could potentially save 33% of the separation energy (§3.2.4), the energy use for CO_2 removal could decrease by 1.1 MJ/Nm^3 CO_2 or 0.6 GJ/t NH_3 (EERE, 2005). In 2020, the practical minimum energy use (e.g., by membranes for CO_2 removal) could be approximately 26.4 GJ/t NH_3. According to (Nieuwlaar, 2001), this figure could be 26.1 GJ/t NH_3.

In Table 3.6 shows tentative outcomes of a hypothetical 'upgrading' of three Ammonia plants.

[5] Uhde's proprietary Ammonia process was developed by exploiting catalyst technology from UK-based Synetix. During 2003 Johnson Matthey acquired Synetix from ICI and formed Johnson Matthey Catalysts.

Topsoe, Inc. – EX1020
Page 26 of 54

Table 3.6 *Potential energy saved by reduced separation energy for three Ammonia plants*

Company	Site	Code/ year built	Energy efficiency before 'upgrade' [GJ/t NH_3]	Energy efficiency after 'upgrade' [GJ/t NH_3]	Estimated investment cost per GJ of energy saved [€/GJ•a]
DSM Agro	Geleen	AFA-2/ 1971			
		AFA-3/ 1983			
		Revamp/ 1997			
		Subtotal	~ 31.7	~ 31.4	50[a]
Yara	Sluiskil	C/ 1973			
		D/ 1984			
		E/ 1988			
		Subtotal	~ 30.5	~ 30.1	50 [a]
Total			~ 31.0	~ 30.6	

a According to (VKP, 2007), the energy efficiency of the Ammonia plants of DSM Agro and Yara Sluiskil is already high in international perspective: between 30 and 32 GJ/t NH_3, compared to BAT 28-31 GJ/t NH_3. Therefore, further energy efficiency improvement - at a disproportionate high investment cost estimated at 50 €/GJ•a - does not seem to be economically viable.

Such a kind of upgrading of three rather efficient Ammonia plants could be characterised by:

- Two-third of the capacity - approximately 5,250 out of 7,985 t NH_3/d - to be upgraded.
- Estimated energy conservation (primarily natural gas): approximately 1 PJ/year.
- Tentative estimate of investment: € 50 mln. Additional operational costs: € 1.25 mln/a.
- 'Upgraded' ammonia plants may remain in the top of the IFA benchmark (Figure 3.6).
- However, the pay-out-time is too long (approx. 7 years) to warrant economical feasibility.

While most Ammonia plants operate at scales in excess of 300 kt/a (900 metric tonne per day, mtpd), improvements in technology enable small-scale manufacture for products aimed at nearby markets by sharing of hydrogen from the syngas generator and the co-production of oxygen for the nitrogen required for the Ammonia plant. In 1999, Petronas Fertiliser became the world's first grassroots plant to co-produce Methanol and Ammonia at Kedah, Malaysia, according to (Othman Abu Bakhar, 1998) and (Internet Source 10). The plant is able to vary methanol production between zero and 200 tonnes per day (0-73 kt/a) and ammonia between 1,125 and 1,350 tonnes per day (400-500 kt/a).

According to (Gregory et al., 2006), (IFDC, 2006), and (Nieuwlaar, 2001), Ammonia plants suitable to substitute current capacity ranging from 900 t NH_3/d (Yara's C plant) to 1,750 t NH_3/d (E plant) could incur investment costs of 175-275 k$/mtpd or $18-28/GJ•a (Table 3.7).

Table 3.7 *Investment cost of Ammonia(Urea) plants for a range of plant capacities*

Option		1	2	3a	3b	4	5	6	'Notore' [a]
Capacity	(compared to NL)				'high'		'low'		
Capacity	[mtpd]	3,300	2,750	2,000	1,829	1,500	1,000	500	1,500
Energy efficiency	[GJ/t NH_3]	(27.2)[b]	(27.4)[b]	(27.6)[b]	27.8	(28.0)[b]	(28.2)[b]	(28.4)[b]	N/A
Investment cost	[US$ mln]	520	477	397	320	343	276	169	100 [a]
Specific investment cost	[1000$/mtpd]	158	173	199	175	229	276	339	67 [a]
	Per GJ input [$/GJ•a]	16.6	18.1	20.5	18.0	23.3	28.0	34.0	

a The since 1996 closed 'Notore plant' of NAFCON (National Fertilizer Company of Nigeria), will -after *refurbishment*- initially produce about 1,700 t of urea per day or 600,000 tons per year (Internet Source 11).

b Except for '3b' - a Trinidad plant (Internet Source 12) - efficiencies are tentative ('best state-of-the-art').

Sources : Gregory and Bunb, 2006; IFDC, 2006; Nieuwlaar, 2001; Internet Sources 11-12.

Topsoe, Inc. – EX1020
Page 27 of 54

Ammonia production in the EU decreased tremendously in the last 10-15 years, except in Belgium and Germany (Abram and Forster, 2005). As fuel prices rise, manufacturers are shutting down production capacity, and move to China[6] and India -based on indigenous coal- or the Middle East (McFarlane et al., 2006). China has several plants based on coal and coke (Koss, 2006) with, e.g., coal gasification technology of Shell (Chhoa, 2006). In the USA, the Great Plains synfuel plant produces 400 kt NH_3 annually from lignite (Thomas and Parks, 2006)[7].

In the 1970s and 1980s, relatively cheap feedstock gas served as a base load for the development of onshore and shallow water offshore gas fields: the nitrogen and methanol industries in the Netherlands served as a base load for the newly developed North Sea gas fields (Prince, 2007). Today, in Europe and North America natural gas is dramatically more expensive than in, e.g., Russia[8] (Larson, 2005). Ammonia plants in Europe, however, are more energy efficient than in Russia (Figure 3.7), and much more than in China (Rong, 2000; Jigang, 2004; Brouwer and Mennen, 2004).

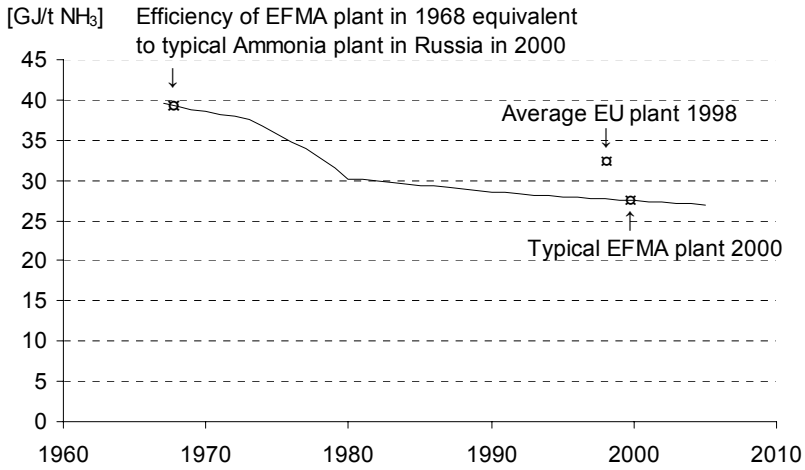

Figure 3.7 *Energy requirement of BAT Ammonia plants 1968-2005*
Note: In 2000, energy use of Russian plants corresponded to the state-of-the-art of 1968 (~40 GJ/t NH_3).
Sources: Kongshaug, 1998; Sukalac, 2005; Aldinger, 2001; EFMA, 2000a.

In practically all industrialised and populous countries where energy has to be imported -in Western Europe but also the USA- feedstock gas industries are coming into direct competition with power generators in a market with sharply increased natural gas prices. Producers of Ammonia or Methanol are generally not able to pass their costs simply to customers, as they operate on the world market with low-cost producers in the Middle East, Russia, etc. Figure 3.8 shows that natural gas is much more expensive in OECD countries than in the Middle East and Russia.

[6] China's energy resource is characterised by 'abundant in coal, in-sufficient in gas and shortage in oil' (Li, 2004).
[7] In 1997, 13.5% of global production capacity was based on coal or coke and 77% on natural gas (Balken, 2007).
[8] Russia will increase its domestic gas prices from $1.41/GJ in 2006 to $1.90/GJ in 2010 (Aldinger, 2006).

Topsoe, Inc. – EX1020
Page 28 of 54

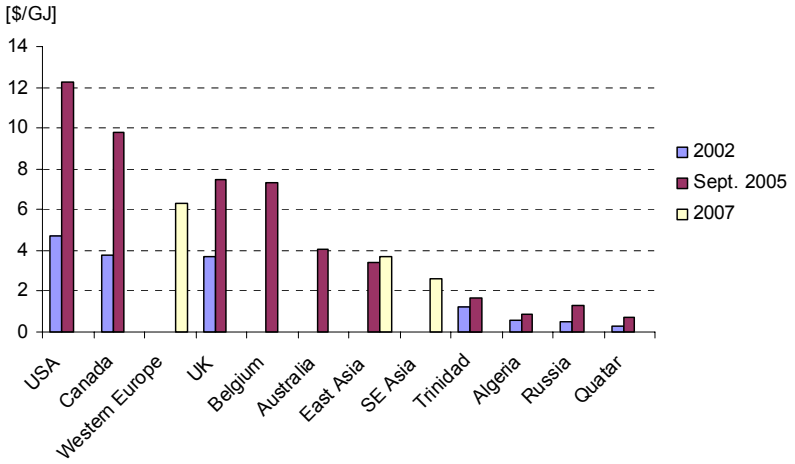

Figure 3.8 *Industrial gas prices ($/GJ) in various countries and world regions*

Notes: For 2002, based on IEA, World Bank, EIA, and private companies (NCEP, 2004), for 2005 on Bloomberg, Economic Times, Fertecon, Financial Times, Pace, Platts (Larson, 2005), and for 2007 on EIA, WGI, NYMEX, British Sulphur (Prince, 2007).

Sources : Prince, 2007 ; NCEP, 2004 ; Larson, 2005 ; Internet Source 13.

Figure 3.9 shows the development of the price of natural gas and of Ammonia in the USA between 1985 and mid 2006 (Huang, 2007). The volatile and upward trend in natural gas prices from 2000 to 2006 has led to a 17% decline in the domestic aggregate supply of ammonia. During that period, U.S. ammonia production declined 44%, while U.S. imports increased 115%.

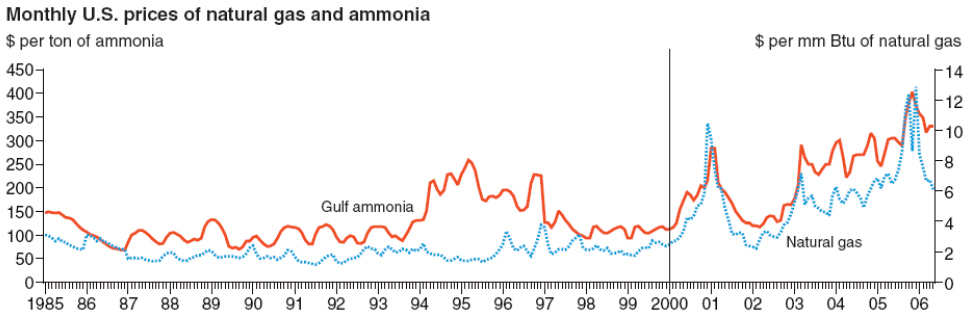

Figure 3.9 *Monthly prices of Ammonia ($/ton, Gulf) and of natural gas ($/MBtu) in the USA*

Source: Huang, 2007.

(Gosnell, 2005) suggest that production capacity may shift to the Middle East and Latin America where gas is available at lower cost. (Larson, 2005) reports that within 42% of the Canadian firms shifting investment offshore was mentioned as an option, actively discussed, planned or actually implemented. In the USA, 17 Ammonia plants were shut down and six temporarily idled in the period 1999-2004 (Linneman et al., 2006; Internet source 14). High gas prices may continue to pressure firms to shift investments offshore (Kramer, 2005; Gosnell, 2005).

3.3 Nitric Acid

In 1991, the capacity of Nitric Acid (HNO_3) manufacturing plants in the USA was 11 Mt/a (EPA, 1997), and in 1999 it stood at 8.1 Mt/year (Internet Source 15). Production was 6.42 Mt/year in 2001, and 6.76 Mt/year in 2002 (Kramer, 2002). Production of Nitric Acid in the EU

Topsoe, Inc. – EX1020
Page 29 of 54

is about 20 Mt/year in approximately 80 plants. Figure 3.10 shows a flow-sheet of an integrated Ammonia/Nitric Acid/Ammonium Nitrate plant (Kirova, 2000).

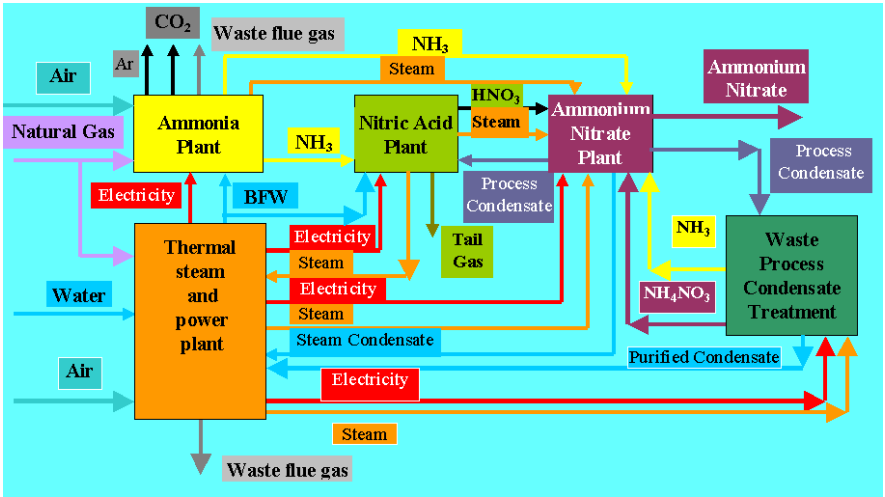

Figure 3.10 *Flow diagram of Nitric Acid and Ammonium Nitrate production*
Source: Kirova, 2000.

Nitric Acid (NA) is commercially available in two forms: azeotropic NA (69% HNO_3) and concentrated NA (> 95 % HNO_3), based on different processes. Azeotropic NA is produced in far greater quantities than concentrated NA (Wiesenberger, 2001). All NA produced for fertiliser production is below azeotropic concentration, more specifically in the range of 53-62%. Figure 3.11 shows applications of Nitric Acid (Maurer and Bartsch, 2001). NA used in the manufacturing of Ammonium Nitrate (AN), Calcium Nitrate (CN) and Potassium Nitrate, which, in turn, are used either as straight fertiliser or mixed into compound fertiliser. Ammonium Nitrate (AN) production in the USA comprises 80 percent of NA produced, Adipic Acid 9%, and aniline and toluene 11% (Internet Source 15). As production of Ammonium Nitrate (AN) is stagnant, Nitric Acid demand in the USA is expected to grow by merely 0.8% annually.

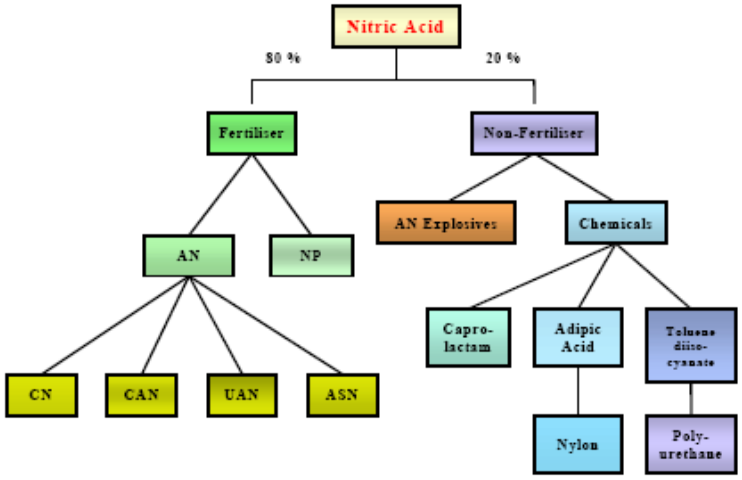

Figure 3.11 *Applications of Nitric Acid*
Note: NP = Nitro Phosphate; CAN = Calcium Ammonium Nitrate; UAN = Urea-Ammonium Nitrate; ASN = Ammonium Sulphate Nitrate.
Source: Maurer and Bartsch, 2001.

Most Nitric Acid is produced by catalytic oxidation of ammonia at high pressure and high temperature. All plants producing Nitric Acid are based on the same basic chemical reactions: oxidation of ammonia with air to give Nitric Oxide (Nitric Monoxide, NO), and oxidation of the Nitric Oxide (NO) to Nitrogen Dioxide (NO_2) and absorption in water to give a solution of Nitric Acid. The oxidation of ammonia also yields (other) by-product nitrogen oxides which are emitted as a tail gas, namely NO and NO_2. Nitrous Oxide (N_2O, a strong greenhouse gas) in the tail gas is a by-product of the ammonia oxidation. The reaction from ammonia to Nitric Acid is exothermic and contributes to a considerable net steam export, which may be considered an energy 'credit' (EFMA, 2000b).

The Nitric Acid process has also undergone significant energy improvements during the last decades, from atmospheric combustion pressure, via mono medium pressure units to dual pressure plants operating with high absorption pressure. The reaction from Ammonia to 60% Nitric Acid theoretically releases 28.5 GJ/t HNO_3-N. However, the energy lost in gas compressors and cooling reduces the net steam export.

Consequently, a modern dual pressure Nitric Acid plant has a net energy export of 11 GJ/t N as high pressure (60 bar) steam. The average net energy export for European plants is about 7 GJ/t N, while the best plants 30 years ago had a net export of 5 GJ/t N. If all the released thermal energy is converted to electricity in a steam turbine, the net energy export is reduced by approximately 65% (Kongshaug, 1998). According to (Wiesenberger, 2001) state-of-the-art Nitric Acid production is characterised by a high degree of energy recovery: a net energy output of 11 GJ/t N as 60 bar steam or 2.4 GJ/t HNO_3 (100 %), as exhibited by Figure 3.12.

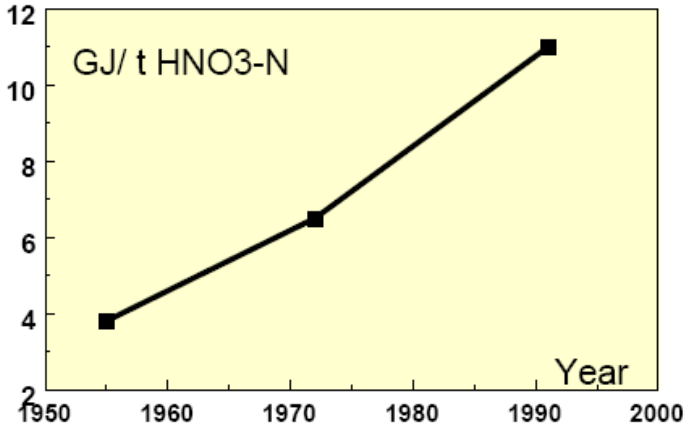

Figure 3.12 *Net energy export of Nitric Acid plants [GJ/t HNO_3-N]*
Sources: Kongshaug, 1998; Wiesenberger, 2001.

By varying the process parameters (heat exchanger surfaces, temperatures, steam flow rates etc.), a process simulator enables the operator to steadily improve the energy efficiency of the plant. This approach has been applied to the nitric acid process for the last four decades, turning a power deficit into a power surplus. Nowadays, however, several practical limits have been reached stopping further significant improvements in energy efficiency. The two major limitations are the inlet temperatures to the tail gas turbine (today around 700°C) and maximum steam pressure (100 bar). The future improvement of the conventional plant is expected mainly to be due to improvements in efficiencies of turbomachinery, according to (Nielsen, 2007b).

PDC, assisted by DSM Agro and Yara, has developed an energy benchmark system for Nitric Acid plants (VKP, 2007). The calculation method is based on an exergy model. In 2004, a benchmark with 83 Nitric Acid plants worldwide was performed. The best plant had an energy

efficiency of -1.83 GJ/t HNO_3 (energy export) and the most inefficient plant had an energy efficiency of +3.8 GJ/t NHO_3 (energy import). Only about 43% of the plants had net energy export. (Internet Source 16) shows that the investment cost of a 100% Nitric Acid plant (Mono pressure process) with a capacity of 900 mtpd in the Czech Republic was about €41 mln (Koruna 1.3 bln). Stagnant markets for AN and Nitric Acid give little incentive for R&D (Appendix C).

3.4 Urea

Urea is produced from NH_3 and CO_2. It is the fertiliser with the highest concentration of nitrogen (46%). From 1959, Stamicarbon in the Netherlands commercialised urea production with full recycle of unreacted reactants in terms of water soluble coal-ammonia salts, resulting in a granulated product by splashing a strong Urea solution in a hollow tower against the air flow - a process called prilling (Internet Source 17).

More recently, process development focused on reducing production costs and emission levels. Emission reduction and introduction of 'total recycling' increased energy consumption, but heat recovery and reduction of utilities reduced overall energy consumption. Today, different Urea processes have almost the same energy requirement (Kongshaug, 1998). The Stamicarbon and Snamprogetti processes captured approximately 76% of the world market (Internet Source 18). Urea, also known as carbamide or carbonyl diamide, is marketed as a solution or in solid form. Most Urea solution produced is used in fertiliser mixtures, with a small amount going to animal feed supplements. Most solids are produced as prills or granules, for use as fertiliser or protein supplement in animal feed, and in plastics manufacturing (Internet Source 19).

In 2000, 62 Urea plants were in operation in Western Europe. The total capacity in 1999/2000 was about 5.8 Mt Urea (EFMA, 2000c). Downstream use of Urea comprises (Mitsubishi, 2004):

- Fertilizer bagging and blending plants.
- Livestock nutrition (cattle/poultry).
- Melamine.
- Coatings and laminate.
- Formaldehyde.
- Building products (particle board and melamine).
- Fuel additives.

Urea is produced from liquid NH_3 and gaseous CO_2 at high pressure and temperature. Both reactants often are obtained from an ammonia-synthesis plant; Urea plants tend to be co-located with Ammonia plants. The CO_2 is a by-product stream, which is vented from the CO_2 removal section of the ammonia plant. The two feed components are delivered to the high-pressure urea reactor usually at a molar ratio of greater than 2.5 to 1. Urea is formed as follows:

$$2NH_3 + CO_2 \leftrightarrow NH_2COONH_4 \text{ (1) and}$$
$$NH_2COONH_4 \leftrightarrow CO(NH_2)_2 + H_2O \text{ (2)}$$

where NH_2COONH_4 is ammonium carbamate. The formation of NH_2COONH_4 and the dehydration to urea take place simultaneously for all practical purposes (USGS, 2004). Reaction 1 is fast, highly exothermic, and goes essentially to completion under normal industrial processing conditions, while reaction 2 is slow, endothermic and usually does not reach thermodynamic equilibrium under processing conditions (Internet Source 18).

In 2002, the Urea production capacity stood at 61.2 Mt N/a, or 131.2 Mt Urea/a (USGS, 2004). In 2002, 1.8% of the global Ammonia production was produced in the Netherlands. The corresponding figure for Urea production was 0.9%, according to (USGS, 2004), see Table 3.8.

Topsoe, Inc. – EX1020
Page 32 of 54

Table 3.8 *Global production and production capacity of Urea (2002)*

Country	Capacity 2002 [Mt N]	Production 2002 [Mt N]	Production 2002 [%]
China	16.300	16.000	31.1
India	9.810	8.580	16.7
U.S.	3.880	3.360	6.5
Indonesia	3.380	2.820	5.5
Russia	2.470	2.110	4.1
Canada	1.940	1.850	3.6
Pakistan	1.930	1.730	3.4
Ukraine	1.550	1.490	2.9
Saudi Arabia	1.200	1.240	2.4
Bangladesh	1.370	1.070	2.1
Egypt	1.120	1.080	2.1
Qatar	0.642	0.799	1.6
Iran	0.812	0.733	1.4
Brazil	0.794	0.594	1.2
Malaysia	0.591	0.567	1.1
Argentina	0.584	0.517	1.0
Venezuela	0.786	0.497	1.0
Netherlands	0.520	0.480	0.9
Romania	1.170	0.444	0.9
Germany	1.070	0.430	0.8
Libya	0.418	0.390	0.8
Others	8.863	4.619	9.0
Total	61.200	51.400	100.0

Source: USGS, 2004.

In a modern total 'recycling' urea process, conversion of ammonia to solid urea requires 7.2 GJ/t N (3.3 GJ/t Urea). (Kongshaug, 1998) assumes that the average requirement for European plants is 9 GJ/t N, and that the best plants 30 years ago operated at 10 GJ/t N. Production of Urea is commonly linked to an Ammonia plant due to the need of CO_2.

Table 3.9 shows the energy use of Urea plants. The energy use of Urea plants is exhibited for three levels of energy efficiency in case of European technology, viz. 'old', 'average', and 'modern'. With regard to Urea production in the Netherlands, it is assumed here that the energy requirement is between 'average' and 'new' of (Kongshaug, 1998) for European plants.

Table 3.9 *Energy efficiency Ammonia and Urea plants in Europe c.q. Netherlands 2002*

Product	Material input	Unit	European technology (Kongshaug, 1998) 'Old'	'Average'	'New'	Average NL Technology 2002
Ammonia (NH_3)	Feed & fuel	[GJ/t N]	50.0	39.0	32.8	~ 37.7 [a]
Urea	Natural gas	[GJ/t N]	10.0	9.0	7.2	~ 8.1 [b]
Urea	Fuel (excl. feed)	[GJ/t N]	60.0	48.0	40.0	~ 45.8 [b]

a Energy efficiency for Ammonia production in 2002 estimated at ~ 31.0 GJ/t NH_3 ≈ 37.7 GJ/t N.
b Energy use for Urea production in the Netherlands ~ 8.1 GJ/t N (total energy requirement ~ 45.8 GJ/t N).
Source: Kongshaug, 1998.

3.5 N fertiliser industry in general

Regarding Nitric Acid it was noted that current processes are based on significant heat recovery. Lower temperature catalysts for ammonia oxidation could be an area for research. However, incentives for further energy efficiency improvement are lacking in a stagnant Nitric Acid market.

With regard to Ammonia, developing a synthesis catalyst that is resistant to poisoning by CO_2, thus eliminating the CO_2 removal unit and methanation entirely is a long-term (>2020) option. (Energetics Inc., 2000) suggests that many low-cost, high-return investments have already been made, or as (Larson, 2005) notes on Canada: '*There are no easy reductions in energy consumption, or low hanging fruit here*'. Deeper efficiency improvement demands drastic changes in process design and innovative R&D. In Table 3.10, the energy use for Ammonia and Urea is compared with the total energy use of the fertiliser industry in the Netherlands in 2002 based on (CBS, 2006).

Table 3.10 *Total energy requirement for Ammonia & Urea in the Netherlands (2002/2005)*

	Specific energy use 2005 [a]	Production 2002	Specific energy use [a] (for NH_3 see Table 3.5)	Production 2002	Energy requirement 2002	Energy requirement 1986
	[GJ/t N]	[1000 t N]	[GJ/t product]	[kt product]	[PJ]	[PJ]
Ammonia (NH_3)	~ 37.6	1,970	~ 31.0	2,395	~ 74.17	93.0
Urea excl. ammonia (NH_3)	8.10	480	3.78	1,029	3.89	2.5
Total Ammonia & Urea					~ 78.06	
Other fertiliser industry [b]					~ 8.15	
Other (mainly NPK)						4.7
Fertiliser industry (CBS)					~ 86.21[c]	100.2

a Merely natural gas, assuming an Ammonia/Urea plant with net steam or electricity import or export.
b Other than Ammonia and Urea, and *in 2002* including combined heat and power at ammonia plants.
c In 2002, the energy use of the fertiliser industry was 86.77 PJ. Considering the efficiency improvement due to application of Automatic Process Control at units D and E at Sluiskil since 2002, the total energy use has been lowered by 0.56 PJ in order to present a more representative figure for 'other fertiliser industry'.

Table 3.6 showed a tentative estimate of the energy efficiency potential - approximately 1 PJ - of more efficient technology for CO_2 separation at three energy-efficient Ammonia plants in the Netherlands. (EERE, 2005) presents an estimate of the energy efficiency potential of pervaporation - hybrid technologies based on membranes and distillation - for the U.S. Urea production of 2 PJ (§2.3.1). Based on the ratio between Urea production in the Netherlands (480 kt N) and the USA (3,260 kt N), approx. 0.3 PJ could be conserved in Dutch Urea production plants. As it is technically easier and more economical to replace distillation with hybrid systems than to totally replace it with an alternative technology, the investment for pervaporation at Urea plants is estimated at no more than € 15/GJ•a and additional O&M cost at € 0.3/GJ (Table 3.11).

Topsoe, Inc. – EX1020
Page 34 of 54

Table 3.11 *Energy efficiency potential Ammonia and Urea production in the Netherlands*

	Stage	Total energy requirement 2002	Tentative estimate of investment	Tentative estimate of specific investment	Tentative estimate of additional O&M	Tentative estimate of additional O&M cost
		[PJ]	[€ mln]	[€/GJ•a]	[€ mln/a]	[€/GJ]
0	Status 2002, Table 3.10	78.06				
A	Pervaporation for Urea production	77.75 (-0.31)	~ 4.7	15	~ 0.1	0.3
B	'Upgrade' Ammonia production (regenerable sorbents, etc.)	77.06 (-1.000)	~ 50	50	~ 1.25	1.25
A+B	Pervaporation (Urea) & 'upgrade' Ammonia	76.75 (-1.31)	~ 54.7	41.8	~ 1.35	~ 1.0

3.6 Roundup and comparison to efficiency potential of ICARUS-4

The efficiency gains made in nitrogen based fertiliser production in the Netherlands confirm to a large extent the energy efficiency potential according to (Nieuwlaar, 2001), 'ICARUS-4'. The main changes in *Ammonia* production plants in the Netherlands since 1997 are (Figure 3.13):

- Revamping of AFA-2 and -3 of DSM Agro at Geleen (1997 and 2001), by amongst others installation of a pre-reformer and a purge gas converter, which increased production capacity from 2,720 to approximately 2,820 t NH_3/day and some small creep projects, which increased production capacity further. Simultaneously, a solution swap to Methyl Di-Ethyl Amine (aMDEA™) was implemented. An advantage is that operation usually leads to a very low CO_2 slip. It is assumed that the average efficiency of DSM's plants was reduced from approximately 33 GJ/t NH_3 before the revamp operation to approximately 31.7 GJ/t NH_3 after that, when production capacity was 3,000 t/d. The investment cost of the total 'revamping' operation was approx. NLG 100 mln (≈ € 45 mln), according to (VKP, 2007).
- Closure of the Ammonia plant of Kemira Oy at Rozenburg, with a production capacity of 1,500 t NH_3/day, by the end of 2000 because of adverse market conditions (Nieuwlaar, 2001).
- Revamping of Yara's unit C in 1996 and application of Automatic Process Control (APC) at Yara's units D and E in 2005. This has been taken together as one step in 1996/1997 (Figure 3.13).

Figure 3.13 highlights the development of the production capacity of Ammonia plants in the Netherlands since 1995.

Topsoe, Inc. – EX1020
Page 35 of 54

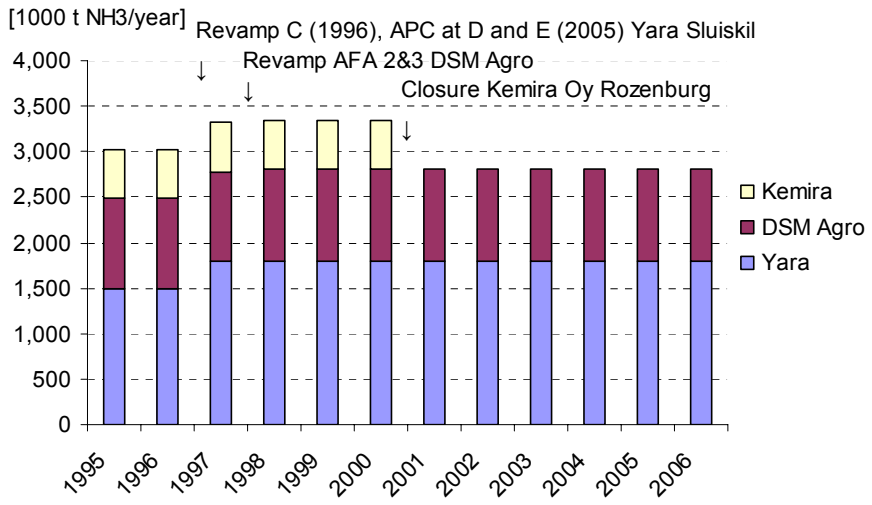

Figure 3.13 *Production of Ammonia plants in the Netherlands [1000 t NH_3/year]*

The energy efficiency potential in Table 3.11, which is rather theoretical (membranes, etc. for separation of CO_2 at ammonia plants) as the technology is not yet developed, is compared to the energy efficiency potential with regard to electricity based on (Nieuwlaar, 2001) in Table 3.12.

Table 3.12 *Energy conservation with regard to electricity in the Dutch fertiliser industry*

Category	Energy use 1995	Efficiency improvement potential	Specific investment cost		Explanation
	[PJ_e] (%)	[PJ_e] (%)	[€/GJ_e•a]	[€/GJ_p•a]	
Pumps	1.55 (42)	0.25 (16)	16	6.4	Approx. 92% of pumps are oversized and controlled by throttling or bypass adjustment. Adjustable Speed Drives (ASD) may reduce consumption of pumps by 16%.
Machine drives	0.89 (24)	0.02 (2)	225	91	Adjustable Speed Drives (ASD) might reduce consumption of machine drives by 2%.
Fans	0.67 (18)	0.07 (10)	45.5	18	High efficiency fans may reduce electricity consumption of fans by 10%.
Compressed air	0.48 (13)	0.10 (20)	16	6.4	Electric compressors are mainly used for compressed air. Savings may be achieved by diminishing leakages, applying different pressured levels, lowering working pressure and using colder air. The energy saving is estimated at 20%.
Lighting	0.11 (3)	0.04 (35)	25	10	Efficient lamps, fittings, and lighting control systems are examples of measures to reduce energy consumption of lighting. The energy saving is estimated at 35%.
Total/ average	3.70 (100)	0.47 (13)	29	12	These measures are assumed not implemented before 1995.

Note: (Nieuwlaar, 2001) presents data in (€/GJ_e•a) as well as (€/GJ_p•a), taking into account a conversion efficiency for electricity generation.
Source: Nieuwlaar, 2001.

With regard to Ammonia production (Nieuwlaar, 2001) presents the following energy efficiency potential (Table 3.13).

Table 3.13 *Energy conservation with regard to Ammonia production in the Netherlands*

Category	Penetration 1995 (percentage of capacity)	Efficiency improvement potential	Specific investment cost	Additional O&M cost	Explanation
	[%]	[%]	[€/GJ•a]	[€/GJ]	
Pre-reformer	18	4	7.5		In 1990 Kemira Oy installed a pre-reformer.
Hydrogen recovery	10	0.8 GJ/t NH_3	10	0.25	Hydrogen recovery by membranes is installed at 10% of capacity.
Process integration	50	4	15	0.5	Penetration is assumed to be 50% in 1995.
Auxiliary steam generation		2.5	45	1.5	Changing boilers to 'hot stand-by' reduces the stand-by capacity.
CO_2 removal with improved solvents	20	30-60 MJ/kmol CO_2	3		Replacement of, e.g., potassium carbonate by aMDEA. Penetration is assumed to be 20% in 1995.

Note: According to (VKP, 2007), aMDEA was introduced in Dutch ammonia plants about 10 years ago.
Source: Nieuwlaar, 2001.

Topsoe, Inc. – EX1020
Page 37 of 54

Furthermore, (Nieuwlaar, 2001) notes that in modern Urea plants energy use may be as low as 2.75 GJ/t Urea. Energy use in Dutch Urea plants is estimated at 3.05 GJ/t Urea. Therefore, an energy efficiency improvement of 11% is deemed achievable. This would entail a specific investment cost of €25/GJ. Urea production is assumed to account for 10% of the energy use for fertiliser production in 1995.

According to (Nieuwlaar, 2001), Nitric Acid and CAN plants may export steam, thereby reducing the energy use of fertiliser production in 1995 by an estimated 4%. The specific investments costs incurred are estimated at €75/GJ.

Topsoe, Inc. – EX1020
Page 38 of 54

4. Conclusions and recommendations

Conclusions

This study focuses on the energy efficiency potential of the Nitrogen (N) fertiliser industry. First, the study presents an overview of the energy efficiency potential of several 'resource-intensive' industries in the USA, based on two in-depth studies. Secondly, the energy efficiency potential of the N fertiliser industry in the Netherlands is analysed, drawing on the generic studies for the USA and country-specific studies and data for the Netherlands. The N fertiliser industry in the Netherlands encompasses Ammonia production, Urea production, etc.

The time horizon is 2020. Therefore, technologies with a long-term potential - e.g., technologies that are in the R&D stage - are not taken into account. The trends observed for the N fertiliser industry as well as the energy efficiency potential that results from the analysis, may be used for models employed by ECN Policy Studies. However, the energy efficiency potentials resulting from the analysis have to be used with care as they prove to be difficult to quantify.

The Dutch N fertiliser industry mainly consists of ammonia plants in Geleen (DSM Agro) and Sluiskil (Yara) that have been built in the 1970s and 1980s when the use of gas for fertiliser production was favoured in order to provide a base load for gas production from the Dutch continental shelf. From the 1990s, several important changes occurred with regard to ammonia production in the Netherlands. First, one of the three ammonia plants in Sluiskil (Yara) was 'revamped', thereby increasing the production capacity. Later on, Yara's other ammonia plants were equipped with Automatic Process Control, and their production capacity was increased too. Secondly, in 1997, DSM executed a revamp of its twin units at Geleen, increasing their capacity and decreasing the net energy use (including utilities, viz. steam and electricity) significantly. Thirdly, in 2000 the ammonia plant operated by Kemira in Rozenburg was closed. In 1991 also the DSM Agro IJmuiden ammonia plant was closed. The production capacity of the five remaining ammonia plants (three in Sluiskil and two in Geleen) increased substantially from 1997 onwards.

Ammonia plants in the Netherlands have an estimated energy use for feedstock and utilities (steam and electricity) of on average 31 GJ/t NH_3. Dutch ammonia plants are energy efficient in comparison to plants in other countries of the world. This can be attributed to continuous energy efficiency improvement at the ammonia plants in Geleen - installation of a purge gas converter, simultaneous solution swap to aMDEA, installation of a pre-reformer, etc - and Sluiskil - solution swap to aMDEA, installation of Automatic Process Control. Recently, a benchmark study for 66 Ammonia plants by Plant Surveys International (PSI) for IFA showed that the average net energy efficiency of these 66 plants was 36.9 GJ/t NH_3, and that of the 10 best-in-class plants approximately 30 GJ/t NH_3.Yara's D and E plants (Sluiskil), are in the first quartile of the corresponding class of the benchmark. This ranking appears to be confirmed by the fact that Ammonia plants that have been revamped exhibit a net energy efficiency of at best approx. 29.7 GJ/t NH_3.

A significant energy efficiency improvement might be the application of new, more easily regenerable sorbents, membranes, etc. instead of the current CO_2 separation by aMDEA. If this type of technology would be developed and applied at three relatively modern ammonia plants in the Netherlands, the energy conserved could amount to 1 PJ/year. However, at this moment this technology is not available yet. Another option is application of pervaporation for Urea production. This could save approximately 0.3 PJ/year, and the pay-out time could be shorter than 7 years (in case of membranes for Ammonia production).

Topsoe, Inc. – EX1020
Page 39 of 54

With regard to Nitric Acid (NA), PDC - assisted by DSM Agro and Yara - has developed an energy benchmark system. The calculation method is based on an exergy model. In 2004, a benchmark with 83 Nitric Acid plants worldwide was performed. The best plant had an energy efficiency of -1.83 GJ/t HNO_3 (energy export) and the most inefficient one had an energy efficiency of +3.8 GJ/t NHO_3 (energy import). Only 43% of the plants had net energy export.

For Dutch Ammonia and Nitric Acid plants, it seems that 'There are no easy reductions in energy consumption, or low hanging fruit…' as an industrial expert noted. An exception may be pervaporation for Urea production. Economically viable energy savings in the N fertiliser industry may amount to 0.5 PJ/year or more, including 0.3 PJ/year from pervaporation for Urea plants.

Recommendations

Cross-cutting technologies like separation technologies with potential for energy conservation in the N fertiliser industry in the Netherlands deserve due attention. This is because studies on energy efficiency improvement in the past mainly focused on incremental energy efficiency improvement. It is noted, that in particular studies in the framework of 'ICARUS-4' of Utrecht University (Utrecht Centre for Energy Research, UCE) remain valuable from the point of view of the methodological approach. However, much of the 'low hanging fruit' already has been harvested, particularly in the N fertiliser industry. Also, profound changes have occurred in the conditions governing the Dutch energy economy, viz.:

- Introduction of carbon trading in January 2005: the European Emission Trading Scheme.
- A steep increase of oil and gas prices, culminating in a temporary maximum oil price of approximately $78 per barrel in 2006 and up to maximum of approx. $145 per barrel in 2008.
- An increased attention for energy conservation and renewable energy - next to other options like advanced coal and nuclear power - in order to combat climate change, reduce the dependence on imported oil and gas, and reduce the cost of energy for the economy.

It may be recommended to take a fresh look at the potential for energy efficiency improvement in (sectors of) the energy or resource intensive industry, based on a distinctive approach:

- Determination of the position of the industrial sector from an international point of view, e.g., taking into account benchmark studies performed or other (international) literature studies.
- Consideration of energy efficiency improvements achieved, like those reported in this study for the Dutch N fertiliser industry, as well as consideration of plans with regard to energy conservation and capacity expansion (e.g., through revamping) in the medium term.
- Quantification of energy conservation potential through a supply curve, if possible (as practised by Utrecht University in the framework of ICARUS-4.

In the past, Utrecht University has applied such an approach for several industrial sectors. However, for the N fertiliser industry their study is more or less outdated. Thus, the energy efficiency potential has to be checked again based on, e.g., benchmark studies, if available, taking into account competition in an international framework, including carbon trading etc.

Topsoe, Inc. – EX1020
Page 40 of 54

Acronyms and abbreviations

CAN	Acrylonitril
ADt	Air Dried tonne
aMDEA	Activated Methyl Diethanol Amine
AN	Ammonium Nitrate
APC	Automatic Process Control
ASD	Adjustable Speed Drives
ASN	Ammonium Sulphate Nitrate
BAT	Best Available Technique
BPF	Berghuizer Papierfabriek
CAN	Calcium Ammonium Nitrate
CapEx	Capital Expenditures
CCE	Cost of Conserved Energy
CCS	CO_2 Capture and Storage
CHP	Combined Heat and Power
CN	Calcium Nitrate
DMFC	Direct Methanol Fuel Cell
DoE	Department of Energy (USA)
EC	European Commission
EDC	Ethylene dichloride
EEI	Energy Efficiency Index
EFMA	European Fertilizer Manufacturers' Association
EO	Ethylene oxide
EU ETS	European Emission Trading Scheme
GHG	Greenhouse gas
IFA	International Fertilizer industry Association
LPG	Liquefied petroleum gas
MEA	Mono ethanolamine
MTBE	Methyl Tertiary Butyl Ether
NA	Nitric Acid
NGL	Natural gas liquid
NP	Nitro Phosphate
O&M	Operation and Maintenance
OpEx	Operating Expenditures
PSA	Pressure Swing Adsorption
PTA	Purified Terephthalic Acid
RD&D	Research, Development, and Demonstration
RTD&D	Research and Technological Development and Demonstration
SHC	Specific Heat Consumption
UAN	Urea-Ammonium Nitrate
UCE	Utrecht Centre for Energy Research
VBE	Verificatiebureau Benchmarking Energie-efficiency

Topsoe, Inc. – EX1020
Page 41 of 54

References

Abram, A., D.L. Forster (2005): *A Primer on Ammonia, Nitrogen Fertilizers, and Natural Gas Markets*. Department of AED Economics, The Ohio State University, USA, September 30, 2005, p. 17.

Aldinger, H. (2006): *The European Fertilizer Sector in a Changing Domestic and Global Environment*. 12th AFA International Annual Conference, Cairo, Egypt, 6-8 February 2006.

Aldinger, H. (2001): *The Fertilizer Sector in Western Europe - Market Trends and Industry Outlook*. 2nd International Conference on The Chemical and Petrochemical Industries of Russia, the CIS and Central & Eastern Europe, Budapest, Hungary, 23-24 April 2001, p. 15.

Balken, H. van (2007): *Best Available Techniques for the production of ammonia*. IFA 2007 Technical Committee Meeting - Workshop on Energy Efficiency and CO_2 Reduction Prospects in Ammonia Production, 12-14 March 2007, Ho Chi Minh City, Viet Nam.

Boot, H. (1994): *Sectorstudie kunstmestindustrie*. Project NEEDIS, TNO Apeldoorn, The Netherlands, October 1994.

Brouwer, M., J. Mennen (2004): *Stamicarbon Revamping Strategy in China*. IFA Technical Conference, Beijing, China, 20-23 April 2004.

CBS (2006): CBS Energiebalans Industrie. CBS, The Hague, 2006.

Chhoa, T. (2006): *Shell Clean Coal Energy in Asia-Pacific*. Shell, VP Clean Coal Energy Asia-Pacific Shell Gas & Power, April 10, 2006. Http://www.gasification.org/Docs/2006_Papers/34CHHO.pdf.

Choate, W. et al (2005): *Materials for Separation Technologies*. ORNL, USA, 2005. http://www.eere.energy.gov/industry/imf/pdfs/separationsreport.pdf#search=%22Materials%20for%20separation%20technologies%22.

Christensen, P.V. (2001): *Design and Operation of Large Capacity Ammonia Plants*. 4th Conference for Development and Integration of Petrochemical Industries in the Arab States, Bahrain, May 7-8, 2001.

DoE (2005): *Separation Technology R&D Needs for Hydrogen Production in the Chemical and Petrochemical Industries*. U.S. Department of Energy (DoE), Washington DC, December 2005.

Dorgan, J.R. et al (2003): *Energy Saving Separations Technologies for the Petroleum Industry: An Industry-University-National Laboratory Research Partnership*. Chemical Engineering and Petroleum Refining Dept. Colorado School of Mines, Golden, Colorado, USA, March 2003.

EERE (2005): *Materials for Separation Technologies: Energy and Emission Reduction Opportunities*. Energy Efficiency and Renewable Energy (EERE), Department of Energy, USA, May 4, 2005.

EFMA (2000a): *Production of Ammonia - Best Available Techniques for Pollution Prevention and Control in the European Fertilizer Industry*. European Fertilizes Manufacturers Association (EFMA), Brussels, Belgium, 2000.

EFMA (2000b): *Production of Nitric Acid*. EFMA, Brussels, Belgium, 2000.

EFMA (2000c): *Production of Urea and Urea Ammonium Nitrate*. EFMA, Brussels, Belgium, 2000.

EFMA (2006): Forecast of Food, Farming and Fertilizer Use in the European Union 2006-2016. EFMA, 2006. http://cms.efma.org/EPUB/easnet.dll/GetDoc?APPL=1&DAT_IM=000E50&DWNLD=EfmaForecast06Site.pdf

Energetics Inc. (2000): *Energy and Environmental Profile of the U.S. Chemical Industry*. Energetics Inc., Columbia, Maryland, USA, May 2000, p. 24.

EPA (1991): *Alternative Control Techniques Document - Nitric and Adipic Acid Manufacturing Plants*. U.S. EPA, Office of Air Quality, Planning, and Standards, Research Triangle, NC. EPA-450/3-91-026, 1991.

FAO (2005): *Current World Fertilizer Trends and Outlook to 2009/10*. Food and Agriculture Organization (FAO), Rome, Italy, 2005.

Furukawa, S.K., R.K. Bartoo (1997): *Improved Benfield Process for Ammonia Plants*. UOP, Des Plaines, Illinois, USA, 1997. http://www.uop.com/objects/85ImprvdBenfieldAmm.pdf.

Gosnell, J. (2005): *Efficient Ammonia Production*. Hydrogen Conference, Argonne National Laboratory. KBR, USA, 13 October 2005.

Gregory, D.I., B.L. Bumb (2006): *Factors Affecting Supply of Fertilizer in Sub-Saharan Africa*. Agriculture and Rural Development Discussion Paper 24, the World Bank, Washington DC, USA, 2006.

Huang, W.-Y. (2007): *Impact of Rising Natural Gas Prices on U.S. Ammonia Supply*. United States Department of Agriculture (USDA), August 2007. Http://www.ers.usda.gov/Publications/WRS0702/

Humphrys, M. (2005): *The Effect of Johnson Matthey Catalysts on the Uhde Ammonia Flowsheet*. 18th AFA International Annual Technical Conference & Exhibition, Casablanca, Morocco, 5-7 July, 2005.

IEA (2006) : *Energy Technology Perspectives 2006*. IEA, Paris, France, 2006.

IFA (2008): *Production and International Trade Committee: World Ammonia Statistics by Region*. International Fertilizer Industry Association (IFA), Paris, France, 2008. http://www.fertilizer.org/ifa/content/download/7832/121893/version/1/file/2006_ammonia_public.xls

IFA (2007): *Medium-Term Outlook for Global Fertilizer Demand, Supply and Trade 2007-2011 - Summary Report*. 75th IFA Annual Conference, Istanbul, Turkey, 21-23 May 2007, A/07/88, June 2007.

IFA (2005a): *Medium-Term Outlook for Global Fertilizer Demand, Supply and Trade - Summary Report*. IFA, Paris, France, June 2005.

IFA (2005b): *World Agriculture and Fertilizer Demand, Global Fertilizer Supply and Trade 2005-2006 - Summary Report*. IFA, Paris, France, December 2005.

IFDC (2006): *IFDC Corporate Report 2005/2006*. International Fertilizer Development Center (IFDC), Muscle Shoals, Alabama, USA, 2006, p. 25.

Jigang, T. (2004): *Energy Saving and Capacity Increase Retrofit for a large-scale Ammonia Plant*. IFA Technical Conference, Beijing, China, 20-23 April 2004.

JVP (2004): *Chemical Bandwidth Study*. JVP International, Inc., New York, USA, December 2004.

Topsoe, Inc. – EX1020
Page 43 of 54

Kirova, Z. (2000): *Thermodynamic Estimation of the Environmental Impact of Mineral Fertilizers Production*. University "Prof. Assen Zlatarov", Bourgas, Bulgaria, 2000. Http://www.chem.ntnu.no/…/R8/14.30-16.00/_THERMODYNAMIC-ESTIMATION-OF-THE-ENVIRONMENTAL-Kirova-Yordanova.ppt.

Kongshaug, G. (1998): *Energy Consumption and Greenhouse Gas Emissions in Fertilizer Production*. Hydro Agri Europe, Norway, 20 July 1998. Http://www.fertilizer.org/ifa/publicat/PDF/1998_biblio_65.pdf.

Koss, U. (2006): *Rectisol expands its Scope in China*. A brief glance on Lurgi's syngas-based activities in China presented at GTC Conference 2006. Washington DC, USA, 2006.

Kramer, D.A. (2005): *Nitrogen*. United States Geological Survey (USGS) Minerals Yearbook 2005, USA, 2005. http:://minerals.usgs.gov/minerals/pubs/commodity/nitrogen/nitromyb05.pdf.

Kramer, D.A. (2002): *Nitrogen*. USGS Minerals Yearbook 2002, USA, 2002. Http://minerals.usgs.gov/minerals/pubs/commodity/nitrogen/nitromyb02.pdf

Larsen, J., et al. (2003) : *Large-scale Hydrogen Plants*. Uhde and UOP's experience. 2003 Spring Meeting, New Orleans, USA, March 30-April 03, 2003. Http://www.uop.com/objects/LgScaleHydroPlnts41b.pdf.

Larson, R. (2005): *The Demand Crunch. Submission to Council of Energy Ministers Meeting*. St. Andrews, Brunswick, Canada, September 20, 2005. Http://www.cfi.ca/files/PDF/CIEC_CEM_2005-English.PDF.

Li, Z. (2004): *Coal-based Ammonia Plants, New Technology and Trend in Ammonia Production in China*. IFA Technical Conference, Beijing, China, 20-23 April 2004.

Linneman, L. et al. (2006): *Ammonia Chain*. University of Wisconsin - Eau Claire, Wisconsin, USA, 17 November 2006. Http://www.uwec.edu/carneymj/Adobe%20handouts/Ammonia%20Chain.pdf.

Lippmann, D., N. Frisse (2004): *First Application of the Uhde Dual Pressure Ammonia Process for the 3300 Mtpd Ammonia Plant for SAFCO in Saudi Arabia*. IFA Technical Conference, Beijing, China, 20-23 April 2004. Http://www.fertilizer.org/ifa/publicat/PDF/2004_tech_beijing_frisse.pdf.

Maurer, R., U. Bartsch (2001): *Enhanced Plant Design for the Production of Azeotropic Nitric Acid*. Heraeus Nitric Acid Conference, Johannesburg, South Africa, November 29-30, 2001.

McFarlane, J., S. Robinson: *Alternative Feedstocks in Chemicals Manufacturing*. Green Chemistry and Green Engineering Conference American Chemical Society, Washington DC, USA, June 27, 2006. Http://www.ornl.gov/~webworks/cppr/y2001/pres/124993.pdf.

Mitsubishi (2004): *Brunei Ammonia/Urea Manufacturing Project*. Mitsubishi Corporation, Japan, 20 September 2004. Http://www.pivot.com.au/zone_files/PDFs/BruneiConsortiumPresentation.pdf.

NCEP (2004): *NCEP Technical Appendix Chapter 4: Expanding Energy Supplies*. Energy and Environmental Analysis, Inc., on behalf of National Commission on Energy Policy (NCEP), Arlington, Virginia, USA, May 2004, p. 109.

Nielsen, S.E. (2007a): *Future Energy Efficiency and CO_2 Reduction Potential*. IFA 2007 Technical Committee Meeting - Workshop on Energy Efficiency and CO_2 Reduction Prospects in Ammonia Production, 12-14 March 2007, Ho Chi Minh City, Viet Nam.

Topsoe, Inc. – EX1020
Page 44 of 54

Nielsen, J.S. (2007b): *Energy Efficiency Measures in Fertilizers Sites*. IFA 2007 Technical Committee Meeting - Workshop on Energy Efficiency and CO_2 Reduction Prospects in Ammonia Production, 12-14 March 2007, Ho Chi Minh City, Viet Nam.

Nieuwlaar, E. (2001): *ICARUS-4 - Sector study for the chemical industry*. NWS-E-2001-19, Utrecht, The Netherlands, September 2001.

Okuzumi, N. et al. (2001): *Start-up of the World Largest Ammonia Plant*. Nitrogen 2001, Tampa Bay, Florida, USA, February 18-21, 2001. http://www.topsoe.com/site.nsf/vALLWEBDOCID/KVOO-5PGF6C/$file/Ammonia4-Start-upoftheWorldsLargestAmmoniaPlant.pdf.

Othman Abu Bakhar, S. (1998): *Economics of Co-Production of Methanol in Ammonia/Urea Complex*. Petronas Fertilizer, Kedah, Malaysia, 1998. Http://www.fertilizer.org/ifa/publicat/PDF/1998_biblio_96.pdf.

Park, M.S., et al. (2002): Oxidative dehydrogenation of ethylbenzene with carbon dioxide over zeolite-supported iron oxide catalysts. *Res.Chem.Intermed.*, Vol. 28, 5, 2002, pp. 461-469.

Prince, A. (2007): *Initiating New Projects in the Ammonia Sector*. IFA 2007 Technical Committee Meeting - Workshop on Energy Efficiency and CO_2 Reduction Prospects in Ammonia Production, 12-14 March 2007, Ho Chi Minh City, Viet Nam.

Rong, M. (2000): *The Development of Fertilizer Industry in China*. International Workshop on Economic Policy Reforms and Agricultural Input Markets: Experiences, Lessons, and Challenges. Cape Town, South Africa, October 16-20, 2000.

Roos, W.F., et al. (2000): *Increasing Ammonia Plant Capacity by Utilizing Purge Gas from Two Adjacent Ammonia Plants*. 45th Annual Safety in Ammonia Plants and Related Facilities Symposium, Tucson, Arizona, USA, September 11-14, 2000.

Sukalac, K.E. (2005): *Technology Transfer to reduce Climate Change Impacts from the Fertilizer Industry*. Knowledge transfer to reduce GHG emissions: lessons from the fertilizer industry. COP11/MOP1 UNFCCC, Montreal, Quebec, Canada, 6 December 2005. Http://regserver.unfccc.int/seors/file_storage/yuq4s8s77zfrj8l.pdf.

Sukumaran Nair, M.P. (2006): Ammonia industry - today and tomorrow. *Hydrocarbon Processing*, April 2006, pp. 47-55.

Thomas, G., G. Parks (2006): *Potential Roles of Ammonia in a Hydrogen Economy*. U.S. Department of Energy (DoE), Washington DC, February 2006.

Turk, B.S. et al (2001) : *Novel Technologies for Gaseous Contaminants Control*. National Energy Technology Laboratory (NETL), Department of Energy, Washington DC, USA, September 2001.

Uhde (2006): *Ammonia*. Uhde, Dortmund, Germany, 2006. Http://www.uhde.biz/cgi-bin/byteserver.pl/archive/upload/uhde_brochures_pdf_en_5.00.pdf.

USGS (2008): Mineral Commodity Summaries: Nitrogen (fixed) — Ammonia. U.S. Geological Survey (USGS), January 2008. Http://minerals.usgs.gov/minerals/pubs/commodity/nitrogen/mcs-2008-nitro.pdf.

USGS (2004): *Mineral Commodity Profiles: Nitrogen*. United States Geological Survey (USGS), Open-File Report 2004-1290, 2004.

Verduijn, W., J. de Wit (2001): *Energy Conservation: Key to Survival for Fertiliser Producers*. The International Fertiliser Society, London, May 10, 2001, ISBN 0 85310 1159.

VKP (2007): *Commentaar conceptstudie ammoniakindustrie Nederland*. Vereniging van Kunstmest Producenten (VKP), Leidschendam, the Netherlands, B-07-00043-MD, October 2007.

Topsoe, Inc. – EX1020
Page 45 of 54

Wiesenberger (2001): *State-of-the-art for the Production of Nitric Acid with regard to the IPPC Directive*. Umweltbundesamt GmbH (Federal Environment Agency Ltd), Monographien Band 150, Vienna, Austria, 2001.

Williams, G., F. Al-Ansari (2007): *IFA Benchmarking of Global Energy Efficiency in Ammonia Production*. IFA 2007 Technical Committee Meeting - Workshop on Energy Efficiency and CO_2 Reduction Prospects in Ammonia Production, 12-14 March 2007, Ho Chi Minh City, Viet Nam.

Yexin, Y. (2004): *Blue Print of CNOOC Oriental Chemical Park: Construction of CNOOC Fertilizers Complex*. IFA Technical Conference, Beijing, China, 20-23 April 2004. Http://www.fertilizer.org/ifa/publicat/PDF/2004_tech_beijing_yang_yexin.pdf.

Internet sources

1. Http://www.chemicalprocessing.com/articles/2006/025.html.
2. Http://www.pubs.acs.org/cen/coverstory/83/8340membranes.html.
3. Http://www.physorg.com/news10485.html.
4. Http://www.dis.anl.gov/ceeesa/programs/hydrogen_markets.html.
5. Http://minerals.usgs.gov/minerals/pubs/commodity/nitrogen/nitromcs05.pdf.
6. Http://minerals.usgs.gov/minerals/pubs/commodity/nitrogen/nitromcs06.pdf.
7. Http://www.ipcos.be/news.html (November 7, 2005).
8. Http://www.iffco.nic.in/applications/iffcowebr5.nsf/622a5cc0ab1610f6e52566a500151fbb/4c4c41bda8dce6c7652570c40047bd41?OpenDocument.
9. Http://www.lurgi.com/website/fileadmin/user_upload/pdfs/09_Ammoniak-E.pdf.
10. Http://www.chemlink.com.au/ammonia.htm.
11. Http://www.africafertilizersummit.org/Online_Press_Room/NOTORE.pdf.
12. Http://www.innovations-report.de/html/berichte/unternehmensmeldung/bericht-59615.html.
13. Http://www.cfi.ca/files/publications/facts_and_issues/cfi_issues-energy_FINAL.PDF.
14. Http://minerals.usgs.gov/minerals/pubs/commodity/nitrogen/nitromcs04.pdf.
15. Http://www.epa.gov/nitrousoxide/pdfs/adipic_nitric_n2o.pdf.
16. Http://www.chemicals-technology.com/projects/lovochemie/
17. Http://www.niik.ru/urea-eng.htm.
18. Http://www.cheresources.com/ureamodeling.pdf
19. Http://www.epa.gov/ttn/chief/ap42/ch08/final/c08s02.pdf.

Topsoe, Inc. – EX1020
Page 46 of 54

Appendix A Energy conservation potential of the U.S. chemical industry

In the framework of the 'Industrial Technologies Program' (ITP), JVP International, Inc. conducted a study on exergy analysis with regard to the U.S. chemical industry (JVP, 2004). Analysis was performed on 25 chemical process technologies associated with the selected chemical products shown in Table B.1. The total potentially recoverable energy identified for the 25 processes is approximately 900 PJ, using average values for multiple technologies when applicable (see Table B.2). Recoverable energy is assumed to be of high enough quality to warrant recovery, *regardless of economic feasibility*. In order to put this potential in perspective, the recoverable energy is compared to the process energy (Table B.2). The next paragraphs address the energy conservation potential for the 25 chemical technologies distinguished in more detail, except for Ammonia production which is covered by §2.3.2.

Ethylene

There are two processes for manufacturing of ethylene, viz. cracking of propane and cracking of naphtha. Cracking of propane is predominant in the USA, based on Natural Gas Liquids (NGLs). In Europe, cracking of naphtha is common[9]. The Kellogg process for cracking of naphtha is more exothermic, and requires less input process energy than the Braun process for cracking of propane. Exergy losses in the Kellogg process, however, are double in cracking and quenching due to the higher compression ratio used (36 versus 10 bar). Total process energy required is about 12 times greater than the theoretical minimum. Substantial losses occur in the de-methaniser column due to the condenser, where the coolant is ethylene refrigerant. Another significant source of losses is cracking and quenching, mostly due to the cracking furnaces and the large towers where temperature differences create exergy losses. The cracked gas compressor inter-stage coolers are large sources of losses.

Large opportunities exist due to high-volume production and energy-intensity of current processes. R&D priorities are (JVP, 2004):

- Low-temperature, more selective retrofit reaction systems to replace pyrolysis and eliminate need for quenching.
- Novel separation concepts (hybrid systems) coupled with new production processes.
- Dehydrogenation or oxide-hydrogenation based on ethane feedstock (dependent on price of NGLs versus petroleum).
- New routes to ethylene based on alternative feedstocks (ethanol, methanol, methane/syngas, higher olefins) coupled with simpler recovery and purification technologies.

Propylene

The endothermic process analysed in (JVP, 2004) is based on the Fina technology for production of propylene from light naphtha fractions (described in the patent literature but not yet commercialised). Most propylene is now produced as a co-product of ethylene in naphtha crackers, and it is uncertain if dedicated production of propylene from naphtha will ever be commercially popular. Total process energy is about 5 times greater than the theoretical minimum (in case of ethylene production, it is 12-13 times greater than theoretical minimum). Most energy losses occur during production separation, mostly due to debutaniser column and coolers. Some level of energy recovery may be possible in this section. The largest exergy loss occurs in the reactor subsection, mostly in the feed pre-heater, coolers and the reactor. Large internal losses in this section are due to wide differences in input and output stream temperatures.

[9] 70% of the feedstock for ethylene in the USA is ethane/propane, whereas in Europe naphtha/condensate feedstocks account for 75% of production (Internet Source 20).

Topsoe, Inc. – EX1020
Page 47 of 54

Table A.1 *Energy & exergy analysis of 25 chemical technologies U.S. chemical industry*

Process	Process energy input Q_{IN}	Process exergy input Q_{EX}	Actual process exergy Q_W [a]	Theoretical minimum energy	Recoverable energy Q_{LOSS} (= Q_{EX} - Q_W)	Ratio of Q_{LOSS}/Q_{IN}	Recoverable energy [b]
	[MJ/kg]	[MJ/kg]	[MJ/kg]	[MJ/kg]	[MJ/kg]	[%]	[PJ/yr]
Ethylene (Braun)	20.13	12.87	0.76	1.51	12.11	60	286.2
Ethylene (Kellogg)	18.93	11.71	0.50	1.51	11.21	59	264.8
Ammonia	10.69	8.24	-0.82	0.96	9.06	86	121.3
Ethylene Oxide	18.01	13.34	-15.63	1.71	28.97	161	103.8
Propylene	10.58	7.09	2.16	1.97	4.93	47	71.1
Terephthalic Acid	4.46	2.69	-11.00	7.09	13.69	307	58.3
MTBE	20.62	5.98	-0.31	0.29	6.29	31	56.6
Methanol (ICI LP process)	11.36	2.03	-10.57	1.87	12.60	111	41.7
Acrylonitrile from propane	12.52	3.24	-30.59	12.81	33.83	270	41.5
Methanol (Lurgi process)	5.29	1.96	-9.61	1.87	11.57	219	38.3
Formaldehyde	1.62	0.27	-7.46	1.87	7.73	476	32.6
Acrylonitrile from propylene	10.15	2.37	-18.64	10.13	21.02	207	25.7
Nitric Acid	0.54	0.48	-3.26	4.54	3.74	694	25.3
Styrene (Fina/Badger)	7.83	4.33	0.86	0.79	3.47	44	17.3
Ethylbenzene (Lummus)	3.55	2.67	-0.50	0.64	3.17	89	17.1
Styrene (Lummus/Monsanto/UOP)	10.93	3.95	0.71	0.79	3.24	30	16.1
Ethylbenzene (Mobil/Badger)	4.13	2.24	-0.74	0.64	2.98	72	16.1
p-Xylene (Isomerisation)	7.51	3.96	-0.31	0.05	4.27	57	16.0
Carbon Dioxide	4.85	1.18	-0.99	N/A	2.17	45	15.3
Vinyl Chloride	6.21	2.27	0.34	0.33	1.93	31	15.1
Acetic Acid	3.75	1.83	-1.19	1.01	3.02	80	6.5
Cumene ($AlCl_3$ Cat.)	2.61	1.02	-0.56	1.22	1.58	61	5.5
Cumene (Zeolite Cat.)	2.47	0.87	-0.58	1.22	1.45	59	5.1
Cumene (SPA Cat.)	1.89	0.76	-0.57	1.22	1.34	71	4.6
Butadiene	3.21	1.09	0.13	N/A	0.96	30	1.8

a A net chemical conversion exergy inflow (negative sign) signals an exothermic reaction.
b The recoverable energy (PJ/yr) is *regardless of economic feasibility*.
Source: JVP, 2004.

Topsoe, Inc. – EX1020
Page 48 of 54

Table A.2 *Production (2002), energy use & conservation potential U.S. chemical industry*

Chemical	Production [kt/yr]	Process energy Q_{IN} [PJ/yr]	Recoverable energy [a, b] [PJ/yr]	Q_{LOSS}/Q_{IN} [c] [%]
Ethylene	23,630	461.5	275.5	60
Propylene	14,420	152.7	71.1	47
Ammonia	13,150	140.9	121.3	86
MTBE	8,980	185.3	56.6	31
Vinyl Chloride	7,850	48.7	15.1	31
Carbon Dioxide	7,030	34.1	15.3	45
Nitric Acid	6,760	3.7	25.3	694
Ethylbenzene	5,400	20.9	16.6	80
Styrene	4,990	46.6	16.7	36
Terephthalic Acid	4,260	19.0	58.3	307
Formaldehyde	4,220	6.9	32.6	476
p-Xylene	3,760	28.3	16.0	57
Ethylene Oxide	3,580	64.5	103.8	161
Cumene	3,490	12.1	5.1	42
Methanol	3,310	27.3	40.0	145
Acetic Acid	2,180	8.1	6.5	80
Butadiene	1,860	6.0	1.8	30
Acrylonitrile	1,220	13.8	33.6	242
Total	120,100	1,280.0	910.0	71

a Using average values for multiple technologies when applicable.
b The recoverable energy (PJ/yr) is *regardless of economic feasibility*.
c Ratio may exceed 100% due to exothermic reaction (net chemical conversion exergy-inflow Table B.1).
Source: JVP, 2004.

MTBE

The exothermic, 'first generation' process for MBTE manufacture uses a liquid acid to catalyse the etherification of isobutylene with methanol. Other technologies practised use an acid ion exchange resin catalyst in a reactor or within a distillation column (catalytic distillation). Process energy input is more than 70 times the theoretical minimum. Nearly all exergy losses occur in the recovery section due to distillation. Reactor effluent is distilled, with MTBE as the bottom product. Losses are due to the low temperature of the overhead streams requiring cooling water, and large temperature differences among the overheads, feed, and bottoms stream temperatures. In the USA, MTBE is being phased out as a fuel (gasoline) additive for environmental reasons.

Vinyl Chloride

The endothermic Vinyl Chloride production process is based on the Hoechst et al process for gas phase pyrolysis (de-hydro-chlorination) of ethylene dichloride (EDC). The total process input energy is about 19 times greater than the theoretical minimum energy required. The reaction is carried in the tubes of a fired furnace and the resulting effluent gases are at a higher temperature than input gases. The largest energy losses are in the quench section where reaction effluent is cooled from over 480°C to 50°C, a temperature too low for steam generation. EDC recovery also has relatively high energy losses (source: four distillation columns). The low-pressure HCl column with a refrigerated condenser accounts for losses in the HCl recovery section.

Propositions to reduce reaction temperature and energy use for separation include:

- Cracking additives.
- Low-temperature catalysts.
- Alternative feedstocks, e.g., catalytic dehydrogenation of ethyl chloride.
- Novel separation systems to reduce distillation.

Topsoe, Inc. – EX1020
Page 49 of 54

Carbon Dioxide (CO_2)
CO_2 is produced by recovery from gas streams where it is a contaminant or by-product. The majority comes from ammonia, H_2 or ethylene oxide producing plants. The total process input energy is about 19 times greater than the theoretical minimum energy required. The most common process is absorption via a physical or chemical solvent. (JVP, 2004) models a process where mono ethanolamine (MEA) is used to recover CO_2 from power plant flue gas. The CO_2 stripper and absorber are large sources of exergy losses. A large exergy loss occurs where hot flue gas is cooled to minimise water content and temperature of flue gas entering the MEA system. Energy recovery could be possible from the associated cooling water recycle, make-up and purge loop.

Solvents for recovering CO_2 are limited and expensive, and could poison recycle gases. Possible areas for research are (JVP, 2004):
- Better solvents, especially adducts.
- Novel separations or hybrid separations with membranes, PSA (Appendix A), etc.

Nitric Acid
The exothermic process for Nitric Acid manufacture is based on a composite of various licensed technologies via oxidation of ammonia to Nitric Oxide (NO) and ultimately Nitric Acid. The total process input energy is less than the theoretical minimum due to significant energy generation made possible by the exothermic reaction. The largest exergy losses are in the heat recovery section, which appears to have considerable additional capacity for energy recovery. In addition, most nitric acid plants utilised a steam turbine and gas expander to drive one or more compressors. Energy losses in the reaction section are due primarily to the nitric acid absorber, which performs the absorption of Nitrogen Dioxide (NO_2) in water while reacting it to form Nitric Acid, generating heat in the process. The heat of reaction is taken out in the partial condenser of the absorber, usually with refrigeration. Large internal exergy losses are due mostly to extreme temperature differences between feed and effluent streams and other exchanged streams in the system (gas coolers, steam super-heaters, evaporators).

A stagnant Nitric Acid market gives little incentive for R&D. Current processes practise significant heat recovery. Lower temperature catalysts for ammonia oxidation could be an R&D area.

Ethylbenzene
There are two ethylbenzene production processes: the vapour-phase Mobil/Badger and the Lummus process. In the most energy-efficient one, the Lummus process, ethylbenzene is produced via liquid-phase benzene alkylation, and the front end of the process differs considerably from the Mobil/Badger process. The reaction systems differ substantially in operating temperature as well as phase of reaction. After the reaction system the processes are very similar. The total process energy input is about 6 times greater than the theoretical minimum (8 times for Mobil/Badger). The benzene fractionator accounts for most exergy losses, similar to the Mobil/Badger technology. This column processes both fresh feed and recycle benzene, and its large condenser operates at a low temperature, inhibiting economic energy recovery. There is some opportunity for medium- to low-pressure steam export from the alkylation reactor.

Ethylbenzene is used exclusively for the production of styrene, and synergies should be considered, as well as the possibility of finding alternative feedstocks for producing styrene. The current process is relatively efficient; finding more active catalysts to lower the alkylation temperature would be a useful future research area.

Styrene
There are two processes for styrene production, viz. the Lummus/Monsanto/UOP and the Fina/Badger process. The most energy efficient of the two, the Fina/Badger process, is an endothermic process that is very similar to the Lummus process, except for modest differences in the reactor section. Total process energy input is about 10 times greater than the theoretical mini-

Topsoe, Inc. – EX1020
Page 50 of 54

mum. The largest energy losses are found in air coolers used to condense and cool the reactor effluent, although the quality of the energy lost is relatively low. The feed preheat is the source of significant exergy losses due to high temperature differences in reactor effluent exchangers and in the dehydrogenation reactors. Losses also occur in the ethylbenzene/styrene stripper column, which must be operated under vacuum, and the large condenser load is removed with cooling water at too low a temperature for heat recovery. The Lummus process uses a higher steam/ethylbenzene ratio than the Fina/Badger technology, and requires higher energy input. However, the Lummus process recovers low-temperature heat from the ethylbenzene/styrene stripper and exergy losses are lower than those in the Fina/Badger unit operation.

The current high-temperature endothermic reaction requires preheating of feed and cooling of effluents with relatively high energy burdens. R&D to reduce energy use includes (JVP, 2004):

- Liquid phase lower temperature process with continuous removal of hydrogen.
- Novel separation technologies to remove hydrogen.
- Process using diluents other than steam.
- Alternative feedstock process.

A process substituting CO_2 as a soft oxidant for CO_2 has been proposed by (Park et al, 2002). Catalytic activity is reported to be greatly improved using zeolite-supported iron oxide catalysts.

Terephthalic Acid

This exothermic process is based on Amoco technology for producing Purified Terephthalic Acid (PTA) via oxidation of p-xylene. It is a complex, energy- and exergy-intensive process. Purification requirements are critical and the current process yields are high. Total process energy input is about twice that of theoretical minimum energy requirements. Large exergy losses occur in the reaction system, mostly due to process irreversibilities associated with the wide range in temperatures and compositions of the various feed streams and the effluent. The oxidation reactor is a main source of losses. In crystallisation, the solvent dehydrator is a primary source of losses. Condensers and slurry vessels account for losses during purification. The high selectivity of the current catalyst system limits the interest in seeking new approaches to producing PTA. Current research is concentrated on further improvements to product purification.

Purification requirements are critical and current yields are approaching stoichiometricity. Purification and catalyst recovery, both complex and energy-intensive, could be improved:

- Novel separation schemes for solvent recovery and dehydration and for refining/purifying PTA (Purified Terephthalic Acid).
- Process requiring less corrosive solvent.
- Entirely new concepts for producing PTA.

Formaldehyde

This exothermic process produces formaldehyde from methanol using a silver-based catalyst, and is based on BASF technology. Total process energy-input is about 4 times greater than theoretical minimum energy requirements. In this relatively simple process configuration, the low temperature quench of the reactor effluent is responsible for most of the energy consumption as well as energy and exergy losses. The very large driving forces around the exothermic reactor contribute to the substantial internal exergy losses.

According to (JVP, 2004), it is uncertain what the process of choice will be for formaldehyde production (mixed-oxide versus silver catalyst). Possible improvements are:

- More selective, longer-life catalysts.
- New ways to recover formaldehyde (without polymerisation).

Topsoe, Inc. – EX1020
Page 51 of 54

p-Xylene
The process for p-xylene manufacture is based on conventional production from a mixture of C8 aromatic isomers (p-xylene, o-xylene, m-xylene, ethylbenzene). The isomerisation reaction is endothermic, but chemical conversion is exothermic due to side reactions. The total process energy-input is 600 times greater than the theoretical minimum due based on isomerisation of a p-xylene-depleted xylene mixture. Energy losses are comparable between isomerisation and fractionation, but exergy losses are much higher in isomerisation due to large temperature differentials between inlet and outlet streams to the reactors and feed pre-heaters. The low external exergy loss indicates little opportunity for further energy recovery in isomerisation. In fractionation, the produce cooler is the largest source of losses. The process temperatures in this cooler are high enough to suggest steam generation or cross-exchange would save energy.

Considerable energy recovery is already practised. New opportunities include (JVP, 2004):
- New separation technologies, e.g., removing p-xylene during isomerisation.
- Couple p-xylene process with downstream terephthalic acid process to achieve reductions in energy use (e.g., unique catalyst for oxidation).

Ethylene Oxide
The exothermic process for Ethylene Oxide (EO) based on Shell technology is based on direct oxidation of ethylene with oxygen. EO plants also produce ethylene glycol in an integrated flow sheet. The process as modelled has half of the product EO as an aqueous stream. This has contributed to unusually high energy and exergy losses. In addition, the process couples the upstream stripping column condenser with the purification column condenser, creating a very large condensing load at too low a temperature for energy recovery. This may not be common practice. Process energy is about 10 times theoretical minimum energy requirements. The EO purification unit accounts for 91% of energy- and 19% of exergy losses. In the stripper section, high internal exergy losses are due to heat exchangers and columns in the recirculating water loop. Relatively low temperatures result in little opportunity for heat recovery. Internal losses could be reduced by larger heat exchangers. Large internal losses in the reactor section area due to large temperature differentials in the inlet gas and exothermic conditions in the reactor.

EO technology must operate at low per pass conversion to maintain selectivity and to control the reaction gas composition outside the flammable region. New processes/process routes are:
- Fluidised bed reactors.
- Liquid-phase (LP) oxidations, LP process using hydro-peroxide or hydrogen peroxide.
- Bioxidation of ethylene.
- Processes for richer EO-containing streams to reduce large recycle.
- Novel separations for richer EO streams, including carbonate system.

Cumene
There are three processes for Cumene production, among which a Solid Phosphoric Acid (SPA) catalysed process and a Zeolite catalysed one. The most energy efficient (exothermic) process is based on propylene alkylation of benzene with a Solid Phosphoric Acid (SPA) catalyst (UOP design). Total process energy input is about 1.5 times greater than the theoretical minimum. The largest energy losses occur in air coolers, primarily due to their low temperatures. Virtually all energy and exergy losses occur in Cumene recovery, primarily due to three distillation columns. Additional energy recovery is possible from the Cumene fractionator, but may not be economical. There may be opportunity for feed preheating in the alkylation section.

All Cumene goes to production of phenol and acetone (JVP, 2004). Demand for phenol is not balanced with demand for acetone (often sold at distress prices). The result is a major thrust to find alternative processes to produce phenol that do not require propylene or produce acetone. Related research topics include alternative (or one-step) routes to phenol and integration with bisphenolA processes.

Topsoe, Inc. – EX1020
Page 52 of 54

Methanol
The main processes for methanol production are the ICI low-pressure and the Lurgi process. The Lurgi process utilises a combined reforming process with two stages of reforming in series, the second with oxygen injection. The heat recovery section exhibits the greatest external exergy losses and indicates potential for low-temperature energy recovery. The methanol column in the refining section also makes a large contribution to energy losses. Condenser steam generation could reduce energy losses. Relatively large losses are also attributed to a process exchanger and combustion furnace in the reforming section, and to methanol reactors, condensers and air coolers in the synthesis section. The process exchanger is a candidate for steam generation with substantial energy recovery. The combustion furnace has a lower energy loss but the high external energy ratio suggests the possible use of a waste heat boiler to recover energy. Exergy losses occur in the reforming and heat recovery sections due to the wide range of inlet and outlet temperatures involved. Preheating the feed within the reactor system is the source of large internal exergy losses in the synthesis section due to large temperature differences.

Expectations for building methanol plants in the USA are not high. Innovations could include:
- Liquid phase processes for methanol production.
- Better process technologies for production of synthesis gas.
- Improved catalysts, including biocatalysts.
- Alternative feedstocks (methane, biomass).
- Novel separation technologies to reduce distillation.

Acetic Acid
The process analysed is the Acetica Process developed by Chiyoda and UOP that is similar to other acetic acid facilities based on carbonylation of methanol. Differences are the bubble column reactor design that eliminates the agitator, and the immobilisation of the catalyst onto solid particles rather than being dissolved in reaction medium. No commercial plants using this technology are currently operating. The total process input energy is about 4 times greater than the theoretical minimum. Acetic acid refining accounts for the largest exergy-losses, primarily due to the crude fractionator. The overhead temperature of the column is too low to reasonably recover the energy in condenser cooling water. Large internal exergy losses are due to large temperature, pressure and composition differences of the streams leaving the column. Large internal exergy losses are also present in the carbonylation reactor, due to large temperature, pressure and composition differences among the recycle, feed methanol and carbon monoxide streams.

Catalyst research continues to improve acetic acid production. Other research needs are:
- Novel separations to improve carbonylation routes (e.g., separation of gases from carbonylation reaction, supplementation of distillation).
- Alternative routes (oxidation of butane, ethylene-based, oxidative dehydrogenation of ethane).
- Acetic acid from biomass via chemical or bio-catalysis.

Butadiene
The Nippon Zeon process is based on extractive distillation with DMF solvent to recover butadiene from mixed C4 streams (butane and derivatives, viz. butene, butylene, butadiene). This is a separation process with no chemical reaction, so no theoretical minimum is given. Distillation columns (butadiene stripping column, butene extractive column, propylene and butadiene product columns) account for large exergy losses in extractive and conventional distillation. The large internal exergy losses reflect wide differences in the composition and temperature of inlet and outlet streams. Large energy losses are due to refrigeration used for condensation in some cases. Most of the column condensers are operating at temperatures too low for energy recovery, except the acetylenes stripping column, where reuse of heat of condensation is possible.

Topsoe, Inc. – EX1020
Page 53 of 54

Almost all butadiene is present in C4 streams from refineries and steam crackers. Improvements could be made in methods of separating butadiene from butane/butane/butadiene mixtures (new solvents, hybrid systems, membranes, PSA).

Acrylonitrile

The process analysed for acrylonitrile (ACN) production is the exothermic propylene ammoxidation process which occurs at high temperatures. This process is based on SOHIO-BP fluidized bed technology, which is now used predominantly. The total process energy input is approximately the same as the theoretical minimum energy required (considerable energy is produced by the exothermic reaction). About 45% of energy losses are recoverable heat and refrigeration of process effluent streams. The largest exergy losses occur in the heat and refrigeration section, primarily due to effects of refrigeration cycles needed to separate the product and by-products at low temperatures. A large source of losses in the ammoxidation section is the quench column overhead cooler, although most exergy losses occur as internal losses in the ammoxidation reactors due to the large number of input and output steams at widely different temperatures. Increased heat exchange to increase the cold feed temperatures could reduce these irreversibilities, if economic. Most of the losses in the ACN separation are due to the HCN stripper column and condenser, which is cooled with refrigeration and is very energy-intensive.

Conversion to ACN requires a rapid quench of reaction gases to lower temperatures with a complex separation scheme (with refrigeration). Novel ideas to reduce the energy intensity are:

- Fluidised beds.
- Recycle process with substitution of oxygen for air.
- Bio-catalytic production of ACN.

Topsoe, Inc. – EX1020
Page 54 of 54