

Petrochemicals from Oil, Natural Gas, Coal and Biomass:

Energy Use, Economics and Innovation

Ren, T.

Petrochemicals from Oil, Natural gas, Coal and Biomass: Energy Use, Economics and Innovation

Utrecht University, Copernicus Institute for Sustainable Development and Innovation,
Department of Science, Technology and Society, Faculty of Science

ISBN: 978-90-393-5019-5

Cover design: Ipskamp Drukkers B.V. en Tao Ren

Cover photo: SECCO petrochemical site in Shanghai, China (Courtesy of Emerson Process Management)

Printed by Ipskamp Drukkers B.V., Enschede, The Netherlands

Petrochemicals from Oil, Natural Gas, Coal and Biomass: Energy Use, Economics and Innovation

Petrochemische Productie vanuit Olie, Aardgas, Steenkolen en Biomassa: Energiegebruik, Kosten en Innovatie

(met een samenvatting in het Nederlands)

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Universiteit Utrecht op gezag van de rector magnificus, prof. dr. J.C. Stoof, ingevolge het besluit van het college voor promoties in het openbaar te verdedigen op woensdag 4 maart 2009 des middags te 2.30 uur

door

Tao Ren

geboren op 2 juni 1974
te Urumqi, China

Promotor: Prof. dr. K. Blok

Co-promotor: Dr. M. K. Patel

Dit proefschrift werd mede mogelijk gemaakt met financiële steun van:

- Energieonderzoek Centrum Nederland (ECN)
- Utrecht Centrum voor Energieonderzoek (UCE)

用石油，天然气，煤炭和生物质能生产传统化工产品: 能效, 经济和创新
(博士毕业论文)

荷兰乌特赫支大学

导师: 孔内乐斯。伯罗克 **Kornelis Blok** (荷兰乌特赫支大学化学系教授)

副导师: 马丁。帕特勒 **Martin Patel** (荷兰乌特赫支大学化学系副教授)

赞助机构: 荷兰能源研究中心 (**ECN**)和乌特赫支能源研究会 (**UCE**)

博士生: 任涛 (1974 年生于中国新疆乌鲁木齐市)

谨将本文献给本人的已故慈父

For the author's father Ben Fu Ren

TABLE OF CONTENTS

CHAPTER 1 INTRODUCTION	1
1.1 TWO CHALLENGES: CLIMATE CHANGE AND SECURITY OF ENERGY AND RAW MATERIALS SUPPLY	2
1.2 DEVELOPMENT OF BASIC PETROCHEMICALS PRODUCTION	3
1.3 PREVIOUS WORK, CENTRAL RESEARCH QUESTION AND OUTLINE	5
1.4 RESEARCH METHOD	7
1.5 TWO PROCESS STEPS	7
1.5.1 Primary Energy Sources	8
1.5.2 Feedstocks.....	9
1.5.3 Basic Petrochemicals.....	10
1.6 APPROACH TO ACCESS MULTIPLE-PRODUCT PROCESSES	11
1.6.1 Naptha Value-Equivalent Feedstocks	13
1.6.2 High Value Chemicals (HVCs).....	13
1.6.3 Electricity.....	14
1.6.4 Yields.....	14
1.7 ENERGY AND ECONOMIC ANALYSIS.....	15
1.7.1 Energy Supply	15
1.7.2 Definitions of Energy Use.....	15
1.7.3 Definitions of CO ₂ Emissions.....	16
1.7.4 Production Costs.....	17
CHAPTER 2 PETROCHEMICALS FROM CRUDE OIL AND STEAM CRACKING: ENERGY ANALYSIS	19
2.1 INTRODUCTION	20
2.2 PROCESS DESCRIPTION OF NAPHTHA STEAM CRACKING.....	22
2.3 DEFINITIONS.....	25
2.4 ENERGY ANALYSIS OF NAPHTHA/ETHANE STEAM CRACKING	31
2.4.1 Specific Energy Consumption (SEC)	31
2.4.2 Breakdown of SEC and Exergy Losses	31
2.4.3 Energy Integration.....	33
2.5 LATEST DEVELOPMENTS OF NAPHTHA STEAM CRACKING	33
2.5.1 State-of-the-Art Naptha Steam Cracking	35
2.5.2 Advanced Naptha Steam Cracking Technologies.....	36
2.6 CATALYTIC AND OTHER TECHNOLOGIES	38
2.6.1 Specific Energy Consumption (SEC)	38
2.6.2 Reactors and Catalysts	42
2.7 CONCLUSIONS	45

CHAPTER 3 PETROCHEMICALS FROM METHANE: ENERGY USE AND PRODUCTION COSTS..... 47

3.1 INTRODUCTION	48
3.2 METHANOL AND OXIDATION ROUTES	49
3.2.1. <i>Methanol Routes</i>	50
3.2.2. <i>Oxidative Coupling of Methane (OCM)</i>	55
3.3 DEFINITIONS.....	58
3.4 ENERGY AND CO ₂ EMISSIONS ANALYSIS	58
3.4.1. <i>Steam Cracking Routes</i>	59
3.4.2. <i>Methanol Routes</i>	59
3.4.3. <i>Oxidative Coupling of Methane (OCM)</i>	66
3.5 RESULTS AND DISCUSSION	66
3.5.1. <i>Results</i>	66
3.5.2. <i>Future Improvement</i>	68
3.6 PRODUCTION COST ANALYSIS.....	70
3.7 CONCLUSIONS	74

CHAPTER 4 PETROCHEMICALS FROM COAL AND BIOMASS: ENERGY USE AND CO₂ EMISSIONS 75

4.1 INTRODUCTION	76
4.2 DEFINITIONS.....	77
4.2.1. <i>Primary Energy Sources, Feedstocks and Petrochemicals</i>	77
4.2.2. <i>Electricity</i>	78
4.2.3. <i>Energy Use and CO₂ Emissions</i>	78
4.3 ROUTE DESCRIPTION	79
4.3.1. <i>Conventional Routes</i>	79
4.3.2. <i>Alternative Routes</i>	82
4.4 ENERGY USE, CO ₂ EMISSION ANALYSIS AND LAND USE.....	87
4.4.1 <i>Results of Energy Analysis</i>	100
4.4.2 <i>Results of CO₂ Emissions Analysis</i>	101
4.4.3 <i>Land Use Analysis</i>	102
4.5 DISCUSSION.....	103
4.5.1 <i>Credit and Allocation Approaches</i>	104
4.5.2 <i>Technological Developments</i>	106
4.6 CONCLUSIONS	108

CHAPTER 5 PETROCHEMICALS FROM OIL, NATURAL GAS, COAL AND BIOMASS: PRODUCTION COSTS IN 2030-2050 109

5.1 INTRODUCTION	110
5.2 DEFINITIONS AND METHODS	111
5.3 ECONOMIC ANALYSIS	112
5.3.1. <i>Range of Energy prices, CO₂ Costs and Production Costs</i>	112
5.3.2. <i>Correlations of Energy prices</i>	114
5.3.3. <i>Monte Carlo Analysis</i>	116
5.3.4. <i>Energy Prices in 2008</i>	124
5.4 RESULTS.....	125
5.4.1 <i>Range and Rankings of Production Costs</i>	125
5.4.2 <i>Production Costs in 2008</i>	127
5.5 POSSIBLE EFFECT OF STAGNANT OIL SUPPLY IN 2030-2050.....	127
5.6 UNCERTAINTIES	129
5.7 CONCLUSIONS	132

CHAPTER 6 ENERGY EFFICIENCY IMPROVEMENT AND PROCESS INNOVATION IN BASIC PETROCHEMICAL PROCESSES 133

6.1 INTRODUCTION	134
6.2 RESEARCH METHODS.....	135
6.3 DEFINITIONS AND SCOPE	136
6.3.1. <i>Basic Chemicals and Petrochemical Processes</i>	136
6.3.2. <i>Innovation Counts and Definitions</i>	138
6.3.3. <i>Improving Existing Processes and Developing New Processes</i>	138
6.3.4. <i>Innovators</i>	140
6.3.5. <i>Drivers and Barriers</i>	141
6.4 INNOVATION PROCEDURE.....	145
6.5 TWO TYPES OF INNOVATION ACTIVITIES, DRIVERS AND BARRIERS.....	147
6.5.1 <i>Improving Existing Processes</i>	147
6.5.2 <i>Developing New Processes</i>	153
6.6 REWARD-TO-RISK RATIO.....	158
6.6.1 <i>Uncertainties in Improving Existing Processes</i>	159
6.6.2 <i>Uncertainties in Developing New Processes</i>	160
6.7 INNOVATION IN JAPAN AND CHINA	164
6.8 COMPARISON WITH EARLIER RESEARCH.....	165
6.9 CONCLUSIONS	167

SUMMARY AND CONCLUSIONS	169
SAMENVATTING EN CONCLUSIES	177
概要.....	185
LIST OF FIGURES	189
LIST OF TABLES	193
GLOSSARY	195
REFERENCES.....	197
ACKNOWLEDGEMENTS.....	217
ABOUT THE AUTHOR.....	219

Chapter 1 Introduction

These days, plastics, rubber, synthetic fibers and other chemical products are made from the so-called building blocks of the chemical industry: basic petrochemicals. The most important basic petrochemicals are light olefins (e.g. ethylene and propylene) and aromatics (e.g. benzene). The dominant production process of these basic petrochemicals, steam cracking, is the backbone of the chemical industry. The production processes of basic petrochemicals (refinery processes and steam cracking) use more process energy in total than the production processes for any other chemicals [1, 2]. Similar to most other energy intensive industrial sectors today, the petrochemical industry is facing dual challenges: it needs to have an answer to both *climate change* and the *security of energy and raw materials supply*. It is therefore of particular interest to study innovative technologies for the production of basic petrochemicals.

The primary objective of this thesis is to provide insight into the potentials of improved or new process technologies for basic petrochemicals to reduce energy use, CO₂ emissions and production costs. In addition, the thesis aims at deepening the understanding of drivers, barriers and energy strategies that affect technological innovations in the petrochemical industry.

This thesis was written with two types of readers in mind. For engineers and energy researchers who are involved in the R&D of new petrochemical processes, the thesis offers a review of emerging technologies and their key techno-economic characteristics. For policymakers and firm managers who are concerned with the pressing challenges of climate change and the security of energy and raw materials supply, the thesis presents a study on innovation issues related to energy efficiency improvement and the utilization of alternative primary energy sources.

In this chapter, we introduce the subject and research methods of the thesis. Section 1.1 describes the motivation for our research. In Section 1.2, we briefly review the history of basic petrochemicals production and steam cracking. Section 1.3 presents the research question and the outline of the thesis. In the rest of Chapter 1, we explain the general methods and definitions that are used in the thesis. A glossary for all the abbreviations and acronyms used in the chapters can be found at the end of this thesis.

1.1 Two Challenges: Climate Change and Security of Energy and Raw Materials Supply

Climate change is essentially caused by greenhouse gas emissions (most importantly by CO₂ emissions) and the most important reason for these emissions is the extensive use of fossil energy [3]. Most of the basic petrochemicals production depends on crude oil for energy and raw material supply. According to many authors [4-8], the demand for crude oil may outpace its supply sometime before 2050. These two challenges, *climate change* and *security of energy and raw materials supply* are critical for the basic petrochemicals production in the long-term future (up to 2050).

The first challenge, *climate change*, is related to the fact that large amounts of fuel used in basic petrochemicals production contribute significantly to global emissions of CO₂. In 2004, the production of basic petrochemicals¹ accounted for about three EJ of primary energy use (due to the combustion of fossil fuels and excluding the calorific value of basic petrochemicals) and about 200 million tons of CO₂ equivalent greenhouse gas emissions² (due to the combustion of fossil fuels) [1, 10]. It can be translated into a fuel energy price of close to 10 billion (10⁹) dollars (US dollars in 2000). Reduction of the CO₂ emissions associated with fossil-fuel use in basic petrochemicals production could help in meeting the 2012 emission targets set by the Kyoto Protocol as well as mitigating climate change in the long-term future.

The second challenge, *security of energy and raw materials supply*, is related to the fact that the production of basic petrochemicals relies on large amounts of feedstocks and process energy supply. If the calorific value of basic petrochemicals is included, the total energy input in basic petrochemicals production currently accounts for nearly 10% of global oil consumption (including petrochemicals produced by both the petrochemicals and oil refinery industry) and nearly 5% of global natural gas consumption [11]. Ethylene (C₂H₄; about 116 million tons) accounted for more than one third of basic petrochemicals produced worldwide in 2006 and this

¹ Basic petrochemicals here refer to ethylene, propylene, butadiene and aromatics produced from steam cracking as well as propylene and aromatics from oil refineries. See details on the definition of basic petrochemicals in Section 1.5.3.

² Three EJ is about 20% of the total final energy use (combusted fuels; calorific value of chemicals excluded) in the global chemical industry while the 200 million tons of CO₂ is about 18% of the total CO₂ emissions from the global chemical industry [1]. Also, three EJ is less than 1% of the global primary energy use while 200 million is less than 1% of the global energy use related CO₂ emissions [1]. Emission factors of production one ton of basic petrochemicals can be found in [9].

is the most important basic petrochemical for making plastics¹, ethylene oxides and other chemicals [13]. The second most important basic petrochemical is propylene (C₃H₆), about 65 million tons of which was produced globally in 2006 [13]. Together, ethylene and propylene are the most important light olefins. Nearly all light olefins are currently produced through steam cracking, but the fluid-bed catalytic cracking (FCC; a refinery process) also represents 30% of propylene produced worldwide [1]. The global capacity of ethylene production doubled in the period of 1990-2005 (at a growth rate of 5-6%) per year. This was largely due to the strong demand growth in Asia, where China and India presented double-digit growth rates, while the market growth in the US and Europe was rather moderate. In recent years, the annual growth rate of the global olefin market slowed down to 3-4% [14, 15]. The annual growth rate of ethylene demand is expected to remain around 3-4% in the coming decades, but that of propylene is expected to be around 4-7% [16-18]. If increased demands indeed outpace crude oil supplies for the basic petrochemicals production in the next decades, alternative energy and feedstock sources may be required to meet the unfulfilled demands.

In response to the challenges mentioned above, two main options can be distinguished. The first option is to apply technologies that have lower energy input and associated emission per unit of product in petrochemicals production than current technologies (energy efficiency improvement). The second option is to make use of alternative feedstocks that lead to lower emissions and/or are less scarce than conventional feedstocks derived from crude oil. In order to examine whether new technologies can help solving the problems mentioned above, we must compare the energy use, production costs and CO₂ emissions of these new technologies for basic petrochemicals production with those of the conventional technologies.

1.2 Development of Basic Petrochemicals Production

Basic petrochemicals production consists of two steps: feedstock production (from primary energy sources to feedstocks) and petrochemicals production (from feedstocks to petrochemicals; details will be explained later). Therefore, its history has always been strongly influenced by the supply of primary energy sources and feedstocks.

¹ Global plastics consumption reached 245 million tons in 2006 and its annual growth rate between 1970 and 2006 was 6% [12].

In 1855, when a fractional distillation process of petroleum was demonstrated at Yale University, the main liquid feedstocks used in today's basic petrochemicals production, naphtha and gas oil (discussed later in details), were first obtained in small volumes along with much tar and gasoline. For the early development of oil refineries, the desired product was primarily gasoline, while naphtha was considered as a worthless byproduct to be discarded or burned as heating fuel. Not until 1936 was naphtha commercially used to produce gasoline through a catalytic cracking process [19].

In 1920, the first cracking process using natural gas-based feedstocks (ethane and propane) to produce ethylene was developed by Linde [20]. In the same year, a similar process was used by Union Carbide to build the world's first ethylene plant, and Standard Oil built the world's first plant to produce isopropyl alcohol from crude oil (which can be converted into propylene by heating it with sulfuric acid) [19, 20].

After the World War II, the growing demand for petrochemicals and the rising supply of naphtha from the newly-built oil refinery industry were major drivers for the use of naphtha as a feedstock in petrochemicals production and the development of naphtha-based steam cracking. Basic petrochemicals became the most important basic chemicals in the chemical industry. Ethylene became so important that the ethylene growth rate was sometimes used as an indicator of economic growth of a nation (it is usually a bit higher than the economic growth rate) [21].

Since the 1960s, ethylene produced from naphtha-based steam cracking has dominated the European ethylene market [20]. In the US where most of naphtha is converted into gasoline, most ethylene is produced by steam cracking of ethane. Globally, more than 60% of all basic petrochemicals produced today come from crude oil-derived feedstocks, naphtha and gas oil [22].

From the 1960s to the beginning of the first oil crisis in 1974, basic petrochemicals production grew about 20% annually in Europe and Japan [20]. However, the two oil crises of the 1970s and 1980s caused a fall by 20-30% in basic petrochemicals production in major industrial countries [20]. During that period, energy efficiency in the existing steam cracking processes was improved [1]. Also, a few pilot plants were built to produce basic petrochemicals using coal

and methane as primary energy sources. Most of them were never widely commercialized due to the drop in oil prices after the crises¹.

In the 1990s, Europe became the largest producer of basic petrochemicals, ahead of the US and Japan. Today, China, India and the Middle East are rapidly building up their own petrochemical capacities, which—next to the increased demand of these countries for oil for transportation—have contributed to the fast growing demand for crude oil and the rise of oil prices.

1.3 Previous Work, Central Research Question and Outline

A number of previous studies in recent years addressed various aspects of improved and new technologies for basic petrochemicals production. Through the use of several best available and emerging technologies, significant energy savings were reported to be possible in the production of crude oil and natural gas-based petrochemicals [22, 23]. New, coal and biomass-based technologies that are still undergoing research and development (R&D) were said to present great differences in energy use and production costs [24-27]. So far, these novel technologies have not been compared in terms of energy use, CO₂ emissions and projected production costs. Moreover, not only the techno-economic parameters are of relevance, but also the circumstances under which these new technologies are adopted (or not) are important. A wide body of literature (e.g. the studies collected in [28]) is available on innovation processes in industrial companies, but the knowledge about the petrochemical industry is limited to the understanding of economic circumstances alone (e.g. the roles of increased competition and cost leadership in driving innovation [19, 29]). No study has yet been undertaken that also considers the impact of energy supply and environmental issues on innovation in the petrochemical industry.

To bridge this knowledge gap, we defined the **central research question** of this thesis as: *what are the prospects of improved and new technologies for basic petrochemicals production in comparison with conventional state-of-the-art technologies?* This question can be broken down into three sub-questions:

¹ The only exception was the coal and methane-based petrochemicals production in South Africa, which could not use crude oil due to the international embargo and continues to operate today. In 1950-1980, there were at least three coal-to-liquids plants with a total capacity of 0.2 mbpd (million barrels per day) to meet 60% of the domestic demand in South Africa. Today, at least two of the three plants are still running. The process used there is similar to the Fischer-Tropsch (FT) processes used in Germany during World War II.

- *Environmental* What is the environmental effect in terms of energy use and CO₂ emissions of improved technologies and innovative technologies utilizing alternative primary energy sources in comparison with conventional state-of-the-art technologies?
- *Economics* What is the economic potential in terms of production costs of the technologies utilizing alternative primary energy sources in comparison with the conventional technologies?
- *Innovation* What drivers, barriers and strategies influence the innovation process of improved and new process technologies?

To address these sub-questions, the outline of the thesis is designed as follows:

Regarding the *economic* aspect, we analyze the production costs of various technologies that convert alternative primary energy sources to petrochemicals. Chapter 3 presents the production costs of the conventional technologies and methane-based olefin technologies that are related to methanol and oxidative coupling. To this end, past and present-day energy prices are considered. Chapter 5 discusses the long-term production costs of the various routes presented in previous chapters. Energy prices according to various energy scenarios are used as the determinants to analyze the distribution and ranking of production costs of various routes for basic petrochemicals production.

Chapter 6 addresses the *innovation* aspect. We discuss the innovation and strategic issues that are involved in the development of basic petrochemical technologies, and analyze the barriers and drivers for innovation with respect of two situations: improving existing processes and developing new processes. In addition, we use the concept of risk-and-reward ratio to describe how energy efficiency and technological innovations are considered differently under different circumstances.

In Chapter 7, we present our conclusions. We briefly summarize the thesis in terms of the three aspects: environment, economics and innovation. Based on the main findings of the previous chapters, we present several recommendations to policymakers and industry managers regarding the future development of petrochemical technologies.

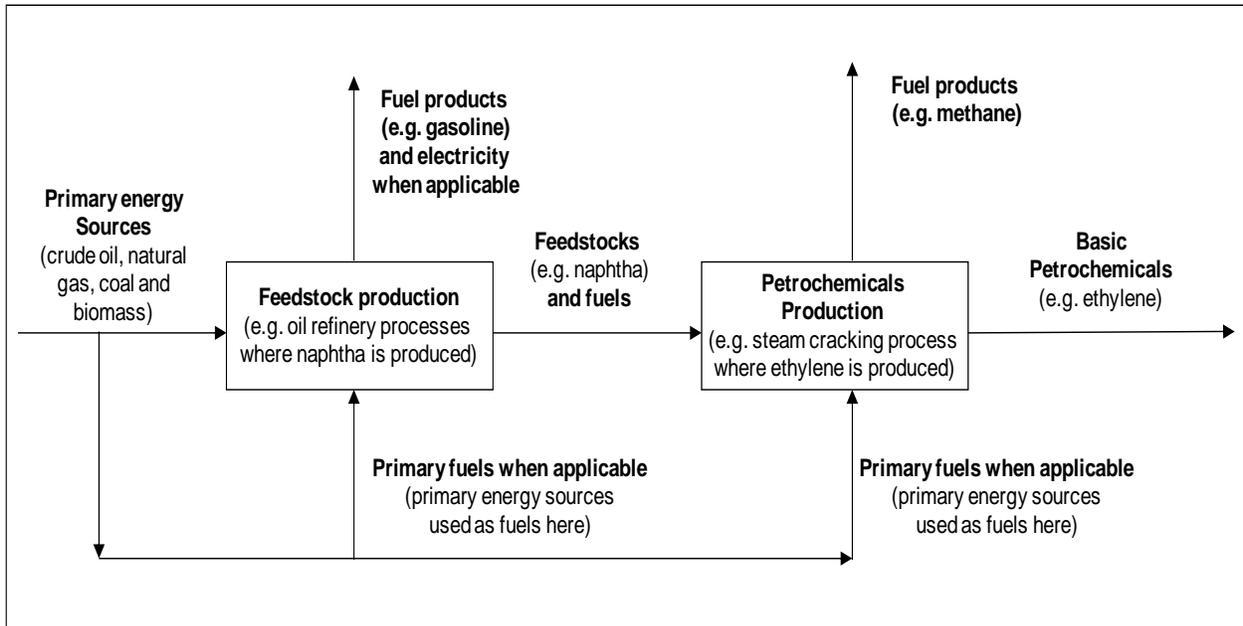
1.4 Research Method

The main research methods used in the thesis are energy and economic analyses (to conduct calculations and draw conclusions). These methods have been described in [30]. When applying this method, we first describe the processes, then characterize them in terms of energy efficiency and CO₂ emissions and finally discuss technological developments or identify areas for potential improvement. The energy data of the state-of-the-art conventional technologies are used as reference in the comparison with alternative technologies. Similarly, for the economic analysis, the production costs of conventional technologies are used as reference. From the data found in the sources, we chose the data sets which we considered to be most reliable and up-to-date. These datasets were then cross checked and adapted to make them consistent and comparable¹.

1.5 Two Process Steps

Figure 1-1 shows that a complete process route for producing basic petrochemicals contains two process steps:

Figure 1-1 Two Process Steps in Basic Petrochemicals Routes



¹ Though not being a research method, personal communication, especially in Chapter 6, has also been used to crosscheck our data quality as well as for our qualitative analysis.

- *Feedstock production* In feedstock production, primary energy sources (i.e. crude oil, natural gas, coal and biomass) are extracted and then converted into feedstocks (e.g. naphtha and methanol). In this step, it is possible for some processes to coproduce electricity and fuels. When applicable, primary energy sources can also be used as fuels here (primary fuels; see Figure 1-1).
- *Petrochemicals production* In petrochemicals production, feedstocks are converted into basic petrochemicals, such as ethylene and aromatics, which are then separated from each other. In this step, it is possible for some processes to coproduce fuels.

The three terms mentioned above, primary energy sources, feedstocks and basic petrochemicals, are defined in the following sections.

1.5.1 Primary Energy Sources

The primary energy sources mentioned in this thesis refer to crude oil, natural gas, coal, biomass and plastic waste. The weights of all primary energy sources referred to in this thesis are expressed on a dry basis, which means free of moisture.

Crude oil in the thesis refers to light crude oil, which has a low wax content. Roughly, 10% of all crude oil is used in basic petrochemicals production (including such production in refineries as well) [11].

Natural gas can be so-called wet gas or dry gas. These terms do not refer to the water content but rather to the ratio of methane as opposed to higher hydrocarbons: Wet gas, mostly from the Middle East, contains more ethane, propane and butane than dry gas, which contains almost only methane and is mostly found in Russia. On average, 95-96% of natural gas (wt.) is methane. The rest of natural gas includes ethane, propane, butane and a small amount of impurities (e.g. water, sulfur, etc.). Roughly, 5% of the natural gas produced worldwide is used in basic petrochemicals production [11].

1.5.2 Feedstocks

Feedstocks in this thesis refer to intermediate raw materials derived from various primary energy sources. These include:

- Ethane (derived from refinery gases or natural gas);
- Naphtha (derived from various primary energy sources);
- Methane (derived from natural gas);
- Methanol (derived from various primary energy sources);
- Ethanol (derived from biomass).

It should be noted that naphtha and methanol are sometimes classified as petrochemicals in the literature and statistics. However, in this thesis they both play the role of feedstock because they still need to be converted into basic petrochemicals as defined in this thesis.

Further details of methane, methanol and ethanol will be given in Chapters 3 and 4. Here we will elaborate on ethane and naphtha, since they are the most widely used conventional feedstocks, and because ethane and naphtha steam cracking processes are used as the benchmark technologies in this thesis.

Ethane (C_2H_6) is mostly produced as a byproduct of natural gas processing. Other gaseous feedstocks are propane (C_3H_8) and butane (C_4H_{10}), which are also mostly produced through separation in natural gas processing plants. A major source of gaseous feedstocks is natural gas liquids (NGLs). NGLs are present in wet gas extracted from oil or gas fields and must be separated from methane because they can cause problems for methane transportation in natural gas pipelines. Gaseous feedstocks also comes from refinery gases and LPG (liquefied petroleum gases consisting mostly of ethane, propane and butane) produced in oil refineries. As the prices of ethane and other gaseous feedstocks are similar to those of methane in the world's natural gas-rich regions in 1995-2006 [16, 31], they are considered to have the same economic value in terms of \$/GJ.

Naphtha is currently obtained in oil refineries as one of the intermediate products from the distillation of crude oil. It is an intermediate between the lighter gasoline and the heavier kerosene. In the world market, several types of naphtha are being traded. There are three kinds of naphtha that are being used in basic petrochemicals production today (they are differentiated here because different kinds of naphtha lead to different mixes of light olefins):

- *Light naphtha* This is also called paraffinic naphtha (in the range C_5H_{12} - C_6H_{14}) and is a byproduct of oil refinery. A small amount of light naphtha also comes from natural gas condensates in oil and natural gas fields. Steam cracking of light naphtha leads to a high yield of light olefins. Naphtha made from Fischer-Tropsch (FT) processes, or FT naphtha, is also a light naphtha that leads to an higher ethylene yield than regular light naphtha (see Chapter 4) [32, 33].
- *Heavy naphtha* This is also called non-normal paraffinic naphtha (in the range of C_7H_{16} - C_9H_{20}). It is richer in aromatics than light naphtha. Since its octane number is low, it cannot directly be used as transportation fuel. Therefore, it is often converted through gasoline reforming into high-octane gasoline. However, it can also be used for petrochemicals production.
- *Full range naphtha* This is a mixture of light and heavy naphtha (in the range of C_5H_{12} - C_9H_{20}). It is the most common type of naphtha used in steam cracking.

Other liquid feedstocks are gas oil (C_{10} - C_{20}), C_4 - C_9 mixed fractions and low-value liquid hydrocarbons, which are far less important than naphtha in terms of the volume used in petrochemicals production. All these liquid hydrocarbons are byproducts of oil refining and petrochemical processes. Heavy liquid feedstocks, such as bitumen and heavy naphtha, can be also derived from oil sands (sometimes called tar sand) and can then be used for petrochemicals production (see Chapter 4). Chapter 4 also discusses naphtha produced from coal and biomass.

1.5.3 Basic Petrochemicals

Petrochemicals in this thesis refer to the most representative basic petrochemicals, i.e. light olefins (most importantly ethylene, propylene and butadiene) and non-olefin chemicals (aromatics).

- *Light olefins* Ethylene and propylene are the most important intermediates in the production of plastics and other chemical products. The current end use of ethylene worldwide is as follows: 58% in polyethylene (used as plastics), 13% in ethylene oxide/glycol (used for PET fiber and plastic), 13% in ethylene dichloride (used for PVC polymer), 7% in ethylbenzene (used for styrenic polymers) and 9% in others [15, 34]. The current end use of propylene worldwide is as follows: 62% in polypropylene (used as plastics), 11% in acrylonitrile, 12% in cumene (used for phenolic resin), 8% propylene oxide (used for PU) and 8% oxo-alcohol [18]. About 30% of ethylene and propylene derivatives are used for durable purposes (e.g. PVC for water pipes), meaning that they last for three or more years. The rest, 70%, is used for non-durable, mainly single applications (e.g. polyethylene garbage bags) [35].
- *Non-olefins* Non-olefin petrochemicals are typically aromatics (benzene, toluene and xylene or simply BTX)¹. Benzene is used in Europe as a gasoline additive in limited amount (maximum 1% of gasoline), but this practice is forbidden in the US. Most benzene is used to make styrene (styrene is used for making polymers and plastics), phenol for resins and adhesives (via cumene), and cyclohexane (cyclohexane is used for making nylon). Smaller amounts of benzene are used to make some types of rubbers, lubricants, dyes, detergents, drugs, explosives and pesticides. Toluene is used as a solvent (for making paint, rubber and adhesives), a gasoline additive or for making toluene isocyanate (toluene isocyanate is used for making polyurethane foam), phenol and TNT. Xylene is used as a solvent and as an additive for making fuels, rubber, leather and terephthalic acid (terephthalic acid is used for making polymers).

1.6 Approach to Access Multiple-Product Processes

All routes addressed in this thesis consist of processes that lead to multiple products. This represents a problem for the assessment: after all, different routes are only comparable if they result in outputs which are equivalent in terms of quantity and quality. To solve this problem, we need a methodology to create a common denominator for the assessment of energy use (and

¹ Aromatics, diesel, kerosene and other C₅₊ hydrocarbons are co-produced along with naphtha and/or light olefins in conventional oil-based refinery processes as well as in methane, coal and biomass-based processes.

likewise CO₂ emissions) and the economics of multiple-product processes. The two main methods as applied for this purpose are the *allocation approach* and the *credit approach* [30]:

- *Allocation approach* The energy use is allocated to the products on the basis of their *economic values* (i.e. the market prices of the products) or, alternatively, a physical property like the *mass* of the products. Since the products discussed have very different economic values, we consider the economic value-based allocation approach to be more suitable for analyzing the technologies discussed in this thesis than the mass value-based allocation approach. Details on these products will be explained in the next few sections.
- *Credit approach* This approach involves two steps. First, the energy use (and likewise CO₂ emissions and any other environmental impact) is determined for the production of each individual co-product (so not the main product) in a standalone process. This is the amount of energy that would have been needed to produce these co-products if they had been produced individually. Second, the energy use determined in this first step is deducted from the *total* energy input. Thus, the remainder is the sum of the calorific value of the main product and the process energy needed throughout the process chain in order to produce it. The deduction in the second step represents a credit (which gives the name to this approach). This credit approach is conceptually identical with the system expansion approach; however, the credit approach usually aims at having only one product as the functional unit, whereas the number of products in the system expansion approach is theoretically unlimited. For those technologies that cogenerate electricity, the *credit approach* is most suitable because electricity can be assumed to be produced in a standalone power plant. However, the *credit approach* is unsuitable for feedstocks and petrochemicals (see the next few sections). Unlike electricity, which is the only product of most power-generation technologies, none of the feedstocks and petrochemicals are produced entirely alone; therefore, they cannot be assumed to have been produced individually in a standalone plant (for example, there is no widespread technology for the production of pure ethylene only).

1.6.1 Naphtha Value-Equivalent Feedstocks

Naphtha is always produced along with other liquid hydrocarbons. Some of these, such as diesel (car fuel), kerosene, gas oil, light/heavy distillates and C₄–C₉ mixed fractions, have 20-year average historical prices similar to naphtha (in the range of \$200/t; all economic values in US dollar in the year of 2000; see Section 1.7.3) [31, 36, 37]. However, it should be noted that in recent years naphtha prices have been much higher than their historic average: the naphtha market price in 2006 was around \$600/t. The other hydrocarbons, such as propane, butane, heavy residue fuel oils, vacuum gas oil and vacuum distillate residues (mostly heavier than C₁₀), have a value which is only roughly half that of naphtha and are therefore typically considered as lower-value products [38].

Due to the large differences between the economic values of naphtha and those of lower-value hydrocarbons, the economic value-based allocation approach is used to consider the products of feedstock production processes. In this approach, 100% weight is given to the mass of naphtha-value-equivalent hydrocarbons, whereas 50% weight is given to the mass of low-value byproduct hydrocarbons, which has roughly half the economic value of naphtha.

1.6.2 High Value Chemicals (HVCs)

There are also large differences between the economic values of basic petrochemicals; therefore, the economic value-based allocation approach is used to consider these chemical products. The historical average prices of non-olefin chemicals (see the definition in Section 1.5.3) (roughly \$200/t) are approximately half as high as those of light olefins (roughly \$400/t)¹ [31, 36, 37]. Accordingly, light olefins are given 100% weighting per unit of mass, whereas non-olefins are given 50% weighting per unit of mass. This definition is different from the definition of HVCs used in [22, 39] where ethylene, propylene, butadiene, benzene and hydrogen are given 100% weighting per unit of mass regardless of their economic values². However, the yield of non-olefins in steam cracking is small in comparison with the total output of the process; consequently, this does not lead to large differences between our results and those in [22, 39].

¹ Due to the high oil prices in 2006, the average prices of light olefins were about \$1,000/t in that year.

² In Chapter 3, both of these two different definitions are used to test the sensitivity of the results to the choice of the definition.

High-value chemicals (HVCs) are defined as petrochemicals with a value equivalent to light olefins.

1.6.3 Electricity

Electricity, either used or cogenerated in a route, is assumed to come from a standalone, natural gas-fired power plant. We assume that the energy efficiency for electricity generation is 55%. Since most technologies discussed in the thesis will only possibly be used on a commercial scale worldwide in the long-term future (up to 2050), an efficiency of 55% is appropriate for a natural gas-fired power plant that will be built in the future. 55% is higher than the energy efficiency of 40% in a standalone, coal-fired electricity plant. Sensitivity tests regarding other energy efficiencies, namely 40% and 60%, will be discussed in Chapter 4.

In the case of electricity cogeneration, the credit approach is used. Several natural gas-based (Chapter 3) and most coal and biomass-based routes (Chapter 4) cogenerate a significant amount of electricity and therefore can export electricity for external use. In this thesis, we assume that these routes avoid the use of natural gas that would otherwise have been needed to produce electricity in a standalone, natural gas-fired power plant¹. Therefore, the energy use that is avoided is subtracted from the actual fossil energy use in these routes. For biomass-based routes, the result can be negative if the actual fossil energy use is less than the avoided use of natural gas. The credit approach described above concerns the calculation of fossil energy use in a route, but it also applies to the calculation of related CO₂ emissions as well. The calculation of production costs in the case of electricity cogeneration will be discussed in Section 1.7.4.

1.6.4 Yields

In this thesis, yield refers to a percentage of the desired output divided by the input, unless otherwise specified. The output refers to the final outcome after the input has gone through conversion, separation, purification and recycling.

¹ In many countries, electricity is made in coal-fired power plants, not in natural gas-fired plants. However, since natural gas-fired power plants are considerably more efficient than coal-fired ones, the choice of natural gas-fired power plants as the reference technology leads to fewer credits for cogenerated electricity in the alternative routes studied. Hence, the chosen approach leads to a conservative assessment of the possible savings of fossil energy use and possible avoided CO₂ emissions offered by the alternative routes.

All yields are on a mass basis. It should be noted that the current chemistry literature often uses per-pass yield on molar basis. Yield in feedstock production refers to the weight of the feedstocks (excluding oxygen when it is used) divided by that of primary energy sources. Yield in petrochemicals production refers to the weight of HVCs (including all light olefin value equivalent chemicals) divided by that of the feedstocks (also excluding oxygen when it is used as a feedstock). All physical units used in the thesis are metric values. A ton means a metric ton.

1.7 Energy and Economic Analysis

1.7.1 Energy Supply

The energy required to drive reactions in various processes can be supplied by external sources (e.g. imported fuel, steam and electricity). Alternatively, it can be supplied by fuel-grade byproducts that are combusted to produce the heat and steam needed for reaction and separation (e.g. in the case of naphtha-based steam cracking process). Imported fuel, unless specified differently, is assumed to be methane.

Steam, if used, is assumed to be produced in boilers at an energy conversion efficiency of 90% in terms of lower heating value (LHV). Oxygen, if used, is assumed to have been produced by the fractional distillation of air in a process that uses electricity. The primary energy used to produce oxygen at 99% purity is about 3 GJ/t oxygen¹ [40].

All energy figures in this thesis are expressed in terms of LHV². Also, unless otherwise specified, they are reported in terms of primary energy (e.g. GJ_e). GJ_e refers to the energy content of electricity—not the primary energy that is needed to make electricity.

1.7.2 Definitions of Energy Use

The main indicator used for the energy analysis in this thesis is *cumulative process energy use*³. This is the sum of the process energy use per ton of product in the two steps of a route from the

¹ Here an electricity consumption of 350 kWh/ton oxygen with an efficiency of 40% for coal-fired electricity production is assumed.

² LHV is defined as the energy released during oxidation of a unit of fuel excluding the heat required for vaporization of the water in the fuel and the water produced from combustion of the fuel hydrogen.

³ Since cumulative process energy use is expressed in primary energy terms in this chapter, it is approximately the same as cumulative process exergy consumption. The concept of cumulative process energy use (in primary energy terms) originates from the concept of gross energy requirements discussed in [41] and from the concept of the cumulative consumption of energy and cumulative exergy consumption discussed in [42].

extraction of primary energy to the basic petrochemicals: *feedstock production* and *petrochemicals production*:

- Process energy use in *feedstock production*: this term refers to the process energy for the conversion of primary energy sources to feedstocks (including also extraction, transportation and preprocessing of primary energy sources) and all the subsequent separation and purification of the feedstocks;
- Process energy use in *petrochemicals production*: this term refers to the process energy for the conversion of feedstocks to olefins/non-olefins (including also the loss of feedstocks) and the subsequent separation and purification of the petrochemicals.

In Chapter 2, all of technologies in Chapter 2 have the same amount of process energy use in *feedstock production*. Therefore, instead of analyzing *cumulative process energy use*, we only need to study *specific energy consumption* (SEC), which refers to energy use in a single step of the process chain (e.g. steam cracking) and is thus only part of the cumulative process energy use. SEC is used as the basis to compare the energy use for the production of petrochemicals by means of steam cracking processes and by means of other technologies in Chapter 2.

In Chapter 3, cumulative process energy use has been chosen as the basis for comparison because the energy use in *feedstock production* is significantly different among the technologies discussed. The comparison of process energy use in *petrochemicals production* alone would lead to distorted conclusions.

In Chapter 4, the main indicator is *total energy use*. *Total energy use* is the sum of cumulative process energy use and the calorific value of the end products derived from HVCs. It is assumed here that the waste treatment of end products derived from HVCs (e.g. the incineration of polyethylene plastic bags) does not lead to any energy recovery. The term *total energy use* is the same as “*cradle-to-grave*” energy use, which is often used in the literature.

1.7.3 Definitions of CO₂ Emissions

Analogous to the definition of cumulative process energy use, *cumulative process CO₂ emissions* is the sum of CO₂ emissions per ton of products in feedstock production and petrochemicals

production. For fossil-based routes, the carbon content of HVCs is not considered since HVCs are not combusted during feedstock production or petrochemicals production. For biomass-based routes, the carbon content of HVCs is deducted from the CO₂ emissions due to fossil energy use because the carbon content of HVCs originates from CO₂ in the atmosphere (CO₂ is captured by biomass during the plant growth). In Chapter 3 and 4, the term *cumulative process CO₂ emissions* is used. This term means the same as “*cradle-to-factory gate*” CO₂ emissions, which is often used in the literature¹.

Similar to the definition of the total energy use, the *total CO₂ emissions* is defined as the sum of *cumulative process CO₂ emissions* and the *CO₂ emissions* due to the combustion of end products derived from HVCs. It is assumed here that the waste treatment of end products derived from HVCs (e.g. polyethylene plastic bags) is incineration and, as a result, the carbon content of HVCs is released into the atmosphere. For fossil-based routes, the CO₂ emissions due to the combustion of end products derived from HVCs are equal to the carbon content of HVCs. For biomass-based routes, the CO₂ emissions due to the combustion of end products derived from HVCs do not add CO₂ to the atmosphere and are in fact zero. After all, the carbon content of HVCs originates from the atmosphere and returns to it through the combustion of end products derived from HVCs. The term *total CO₂ emissions* is used in Chapters 4 and 5 and is the same as “*cradle-to-grave*” CO₂ emissions, which is often used in the literature.

1.7.4 Production Costs

Production costs consist of the following three components:

- *Energy Prices* For feedstock production, the term energy prices refer to the costs of primary energy sources and the costs of process energy use. For petrochemicals production, we refer to energy prices as the total of feedstock costs and the cost of process energy use. Prices of primary energy sources are specified in individual chapters. Other variable costs, such as utilities (electricity, steam, etc.), are included here as well.

¹ The term *cradle-to-factory gate* energy use is defined in several ways in the literature. Some sources include the calorific value of the products and others do not. To avoid confusion, the term is not mentioned here.

- *Operation and Maintenance (O&M)* This refers to the costs of labor, operation and maintenance. If they are not specified in the referred original sources, they are assumed to be about 4% of capital costs (excluding interests).
- *Capital Costs* The main assumptions for capital costs are: capital recovery factor of 13%¹ and an operating rate of 90% (8000 hours per year).

Several natural gas-based (in Chapter 3) and most coal and biomass-based routes (in Chapter 4) cogenerate both electricity and chemicals. To calculate the production costs of chemicals, it is necessary to deduct the production costs of electricity from the total production costs of chemicals and electricity².

In Chapter 3, to calculate the production costs of chemicals, the estimated production costs of a natural gas-fired power plant are deducted from the total production costs of two natural gas-based technologies. Chapter 3 focuses exclusively on the production costs of methane-based new technologies, but in Chapter 5, the production costs of natural gas, coal and biomass-based new technologies are compared. The average production costs of coal and natural gas-fired power plants³, \$0.03-0.05/kWh, are deducted from the total production costs of those technologies with power cogeneration [43]. Here the average production costs of coal and natural gas-fired power plants are used since the production costs of these plants are nearly the same in the long term (2010-2050)⁴.

All economic values in the entire thesis are expressed in terms of constant US dollars of the year 2000. To correct nominal dollar values to the constant US dollars of the year 2000, an inflation rate of 2% is used. With a billion, giga (G), 10⁹ is meant.

¹ A capital recovery factor (annuity factor) of 13% (meaning the interest rate is 10%) leads to a return on investment (ROI) of 10% for an investment with a depreciation period of 15 years.

² We did not choose to deduct the market prices of electricity from the total production costs. First, the purpose of the economic analysis presented in this thesis is to study the production costs. Second, an equilibrium where energy prices are consistent with each other provides a level playing field for various technologies to compete with each other. Third, market prices of electricity are volatile due to many short-term issues (e. g. marginal production costs, capacity availability, fuel prices and market characteristics).

³ Coal and gas-fired power plants are chosen here because 80% of the electricity worldwide is currently made from coal and natural gas [11]. It is expected that coal and natural gas will continue to be the most important fuels for electricity production in the long-term future (2010-2050) [43].

⁴ According to a 2005 publication by the IEA (International Energy Agency) and NEA (Nuclear Energy Agency), projected production costs of coal-fired power plants are \$0.003-0.004/kWh (US dollar in the year of 2000) lower than those of gas-fired power plants in 2010-2050 [43].

Chapter 2 Petrochemicals from Crude Oil and Steam Cracking: Energy Analysis¹

ABSTRACT

Conventional routes converting crude oil and natural gas to olefins and other basic petrochemicals (i.e. aromatics) currently account for more energy use in total than any other production process in the chemical industry. To understand the potential for energy efficiency improvement and CO₂ emission mitigation in petrochemicals production, we compared the energy use in conventional steam cracking and innovative olefin technologies that utilize crude oil and natural gas-derived feedstocks. The basis for comparison is the specific energy consumption to produce one ton of high value chemicals (olefin-value equivalent). Only fuel use is considered while the calorific value of chemicals is not considered. The main findings are:

- State-of-the-art naphtha steam cracking technologies can lead to savings of about 20% compared to the current world average energy use in steam cracking.
- Alternative processes utilizing low-cost, crude oil-derived heavy feedstocks, i.e. catalytic olefin technologies, can lead to savings of up to about 20% compared to the energy use in state-of-the-art naphtha steam cracking technologies.
- Advanced naphtha steam cracking technologies in the pyrolysis section, such as advanced coil and furnace materials, can together lead to savings of up to about 20% compared to the energy use in state-of-the-art naphtha steam cracking technologies. Together with the potential improvements in the compression and separation sections, savings of up to 30% are possible compared to the energy use in state-of-the-art naphtha steam cracking technologies.

The innovative technologies mentioned above, which either have already been applied to a certain extent or are being offered for commercialization, have significant energy savings potentials and can be widely used in the coming decades.

¹ This chapter is a longer version of the paper, Ren T, Patel M, Blok K. “*Olefins from conventional and heavy feedstocks: Energy use in steam cracking and alternative processes*” *Energy*, 2006;31(4): 425-451.

2.1 Introduction

Steam cracking utilizing naphtha and ethane as feedstocks is the most dominant technology today for the production of light olefins [15]. The share and energy use of naphtha and ethane-based steam cracking in the current global olefin production are shown in Table 2-1. Given this great energy use, we are interested in studying energy use in existing steam cracking as well as the energy saving potentials offered by recent technological improvements.

Many technical articles have described various petrochemical processes with an emphasis on technical details of catalysis and engineering [44]. Some studies on various ethylene processes were conducted in the 1980s [24]. Several new olefin production technologies were also considered with respect to their recent development [23, 26, 45]. However, what is still missing is an updated, thorough comparison of improved olefin technologies and steam cracking that takes into account energy allocation to byproducts and all steps of feedstock production. Therefore, the research question in this chapter is defined as: *What are recent technological developments in steam cracking and in alternative processes that utilize crude oil and natural gas-derived feedstocks and do these developments offer any opportunities for energy savings in the coming decades?*

For confidentiality reasons, only a few articles in the open literature have presented quantitative energy analyses of steam cracking. Sources used in this chapter fall into the following categories: government reports, scientific and technical journals, and conference proceedings. Personal communications were also found to be helpful.

The scope of technologies in this chapter is limited to those that produce olefins from conventional feedstock and low-cost, crude oil-derived heavy feedstocks. Moreover, due to large shares of naphtha and ethane as feedstocks (see Table 2-1), naphtha and ethane steam cracking are the main subjects.

This chapter first gives a process description for naphtha steam cracking in Section 2.2. Definitions are given in Section 2.3, and Section 2.4 presents the results of energy analysis. In section 2.5, state-of-the-art and advanced naphtha steam cracking technologies are described, and Section 2.6 discusses catalytic technologies.

Table 2-1 Estimated Global Energy Use and CO₂ Emissions in Olefins Production in 2004

	World	US	Europe (EU and Former Soviet Union States)
Total feedstocks^b (in million tons)	310	85	90
Breakdown of Feedstocks (wt. %)	naphtha 55, ethane 30, LPG 10, gas oil 5	ethane 55, naphtha 23, propane 15, gas oil 5	naphtha 75, LPG 10, gas oil 9, ethane 5
Ethylene capacity (in million tons)	113	30	32
Propylene capacity (in million tons)	77	20	20
Total process energy use^a (fuel combustion during the olefin production process) (EJ)	3	0.6	0.8
Total CO₂ emissions (due to fuel combustion during the olefin production process; in million tons)	200	45	55

^b Feedstock use was estimated [1, 10].

^a Energy use and CO₂ emissions and the production of basic petrochemicals in 2004 are based on [1].

2.2 Process Description of Naphtha Steam Cracking

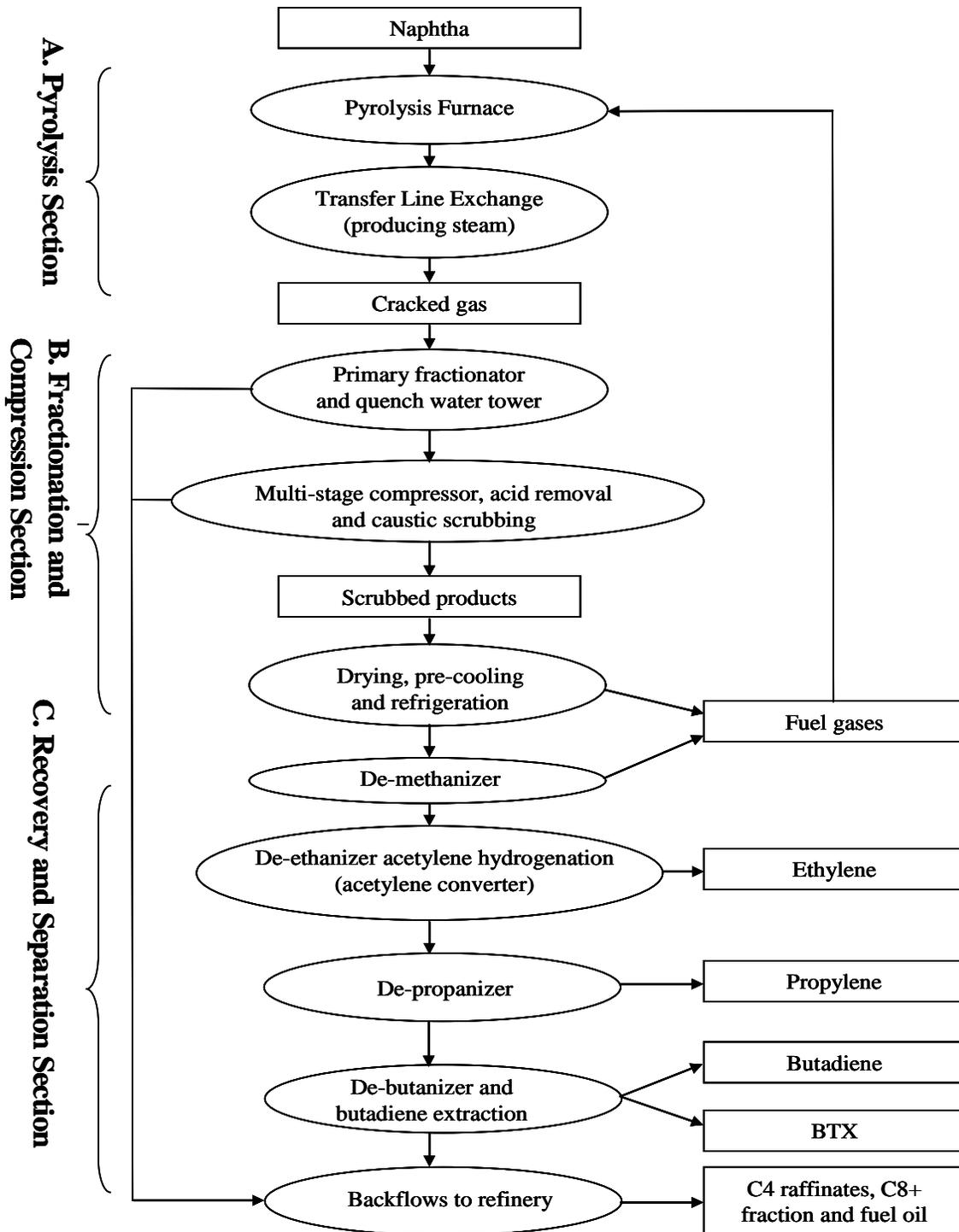
Steam cracking typically refers to all processes inside the battery limits of a steam cracker. Figure 2-1 shows a typical naphtha steam cracker, which consist of three sections: pyrolysis (A), primary fractionation/compression (B) and product recovery/separation (C). They are described as follows.

Pyrolysis Section (A) This is the heart of a steam cracker. Naphtha first enters the convection section of a pyrolysis furnace. Here naphtha is vaporized with slightly superheated steam and is passed into long (12-25 meters), narrow (25-125 mm) tubes, which are made of iron, chromium and nickel alloys. Steam is added to reduce partial pressure of products. Pyrolysis takes place mainly in the radiant section of the furnace where tubes are externally heated to 750-900 °C (up to 1100 °C). No catalysts are used. Depending on the severity¹, large molecules of naphtha are broken down (or cracked) to smaller molecules via a pyrolytic decomposition mechanism. This mechanism means that carbon bonds are broken symmetrically and thus pairs of free radicals are formed. The free radicals are electronically neutral species. They then undergo complex rearrangement and eventually lead to the formation of light olefins and aromatics in the gaseous state. After leaving the furnace, the hot gas mixture is quenched in the transfer line exchangers (TLE) to about 350 °C. TLEs are in fact a series of heat exchangers. Heat transfer activities in TLEs avoid degradation by secondary reactions and at the same time generate high-pressure steam for driving compressors, etc. However, TLEs are prone to fouling², which means coking here (see in next page). Further cooling of gas mixtures is done by liquid oil quench.

¹ High severity (characterized by residence time of less than 0.5 second and temperature up to 900-1100 °C) conditions increase ethylene yield (max. 5% increase) and lowers propylene yield. Such severity favors the production of ethylene and benzene. Low severity has temperatures at lower than 800 °C and approximately one second residence time [46]. Such severity favors the production of propylene, C₄ and liquid hydrocarbons. The degree of severity is described by the P/E ratio (propylene/ethylene). A P/E around 0.7 is low severity and any value below 0.5 is high severity. In Western Europe, the average severity for steam crackers is around 0.52 [22]. Severity is strongly limited by metallurgy of the tubes and rapid coking tendency in the coils. Newly built furnaces can reach very high severity with extremely short residence time, or milliseconds. A millisecond is one thousandth (10⁻³) of a second. It means here that gas velocities reach speeds beyond the speed of sound.

² Fouling is still an unresolved problem in the chemical process industry. Simply explained, it represents the buildup of polymers or coke on the heat transfer surface. It leads to lower heat conductivity and higher hydraulic resistance and hence results in higher energy use than what would have been necessary [47].

Figure 2-1 Typical Flow Diagram for a Naphtha Steam Cracker [22, 48]



- *Primary Fractionation/Compression (B)* Primary fractionation applies to liquid feedstocks such as naphtha and gas oil only and not for gaseous feedstocks such as ethane. In the primary fractionator, gas mixtures are first cooled to around 150 °C and most BTX and fuel oil are condensed. In the quench water tower, water from dilution steam is recovered for recycling. Here heat is recovered and used for feedstock heating, steam generation and separation sections. Then, this gaseous steam is passed through four or five stages of gas compression with temperatures at approximately 15-100 °C, then cooling and finally cleanup to remove acid gases, carbon dioxide and water. A common problem with compression is fouling in the cracked gas compressors and after-coolers. Fouling here means the buildup of polymers, which results in energy losses as well as mechanical problems such as vibration [49]. Wash oil and water are used to reduce fouling.
- *Product Recovery/Separation (C)* This is essentially a separation process through distillation, refrigeration and extraction¹. Equipment includes chilling trains and fractionation towers, which include refrigeration, de-methanizer, de-ethanizer, de-propanizer and finally a de-butanizer (see Figure 2-1). De-methanization requires very low temperatures, e.g. -114 °C. C₂ compounds, or ethylene and ethane, separation often requires large distillation columns with 120-180 trays and high reflux ratios. Undesired acetylene is removed through catalytic hydrogenation or extractive distillation. Similarly, C₃ compounds, or propane and propylene, are re-boiled with quench water at approximately 80 °C and separated in the de-propanizer. Ethylene and propylene refrigeration systems can be operated at low temperatures within -10 °C and -150 °C for cooling and high pressure with 15-30 bar for compression. Ethane and propane are either recycled as feedstocks, or burned (or exported) as fuels. A considerable amount of ethylene is condensed and recovered through turbo-expanders [49]. Methane and hydrogen are separated at cryogenic temperatures by turbo-compressors. As fuel grade

¹ There are many different designs of the separation section that aim at optimal economics by minimizing capital and operating costs. For example, front end de-methanizer has advantages of in capital investment and ease of operating, but it is not the most energy efficient. Front end de-propanizer can reduce separations energy and capital in some cases. This is a difficult separation step because of the close boiling point of C₃ compounds. Often two de-propanizers are required to avoid excessive height [49, 50]. Feedstock composition, energy integration with the site and projected energy price and are important considerations in the selection of the separation sequences [49].

byproducts, they are often used as fuel gas in the pyrolysis process, but they can also be exported. Butadiene, other C₄/C₅ compounds and aromatic gasoline are separated in the end. Butadiene extraction is not typically part of a steam cracker [50]. The total product yields from naphtha steam cracking differ depending on the paraffin and aromatic content of the naphtha and on the severities.

Generally, ethane steam cracking also requires three sections that are similar to those in the case of naphtha steam cracking process. However, ethane steam cracking requires slightly higher temperature in the furnace, a higher capacity of the de-ethanizer but less infrastructure facilities. Primary fractionator, storage tanks or recovery equipment for propylene, butadiene and BTX aromatics are not needed. Only the water quench tower is required. Also, an ethane vaporizer and a super-heater are required.

An additional issue is coking. Coking forms carbon on the furnace coils and therefore reduces its effectiveness. Although the use of steam reduces some coking, regular decoking still is required in various parts of the pyrolysis section. Before decoking, feedstocks are removed from the furnace. Then, high pressure steam and air are fed to the furnace as it is heated up to 880-900 °C (or even up to 1100 °C). Coke on the inner surfaces of the wall and tubes is either washed away with high pressure water or removed mechanically. Decoking process can take up to three days for a naphtha steam cracker. Decoking for steam cracking furnaces is required every 40-80 days on average. Typically, a naphtha pyrolysis furnace is decoked every 15-40 days. Maximum cycle time is around 60-100 days. A typical steam cracker has 6-8 furnaces to accommodate decoking and maintenance [49]. Similar decoking, though far less frequent, is also required for TLEs associated with furnaces because of fouling (see the previous page).

2.3 Definitions

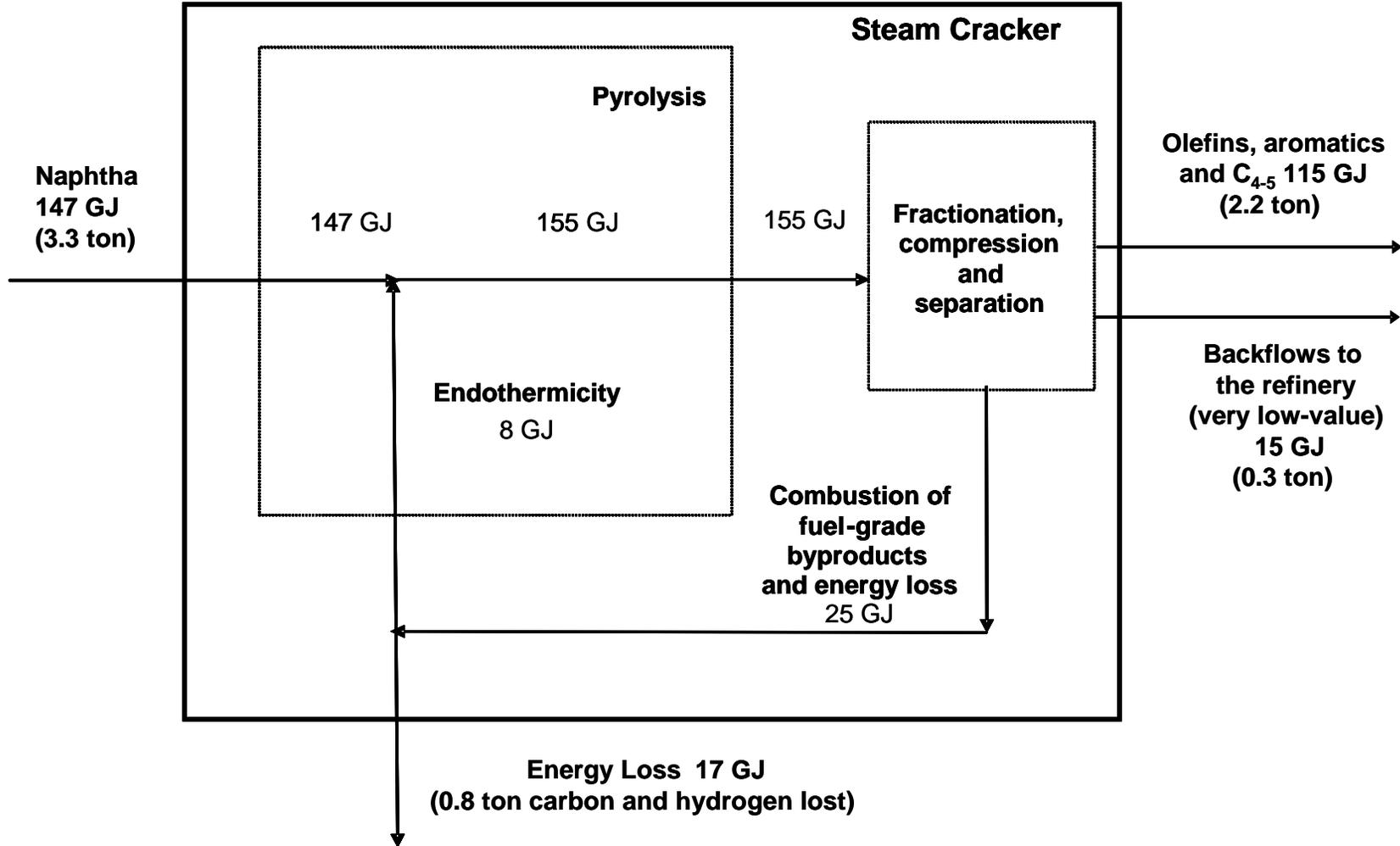
Cumulative process energy use is the sum of *energy use in feedstock production* and *energy use in petrochemicals production* in specific terms (as defined in Chapter 1). In this chapter, we focus on *energy use in petrochemicals production* in specific terms only. The reason is that all the technologies discussed in this chapter have the same amount of *energy use in feedstock production* in specific terms (or about 2-3 GJ/t feedstock [51], which contributes to less than half

of the cumulative process energy use in any technologies discussed in this chapter). The real difference between these technologies lies in *energy use in petrochemicals production* per ton of HVCs (i.e. high value chemicals as defined in Chapter 1). Please note that energy use in petrochemicals production refers only to the energy use in the conversion of feedstocks to HVCs and all the subsequent processes (i.e. compression, recovery and separation), while excluding feedstock production as such.

In the open literature, specific energy consumption (SEC) in steam cracking is the most commonly used term for comparing energy efficiency of ethane and naphtha-based steam crackers [22, 52]. To make this analysis comparable with the literature, the term SEC is the basis for comparison to compare energy use in all technologies discussed in this chapter. The SEC is the calorific value of fuels that are used in a steam cracker for conversion of feedstocks to HVCs and all the subsequent processes (this includes also the primary energy equivalent of the relatively small amounts of power required). However, the SEC in the case of steam cracking differs from *energy use in petrochemicals production* in specific terms as defined in Chapter 1 because the SEC in the case of steam cracking includes both *energy use in petrochemicals production* and the effect of *endothermicity* (all expressed in specific terms) [10]. *Endothermicity* refers to the theoretical thermodynamic energy requirement in an endothermic reaction, which is the minimum energy input required for converting feedstock to desired products [10]. Endothermicity originates from the energy released by the combustion of fuels. After the whole steam cracking process is completed, endothermicity remains in the final products as part of their calorific value. Therefore, endothermicity is not part of energy use in petrochemicals production. An illustration of the energy flow in a typical naphtha steam cracking process is shown in Figure 2-2. It shows that endothermicity is 8 GJ/t ethylene (or 5 GJ/t HVCs) in the case of a typical naphtha steam cracking. A similar amount of endothermicity (about 4-5 GJ/t HVCs) occur in all technologies discussed in this chapter.

Energy use in non-steam cracking processes discussed in this chapter is also expressed in specific terms. Some of these processes import oxygen, hydrogen, electricity and steam. Primary energy use in the production of these imports is counted as part of the SEC in these non-steam cracking processes.

Figure 2-2 Energy Flow in a Typical Naphtha Steam Cracker with Fuel Use of 25 GJ/t Ethylene (fuel use is the energy loss plus endothermicity; one ton ethylene is produced) [10]



As stated earlier, the degree of energy efficiency is measured by SEC in GJ/t. In this chapter, several measures of SEC are used, e.g. GJ/t feedstock, GJ/t ethylene or GJ/t high value chemicals (HVCs). In the literature, SEC in steam cracking is often expressed in GJ/t ethylene. This means that energy use is allocated to ethylene only and all other byproducts are produced “for free” in terms of energy use. This indicator is not suitable for comparing ethane cracking (which has a high yield of ethylene) and other processes that produce large quantities of other valuable chemicals. For example, naphtha cracking produces considerable amounts of valuable byproducts (mostly propylene and aromatics). Unlike the case of electricity mentioned earlier, none of these byproducts is produced entirely alone and therefore they cannot be assumed to be produced by a standalone plant. For these reasons, alongside the commonly used GJ/t ethylene, the term GJ/t HVCs is used as the primary indicator for specific energy consumption in this chapter. Our estimates for energy savings are expressed in terms of GJ/t HVCs.

In addition, this chapter shows the results of exergy analyses of the naphtha steam cracking process based on the data from two sources. Definitions, reference state and equations used in the two sources are described in the sources themselves or in the references quoted by these two sources [53, 54]. For the calculation of the exergy value¹ of each material flow E_m , both sources used the formula: $E_m = h - h_0 - T_0(s - s_0)$

- h_0 is the reference enthalpy; h is enthalpy of the flow;
- s_0 is the reference entropy; s is the entropy of the flow;
- T_0 is the reference temperature.

The reference conditions for s_0 are the standard ambient conditions, i.e. temperature T_0 at 25 °C and pressure at 1 bar. The exergy values of the air, water and CO₂ are assumed as zero. The full details of calculations can be found in [53, 54]. In this chapter, we will try to identify the locations of exergy losses so as to find out in which process significant exergy savings can be possible.

¹ The exergy of a system is commonly defined as the maximum amount of work that is obtainable when the system is brought into equilibrium with the reference state [55]. Unlike energy, exergy can be lost according to the Second Law of Thermodynamics.

Table 2-2 Characteristics of Ethane and Naphtha-based Steam Cracking Processes

	Ethane	Naphtha
SEC (GJ/t ethylene)^a	17-21 (typical); 15-25 (maximum)	26-31 (typical) and 20-40 (maximum)
SEC (GJ/t HVCs)	16-19	14-17
CO₂ emission (tons CO₂ per ton ethylene)^b	0.9-1.2	1.0-2.0
CO₂ emission (tons CO₂ per ton HVCs)	0.9-1.2	0.8-1.8
Ethylene yield (wt. %)^c	80-84%	29-34%
Propylene yield (wt. %)	1-1.6%	13-16%
Butadiene yield (wt. %)	1-1.4%	4-5%
Aromatics and C4+ yield (wt. %)	2-3%	10-16%
Methane yield (wt. %)	4.2%	13-14%
Hydrogen yield (wt. %)	4.3%	1%
HVCs final yield (wt. %)	82%	55-65% ^d
Backflows to the refinery (not HVCs) (wt. %)	0%	8-10%
Losses (due to fouling, coking, etc.) (wt. %)	1-2%	1-2%

^a Energy use is based on [56, 57]. SEC here only refers to process energy use in pyrolysis and separation.

^b Emissions are calculated based on [56, 58]. Emissions are the result of fuel combustion and utilities, both of which use fossil fuel. Ethane steam cracking results in higher hydrogen and ethylene content, therefore less CO₂ emission per ton of ethylene, than naphtha steam cracking does.

^c Yield data is based on [56, 59]. Yields are on mass basis and are all final yields.

^d The backflows are low-value products (half as valuable as naphtha). To calculate the yield of high value chemicals (HVCs), we subtracted half of their weight from the weight of naphtha. The result is that the yields of HVCs become slightly higher than typical yields which are reported in [22, 60].

Table 2-3 Breakdown of Specific Energy Consumption (SEC) and Exergy Losses in a Steam Cracker

Sections		Ethane	Naphtha						
		SEC ^a	Sub-Sections	Exergy Loss			SEC		
References		[61]		Our own ^b	[53]	[54, 62]	[63]	[50]	[64]
Pyrolysis	Heat of reaction	23% ^c	Fuel combustion and heat transfer to the furnace		75% (or 15 GJ/t ethylene)	73%	65%	65%	50-60%
	Steam, losses, etc.	24%		Heat exchange with steam, TLEs and heat loss to flue gas		27%			
Fractionation and Compression		22% ^d	Fractionation ^f and Compression	25% (2 GJ/t ethylene in compression and the rest of separation processes)	Not applicable	19%	15% ^e	40-50%	Major driver shaft work 11%; process use 13%
Separation		31%	De-methanization			12%			
			De-ethanizer			23%			
			De-propanizer			10%			
			De-butanizer			3%			
			Ethylene refrigeration			5%			
			Propylene refrigeration			30%			
Total		100%	Total exergy losses	100% or 17 GJ/t ethylene	100% (only pyrolysis section)	100%	100%	100%	

^a All energy figures in the table are in primary energy terms. Generally speaking, the contribution of electricity is very small, around 1 GJ/t ethylene [57]. Steam is produced internally and is in balance. Almost all process energy (including steam) originates from combustion of fuel-grade byproducts and extra fuel (only in case of ethane steam cracking). The distribution of byproduct/fuel calorific values is represented by the percentages in the table.

^b Our estimate on the pyrolysis section is based on [53]. Our estimate on the compression and separation sections is based on [54, 62].

^c Another figure for heat of reaction given in [24] is 21%. Energy use for “heat of reaction” refers to the energy used to convert feedstocks into desired products.

^d Another figure for compression given in [24] is 16%.

^f Data on the exergy loss in fractionation and quench towers was not found. We estimated the exergy loss here is below 0.2 GJ/t ethylene.

^e Another figure for compression given in [24] is 13%.

2.4 Energy Analysis of Naphtha/Ethane Steam Cracking

2.4.1. Specific Energy Consumption (SEC)

There is little data in the public literature on the specific energy consumption SEC that represents the current energy use in a typical naphtha steam cracker. Data that are publicly available are usually expressed in SECs (in terms of GJ/t ethylene) within a very wide range, but yields and methodologies are often not reported in details. The world average SECs, excluding Japan and Korea¹, in 1995 was approximately 30-36 GJ/t ethylene for naphtha steam crackers [39]. If one assumes an efficiency improvement rate of 1.7% per year for typical steam crackers in the past thirty years [22] and typical yields of HVCs in Table 2-2, then the SECs for a typical naphtha steam cracker should be approximately within the range of 26-31 GJ/t ethylene and 14-17 GJ/t HVCs.

As stated earlier, the *SEC* in the case of naphtha steam cracking is the sum of theoretical thermodynamic energy requirement and energy loss. The theoretical thermodynamic energy requirement for naphtha steam cracking is approximately 8 GJ/t ethylene or approximately 5 GJ/t HVCs. This is roughly a third of the SEC in the naphtha steam cracking as shown in Table 2-2. The other two thirds of the SEC, approximately 17 GJ/t ethylene or 8 GJ/t HVCs, is energy loss. In the case of naphtha steam cracking as specified in Table 2-3, the value of the total exergy losses is also 17 GJ/t ethylene. The breakdown of exergy losses is explained below.

2.4.2. Breakdown of SEC and Exergy Losses

The breakdown of SEC and exergy losses by each process helps identify in which process significant energy saving are possible. Data for a breakdown of SEC and exergy losses found in literature are summarized in Table 2-3. Regarding energy analysis, pyrolysis accounts for approximately 2/3 of the SEC of naphtha steam crackers. The remaining 1/3 is consumed in compression and separation sections. The compression section uses approximately 15% of the SEC in naphtha steam cracking. This is slightly less than energy use in the separation section, which is approximately 1/5 of the SEC in naphtha steam cracking.

¹ The SECs of naphtha steam crackers in Japan and Korea in 1995 are exceptionally low, namely approximately 25 GJ/t ethylene [39]. About 40% of steam crackers in Europe have an SECs of approximately 31-35 GJ/t ethylene [22]. Naphtha and gas oil steam crackers in the US have SECs at approximately 32 GJ/t [57].

Regarding exergy analysis, approximately 75% of the total exergy loss occurs in the pyrolysis section. Fuel combustion is the main cause. These large exergy losses can be illustrated by the high temperature drops across heat exchangers, which are mostly in the range of 100-300 °C and even near 500 °C in the TLEs. Throughout the whole pyrolysis process, the total temperature drop is more than 1100 °C and the total pressure drop is nearly 7 bar.

With respect to exergy use in other sections of naphtha steam crackers, most significant losses occur in propylene refrigeration, de-ethanization and compression. Losses in the compression and separation sections are caused by the use of electricity (or steam) for refrigeration and compression. These losses are not surprising if we consider the energy consuming conditions in the separation and compression sections. As the process description has indicated, cryogenic refrigeration is characterized by low temperatures (as low as -150 °C) and high pressure (up to 30 bar).

In the case of ethane steam cracking, nearly half of the SEC occurs in the pyrolysis section, which is less than that in the case of naphtha steam cracking. The contribution of the compression and separation sections to the SEC is slightly higher in the case of ethane steam cracking compared to naphtha steam cracking. The chiller that condenses and separates ethylene and ethane uses up to approximately 21% of the total energy consumption [61]. As mentioned in the process description, ethylene and ethane have similar boiling points, which causes the separation to be very energy consuming.

As mentioned in the process description of steam cracking, additional energy used in decoking/de-fouling, shutdowns/restarts and related maintenance for various sections of a steam cracker account for approximately 2-3% of the SEC [49]. Energy use in decoking and de-fouling is always included as part of the SEC in the steam cracking processes reported in the open literature [50]. Decoking and shutdowns also lead directly to large monetary losses. It is said that the greatest challenge for steam-cracker engineers today is to improve the on-stream factors or intervals between shutdowns by reducing coke formation and to extend furnace life between tube replacements.

2.4.3. Energy Integration

In the case of naphtha steam cracking, energy used in the pyrolysis section is provided through combusting significant volumes of fuel gases, which are fuel-grade byproducts. These byproducts, together with flue gases and waste heat, contribute approximately 95% of the fuel use in a naphtha steam cracker. These fuel-grade byproducts amount to approximately 20-25% of the calorific value of naphtha. The LHV of naphtha is approximately 44 GJ/t. Energy for the compression and separation sections is provided by steam, almost all of which is produced in the TLEs. Typically, steam is in balance, which means that there is no net steam import or export. However, in some cases, such as when ethane and propane are burned as fuels or in case of a highly efficient steam cracker, some surplus steam is exported. A small amount of electricity needed is provided from external sources. Electricity is used primarily for running compressors, cooling water and quench oil pumps. It amounts to primary energy use of no more than 1 GJ/t ethylene. Backflows to the refinery and energy export together can amount up to approximately 9-10 GJ/t ethylene for naphtha steam cracking [57]. In contrast to naphtha steam cracking, ethane steam cracking is not energy self-sufficient and therefore requires energy import (e.g. in the form of methane) of up to 15% of the SEC of the ethane steam cracking [56]. Electricity use and imported/exported steam (if applicable) together are considered as utilities and represent about 10% of the SEC in a typical steam cracker [50].

2.5 Latest Developments of Naphtha Steam Cracking

After we identified the processes where energy and exergy losses occur and understood the energy integration, we are now able to study processes that can reduce these losses. We first collected data on the latest technological developments of steam cracking itself. A number of them were chosen on the basis of the following criteria: using conventional or other petroleum feedstocks, undergoing active research and being highly visible in recent publications, recently emerging or being commercialized and possibly having significant impacts on energy use. In the following sections, these technologies are distinguished in two categories: (6.1) state-of-the-art naphtha steam cracking processes (Table 2-4); (6.2) advanced technologies in specific sections of naphtha steam cracking.

Table 2-4 Licensors for State-of-the-Art Naphtha Steam Cracking Technologies^a

Licensors	Technip-Coflexip ^b	ABB Lummus ^c	Linde AG ^d	Stone & Webster ^e	Kellogg Brown & Root ^f
Coil related furnace features	Radiant coils pretreated to reduce coking with a sulfur-silica mixture	Double pass radiant coil design; online decoking reduces emissions	Twin-radiant-cell design (single split) is 13m (shorter than the average length 25m)	Twin-radiant-cell design and quadra-cracking	Coil design (straight, small diameter), low reaction time; very high severity
De-methanizer Separation features	Double de-methanizing stripping system	De-methanizer with low refrigeration demand	Front-end de-methanizer and hydrogenation	De-methanization simultaneous mass transfer and heat transfer	Absorption-based demethanization system with front-end design
Gas Turbine	No data found	Approximately 3 GJ/t ethylene saved	No data found	Offered but no data	No data found
Ethylene Yield (wt. %)	35%	34.4%	35%	No data found	38%
SEC (GJ/t ethylene)^g	18.8-20 (best) or 21.6-25.2 (typical)	18 (with gas turbine); 21 (typical)	21 (best)	20-25	No data found

^a For the conventional naphtha steam cracking, ethylene yield is typically 30%. HVCs yield is typically 55%.

^b Technip data come from [59]. According to Technip, SECs vary depending on the processing scheme, extent of heat integration and climatic conditions.

^c ABB data come from [59]. Other yields are 14.4%, butadiene 4.9% and aromatics 14%. The total HVCs yield is 60.7%. Gas turbine data based on [65].

^d Linde data come from [59];

^e Stone & Webster data come from [59];

^f Kellogg & Brown Root come from [59];

^g The average SEC in the industry today is around 26-31 GJ/t ethylene for naphtha steam cracking.

2.5.1. State-of-the-Art Naphtha Steam Cracking¹

Table 2-4 is a summary of state-of-the-art technologies for naphtha steam cracking sorted by licensors. It contains only publicly available information. For the separation section, only information on the de-methanization was available for each licensor. Regarding pyrolysis furnaces, most technologies focus on the design optimization of furnace coils, which are located in the radiant section where cracking occurs (see process description in Section 2.2). The goal is to improve heat transfer, raise severity, minimize coking and maximize olefin yields. As Table 2-4 shows, small, double coils and double radiant cells seem to be common features. With respect to improvements in the separation processes, front-end de-methanization reduces refrigeration needs and therefore energy demand. For example, ABB Lummus claims a 75% cut in refrigeration needs [59]. However, traditional energy-consuming refrigeration and distillation as the main separation method remain unchanged. Further, no significant changes in the subsequent sections, such as compression and C₂, C₃ and C₄ separation, are reported as part of state-of-the-art naphtha steam cracking technologies.

The processes in Table 2-4 can reach SECs in the range of approximately 18-25.2 GJ/t ethylene, which is equivalent to savings of approximately 20% compared to the current world average SEC (26-31 GJ/t ethylene). The gas turbine mentioned in Table 2-4 is not commonly offered by every licensor. It will be discussed again in the next section. Without considering gas turbines, the average SEC for state-of-the-art naphtha steam cracking is approximately 20-25 GJ/t ethylene and 11-14 GJ/t HVCs. HVCs yields used in the calculation are based on data reported by ABB Lummus². The SEC figures (11-14 GJ/t HVCs) for state-of-the-art naphtha steam cracking technologies are still far more than the absolute theoretical thermodynamic energy requirement for naphtha to olefin conversion mentioned earlier (5 GJ/t HVCs).

In addition to data given in Table 2-4, a trend can be observed that the sizes of state-of-the-art crackers are increasing. While the current average steam cracker has capacity of around 500,000 tons ethylene per year [22], new naphtha steam crackers can produce over one million tons of ethylene annually. Technip built a plant with an ethylene capacity of over 1.2 million tons of

¹ State-of-the-art is technologies that are offered as standard, widely accepted processes and would be used if a new plant is to be built nowadays (see examples and licensors in [59]).

² ABB Lummus' steam cracking technology is said to be used in over 40% of the world's olefin plants [59].

ethylene per year in Iran¹ [66]. KBR (Kellogg Brown & Root) claims that they can able to build an ethylene plant with a capacity of two million tons of ethylene per year [67]. The same trend is observed for ethane crackers. Stone & Webster built an ethane cracker for NOVA in Canada with a capacity of 1.27 million tons of ethylene per year.

2.5.2. Advanced Naphtha Steam Cracking Technologies

Advanced technologies in specific sections of a naphtha steam cracker are not being offered by major licensors as part of standard commercialized processes. In fact, many of them are commercially available, but due to high costs, most of them are not yet widely implemented. Some are still new and their techno-economic feasibility has yet to be proven. Nevertheless, these new technologies have potentials to reduce energy use in specific sections of steam cracking where energy and exergy losses occur.

With respect to the pyrolysis section, there are a few significant innovations and all of them are aimed at improving heat transfer and raising severity. There are circulating solids such as sand, coke and other carriers, circulating beds [68], selective radiant coils (allowing better control of the propylene/ethylene ratio) [69], ceramic coated tubes/coils and other advanced furnace materials [70, 71]. Here only *advanced furnace materials* are discussed. Reducing coking can greatly improve heat transfer in furnaces. Traditionally, coking can be partially inhibited by a sulfur-compound based chemical treatment of inner walls of tubes/coils. Advanced tubes and coils in various shapes such as cast-fins are coated with ceramics such as aqueous salt metals, silicon and phosphorus compounds. They do not need chemical treatment. Coating could reduce energy use by 3-4% through reflecting heat inwards (toward the furnace) and reducing radiant energy losses to the outside² [50]. Coating can also have catalytic effects for olefins selectivity. Also, coating could allow higher severity and thereby enhance ethylene yields. Sintered silicon carbide ceramics, for instance, offer maximum temperature up to 1400 °C, high conductivity and low surface catalytic activity [72]. Conventional pyrolysis tubes made of Cr-Ni alloys allow the maximum skin temperature only up to 1100 °C. It is estimated that these advanced materials

¹ Technip claims the SEC of their crackers is 20 GJ/t ethylene as opposed to the average 30 GJ/t ethylene. It also claims that their mega crackers have lower product loss, which is 0.25% in comparison with the average 1%, as well as lower CO₂ emission, which is half of the average 1.6 t CO₂/t ethylene in Table 2-2 and lower operational cost advantages because of economy of scale [66]. It also claims that the maximum capacity cannot exceed two million tons of ethylene due to the limits of compressors.

² Some, however, doubt whether coating will reduce the production of steam needed while fuel use is reduced [50].

could lead to savings of up to approximately 10% (2-3 GJ/t ethylene) compared to the current world average SEC [69].

An additional new technology is *gas turbine integration*. When applicable, gas turbine integration can lead to the export of both steam and electricity. Also, it produces hot combustion gas for feedstock heating in a pyrolysis furnace. It can possibly save approximately 3 GJ/t ethylene, or 13% of the SEC of state-of-the-art steam cracking technologies [65]. If both advanced furnace materials and gas turbine integration are applied, savings of 20% (or 4 GJ/t ethylene) compared to the SEC of state-of-the-art naphtha steam cracking is possible.

With respect to the compression and separation section, possible improvements are: Vacuum Swing Adsorption Process (VSA), mechanical vapor recompression (MVR), advanced distillation columns, membrane and combined refrigeration systems. VSA uses solid sorbents for selective adsorption of ethylene and propylene over paraffins, such as ethane and propane. MVR could be used in a de-propanizer and could lead to savings of approximately 5% (or 1 GJ/t ethylene) compared to the SEC of state-of-the-art steam cracking [73]. However, some argue that it is not necessary since de-propanizer is currently using hot water circuit which would otherwise be wasted [50].

Advanced distillation column technology has been studied since the 1930s. One type of such columns is “divided-wall” distillation columns for butadiene extraction. They could save approximately 16% of the SEC in the conventional butadiene distillation section [74]. Another type of such advanced distillation columns is the Heat Integrated Distillation Column (HIDiC). Two variations of HIDiC developed in the Netherlands are called *Plate Fin* and *Concentric*. These advanced columns improve heat transfer by building heat exchangers between the stripping and rectifying sections. They can be applied in the de-ethanizer and the de-propanizer. It is generally estimated that HIDiC saves approximately 0.1-0.3 GJ/t ethylene, or 60 to 90% of the SEC of a conventional propylene/propane distillation column, which is known for poor energy efficiency (approximately 20-30%) [75, 76]. With HIDiC, it is even possible to save approximately 0.15 GJ/t ethylene, or 50% of the SEC in modern distillation columns with heat pumps.

Membranes are rarely applied in steam cracking. Membrane materials are often made of polymer or inorganic materials. Membranes can possibly be applied in separation of olefin/paraffin, gases (hydrogen recovery¹, acids, etc.) and coke/water [78]. Membranes could combine high selectivity with high permeability. With regard to membrane application in the C₂ and C₃ separation alone, savings of approximately 8% (or 1.5 GJ/t ethylene) compared to the energy use in a conventional naphtha steam cracker are expected [79]. However, membrane separation is widely believed to be an immature technology because membranes are unable to withstand severe operating conditions and need regular replacement due to erosion, etc. Therefore, membranes are not yet licensed by any steam cracking licensors.

Energy integration of a steam cracker with another industrial process can also save energy. *Combined refrigeration* synchronizes the cryogenic natural gas liquid plant, natural gas liquid fractionation and ethylene plants into a single unit [80]. It is claimed that 60-80% of the total refrigeration requirement by a conventional ethylene plant can be reduced, i.e. approximately 1 GJ/t ethylene can be saved [80].

Considering the energy saving potential of advanced steam cracking technologies mentioned above and the distribution of SEC in a typical steam cracker as described in Table 2-3, we estimate that by applying these advanced steam cracking technologies, it is possible to reach savings of approximately 30% compared to the SEC of a state-of-the-art steam cracking process.

2.6 Catalytic and Other Technologies

2.6.1. Specific Energy Consumption (SEC)

As alternatives to conventional steam cracking technologies, catalytic and other new olefin technologies can process conventional or other petroleum feedstocks. Table 2-5 is a list of these technologies in the order of feedstock weight from light (left) to heavy (right). Note that the technologies in Table 2-5 differ only from the pyrolysis furnace of a steam cracker. The rest, including compression and separation sections, are assumed to be similar to those of state-of-the-art steam cracking.

¹ Hydrogen recovery could be among the first wide-scale commercial applications of membranes [77].

Table 2-5 Catalytic and Other Olefin Technologies Using Conventional and Other Petroleum Feedstocks^a

	Gas Stream Technologies ^b	Ethane Oxidative Dehydrogenation ^c	Propane Oxidative dehydrogenation ^d	Catalytic cracking of naphtha ^e	Hydro-pyrolysis of naphtha ^f	Byproduct upgrading ^g	Catalytic Pyrolysis Process (CPP) ^h
Feed-stocks	Ethane and other gas feedstock	Ethane and oxygen	Propane and oxygen	Naphtha	Naphtha	C ₄₋₉ (from steam cracking, refinery, etc.)	Refinery heavy oils, residues, atmospheric gas oil, vacuum gas oil and bitumen
Reactor	Shockwave, combustion gas; shift syngas; plasma; etc.	Alloy Catalyst Reactor with hydrogen co feed	Both a stem reformer and an (oxy-reactor); or, cyclic fixed-bed	Fluidized bed	Reactors with hydrogen co feed but less steam	Fixed or fluidized bed	Riser and transfer line reactor
Catalysts	Not applicable	Mordenite zeolite	Zinc and calcium aluminate based	Zeolite (or various metal oxides)	Not applicable	Zeolite	Acidic zeolite
Specific energy consumption (SEC)ⁱ	Shockwave: approximately 8-10 GJ/t ethylene or HVCs	Dow: approximately 10-12 GJ/t ethylene of HVCs	Uhde: approximately 8-10 GJ/t propylene; approximately 8-10 GJ/t HVCs	KRICT: approximately 19 GJ/t ethylene and approximately 10 GJ/t HVCs	Blachownia: approximately 16-20 GJ/t ethylene and approximately 10-13 GJ/t HVCs	No data found	CPP: approximately 35 GJ/t ethylene and approximately 12 GJ/t HVCs
Yield (wt. %)^j	Shockwave: highest ethylene yield approximately 90%	Dow: ethylene yield approximately 80%	Uhde: propylene yield approximately 84%	KRICT: ethylene 38%, propylene 17-20%, aromatics 30% and HVCs 73%	Blachownia: Ethylene yield 36-40% and HVCs yield 70%	UOP: propylene yield from steam cracking is 30% and HVCs yield 85%	CPP: ethylene 21%, propylene 18%, C ₄ 11%, aromatics 15% and HVCs yield 60%
Status	Lab	Lab	Commercial	Pilot plant	Commercial	Commercial	Lab

^a A steam cracker has a large, tubular fired furnace; feedstock is indirectly heated; no catalysts use in pyrolysis; temperature 750-1100 °C; no hydrogen or oxygen need. Process energy for the average naphtha steam cracking technology is approximately 9 GJ/t naphtha.

^b Gas stream data come from [81]. Shockwave data come from [82]. Combustion gas could save 0.3 GJ/t ethylene [83].

^c Per pass ethylene yield on mol basis is typically approximately 30%. Data is based on [84, 85]. Oxygen production needs energy use of 3-4 GJ/t oxygen and this is accounted for.

^d Per-pass propylene yield on the mol basis is typically approximately 30-40%. Data is based on [86, 87]. Oxygen production needs 3-4 GJ/t oxygen and this is accounted for. Propane steam cracking has a SEC of 20-25 GJ/t ethylene and 15-18 GJ/t HVCs with the yields of ethylene 42% and propylene 11% [56]. Others include Oleflex by UOP, Catofin by ABB Lummus, etc.

^e KRICT data is based on [88, 89]. Also, LG claims ethylene up by 20% yield and propylene yield up by 10% and 10% energy savings on the current SECs of naphtha steam cracking in Korea [90, 91]. The SEC 7.5 GJ/t naphtha is assumed based on [92]. Other processes are: AIST ethylene/propylene yield together 60-70% and 20% energy savings per ton of ethylene and propylene is claimed [92, 93]. VNIOS ethylene yield 30-34% and propylene yield 18-20% [94]; Asahi ethylene 22%, propylene 20-40% [68].

^f Hydro-pyrolysis was used in Blachownia Chemical Works in Poland, which claims a 20% increase of the average ethylene yield and approximately 30% less energy use [95]. The technology is not offered by major licensors.

^g Olefins upgrading data is based on [96, 97]. A similar industrial process is Metathesis [98]. Metathesis is an olefin conversion process, which in this case converts ethylene and butane-2 to propylene [46]. It is basically an extension of naphtha steam cracking to increase the yield of propylene.

^h CPP data comes from [99-101]. A SEC 7.5 GJ/t feedstock is estimated. Data on similar processes can be found in [102]. There are doubts about the estimated energy use in CPP [49, 50].

ⁱ Typically, current ethane steam cracking has an average SEC 17-21 GJ/t ethylene and 16-19 GJ/t HVCs. Naphtha steam cracking has a SEC 26-31 GJ/t ethylene and 14-17 GJ/t HVCs. The state-of-the-art naphtha steam cracking has 20-25 GJ/t ethylene and 11-14 GJ/t HVCs.

^j Typically, ethane steam cracking has 81% ethylene yield. Naphtha steam cracking has 30% ethylene and 15% propylene yield.

The first three technologies use gaseous feedstocks:

- *Gas stream* technologies
- *Shockwave* technologies
- *Oxidative dehydrogenation* technologies

Gas stream technologies use gases as heat carriers to provide enthalpy needed for pyrolysis [81]. *Shockwave* technology uses steam at supersonic speed as heat carrier and the process is volumetric, not limited by heat transfer through metal walls and tubes as for the conventional steam cracking. If primary energy use for steam production is included, the SEC of shockwave technology is approximately 45% less than the SEC of state-of-the-art steam cracking [82]. Olefin producers are concerned about the large requirement of steam (approximately 5-10 times of the steam requirement by conventional steam cracking) that needs to be generated, superheated and separated from the final products [49, 103]. R&D on shockwave technology was stopped in 1998.

The third type of technology using gaseous feedstocks is *oxidative dehydrogenation* process. Such processes require high-purity oxygen (approximately 90%). There are two major oxidative dehydrogenation processes:

- *Ethane oxidative dehydrogenation* results in savings of about 35% compared to the SEC of state-of-the-art ethane steam cracking [104]. However, if the CO₂ emissions from oxygen usage are included, the CO₂ emissions from ethane oxidative dehydrogenation are 0.31 ton CO₂ per ton ethylene produced. This is 15% higher than that for ethane steam cracking. Ethane steam cracking emits less CO₂ due to combustion of hydrogen although it uses more energy per ton of ethylene than ethane oxidative dehydrogenation [104]. Oxygen production requires electricity, which is approximately 3 GJ/t oxygen in primary energy terms (see Chapter 1) [40]. The emission factor of natural gas for electricity generation is assumed to be 0.056 CO₂/GJ [210]. In the future, oxygen can be possibly produced by membrane processes or other processes (e.g. using solar energy).

- Another process is *propane oxidative dehydrogenation*. This process produces primarily propylene and only little ethylene. Similar to ethane oxidative dehydrogenation, oxygen is required in propane oxidative dehydrogenation as well. Despite of energy consumption in oxygen production, propane oxidative dehydrogenation still has the potential to lead to savings of approximately 45% compared to the SEC in conventional propane steam cracking. The SEC in conventional propane steam cracking is 15-18 GJ/t HVCs. Ethylene yield from conventional propane steam cracking is up to 45% and propylene yield is 12% [56].

The rest of the technologies in Table 2-5 uses naphtha or other petroleum feedstocks. SEC by *catalytic cracking of naphtha* is estimated to be 10-11 GJ/t HVCs. This is approximately 10-20% less than the SEC by the state-of-the-art naphtha steam cracking (11-14 GJ/t HVCs). Some of these processes, developed by LG (a major Korean chemical company) and AIST (a Japanese research institute), are claimed to have the potential to be commercialized soon.

Hydro-pyrolysis can save approximately 9% of the SEC in state-of-the-art naphtha steam cracking. Several factors enable these energy savings: higher yields, lower temperature in the furnace, low coking and lower steam requirement [95]. It is a non-catalytic process.

Byproduct upgrading technologies produce olefins by processing the byproducts (ranging from C₄ to C₉) from conventional steam cracking or from a refinery [97]. As an add-on process to naphtha steam cracking, byproduct upgrading technologies can raise the total propylene yield of naphtha steam cracking from the world average 15% to 30%. This process has a potential saving of approximately 7-10% compared to the SEC in state-of-the-art naphtha steam cracking.

Using heavy oils as feedstocks, the *catalytic pyrolysis process (CPP)* saves approximately 12% of the SEC of state-of-the-art naphtha steam cracking [99, 100]. In the pyrolysis section, the reaction temperatures required for CPP are around 650-750 °C while those for steam cracking are around 800-1100 °C [99, 100]. The mild reaction condition in CPP is the main reason for energy saving (see details in next section).

The energy savings estimated here the results of energy efficiency improvement in the pyrolysis section. If advanced separation technologies (mentioned under 6.2) are also applied, then the

energy savings by catalytic olefin technologies compared to the SEC of state-of-the-art naphtha steam cracking could be up to 40%. Among the olefin technologies discussed, gas stream and hydro-pyrolysis have not been actively pursued by the industry in recent years. However, catalytic olefin technologies are under intensive R&D, especially in China, Korea and Japan.

2.6.2. Reactors and Catalysts

It is interesting to discuss further possibilities for energy saving by the catalytic olefin technologies just mentioned. The emergence of catalytic olefin technologies is in line with the recent discussion on energy saving through process intensification¹. Catalytic olefin technologies basically can be divided into two categories: acidic catalytic cracking and thermal catalytic pyrolysis [88].

- Acidic cracking is associated with zeolite catalysts, FCC-like riser/bed reactors and other petroleum feedstocks.
- Thermal catalytic pyrolysis is associated with various kinds of metal oxide catalysts and naphtha.

The reactors are often similar to tubular furnaces used in steam cracking, but FCC-like reactors are also being tested. The reactors and catalysts used in these new technologies (in Table 2-5) share features with conventional refinery FCC reactors, which are fixed or fluidized bed catalytic cracking reactors. China's SINOPEC has named its catalytic olefin technologies "FCC family techniques" [102].

FCC reactors are usually larger than pyrolysis furnaces. In FCC reactors, moving beds and catalysts used enable intensive contact between catalysts, reactors and feedstocks (by maximizing contact surface) and thereby leads to highly efficient heat transfer. The yield of propylene from FCC can be as high as 17-25% (over 70% of the products are LPG, gasoline and naphtha) [76]. FCC reactors are known for using less energy in terms of SEC/t feedstock (SEC approximately 2-3 GJ/t feedstock) than steam cracking furnaces (SEC approximately 5-9 GJ/t ethane or naphtha). It is mainly because FCC reactors usually operate at lower temperatures than

¹ This term basically means that better heat and mass transfer in smaller and faster reaction systems with less steps lead to higher conversion, better efficiency, less waste and safer control systems [105].

steam cracking. FCC reactors operate at low temperatures: approximately 450-600 °C, which is 200-400 °C less than the temperatures in steam cracking [106].

Acidic zeolite catalysts, such as zeolite FCC catalysts, have been used to save energy in oil refineries. Zeolite FCC catalysts adopted by US refineries in 1977 have helped save 200 million barrels of crude oil, or 30 million tons in the US alone [107]. Zeolite catalysts are complex alumino-silicates, large lattices of aluminum, silicon and oxygen atoms. Such catalysts promote a heterolytic mechanism, which in contrast to the homolytic mechanism in steam cracking, breaks down large hydrocarbon molecules asymmetrically into pairs of carbonium ions of opposite charge (i.e. a carbocation and a hydride anion). These carbonium ions then recombine to form FCC gasoline, LPG, naphtha and olefins.

Derived from experiences in the use of zeolite FCC catalysts, many of the catalytic technologies shown in Table 2-5 use similar catalysts or combine zeolites with other catalysts. The combined use of zeolite and other catalysts lead to formation of both carbonium-ions and free-radicals. They are then reorganized and eventually lead to light olefins, aromatics and other products.

Similar to FCC, catalytic olefin technologies can reduce activation energy use in the pyrolysis section of conventional steam cracking processes¹. The reasons for energy saving are:

- First, these catalysts provide an alternative route to steam cracking with the use of lower activation energy for C-C bonds rupture. In the case of CPP, this means the cracking can be carried out at moderate temperature and pressure in comparison with steam cracking. Also, most of the catalysts cannot withstand extremely high temperatures and pressures as in steam cracking (up to 1,100 °C and 700 bar). Consequently, the temperatures for the new catalytic naphtha steam cracking processes are 150-250 °C lower than those for steam crackers (Table 2-5).
- Second, catalysts improve selectivity to desired products, such as propylene. If the same operating conditions as those of steam cracking are applied for catalytic

¹ The activation energy is provided by fuel combustion, which always leads to exergy loss. Although part of the heat (or the activation energy) in the pyrolysis section is recovered and used later in other sections, exergy loss is irreversible. Therefore, to be more precise, catalytic olefins technologies reduce exergy loss in the pyrolysis section of the conventional steam cracking processes.

cracking, the total olefin yield by LG's catalytic pyrolysis technology can be enhanced by at least 15% [90].

Earlier attempts to catalytically convert heavy hydrocarbons to light olefins often showed that the use of catalysts was quite problematic due to various reasons, such as thermodynamic equilibrium limitations, coking, low yields of olefins and high yield of low-value byproducts¹ [102, 108]. The new catalytic technologies in Table 2-5 have made some progress in solving these problems, but more improvement is still needed.

- Regarding the equilibrium limitation, oxygen is used to drive the reaction towards the desired direction and to take advantage of heat generated by oxidation. As a result, excessive heating and high pressure are not required and thereby energy efficiency is improved [106]. At the same time, oxygen can also be used to burn off coke on the catalysts. Also, reactors that use inorganic catalytic membranes can separate oxygen, ethane/naphtha, hydrogen and other products while reducing undesired reactions and improving the conversion in the equilibrium limited reaction. However, their technical feasibility has yet to be demonstrated.
- Older metal oxide catalysts were prone to coking and quickly deactivate. As stated earlier, coke lowers energy efficiency by hindering heat transfer and by decreasing catalyst activities. Therefore, high severity (i.e. high temperatures and short residence time) was required to reduce coking or to remove coke (catalyst regeneration/decoking). However, high temperatures (800 °C or above) and extremely short residence time (in milliseconds) are often very harsh on catalysts and result in quick deactivation of catalysts and a short lifetime. Recently, new zeolite catalysts, such as metal, silica and hybrid, have shown to cause less coking and to be more effective under higher temperatures [99, 109]. One recent patent on catalytic olefin technologies claims that new catalysts can reduce CO₂ and methane contents in the air stream from catalyst

¹ Coke can be significant even at high reaction temperatures. It can currently only be burned through catalyst regeneration and is very problematic if it remains in the final products. Catalytic olefin technologies often yield large amount of methane and hydrogen, which need much energy at cryogenic conditions for separation. Other low-value byproducts, such as aromatic-rich gasoline is difficult to use due to instability caused by olefins and additional processing will lead to high costs.

regeneration by 90% and 50% respectively in comparison with the air stream from steam cracking [106].

- Older catalysts often show strong selectivity to undesired methane, excessive aromatics and very heavy hydrocarbons instead of light olefins. Undesired methane takes much high-value hydrogen away and, subsequently, excessive aromatics with low hydrogen content are produced. This is still a technical challenge because high temperature and short residence can reduce methane yield, but they also can be too harsh for most of catalysts. New catalysts, such as Ga-P zeolite, may prove to be able to suppress aromatization and therefore provide relatively high yield of ethylene and propylene.

2.7 Conclusions

This analysis of olefin technologies was initiated in view of the large energy use, costs and CO₂ emissions of olefin production. The results of the energy analysis indicate the most energy-consuming sections, such as the pyrolysis section, which accounts for approximately 50-65% of the SEC and approximately 75% of the total exergy losses. An overview of state-of-the-art naphtha steam cracking technologies offered by licensors shows that energy savings of approximately 20% are possible compared to the current world average energy use. Advanced naphtha steam cracking technologies in the pyrolysis section, such as advanced coil and furnace materials, could together lead to savings of up to approximately 20% compared to the energy use of state-of-the-art technologies. Together with potential improvements in the compression and separation sections, savings of up to 30% are possible compared to the energy use in state-of-the-art naphtha steam cracking. Catalytic naphtha steam cracking could possibly lead to savings of up to approximately 20% compared to the energy use in the state-of-the-art naphtha steam cracking. Several other catalytic olefin technologies apply special reactors, catalysts or additional materials (e.g. oxygen and hydrogen) to crack both conventional and low-cost heavy feedstocks. These innovative technologies can lead to higher yields of valuable chemicals such as propylene at lower reaction temperatures. These technologies, which either have already been applied or are being offered for commercialization, have significant energy savings potentials and can be widely used on a commercial scale in the coming decades.

Chapter 3 Petrochemicals from Methane: Energy Use and Production Costs¹

ABSTRACT

Conventional routes converting crude oil and natural gas to basic petrochemicals currently account for more energy use in total than any other production processes in the chemical industry. Recently, methane-to-olefins routes via methanol and oxidative coupling have attracted much attention, but few studies have compared these routes with the conventional routes. In this chapter, we compare these methane-to-olefins routes with naphtha and ethane-based routes (discussed in the previous chapter) with respect to their cumulative process energy use, CO₂ emissions and current production costs per ton of high value chemicals (olefin-value equivalent). The calorific value of the petrochemical products is not considered as part of the cumulative process energy use. Electricity is assumed to be produced in a natural gas-fired power plant. Two energy efficiencies for electricity cogeneration, 55% and 60%, are tested. The main findings are:

- To produce one ton of high value chemicals, the most efficient natural gas-to-olefins-via-methanol route uses more than twice as much process energy as state-of-the-art steam cracking routes.
- Natural gas-to-olefins via methanol routes are unattractive for Europe and the US, where natural gas prices are currently very high. Methane-based routes can be economically attractive in remote, gas-rich regions where natural gas is available at low prices and methanol can be produced at \$75-100/ton methanol. The development of liquefied natural gas (LNG) may increase natural gas prices in these locations.
- Oxidative coupling routes are currently still immature due to low ethylene yields and other problems. They are currently not economically attractive, although sales of cogenerated electricity at high prices can improve the picture.

¹ This chapter is a longer version of the paper, Ren T, Patel M, Blok K. “*Steam cracking and methane to olefins: energy use, CO₂ emissions and production costs*”. *Energy*, 2008:33(5): 817-833.

3.1 Introduction

The previous chapter was a comparison of the specific energy consumption of various olefin technologies that utilize conventional and other petroleum feedstocks. Such feedstocks are either derived from crude oil or separated from natural gas. The current chapter will address energy use in various olefin technologies that utilize feedstocks derived from methane (accounting for approximately 90% of natural gas on the mass basis) through the so-called C_1 routes (methane contains one carbon). C_1 routes have often been hailed as the “holy grail” of the chemical industry due to their potential to utilize methane in remote locations¹[22]. Recently, C_1 routes via methanol (referred to as methanol routes) have been demonstrated and commercialization plans have been made. Oxidative coupling of methane (referred to as oxidation routes) is also undergoing intensive R&D.

In view of these developments, the objective of this chapter is to compare several C_1 routes in terms of cumulative process energy use, cumulative process CO_2 emissions and production costs. A few studies conducted in the late 1980s and early 1990s estimated energy use in C_1 routes [24, 112, 113]. However, an updated comparison of the cumulative process energy use and CO_2 emissions of the most recently developed C_1 routes and steam cracking is still missing. Production costs of C_1 routes and steam cracking have been studied separately by several licensors, consultancies and producers [114-117]. It is interesting to use the data contained in these sources for a comparative analysis of the production costs of various routes.

The research question in this chapter is defined as: *How do the cumulative process energy use, cumulative process CO_2 emissions and production costs of methane-to-olefin routes compare to those of naphtha and ethane-based steam cracking routes?*

In the current chapter, energy use in world average and state-of-the-art steam cracking routes are used as the benchmark for the comparison with C_1 routes. The production cost analysis is performed with various assumed prices of natural gas, crude oil and electricity to test the sensitivity of production costs to these assumptions. The effect of energy prices in the future will be discussed in Chapter 5.

¹ Recoverable natural gas reserves in the world could be 5,000-6,000 EJ over the next 60-160 years. Additionally, it is also possible to derive 840,000 EJ of methane from unconventional resources, such as coal-beds and hydrates [110, 111].

The technical and economic data used in the analysis were found in publicly available literature. Most of the sources were found on the Internet, in libraries and at conferences, and they belong to the following categories: journals (e.g. Oil & Gas Journal and Hydrocarbon Processing), US and European Patent Offices, conferences and seminar proceedings, and publications by producers and licensors (e.g. UOP and Lurgi). A small number of personal communications with experts are also used as references.

There are two types of C_1 routes through which natural gas can be converted into olefins: *indirect* routes (via syngas or ethane) and *direct* routes (directly from methane to light olefins)¹. In this chapter, we focus on several *indirect* routes that are frequently discussed in the open literature: three designs of methanol-to-olefins and two designs for oxidative coupling of methane via ethane. Another *indirect* route is methane to olefins via Fischer-Tropsch (FT) liquids and the subsequent conversion to high value chemicals by means of steam cracking. This route will be discussed in Chapter 4 along with other FT-related routes that utilize coal and biomass. The *direct* route from methane to olefins is a modified Fischer-Tropsch reaction. This route is technically difficult because of low selectivity to light olefins and high yield of heavy hydrocarbons [125]. Today, the chemistry of the direct route remains one of the world's major scientific challenges and very few publications are currently available on the topic [126]. The idea is over sixty years old, but there has been no commercialization so far [127].

The content of this chapter is as follows. First, the processes of C_1 routes are briefly described. Second, their energy use and CO_2 emissions are compared with those of steam cracking. Some possibilities for further energy-efficiency improvement are also discussed. Finally, their production costs are compared with those of steam cracking.

3.2 Methanol and Oxidation routes

The two routes discussed in this chapter are the following:

¹ Some C_1 processes require extremely high temperatures, such as thermal pyrolysis (1,000-1,200 °C), oxyprolysis (850-900 °C), and chloropyrolysis of natural gas (900 °C) [118]. Some of them, such as those via syngas [119, 120], via syngas/methanol-derived ethanol [121] and methyl-chloride CH_3Cl [122], have very low once-through yield. In the catalytic conversion of CO_2 (captured from other processes or from air) and other gases (e.g. ethane and propane) to petrochemicals, there is also the problem of a low yield [123, 124]. Low yield requires much recycling, which means much energy use and great capital investment. For these reasons, these processes will not be discussed in this thesis.

- *Methanol Route:* First, methanol is produced and then is converted to olefins through methanol-to-olefins (MTO) processes. The recent development of methanol routes is summarized in Table 3-1. Research on methanol routes started 20-30 years ago and two pilot plants in Norway are currently in operation (Table 3-1). Three major emerging designs of methanol routes are described in Section 3.4.2.
- *Oxidation Route:* Oxidative coupling of methane (OCM) is sometimes called partial oxidation of methane to ethylene or catalytic oxidative dimerization of methane [128]. OCM has attracted much attention from both academia and industry¹ [131]. Table 3-1 lists a number of major companies involved in R&D on OCM. Currently, no breakthroughs are foreseen. No pilot plants have been described in recent literature.

3.2.1. Methanol Routes

The methanol route, as illustrated in Figure 3-1, consists of three steps:

- *Methanol Production (A)* An example of a state-of-the-art methanol process is Lurgi's Mega-Methanol process. Methane is first fed into a pre-reforming reactor where it is partially reformed with steam to syngas (with a H₂/CO₂ ratio around 3-5). Pre-reforming reduces coking in the subsequent steps. Unreformed methane is further converted to syngas in the auto-thermal reforming reactor with oxygen as a reforming agent at about 1000 °C. Auto-thermal reforming has two stages. First, in a partial oxidative, non-catalytic process, methane is partially oxidized to produce syngas. This is an exothermic reaction (about 5-6 GJ/t methane) and the heat can be used for further processing or export. Second, in a catalytic steam reforming process, unconverted methane is further reformed into syngas. This is an endothermic reaction (about 30 GJ/t methane). After these two stages, syngas is converted into raw methanol (not yet dewatered) through an exothermic synthesis process with a temperature range of 200-280 °C.

¹ The number of publications and patents reached a peak in 1988-1992 and then started to decrease [128]. Researchers in the Netherlands produced some optimistic studies in the early 1990s [112, 129, 130].

Table 3-1 Historical Development in Methanol to Olefins and Oxidative Coupling of Methane Routes

Year	Companies	Technologies	Capacity/status	Location	Sources
1970s- 1980s	Mobil, ICI, BP, Union Carbide, BASF, Hoechst, etc.	Various catalysts for converting methanol to olefins	R&D only; no commercial scale (olefin yields were very low)	Various	[132-134]
1980-now	ARCO, Akzo, BP, DSM, UOP LLC, ExxonMobil, etc.	Oxidative coupling of methane to olefins	R&D since 1980; approximately 20 patents were filed since 1986	Various	[131, 135, 136]; BP [118]; DSM [116]
1990s-now	S. C. ZECASIN	ZECASIN (Methanol to olefins)	In operation but information unavailable	Romania	[137]
1990s-now	ExxonMobil and UOP LLC	Methanol to olefins and gasoline	Extensive R&D	Various	[138-141]
2000-now	UOP LLC/Norsk Hydro and DICP	Methanol to olefins	Pilot plants: olefins 300 t/year by UOP/Norsk; olefins 7000-8000 t/year by DICP	Norway and China	[49, 81, 142]
2002-now	Lurgi and Statoil	Methanol to propylene	Capacity of a pilot plant undisclosed; offered for commercialization	Norway	[143, 144]
2003-now	UOP LLC and Eurochem	Methanol to olefins (plus poly-olefin production)	800-1,000 Kt olefins per year (planned) ^a	Nigeria	[145]
2003-now	UOP LLC and EATCO Suez	Methanol to olefins (plus poly-olefin production)	400-550 Kt olefins per year (planned)	Egypt	[146, 147]

^a The total capacity of the plants in Nigeria and Egypt together represents approximately 1% of the world olefin capacity in 2004.

Figure 3-1 Natural Gas via Methanol to Olefins Based on Lurgi MegaMethanol, UOP MTO, Lurgi MTP and ExxonMobil MTO (Section A is Lurgi MegaMethanol [148]; Section B and C represents UOP MTO [149] and Lurgi MTP [144]; Section C includes UOP/Total Olefin Upgrading Unit [97, 150]; see ExxonMobil MTO in [138-140])

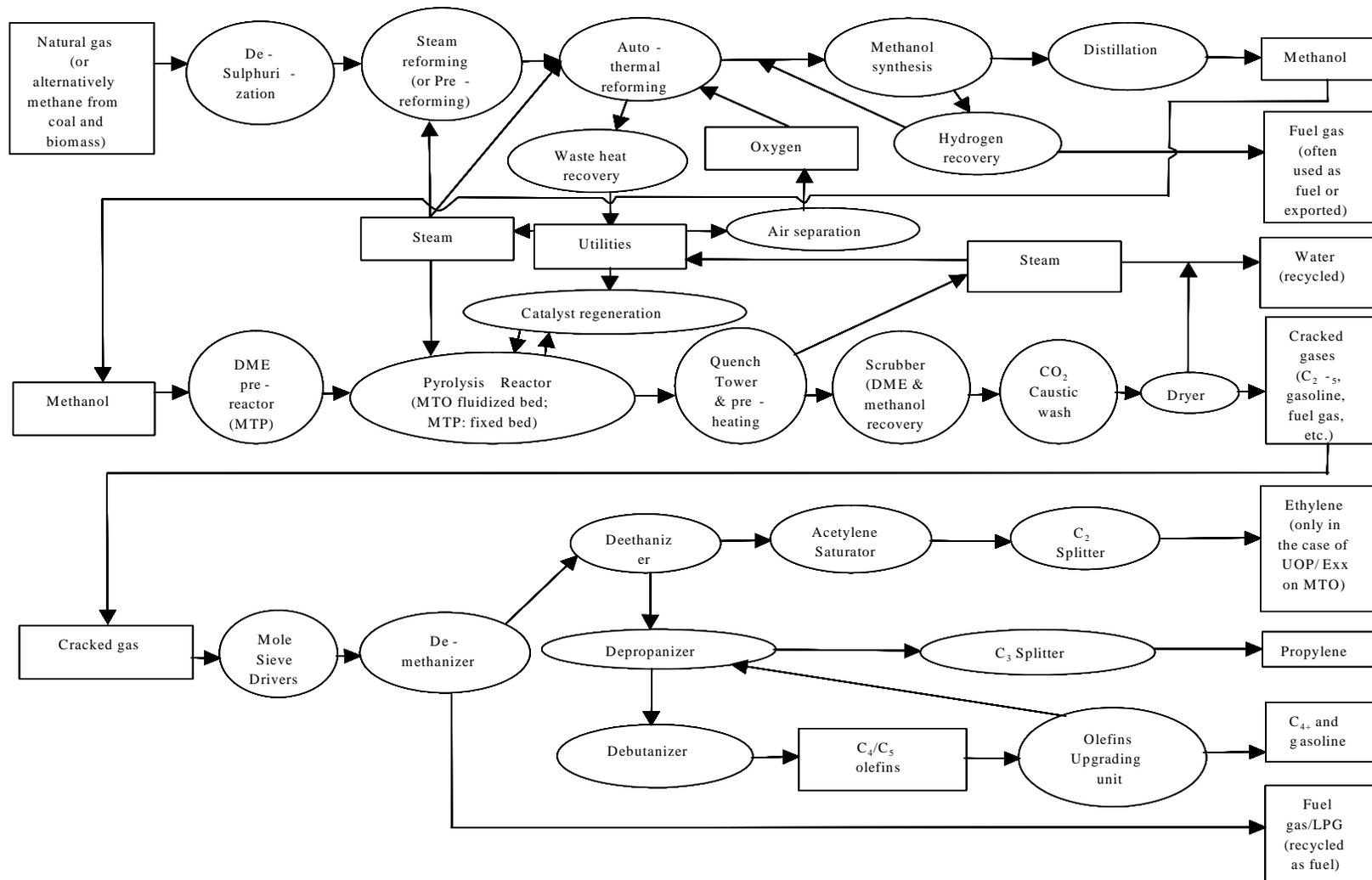


Table 3-2 Summary of Natural Gas-to-Olefins Routes (All yields are maximum yields and are given as the mass of products divided by that of natural gas)

Feedstock	Natural gas to methanol via syngas ($\text{CH}_4+\text{H}_2\text{O}\rightarrow\text{CH}_3\text{OH}$, methanol yield 145%)			Natural gas and oxygen
Technologies	UOP MTO ^a	ExxonMobil MTO ^b	Lurgi MTP ^c	BP OCM ^d
Intermediate	Via methanol and DME	Via methanol and DME	Via methanol and DME	Via ethane
Desired reactions	$\text{CH}_3\text{OH}\rightarrow\text{H}_3\text{COCH}_3+\text{H}_2\text{O}$; H_3COCH_3 is converted into C_2H_4 and C_3H_6 ; water is also produced		$\text{CH}_3\text{OH}\rightarrow\text{H}_3\text{COCH}_3+\text{H}_2\text{O}$; H_3COCH_3 is converted into C_3H_6 , water is also produced	$2\text{CH}_4+1/2\text{O}_2\rightarrow\text{C}_2\text{H}_6+\text{H}_2\text{O}$; $\text{C}_2\text{H}_6+1/2\text{O}_2\rightarrow\text{C}_2\text{H}_4+\text{H}_2\text{O}$
Reactors	Fluidized bed	Fixed bed and fluidized bed	Fixed bed	Fixed bed
Catalysts	silico-aluminophosphate (SAPO-34 or MTO-100)	ZSM-35 (zeolite) and SAPO	ZSM	Metal oxides (e.g. MgO)
Temp. (°C)	350-525	350-500	400-450	650-850
Ethylene yield	26% w/t C _{4,5} upgrading	14%	Negligible	50% per-pass yield
Propylene yield	33% w/t C _{4,5} upgrading	18%	46%	7%
C _{4,5} yield	9% (w/o upgrading)	Negligible	Negligible	2%
Gasoline yield	Negligible	29%	20%	Negligible
Fuel gas yield	2%	0.1%	6%	H ₂ 3% and others 7%
Water yield	83%	81%	81%	Water 180%; CO and CO ₂ 70%
Total HVCs Yield	62%	45% (61% if gasoline weighted 100%)	57% (65% if gasoline weighted 100%)	Per pass 18%

^a UOP MTO data is based on [151, 152]. Olefin upgrading data is based on [97, 150].

^b ExxonMobil MTO data is based on [127, 153].

^c Lurgi MTP data is based on [143, 144, 154].

^d BP OCM data is based on [155]. No energy data is given. Methane/oxygen ratio and ethylene yield are close to those of DSM OCM I. Conversion rate is 22% and selectivity is 74%. DSM OCM I & II have a conversion rate of 30% and a selectivity of 50% [116].

- Conversion of Methanol to Olefins and Gasoline (B)* The heat from methanol synthesis can be used to convert part of methanol into DME (dimethyl-ether CH_3OCH_3) and water. Then, DME is converted into olefins through olefin synthesis reactions. A fluidized or fixed bed reactor is used. Severity conditions are milder than those in the case of steam cracking. Temperature is controlled to no higher than $600\text{ }^\circ\text{C}$ as opposed to $750\text{-}900\text{ }^\circ\text{C}$ in steam cracking. Pressure is about 1-3 bar. As in the steam cracking process mentioned earlier, high severity (high temperature, low pressure and short resident time) favors ethylene over propylene. In this process step, dehydration catalysts are used. There are basically two major catalyst families, ZSM (zeolite silicon micro-spores doped with metal ions such as Mn, Sb, Mg or Ba) and SAPO (silico-aluminophosphate molecular sieve doped with metal ions such as Mn, Ni or Co). The main differences between ZSM and SAPO catalysts are pore sizes and acidity, which are the main causes for shape selectivity. ZSM catalysts have a shape selectivity favoring propylene and heavy hydrocarbons over ethylene. Also, they reportedly lead to less formation of aromatic coke and carbon oxides than SAPO catalysts do [142]. SAPO catalysts have a shape selectivity favoring light olefins over heavy hydrocarbons.
- Product Recovery and Separation (C)* The subsequent cooling, recovery and separation processes are quite similar to those of steam cracking. One difference is that after the recovery and separation of C_4/C_5 , the olefin upgrading (sometimes called olefin conversion) process converts C_4/C_5 to ethylene and propylene [97]. Most of the energy required here is supplied by olefin synthesis in the last step. Composition and yield of final products depend on catalysts, reactor configurations (dilution by steam, aromatics, etc.) and severity (temperature, residence time, etc.). Polymer-grade light olefins of high purity (97-99%) are the major products.

The process steps as described above apply to all three designs of methane-to-olefin routes via methanol discussed in this thesis:

- UOP LLC and Norsk Hydro's methanol-to-olefins process (referred to hereinafter as UOP MTO);

- ExxonMobil's methanol-to-olefins and gasoline process (referred to hereinafter as ExxonMobil MTO);
- Lurgi and Statoil's methanol-to-propylene process (referred to hereinafter as Lurgi MTP).

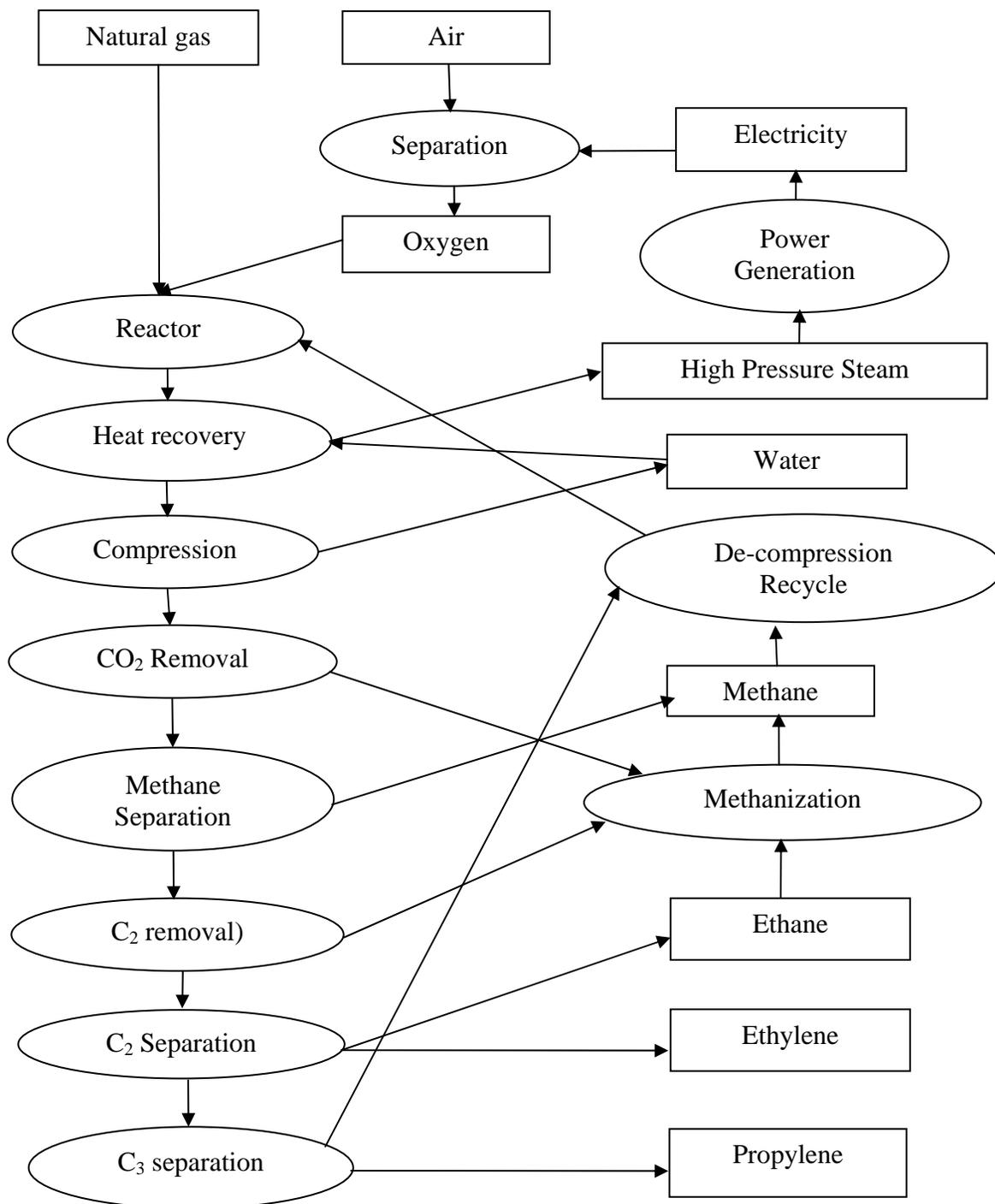
The differences between UOP MTO, ExxonMobil MTO and Lurgi MTP are summarized in Table 3-2. The most important difference is the product yields, which depend on the reactor and catalyst used.

3.2.2. Oxidative Coupling of Methane (OCM)

Figure 3-2 shows a generic OCM route diagram with integrated electricity cogeneration and air separation for oxygen production. Table 3-2 shows a summary of data on OCM routes. These routes can be summarized as follows:

- *Production of Methane and Oxygen* First, methane is separated from natural gas and is purified. Oxygen is separated from air cryogenically at a pressure of approximately six bars and very low temperatures (about $-185\text{ }^{\circ}\text{C}$). Electricity or steam produced in later steps can be used for air separation. The ratio of methane to oxygen (99% purity) should be controlled at about 2.5:1 in order to lower the risk of explosion [156] and to reach desired selectivity to ethylene [49].
- *Oxidative Coupling* A common oxidative coupling reactor design has a fluidized bed, though many other designs are also being considered. In the reactor, methane (CH_4) and oxygen react over a catalyst to form water and a methyl radical (CH_3). This reaction is often called partial oxidation of methane. The methyl radicals combine to form a higher alkane, mostly ethane (C_2H_6), which dehydrogenates into ethylene (C_2H_4). The function of the catalysts is to control oxygen-ions so that reactions can be kept on the desired path. Complete oxidation (rapid formation of CO_2 before the radicals link up to form ethane and ethylene) is an undesired reaction. Catalysts used are mostly oxides of alkali, alkaline earth and other rare earth metals. Hydrogen and steam are sometimes added in order to reduce coking on catalysts. After one pass, approximately 80% of the total oxygen feed by mass is consumed [156].

Figure 3-2 Oxidative Coupling of Methane to Olefins (based on [116, 155]. Electricity cogeneration based on [116]. CO₂ methanization based on [135])



Ideally, 100% is desired since oxygen is difficult to separate and can cause undesired combustion or even explosion later on [49]. The per-pass ethylene yield on the mass basis of methane is approximately 30% due to low conversion and poor selectivity to ethylene¹ [155, 158].

- *Compression, Separation and Recovery* These processes are similar to those of ethane steam cracking except for the sections for water/CO₂ removal and methanization. Ethylene-containing gas streams are compressed and water is condensed. Then, the gases pass through an acid gas removal system where CO₂ is removed. Additional water is removed in a refrigeration unit and then completely removed along with CO₂. In the methanization section, CO, CO₂ and H₂ are converted to methane, which is recycled as a feedstock to increase the total yield [116, 135]. From the remaining stream, ethylene, ethane, propylene and propane are separated through C₂ and C₃ separation respectively.

Given the absence of OCM pilot plants, this analysis is based on two designs by G. Swanenberg in a DSM-sponsored feasibility study [116] (referred to as DSM OCM I & II in this chapter). Both DSM OCM I & II produce ethylene, water, CO₂ and heat. Heat is used for electricity production. Oxygen required for this route is imported. The principle differences between DSM OCM I and II are:

- Methane/oxygen ratios in DSM OCM I and II are 1:2.2 and 1:0.56, respectively.
- The recycling/methanization section is included in DSM OCM I but not included in DSM OCM II [116]. In DSM OCM II, all non-ethylene effluent (unconverted methane, etc.) is combusted for heat export without going through separation, recycling and methanization.
- The final products of DSM OCM I are ethylene and electricity (approximately 19 GJ_e/t ethylene). About 2.3 ton CO₂ per ton ethylene is also produced. In DSM OCM I, a

¹ In this chapter, ethylene final yield from OCM is calculated by dividing the weight of ethylene by the mass weight of feedstock methane on the yearly basis. This definition is used in this chapter to compare OCM with other processes. However, chemistry literature often reports ethylene yields on the molar basis, which is determined by conversion rate of methane and selectivity to ethylene. For example, it is said that the maximum yield of ethylene is typically close to 15-20% on the molar basis, which refers to a methane conversion rate of 20-30% and selectivity to ethylene of 70-80% [155, 157].

CO₂ separation unit is included so that CO₂ can be separated and be sold if a market exists [116]. However, DSM OCM II does not have a CO₂ separation unit. In order to make DSM OCM I & II comparable, energy used in the CO₂ separation unit in DSM OCM I is not considered in this analysis.

- The final products of DSM OCM II are ethylene and electricity (approximately 148 GJ/t ethylene). About 15 ton CO₂ per ton ethylene is also produced. Given its product distribution, DSM OCM II is in fact a combined-cycle power plant with ethylene as a byproduct.

3.3 Definitions

The terms allocation approach and credit approach were defined in Chapter 1. For the energy, CO₂ emission and production cost analysis in the current chapter, these terms are applied in the following ways:

- *DSM OCM I & II* For all analyses, the credit approach is applied (note that electricity and ethylene are the only products). In Section 3.4.4, we tested the sensitivity of using different energy efficiency of electricity production, namely 55% and 60%.
- *All other routes* For the energy and CO₂ emission analysis, both mass value and economic value-based allocation approaches are applied in order to test whether our results are sensitive to the choice of definitions or not. The economic value-based allocation approach means that 50% weight is given to the mass of non-olefins while the mass value-based allocation approach means that 100% weight is given to the mass of non-olefins (100% weight given to the mass of olefins in both cases). This test is only relevant to naphtha steam cracking, ExxonMobil MTO and Lurgi MTP because their non-olefin yields are significant and those of others are negligible. For the production cost analysis, only the economic value-based allocation approach is applied.

3.4 Energy and CO₂ Emissions Analysis

The data used to calculate the cumulative process energy use in C₁ and steam cracking routes are listed in Table 3-3, 3-4 and 3-5. The following three sections explain how the data were chosen

and how the calculations are done for the energy and emissions analysis. The results of the analysis will be discussed in Section 3.4.4.

3.4.1. Steam Cracking Routes

Data on naphtha and ethane steam cracking at world average and state-of-the-art levels come from Chapter 2. CO₂ emissions from naphtha and ethane steam cracking routes are estimated based on the emission factors listed in Table 3-6.

3.4.2. Methanol Routes

Cumulative process energy use in the methanol routes is the sum of process energy use in *methanol production* and in the conversion of *methanol to olefins*.

- Methanol Production* Energy use for methane production is assumed to be 5% of the calorific value of natural gas (or approximately 1 GJ/t methanol)¹. For methanol production from methane, we assumed the Lurgi MegaMethanol technology, which has a SEC of 9 GJ/t methanol (including energy use in oxygen production and excluding the calorific value of methanol 20 GJ/t and the energy use for methane production 1 GJ/t) [148]. 9 GJ/t methanol is slightly lower than that given by Topsoe (10 GJ/t methanol) and ICI (10-14 GJ/t methanol) [164]. Today, Lurgi, ICI and Topsoe dominate the global market for methanol technology. The current world average (not state-of-the-art) is approximately 15 GJ/t methanol [25].
- Methanol to Olefins* The SEC for the conversion of methanol to olefins is in the range of 12-15 GJ/t ethylene (11.6 GJ/t ethylene [24], 12.3 GJ/t ethylene [112] and 14.5 GJ/t ethylene [155]). In the case of UOP MTO, we use the lowest figure (12 GJ/t ethylene). In the case of ExxonMobil MTO, it is about 25 GJ/t ethylene [127]. The large difference between the SECs in the UOP MTO and the ExxonMobil MTO routes is the result of different product yields (see Table 3-2). Energy use in olefin upgrading processes used in UOP MTO is estimated to be approximately 0.5 GJ/t C₄ and C₅ byproducts [97].

¹ Primary energy required in GJ/GJ delivered natural gas ranges widely from 0.2% to 26% depending on location [159-163]. We assumed 5% since this is close to the average in Western Europe and the US.

Table 3-3 Cumulative Process Energy Use in Steam Cracking Routes (the calorific value of feedstocks and HVCs is excluded from cumulative process energy use)

Naphtha-based steam cracking				Ethane-based steam cracking			
Steps	Energy use per step (GJ/t product)	Yield	GJ/t HVCs aromatics weighted 50% (or if weighted 100%)	Steps	Energy use per step (GJ/t product)	Yield	GJ/t HVCs (aromatics or gasoline negligible)
Naphtha production ^a	3 GJ/t naphtha (state of the art)	Naphtha 8% of crude oil ^b	5 (or 5) (state of the art)	Ethane production	2 GJ/t ethane ^c	Ethane 1% of natural gas	3
	4 GJ/t naphtha (world average)		7 (or 7) (world average)				
Naphtha to HVCs ^d	12 GJ/t ethylene (state of the art)	Ethylene 33% and HVCs 60% of naphtha (or 63% if aromatics weighted 100%)	6 (or 6) (state of the art)	Ethane to HVCs	10 GJ/t ethylene (state of the art)	Ethylene 80%; HVCs 84% of ethane	9 (state of the art)
	22 GJ/t ethylene (world average)		12 (or 12) (world average)		15 GJ/t ethylene (world average)		14 (world average)
Total (GJ/t HVCs)	Not applicable		11 (or 11) (state of the art)	Total (GJ/t HVCs)	Not applicable		12 (state of the art)
			19 (or 18) (world average)				18 (world average)

^a Estimation is based on [51]. Energy use for crude oil extraction, transportation and pre-processing is assumed to be 1% of crude oil on an energy basis (other assumptions do exist [159-163]).

^b Estimation is based [165].

^c Estimation is based on [57]. Energy use for natural gas extraction, transportation and pre-processing (assumed to be 5% of natural gas on an energy basis) are included [51].

^d All data on steam cracking are based on the analysis in Chapter 2. Endothermicity is not included as part of cumulative process energy use. Please see details on endothermicity in Chapter 2.

Table 3-4 Cumulative Process Energy Use in Natural Gas-to-Olefins Routes - UOP MTO and ExxonMobil MTO (the calorific value of feedstocks and HVCs is excluded from cumulative process energy use)

Natural gas-to-Olefins (UOP MTO)				Natural gas-to-Olefins (ExxonMobil MTO)			
Steps	Energy Use per step (GJ/t product)	Yield (t/t natural gas *100%)	GJ/t HVCs (aromatics or gasoline negligible)	Steps	Energy use per step (GJ/t product)	Yield (t/t natural gas *100%)	GJ/t HVCs gasoline weighted 50% (or 100%)
Natural gas production and Methanol production ^a	10 GJ/t methanol	Methanol yield 145% of natural gas ^b	23 ^c	Natural gas production, Methanol production	10 GJ/t methanol	Methanol yield 145% of natural gas	32 (or 24)
Methanol to HVCs	13 GJ/t ethylene ^d	Ethylene 26% and HVCs 62% of natural gas	5 ^c	Methanol to HVCs	25 GJ/t ethylene ^e	Ethylene 14% and HVCs 45% of natural gas (or 61% if gasoline weighted 100%)	8 (or 6)
Total (GJ/t HVCs)	Not applicable		29	Total (GJ/t HVCs)	Not applicable		40 (or 30)

^a Methanol data is based on [148]. Energy use for natural gas extraction, transportation and pre-processing (assumed to be 5% of natural gas on an energy basis) are included [51].

^b Methanol yield is expressed by the weight of methanol divided by that of natural gas, which is larger than 100% because methanol contains oxygen [25].

^c As an example, we present the calculation for this case: in the first step, one ton of natural gas can be converted into 1.45 ton methanol and the process energy required in this step is 10 GJ/t methanol; in the second step, methanol is converted into HVCs and the process energy used for this step is 13 GJ/t ethylene or 5 GJ/t HVCs. Therefore, we calculate: (1.45 t methanol) / (1.00 t natural gas) * (10 GJ / t methanol) * (1 t natural gas) / (0.62 t HVCs) = 23 GJ/(t HVCs); 13 GJ/(t ethylene)*26% ethylene yield/62% HVCs yield = 5 GJ/(t HVCs). The calculations for other cases are similar to this case.

^d Estimation is based on [152, 166]. Energy use in olefin upgrading, approximately 0.5 GJ/t C₄₋₅, has been considered [97].

^e Estimation is based on [127].

Table 3-5 Cumulative Process Energy Use in Natural Gas-to-Olefins Routes – Lurgi MTP and DSM OCM I & II (the calorific value of feedstocks and HVCs is excluded from cumulative process energy use)

Natural gas-to-Olefins (Lurgi MTP)				Natural gas-to-Olefins (DSM OCM I & II)			
Steps	Energy Use per step (GJ/t product)	Yield (t/t natural gas *100%)	GJ/t HVCs gasoline weighted 50% (or 100%)	Steps	Energy Use per step (GJ/t product)	Yield (t/t natural gas *100%)	GJ/t HVCs (aromatics or gasoline negligible; electricity production efficiency of 55% and 60%)
Natural gas production, Methanol production	10 GJ/t methanol	Methanol yield 145% of methane	25 (or 22)	Natural gas production	2 GJ/t methane ^a	Not applicable	3 ^b and 3 (DSM I)
				Oxygen production	3 GJ/t oxygen ^d		2 ^c and 3 (DSM II)
							14 ^e (DSM I)
							11 ^f (DSM II)
Methanol to HVCs	10 GJ/t propylene ^g	Propylene 46% and HVCs 57% of methane (or 65% if gasoline weighted 100%)	8 (or 7)	Conversion to ethylene	17 and 20 GJ/t ethylene ^h	HVCs 50% of methane (DSM I)	17 and 20 (DSM I)
					14 and 36 GJ/t ethylene	HVCs 15% of methane (DSM II)	14 and 36 (DSM II)
Total (GJ/t HVCs)	Not applicable		33 (or 30)	Total (GJ/t HVCs)	Not applicable		33 and 36 (DSM I)
							27 and 51 (DSM II)

^a For DSM I, 2.0 tons of methane is needed as the total methane input to produce one ton of ethylene [116]. For DSM II, 6.6 tons of methane is needed to produce one of ethylene.

^b DSM I: [2.0-(19 GJ/55%/50 GJ/t methane)] ton methane/ton ethylene*2.0 GJ/t methane = 3 GJ/t ethylene. The same can be done for 60% to reach 3 GJ/t ethylene.

^c DSM II: [6.6-(149 GJ/55%/50 GJ/t methane)] tons methane/ton ethylene*2.0 GJ/t methane = 2 GJ/t ethylene. The same can be done for 60% to reach 3 GJ/t ethylene.

^d Estimation is based on [40]. Methane/oxygen ratios in DSM OCM I and II on the mass basis are 1: 2.2 and 1: 0.56 respectively [116].

^e DSM I: 2.0 ton methane/ton ethylene*2.2 ton oxygen/ton methane*3.0 GJ/t oxygen = 14 GJ/t ethylene.

^f DSM II: 6.6 ton methane/ton ethylene *0.56 ton oxygen/ton methane*3.0 GJ/t oxygen = 11 GJ/t ethylene.

^g Estimation is based on [25, 143].

^h Estimation for DSM OCM I & II is based on [116]. For power generation, we used an efficiency of 55% as the default and used 60% to test the sensitivity to the efficiency.

Table 3-6 Emission Factors for Steam Cracking and Natural Gas-to-Olefins Routes (ton CO₂ per GJ energy used)

	Naphtha based steam cracking ^a	Ethane based steam cracking ^b	Natural gas-to-olefins		
			UOP MTO, ExxonMobil MTO and Lurgi MTP	DSM OCM I	DSM OCM II
Feedstock production	0.069 (combustion of refinery gas for naphtha production)	0.056 (combustion of natural gas for ethane production)	0.056 (combustion of natural gas for methane and oxygen production) ^c	0.056 (combustion of natural gas for methane production)	
			0.042 (combustion of natural gas and partial oxidation of methane for methanol production) ^d	0.056 (combustion of natural gas for oxygen production)	
Petrochemicals Production	0.053 (combustion of fuel-grade byproducts)	0.047 (combustion of fuel-grade byproducts)	0.056 (combustion of natural gas and a small amount of fuel gas byproducts for product recovery and separation)	0.021 and 0.026 (electricity production with an efficiency of 55% and 60% respectively; combustion of all non-methane and non-ethylene byproducts) ^e	-0.004 and 0.033 (electricity production with an efficiency of 55% and 60% respectively; combustion of all non-methane and non-ethylene byproducts) ^f

^a Data is based on [167]. Refinery gases have higher carbon content than natural gas.

^b Data is based on [167]. The difference between CO₂ emission factors of naphtha and ethane cracking is due to different fuels used. Ethane cracking emits 6 kg CO₂/GJ less than naphtha cracking because the hydrogen content in the fuel grade byproducts from ethane cracking is higher than that from naphtha cracking.

^c Here we assume natural gas as the combusted fuel, which is typical for natural gas-fired heaters used in the chemical industry.

^d Data is based on [167]. This emission factor is smaller than that of natural gas due to auto-thermal reforming, partial oxidative reaction and CO₂ recycling.

^e Data is based on [116]. These emission factors are considerably lower than those of steam cracking. This is due to both the endothermicity (Chapter 2) and partial oxidation reactions in Table 3-2.

^f Data is based on [116]. These emission factors are considerably lower than those of steam cracking. This is due to both the endothermicity (Chapter 2) and partial oxidation reactions in Table 3-2.

Figure 3-3 Comparison of Cumulative Process Energy Use in Steam Cracking and C₁ Routes with Sensitivity Analysis for Different Definitions of High Value Chemicals and Power Generation Efficiencies (the calorific value of HVCs excluded. Data come from Tables 3-3, 3-4 and 3-5. HVCs have a calorific value of approximately 50 GJ/t. The solid error bars for naphtha cracking, ExxonMobil MTO and Lurgi MTP are the results if 100% (weight) of aromatics and gasoline is counted as HVCs. The dotted error bars for DSM OCM I & II are the results when a power generation efficiency of 60% is used. In the default bars, the results are based on a power generation efficiency of 55%)

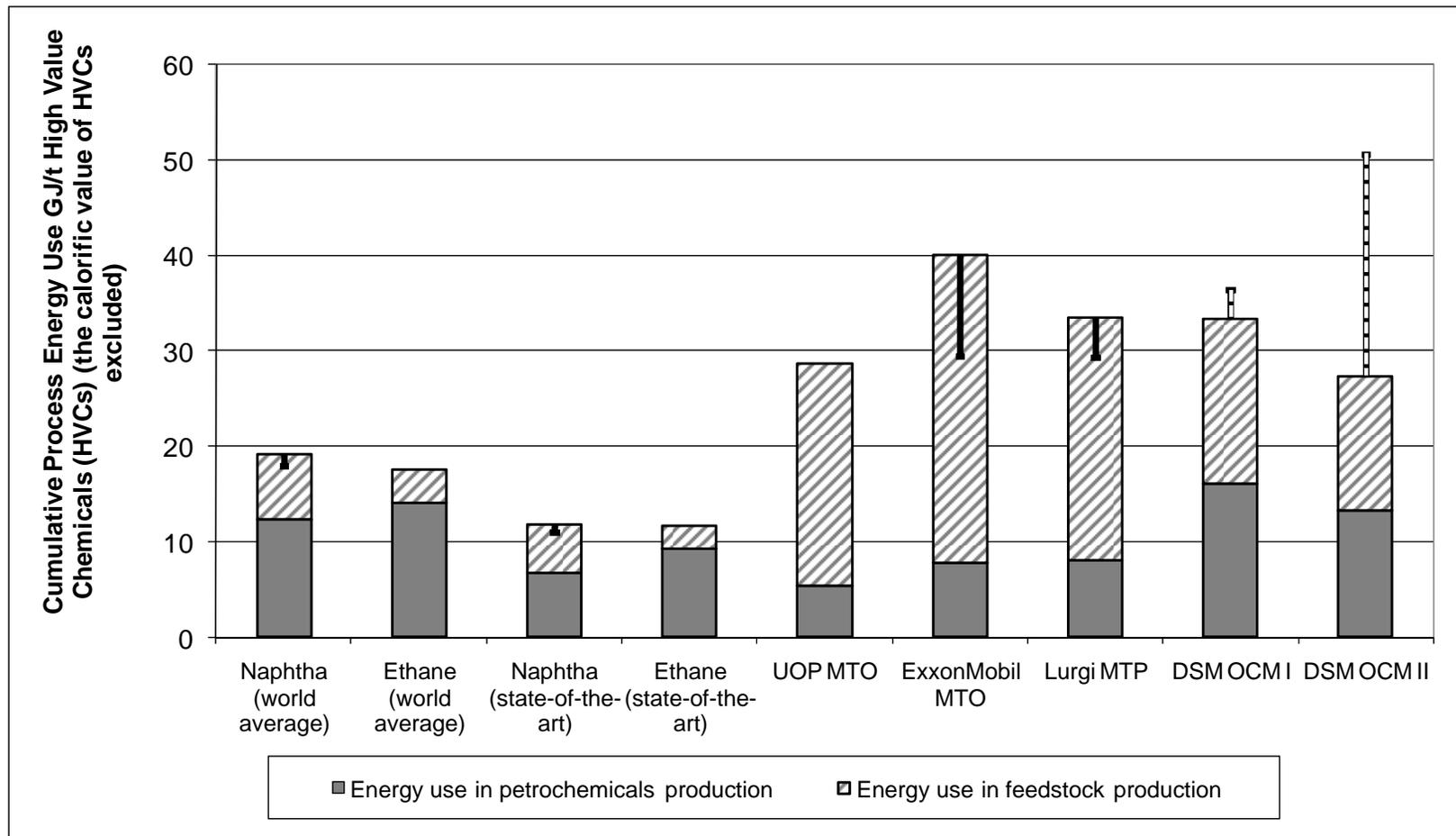
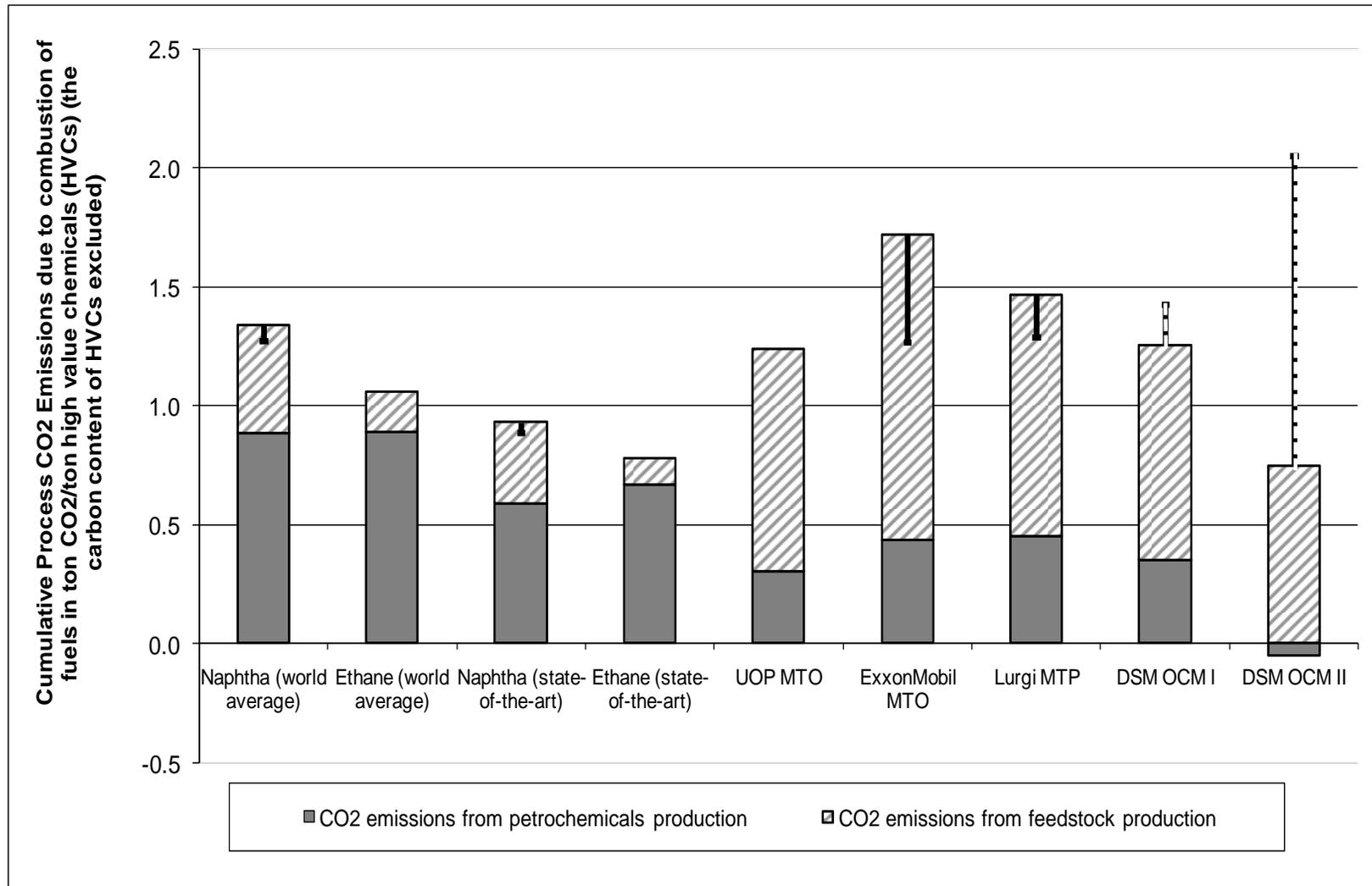


Figure 3-4 Comparison of Cumulative Process CO₂ Emissions in Steam Cracking and C₁ Routes with Sensitivity Indication for Different Definitions of High Values Chemicals and Electricity Cogeneration Efficiencies (Data is based on data in Table 3-3 to Table 3-6. The error bars represent the same sensitivity analyses as those in Figure 3-3. See Table 3-6 for emission factors.)



3.4.3. Oxidative Coupling of Methane (OCM)

Cumulative process energy use in an OCM route is the sum of all energy use for feedstock, i.e. methane and oxygen production and the conversion of methane to olefins.

- *Methane and oxygen production* Energy use for methane production is the same as in the methanol routes. Primary energy use for production of high-purity oxygen (99%) with the use of electricity is about 3 GJ/t oxygen [40].
- *Methane to ethylene* Here we applied the credit approach: we assume that the electricity would otherwise have been produced by a standalone, state-of-the-art power plant with an energy efficiency of 55%. We also assumed 60% to test the sensitivity of the result to the efficiency chosen. Based on these assumptions, we calculated the process energy use in the conversion of methane to ethylene for DSM OCM I to be 17 and 20 GJ/t ethylene and for DSM OCM II to be 14 and 36 GJ/t ethylene for the energy efficiency at 55% and 60%¹ respectively.

CO₂ emissions from the conversion of methane to ethylene are allocated in the same way as the calculation of SEC. For calculating CO₂ emissions from electricity production in OCM I and II, we also considered the same two power plants as mentioned above: one plant with an efficiency of 55% while another with an efficiency of 60%. These emissions are then deducted from the total emissions by DSM OCM I and II.

3.5 Results and Discussion

3.5.1. Results

Our estimates for cumulative process energy use and cumulative CO₂ emissions in terms of per ton of HVCs in UOP MTO, ExxonMobil MTO and Lurgi MTP are presented in Figure 3-3 and Figure 3-4. CO₂ emissions from these routes are calculated on the basis of emission factors listed in Table 3-6. The key findings are:

¹ Our estimates for energy use in DSM OCM I and II are much higher than two early studies on different designs of oxidative coupling [112, 129]. These two studies estimated that energy use in an oxidative coupling process is about 5 GJ/t ethylene. A final ethylene yield of 70% (much higher than those of DSM OCM I and II) after recycling ethane and methane was assumed by these studies. Also, energy use in the production of methane and oxygen was not counted by these studies.

- Energy use and CO₂ emissions in all C₁ routes are much higher than those of steam cracking routes. Methane-based routes use more than twice as much energy than state-of-the-art steam cracking routes do. Methane-based routes lead to 60-85% more CO₂ emission than the state-of-the-art ethane cracking¹.
- Among the methanol routes, UOP MTO is the most efficient, but its energy use is still about 150% higher compared to state-of-the-art naphtha-based steam cracking. Methanol routes have similar energy use, but cause slightly higher CO₂ emissions than DSM OCM I and II do.

Regarding methanol routes, Figure 3-3 shows that most of energy use in these routes is caused by methanol production. The same can be concluded about the CO₂ emissions from methanol routes.

Regarding DSM OCM I and II, several points on Figure 3-3 and 3-4 can be made:

- Half of the cumulative process energy use occurs in the feedstock production (mostly for oxygen production) of DSM OCM I and II. The rest of energy use occurs mostly in recycling and/or separation processes: DSM OCM I has recycling of un-reacted methane and the separation of ethylene and the rest of the products while DSM OCM II has no recycling of un-reacted methane but has the separation of ethylene and the rest of the products.
- When 55% efficiency for electricity cogeneration is assumed, energy use and CO₂ emissions of DSM OCM I are higher than those of DSM OCM II. When 60% is assumed, the situation reverses. Energy use and CO₂ emissions per ton of HVCs in the two cases are different because the original source has modeled the two processes using different configurations (see the last point) and different efficiencies for electricity cogeneration: 56% for DSM OCM I and 53% for DSM OCM II [116]. Energy use and CO₂ emissions per ton of HVCs in DSM OCM II are much more sensitive to the chosen

¹ The difference between the two results (“more than twice” and “60-85%”) is due to both the endothermicity (high emission factors of steam cracking; see Chapter 2) and partial oxidation reactions (low emission factors for methane-base routes; in Table 3-2).

efficiency than DSM OCM II does because the former cogenerates 8 times as much electricity as in the case of the latter.

- Figure 3-4 shows that CO₂ emissions from petrochemicals production in the case of DSM OCM II are slightly negative when 55% efficiency for electricity cogeneration is assumed. This means that with 55% as efficiency for electricity generation, all CO₂ emissions from petrochemicals production is allocated to electricity. However, if a higher efficiency for electricity cogeneration 60% is assumed, much more CO₂ emissions are allocated to HVCs and therefore negative CO₂ emissions per ton of HVCs immediately disappear (as the dotted error bars in Figure 3-4 show).

3.5.2. Future Improvement

3.5.2.1. Methanol Routes

For methanol routes, considerable potential seems to exist for energy savings. The key step for the reduction of energy use is the conversion of methane to syngas, which is currently done through steam reforming. Steam reforming accounts for 50-70% of the total exergy losses in methanol production (exergy loss is the result of methane combustion; approximately 30 GJ/t methane is combusted to provide heat) [168-170].

Tandem reforming is reported to be able to use only 7-8 GJ/t methanol, which is approximately 20% less than in traditional steam reforming [171]. Also, a so-called “sono-chemical” process can convert methane to methanol using high-intensity ultrasound [172]. However, no energy use data is published on this process. Dry reforming instead of steam reforming¹ is reported to allow curbing CO₂ emissions in methanol production. Further potentials for energy saving exist in the optimized heat integration between methanol production and methanol-to-olefins processes.

Despite these technological developments and potential further improvements, we have so far not found any technological breakthroughs that can drastically reduce energy use in methanol production. The theoretical overall minimum exergy consumption of a methane-to-methanol

¹ Mitsubishi has filed patents on a so-called oxo gas process, which recovers CO₂ from both flue gas and steam reforming [173]. The oxo process is also called dry reforming as opposed to steam reforming. The formula for the reaction is: $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$. Mitsubishi claims that this process has the potential to drastically reduce CO₂ emissions. Also, air can be used instead of pure oxygen and therefore CO₂ emissions from oxygen production are also avoided.

reaction is approximately 3 GJ/t methanol [46, 168] (by comparison: 9 GJ/t methanol as mentioned earlier). If it were possible to reduce the energy use in methanol production to this theoretical value, then methanol routes would be as efficient as the state-of-the-art naphtha steam cracking. It is therefore questionable whether methanol routes will ever be more energy efficient than the steam cracking routes.

3.5.2.2. Oxidative Coupling of Methane Routes

The current performance of OCM routes in terms of energy use is poorer than that of state-of-the-art steam cracking primarily due to the following problems:

- *Low yields* There is a trade-off between methane conversion and selectivity to ethylene [174, 175]. Under 600 °C, the rate of reaction is slow, but above 600 °C undesired oxidations dominate the reactions [46];
- *Separation* Relatively high energy use in separation and recycling [174, 176];
- *Catalysts* Additional oxygen and hydrogen are required for reducing coking on catalysts [177, 178]. High temperatures at 750-1,000 °C require catalysts with high thermal stability [174].

Other issues concern safety (possible explosion due to the mixture of oxygen and hydrocarbons), environmental pollution (CO and CO₂ emissions, aromatic hydrocarbons, acid gas and organic acid), and operability [118].

Currently, many experiments are being conducted to tackle these problems:

- *Raising Yield* New energy efficient catalysts may raise conversion and selectivity above 20-30% and 80-90% respectively [157, 174]. Oxygen-permeable membrane reactors could eliminate the need for oxygen plants and enhance the selectivity to ethylene [179]. This could result in ethylene yields up to 50% [180] though the slow oxygen flux might require a large reactor, which implied higher investments [181]. If oxygen-permeable membrane reactors could be integrated with an OCM plant, they would reduce approximately 20% of the energy use in a DSM OCM I plant without membrane reactors, i.e. 6.5 GJ/t ethylene out of 33-36 GJ/t ethylene can be saved [181].

- *Separation* Membrane may also be applied in the recycling and separation sections where ethylene is removed from final product streams. An ethylene yield of up to 75% has been claimed [158]. In addition, experiments are being conducted to try out several AgNO₃ sorbents for ethylene absorption [182].
- *Retrofitting* OCM technologies can be retrofitted with conventional ethane or naphtha steam crackers for energy optimization (e.g. through heat transfer from oxidative coupling to the cracking furnace or through the combination of oxygen production and separation processes of steam crackers) [130, 183-185]. However, some say that this is difficult because steam crackers have only limited capacities to process light gases [49].

We do not have enough data to study these technological possibilities in detail. If implemented, these new technologies could bring considerable improvements in terms of yield, energy use and CO₂ performance. However, at this moment, none of these possibilities have been demonstrated and commercialized. Within the short term (the next 5-10 years), none of these methane-based routes is likely to become more energy efficient or lead to less CO₂ emissions than steam cracking routes do.

3.6 Production Cost Analysis

This analysis is based on economic data in the open literature. For the comparison of production costs, we consulted various publications, industrial experts and consultancy firms and found only relatively minor differences among these sources. These differences do not change the overall picture because feedstock costs (and electricity costs in the case of DSM OCM I & II) dominate the results. We distinguish three sets of feedstock costs and electricity production costs (Table 3-7) in order to compare the historical average situation (referring to 1970-2005) of energy prices in the US and Europe with other more extreme situations (high and low gas prices). The situations with high gas prices represent the average situation in 2006 while the situations with low gas prices represent the “stranded gas” situation.

“Stranded gas” refers to natural gas that is located in remote, gas-rich regions (such as the Far East area of Russia) where natural gas is abundant and local gas consumption is low. Natural gas in these regions accounts for as much as 60% of global natural gas reserves and is currently

available at \$0.5-1.0/GJ, so subsequently methanol can be produced at below approximately \$75/t methanol [114, 127, 128, 186]. However, due to the rapid development of liquefied natural gas (LNG)¹, such low gas prices in these locations may not continue to exist for long in the coming decades.

Feedstock costs refer to the production costs of feedstocks (see Figure 3-5). O&M costs include labor, operation and maintenance. We assumed a lifetime of the petrochemical plant to be 15 years (see Chapter 1).

The approaches described in Section 3.3 are applied for the economic analysis. For DSM OCM I and II, the credit approach is applied: electricity costs are deducted from the total production costs. Assumptions for electricity production costs are shown in Table 3-7. These electricity production costs are strongly dependent on the prices of natural gas used for electricity generation. For all other routes, the economic value-based allocation approach is applied.

Figure 3-5 show that feedstock costs dominate production costs for these routes. There are three interesting findings:

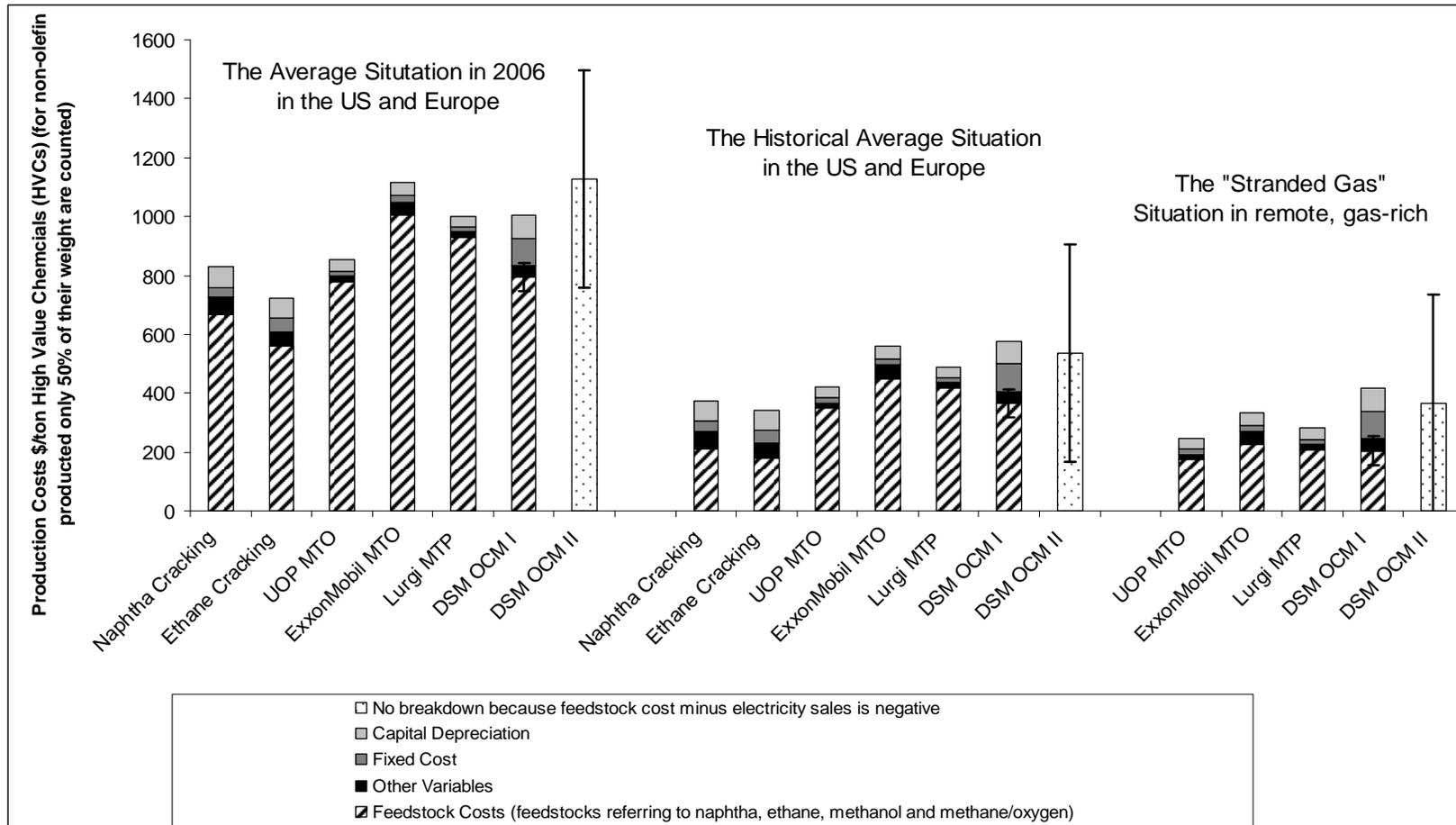
- First, the production costs of HVCs under the situation in 2006 made twice as much as those under the historical average situation.
- Second, under the “stranded gas” situation when the natural gas price is at \$0.75/GJ, C₁ routes can lower production costs to \$300-400/t HVCs. Clearly, the economics of C₁ routes are highly economically attractive in those remote, gas-rich regions.
- Third, due the cogeneration of large amounts of electricity, DSM OCM II is extremely sensitive to the change of electricity production costs: the error bars in Figure 3-5 show the effect of electricity production costs when deviating +/- \$0.01/kWh from the assumptions in Table 3-7. This shows once more that DSM OCM II is rather a power plant than a petrochemical plant. Therefore, electricity sales at very high prices can significantly reduce its total production costs.

¹ The LNG transportation cost from gas-rich countries to the US and Europe is currently about \$3-4/GJ natural gas while the cost of transporting natural gas through conventional gas pipelines is about \$0.5-2/GJ (depending on the distance) [141].

Table 3-7 Three Sets of Assumptions for Energy/Feedstock and Electricity Production Costs (all values in US\$ of 2000)

	The average situation in 2006 in the US and Europe	The historical average situation in the US and Europe (1970-2005)	The “stranded gas” situation in remote, gas rich regions
Crude oil	\$60/bbl (\$440/t) [187]	\$20/bbl (\$147/t) [187, 188]	Not applicable
Naphtha (price \$/t =10 * oil prices in \$/bbl as a rule of thumb derived from [22])	\$600/t	\$200/t	
Ethane (110% of natural gas prices in \$/GJ = 110%*1/6 * oil prices in \$/bbl as a rule of thumb derived from [187])	\$10/GJ (or \$450/t)	\$3/GJ (or \$135/t)	
Natural gas	\$400/t (or \$8/GJ) [187, 189]	\$125/t (or \$2.5/GJ) [187, 189]	\$35/t (or \$0.75/GJ) [187, 189]
Methanol (estimated on the basis of methanol production costs: O&M costs together at \$15/t and capital cost at \$40/t [171])	\$355/t	\$150/t	\$75/t
Electricity production costs (estimated on the basis of [43])	\$17/GJ _e (\$0.06/kWh)	\$8/GJ _e (\$0.03/kWh)	\$5/GJ _e (\$0.02/kWh)
Oxygen (estimated on the basis of oxygen production costs: 350 kWh/t plus O&M and capital costs together at \$50/t [40])	\$70/t	\$60/t	\$55/t

Figure 3-5 Comparison of Production Costs by Steam Cracking and C₁ Routes (based on Table 3-7; error bars showing the effect of electricity production costs deviating +/- \$0.01/kWh from the price assumptions in Table 3-7; all in US\$ of year 2000)



However, the uncertainty of production costs for C_1 routes is high because of the following two reasons: first of all, low production costs are only possible in very remote, gas-rich regions in the Middle East, Russia and other countries. However, as stated earlier, the prices of “stranded gas” in the long term (the coming decades) might not continue to be so low in these locations anymore because of rapid development of LNG there. Secondly, DSM OCM I and II are immature technologies (e.g. low yield problems as mentioned earlier). Up to today, there are no generally accepted designs of oxidative coupling of methane for ethylene production on a large, commercial scale.

3.7 Conclusions

By conducting a comparative analysis of the energy use, CO_2 emissions and production costs of C_1 technologies and naphtha and ethane-based steam cracking technologies, we found that methane-based routes use more than twice as much process energy than state-of-the-art steam cracking routes (the calorific value of products has been excluded). Oxidative coupling routes are currently still immature due to low ethylene yields and other problems, although electricity sales at very high prices may improve the picture. Methane-based routes can be economically attractive in remote, gas-rich regions where natural gas is available at low prices. The development of liquefied natural gas may increase the prices of natural gas in those locations. Although there are several possibilities for energy efficiency improvement, none of these natural gas-based routes is likely to become more energy efficient or lead to less CO_2 emissions than steam cracking routes.

Chapter 4 Petrochemicals from Coal and Biomass: Energy Use and CO₂ Emissions¹

ABSTRACT

Coal and biomass-based routes have recently attracted much attention as alternatives to the conventional routes for producing high value chemicals (HVCs or olefin equivalent chemicals), but few studies have compared them with the conventional routes in terms of energy use and CO₂ emissions. In this chapter, 15 coal and biomass-based routes are compared with three conventional routes and six innovative crude oil or natural gas-based routes. This comparison is based on two indicators: *total energy use* (the sum of cumulative process energy use and the calorific value of HVCs 50 GJ/t) and *total CO₂ emissions* (the sum of cumulative process CO₂ emissions and the carbon content of HVCs). The main findings are as follows:

- The total energy use of the conventional routes is the lowest (about 60 GJ/t HVCs), whereas that of methane-based routes is 30% higher and that of the coal and biomass-based routes is about 60-150% higher;
- The total CO₂ emissions of conventional and methane-based routes are about 4 to 5 tons CO₂ per ton HVCs, whereas those from biomass-based routes range from 2 tons CO₂ per ton HVCs (a maize-based ethanol related route) to 4 tons of *avoided* CO₂ per ton HVCs (a lignocellulosic biomass-based Fischer-Tropsch route). Avoided CO₂ emissions are due to electricity cogeneration;
- The total CO₂ emissions of coal-based routes are by far the highest (8-11 tons CO₂ per ton HVCs). An exception is a route with CO₂ capture and storage, for which CO₂ emissions are similar to those of the conventional routes.

Given these large differences, more research into energy efficiency improvement of coal and biomass-based routes is recommended. However, the total energy use of biomass and coal-based routes is unlikely to match that of the conventional routes anytime soon.

¹ Co-author: Dr. Martin Patel (Utrecht University).

4.1 Introduction

With the aim of understanding the energy use and CO₂ emissions in the production processes of petrochemicals, we focused on the conventional routes in Chapter 2 and compared them with several methane-based routes via methanol and oxidative coupling in Chapter 3. In this chapter, we will additionally study coal and biomass-based routes for producing petrochemicals. We will apply a common framework to assess these routes in comparison with conventional routes and innovative crude oil and natural gas based routes.

With respect to biomass-based alternative routes that produce petrochemicals via ethanol and syngas (Fischer-Tropsch synthesis), a number of recent studies indicate that the CO₂ emissions of these routes can be quite low [26, 27, 190]. With respect to making feedstocks suitable for petrochemicals production, one study argued that not only biomass-based technologies, but also coal-based technologies with CO₂ capture and storage can potentially reach very low CO₂ emissions [191]. We did not find any studies that compared both energy use and CO₂ emissions of methane, biomass and coal-based routes with those of steam cracking routes using naphtha derived from crude oil or ethane derived from natural gas.

Give this knowledge gap, the research question addressed in this chapter is: *How do alternative routes score in comparison with conventional routes in terms of energy use and CO₂ emissions?* The conventional routes here refer to the most commonly used routes, which utilize the conventional primary energy sources (e.g. crude oil) that are currently dominant in the production of basic petrochemicals. For conventional routes, the state-of-the-art technologies are assumed (addressed in Chapter 2). The alternative routes refer to those routes that utilize alternative primary energy sources (i.e. methane, coal, biomass and plastic waste), which have not yet been used in the current production of basic petrochemicals on a commercial scale and are therefore alternatives to conventional primary energy sources.

The main research method used in this chapter is energy and CO₂ emission analysis. The main indicators are the total energy use and the total CO₂ emissions per ton of high-value chemicals, or HVCs. The method and indicators have been described in Chapter 1 in detail.

The analysis in this chapter is based on publicly available data, which were found in scientific and technical journals, books, conference proceedings and technical papers published by petrochemical firms. For comparison purposes, we have chosen technologies that have recently been researched and that are relatively well-understood (meaning that there are sufficient data for analysis; Section 4.3 gives specific reasons why individual technologies have been chosen).

The state-of-the-art conventional steam cracking routes utilizing naphtha derived from crude oil and ethane derived from natural gas are being used as the benchmark for comparison. As far as the alternative routes are concerned, this chapter is a prospective study. Although it is impossible to predict exactly when these routes will be used, it is nevertheless of interest to study their energy use and CO₂ emissions based on current knowledge. The economics of these routes will be studied in Chapter 5.

The content of this chapter is as follows. First, the definitions and methodologies used in this chapter are explained in Section 4.2. Then, 24 routes based on crude oil, natural gas, coal and biomass as primary energy sources are briefly described in Section 4.3. In Section 4.4, the alternative routes are compared with the conventional routes in terms of their energy use and CO₂ emissions. Section 4.5 addresses uncertainties and technological developments. Finally, the conclusions and recommendations are given in Section 4.6.

4.2 Definitions

4.2.1. Primary Energy Sources, Feedstocks and Petrochemicals

In this chapter, the term *primary energy sources* refers to crude oil, natural gas, coal, biomass and plastic waste. *Feedstocks* refers to intermediate products, such as naphtha, ethane, methanol and ethanol (the same as defined in Chapter 1). Their calorific value on a dry basis, expressed as lower heating values (LHVs), is shown in Table 4-1. When mentioned in this chapter, coal refers to black bituminous coal. It should be noted that the black coal found at different locations can have different calorific values (see Table 4-1) and chemical compositions (see Table 4-3). HVCs are defined on the basis of their economic values, meaning that light olefins are given 100% weighting per unit mass, whereas non-olefins are given 50% weighting per unit mass (see Chapter 1).

4.2.2. Electricity

Excess electricity is treated with the credit approach (as defined in Chapter 1), whereby electricity is assumed to come from a standalone natural gas-fired power plant with an energy efficiency of 55%. Sensitivity tests regarding other energy efficiencies will be discussed in Section 4.5. Depending on whether electricity is imported or cogenerated, energy use for electricity production is either added to or subtracted from the actual input of fossil energy. For some biomass-based routes, the input of fossil energy is less than the fossil energy use avoided (fossil energy use is avoided because biomass energy is used to produce electricity that would otherwise have to be produced using fossil fuels), the total fossil energy use is therefore negative (these cases are shown in Table 4-4). Oxygen, if used, is assumed to have been produced by the fractional distillation of air in a process that uses electricity.

4.2.3. Energy Use and CO₂ Emissions

The term *cumulative process energy use* refers to the sum of process energy use in the two steps of a whole route (i.e. feedstock production and petrochemicals production). Accordingly, the term *cumulative process CO₂ emission* refers to the sum of CO₂ emissions from the same two steps. In this chapter, *total energy use* and *total CO₂ emissions* are used as the main indicators. The term “total fossil energy use (the calorific value of HVCs excluded)” and the term “total biomass-derived energy use (the calorific value of HVCs excluded)” refer to the fossil and biomass-derived energy use respectively, both of which are part of the cumulative process energy use.

The term *total energy use* is the sum of cumulative process energy use and the calorific value of HVCs. However, the calorific value of HVCs is assumed to be lost here as we assume waste incineration of end products derived from HVCs without energy recovery¹. The term *total energy use* refers to the sum of fossil and biomass-derived energy use.

For fossil energy-based routes, *the total CO₂ emissions* are the sum of *cumulative process CO₂ emissions* and CO₂ emissions from the combustion of end products derived from HVCs (i.e. the

¹ Many different methods for waste management exist and their effects are significantly different from each other. If a single method is applied for all of the routes, then its effect for each route would have been the same. For the purpose of cross comparison between various routes, it is sufficient here to assume a single waste management method in this thesis.

carbon content of HVCs released into the atmosphere). For biomass-based routes, the *total CO₂ emissions* are the emissions from fossil energy use only. The combustion of final products made from biomass-based HVCs does not add CO₂ to the atmosphere. The carbon content of HVCs originates from CO₂ existing in the atmosphere and was captured by biomass during plant growth. When end products derived from HVCs eventually become waste and if they are incinerated, the CO₂ emitted will cancel out the CO₂ captured by biomass earlier. Therefore, the waste incineration of biomass-derived products does not lead to net CO₂ emissions—unlike the waste incineration of products derived from fossil energy.

4.3 Route Description

This section will describe conventional routes and alternative routes. Conventional and several methane-based routes were already discussed in Chapter 2 and 3, so they are briefly described here. The main focus is on alternative routes that utilize coal and biomass. The schemes of all routes are shown in Figure 4-1 (mostly naphtha related) and Figure 4-2 (mostly methanol and ethanol related). In the following sections, each route will be described in two steps: the first step is *feedstock production* and the second step is *petrochemicals production*. In the first step (*feedstock production*), naphtha, methanol or ethanol is produced. In the second step (*petrochemicals production*), naphtha steam cracking, ethanol dehydration or methanol-to-olefins process is used to produce petrochemicals. Data for the first steps are shown in Table 4-2, 4-3 and 4-4 while data for the second step are shown in Table 4-5, 4-6 and 4-7.

4.3.1. Conventional Routes

The conventional routes are the basis for comparison with all other routes. Steam cracking of naphtha derived from crude oil as a feedstock is referred to as Oil Naphtha SC. Similarly, Ethane SC is steam cracking of ethane derived from natural gas and catalytic cracking is termed Oil Byproduct CC (discussed in Chapter 2). In the petrochemicals production step of Oil Byproduct CC, the catalytic pyrolysis process (CPP) is used. This is currently only applied at a few locations in the world. Oil Byproduct CC is considered a conventional route in this chapter because its feedstocks (e.g. heavy oils, etc.) are byproducts derived from crude oil, which is a conventional primary energy source used for petrochemicals production.

Figure 4-1 Naphtha Related Conventional and Alternative Routes to Basic Petrochemicals (solid lines refer to technologies that are already commercialized; dashed lines refer to technologies that are not yet commercialized; the oil sands route only briefly discussed)

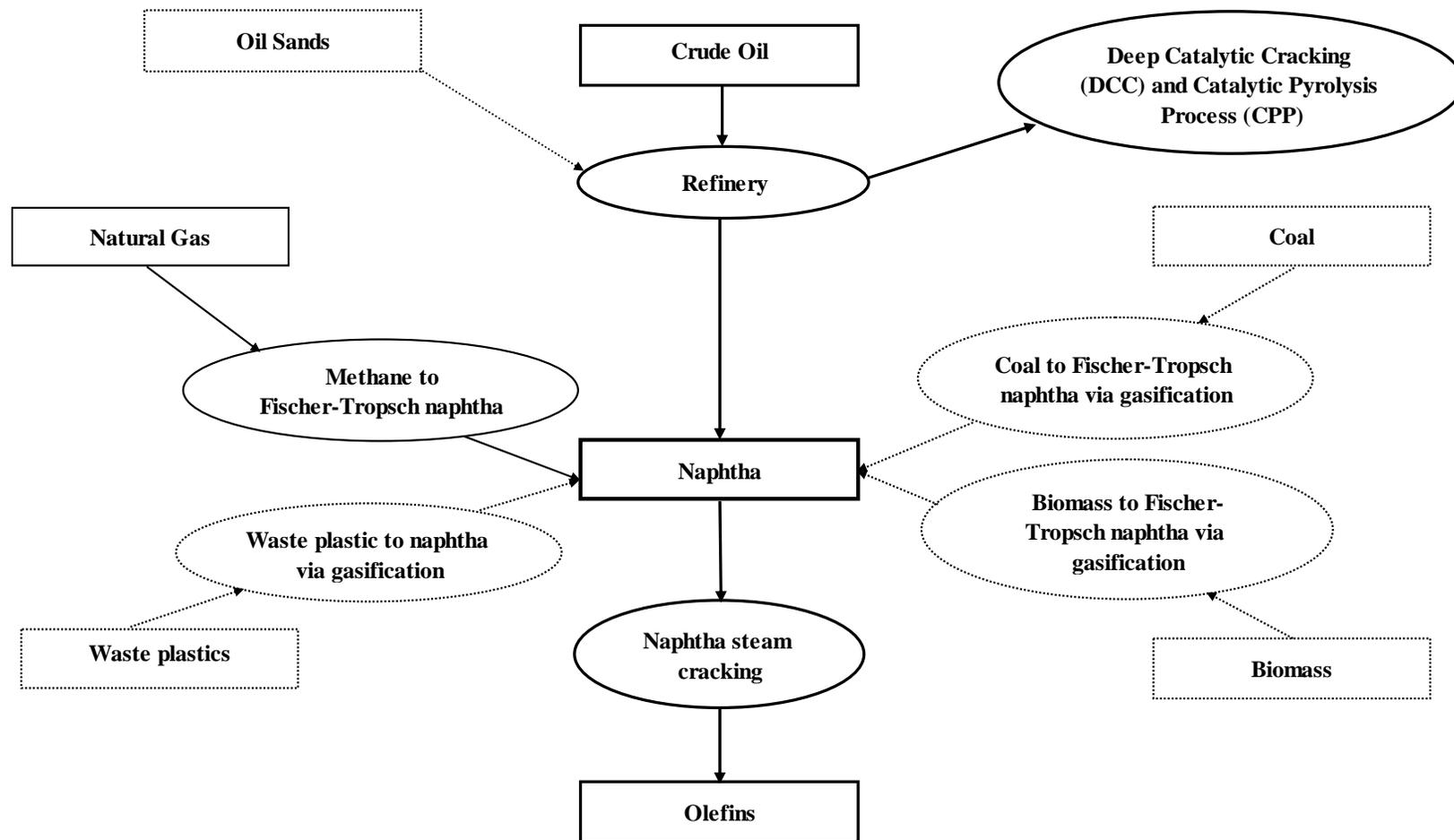
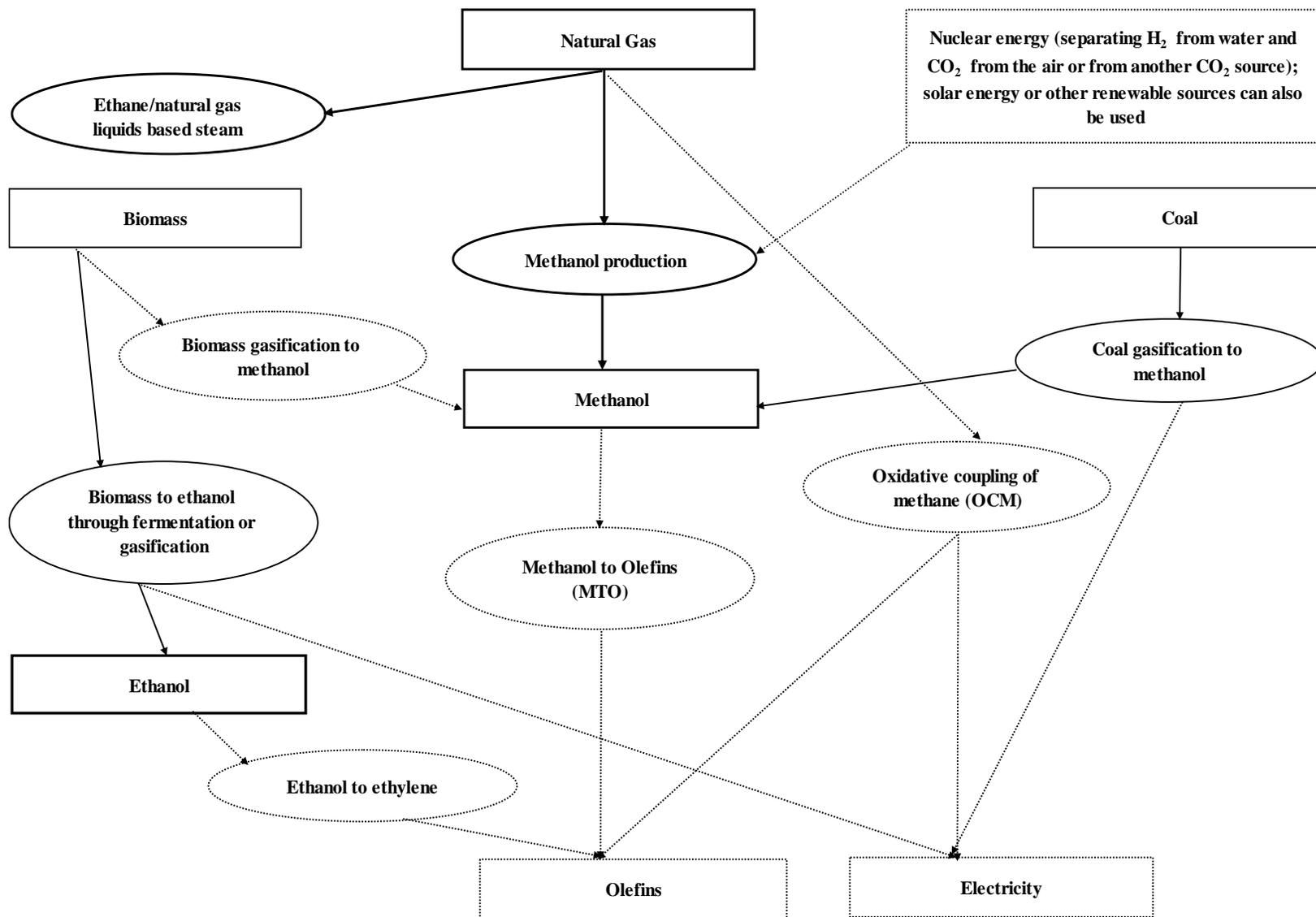


Figure 4-2 Ethane, Methanol and Ethanol Related Routes to Basic Petrochemicals (solid lines refer to technologies that are already commercialized; dashed lines refer to technologies that are not yet commercialized)



4.3.2. Alternative Routes

In contrast to conventional routes, the feedstocks used in alternative routes are derived from alternative primary energy sources. Alternative routes can be categorized into *naphtha*, *methanol* and *ethanol*-related routes and methane processing by *oxidative coupling*.

4.3.2.1. Naphtha Routes: from Methane, Plastic Waste, Coal and Biomass

All the naphtha-related alternative routes are based on the same feedstock (naphtha) and the same petrochemicals production process (naphtha steam cracking) as the second step (see Figure 4-1). However, the first step in these routes, naphtha production, is based on very different primary energy sources, namely methane, plastic waste, coal and biomass.

Methane (i.e. 80 to 100% of natural gas found worldwide) can be converted into naphtha through natural gas-to-liquids (GTL) processes as follows:

- First, methane is converted into syngas. There are two main reactions (see the reaction equations in Table 4-2). One reaction is partial oxidation of methane, which is an exothermic reaction. Another reaction is the well-known steam reforming of methane, which is an endothermic reaction.
- Syngas is then converted into long chains of “-CH₂-” through Fischer-Tropsch (FT) synthesis (see the reaction equations in Table 4-2). FT liquid fuels (i.e. diesel, kerosene and gasoline) are produced through hydrocracking and a series of separation processes. Up to 30% FT naphtha is also formed. Several types of cobalt-based catalysts are used in this step.

FT naphtha contains only paraffins (meaning saturated hydrocarbons with un-branched chain structure) and no aromatics. These properties make FT naphtha ideal for producing light olefins through steam cracking. The ethylene yield from steam cracking of FT naphtha is about 40%, nearly 10% higher than that of oil-derived naphtha [32, 33]. However, due to the lack of aromatics, the total yield of HVCs is only 5% higher than that of Oil Naphtha SC. We chose a natural gas-to-liquids (GTL) process with a maximum naphtha yield and high energy efficiency

as the design of the first process step in the route. The route will be referred to hereinafter as Methane FT Naphtha SC. This route has been applied by Shell in Malaysia and by Mossgas in South Africa. The most recent overviews are presented in [192, 193].

Plastic waste, especially polyolefins (e.g. the polypropylene used in plastic bags), can be converted into naphtha and other hydrocarbons (e.g. mostly high-boiling oils) through a series of liquefaction, pyrolysis and separation processes. Hydrogen, steam and catalysts are needed here. The naphtha produced is similar to naphtha derived from crude oil and, if used in steam cracking, can lead to a similar yield of light olefins. This route will be referred to hereinafter as Waste Naphtha SC. The technology was developed by BASF to comply with regulations in Germany, but was later abandoned [194, 195]. It is not yet used on a commercial scale. Currently, the dominant methods to dispose of plastic waste are landfills, incineration or making secondary plastics. The utilization of plastic waste for the production of naphtha and petrochemicals is a potential method for plastic waste disposal.

Coal can be converted into naphtha via either direct or indirect liquefaction¹ [196-198]. Black sub-bituminous coal (geologically young) and brown coal (lignite) are more suitable for direct coal liquefaction than bituminous coal. As shown in Table 4-1, their calorific values are different from that of bituminous coal.

Several designs for direct coal liquefaction² have been studied in recent decades. A well-known design is the Bergius process in which coal is first ground into fine particles and then mixed with a heavy, aromatic solvent (recovered later) at about 450 °C to form a slurry that is rich in aromatics. Through a low-severity, catalytic hydrogenation process, the slurry is refined into liquid transportation fuels and naphtha. The hydrogen and electricity used in this process are generated internally. In contrast to FT naphtha (with no aromatics), the naphtha produced by this route is rich in aromatics. When used in steam cracking, aromatics-rich naphtha leads to lower HVCs yields than oil-derived naphtha (estimated to be 15% lower than that of Oil Naphtha SC

¹ At the end of the World War II, there were 9 indirect and 18 direct coal liquefaction plants in operation with a total capacity of 0.2 mbpd (million barrels per day) to meet 90% of domestic needs in Germany.

² There are two other major coal direct liquefaction processes. One is the SRC (Solvent Refined Coal) process, which was developed by Gulf Oil and implemented in pilot plants in the US in 1960-1970s [199]. The other is the low temperature carbonization (LTC) or Karrick process, which was developed in the 1920s [200]. No recent data on these processes were found.

[201]). This route will be referred to hereinafter as Coal Direct Naphtha SC and has not yet been applied on a commercial scale.

Coal can also be converted into naphtha via FT processes, or so-called indirect liquefaction. Similar to Methane FT Naphtha SC, coal is first converted into syngas (through gasification) and the syngas is then converted into FT liquids that are similar to those from natural gas-to-liquids (GTL) processes. As with FT naphtha derived from methane, steam cracking of FT naphtha derived from coal can lead to a high yield of light olefins. In contrast to natural gas-to-liquids (GTL) processes, FT naphtha production from coal requires extensive gas cleanup after coal gasification (e.g. removal of sulfur and other impurities such as metals with the use of solvents and absorbents). Three designs, Coal FT Naphtha SC I, Coal FT Naphtha SC II and Coal-ligno FT Naphtha SC, have been selected. Coal FT Naphtha SC I has been chosen because only FT liquids are produced and very little electricity is cogenerated [202]. Coal FT Naphtha SC II has been chosen as a relatively small output of FT liquids is produced and a large amount of electricity is cogenerated [198]. In the case of Coal-ligno FT Naphtha SC, coal and lignocellulosic biomass (e.g. switchgrass) are used to produce FT liquids and a moderate amount of electricity is cogenerated while nearly all CO₂ is captured and used for the purpose of enhanced oil recovery (EOR) [191, 203]. Moreover, Coal-ligno FT Naphtha SC has been selected because it has the flexibility to use both coal and biomass. So far, none of the three coal-based routes (Coal FT Naphtha SC I, II and Coal-ligno FT Naphtha SC) has been used on a commercial scale.

Similar to methane and coal, biomass can also be converted into FT naphtha through FT processes. As with FT naphtha derived from methane and coal, the FT naphtha derived from biomass has a high paraffinic content and leads to high yields of light olefins if it is used in steam cracking. However, FT naphtha production from raw biomass must deal with the high water content of the biomass. The most recent, comprehensive study found so far is [204]. Among the many designs covered in [204], there is one design that has the greatest output of FT liquids and the least net electricity cogeneration, and another that has the greatest electricity cogeneration and the least output of FT liquids. In this chapter, the two routes with these two

designs will be referred to hereinafter as Ligno FT Naphtha SC I and II, respectively. These two routes have not yet been used on a commercial scale.

4.3.2.2. Methanol Routes: from Methane, Coal and Biomass

Five of the six methanol-related routes discussed in this chapter are based on the same process for petrochemicals production: the “Methanol-To-Olefins” (MTO) technology developed by UOP LLC. This technology has been chosen because of its high energy efficiency and high light olefin yield. The natural gas-based methanol route (i.e. methanol production from methane plus MTO) will be referred to hereinafter as Methane MTO. This route has been extensively described in Chapter 3. Another route described in Chapter 3, based on Lurgi’s Methanol-to-propylene (MTP), has been chosen because of its high propylene yield. It will be referred to hereinafter as Methane MTP. Since these process technologies have been extensively described before, we will focus only on the first step in this chapter (i.e. methanol production from coal and biomass).

Methanol can be produced from coal via syngas. Similar to the FT naphtha production from coal mentioned earlier, coal is first gasified to produce syngas and the syngas is then converted into methanol. The most recent and most comprehensive study found so far is [205]. From the six designs described in [205], we chose three for methanol production, since they cover a wide range of technical specifications, such as electricity cogeneration, recycling and CO₂ capture¹. These three routes will be referred to hereinafter as Coal MTO I (with recycling, without CO₂ capture and with the least net electricity cogeneration), Coal MTO II (without recycling, without CO₂ capture and with the greatest net electricity cogeneration) and Coal MTO CCS (with recycling, with CO₂ capture and with the greatest net electricity import). These routes are new, but there are plans to use some of them on a commercial scale in China [197].

All kinds of biomass can be converted into methanol via processes that are similar to coal-based methanol production, i.e. by gasification to produce syngas and subsequent methanol synthesis processes. Biomass-based methanol production has been described in detail in [27, 204]. From the designs described in [204], we chose a design with the highest energy efficiency for this

¹ For the purpose of illustration only. It is technically possible to add CO₂ capture and storage to any of the routes mentioned.

analysis. In this chapter, the route is referred to as Ligno MTO. It has not yet been used on the commercial scale.

4.3.2.3. Ethanol Routes: from Biomass

All ethanol related routes use the same petrochemicals production process as the second step where ethanol is converted into ethylene through a rather well-known dehydration process (ethanol to ethylene or ETE) [27]. Their differences lie in the first step, feedstock production or, in this case, ethanol production. There are three well-known methods to convert biomass into ethanol:

- Direct fermentation of sugar/starch rich biomass (e.g. sugar cane, sugar beet or maize starch) to ethanol [27], in which micro-organisms convert carbohydrates to ethanol under anaerobic conditions. The reaction formulas can be found in Table 4-4;
- Hydrolysis of lignocellulosic biomass (e.g. agricultural waste, wheat and wood), followed by fermentation to ethanol. Here again micro-organisms convert carbohydrates to ethanol under anaerobic conditions. The reaction formulas can be found in Table 4-4;
- Gasification of lignocellulosic biomass, followed by either fermentation or chemical catalysis to ethanol. This method is only briefly discussed in Section 4.5 due to limited data.

Regarding the first method, two improved ethanol process designs were chosen (the energy requirements of these designs are 5-6 GJ/t ethanol lower than the current technologies) [27]. One utilizes maize starch while the other utilizes sugar cane. In this chapter, they will be referred to hereinafter as Maize Starch ETE and Sugar Cane ETE, respectively. Unlike the Maize Starch ETE route, the Sugar Cane ETE route has electricity cogeneration. The ethanol production technologies applied in these two routes are currently used at many locations throughout the world. However, at present there is no known ethylene production from biomass-derived ethanol in a commercial-scale operation. Ethylene plants based on ethanol derived from sugar cane in Brazil were in operation during the 1980s and were shutdown in the early 1990s when the oil prices fell. Currently, this route may be experiencing a comeback. In 2007, plans

for the construction of three such plants in Brazil were announced (to be in operation in 2009-2011 with a total capacity of 600,000 tons of ethylene) [206-208].

Three designs were chosen for the second method mentioned above: one design has the least electricity cogeneration, another has the most electricity cogeneration and the last has moderate electricity cogeneration [27, 204]. They were chosen because they include the full range of technical options regarding electricity cogeneration. The three routes will be referred to hereinafter as Ligno ETE I (with the least electricity cogeneration), Ligno ETE II (with the greatest electricity cogeneration) and Ligno ETE III (with rather moderate electricity cogeneration). The ethanol production technologies based on lignocellulosic biomass are still undergoing development and these technologies have not yet been used to produce ethylene on a commercial scale¹.

4.3.2.4. Oxidative Coupling routes: from Methane

Rather than being converted into HVCs via naphtha or methanol, methane can also be converted to ethylene through the oxidative coupling chemistry described in [116]. Two oxidative coupling routes, DSM OCM I and II (see details in Chapter 3) will be compared with other routes in this chapter. They will be referred to hereinafter as Methane OCM I and II. These routes have not yet been used on a commercial scale.

4.4 Energy Use, CO₂ Emission Analysis and Land Use

Data used in the analysis of energy use and CO₂ emissions for various routes are shown in Table 4-2 to 4-7. Lower heating values (LHVs) and emission factors are shown in Table 4-1. Data on feedstock production, or the first step of each route, are shown in Table 4-2 (oil and natural gas), Table 4-3 (coal) and Table 4-4 (biomass). Data on petrochemicals production, or the second step of each route, are shown in Table 4-5 (oil and natural gas), Table 4-6 (coal) and Table 4-7 (biomass).

¹ There are currently several pilot plants in operation and a number of plans have been announced for the construction of commercial-scale (above 10 million gallons ethanol per year) lignocellulosic ethanol plants [209].

Table 4-1 Overview of Primary Energy Sources, Feedstocks and High Value Chemicals (HVCs) On a Dry Basis

Routes	Oil Naphtha SC, Waste Naphtha SC, Oil Byproduct CC	Ethane SC	FT Naphtha SC	Methane MTO, MTP	Methane OCM I and II	Coal MTO I, II and CCS	Coal Direct Naphtha SC	Coal FT Naphtha SC I	Coal FT Naphtha SC II SC and Coal-ligno FT Naphtha SC	Ligno FT Naphtha SC I and II	Ligno MTO, ETE I, II, III, Maize Starch ETE and Sugar Cane ETE
Primary energy source	Crude Oil (not used for combustion)	Natural Gas (CO ₂ emission factor of methane 0.056 t CO ₂ /GJ [210]; ethane not used for combustion)			Coal (CO ₂ emission factor 0.092 t CO ₂ /GJ) [205]	Coal (CO ₂ emission factor 0.087 t CO ₂ /GJ)[196]	Coal (CO ₂ emission factor 0.118 t CO ₂ /GJ) [202]	Coal (CO ₂ emission factor 0.092 t CO ₂ /GJ) [198, 203]	Biomass (no CO ₂ emission assumed)		
Calorific value (LHV; GJ/t primary energy source)	43 (typical) [210, 211]		44 typical for natural gas, which consists of methane, ethane, natural gas liquids, water, etc. (50 GJ/t for pure methane) [210]			26 [205]	32 [196]	20 [202]	29 [198, 203] (Coal FT Naphtha SC II SC: sulfur 9 GJ/t)	Lignocellulosic biomass 18 [211]; maize 16 and sugar cane 18 [212]	
Energy use for producing primary energy source	0.4 GJ/t crude oil; assumed to be refinery gas (i.e. 1% of crude oil on the energy basis; see details in Chapter 3)		2 GJ/t natural gas; assumed to be methane (i.e. 5% of natural gas on the energy basis; see details in Chapter 3);			0.1 GJ coal to produce 1 GJ coal [213] (multiply the calorific values of different types of coal by 0.1 to get GJ/t for each type of coal)				1 GJ/t sugar cane, 2 GJ/t lignocelluloses and 3 GJ/t maize [27, 204, 219]; assumed to be diesel (CO ₂ emission factor 0.074 t/GJ)	
Feedstock	Naphtha (H ₂ needed for Waste Naphtha SC)	Ethane	Methane	Methanol	Methane	Methanol	Naphtha			Methanol	Ethanol
LHVs (GJ/t feedstock) [211]	45 GJ/t naphtha (120 GJ/t H ₂ ; energy use for making H ₂ is 62 GJ/t H ₂ [25])	47 GJ/t ethane	45 GJ/t naphtha	20 GJ/t methanol	50 GJ/t methane	20 GJ/t methanol	45 GJ/t naphtha			20 GJ/t methanol	26 GJ/t ethanol
LHVs (GJ/t HVCs) [211]	47 GJ/t for ethylene, propylene and other basic petrochemicals; On average 50 GJ/t for HVCs produced by naphtha and methanol related routes (only negligible differences) (these routes also produce aromatics and other non-olefins, 50% of whose weight are counted as HVCs)										47 GJ/t ethylene
Carbon content of HVCs [210]	CO ₂ emissions due to combustion of HVCs: 3.1 ton per ton ethylene, 3.2 ton per ton propylene and 3.5 ton per ton HVCs on average										

Table 4-2 Feedstock Production in Crude Oil and Natural Gas-based Routes (the 1st step of a route)

Primary energy source	Crude Oil (see details in Chapter 2)				Natural gas (see details in Chapter 3)		
Routes	Oil Naphtha SC	Waste Naphtha SC	Oil Byproduct CC	Ethane SC	FT Naphtha SC	Methane MTO and methane MTP	Methane OCM I and methane OCM II
Feedstock	Naphtha		Byproducts	Ethane	Naphtha	Methanol	Methane
Feedstock Production	Crude oil distillation	Hydrogen pyrolysis (hydrogenation)	Separation from refinery/ petrochemical products	Separation from natural gas	Syngas production and Fischer-Tropsch process	Methanol synthesis	Natural gas process (separation and purification of methane)
Reaction	Separation of paraffinic rich C ₅ -C ₁₁	Breaking up of polymers (C ₂ H ₄) _n or (C ₃ H ₆) _n	Separation of C ₄ -C ₉ or heavier than C ₁₀	Separation of C ₂ H ₆ from others	$CH_4 + O_2 \rightarrow CO + 2H_2O;$ $CH_4 + H_2O \rightarrow CO + 3H_2$ $nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$		Separation and purification of CH ₄ from natural gas
Yield of feedstock (wt.)	Naphtha is 10% of refinery products	45% (35% aromatics and conversion gases; 80% naphtha-value equivalent)	Up to 70% (depending on the chemical composition of byproducts)	1-15% (depending on the chemical composition of natural gas)	15-30% (81% naphtha-value equivalent)	Methanol 145% of natural gas	Methane 80-95% (depending on the chemical composition of natural gas)
Fossil energy use (GJ/t feedstock); calorific value of feedstock excluded; No electricity cogeneration	3 [2, 76]	8 [195]	3 [100]	2 [2, 76]	17 (energy use of current technologies is 10-20% higher than 17 [192])	10 [148]	2 GJ/t methane [116]; 3 GJ/t oxygen [40]

Table 4-3 Feedstock Production in Coal-based Routes (the 1st step of a route)

Primary energy source	Coal						Coal and Biomass
Content (wt. excluding minerals/metals)	C:75-85% in bituminous, 70-80% in sub-bituminous and 65-70% in lignite (lignite used for Coal Direct Naphtha SC only); H: 4-5% in bituminous, sub-bituminous and lignite; O: 5-10% in bituminous, 10-20% in sub-bituminous and 20% in lignite; N: 1-2% in bituminous, sub-bituminous and lignite; S: 1-10% in bituminous, sub-bituminous and lignite (C: 80-90% H: 3-4% and O: 2-5% in anthracite; not suitable for Coal Direct Naphtha SC, but suitable for others)						
Routes	Coal MTO I	Coal MTO II	Coal MTO CCS	Coal direct Naphtha SC	Coal FT Naphtha SC I	Coal FT Naphtha SC II	Coal-ligno FT Naphtha SC
Feedstock	Methanol			Naphtha	FT Naphtha		
Feedstock Production	Methanol production (via syngas)			Direct Liquefaction (no syngas involved)	Fischer-Tropsch (via syngas)		
Main Reactions	(CH _{0.8})O _x S _y N _z is gasified and cleaned; 12C ₆ H ₅ +36O ₂ →72CO+30H ₂ ; there are also CO ₂ , SO _x , NO _x and other less valuable byproducts; CO+2H ₂ →CH ₃ OH			C _m H _n O _p S _p N _q is converted into C _n H _{2n} and other C ₄ -C ₂₂ liquids (also CO ₂ , SO _x , NO _x and other less valuable byproducts);	(CH _{0.8})O _x S _y N _z is gasified and cleaned; 12C ₆ H ₅ +36O ₂ →72CO+30H ₂ ; there are also CO ₂ , SO _x , NO _x and other less valuable byproducts; CO+2H ₂ →CH ₃ OH		
Yield of feedstock (wt.)	74%	30%	74%	Naphtha 10% (the total yield of naphtha-value equivalent products is 42%)	Naphtha 9% (the total yield of naphtha-value equivalent products is 31%)	Naphtha 5% (the total yield of naphtha-value equivalent products is 18%)	
Energy use (GJ/t feedstock) before deducting fossil energy use for electricity production (calorific value of feedstock excluded); all fossil energy	17	70	18	38	30	124	88
Electricity cogenerated (GJ/t feedstock)	0.2	20	0	0	0	36	19
Energy use (GJ/t feedstock) after deducting energy use for electricity production (calorific value of feedstock excluded) ; all fossil energy	17	34	18	38	30	59	53 (32 from coal and 21 from biomass)
References	[205]			[196]	[198, 202]		[191, 203]

Table 4-4 Feedstock Production in Biomass-based Routes (the 1st step of a route)

Biomass routes	Ligno FT Naphtha SC I	Ligno FT Naphtha SC II	Ligno MTO	Ligno ETE I	Ligno ETE II	Ligno ETE III	Maize Starch ETE	Sugar Cane ETE
Feedstocks	FT naphtha [204]		Methanol [204]	Ethanol [25, 27, 204]				
Feedstock Production	Fischer-Tropsch (via syngas)		Methanol production (via syngas)	Ethanol (C ₅ H ₁₀ O ₅) production through hydrolysis and fermentation (no syngas involved)				
Main reactions	Lignocelluloses C ₆ H ₁₀ O ₅ is gasified; the products are syngas (a mixture of CO and H ₂) and a small amount of CO ₂ , CH ₄ and H ₂ O.		Lignocelluloses (C ₆ H ₁₀ O ₅) _n +nH ₂ O→n(C ₆ H ₁₂ O ₆); Glucose/sugar C ₆ H ₁₂ O ₆ →2C ₂ H ₅ OH+2CO ₂ ; Sugar/starch 3C ₅ H ₁₀ O ₅ →5C ₂ H ₅ OH+5CO ₂					
	nCO+2nH ₂ →C _n H _{2n} +nH ₂ O							CO+2H ₂ →CH ₃ OH
Yield of feedstock (wt.)	Naphtha 3% (the total yield of naphtha-value equivalent products is 12-14%)		49%	31%	25%	27%	46%	19%
Energy use GJ/t feedstock before deducting fossil energy use for electricity production (calorific value of feedstock excluded)	17 (fossil)	13 (fossil)	6 (fossil)	9 (fossil)	8 (fossil)	8 (fossil)	20 (fossil)	7 (fossil)
	100 (biomass-derived)	124 (biomass-derived)	21 (biomass-derived)	32 (biomass-derived)	47 (biomass-derived)	33 (biomass-derived)	9 (biomass-derived)	61 (biomass-derived)
Electricity cogenerated (GJ_e/t feedstock)	12	38	0	3	14	3	0	10
Energy use GJ/t feedstock after deducting fossil energy use for electricity production (calorific value of feedstock excluded)	-5 (fossil)	-56 (fossil)	6 (fossil)	4 (fossil)	-18 (fossil)	2 (fossil)	20 (fossil)	-11 (fossil)
	100 (biomass-derived)	124 (biomass-derived)	21 (biomass-derived)	32 (biomass-derived)	47 (biomass-derived)	33 (biomass-derived)	9 (biomass-derived)	61 (biomass-derived)

Table 4-5 Petrochemicals Production in Crude Oil and Natural Gas-based Routes (the 2nd step of a route)

Primary energy sources	Crude Oil (see details and references in Chapter 2)				Natural gas (see details and references in Chapter 3)				
	Oil Naphtha SC	Waste Naphtha SC	Oil Byproduct CC	Ethane SC	FT naphtha SC	Methane MTO	Methane MTP	Methane OCM I	Methane OCM II
Petrochemical Production	Steam cracking		Catalytic cracking	Steam cracking		Methanol dehydration		Oxidative coupling	
Reactions	C ₅ -C ₁₁ cracked into C ₂ H ₄ , C ₃ H ₆ , etc.		C ₄ -C ₉ catalytically cracked into C ₃ H ₆ , etc.	C ₂ H ₆ cracked into C ₂ H ₄	C ₅ -C ₁₁ cracked into C ₂ H ₄ , C ₃ H ₆ , etc.	2CH ₃ OH→H ₃ COCH ₃ +H ₂ O; H ₃ COCH ₃ is dehydrated and the main products are C ₂ H ₄ and C ₃ H ₆ (in the case of MTP, no C ₂ H ₄ is produced)		2CH ₄ + 1/2O ₂ →C ₂ H ₆ +H ₂ O; C ₂ H ₆ +1/2O ₂ →C ₂ H ₄ +H ₂ O	
Yield (wt.) of HVCs as % of feedstocks	70%		50%	84%	75%	43%	40%	50% (19 GJ _e /t HVCs co-generated)	15% (148 GJ _e /t HVCs cogenerated)
Energy use (GJ/t HVCs); no electricity cogeneration except for Methane OCM I/II; calorific value of HVCs excluded	6		5	9	6	5	9	17 (energy use for electricity production 35 excluded)	14 (energy use for electricity production 269 excluded)

Table 4-6 Petrochemicals Production in Coal-based Routes (the 2nd step of a route)

Primary energy sources	Coal		
Routes	Coal MTO I, Coal MTO II and Coal MTO CCS	Coal Direct Naphtha SC	Coal FT Naphtha SC I, Coal FT Naphtha SC II and Coal-ligno FT Naphtha SC
Feedstock	Methanol	Naphtha	FT naphtha
Petrochemical Production	Methanol dehydration	Steam cracking	
Reactions	$2\text{CH}_3\text{OH} \rightarrow \text{H}_3\text{COCH}_3 + \text{H}_2\text{O}$; H_3COCH_3 is dehydrated and the main products are C_2H_4 and C_3H_6	Fischer-Tropsch liquids ($\text{C}_5\text{-C}_{11}$) are cracked into C_2H_4 , C_3H_6 , etc.	
Yield (wt.) of HVCs as % of feedstock	43% (see details in Chapter 3 regarding MTO)	55% [201]	75% (see details in Chapter 2 regarding naphtha steam cracking)
Energy use (GJ/t HVCs); no electricity cogeneration; calorific value of HVCs excluded	5 (see details in Chapter 3 regarding MTO)	8 (higher than 6 in the right column because heavy naphtha is used; see details in Chapter 2 regarding naphtha steam cracking)	6 (in the case of Coal-ligno FT Naphtha SC, 3.6 comes from coal and 2.4 comes from biomass; see details in Chapter 2 regarding naphtha steam cracking)

Table 4-7 Petrochemicals Production in Biomass-based Routes (the 2nd step of a route and a summary of both steps)

Primary energy source	Biomass							
Routes	Ligno FT Naphtha SC I	Ligno FT Naphtha SC II	Ligno MTO	Ligno ETE I	Ligno ETE II	Ligno ETE III	Maize Starch ETE	Sugar Cane ETE
Feedstock	FT naphtha		Methanol	Ethanol				
Petrochemical Production	Steam cracking		Methanol dehydration	Ethanol dehydration				
Reactions	C ₅ -C ₁₁ is cracked into C ₂ H ₄ , C ₃ H ₆ , etc.		2CH ₃ OH→H ₃ COCH ₃ +H ₂ O; H ₃ COCH ₃ is dehydrated and the main products are C ₂ H ₄ and C ₃ H ₆	C ₂ H ₅ OH→C ₂ H ₄ +H ₂ O				
Yield of HVCs as % of feedstock (wt.)	75% (see details in Chapter 2 regarding naphtha steam cracking)		43% (see details in Chapter 3 regarding MTO)	61% [27]				
Energy use in the 2nd step (GJ/t HVCs); electricity use negligible; calorific value of HVCs excluded	6 (biomass-derived energy; see details in Chapter 2 regarding naphtha steam cracking)		5 (fossil energy) (see details in Chapter 3 regarding MTO)	2 (fossil energy) [27]				
Total fossil energy use in the 1st and 2nd steps (GJ/t HVCs); calorific value of HVCs excluded	-6	-72	14	8	-27	4	37	-17
Total biomass-derived energy use in the 1st and 2nd steps (GJ/t HVCs); calorific value of HVCs excluded	137	170	53	51	76	54	12	100

Figure 4-3 Total Energy Use in Various Routes to High-Value Chemicals (HVCs) (both fossil and biomass-derived energy; error bars represent the result of using an economic value-based allocation approach to allocate the total energy use to electricity and HVCs)

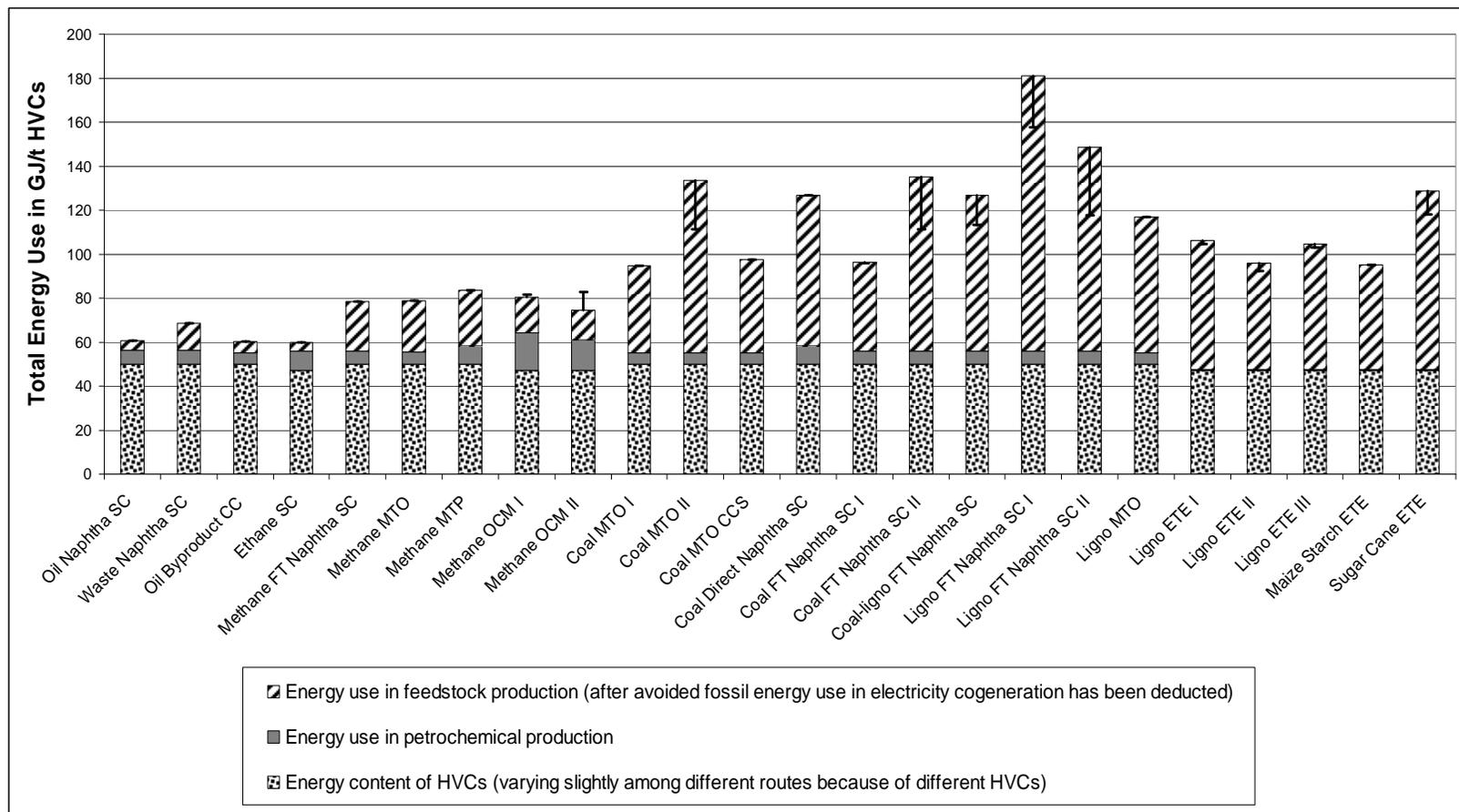


Figure 4-4 Cumulative Process CO₂ Emissions (Cradle-to-factory gate) in Various Routes for Production of High-Value Chemicals (HVCs) (CO₂ emissions from feedstock production and petrochemicals productions; the carbon content of HVCs for fossil-based routes is excluded; the carbon content of HVCs for biomass-based routes originates from the atmosphere and is sequestered in HVCs)

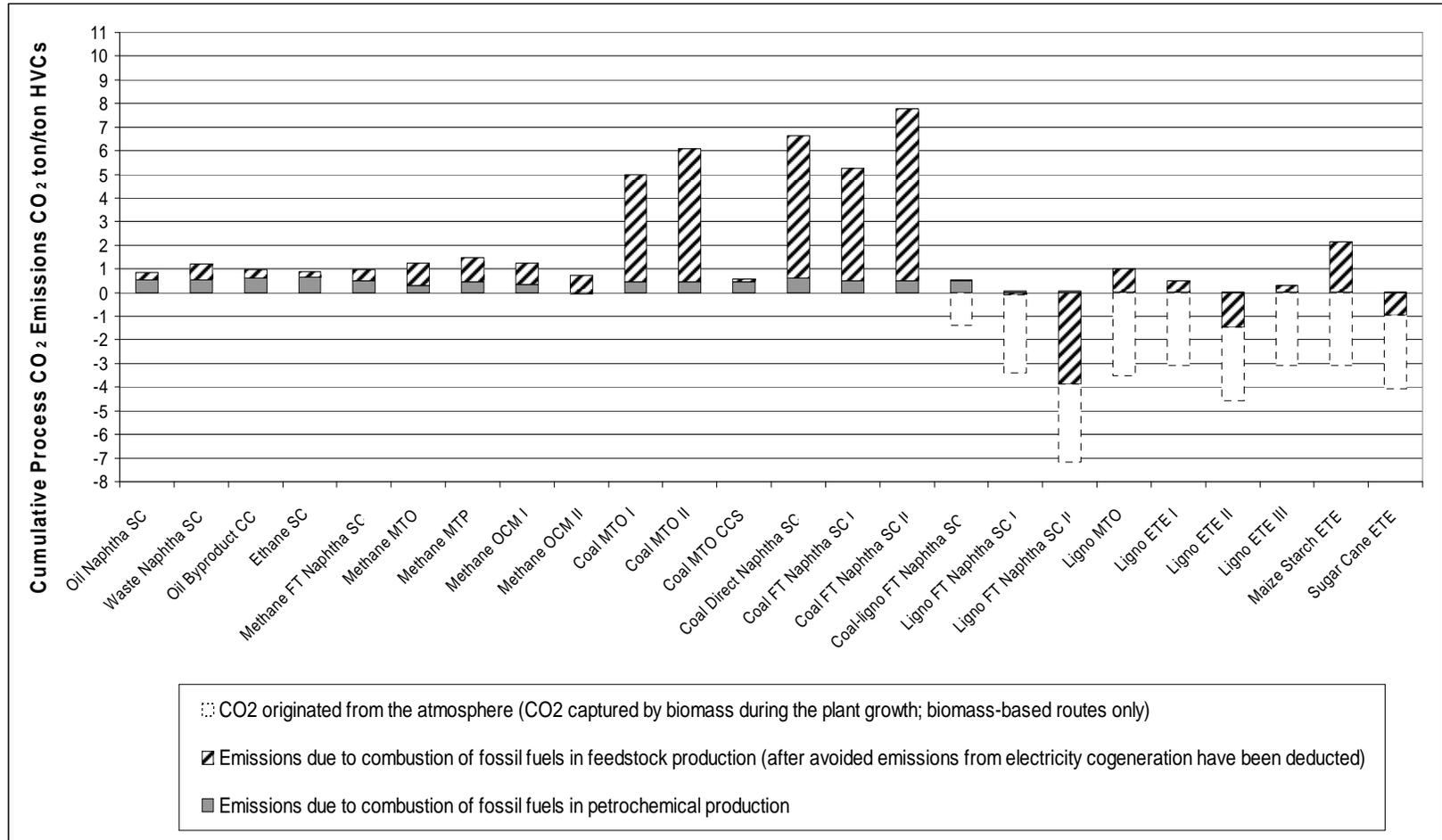


Figure 4-5 Total CO₂ Emissions (Cradle-to-grave) in Various Routes for Production of High-Value Chemicals (HVCs)
 (including the CO₂ emissions from feedstock production and petrochemicals productions as well as the carbon content of HVCs; dotted bars represent fossil carbon physically embodied in HVCs; the carbon content of HVCs from biomass-based routes is zero since it originates from the atmosphere)

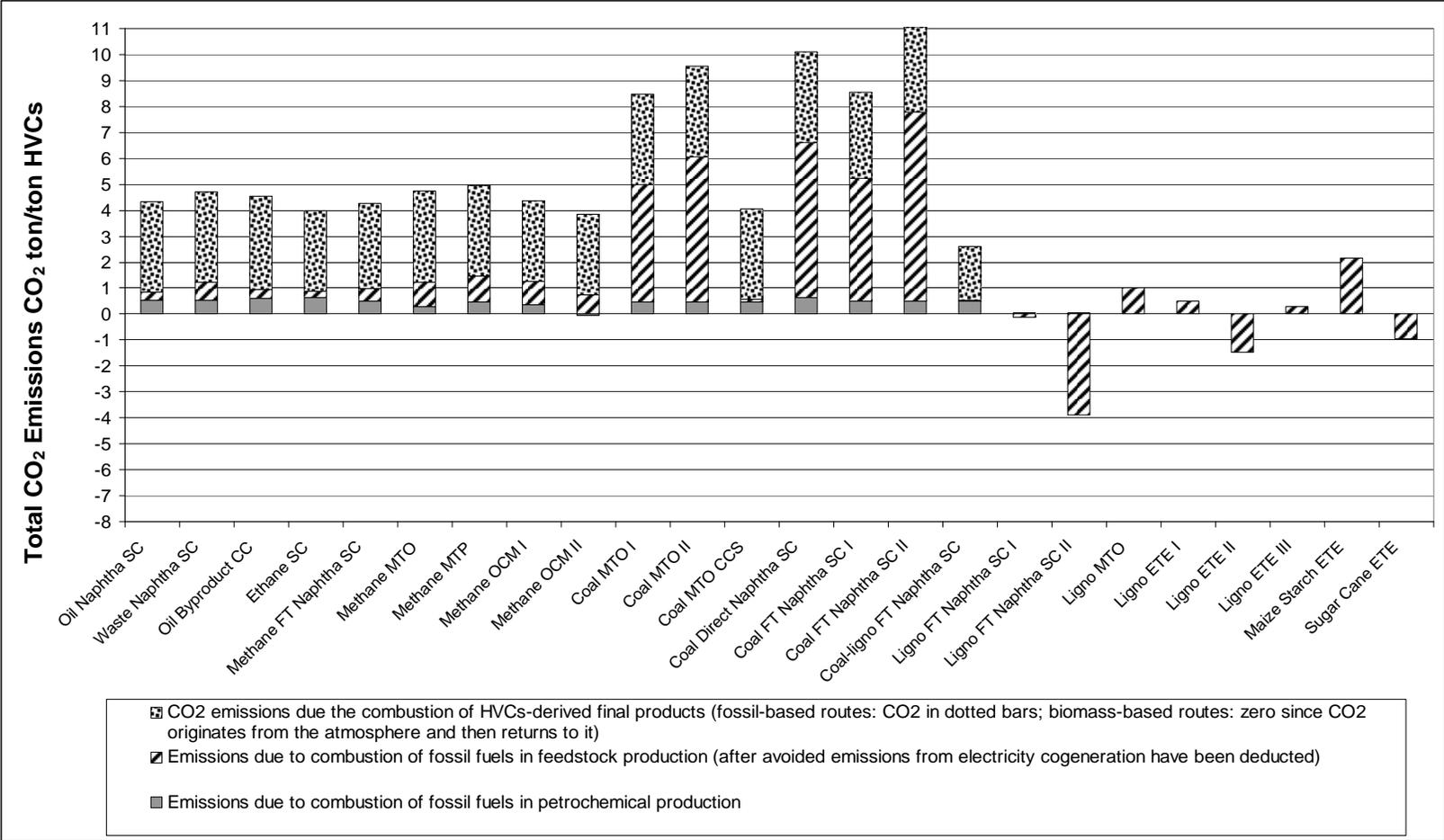


Figure 4-6 Land Use for Growing Various Type of Biomass for Biomass-based Routes to High-Value Chemicals (HVCs) (the default is large round dots; the distance between two large round dots for each route represents a possible range of land use if the total energy use is allocated to HVCs only; the distance between the ends of error bars represents the land use if an economic value-based allocation approach is used to allocate the total energy use to both electricity and HVCs; see Section 4.5.1)

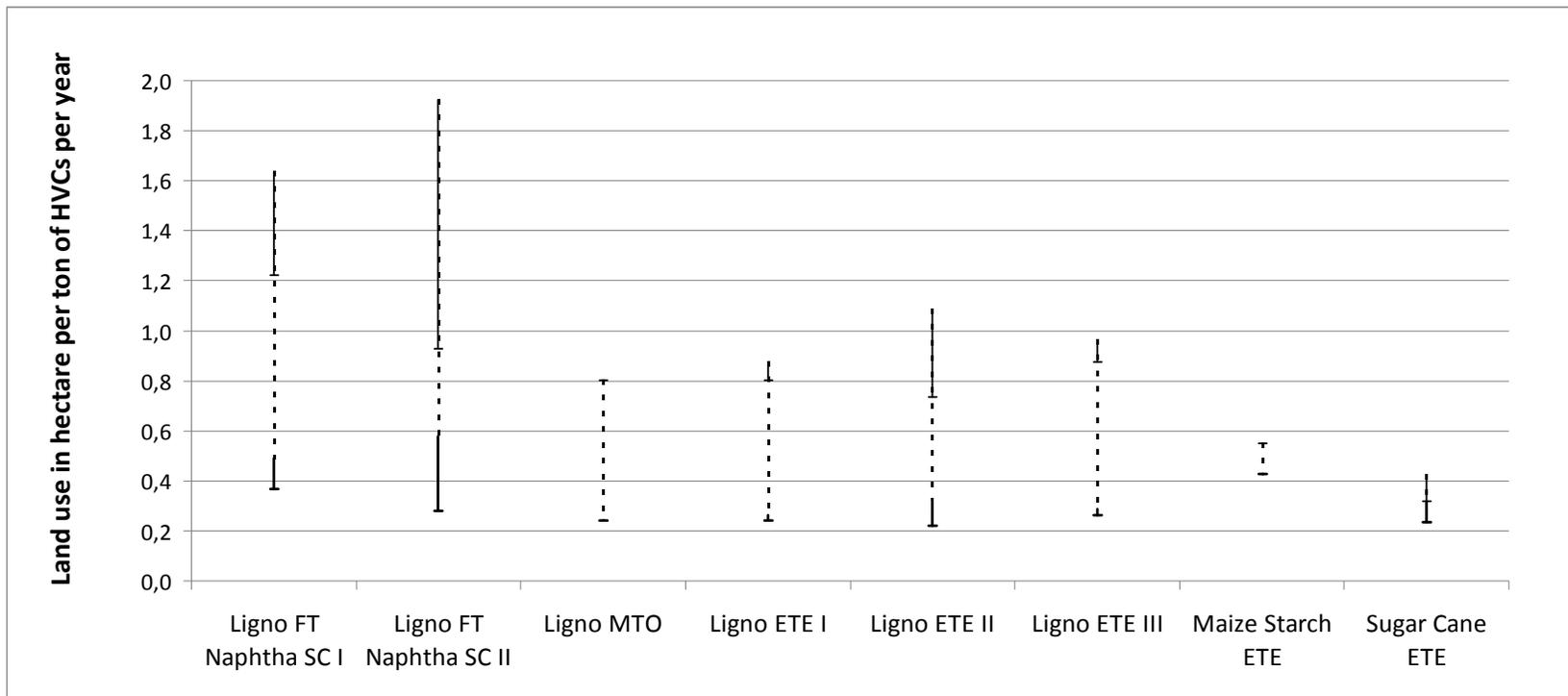
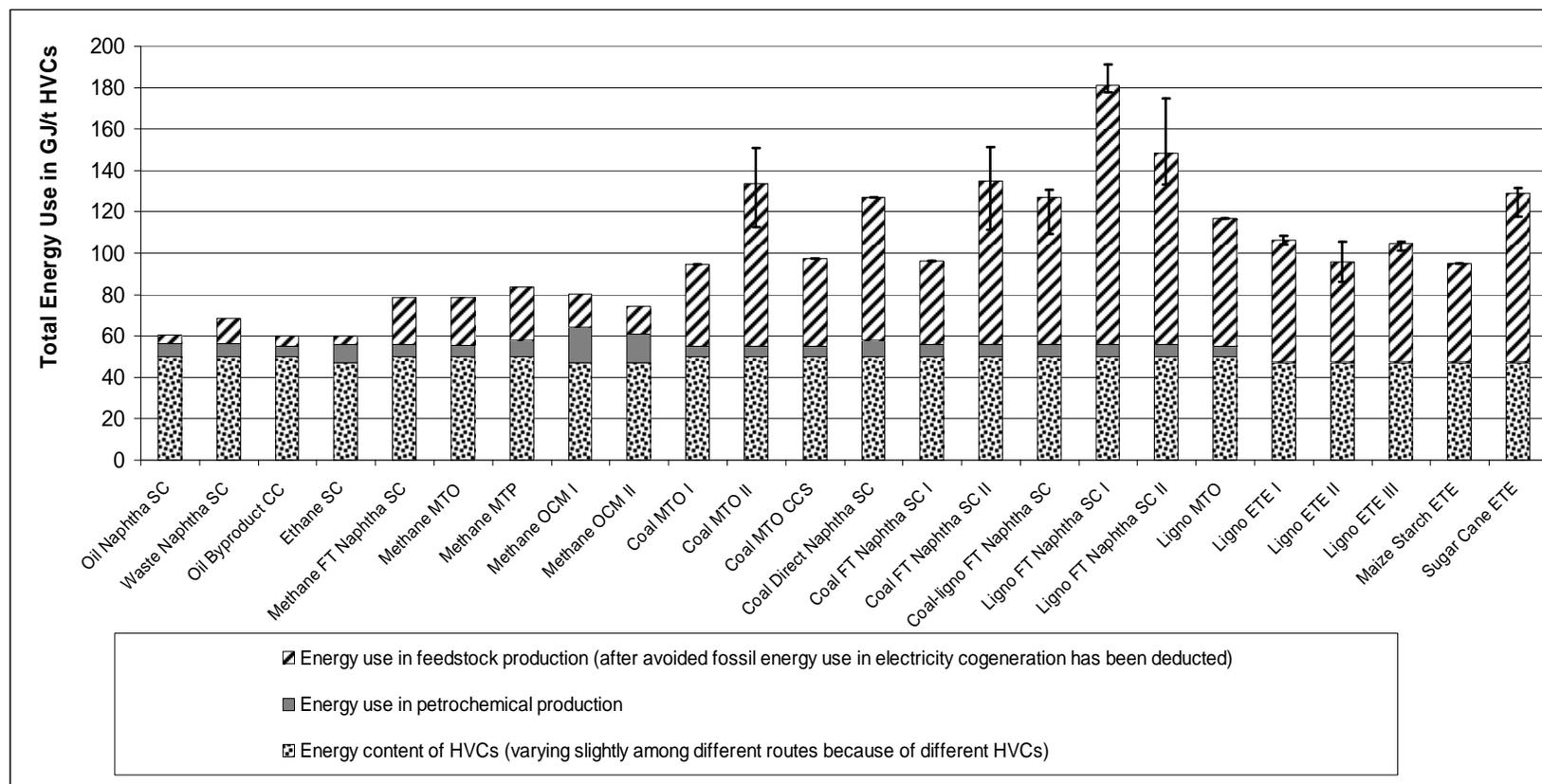


Figure 4-7 Total Energy Use in Various Routes to High-Value Chemicals (HVCs) (both fossil and biomass-derived energy; the upper and lower ends of the error bars represent respectively the results of using the energy efficiency of 60% and 40% for electricity production in coal and biomass-based routes)



4.4.1 Results of Energy Analysis

The overall results of energy analysis for the routes discussed in this chapter are shown in Figure 4-3. When the total energy use (consisting of fossil and biomass-based energy) is compared, the conventional routes (based on crude oil and ethane) are the most energy efficient. The total energy use of the conventional routes is about 60 GJ/t HVCs (the *cumulative process energy use* of 10 GJ/t HVCs plus the calorific value of HVCs about 50 GJ/t HVCs). The total energy use for Waste Naphtha SC is relatively high due to the use of hydrogen.

The total energy use of methane (natural gas) based routes is about 80 GJ/t HVCs. This is about 30% more than that of the conventional naphtha steam cracking route (based on naphtha derived from crude oil). This is in contrast to the current electricity production based on various primary energy sources where power plants fired by natural gas (mostly methane) are the most energy efficient.

Figure 4-3 shows that the *total energy use* of coal and biomass-based routes is roughly 60 to 150% higher than that of conventional routes. The total energy use (consisting of fossil and biomass-based energy) of most of coal and biomass-based routes is in the range of 90-130 GJ/t HVCs. The *cumulative process energy use* of most of the coal and biomass-based routes can even be 4 to 8 times as much as that of conventional routes. The routes with the highest total and cumulative process energy use are Ligno FT Naphtha SC I and II. Their total energy uses are about 180 and 150 GJ/t HVCs respectively. This is due to the low yields (12% to 14%) of feedstock production (FT naphtha production) in these routes, which are much less than the yields of feedstock in most of other routes (see Tables 4-2 through 4-4).

Figure 4-3 show that the CO₂ separation unit of Coal MTO CCS does not lead to substantially higher energy use than other two coal-based methanol routes. About 6% of the total coal input in primary energy terms is used in recycling and CO₂ capture in the case of Coal MTO CCS [205]. Electricity use for drying and compressing CO₂ is about 0.4 GJ_e/t CO₂. The total electricity consumption in Coal MTO CCS is 3.2 GJ_e/t methanol (2.7 GJ_e is cogenerated and 0.5 GJ_e is imported). The energy impact of CO₂ separation is limited because the concentration and pressure of CO₂ are high after gasification [214].

For ethanol production in ethanol-related routes, Table 4-4 indicates that the cumulative process energy use is 29 to 37 GJ/t ethanol¹ (note: it is 50 GJ/t for Sugar Cane ETE). This is 10 to 18 GJ higher than ethanol production from methane via syngas (18.5 GJ/t ethanol)² [215]. High energy use in ethanol production from biomass is largely due to the energy-consuming separation of ethanol from the fermentation broth at relatively low ethanol yields. While cumulative process energy use amounts to 29-37 GJ/t ethanol and is more than the calorific value of ethanol (26 GJ/t ethanol), the fossil energy use is only 7 to 20 GJ/t ethanol, which is still 6 to 19 GJ/t less than the calorific value of ethanol (26 GJ/t). This confirms that ethanol production from biomass avoids the use of fossil energy [216, 217].

4.4.2 Results of CO₂ Emissions Analysis

Figure 4-4 shows the cumulative process CO₂ emissions (cradle-to-factory gate) of all routes. Figure 4-5 shows the total CO₂ emissions (cradle-to-grave) of all routes. For biomass-based routes, the white bars in Figure 4-4 indicate that the carbon content of biomass-derived HVCs originates from the atmosphere (carbon captured by biomass from the air during the plant growth) and is then sequestered in HVCs. When the products derived from HVCs are incinerated for waste treatment, the carbon content of HVCs is released into the atmosphere and finally cancels out the carbon that was originally captured by biomass (see the result in Figure 4-5).

Figure 4-4 and 4-5 show that CO₂ emissions from feedstock production due to the combustion of fossil fuels in several biomass-based routes are negative. This is because the CO₂ emissions avoided by electricity cogeneration are larger than the CO₂ emissions due to the use of fossil energy use. As stated earlier, electricity is always assumed to have been produced by a natural gas-fired power plant and electricity cogeneration leads to CO₂ emissions being avoided. Not all biomass-based routes have electricity cogeneration. The more electricity a biomass-based route cogenerates, the more avoidance of the CO₂ emissions it leads to. As Figures 4-4 and 4-5 show, biomass-based route with the most electricity cogeneration, Ligno FT Naphtha SC II, avoided the most CO₂ emissions.

¹ 29-37 GJ/t ethanol is the sum of fossil and biomass-derived energy use shown in the lowest two rows in Table 4-4.

² Ethanol for industrial use nowadays is mostly made from ethylene, which is the desired final product for this thesis.

The total CO₂ emissions of conventional routes are slightly more than 4 tons CO₂ per ton HVCs. The total CO₂ emissions of methane-based routes are about 10% more than those of conventional routes (see details in the previous chapter). CO₂ emissions of coal-based routes are the highest (8 to 11 tons CO₂ per ton HVCs¹) with an exception of Coal MTO CCS (with CO₂ capture and storage), for which total CO₂ emission is nearly the same as that of the conventional routes. It is technically possible to equip any route, including biomass-based routes, with CO₂ capture and storage to achieve very low CO₂ emissions.

Table 4-2 and Figure 4-3 show that the energy use in feedstock (naphtha) production² of Methane FT Naphtha SC is 17 GJ/t naphtha, which is nearly 6 times that of Oil Naphtha SC (3 GJ/t naphtha). However, Figure 4-4 shows that CO₂ emissions for naphtha production from the former are only slightly higher than for the latter. In the case of naphtha production using Methane FT Naphtha SC, only 6 out of 17 GJ/t is supplied by the combustion of methane and the rest (11 GJ/t naphtha) is supplied by partial oxidation of methane. Partial oxidation of methane leads to the formation of water and hydrocarbon liquids, but not CO₂ (see Table 4-2 for reaction equations). In the case of naphtha production by Oil Naphtha SC, 3 GJ/t naphtha is supplied by the combustion of refinery gas. Because the emission factor of methane is lower than that of refinery gas, the CO₂ emissions from naphtha production in these two routes are only slightly different.

4.4.3 Land Use Analysis

Based on the yields of feedstock per ton of biomass (see Table 4-4) and the yields of HVCs per ton of feedstocks (see Table 4-7), one can calculate the yield of HVCs per ton of biomass can be calculated. The reasonable ranges of biomass yield in terms of tons/hectare/year in the medium term (now–2030) and long term (2030-2050) are expected to be 6 to 20 (lignocellulosic), 7 to 9 (maize) and 20 to 27 (sugar cane) [204, 218, 219]. Using these data, a figure can be calculated for land use per ton of HVCs for each of the biomass-based routes (see large round dots in Figure 4-6). With the exception of Ligno FT Naphtha SC I/II and Ligno ETE II, all other routes use about 0.3-0.8 hectare to produce one ton of HVCs.

¹ CO₂ emissions of Coal-ligno FT Naphtha SC are low because nearly all CO₂ is captured (as said in Section 4.3.2).

² As defined in Chapter 1, energy use in feedstock production is process energy and excludes the calorific value of feedstocks.

The values represented by large round dots in Figure 4-6 are not fully comparable. In Figure 4-6, the yield of HVCs per total input of biomass has been considered (i.e. all biomass use is allocated to HVCs) while several routes (i.e. Ligno FT Naphtha SC I/II and Ligno ETE II) cogenerate large amounts of electricity. This is the reason why the land use for Ligno FT Naphtha SC I/II and Ligno ETE II can be greater than one hectare per ton of HVCs. It is possible to allocate biomass use to both HVCs and electricity through the use of an economic value-based approach. The results will be discussed in Section 4.5.1.

Figure 4-6 shows that the land use of lignocellulosic biomass-based routes can reach 0.2 to 0.4 hectare per ton of HVCs per year as the lignocellulosic biomass yield approaches 20 ton/hectare/year. The range of 0.2 to 0.4 is rather low when compared to the land requirement of several other interesting biomass-based bulk chemicals [27, 220]. The lignocellulosic biomass yield of 20 tons/hectare/year can only be obtained with favorable conditions in terms of fertilization effects, technological improvement, climate and soil quality [218, 219]. It is therefore quite a challenge to reach a land use figure of 0.2 to 0.4 hectares per ton of HVCs per year.

Different biomass grows on different types of land. Maize and sugar cane are generally grown on high-quality agricultural land (hence resulting in high yields). Moreover, sugar cane only grows in tropical and sub-tropical climates. Lignocellulosic biomass can be grown on poor land, but it can also come from agricultural wastes or forests (forest land is generally unfit for agricultural purposes).

4.5 Discussion

The data on individual routes can be affected by various uncertainties to some extent, as indicated in the sources cited for this analysis. However, whether alone or combined, these uncertainties do not change the overall results in Section 4.4 (e.g. Figures 4-3 through 4-5 show the significant differences between the feedstock production steps of conventional and alternative routes). The only significant uncertainty introduced by ourselves is the assumed energy efficiency in electricity cogeneration. In the following sections, we will first discuss an

alternative method for treating electricity in energy allocation. Then, we will discuss several possibilities for technological developments.

4.5.1 Credit and Allocation Approaches

The results presented so far were calculated by applying a credit approach for the routes with electricity cogeneration. This poses two problems:

First, while we applied the physical property-based credit approach for the routes with electricity cogeneration, we also took the economic value-based allocation approach in the definition of naphtha value-equivalent feedstocks and of olefin value-equivalent HVCs. This means that we have in fact used both the credit approach and allocation approach in Section 4.4. The combination of one physical property-based approach and another economic value-based approach could therefore raise questions about consistency.

Secondly, while using the credit approach, we have assumed a default energy efficiency of 55% for the use of natural gas for electricity production. However, as discussed in the last section, 55% is not valid as the energy efficiency for electricity production from coal or biomass, which is generally known to be lower than that of electricity production from natural gas. Testing using values of 40% and 60% for those coal and biomass-based routes with electricity cogeneration against the default energy efficiency of 55% indicated that the total energy use in these routes is quite sensitive to the energy efficiency assumed for electricity cogeneration (see Figure 4-7). The test results nevertheless do not change our earlier finding that coal and biomass-based routes use much more energy than the conventional routes.

One way to tackle the two problems described above is to apply only the economic value-based allocation approach for all routes for allocating the total energy use to both the production of HVCs and electricity generation (therefore not using the credit approach at all). This requires the values of HVCs and electricity to be expressed in common units. The unit cannot be \$/ton (which would be meaningless for electricity), so \$/GJ is a more suitable common unit for expressing the values.

The average projected production costs of HVCs in 2030-2050 are roughly in the range of \$500/t HVCs to \$800/t HVCs (without considering CO₂ costs, see Chapter 5), which is \$10/GJ to

\$16/GJ if expressed in terms of \$ per GJ of calorific value of the HVC products. The projected electricity production of coal and gas-fired power plants in 2010-2050 are roughly in the range of \$0.03/kWh to \$0.05/kWh [43], which is \$8/GJ_e to \$14/GJ_e if expressed in terms of \$ per GJ_e of electricity. Based on these data, HVCs and electricity can be considered to have roughly the same economic values in terms of \$/GJ. As a thought experiment, in terms of \$/GJ, electricity can be simply treated as HVCs. This allows one to apply the allocation approach based on the calorific content of HVCs and the energy content of the cogenerated electricity.

The result of using the economic value-based allocation approach is represented by the error bars in Figure 4-3. Applying the economic value-based allocation approach leads to a convergence of energy use among these routes. As the error bars in Figure 4-3 show, the total energy use of all methane-based routes is about 80 GJ/t HVCs and that of all biomass and coal-based routes (except for Ligno FT Naphtha SC I) is now in the range of 90 to 130 GJ/t HVCs.

The economic value-based allocation approach mentioned above can also be used to correct the land use for those biomass-based routes that cogenerate large amounts of electricity (see Section 4.4.4 and Figure 4-6). When the economic value-based allocation approach is used, cogenerated electricity is converted to tons of HVCs equivalent since their market prices in \$/GJ are nearly the same (as explained above). The error bars in Figure 4-6 represent the result of applying the economic value-based allocation approach. The range of land use has been narrowed to an extent that means all of the biomass-routes (except for Ligno FT Naphtha SC I) use a similar range of areas (about 0.3-0.8 hectare) to produce one ton of HVCs.

If the economic value-based allocation approach is used, cogenerated electricity is considered as equivalent to HVCs and is not used to calculate any avoidance of fossil energy use that would have been used to produce electricity (as in the credit/allocation combined approach used in Section 4.4). Therefore, if fossil energy use and biomass-derived energy use are to be distinguished, the economic value-based allocation approach is less suitable than the credit/allocation combined approach used in the main analysis. For the same reason, the economic value-based allocation approach cannot be used for CO₂ emissions analysis.

4.5.2 Technological Developments

In Chapters 2 and 3, several possibilities to improve petrochemicals production (the second step of a route) in crude oil and natural gas-based routes were discussed, but none of these will affect the overall results indicated in Section 4.4. As Figures 4-3 through 4-5 show, the biggest difference between the various routes is caused by feedstock production (the second step of a route). It is therefore interesting to further consider the technical developments in feedstock production. Possible technological developments will be discussed in this section.

CO₂ emissions in syngas-related routes (i.e. where methanol and FT liquids are used as feedstocks) can be reduced further since syngas technologies are still undergoing R&D and offer considerable room for improvement. Specifically for FT liquids production processes, a recent study reports that — theoretically speaking — optimized CO₂ recycling (methane reacting with CO₂ to form syngas¹) and hydrogen usage in a methane/coal co-fed FT liquid plant could allow the ultimate process CO₂ emissions to be reduced to zero [221]. For all the twelve syngas-related routes discussed in this chapter, CO₂ recycling can theoretically be applied and CO₂ emissions per ton of HVCs can be halved. One possible use of CO₂ recycling for methanol production is now undergoing intensive R&D (see Section 3.5.2 in Chapter 3).

Heavy liquid feedstocks, such as bitumen and heavy naphtha derived from oil sands in Canada and Venezuela, can be used for producing petrochemicals. However, a comparative analysis could not be conducted due to the lack of data in the second step (petrochemicals production). The estimates are as follows. In the first step (feedstock production), energy use in the production process of bitumen and crude oil from oil sands was reported to be about 12 GJ/t oil equivalent and the associated CO₂ emissions are reported to be about 0.8 tons CO₂/t oil equivalent [222]. For the second step (petrochemicals production), data on energy use are incomplete [223]. The process described in the source is similar to the catalytic cracking process used in the Oil Byproduct CC route. However, the feedstocks used here are highly naphthenic/aromatic and are very different from the paraffinic feedstocks used in the Oil Byproduct CC route. An unknown and possibly a large amount of hydrogen is needed. The

¹ See Section 3.5.2 in Chapter 3. CO₂ recycling is based on the oxo process, which is also called dry reforming as opposed to steam reforming. The formula for the reaction is: $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$.

maximum HVCs yield in this step is 45% [223], or 5% lower than the Oil Byproduct CC route. Excluding the energy use and CO₂ emissions from hydrogen production, the cumulative process energy use of the entire oil sands-based route is estimated to be at least 32 GJ/t HVCs and its cumulative process CO₂ emissions are estimated to be at least 1.6 t/t HVCs (meaning that the total energy use is at least 80 GJ/t HVCs and the total CO₂ emissions are at least 5.0 tons CO₂ per ton HVCs). Therefore, we estimate that the cumulative process energy use and CO₂ emissions are higher for the oil sands-based route than for most of the natural gas-based routes.

Besides the two methods for biomass-derived ethanol production (direct fermentation and hydrolysis) described in the main analysis earlier, another possible method is the gasification of lignocellulosic biomass. Lignocellulosic biomass is first gasified into syngas, which is subsequently converted into ethanol by either microbial conversion (fermentation) [224, 225] or chemical conversion (with a proprietary catalyst) [226, 227]. However, there are no detailed data on the gasification of biomass available, which makes it impossible to conduct a comparative analysis with the other two methods, direct fermentation and hydrolysis of biomass. In the literature, several ethanol yields from the gasification of lignocellulosic biomass were claimed:

- *Microbial conversion* 30% based on various types of biomass [224] and 22% based on lignocellulosic biomass and municipality waste [225];
- *Chemical conversion* 27% based on wheat straw [226] and 24-30% based on rice straw [227].

These yields are similar to those of the ethanol processes discussed in this chapter (see Table 4-4). However, because gasification requires more energy than direct fermentation and hydrolysis, we expect the cumulative process energy use and CO₂ emissions of the gasification routes to be higher than those of the direct fermentation and hydrolysis routes discussed earlier in this chapter. Recently, plans have been announced for the construction of commercial-scale ethanol plants (above 20 million gallons of ethanol per year) [224, 226].

CO₂ can be captured from the air and used in petrochemicals production in a nuclear energy-based route [228]. In this route, H₂ and CO₂ are made first. H₂ is produced through nuclear

energy-powered thermal cracking of water and CO₂ is produced through air separation [228]. Subsequently, methanol and water are produced through the following reaction: $3\text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$. Finally, ethylene and propylene are produced through methanol dehydration, which is the same MTO process as mentioned in Chapter 3. It was reported that if CO₂ was captured from the air ¹, a plant with a capacity of 500,000 tons of ethylene per year would require a nuclear power plant with a capacity of 2.4 GW_e [229]. This leads to a nuclear energy-derived electricity consumption of 151 GJ/t HVCs and the capture of 3.5 tons CO₂ per ton HVCs. Alternatively, other carbon-neutral energy sources, such as solar energy [230] and biomass-derived energy, can also be used to produce the electricity needed to capture CO₂ and use it in the process described above.

4.6 Conclusions

To answer the research question of this chapter, a comparative analysis is required of the alternative routes (utilizing methane, coal and biomass) and conventional routes (utilizing naphtha and heavy feedstocks derived from crude oil and ethane derived from natural gas). Our analysis shows that the conventional routes are far more energy efficient than any of the alternative routes and that biomass-based routes use far less fossil energy than other routes. While cradle-to-grave CO₂ emissions from coal-based routes are by far the highest, those of the biomass-based routes are much lower than those of conventional routes, due to the use of biomass. The land use per ton of high-value chemicals produced is likely to be about 0.3-0.8 hectare for most biomass-based routes. The energy efficiency of state-of-the-art conventional routes (i.e. utilizing naphtha derived from crude oil and ethane derived from natural gas) and that of coal and biomass-based routes will be improved in the coming decades. Given the significant differences between them, the total energy use of biomass and coal-based routes is unlikely to match that of the conventional state-of-the-art routes anytime soon. Moreover, the economics of these routes should be studied.

¹ Capturing CO₂ from other fossil fuel-based sources (e.g. an integrated coal gasification combined cycle power plant) would have been a more efficient way to produce CO₂ than extracting it from the air. The study [229] cited three reasons for using air as a CO₂ source: 1) large scale availability of CO₂ in the air; 2) a closed CO₂ cycle and 3) guaranteeing CO₂ emission reductions.

Chapter 5 Petrochemicals from Oil, Natural Gas, Coal and Biomass: Production Costs in 2030-2050¹

ABSTRACT

In this chapter, we compare the production costs of 24 routes that utilize oil, gas, coal and biomass to produce petrochemicals. To this end, we use a wide range of projected energy prices for 2030-2050 found in the open literature. The basis for comparison is the production cost per ton of high value chemicals (HVCs or light olefin-value equivalent). A Monte Carlo method was used to estimate the ranking of production costs of all 24 routes with 10,000 trials of varying energy prices and CO₂ emissions costs (assumed to be within \$0-100/t CO₂; the total CO₂ emissions, or cradle-to-grave CO₂ emissions, were considered). High energy prices in the first three quarters of 2008 were tested separately. The main findings are:

- *Production costs* While the production costs of crude oil and natural gas-based routes are within \$500-900/t HVCs, those of coal and biomass-based routes are mostly within \$400-800/t HVCs. The production costs of coal and biomass-based routes are quite similar. Among the top seven most expensive routes, six are oil and gas-based routes. Among the top seven least expensive routes, six are coal and biomass-routes.
- *CO₂ emissions costs* The effect of CO₂ emissions costs was found to be strong on coal-based routes and also quite significant on biomass-based routes. However, the effect on oil and gas-based routes is found to be small or relatively moderate.
- *Energy prices in 2008* Most of coal-based routes and biomass-based routes (particularly sugar cane) still have much lower production costs than the oil and gas-based routes (even if international freight costs are included).

To ensure the reduction of CO₂ emissions in the long term, we suggest that policies for the petrochemicals industry focus on stimulating the use of biomass as well as CO₂ capture and storage for coal-based routes.

¹ Co-authors: Dr. Bert Daniels (ECN, or Energy Research Center of the Netherlands), Dr. Martin Patel (Utrecht University) and Prof. dr. Kornelis Blok (Utrecht University).

5.1 Introduction

In previous chapters, energy use and CO₂ emissions of basic petrochemicals production routes based on crude oil, natural gas, coal and biomass were discussed. Chapter 3 considered the production costs of oil and natural gas-based routes using historical and current energy prices. The present chapter will compare the production costs of these conventional and alternative routes as a function of projected energy prices (crude oil and natural gas) and CO₂ emissions costs (with greenhouse gas mitigation policies) in the long-term (up to 2050). This subject has so far not been covered by any publication known to us.

Two recent studies have offered some insights into the effect of climate policies on the future of conventional and alternative routes up to 2020 and 2025, respectively [190, 231]. One study concluded that if conventional routes continue to be used in the USA before 2020, it may be more effective for CO₂ emission reduction in the US petrochemical industry to promote the investment in new and improved technologies than to implement policies, e.g. CO₂ taxes [231]. Another study argued that imposing global CO₂ emissions charges (at \$65-130/t CO₂) could lead to widespread use of biomass-based (alternative) routes, which could halve the total CO₂ emissions from the global petrochemicals production up to 2025 [190]. These studies considered neither the production of petrochemicals from coal, nor projected energy prices in 2030-2050.

Given this knowledge gap, the aim of the current chapter is to explore the economic prospects of all routes for making basic petrochemicals (discussed in previous chapters) in the period of 2030-2050. We are particularly interested in the effect of possible global CO₂ emissions costs on the production costs of conventional and alternative routes. Our objective is to identify those routes that are relatively robust under a variety of plausible scenarios for energy prices as well as a wide range of CO₂ emissions costs. Accordingly, the research question of the current chapter is defined as: *Which routes for the production of basic petrochemicals are economically favorable, based on projected energy prices and CO₂ emissions costs in the period of 2030-2050?*

The outline of this chapter is as follows. First, we will briefly explain the research methods and definitions used. Then, we will use energy prices found in the open literature to analyze the production costs of various routes. Finally, uncertainties in this analysis will be discussed.

5.2 Definitions and Methods

The 24 routes discussed in this chapter are identical with those of Chapter 4 and the same abbreviations are used to denote the routes. Technical data (e.g. energy use, yields and CO₂ emissions) are summarized in Table 5-1 (crude oil and natural gas-based routes) and Table 5-2 (coal and biomass-based routes). Economic data (e.g. O&M and capital costs) are summarized in Tables 5-3 (crude oil and natural gas-based routes) and 5-4 (coal and biomass-based routes).

We conducted a production cost analysis to assess the economics of the various routes from primary energy sources to basic petrochemicals. Since the prices of primary energy sources are projected to vary widely, a computational algorithm, the Monte Carlo analysis, is used to study the range and ranking of production costs. Details will be explained in Section 5.3. In this chapter, the same definitions of production costs are used as in Chapter 1¹. Data used in this chapter were found in reports (e.g. by the US Department of Energy and International Energy Agency), scientific and technical journals as well as conference proceedings.

For the economic analysis of crude oil, natural gas and coal-based routes, the global market prices of these primary energy sources found in various scenario studies are used to calculate the production costs of basic petrochemicals in 2030-2050². Due to the lack of comparable data, for the economic analysis of biomass-based routes, we used production costs of biomass energy crops, which consist of costs of labor, capital, land rent and local transportation (50 km) [218]. We expect the biomass market prices in the future to differ strongly depending on the local conditions. Therefore, we chose a wide range of biomass production costs (\$1-5/GJ) for 2030-2050. Besides the projected energy prices for 2030-2050 found in scenario studies, the high energy prices of the first three quarters of the year 2008 will also be used to calculate the production costs. These energy prices are higher than those projected for 2030-2050.

In addition to energy prices, we will test the possible impact of climate policies regarding CO₂ emissions costs on the production costs of various routes. For the main analysis, the most stringent climate policies in 2030-2050 are assumed: producers must pay CO₂ emissions costs

¹ In order to calculate the production costs for high value chemicals (HVCs), the production costs of electricity by coal and gas-fired power plants are deducted from the total production costs of those routes that cogenerate electricity.

² Global average transportation costs for crude oil, natural gas and coal have been considered in their market prices.

for the total (or cradle-to-grave) CO₂ emissions¹. The current, less stringent climate policies are discussed in Section 5.6.

5.3 Economic Analysis

To conduct the economic analysis, we first define the projected energy prices and CO₂ emissions costs in 2030-2050. Then, we determine the correlations of energy prices and use a Monte Carlo approach to calculate the production costs of the routes. Finally, the result of using energy prices as seen in 2008 will be discussed.

5.3.1. Range of Energy prices, CO₂ Costs and Production Costs

While recognizing that it is impossible to predict the exact range of production costs of various routes in 2030-2050, we are interested in comparing the production costs of various routes under a set of energy and policy scenarios which consistently account for energy supply, demand and market equilibrium.

Energy prices in Tables 5-3 and 5-4 are derived from various energy and economic scenarios shown in Table 5-5. Table 5-5 shows a wide range of energy prices (in US\$ of the year 2000) for industrial users found in energy and policy scenario studies for 2030-2050. On the basis of different economic growths in 2030-2050 assumed in these studies, they were grouped in Table 5-5. Since we look for the most robust technological routes, all of energy prices in Table 5-5 should be considered as input data to compare the production costs of the various routes.

The production costs of electricity are projected to be within \$0.03-0.05/kWh for both coal and natural gas-fired power plants during the period of 2030-2050 in major industrialized countries² (corresponding to coal prices of \$1-2/GJ and natural gas prices of \$4-8/GJ). Electricity production costs below \$0.03/kWh and above \$0.05/kWh are considered to be extreme (outliers in the 2030-2050 context) [43] (see Section 5.6).

¹ If the total CO₂ emissions are negative (due to electricity cogeneration), negative CO₂ emissions costs are awarded. Definitions of CO₂ emissions were given in Chapter 1. The results of the CO₂ emissions analysis were presented in Chapter 4.

² The production costs of electricity at \$0.03-0.05/kWh are the levelised production costs in 21 countries (19 of which are OECD countries) for coal and natural gas-fired power plants that are assumed to be commissioned in 2010 and reach the end of the plant economic lifetime in 2050 at a discount rate of 10% [43]. By comparison, during the last few years, the electricity wholesale prices for large industrial users in major industrialized countries were within \$0.04-0.08/kWh (electricity is based on major fuels, e.g. coal, natural gas, nuclear and oil) [11, 38, 187, 232, 233]. Electricity prices at \$0.01-0.03/kWh usually refer to prices in countries with energy subsidies [36, 38]. Some studies expect electricity prices to be at \$0.04-0.06/kWh in 2030 [188, 234] while one study expects electricity prices to increase to as much as \$0.09-0.12/kWh in 2040 [235].

The global historical prices and projected 2030-2050 prices of plastic waste are not available. The average prices in the US and Western Europe were found to be \$120-220/t (or \$3-5/GJ; the calorific value of plastic waste is about 45 GJ/t) in 1995-2005 when the oil prices were at \$26-60/bbl [236]. Since the oil prices are projected to be at \$26-60/bbl in 2030-2050, we assume that the prices of waste plastic will be at \$120-220/t (or \$3-5/GJ) in 2030-2050.

Taking all this into consideration, we can determine the ranges of energy prices as:

- crude oil \$26-60/bbl¹,
- natural gas \$4-8/GJ²,
- coal \$37-57/t,
- biomass \$1-5/GJ³,
- plastic waste \$120-220/t,
- electricity production costs \$0.03-0.05/kWh.

The prices are listed in Tables 5-1 and 5-2 in terms of \$/GJ as well. There are three reasons why these ranges are consistent. First, the ratio of oil prices in \$/bbl to natural gas prices in \$/GJ is around 6:1, which is used as a rule of thumb to estimate energy prices [22]. This is especially true in the US and Europe where prices of natural gas and oil are strongly correlated [237]. In \$/GJ terms, crude oil and natural gas prices are comparable: crude oil at \$4-10/GJ (the calorific value of crude oil is 6 GJ/bbl) and natural gas at \$4-8/GJ.

Second, the projected future prices of natural gas are higher than the historical average (\$2-4/GJ) in industrialized countries. The rising natural gas prices are driven by the consumption growth in the electricity and transportation fuel sectors (the growth is partially due to more stringent environmental regulations e.g. reduced emissions of SO_x and particulate matter). The strong demand for natural gas has led to the rapid development of GTL technologies (natural gas

¹ The maximum oil price of \$88/bbl in 2030 shown in Table 5-5 (see “slow economic growth”) is much higher than \$26-60/bbl. Therefore, as an outlier, it is excluded from consideration. By comparison, the average oil price in 1970-2001 (see Table 3-7 in Chapter 3) was \$20/bbl oil.

² The current prices of stranded (natural) gas, found only in remote locations in the Middle East, Africa and Russia, are at \$0.5-1/GJ. Natural gas prices were above \$8/GJ in the US in late 2005. These prices are extreme (outliers); therefore, they are excluded from this analysis. By comparison, natural gas prices in 1970-2001 were \$2-3/GJ (Table 3-7 in Chapter 3).

³ Biomass prices below \$1/GJ (e.g. possibly in some part of Africa or the former USSR countries) or above \$5/GJ (e.g. in Japan) as estimated in [218] are extremely low or high and therefore are excluded as outliers.

conversion to transportation fuel liquids) and of LNG technologies (liquefied natural gas which is related to natural gas transportation and electricity production).

Third, the prices of coal in \$/GJ terms have a much narrower range than those of crude oil, natural gas and biomass. Historically, coal prices have been very stable due to the abundant supply of coal and the widespread availability of coal reserves around the world [36]. Based on these three reasons, we assume that energy prices in 2030-2050 will fluctuate but not exceed the range quoted above.

5.3.2. Correlations of Energy prices

The ranges of the production costs of the 24 routes in Figure 5-1 were calculated based only on the ranges of energy prices. Correlations of energy prices were not considered. It is widely accepted that due to substitution effects and long-term international contracts, price correlation by indexing can set the limits for price fluctuation of primary energy sources (e.g. crude oil, natural gas and coal) and electricity. Historically, oil and natural gas prices were clearly linked though not fully correlated [238]. However, due to increased inter-fuel competition and the continuing widespread use of oil-price indexation in mid and long-term gas supply contracts, in the future oil and natural gas prices will be linked more strongly than before [237]. Furthermore, many LNG and GTL projects will come on stream over the next decade and this will make natural gas a global commodity that influences both the world oil market and local electricity markets [237]. Based on the information above, strong correlations between energy prices in 2030-2050 can be projected.

For the purpose of this analysis, we will try to define these correlations within the given ranges of energy prices through statistical means. Here we distinguish two types of correlations: *perfect correlation* and *adjusted correlation*:

For *perfect correlation*, we assume that in 2030-2050, there will be a market where firms have access to perfect information on all primary energy sources. The costs of all energy sources in Table 5-5 are “pegged” with the oil price. First, a random number¹ (R) is generated. Then, this random number R is used to determine an energy price for each type of energy source. For

¹ In Excel®, the function RAND() can be used to generate a random number between 0 and 1 with a uniform distribution.

example, if R is 0.5, then the price of natural gas is $R*(8-4)+4=6$ in \$/GJ. The same random number is used to determine the prices for the other energy sources. For this reason, we call this approach *perfect correlation*. This approach does not reflect the weaker correlation found in reality; in the international market, many different energy prices for natural gas can be found, even though the price for a barrel of crude oil remains the same.

For *adjusted correlation*, we assume that the prices for other types of energy sources can vary greatly while the oil prices remain the same (this is a better simulation of the actual market than perfect correlation). These costs, however, must not deviate too far from those identified under perfect correlation, or there will be no correlation at all. Therefore, deviations must be defined within a reasonably small range. To calculate energy prices under the adjusted correlation, we define the maximum deviation from the prices found under the perfect correlation as 12.5% of the difference between the upper and lower price ranges of natural gas, coal, biomass and plastic waste¹. This means that the energy prices determined for the perfect correlations need to be adjusted by +/-12.5% of the difference between the upper and lower price ranges. As a result of this adjustment, energy prices under the adjusted correlation can fall outside the original ranges of energy prices. To prevent this, the range of energy prices needs to be adjusted². Under the adjusted correlation, oil prices are the reference for adjusting coal, gas and biomass prices. Therefore, the calculation procedures described above are applied only to coal, gas and biomass, while oil prices are determined by perfect correlation only.

In the future, production costs can be affected not only by energy prices but also by CO₂ emissions costs. In order to test the effect of CO₂ emissions costs, we assume that in 2030-2050

¹ The maximum deviation is \$0.5/GJ (12.5% of \$4/GJ) for natural gas and \$2.5/t (12.5% of \$20/t) for coal. These deviations are based on the changes in natural gas and coal prices worldwide in 1998-2006 and on the changes in expected prices in 2004-2030 [36, 188]. There are no comparable historical or future prices available for biomass and plastic waste. These four primary energy sources can all be regarded as substitutes for each other if used for electricity production in the future. Currently, about 80% of electricity worldwide is produced from coal and natural gas [11].

² The prices of natural gas can serve as an illustration. There are three steps: 1) The gas prices can vary within the range \$4/GJ to \$8/GJ. A reasonably small range of deviation is set as 12.5% of \$4/GJ (i.e. \$0.5/GJ). To prevent gas prices from falling outside the range \$4/GJ to \$8/GJ (e.g. \$4/GJ-\$0.5/GJ < \$4/GJ), it is necessary to add \$0.5/GJ to \$4/GJ and subtract \$0.5/GJ from \$8/GJ. Therefore, the adjusted range of the gas price is \$4.5/GJ to \$7.5/GJ. After the deviation +/-0.5/GJ is applied to \$4.5/GJ to \$7.5/GJ, the actual range of all adjusted gas prices is again \$4/GJ to \$8/GJ (the same as the original range); 2) A random value is generated to determine the gas price. For example, 0.3 is generated and leads to \$6/GJ (i.e. $0.3*(7.5-4.5) + 4.5 = 5.4$); 3) Another random value (always between 0 and 1) is generated from which a fixed value 0.5 is subtracted to generate a random value between -0.5 and 0.5. This is then multiplied by the maximum deviation (\$0.5/GJ) and then multiplied by 2 to cover both plus and minus sides of the maximum deviation. For example, 0.2 is generated and \$5.4/GJ should be then adjusted by \$-0.3/GJ ($(0.2-0.5)*\$0.5/GJ*2 = \$-0.3/GJ$), which is \$5.1/GJ.

these costs will fluctuate randomly in the range of \$0-100/t CO₂ and that there is no correlation between CO₂ emissions costs and energy prices.

5.3.3. Monte Carlo Analysis

Once the correlations between energy prices are determined, energy prices are fluctuated and the production costs of the routes are compared. In the current literature, breakeven analysis and sensitivity analysis are often used to compare the production costs of different technologies. These methods are primarily suitable to single out the influence of one input variable while keeping the others constant. However, they are not suitable to answer the research question addressed by this chapter. For each oil price, there are many combinations of natural gas, coal and biomass prices (as well as electricity costs and CO₂ emissions costs) that can lead to numerous breakeven points (see Figure 5-1). This type of multi-variable problem is typically dealt with by the Monte Carlo analysis method¹ [239].

In this chapter, the Monte Carlo analysis method is applied by making a large number of random draws from various energy prices (input variables) within the ranges of projected energy prices, then calculating the production costs of the routes (output variables) and finally ranking on price. In Monte Carlo simulations, the number of necessary trials is usually determined by the standard error of the mean and the range of the values. @RISK® and Crystal Ball® recommend 10,000 trials. For the range of the values used in this analysis, 10,000 trials are more than enough to reach less than 2% of standard error of the mean. Therefore, we generated 10,000 sets of energy and CO₂ emissions costs and then used these to calculate 10,000 sets of production costs. The ranking of the production costs of various routes against each other is determined by the ranking of their relative cost advantages from the least expensive (or the 1st) to the most expensive (or the 24th). These rankings are then summed up for all of the 10,000 calculations and they are then divided by 10,000 to determine the average ranking for each route (with and without CO₂ emissions costs).

¹ Monte Carlo analysis is a computer-based analysis method developed in the 1940s that uses statistical sampling techniques to obtain a probabilistic approximation to the solution of a mathematical equation or model. It uses a class of computational algorithms that rely on repeated random sampling. It is often used when physical and mathematical systems are simulated. Its purpose is to analyze the distribution of the results.

Table 5-1 Technical Data for Routes from Crude Oil and Natural Gas to Basic Petrochemicals (energy efficiency for electricity production at 55%; calorific value and carbon content of HVCs excluded; details on calculations can be found in Chapters 2, 3 and 4)

Primary energy sources		Crude Oil			Natural gas					
Routes		Oil naphtha SC (steam cracking)	Waste Naphtha SC (steam cracking)	Oil Byproduct CC (catalytic cracking)	Ethane SC (steam cracking)	Methane FT naphtha SC (steam cracking)	Methane MTO	Methane MTP	Methane OCM I	Methane OCM II
Feedstock Production		Distillation	Hydrogen pyrolysis of plastic waste	Byproducts from refinery and petrochemicals production	Separation from natural gas	Fischer-Tropsch	Methanol production (oxygen separation from air needed)		Methane from natural gas (oxygen separation from air needed)	
Yield of feedstock as % (wt.) of primary energy sources		10%	45% (80% naphtha-value equivalent)	10-70%	1-15%	15-30% (81% naphtha-value equivalent)	145%		80-95%	
Petrochemicals production		Steam cracking		Catalytic cracking	Steam cracking		Methanol dehydration		Oxidative coupling of methane	
Yield of HVCs as % (wt.) of feedstocks		70%		50%	84%	75%	43%	40%	50%	15%
Total CO ₂ emissions (t/t HVCs) (cradle-to-grave; after the subtraction of CO ₂ emissions avoided by electricity cogeneration)	Cumulative process CO ₂ emissions (t/t HVCs) (cradle-to factory gate)	0.8	1.2	1.0	0.9	1.0	1.2	1.5	1.3	0.7
	CO ₂ emissions due to the combustion of end products derived from HVCs	3.5 ton per ton HVCs on average							3.1 ton per ton ethylene (ethylene is the only HVC produced)	
Electricity cogeneration (GJ/t HVCs)		0							13	147

Table 5-2 Technical Data for Routes from Coal and Biomass to Basic Petrochemicals (energy efficiency for electricity production at 55%; calorific value and carbon content of HVCs excluded; details can be found in Chapters 2, 3 and 4)

		Coal						Biomass								
Routes		Coal MTO I	Coal MTO II	Coal MTO CCS	Coal Direct Naphtha SC	Coal FT Naphtha SC I	Coal FT Naphtha SC II	Coal-Ligno FT Naphtha SC	Ligno FT Naphtha SC I	Ligno FT Naphtha SC II	Ligno MTO	Ligno ETE I	Ligno ETE II	Ligno ETE III	Maize Starch ETE	Sugar Cane ETE
Feedstock Production		Methanol production (oxygen separation from air needed)			Direct Liquefaction	Fischer Tropsch (oxygen separation from air needed)				Methanol production	Hydrolysis and fermentation for ethanol production					
Yield of feedstock as % (wt.) of primary energy sources		74%	30%	74%	10% (42% naphtha-value equivalent)	9% (31% naphtha-value equivalent)	5% (18% naphtha-value equivalent)	3% (12% naphtha-value equivalent)	3% (14% naphtha-value equivalent)	49%	31%	25%	27%	46%	19%	
Petrochemicals production		Methanol dehydration			Steam cracking					Dehydration						
Yield of HVCs as % feedstocks (wt.)		43%			55%	75%				43%	61%					
Total CO₂ emissions (t/t HVCs) (cradle-to-grave; after the subtraction of CO ₂ emissions avoided by electricity cogeneration)	Cumulative process CO₂ emissions (t/t HVCs) (cradle-to factory gate)	5.0	6.1	0.6	6.6	5.2	7.8	0.5	-0.1	-3.8	1.0	0.5	-1.4	0.3	2.1	-0.9
	CO₂ emissions due to the combustion of end products derived from HVCs	3.5 ton per ton HVCs on average										3.1 ton per ton ethylene (ethylene is the only HVC produced)				
Electricity cogeneration (GJ/t HVCs)		0	46	0			48	26	16	50	0	4	22	5	0	16

Table 5-3 Assumptions for Calculating Production Costs of Routes that Convert Crude Oil and Natural Gas into Basic Petrochemicals (yield of feedstock as % of primary energy sources and yield of HVCs as % of feedstocks shown in Table 5-1)

Primary energy sources	Crude Oil			Natural gas					
Routes	Oil naphtha SC (steam cracking)	Waste Naphtha SC (steam cracking)	Oil Byproduct CC (catalytic cracking)	Ethane SC (steam cracking)	FT naphtha SC (steam cracking)	Methane MTO	Methane MTP	Methane OCM I	Methane OCM II
Prices of primary energy sources and electricity production costs	\$26-60/bbl, \$5-11/GJ or \$190-440/t crude oil	\$3-5/GJ or \$120-220/t plastic waste	Assumed to be half of naphtha prices (byproducts typically worth half of naphtha [38]; see Chapters 1 and 2 for details); 5x crude oil prices (\$/bbl) (see the column for Oil Naphtha SC); O&M and capital not applicable	\$4-8/GJ or \$200-400/t natural gas					
				Electricity costs at \$0.03-0.05/kWh					
Costs for feedstocks and O&M (\$/t feedstock) for feedstock production	Assumed to be 10x crude oil prices (\$/bbl) (or \$220-640/t); O&M and capital not applicable; according to the rule of thumb [22] (see details in Chapter 3)	O&M 198; Capital 70; [195]		Assumed to be 110% of natural gas prices; O&M and capital not applicable; according to the estimation [187] (see details in Chapter 3)	O&M 51; capital 65; [193]	Methanol: O&M 17; capital 40 [171]		Methane: see above (O&M and capital not applicable); Oxygen: electricity use 350 kWh/t times electricity costs; O&M and capital \$50/t oxygen [40]	
O&M and capital costs of petrochemicals production (\$/t HVCs) (see details on calculations in Chapter 3 and 4)	O&M 28; capital 59 [117]		O&M 33; capital 83 [240]	O&M 45; capital 68 [117]	O&M 27; capital 55 [117]	O&M 19; capital 37 [151, 152]	O&M 16; capital 39 [127, 153]	O&M 93; capital 79 [116]	O&M 328; capital 287 [116]

Table 5-4 Assumptions for Calculating Production Costs of Routes that Convert Coal and Biomass into Basic Petrochemicals (yield of feedstock as % of primary energy sources and yield of HVCs as % of feedstocks shown in Table 5-2)

Primary energy sources	Coal							Biomass							
Routes	Coal MTO I	Coal MTO II	Coal MTO CCS	Coal Direct Naphtha SC (steam cracking)	Coal FT Naphtha SC I	Coal FT Naphtha SC II	Coal-Ligno FT Naphtha SC	Ligno FT Naphtha SC I	Ligno FT Naphtha SC II	Ligno MTO	Ligno ETE I	Ligno ETE II	Ligno ETE III	Maize Starch ETE	Sugar Cane ETE
Energy prices	\$1-2/GJ or \$37-57/t coal							\$1-5/GJ or \$17-95/t biomass							
	Electricity costs \$0.03-0.05/kWh														
Costs of O&M and capital for feedstock production (\$/t feedstock)	O&M 23; capital 84	O&M 70; capital 254	O&M 21; capital 78	O&M 26; capital 95	O&M 31; capital 78	O&M 87; capital 306	O&M 11; capital 384	O&M 60; capital 217	O&M 72; capital 261	O&M 24; capital 68	O&M 29; capital 110	O&M 99; capital 165		O&M 5; capital 123	
References	[205]		[196]	[198, 202]		[191, 203]	[25, 204]					[27]			
O&M and capital costs of petrochemicals production (\$/t HVCs)	O&M 19; capital 37			O&M 37; capital 75	O&M 28; capital 59				O&M 19; capital 37	O&M 26; capital 41					
References	[151, 152]			[117]					[151, 152]	[27]					

Table 5-5 A Summary of Energy and Policy Scenarios for 2030-2050 (expressed in US\$ of the year 2000)

<p>Moderate Economic Growth</p> <ul style="list-style-type: none"> ○ Alternative Policy 2030 (oil \$46/bbl; natural gas \$7/GJ; coal \$51/t) [7]; ○ Kyoto Protocol Case 2030; other comparable data not found in [188, 234]; ○ B1 2050 (oil \$53/bbl; natural gas \$7/GJ; coal \$51/t; biomass \$4/GJ) [241]; ○ Abandoned Land (biomass \$1-2/GJ) [218] ○ Strong Europe 2040 (moderate growth; good geopolitical relations; renewable energy use high; much improved energy efficiency; oil \$26/bbl; natural gas \$4/GJ; coal \$47/t) [235] 	<p>High Economic Growth</p> <ul style="list-style-type: none"> ○ Reference 2030 (business as usual; oil \$47/bbl, natural gas \$8/GJ; coal \$52/t) [7]; ○ Reference Case 2030 (oil \$53/bbl, natural gas \$6/GJ and coal \$43/t) [188, 234]; ○ A1 2050 (oil \$60/bbl; natural gas \$8/GJ; coal \$57/t; biomass \$4/GJ) [241]; ○ Abandoned Land (biomass \$1-2/GJ) [218]; ○ Global Economy 2040 (high growth; excellent geopolitical relations; very high energy efficiency; oil \$34/bbl; natural gas \$5/GJ and coal \$47/t) [235]
<p>No Economic Growth</p> <ul style="list-style-type: none"> ○ Depressed Economy 2030 (oil \$40/bbl; natural gas \$6/GJ; coal \$44/t if Alternative Policy-based abatement costs do not exist) [7]; ○ Low Case 2030 (oil \$31/bbl, natural gas \$5/GJ and coal \$37/t) [188, 234]; ○ B2 2050 (oil \$53/bbl; natural gas \$7/GJ; coal \$51/t; biomass \$3/GJ) [241]; ○ Abandoned Land (biomass \$2-5/GJ) [218]; ○ Regional Community 2040 (no growth; geopolitical relations not so good; fossil use down; much improved energy efficiency; oil \$30/bbl; natural gas \$5/GJ and coal \$47/t) [235] 	<p>Slow Economic Growth</p> <ul style="list-style-type: none"> ○ Deferred Investment 2030 (oil \$52/bbl; natural gas \$8/GJ and coal \$57/t) [7]; ○ High Case 2030 (oil \$88/bbl, natural gas \$7/GJ and coal \$46/t) [188, 234]; ○ A2 2050 (oil \$52/bbl; natural gas \$7/GJ; coal \$48/t and biomass \$3/GJ) [241]; ○ Abandoned Land (biomass \$2-3/GJ) [218]; ○ Transatlantic Market 2040 (slow growth; bad OECD-Middle East geopolitical relations; coal use up; reasonable energy efficiency; oil \$33/bbl; natural gas \$6/GJ and coal \$47/t) [235]

Figure 5-1 Range of Production Costs Based on Various Energy Prices in January-August of 2008 and in 2030-2050 (US\$ of the year 2000; CO₂ costs are calculated on the basis of cradle-to-grave CO₂ emissions)

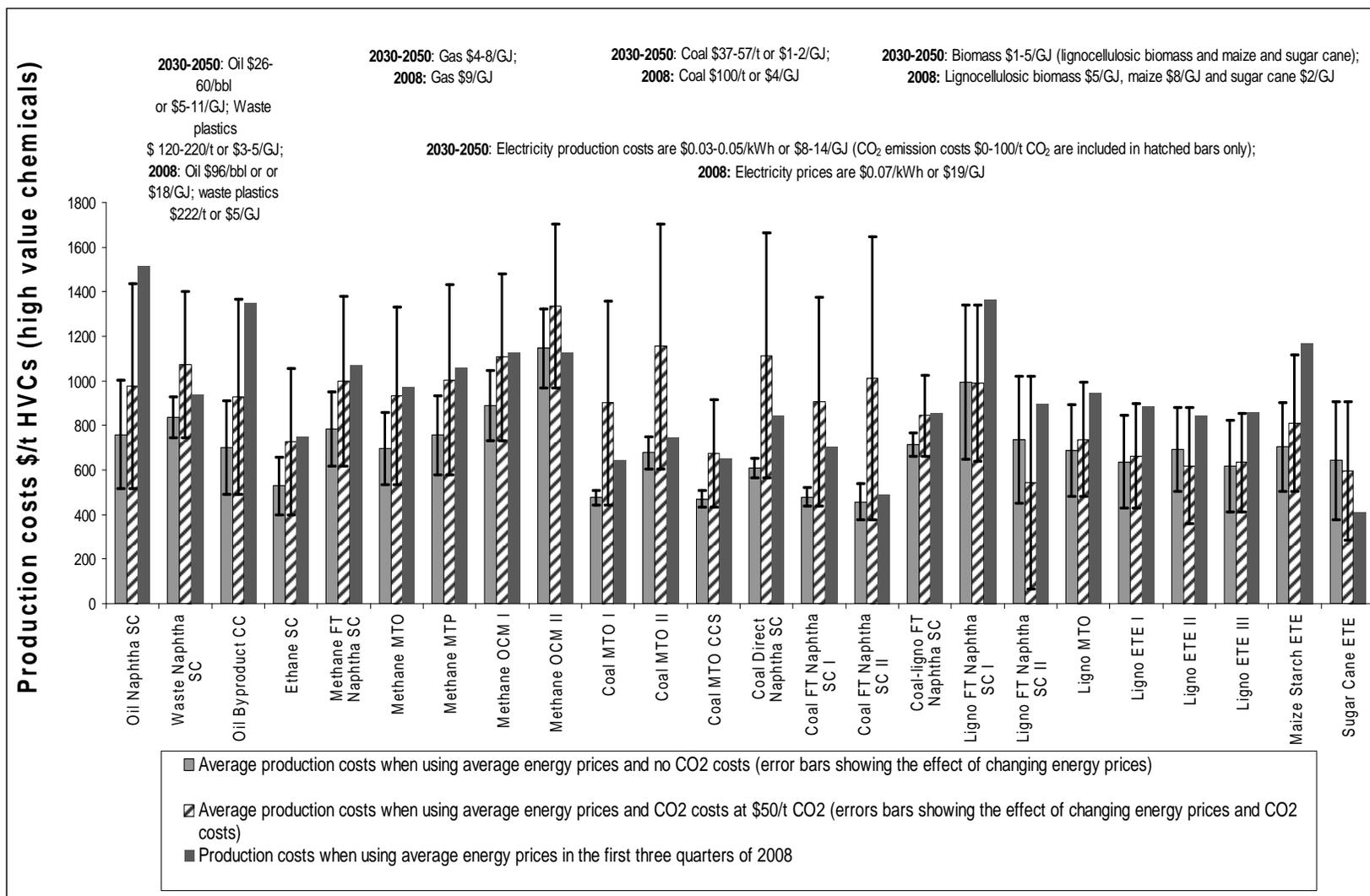
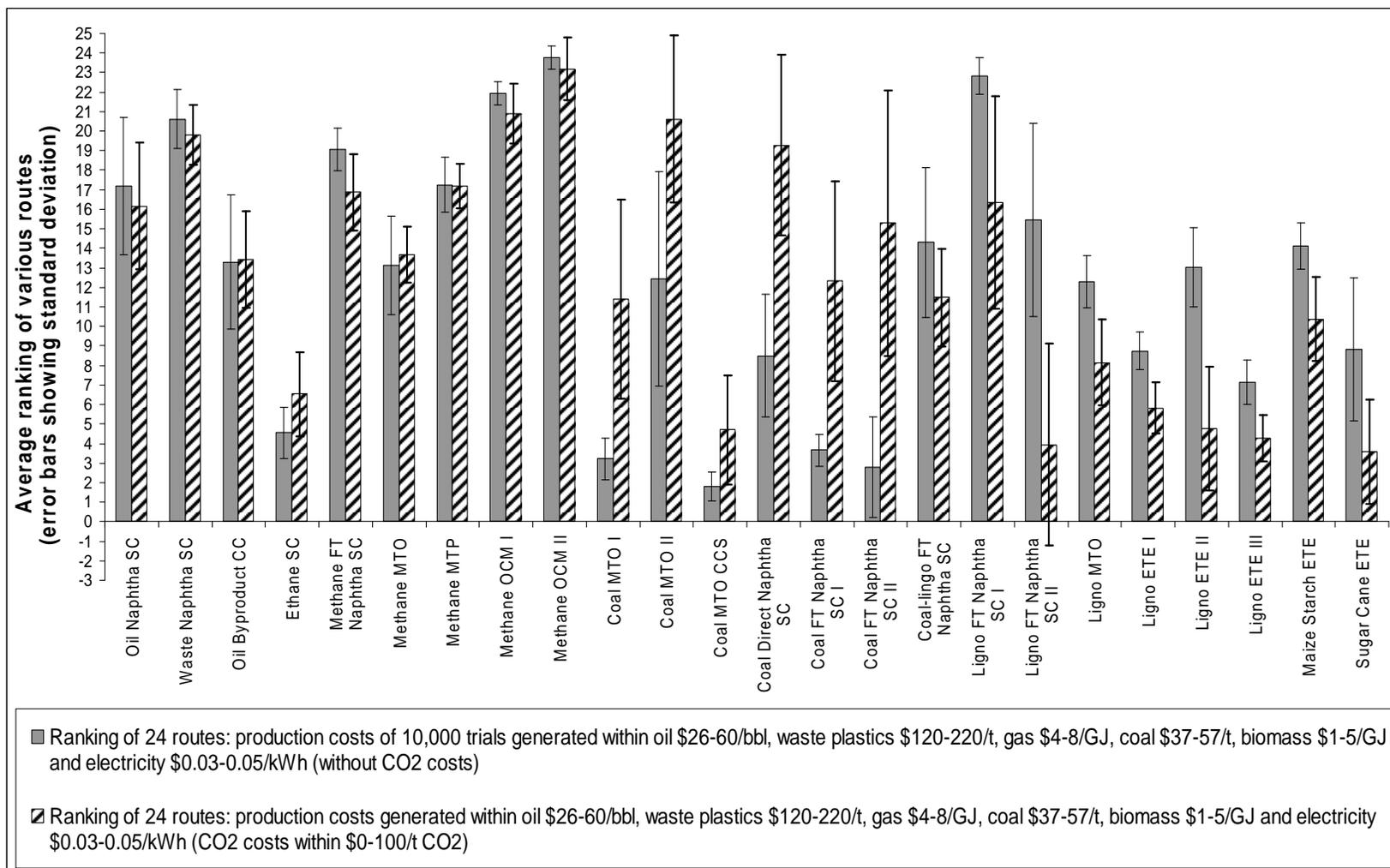


Figure 5-2 Ranking of Production Costs of Basic Petrochemical Routes through Comparing Their Production Costs with Each Other by Using Projected Energy Prices in 2030-2050 (US\$ of the year 2000; CO₂ costs are calculated on the basis of cradle-to-grave CO₂ emissions)



5.3.4. Energy Prices in 2008

In the first three quarters of 2008, in many countries energy prices were significantly higher than those used in the analysis for the period of 2030-2050. It is interesting to use the high energy prices of 2008 to calculate the production costs. The average energy prices in the first three quarters of 2008 expressed in US dollars of the year 2000 (with 2% average annual inflation as defined in Chapter 1) are: crude oil at \$96/bbl¹, natural gas at \$9/GJ², plastic waste at \$222/t³, coal at \$100/t (\$4/GJ)⁴ and lignocellulosic biomass at \$5/GJ⁵. When the coal prices are at \$4/GJ and natural gas prices are at \$9/GJ as mentioned above, the average electricity prices of coal and gas-fired power plants in most industrialized countries are about \$0.07/kWh [232, 246]⁶.

Global market prices for the whole maize plant and the dry cane are not available; therefore, they have to be estimated. Based on the prices for food-grade maize in the first three quarters of 2008 (\$210/t⁷), the price for the whole maize plant is estimated to be \$8/GJ⁸. Based on the raw sugar prices in the first three quarters of 2008 (\$265/t⁹), the price for the whole sugar cane plant is estimated to be \$2/GJ¹⁰.

While the oil, gas, lignocellulosic biomass and maize prices mentioned above are valid for major petrochemical consuming countries such as Western Europe and the US, the coal prices are valid for coal-exporting regions such as Australia and South Africa and the sugar cane prices are valid for South America. Freight costs for transportation from these regions to Western Europe or the US have not been included. Let us assume Western Europe to be the final destination of basic petrochemicals. If the freight cost for transporting coal from South Africa and Australia to Western Europe (about \$30/t coal in the first three quarters of 2008 [242, 247] or \$1/GJ coal) is

¹ The average of three oil prices: Dated Brent, West Texas Intermediate and the Dubai Fateh [242] (global oil prices are mostly the same [243]).

² The average of Russian natural gas border price in Germany and spot price at the Henry Hub terminal in Louisiana [242].

³ The average price of used plastic films and plastic bottles in the UK [244]. Average global prices are unavailable.

⁴ The average price of Australian thermal bituminous coal FOB prices and South African bituminous coal FOB price [242] (LHV of coal at 27 GJ/t). FOB means free on board or without freight costs.

⁵ The average global price of pulpwood fiber (LHV 18 GJ/t) (The largest producer, North America, accounts for 40%) [245].

⁶ To calculate the production costs of the various routes in 2008, electricity prices are used. The electricity sales are deducted from the total production costs of the routes with power cogeneration. This approach is different from the previous case of 2030-2050 where electricity production costs were deducted from the total production costs of the routes with power cogeneration. The reason is that in the case of 2008 the real market energy prices are used while in the case of 2030-2050 the projected energy prices were used.

⁷ The sum of the average price for US maize No. 2 Yellow FOB (\$210/t) [242].

⁸ The price of maize stover is 25% that of the maize kernel while the weight of maize stover is similar to that of maize kernel, or about 50% that of the whole plant [27].

⁹ The average raw sugar price of Coffee Sugar and Cocoa Exchange contract No. 11 prices nearest future position (FOB) [242].

¹⁰ The price of dry sugar cane (the whole sugar cane plant) has always been 14% of raw sugar prices in 1990-2003 [27].

added to the 2008 coal price mentioned earlier (\$4/GJ), the resulting price will be \$5/GJ. If the freight cost for transporting sugar cane from South America to Western Europe (\$380/t raw sugar in the first three quarters of 2008 [242] or \$3/GJ sugar cane) is added to the 2008 sugar cane price mentioned earlier (\$2/GJ sugar cane), the resulting price would be \$5/GJ sugar cane.

The freight costs of \$1/GJ for coal and \$3/GJ for sugar cane in 2008 are quite significant if compared to the range of biomass and coal prices projected for 2030-2050 mentioned earlier (\$1-5/GJ and \$1-2/GJ respectively for biomass and coal). Therefore, it is interesting to consider the effect of the freight costs on the production costs of the sugar cane-based and coal-based routes. However, in view of the high freight cost, the transportation of sugar cane is extremely unlikely to happen. Therefore, as an alternative to adding freight costs of sugar cane to the production costs, the freight costs for transporting basic petrochemicals from sugar-exporting countries to Western Europe can be considered—assuming that sugar-exporting countries will produce basic petrochemicals from sugar cane and then export them to Western Europe. The same procedure can be followed for coal. The freight cost of shipping liquid chemicals (e.g. basic petrochemicals including ethylene and propylene) to Western Europe via Atlantic routes in the first three quarters of 2008 was about \$30-50/t chemicals [243].

5.4 Results

5.4.1 Range and Rankings of Production Costs

Figures 5-1 and 5-2 indicate the ranges and ranking of the production costs of all 24 routes of basic petrochemicals production under the assumptions made for 2030-2050 as described earlier. The overall results derived from Figures 5-1 and 5-2 are discussed below. This refers to the first two bars in Figure 5-1 and both bars in Figure 5-2; the results based on 2008 energy prices, i.e. the third bar in Figure 5-1, will be discussed later:

- *Range* While the costs of crude oil and natural gas-based routes are mostly within \$500-900/t HVCs¹, those of coal and biomass-based routes are mostly within \$400-800/t HVCs. If CO₂ emissions costs are added, the costs for most coal-based

¹ By comparison, the market prices of HVCs during 1990-2006 ranged between the lowest price \$400/t HVCs (corresponding to oil price at \$20/bbl in 1999) and the highest price \$1200/t HVCs (corresponding to oil prices \$70/bbl in 2005) [15]. In 2008, these prices have sometimes been higher than \$1,500/t HVCs. However, such high prices are not used in the analysis since they represent short-term prices only.

routes are unlikely to be below \$800/t HVCs and those for oil and natural gas-based routes are unlikely to be below \$900/t HVCs. CO₂ emissions costs do not have a strong impact on most of the biomass-based routes.

- *Ranking* Among the top seven most expensive routes, six are crude oil and natural gas-based routes. Among the top seven least expensive routes, six are coal and biomass-routes. If CO₂ emissions costs are added, the positions of the coal-based routes worsen by 7 ranks on average while the positions of the biomass-based routes improve by 6 ranks on average. Adding CO₂ emissions costs has no strong impact on most oil and natural gas-based routes (worsening by 1-2 ranks). Ethane SC is the least expensive route among all the oil and gas-based routes.
- Without CO₂ emissions costs, Coal FT Naphtha SC II, Coal MTO CCS and Coal MTO I are the most favorable routes (standard deviations in Figure 5-2 should be considered).
- If CO₂ emissions costs are added, Ligno FT Naphtha SC II, Sugar Cane ETE and Ligno ETE II are the most favorable routes due to the combination of biomass use and electricity cogeneration (both leading to the deduction of CO₂ emissions costs from the total production costs).

Figures 5-1 and 5-2 show that most of biomass-based routes are quite favorable if compared to oil and gas-based routes. This is consistent with the conclusion in [190], which was mentioned in Section 5.1. Ligno FT Naphtha SC I is not favorable because its electricity cogeneration is 2/3 less than that of Ligno FT Naphtha SC II. However, the total yields of HVCs (ton HVCs per ton total biomass input) in these two cases are quite close: about 9% for Ligno FT Naphtha SC I and about 10% for Ligno FT Naphtha SC II [204].

It should be pointed out that some of biomass-based routes require much fossil energy input, but they do not cogenerate any electricity, which can offset at least some of the fossil energy use. The fossil fuel use of Maize Starch ETE is 37 GJ/t HVCs (no electricity cogeneration) [27] whereas the fossil fuel use of Ligno MTO is 15 GJ/t HVCs (no electricity cogeneration) [25].

5.4.2 Production Costs in 2008

The result of using energy prices as seen in 2008 is represented by the dark gray bars (the third bar from the left) in Figure 5-1. The production costs of most of the coal-based routes are about \$200/t HVCs lower than those of most of the biomass-based routes, about \$300/t HVCs lower than those of the gas-based routes and about \$800/t HVCs lower than those of the Oil Naphtha SC route. Compared to the large cost-advantage of coal-based routes over the oil and gas-based routes shown above, the freight costs of transporting coal (\$1 GJ/t coal or \$100/t basic petrochemicals) or basic petrochemicals (\$30-50/t basic petrochemicals) from coal-exporting countries to Western Europe are insignificant.

In particular, the production cost of Sugar Cane ETE is only about \$400/t. Even if the freight costs for transporting sugar cane from South America to Western Europe (\$3/GJ sugar cane or \$440/t HVCs) is added (as said before, such transportation is very unlikely to occur), the production cost of Sugar Cane ETE will be still \$250/t HVCs lower than those of gas-based routes and about \$650/t HVCs lower than that of the Oil Naphtha SC route. The cost advantage of sugar cane-based routes over conventional routes have been validated by the fact that three large-scale “sugar cane to ethylene” projects are being constructed in Brazil since 2007 (to be in operation in 2009-2011 with a total production capacity of 600,000 tons of ethylene [206-208]).

It should be stressed that as stated in Chapter 4, out of the 24 routes discussed, only Oil Naphtha SC and Ethane SC are widely used on a commercial scale. Oil byproduct SC and Methane FT Naphtha SC are used in only a few locations. There are plans for commercial use and ongoing investments for some other routes (e.g. Sugar Cane ETE as said above). The rest are still undergoing research and development.

5.5 Possible Effect of Stagnant Oil Supply in 2030-2050

It is widely expected that the global demand for petrochemicals will continue to grow in the future. To meet this demand, the energy supply for petrochemicals will have to increase accordingly. As a thought experiment, it is therefore interesting to briefly consider the possible

effect of a stagnating oil supply in 2030-2050 on the petrochemical industry¹. For this discussion, three specific assumptions are made:

- *Crude Oil* The oil supply will reach a plateau at about 125 million barrels per day (mbpd) in 2030-2050² [4, 6, 251]. As in the past, about 10% of crude oil will be used for petrochemicals production³ [11, 188, 234];
- *Natural Gas* The supply of natural gas will be between 75 and 165 mbpd oil equivalent in 2030-2050 [4, 6, 251]. As in the past, 5% of natural gas (i.e. ethane and NGLs derived from natural gas) will be used for petrochemicals production [11]. In addition, about 1-2% of methane will be used for petrochemicals production in 2030 and 3-6% will be used in 2050 according to the current projections up to 2030⁴. Together, roughly 6-7% of natural gas will be used for petrochemicals production in 2030 and 8-11% will be used in 2050.
- *Demand for Petrochemicals* The global demand for petrochemicals will grow by 3% annually in 2008-2050 (assuming that 200 million tons of basic petrochemicals will be produced in 2008; estimated on the basis of a number of historical and forecast data sources [7, 12, 16, 17, 254, 255]). The total demand will be approximately 400 million tons in 2030 and 700 million tons in 2050.

Based on these assumptions, the total share of oil and natural gas-based routes in global petrochemicals production will be 85% in 2030 and 70% in 2050. Therefore, the remaining

¹ Although some analysts, such as C. Campbell, K. Deffeyes, J. Laherrère and M. Simmons, argue for “peak oil production” before 2020, a number of official and consultancy sources expect that oil production will likely stagnate or start to decrease after 2020-2030 [4, 7, 8] or between 2030 and 2050 [4-6, 248, 249]. This thesis will address the possibility of stagnated oil supply only.

² Oil shale is excluded due to high uncertainties but other types of unconventional oil reserves such as oil sands-derived bitumen are included. The current oil supply is about 80 mbpd [237] and that of paraffinic naphtha over 250 million tons [250].

³ Currently, besides the use of crude oil in petrochemicals production (10%), 50% of crude oil is used in the transportation sector and the remaining 40% is used for heat and power generation. Little change is expected in the future [11, 188, 234].

⁴ Methane is currently used in the electricity, fertilizer, methanol and transportation sectors. The electricity sector uses more natural gas (about 30%) than any other sector and its share will reach 35% to 45% by 2030 [237, 252]. The global consumption of ammonia and urea is increasing by 7-8% per year [11]. Methanol production has been growing by 3% annually since 1991 and was 47 million tons in 2008 [253]. In the future, methanol may be used in the electricity sector via fuel cells or in the transportation sectors either directly or via methanol-derived gasoline. These chemicals together will use about 25% of methane by 2030 [237]. Also, cars that run on natural gas or natural gas-derived transportation fuels (GTL) can compete for gas in the future. The current global GTL capacity (mostly using low-cost stranded gas) is about 0.2 mbpd in 2006 and another 2-3 mbpd capacity will come on stream by 2010 [234, 237]. The annual growth rate of GTL capacity is expected to be roughly 7% in 2010-2030 and by 2030, 5-10% of natural gas worldwide will be used to produce GTL [237]. About 15-30% of GTL is suitable for producing basic petrochemicals (see Chapter 4). Based on all this, it can be estimated that 1-2% of methane produced will be used in petrochemicals production in 2030. If this trend is assumed to continue to 2050, it can be estimated that 3-6% of the petrochemicals production in 2050 will be based on feedstocks from GTL.

energy demand for the global petrochemicals production unmet by oil and natural gas (15% in 2030 and 30% in 2050) will have to be met by coal and biomass:

- *Coal* The supply of coal-derived liquids (used as transportation fuels and feedstocks for petrochemicals production) has been growing by 5% annually in recent years and is expected to reach about one mbpd oil equivalent in the US by 2030 [188, 234] and about four mbpd oil equivalent globally by 2030 [202]. If this growth continues in 2030-2050 and all coal-derived liquids are used for making petrochemicals¹, coal will be sufficient to meet the remaining energy demand for global petrochemicals production (i.e. 15% in 2030 and 30% in 2050; unmet by oil and natural gas).
- *Biomass* If a conservative crop productivity of about 200 GJ/ha/year is assumed, about 46 million hectares (Mha) in 2030 and 166 million hectares in 2050 are needed to meet the remaining energy demand for global petrochemicals production (i.e. 15% in 2030 and 30% in 2050; unmet by oil and natural gas)² [218].

The discussion above is based on the assumptions made by various historical and forecast studies. However, numerous other development paths are possible. Major changes in other sectors in 2030-2050 may significantly affect the petrochemicals industry. For example, new discoveries of large oil or gas reserves could mean that even if the global demand for petrochemicals continues to increase, coal or biomass would not be needed at all for making petrochemicals in the future. However, the discussion of these possibilities goes beyond the scope of this thesis.

5.6 Uncertainties

The uncertainties regarding the technical data presented in Tables 5-1 and 5-2 have been discussed in the previous chapters and will be not repeated here. The uncertainties regarding the

¹ Not all these coal-derived liquids are suitable for use as petrochemical feedstocks (see Chapter 4).

² The land use for producing HVCs is 0.3-0.8 ha/t HVCs (see Figure 4-6 in Chapter 4). A land use of 0.8 ha/t HVCs is possible if energy crop productivity is about 200 GJ/ha/year. About 46 Mha in 2030 and 166 Mha in 2050 of the so-called rest land (grasslands) is needed to meet the remaining energy demand for the global petrochemicals production (i.e. 15% in 2030 and 30% in 2050; unmet by oil and gas). A land use of 0.3 ha/t HVCs is possible if energy crop productivity is about 400 GJ/ha/year. About 17 Mha in 2030 and 62 Mha in 2050 of abandoned agricultural land is needed for the same demand mentioned above [218]. Because it is more conservative, 46-166 Mha is chosen here rather than 17-62 Mha. The land use of 17-166 Mha is about 1-4% of the total global land use for agriculture (around 3,000-4,000 Mha in 2050) [218].

energy prices¹ in Tables 5-3 through 5-5 are inherently high. An extensive discussion on these energy prices and their fluctuations is outside the scope of this chapter. Several other uncertainties will be discussed in the following paragraphs.

With electricity production costs at \$0.02-0.04/kWh (lower than the \$0.03-0.05/kWh used in the main analysis) and no CO₂ emissions costs (all of the energy prices remaining the same), those routes that cogenerate large amounts of electricity (e.g. Methane OCM I and II, Coal MTO II and Ligno FT Naphtha SC II) become quite unfavorable. The three most favorable routes are Coal MTO CCS, Coal MTO I and Coal FT Naphtha I.

When electricity production costs are very high at \$0.06-0.10/kWh (other conditions mentioned remaining the same), then those routes that cogenerate large amounts of electricity (i.e. Methane OCM II, Coal FT Naphtha SC II, Ligno FT Naphtha SC II and Coal MTO II) become highly favorable—their production costs are very low and can even be negative.

We tested a wide range of deviations of energy prices by assuming the condition of perfect correlation (explained in Section 5.3.1). If the deviations increase, the correlations between prices of various primary energy sources weaken. However, the overall finding that most of coal and biomass-based routes are more favorable than oil and gas-based routes still holds.

Regarding the capital investment costs of alternative routes shown in Table 5-3 and Table 5-4 (mostly \$200-500/t HVCs in total²), the sources quoted in this chapter gave a rather high uncertainty of 20-30%, citing the effects of technological learning and economy of scale [204]. The effect of these uncertainties on the overall production costs of the alternative routes might have been presented with error bars added to Figure 5-1. We chose not to do this because the effect of these uncertainties (i.e. \$40-150/t HVCs) is small in comparison to the effect of fluctuating energy prices on the overall production costs of methane and biomass-based routes which are indicated by error bars in Figure 5-1 (i.e. about \$300-400/t HVCs). For most of the coal-based routes where the capital costs are about \$200/t HVCs, an uncertainty of \$40-60/t

¹ The fossil energy prices used in this chapter are well within the price ranges that were estimated for 2020-2030 by: Altos Partners, Energy & Environmental Analysis Inc., Energy Ventures Analysis, Deutsche Bank AG, Petroleum Economics Ltd., Petroleum Industry Research Associates Inc., Strategic Energy and Economic Research Inc. and Global Insight Inc.

² Those alternative routes that cogenerate electricity have large capital costs (about \$300-600/t HVCs) due to the capital investment in the electricity cogeneration facilities. Their production costs are lowered due to the sales of cogenerated electricity.

HVCs (i.e. 20-30% of \$200/t HVCs) compared to the effect of varying coal prices (i.e. about \$60-100/t HVCs) is considerable, but it is much less than the difference between the production costs of coal-based routes and oil and gas-based routes, which is about \$200/t HVCs on average. Therefore, even if the capital costs of coal-based routes increase by \$40-60/t HVCs, our results on the cost advantage of coal-based routes over the oil and gas-based routes still hold¹.

Regarding the competition between 10-15 years old, fully depreciated capacities based on conventional routes (i.e. without capital costs) and newly built, green-field capacities based on alternative routes (i.e. with capital costs), our results also hold. Capital costs of conventional routes, around \$60-80/t HVCs, are not critical for the overall production costs. As shown in Figure 5-1, the effect of energy prices indicated by the error bars is much larger than \$60-80/t HVCs.

Regarding future policies on CO₂ emissions costs, we assumed in our main analysis that producers must pay for CO₂ emissions during feedstock production and petrochemicals production as well as for CO₂ emissions due to the combustion of end products derived from HVCs. However, the current CO₂ policies do not impose the costs of CO₂ emissions due to the combustion of end products derived from HVCs on producers or waste incinerators (e.g. the current EU Emissions Trading Scheme excludes the waste management sector²). Neither are any CO₂ credits being awarded to plastics made from biomass. Only the CO₂ emissions due to the combustion of fossil fuels during feedstock production and petrochemicals production are subject to CO₂ emissions constraints. In addition, subsidies are given to the cogeneration of heat and power and biomass-fired electricity production in some countries (e.g. the UK). If the same policies, including awarding CO₂ credits to the cogeneration of heat and power, are assumed for 2030-2050, then the CO₂ emissions costs due to the combustion of end products derived from HVCs should be removed for all routes (no effect on biomass-based routes since CO₂ credits are cancelled out). The positions of coal-based routes would improve slightly by 2 ranks on average

¹ This means that the overall production costs of coal-based routes will still be \$60-140/t HVCs less than those of conventional routes.

² Under the current climate policies (e.g. the EU Emissions Trading Scheme), producers need to acquire permits for CO₂ emissions from large installations such as fossil fuel-fired power plants and petrochemical plants. The waste management sector is currently excluded, but may be included by 2013. For producers, it is difficult to track the final destination of the carbon content of HVCs due to the diversity of waste management practices and the global trade of chemical products. It also depends on the country whether HVCs-derived end products will be combusted or used for landfill and whether energy recovered from the combustion of HVCs-derived end products will be used to substitute fossil energy use (i.e. incineration with energy recovery).

and those of oil and gas-based routes also by 1 rank on average while those of biomass-based routes worsen by 3 ranks on average. The general findings and the most favorable routes (i.e. Ligno FT Naphtha II, Ligno ETE II and Sugar Cane ETE) described in the main analysis remain the same.

Regarding the possible use of nuclear energy in producing petrochemicals mentioned in Chapter 4, there are many uncertainties related to costs/benefits, environmental effects and public acceptance. Nevertheless, it remains an interesting topic for discussion since the production of chemicals using nuclear energy has several environmental advantages comparable to biomass: utilizing CO₂ and avoiding the use of fossil energy. Using the data on methanol production in [229] and our data on MTO processes in Chapter 3, we found that the projected production cost of a nuclear energy-based route is in the range of \$560-950/t HVCs. This is quite similar to the production costs of crude oil-based conventional routes in the period of 2030-2050 shown in Figure 5-1. If CO₂ emissions due to the combustion of end products derived from HVCs are considered, the nuclear energy-based route will have an economic advantage over the fossil energy-based routes similar to biomass-based routes.

5.7 Conclusions

We have used a wide range of energy prices to calculate the production costs of 24 routes for producing basic petrochemicals and found that most of the coal and biomass-based routes are less expensive than most of the crude oil and natural gas-based routes. The difference between the ranges of their production costs is roughly \$100-200/t HVCs. The effect of CO₂ emissions costs is strong for coal-based routes and is also quite significant on biomass-based routes, but is relatively moderate for oil and natural gas-based routes. To ensure the reduction of CO₂ emissions in the long term, we suggest that policies for the petrochemicals industry focus on stimulating the use of biomass as well as the use of CO₂ capture and storage for coal-based routes.

Chapter 6 Energy Efficiency Improvement and Process Innovation in Basic Petrochemical Processes¹

ABSTRACT

Energy efficiency improvement and process innovation are among the key options to reduce greenhouse gas emissions in the production of basic petrochemicals. The previous chapters have covered the technical and economic potential of energy efficiency and innovative process technologies. However, it is unclear why some of these process technologies are being developed or implemented whereas others are not, despite their promising techno-economic potential. This chapter presents some of the main barriers and drivers for energy efficiency improvement and process innovation in the basic petrochemical industry. The guidelines of the Oslo Manual published by OECD in 1997 were followed. The main findings are:

- *Improving existing processes* The main drivers are: energy savings, tight supply of gas feedstocks and the personal commitment of individuals. The main barriers are: shortages of staff and time, competition from other prioritized projects and unwillingness to change existing process configurations.
- *Developing new processes* The main drivers are: the use of low-cost feedstocks to produce high-value chemicals, competition among firms and the wish to broaden the application of existing knowledge. The main barriers are: unfavorable economic situations, insufficient modeling tools and concerns about job security.
- *Energy Efficiency* For both types of innovation, energy efficiency is always a highly desirable and possible outcome, but in itself it is not necessarily always a major priority. As far as strategic scenario planning is concerned, feedstock economics of new processes are of strategic importance, while energy efficiency is considered much less important.

¹ A shorter version of this chapter with the title “*Process Innovation and Energy Efficiency Improvement: the Case of the Petrochemical Industry*” has been accepted for publication by the Journal of Engineering and Technology Management.

6.1 Introduction

In the previous chapters, we have analyzed the energy use and production costs of various routes for petrochemicals production. As far as energy efficiency is concerned, most of the alternative routes are much less energy efficient and emit more CO₂ than conventional routes. This means that energy efficiency does not play the decisive role in the technological innovations of alternative routes. While some of those alternative routes are being developed or implemented, others are not. This leads us to the question: Which issues are important for firms to consider when they decide whether or not to invest in such innovations?

Most previous work on innovation in the basic petrochemical industry had an economic perspective. Stobaugh argued that increased competition in the petrochemical industry has propelled innovation throughout history, such as in the case of methanol [19]. The European Community Innovation Survey I (CIS I) concluded that cost leadership and financial factors were the primary concerns for innovations in the 1990s [29]. While these studies had an economic perspective, a number of publications have addressed innovation in the petrochemical industry from an environmental perspective. These studies suggest that energy efficiency improvement (e.g. advanced thermal integration and coproduction of multiple products) and the use of biomass-derived feedstocks are among the most promising innovation solutions in chemical engineering [27, 256, 257]. Together, these economic and environmental perspectives lead to the question: Have the environmental issues been considered in the overall economic context of innovation? Or, more broadly: what factors encourage or hinder innovation?

Given this gap in knowledge, our research question is: *Which are the drivers for and barriers to innovation regarding the energy efficiency improvement in petrochemical processes?* Exploring the answer to this question will provide policymakers with some insight into ways of stimulating energy efficiency improvement and process innovation in the industrial process.

Basic petrochemical processes are used as a case study due to large amounts of energy used in these processes. Although our focus is on basic petrochemical processes, this chapter will go beyond just basic petrochemicals production and will place the innovation of basic petrochemical processes in the greater context of basic chemicals as well as that of the whole chemical industry.

The outline of this chapter is as follows. First, the methods and definitions are presented. Then, the barriers and drivers for innovation activities are described. Implications for energy efficiency are explored, and, finally, uncertainty issues are discussed.

6.2 Research Methods

The guidelines provided by the Oslo Manual published by the OECD in 1997 are the most widely recognized for collecting and using data on innovation [258]. These guidelines are primarily used for conducting nationwide, large-scale surveys for statistical purposes. Instead of conducting this type of survey, we applied these guidelines for definition purposes: the definitions of innovation, innovation activities, innovation firms and factors that influence innovation activities (i.e. drivers and barriers). The final discussion on the drivers and barriers involves the concept of reward-to-risk ratio (this concept is not mentioned in the Oslo Manual).

One main method for acquiring data is through interviews. We used interviews to identify drivers and barriers to process innovation and energy efficiency improvement in the case of the basic petrochemical industry. Our interviewees¹ were experts from petrochemical manufacturers, engineering firms, consultancies, universities and governmental bodies. They were defined using a “following-the-actors” approach, which is often used in actor-network technological studies [259]. Over 30 personal communications², including face-to-face interviews, telephone conversations and emails, were conducted in 2003-2005. Over 70% of these contacts were from the two core groups of innovators (in the center of Figure 6-1). Face-to-face interviews were held at least once with a person from eight out of the eleven firms (listed in Table 6-2).

In addition to the interviews, we collected data (e.g. innovation counts, R&D spending, sales and patents) through a literature review. The sources used can be divided into four categories: statistical and patent sources³ (e.g. US National Science Foundation, OECD and Eurostat),

¹ Most interviewed experts were found among or via those who attended the Texas Technology Showcase Conference in 2003, the 5th EMEA European Petrochemical Technology Conference in 2003, and the American Institute of Chemical Engineers (AIChE) Spring Meeting in 2005. The statements of our interviewees represent their personal opinions only and do not represent the views of the institutions they were affiliated to.

² Issues of confidentiality, legality and national security in the US and European chemical industry prevented us from being granted more access to personnel and to industrial sites. This was especially true in the US. For the same reason, we were not permitted to publish all the data collected.

³ There is no specific, comparable data related to engineering, procurement, machinery and construction services.

economic studies (e.g. EU Joint Research Center), patent databases (e.g. US and European Patent Office) and industry conference proceedings (e.g. those of American Institute of Chemical Engineers conferences).

Regarding patent databases, there are no standardized statistical indicators or commonly agreed methodologies for studying innovation in a specific production process. We did not do an extensive patent count. We conducted a preliminary patent review. Several keywords, such as methane, ethylene, olefins and firm names, were used to search for relevant patents and patent applications on petrochemical processes.

Regarding geographical coverage, this chapter concentrates on large US and European firms because of their global significance. The global significance of the large US and European firms concerns three aspects. First, petrochemical capacities located in Europe and the US have over 50% of the global market share [14]. Second, the majority of players involved in the innovation of petrochemical processes (see Table 6-2 and 6-3) are based in Europe and the US. Third, these players currently dominate the world petrochemical market. Since several major petrochemical firms are based in Asia, we will briefly discuss innovations in Japan and China in Section 6.7.

6.3 Definitions and Scope

6.3.1. Basic Chemicals and Petrochemical Processes

The Oslo Manual recommends economic activity (by industrial classification) as the most important variable for classifying innovation [258]. International classification codes contain many different definitions of chemicals (see Table 6-1). These codes are used throughout the figures and tables shown in this chapter. Therefore, it is necessary to describe the definitions of basic chemicals (including basic petrochemicals) and non-basic chemicals. These codes and definitions used in this chapter are shown in Table 6-1. Chemicals with little significance for energy use, such as pesticides and pharmaceuticals, are excluded.

In this chapter, we choose the energy efficiency improvement and innovation in basic petrochemical processes as a case study; however, the results are generally applicable to other basic chemical processes as well.

Table 6-1 Definitions of Basic Chemicals and Non-basic Chemicals: Definitions Used in this Chapter and in [260, 261]

Definitions used in this chapter	NACE (EU)	ISIC (UN)	NAICS (N. America)	SIC (recently replaced by NAICS)
<p>Basic chemicals (Petrochemicals and all others listed on the right are included, except pesticides. This definition is used in this chapter. Sources quoted in this chapter, however, used various definitions as listed on the right)</p>	Basic chemicals 24.1	Basic chemicals 241 (including industrial gases, dyes and pigments, other inorganic basic chemicals and other organic basic chemicals)	Basic chemicals 3251	Not applicable
	Industrial gases 24.11		Industrial gases 32512	Industrial inorganic chemicals 281
	Dyes and pigments 24.12		Dyes and pigments 32513	
	Other inorganic basic chemicals 24.13		Other inorganic basic chemicals 32518	
	Other organic basic chemicals 24.14		<i>Petrochemicals</i> 32511 and Other organic basic chemicals 32519	Industrial organic chemicals 286 (e.g. cyclic crude and intermediates)
	Fertilizers and nitrogen compounds 24.15	Fertilizers and nitrogen compounds 2412	Agricultural chemicals 3253 (including fertilizers and pesticides)	Agricultural chemicals 287 (including fertilizers)
	Plastics in primary forms 24.16	Plastics in primary forms 2413	Plastic material, resin, synthetic rubber, etc. 3252	Plastics material and synthetics 282
	Synthetic rubber in primary forms 24.17	Synthetic rubber in primary forms 2413		
<p>Non-basic chemicals (including all on the right except pharmaceuticals)</p>	Chemicals products and man-made fibers 24.2-a24.7	Chemicals products and man-made fibers 242-243	Chemicals products 3252-3259	Pharmaceuticals 283; soap, etc. 284; paints 285; miscellaneous 289

6.3.2. Innovation Counts and Definitions

There are over 100 definitions of innovation used in the literature [262]. The definitions accepted and used most widely are those of the Oslo Manual, which are the criteria for counting technological product and process (TPP) innovations [258]. The Oslo Manual defines TPP innovations as follows [258]:

TPP innovations comprise implemented technologically new products and processes and significant technological improvements in products and processes. A TPP innovation has been implemented if it has been introduced to the market (product innovation) or has been used within a production process (process innovation). The minimum entry is that the product or process should be new (or significantly improved) to the firm (it does not have to be new to the world). A technological process innovation is the adoption of technologically new or significantly improved production methods, including methods of product delivery. A technological process innovation in ancillary activities is included.

The Oslo Manual definitions of innovation serve as the basis for the process innovation in the basic petrochemicals production discussed in this chapter. The definitions are used to collect data from official statistic sources. Official statistics sources (such as the European Community Innovation Surveys) provide data (e.g. innovation counts) by following international classification codes (see Table 6-1).

It is necessary to point out that according to the Oslo Manual definition, the minimum entry is that the product or process should be new (or significantly improved) to the firm (it does not have to be new to the world). This is one of the issues that have been extensively discussed in recent work [262-264]. We will not go into this issue here. In this chapter, we accept the minimum entry for innovation described above. Moreover, we accept the methods recommended in the Oslo Manual by adapting them within the context of innovation in basic petrochemical processes (see the next section).

6.3.3. Improving Existing Processes and Developing New Processes

The Oslo Manual suggests that TPP innovations and innovation activities should be differentiated by two types of novelty: “significantly technologically improved” and

“technological new” [258]. Based on this suggestion, we distinguish between two types of innovation activities regarding basic petrochemical processes: *improving existing processes* and *developing new processes* in the context of basic petrochemicals production (see Table 6-3). *Improving existing processes* involves significantly improved equipment, different engineering designs (e.g. reaction conditions) and unit operations while the same feedstocks and the same or similar basic engineering principles are used [19]. “Significantly” improving existing processes is here interpreted as: capable of improving energy efficiency by at least 5%. Examples can be found in the two left columns in Table 6-3. Technologies in these columns can be differentiated by their energy saving potentials. It should be noted that with respect to basic petrochemical processes, installing gas turbines (cogeneration of steam/electricity) falls under the Oslo Manual definition of innovation, but is still a secondary activity and therefore far less innovative than the implementation of ceramic furnace coils in a steam cracker, which is a core activity. Gas turbine integration in steam cracking has existed in Japan and elsewhere since the 1970s. However, ceramic coils are hardly implemented (due to erosion problems) and are still undergoing R&D today. Activities involving non-innovative, energy efficient technologies, such as fixing a steam leak with commonly used materials, are not counted as innovation. Also, non-energy related activities that affect safety, health, air/water pollution and waste treatment are excluded from this chapter.

Developing new processes involves radically new equipment, fundamentally different unit operations and engineering designs (e.g. reaction conditions), while the feedstocks used can be the same, similar or completely new as before [19]. Examples can be found in the two columns on the right in Table 6-3. Technologies in these columns can be differentiated by their feedstocks. New processes can use either conventional or alternative primary energy sources. In Chapter 2, new processes using conventional energy sources were referred to as conventional routes (e.g. steam cracking and catalytic olefin technologies). New processes using alternative primary energy sources were discussed as alternative routes (e.g. natural gas, coal or biomass to petrochemicals) in Chapters 3 and 4. However, as was shown in these chapters, alternative routes, though counting as process innovation, are not necessarily more energy efficient than the conventional routes.

Innovation related to basic chemicals is dominated by process innovation rather than product innovation [265, 266], although some product innovation does occur for polyethylene and polypropylene with new properties. Currently, no new basic chemicals or basic petrochemicals are expected to substitute conventional basic petrochemical products such as ethylene. It is reported that 46 out of the top 50 high-volume basic chemicals in 1977 remained in the top 50 in 1993 [254]. New chemicals, such as bio-based poly-lactic acid, have some functions of basic chemicals, but cannot yet be classified as basic chemicals due to their small production volume, physical properties and special functions. Innovation in new basic chemicals is outside the scope of this chapter. The focus is instead on innovation in basic petrochemical processes that can substitute conventional processes.

6.3.4. Innovators

The Oslo Manual suggests that innovators, or innovating firms, can be identified and classified on the basis of their economic activities (by international industrial classification codes) [258]. Based on this suggestion, innovators were identified through interviews and literature review. In Figure 6-1, they are grouped on the basis of their main activities and are linked on the basis of their relationships. The lines between innovators represent innovation and energy-efficiency improvement-related relationships. The thick lines indicate the great importance of two core groups of innovators (in the center of Figure 6-1) and their intensive interactions.

The two core groups of innovators are *licensing firms* and *producers*, shown in the center of Figure 6-1. *Licensing firms*, known as licensors, own patented technologies, or so-called proprietary processes. Some of the licensors are also chemical producers (see Table 6-2). The firms can use the processes internally if they are also producers, but usually they transfer these processes to others through licensing contracts.

Licensors have in-house capacity for certain types of research and development as well as for *engineering, procurement* and *construction* service (commonly known as the EPC service). Nearly all basic chemical projects and 80% of petrochemical projects in the world during 1980-1990 were licensed by these firms (the rest of projects were carried out through internal use of licenses) [267]. Regarding steam cracking processes used in the production of basic

petrochemicals, five licensors currently dominate the world market [268]. These five licensors are listed in Table 6-2.

The term *producers* in this chapter refers to producers of basic petrochemicals. Producers decide whether or not to use improved or new processes that are licensed by their own engineering departments or by licensors from outside (see Section 6.4). No producers own the license of a steam cracking process simply because none of them needs to build a new steam cracker every year. The top ten producers of petrochemicals have half of the world's production capacity (the rest belong to national firms) [34, 269]. Six of these firms are listed in Table 6-2. No comparable data about the other four producers were found. The sales of basic petrochemicals represent roughly 10-20% of the total sales of the major oil firms listed in Table 6-2.

6.3.5. Drivers and Barriers

The Oslo Manual recommends that information should be collected on factors assisting or hampering innovation activities [258]. On the basis of this recommendation, drivers and barriers discussed in this chapter are defined as follows. *Drivers* are defined as factors that positively influence a firm's intention to innovate and therefore assist innovation activities. *Barriers* are defined as factors that negatively affect a firm's intention to innovate and therefore hamper innovation activities.

The Oslo Manual points out that a factor may assist in one case and be an obstacle in another [258], and this holds true for innovation in basic petrochemical processes as well. Innovators often have overlapping roles and are inseparably linked to each other via networks and feedbacks. For certain technologies and firms, specific drivers and barriers apply. Therefore, these cases will be mentioned individually.

The drivers and barriers presented in this chapter are commonly agreed upon by nearly all of the interviewees we have had contact with (listed in the Reference). Therefore, we consider these drivers and barriers as representing the common perceptions of industry experts on technological innovations in petrochemical processes. Individual interviewees are only cited for certain statements that they have made on specific technologies.

Figure 6-1 Innovators and Networks for Innovation in Petrochemical Processes (based on various interviews)

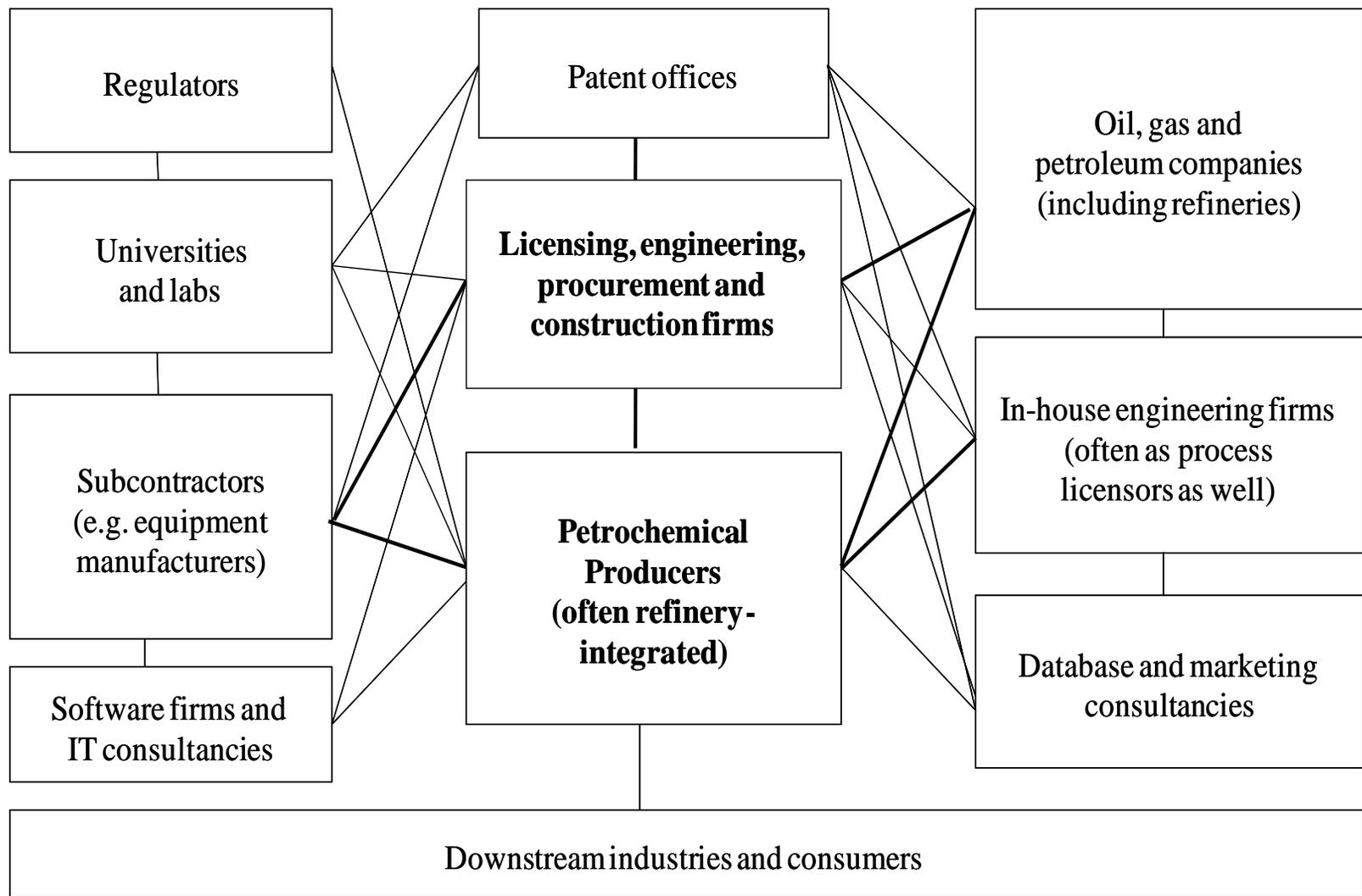
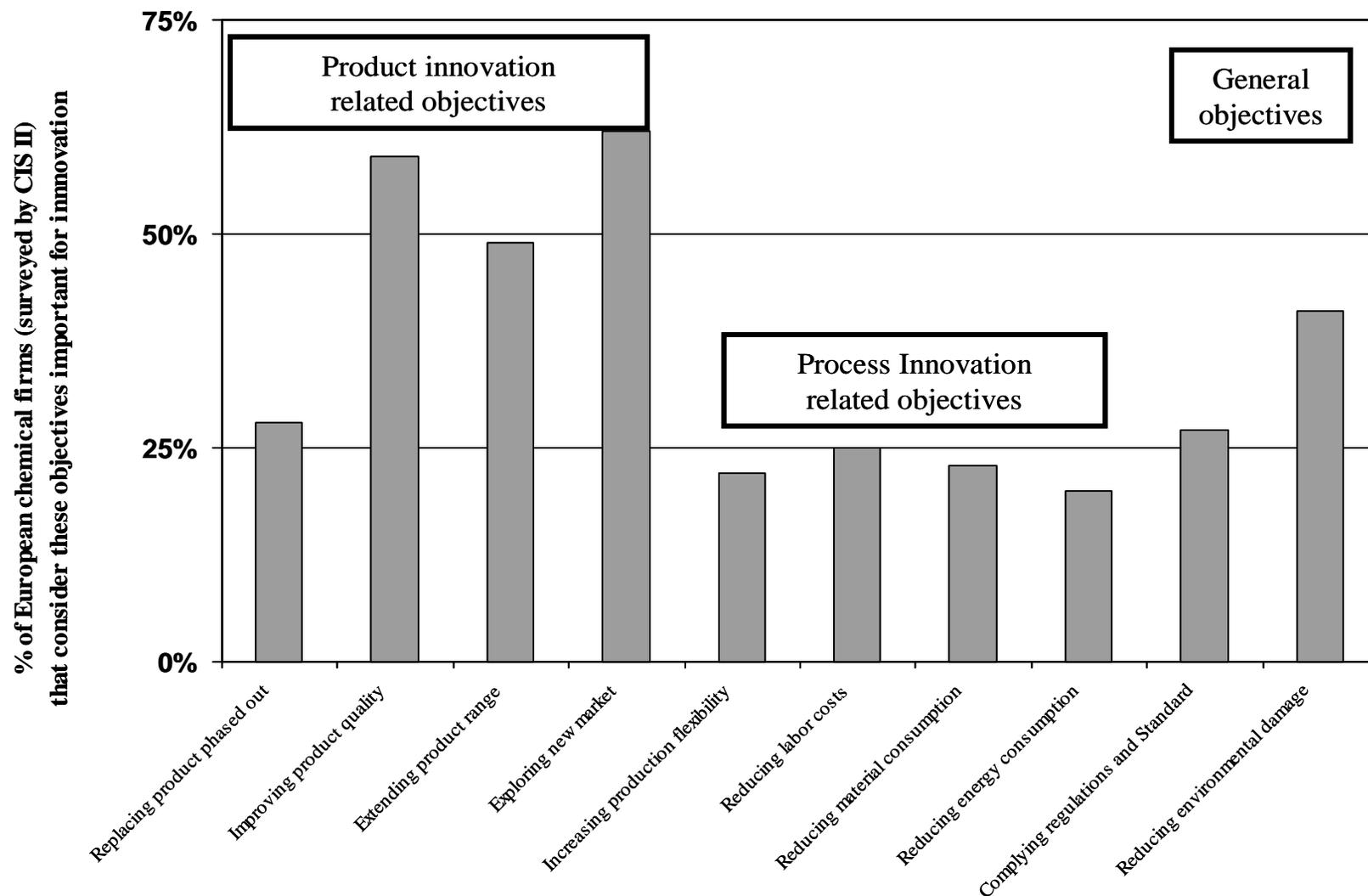


Table 6-2 Major Firms Involved In Petrochemicals Production and Processes (based on [270-272] and various annual reports)

	Firms (2003)	Sales from chemicals or services (in M\$ 2003)	Licensing as % of total technology use (1998)	Core business (2003)	Ethylene capacity (in MT) (2002)	R&D spending (in M\$ 2003)	R&D/sales (%) (2003)
Chemical producers (global top two in 2003)	BASF	38318	50	Diversified (including petrochemicals)	4.4	1250	3.3
	Dow	32632	35		13	979	3.0
Petrochemical producers	ExxonMobil	20190	65	Oil, natural gas, chemicals and process licensing	12	630 (2000)	0.4 (2000)
	BP	77500	65		4.6	310	0.4
	Shell	10100 (2000)	55		6.7	505 (2000)	0.5 (2000)
	Chevron	7018	70		3.5	182 (2000)	0.6 (2000)
Petrochemical process licensors and engineering firms	Halliburton (owner of KBR)	14333	Data not available; estimated to be close to 100%	Process licensing, engineering, procurement and construction services	No data	258 (2000)	1.8 (2000)
	Linde	7103				206	2.9
	Technip	5516				171	3.1
	Shaw (owner of Stone & Webster)	3307				No data	No data
	ABB Lummus	1164				93	8.0

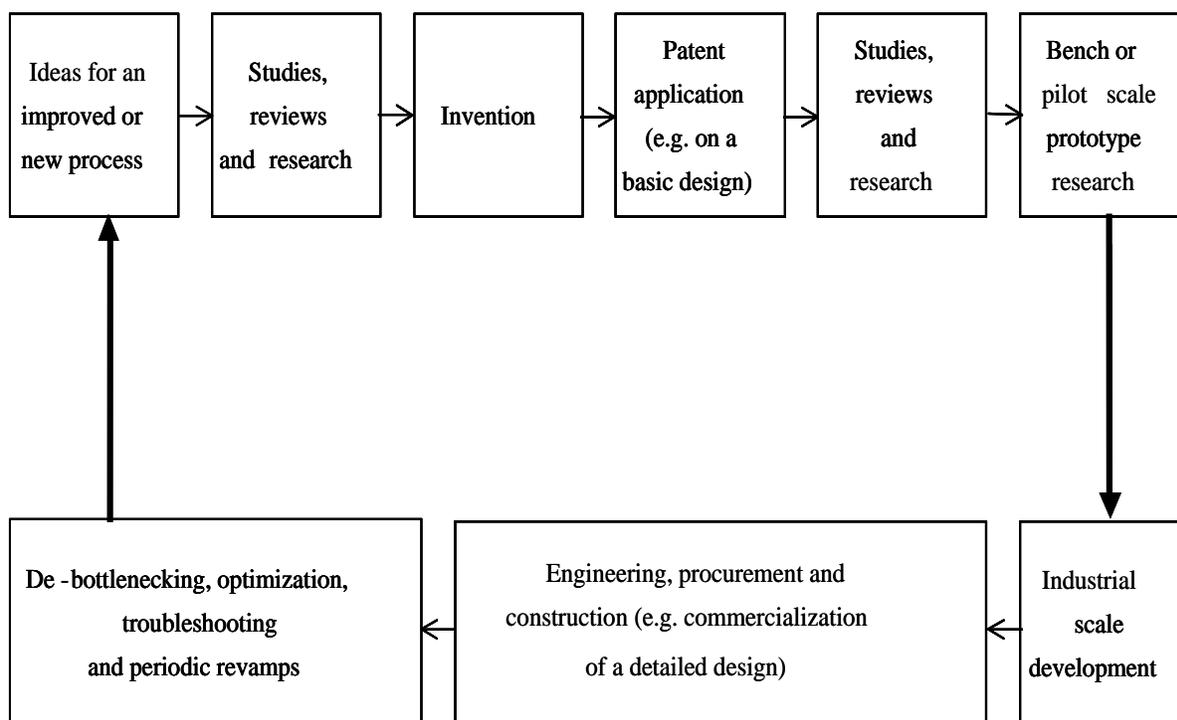
Figure 6-2 Objectives of Innovation in the European Chemical Industry [263]



6.4 Innovation Procedure

The Oslo Manual recommends that various components of TPP innovation activities should be distinguished [258]. Based on this recommendation, we identified the main phases of an innovation procedure in the petrochemical industry through interviews and a literature review (see Figure 6-3). Only major feedback-related activities are shown here.

Figure 6-3 A Simplified Procedure for Innovation in Petrochemical Processes (based on interviews; feedbacks between various steps omitted)



The core characteristics of a typical innovation procedure are as follows:

- For every patent, roughly five patent applications and 15 inventions are needed. The number of inventions is typically halved in each of the first two reviews. 10% of inventions are chosen for R&D investment and half of R&D spending ends up in commercialization projects [273, 274]. So in total, about 5% of inventions is commercialized in the end.

- Many interviewees remarked that innovators in various consortia of contractors, service firms and technology centers of large firms (sometimes together with universities) mostly conduct applied research that is target-specific or troubleshooting in nature. They noted that universities and a few companies such as ExxonMobil carry out fundamental research as well.
- R&D spending is 55% of the total expenditure in an innovation project for a basic petrochemical process [275]. The rest of the expenditure is for training (20%), engineering design (12%), market analysis (8%) and patents/licenses (5%). One source said that 20% of R&D is spent on research and the rest on development [276]. Various interviewees noted that R&D spending devoted to energy efficiency in petrochemical processes is relatively low, whereas most of R&D is spent on de-bottlenecking, troubleshooting, NO_x reduction, safety, regulatory compliance and the reduction of construction and equipment costs.
- Capital spending in investment projects is largely the responsibility of financial managers, rather than of their technical colleagues [277]. Investment in the petrochemical business follows a cyclic pattern [278]. First, capital is made available by the growth of total sales and profitability, which is in turn positively related to market demand and prices. Market growth is then positively related to the overall economic growth. If economic growth leads to too much capital investment and too much new capacity, an oversupply will follow and operating rates (or capacity utilization) will be discouraged. Investment falls until capacity is too low or market demand and prices rise again.
- The execution of a commercial-scale basic petrochemical project usually involves only one licensor (often acting as the contractor as well) and one or two large producers through a so-called turnkey contract. Almost all existing steam-cracking plants use processes provided by licensors though sometimes producers also apply their own technologies in certain sections of a plant. A major producer usually needs no more than one new plant or large expansion project every several years. Given the high cost of acquiring the entire steam cracking process, it is cost-efficient for producers to simply

buy processes provided by licensors [273]. In the first 3-4 years after the project has been finished, producers continue to receive services from licensors. Sometimes they may also give knowledge gained through operational experience back to licensors based on “grant-back” contract provisions [279].

- All in all, it is fair to say that with respect to the entire steam cracking process, the five licensors (and their contractors) are primarily responsible for innovation. Producers make important contributions to the improvement of various sections in the steam cracking process.

6.5 Two Types of Innovation Activities, Drivers and Barriers

6.5.1 Improving Existing Processes

The definition of improving existing processes is given in Section 6.3.3. Examples are given in Table 6-3. The core characteristics of improving existing processes are as follows.

- A large improvement project leads to 5% or more energy efficiency improvement (qualified as process innovation as defined earlier). Such a project often costs 20-200 million dollars. Typical examples are improved furnaces, integration of refinery and petrochemical complexes and cogeneration of heat, steam and power. In terms of savings as a percentage of total annual energy costs, 10-20% is often used as criterion to make an investment decision [280]. In terms of savings as a percentage of the total annual production costs, a similar range of 10-15% is used as criterion [240, 276]. A payback time of 5-6 years is often accepted [280, 281]; however, in many recent cases a payback time of 2-3 years was required.
- Most projects aimed at improving existing processes are implemented during revamps (usually together with de-bottlenecking) of an existing petrochemical plant. Plants are revamped every 5-6 years to make major add-ons and retrofitting possible. This requires a shutdowns of six weeks to two months [282]. The total cost of a major revamp can be 300 million dollars [240].

Many interviewees mentioned work on the implementation of improved processes in petrochemical plants. Combined heat and power (CHP) generation was a dominant subject during interviews. When asked about inventions and R&D issues, interviewees stressed that activities aimed at existing processes mostly concentrate on engineering and implementing those already widely commercialized technologies rather than on R&D.

The following drivers and barriers are generally applicable to all the technologies listed in the two columns under “Improving Existing Processes”. Specific drivers and barriers are discussed afterwards.

6.5.1.1 Drivers

The most important driver for improving existing processes is cost savings as a result of reducing energy use per ton of products (the calorific value of petrochemical products is excluded from consideration because it is a physical property of the petrochemical products and it cannot be reduced). Installing cogeneration could save 5-25 million dollars annually out of yearly energy costs of several hundred million dollars in a large firm (the calorific value of products excluded), or up to 15% of the total annual energy costs in a single plant [281, 283, 284]. Installing furnace coils that require a shorter residence time (reducing energy use per ton of product per second) and more efficient distillation columns (with better heat integration) could save 10-20% of the cumulative process energy use in conventional processes (see Chapter 2). Some examples can also be found in Table 6-3. As in any type of process cost savings (through either non-innovative or innovative technologies), the reduction of energy costs directly increases profits, or earnings before income tax, a key indicator of performance [273]. In fact, process energy cost is one of a few elements of production costs that can be reduced—other than costs of feedstock and maintenance. Process energy costs (the costs of combusted fuels and electricity) were roughly 20% of the total production cost of a naphtha-based steam cracking process in 2000 [117]. In the period of 1999-2003, the costs of fuels and electricity per ton of ethylene together more than doubled in the US and rose over 50% in Europe and Japan [285].

Another strong driver for improving existing processes is the tight supply of gas feedstocks (i.e. ethane and propane derived from natural gas and LPG). This driver is generally applicable to

any type of energy efficiency measures (either innovative or non-innovative technologies) taken by petrochemical producers. This is especially true in the US where 70% of feedstocks (wt.) in steam cracking are based on ethane and propane. Gas feedstock supplies become tight mainly due to the increasing use of natural gas for the production of electricity and of natural gas liquids (used for producing LPG) for transportation fuel production. During the past 30 years, ethane prices in the US were around \$1-3/GJ. The average US steam cracker was found to be 25% less energy efficient than its equivalent in Japan and 16% less energy efficient than its European equivalent [285]. However, since 1999, the prices of gas feedstocks in the US have become extremely volatile. The prices repeatedly went above \$10/GJ. This has caused the five-year-average spending on energy conservation in US petrochemical plants in 1999-2003 to increase by 4.5 times compared to that in 1994-1998¹ [285].

A third driver is the personal commitment of individuals. This driver is generally applicable to any type of changes made to existing processes through either innovative or non-innovative technologies. Some process engineers and energy managers are committed as a result of bonuses based on energy savings [281]. Others are committed owing to their increasing fear of losing local employment to competition from overseas [280]. Commitment from the top leadership or a leading coordinator in energy savings can also be important [286, 287]. This confirms a well-known notion that innovations are often triggered by people inside the companies [29].

The drivers mentioned above were chosen because they are generally applicable to all of the technologies discussed. Several interviewees also noted that other specific drivers exist for specific technologies. For instance, revenue (from selling steam or electricity in a favorable local market) is a driver for adopting cogeneration. Also, improved reactor kinetics, increased yields (i.e. selectivity and conversion of high value chemicals), less undesired low-value byproducts (e.g. coking or dry gas) and higher flexibility (i.e. higher degree of freedom) are important drivers for the adoption of advanced process optimization tools, reactors and product recovery.

¹ Technologies that were used for such energy conservation, whether they can be counted as innovation or not, were not given.

Table 6-3 Drivers and Barriers to Improving Existing Processes and Developing New Processes

	Improving Existing Processes		Developing New Processes	
Commercial Status	Widely commercialized; very often implemented	Mostly commercially available; some implementations	Mostly commercially available; rarely implemented	Some commercially available; a few implementations completed or planned
Feedstocks	Derived from conventional energy sources (e.g. crude oil and ethane/propane/butane-rich natural gas)		Low-cost feedstocks derived from crude oil or other conventional energy sources	Low-cost feedstocks derived from alternative primary energy sources (e.g. natural gas, coal and biomass)
Potential for energy savings by each technology	Savings of 5-15% compared to conventional processes	Savings of 10-20% compared to conventional processes	Savings of up to 20% compared to conventional processes	Methane-based process routes use 30-40% more energy and coal/biomass-based process routes use 60-150% more energy than crude oil-based conventional process routes
Innovating firms and technologies	<p>Lockwood Green, BASF and Atofina: cogeneration integrated into a steam cracker site</p> <p>GE/ExxonMobil: residue gasification for cogeneration</p> <p>Air Liquide, Dow and Shell: combined-cycle cogeneration</p> <p>ASPEN Tech: real-time plant process control and energy management system</p> <p>UOP: integration of petrochemical and refinery complex</p>	<p>Hamworthy: burner design</p> <p>FM: coated furnace coils</p> <p>Linde: short coil tubes</p> <p>ABB Lummus: online decoking; gas turbine integration</p> <p>Stone & Webster: advanced product recovery</p> <p>gas turbine integration</p> <p>KBR: short residence time</p> <p>Technip: distillation schemes</p> <p>Shell/ECN: integrated distillation columns for separation</p>	<p>ExxonMobil, Shell, ABB Lummus, KBR, UOP, DSM, Linde and S&W/Sinopec: low-value hydrocarbons (e.g. C₄₋₉ refinery or steam cracking byproducts) to petrochemicals in FCC-like reactors at lower temperatures than steam cracking therefore saving energy;</p> <p>KRICT, LG, AIST, VNIOS and ASAHI: catalytic cracking of conventional, C₄/C₅ streams and heavy feedstocks</p> <p>Dow and ExxonMobil: catalytic oxidative dehydrogenation of ethane and propane</p> <p>BP/MTR: membrane separation</p>	<p>ExxonMobil, BP, ConocoPhillips, Rentech, Sasol/Chevron, Statoil, Syntroleum, Moss gas and Shell: methane to liquid fuels and petrochemical feedstocks via syngas</p> <p>UOP and Lurgi: methane to light olefins and fuels via methanol</p> <p>DSM: partial oxidation of methane to ethylene and electricity cogeneration</p> <p>Synfuel/A&M University: methane to ethylene or fuels via acetylene</p> <p>Bechtel: coal to fuels, electricity and petrochemical feedstocks</p>
Drivers	<p>Energy cost savings;</p> <p>Tight supply of gaseous feedstocks</p> <p>Personal commitment of individuals</p>		<p>The conversion of low-cost feedstocks to high-value chemicals</p> <p>Competition among process licensors and engineering firms</p> <p>The wish to broaden the application of existing knowledge</p>	
Barriers	<p>Shortage of staff and time</p> <p>Competition from other prioritized projects</p> <p>Existing configurations</p>		<p>Unfavorable economic situations</p> <p>Insufficient tools for decision making and process modeling</p> <p>Concerns for job security</p>	

6.5.1.2 Barriers

All out interviewees agreed that shortage of staff and time is a general barrier to improving any kind of existing process. Employment in the US basic chemical industry was reduced by 4% during 1994-2004¹ [288], even though labor cost is less than 1% of the total petrochemicals production costs [117, 282]. Engineers in petrochemical plants are often occupied with the “putting out fires” type of urgent or critical tasks [289]. Consequently, little time is left for understanding current energy use or collecting information on innovative, energy efficient technologies [282]. This is especially true when market demand is strong and the operating rates are high (higher than 90%) [282]. Small projects receive even less manpower than larger projects [50]. In many large firms, no more than ten people specialize in coordination and management tasks aimed at energy-efficiency improvement [281]. Labor shortages also occur at contractor and engineering firms. Finding experienced engineers to meet labor demand [286, 287] or to replace retired personnel [290] has already become quite difficult in recent years.

Another barrier to improving existing processes is a lack of prioritization. Priorities such as capital investment in new capacity can lead to a higher internal rate of return and more sales than those listed in Table 6-3 and, therefore, they are often the first to receive available investment funds. In 2004, ExxonMobil posted a return on capital investment of 23% [291], which is much higher than the average return from many improvement projects; for example, heat and power cogeneration has returns up to 15% [279]. Furthermore, as one interviewee said, improving existing processes may lead to better energy efficiency and higher profits (or other benefits such as higher reliability and safety), but it does not necessarily increase the sales of basic petrochemicals [273]. Sales are used to make investment decisions, but are determined mainly by factors such as market share, prices and demand. Also, since many firms expect diminishing returns from investing in existing processes and less volatile (or lower) energy prices in the long term (meaning several decades), any capital spending on existing processes is unlikely to stay high or to increase forever [283]. This idea is reflected in a 2005 Solomon report stating that the

¹ No comparable data are available for the petrochemical or basic chemical industry in Europe and Japan. The reduction of employment in the chemical industry in these regions was 5% in 1994-2000 [288]. There are various reasons for this reduction, such as lean management, downsizing and cost-motivated restructuring (i.e. mergers, acquisitions or divestment).

five-year average of planned capital spending on energy conservation in US petrochemical plants in 2004-2008 was reduced by 66% from that in 1999-2003¹ [285].

A third barrier is that relying on proven configurations and operation control is considered more important than the potential benefits from implementing energy efficient technologies. One example is adopting new high-performance furnace coils (e.g. with millisecond residence time), which may cause problems in other parts of the steam cracking process that are incompatible with the new coils [280]. Another example is integration, such as integration of refinery and petrochemical processes or cogeneration of heat, steam and electricity via gas/steam turbine. Such integration is impossible if the refinery and petrochemicals plants are too far from each other. Even if possible, such integration adds complexity, reduces flexibility and sometimes causes upsets. When units are linked either directly or indirectly, an upset in one unit can lead to unexpected disruptions at another unit (or even to a shutdown of the whole plant) [292]. Plant operators are very reluctant to adopt such integration since it is very important to them to have the flexibility to shut down part of the plant while still allowing other parts to run. Additional examples of the importance of proven configurations is the adoption of combined distillation and evaporation columns or liquid membrane separators, which tend to have low flux and could, therefore, slow down throughput if they are not well synchronized with the rest of the plant [282]. Economically, throughput is far more important than the benefits from energy savings. Economic losses due to disruptions and shutdowns are usually in the range of hundreds of thousands to millions of dollars per month for a plant [282]. The full benefits from using new equipment in the existing configurations are often achievable only by replacing other related older equipment, which incurs so-called “hidden costs”, meaning costs other than buying and operating the new technologies themselves. Worried that hidden costs will outweigh the benefits from improving existing processes, plant operators are often reluctant to adopt any kind of changes, whether innovative or not [292].

The barriers mentioned above were found to be generally applicable to all the technologies discussed. Several interviewees also noted that other specific barriers exist for specific technologies. For instance, the high initial investment cost is a barrier to adopting a large

¹ The technologies that were used for such energy conservation, and whether they can be counted as innovation or not, were not given.

cogeneration plant for a firm that is short of funds. Lack of electricity demand and low energy prices in certain areas of the US can be another barrier to the implementation of heat and power cogeneration. Expensive equipment and high maintenance costs are important barriers to carrying out R&D on highly efficient steam crackers and ceramic coils, and this is an especially strong barrier to innovation by relatively small firms.

6.5.2 Developing New Processes

The definition of developing new processes is given in Section 6.3.3. Examples are given in Table 6-3. The core characteristics of developing new processes are as follows:

- Developing new processes involve radically different or new engineering designs, e.g. new reactors and catalysts. Some new processes are catalytic processes that use oil and natural gas-derived feedstocks, e.g. naphtha and ethane. Other new processes convert low-cost, alternative feedstocks to high-value petrochemical products.
- New processes that use conventional feedstocks lead to savings of up to 20% compared to the energy use in state-of-the-art steam cracking technologies (see Chapter 2). Several other new processes, e.g. Omega (Only-MEG-Advanced) processes for conversion of ethylene to mono ethylene glycol (MEG) and MPG via the carbonate route, can save up to 80% of the energy use in conventional processes [293].
- New processes that use methane, coal and biomass-derived feedstocks do not lead to energy savings (see Table 6-3). Methane-based olefin process routes use about 30% more energy than conventional naphtha or ethane-based existing processes, while coal and biomass-based olefin process routes use 60-150% more energy (see Chapters 3 and 4).
- The size of a pilot plant depends on how well understood the scale-up effect of new processes is. A large pilot plant based on new processes such as gas-to-liquids (GTL) runs about 5,000-10,000 tons per year, while a small one may run only half of that or less. A plant on such a scale can cost tens of millions and sometimes even hundreds of millions of dollars. However, even if a pilot plant is running successfully, the new

processes are not yet seen as “tried-and-proven” since the only convincing proof is the successful construction and running of a full-scale, commercial-size plant [294].

- The equipment for a full-scale petrochemical plant using new processes (in Table 2) costs 1-2 billion dollars. If it is integrated into a refinery plant using natural gas, coal or biomass-to-liquids technologies, the total equipment cost will amount to 6-7 billion dollars. In addition, indirect costs and contingency costs could add another 20-30%.
- Add-ons using small new processes typically cost approximately 200-500 million dollars [240]. A test furnace costs 2-3 million dollars. A commercial-size furnace costs 12 million dollars and seven to eight furnaces are needed for a world-scale ethylene plant (i.e. with a capacity of one million tons ethylene or more per year) [295]. The average payback period ranges from four to seven years. The costs of logistics, such as naphtha, natural gas and olefin pipelines, can also be in the range of billions or tens of billions of dollars depending on the distance covered.
- One interviewee remarked that developing new processes typically takes 10-15 years to reach an early stage of commercialization [273]. It takes another eight years for a new process to reach full commercialization [295]. Making the decision to invest in a new process could take up to 5 years [273], and project execution and construction could take 3-4 years [296]. However, methane-to-chemicals and fuels processes have been undergoing R&D since the mid 1970s and are still not commercialized worldwide.

Many interviewees quoted here work on R&D and project development that involve new processes (see Table 6-3). There are fewer consensuses among the interviewees on the status of these new technologies than on the improvement of the existing processes. The most disputed technical issues among the interviewees are the level of yields, effectiveness of different catalysts and coking problems. The most disputed economic issues concern the prices of energy sources, feedstocks and products. The following drivers and barriers are applicable to all of the new technologies listed in the two columns under “Developing New Processes” in Table 6-3.

6.5.2.1 Drivers

The strongest driver for both producers and engineering firms is the possible economic gain from the conversion of low-cost feedstocks to high-value basic petrochemicals. One example of such a feedstocks is so-called “stranded gas”, which is found in remote locations in the Middle East or Eastern Europe where the available natural gas far exceeds local demand but is too costly to transport [114]. As discussed in Chapter 3, stranded gas is 50-80% cheaper than ethane or naphtha in \$/GJ terms. The low cost of stranded gas is the main driver for UOP (a major engineering firm) to develop a natural gas-to-olefins via methanol process [297]. Another example of such feedstocks is low-value heavy hydrocarbons from refineries and steam cracking, which are about 50% cheaper than naphtha in \$/ton feedstock terms (see also Chapters 2 and 4). Methanol or naphtha made from coal-derived syngas is another example. In the last two decades, coal prices have often been one fifth to one third of oil and natural gas prices in \$/GJ terms. The production cost of olefins made from coal via methanol is estimated to be only about 50% of that of olefins made from the weighted average of US feedstocks (mainly ethane and naphtha) in 1997-2005¹ [240]. These processes are promoted as stabilizing profits when prices of conventional energy sources and feedstocks are high relative to those of the alternatives. Therefore, securing feedstock supply and stabilizing profits have always been considered to be of strategic importance for the future of the basic petrochemical industry [20].

Another strong driver for developing new processes is fierce competition between process licensors and engineering firms as well as between producers. The survival of these firms, especially independent engineering firms such as ABB Lummus and UOP, depends heavily on contracts for new projects. It is widely expected that a number of new projects will be announced in the coming years. Global petrochemical capacity is expected to grow about 20% (in physical terms) in 2001-2007 (based on known start-ups and planned projects), but the global market demand for petrochemicals is expected to grow 25-40% (3-5% annually) during the same period. In particular, the annual growth in demand for propylene is expected to be 5-6%, while that of ethylene will be 4% [298]. Targeting upcoming propylene projects, several firms have recently offered catalytic technologies with high yields of propylene for commercialization (see

¹ Production cost by using coal as the feedstock is about \$260/t ethylene (based on \$125/t methanol and \$40/bbl crude oil) [240].

the left column in Table 6-3 under “Developing New Processes”). These processes, such as catalytic cracking of low-value C₄/C₅ byproduct, metathesis and methanol-to-propylene, are often referred to as propylene-on-purpose processes [296]. These firms intend to use new processes to compete with conventional processes (and other new processes) in several areas: costs of capital investment, energy efficiency, flexibility of feedstocks and products, effectiveness of catalysts, yields, length of construction time and maintenance costs [293, 296]. Among producers, competition for “stranded gas” is also extremely fierce (see the right column “Developing New Processes” in Table 6-3).

A third driver is the wish to broaden the application of existing knowledge on catalytic processes, which stimulates engineering firms and producers to innovate. Using existing knowledge allows for maximal utilization of the R&D and operational experiences gained in the past, but also leads to a better understanding of the risks that are involved in the development of new processes. This effect was observed both by interviewees and in our earlier techno-economic feasibility studies. Many interviewees remarked that currently well-understood refinery processes, such as Fischer-Tropsch (conversion of natural gas, coal and biomass to syngas, fuels and basic petrochemicals), partial oxidation and related catalysis knowledge were either transformed or stretched into new processes that convert low-value feedstocks to basic petrochemicals (see both columns of new processes in Table 6-3) [294, 296, 297, 299]. Firms that are active in new processes, such as those listed in Table 6-2 and 6-3, already have extensive knowledge on refinery and catalytic processes.

6.5.2.2 Barriers

Due to recurring unfavorable economic situations (i.e. low profit margins and uncertain market prospects), firms in the petrochemical industry have been reluctant to invest in the development of new processes. For many large firms, the petrochemical business has become less profitable due to the recent globalization of the market. Since 1970s, the supply of and demand for petrochemicals became increasingly globalized as new players emerged in the Middle East and Asia. These players have demonstrated their strong advantages in low energy price or rapid market growth (5-10% annually). As a result, average profit margins of large firms fell by 2% per year between 1986 and 1996 [37, 300, 301]. In industrialized countries, market demand for

chemicals grew slowly, at roughly 2% annually in the 1990s, so there has been much fear of overcapacity. Overcapacity (roughly 10-15% of demand) and low operating rates (less than 90%) are constantly threatening the profitability of existing plants [34]. One interviewee estimated that 95% of innovation failure is due to overcapacity and related losses [268]. Even if new capacity is needed to meet growing demand, old processes are still preferred since investing in the de-bottlenecking of existing processes usually requires less capital. For example, the de-bottlenecking of FCC operations in US refineries (to produce more propylene) could obviate the need for new propylene-on-purpose processes [296]. Increased use of ethane steam cracking in the Middle East could prevent ethane partial oxidation from being commercialized [302]. The emergence of coal-to-chemicals processes in China could prevent biomass-based processes from being used there [302]. In addition, past price fluctuations and unfavorable outlooks of market demand worry many firms [303]. Given the uncertain business conditions described above, firms have become quite risk-averse regarding investing in new processes [50]. Hence, the unfavorable economic situation in the petrochemical industry are a strong barrier to developing new processes.

A second barrier is that conventional tools for modeling processes and making decisions are seen by producers and engineering firms as insufficient to deal with the high uncertainties inherent in the decades-long development of new processes. It is well known that a lack of sufficient tools can discourage firms from engaging in innovation. Developing such tools is much more difficult and expensive than buying them. Technip controls about 70% of the steam cracking simulation tools market and Aspen TECH has 80% of the continuous process flow sheet market. These conventional process-modeling tools, though highly optimized, may not be suitable for the simulation of radically new processes [282, 302] such as catalytic processes [201]. Similar problems exist in the case of conventional decision-making tools for economic analysis. Such tools typically consist of extrapolative methods such as history-based forecasting, net present value analysis and utility theory [304]. These tools are suitable for analyzing relatively regular business cycles and for forecasting market demand for the coming five years. They typically give quantitative recommendations that target small rewards, such as those gained through improving existing processes. However, these tools are unable to address the complexities or the

likelihood of market entry in the long term by new processes using alternative feedstocks such as natural gas or coal [294]. They also fail when facing sensitive issues, such as market deregulations, CO₂ emissions costs and energy taxes. Small firms that do not possess reliable software tools to compensate (at least partially) for the lack of operational experience and economic certainty often find it difficult to assess the overall cost/benefit of any innovation project [302].

A third barrier is concern for job security. This is especially significant for the petrochemical industry because R&D on petrochemical process usually requires large investments in time and capital. Engineers and managers at big firms have worked on natural gas-to-chemicals and fuels processes using Fischer-Tropsch (FT) chemistry since the 1970s. Major firms have spent over two billion dollars on R&D on FT processes since the early 1980s [305]. ExxonMobil claims to have spent over 600 million dollars and acquired over 3,500 patents worldwide on FT and gas-to-liquid technologies [305]. Others firms, such as those listed in Table 6-3 (in the first column from the right), spent more than one billion dollars on R&D and they now own over 1,000 patents on FT processes. When a non-FT process, “ECLAIRS”, was presented to managers and engineers from some of these big firms, it was ignored. According to some interviewees, this is the familiar “not-invented-here syndrome”: managers and engineers of big firms are afraid of losing their jobs if they agree that ECLAIRS is better than their own technologies, so they refuse to accept it [306]. However, according to another interviewee, this syndrome is often used as a marketing technique and those who cite it are afraid of losing their own jobs as well [294]. A similar observation is that executives believe their jobs are safer if they develop the same technologies that others are working on. They are quoted as saying: “if everyone is wrong, then no one is better than us” [307].

6.6 Reward-to-Risk Ratio

The drivers for and barriers to improving existing processes and to developing new processes are very different from each other. For example, energy cost savings are a driver for improving existing processes, but not for developing new processes. This raises the question why these barriers and drivers in the two cases are so different. How important is energy efficiency to process innovation? What is the place of factors in the overall economic consideration? To find

answers to these questions, we need to take a step back and look at the fundamental rationale for making a decision concerning the investment in process innovation. This is explained here in terms of the reward-to-risk ratio¹. The reward-to-risk ratio, a risk-adjusted indicator of returns for a firm, is *reward* minus *opportunity costs* divided by *variability of competitors*.

- *Reward* is the result of subtracting opportunity costs from potential returns in the case of an innovation activity [308].
- *Opportunity costs* refers to the interest that the firm could obtain by depositing cash in a savings bank account or buying government bonds—instead of investing it in innovation [308]. This is the reference situation in which the firm does not engage in any innovation activities and therefore takes no risk.
- *Variability of competitors* refers to the market situation the firm faces [308]. It is expressed as the standard deviation, or the average differences of the profit performance among the firm's competitors.

Potential returns from an innovation activity are first adjusted by the risks of incurring opportunity costs and then by the risks of falling behind its competitors. The reward-to-risk ratio is an indicator of the comparative advantage that a firm gains over its competitors by investing and engaging in innovation activities. The uncertainty of the reward-to-risk ratio is ultimately determined by the level of knowledge the firm has on the three components of the reward-to-risk ratios: potential returns, opportunity costs and the profit performance of competitors.

6.6.1 Uncertainties in Improving Existing Processes

In the case of improving existing processes, the uncertainty regarding reward-to-risk ratios is often low because much of the required knowledge on the three components of this ratio already exists.

- First, the *reward* from adopting most of the technologies involved in improving existing processes is rather well known. Figures on returns (i.e. costs and benefits) are

¹ This concept is derived from the Sharpe ratio or the reward-to-variability ratio. The Sharpe ratio is used to evaluate the risk-adjusted performance of an investment asset, or a trading strategy in the financial market [308]. It can also be used by non-financial firms, such as petrochemical manufacturers, to make decisions regarding the investment in innovation activities.

given in Section 6.5.1. Most of these technical and economic data have been “tried and proven” through various scales of commercialization and therefore can be used to calculate potential returns.

- Second, *opportunity costs* can also be seen as quite certain over the next few years. Improving existing processes typically requires a payback period of less than a year or a few years. The interest on a risk-free investment over this time scale is rather well-known.
- Third, *variability of competitors* is insignificant in this case. As stated earlier, revamp is a common practice and the costs involved in revamps are similar for each existing plant. The risks of falling behind each other can be seen as being shared, or equally distributed among the competitors. Such a low variability (the denominator) leads to high reward-to-risk ratios.

Given this knowledge on the rewards and risks involved in improving existing processes, firms are often rather certain about the significance of reward-to-risk ratios (see drivers in Section 6.5.1.1). Energy efficiency improvement is often the primary source of returns from improving existing processes. In virtually all firms contacted for this study, improving energy efficiency in existing processes, regardless whether it is innovation or not, is appreciated as giving a competitive advantage, although it is not always at the top of the priority list (see barriers in Section 6.5.1.2). This perception is reflected in a common remark made by our interviewees: energy efficiency improvement is usually carried out as a routine activity to improve operational performance in most firms and is always a highly desirable and possible outcome of improving existing processes. In contrast to developing new processes, improving existing processes essentially concerns operational performance, and is not of strategic importance.

6.6.2 Uncertainties in Developing New Processes

In contrast to improving existing processes, the uncertainty regarding reward-to-risk ratios is often high in the case of developing new processes since much of the required knowledge on the three components of the reward-to-risk ratio either does not exist or is still being developed.

First, the *reward* from developing new processes is much more difficult to assess than that from improving the existing processes. This is illustrated by the large ranges of investment costs as given in Section 6.5. In an unfavorable economic situation, there is no or little reward for developing new processes that reduce CO₂ emissions (see Section 6.5.2).

Second, due to the long period of time required for developing new processes, *opportunity costs*, or long-term interest rates over several decades, have to be estimated. Development of methane-to-chemicals and fuels technologies has taken over 30 years (see Section 6.5.2).

Third, *variability of competitors* is high and the market situation is complex because of globalization in the petrochemical industry. There are so far no clear signs of policy incentives that can encourage developing new processes in the face of low ethane costs in the Middle East and the lack of level playing field (see Section 6.5.2).

Given that in developing new processes there is so little knowledge on rewards and risks, firms are naturally highly uncertain about rewards and risks (see barriers in Section 6.5.2.2). In fact, they do not calculate reward-to-risk ratios merely on the basis of the energy efficiency of any individual new process, but instead first consider reward-to-risk ratios as part of their strategic scenario planning.

In contrast to conventional planning and decision-making tools that try to predict a single future based on extrapolation, strategic scenario planning is a way to imagine multiple possible futures. Scenario planning is not the magic solution to uncertainty problems, but it helps firms prepare themselves for a wider range of possibilities than traditional tools do. Scenario planning lays the groundwork for developing an innovation strategy. Long-term (several decades), innovation-based scenario planning helps guide a firm to prepare its energy/feedstock supply and technological capabilities and ensures high reward in the future regardless of which scenario will come true. Innovation strategies are often discussed as part of scenario planning and risk management [309, 310]. The execution of such strategic planning is currently a main obstacle [311].

In a strategic scenario planning, multiple possible scenarios on feedstock supply, economic growth rates and competitor behavior are considered—so that returns and risks can be estimated

or defined (i.e. opportunity costs and market situation). An example of such planning is shown in Figure 6-4. By considering various possibilities, strategic scenario planning can help guide the overall direction of innovation, estimate reward-to-risk ratios and create certainties for making investment decisions. Strategic scenario planning has led major firms to invest billions of dollars in the development of natural gas, coal and biomass-to-chemicals and fuels processes (see Table 6-3). These innovation activities are known as “option values”, which means firms invest in new processes that use low-cost, alternative feedstocks in order to hedge the risk of falling behind their competitors who might do the same.

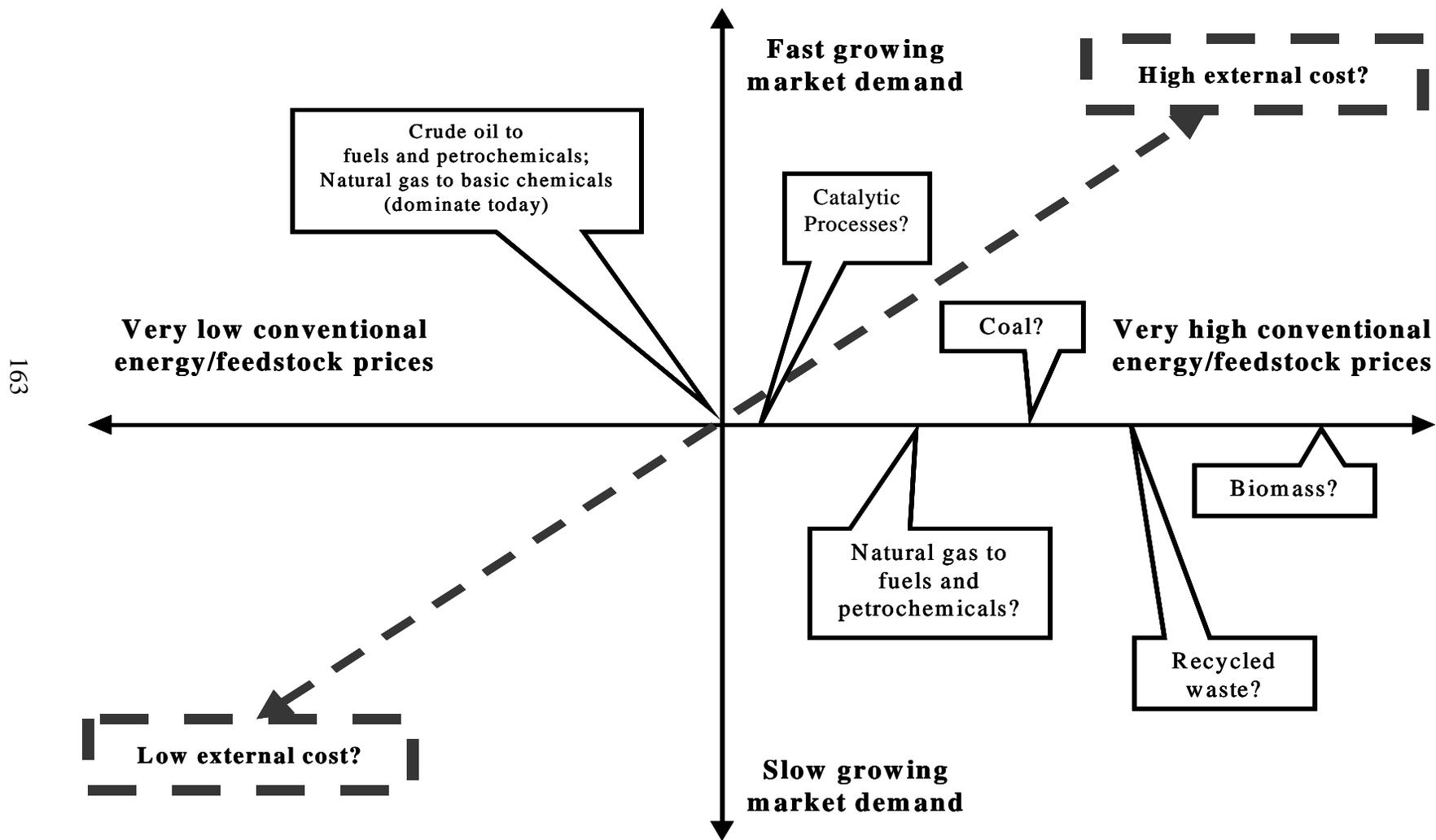
Since many important issues other than energy efficiency are involved in developing new processes, it is not surprising that none of the companies contacted for this study treats energy efficiency as a major priority or the primary source of returns when developing new processes. The competitive advantage of new processes over conventional processes is not related to energy efficiency as in the case of improving existing processes. Rather, their competitive advantage lies in the relatively low feedstock costs (see drivers in Section 6.5.2.1).

The rate of return from using a new, low-cost feedstock is about 4-5 times larger than that from using a more energy efficient technology in existing processes (see figures in Section 6.5.1.1 and 6.5.2.1). Many of our interviewees agreed that energy efficiency is always relevant to the development of new processes, but the weight given to energy efficiency is determined by the specific technological and economic context. This means that feedstock economics (e.g. coal-derived naphtha is relatively inexpensive in comparison with naphtha derived from crude oil) is considered first and that energy efficiency in itself is not necessarily the primary source of returns when new processes are developed.

As mentioned above, as far as strategic scenario planning is concerned, feedstock economics is of strategic importance. Therefore, developing new processes should be seen as a strategic innovation¹. The greater strategic importance of feedstock economics over energy efficiency explains why new processes are of great importance to companies, even though they are often less energy efficient than the existing processes.

¹ Strategic innovation refers to technological innovations with a specific, strategic purpose as defined in strategic scenario planning. It is different from strategic science research, which refers to “basic research carried out with the expectation that it will produce a broad base of knowledge likely to form the background to the solution of recognized current or future practical problems” [312].

Figure 6-4 an Example of Strategic Scenario Planning in a Petrochemical Firm



6.7 Innovation in Japan and China

As stated earlier, our case study was limited to the US and Europe, and our main findings related to big, global firms. There is very little public literature on innovation in basic petrochemical processes in other regions, such as East Asia, where several important petrochemical producers are located. Nevertheless, it is necessary to add a few words on the situation in East Asia. Some of the interviewees had worked in these regions, and they have given us some interesting insights.

Japan has no own energy resources and for a long time it has relied on global engineering firms such as ABB Lummus and Stone & Webster to acquire petrochemical processes. Their own R&D and equipment manufacturing started in the late 1980s. As stated earlier, several Japanese petrochemical producers have adopted gas turbines in steam crackers since the 1970s. Today, Japanese steam crackers are among the most efficient in the world [296]. Japanese firms are very active in R&D on energy efficient catalytic cracking of naphtha. However, energy efficiency improvement is not without its challenges. The adoption of gas turbine requires expensive natural gas. When electricity has to be sold, there is the competition from nuclear power plants. Energy savings and catalysis were ranked as the least important area for Japanese government-sponsored R&D in 2003, and only 12% of all R&D budget targeted energy savings and catalysis-related environmental technologies [313]. The percentages of sales spent on R&D in large Japanese firms are usually either similar to or lower than those of their American or European competitors [314].

Only occasionally is the reduction of CO₂ emissions claimed to be a primary objective for innovation in Japan. An example is Mitsubishi's CO₂-free gas-to-liquids process [173] (discussed in Chapter 3). This process avoids oxygen production and includes CO₂ separation and recycling. The benefits from electricity savings and increased yield outweigh the additional cost of energy that is used to recover CO₂. We argue that investment cost savings and carbon efficiency are the fundamental objectives in this case. Reduction of CO₂ emissions is merely an additional benefit.

In China, firms have also relied on technology transfer of chemical processes from the former Soviet Union and Western countries in the past. However, since the early 1990s, Chinese firms have adopted the international practice of acquiring licenses for proprietary processes while setting up joint-ventures with foreign firms [296]. In recent years, China's own capacity in engineering, equipment manufacturing and construction has been growing fast. In many recent projects, Chinese firms have been using their own engineering and equipment while purchasing only licenses. Like most producers in the world, Chinese firms are risk-averse as they mostly prefer only "tried-and-proven" technologies. There is much state-funded R&D on basic petrochemical-related processes while firm-based R&D only began very recently. Little official data on R&D spending was published. In recent years, new processes using low-value feedstocks, such as heavy oils and coal-to-chemicals, have undergone intensive R&D. Plans have been made for large-scale plants.

The implementation of innovative technologies has been very slow in China. Chinese producers fear for domestic overcapacity since the low-cost Middle East producers are also adding new plants. Recently, the Chinese government has emphasized the development of high-value fine and specialty chemical sectors. Investment opportunities in the refinery, logistics and transportation sectors are restricted by the government. An Energy Conservation Law was passed in 1997 to promote long-neglected energy efficiency improvement and related innovations. A Renewable Energy Law was passed in 2005 to stimulate the development of alternative energy. Detailed guidelines for the implementation of these laws are still being developed. Besides all this, there are many more institutional, policy and infrastructure barriers to innovation in China. Further research in this area is much needed.

6.8 Comparison with Earlier Research

Our findings are now compared with earlier research on drivers for innovation in the chemical industry. Energy cost savings as a driver for improving existing processes (Section 6.5.1.1) are consistent with two of the main drivers for process intensification mentioned in [315]. The drivers for developing new processes (Section 6.5.2.1) are similar to the top five drivers¹ for

¹ These five drivers are previous innovation expertise in related fields, market demand, technological advances, raw material advantages and competition [316].

radical innovations in the chemical industry in 1930-1985 discussed in [316], but in reverse order due to increased interest in energy and environmental issues since the 1990s. The conclusion that innovation is driven by reduction of production costs is similar to the conclusion of other studies [29, 317, 318]. However, the findings of this chapter place specific emphasis on energy costs and energy efficiency. In addition, these results are consistent with the earlier conclusion that the reduction of uncertainty is a central feature in innovation in petrochemical products [19]. These findings specified two areas with the highest uncertainty: costs and supply of energy/feedstocks; prospects of economic growth and market demand.

Next, our findings are compared with earlier research on *barriers*. This chapter focuses on energy efficiency issues more than other studies did. The barriers we found to improving existing processes confirm the results of the European Community Innovation Survey II (CIS II), which concludes that chemical firms in Europe do not consider changes in material consumption and energy efficiency improvement as important objectives for process innovation [263]. The US Manufacturing Energy Consumption Survey drew similar conclusions [319]. Although these barriers have some overlapping with those identified by engineering experts [315, 320], they are more specific and can be used directly for considerations on energy efficiency related issues. Furthermore, the barrier of a “lack of staff and time” from these findings is related to “the lack of information”, which was considered to be the most important barrier to energy efficiency improvement in Europe [321].

Additionally, this study’s results can explain the economic barriers that were previously found. The top two barriers to innovation in new or improved basic chemical processes identified by the European Community Innovation Survey I (CIS I) were high costs of innovation and a lack of financial resources [29]. According to the innovation procedure described in Section 6.4, low rates of success can cause high costs of innovation (see costs of innovation in Section 6.5.2). A lack of financial resources is indicated in Table 6-2 by low R&D spending and intensity (all within 0.4%-3.1%, except for 8% at ABB). Barriers listed in Section 6.5.2.2 can at least partially explain the reason for the results of CIS I.

Finally, these results can also provide some explanations for other barriers to innovations in the general chemical industry. The top three barriers to alternative synthetic pathways identified by

an IPTS expert inquiry are as follows: lack of incentives/pressures to be environmentally friendly, lack of research funds and structural/industrial/commercial barriers [322]. Our review of the chemical industry related regulations also indicated that previous regulations have not provided strong incentives for energy efficiency improvement in basic chemical processes. Regarding structural/industrial/commercial barriers, our findings show that these barriers are strongly related to ever-intensifying globalized competition and that there is a lack of new modeling tools to deal with uncertainties.

6.9 Conclusions

In this chapter, we have identified a number of drivers and barriers to energy efficiency improvement and innovation in basic petrochemical processes. The basic differences between these drivers and barriers can be understood in terms of different levels of knowledge and uncertainties regarding the reward-to-risk ratios. Improving existing processes concern innovations that are much better known and involve lower risks than the innovations needed for the development of new processes.

We conclude that for both types of innovation, energy efficiency is always a highly desirable and possible outcome. However, because its importance is determined by the technological and economic context, in itself it is not necessarily always a major priority. In the case of strategic innovations (i.e. developing new processes using low-cost feedstocks), relative feedstock economics are considered first because of their importance for the long term. This explains why new processes are often less energy efficient than the existing processes. Nevertheless, they are strategically important. Therefore, these new processes deserve much attention from policymakers who are interested in stimulating innovations in the chemical industry.

Summary and Conclusions

Many chemicals (e.g. plastics, rubber, solvents) that we use every day are made from basic petrochemicals, the so-called building blocks of the chemical industry. Important basic petrochemicals are light olefins (e.g. ethylene and propylene) and aromatics. Hence, the technologies for producing these chemicals are seen as the backbone of the chemical industry. Most basic petrochemicals are currently produced from crude oil and natural gas-derived naphtha and ethane through the use of conventional technologies such as oil refinery processes and steam cracking. In 2004, basic petrochemicals accounted for more process energy use (about 3 EJ fuels combusted) and CO₂ emissions (about 200 million tons) in total than any other type of chemical. Like all other highly energy-intensive industries, the petrochemical industry is facing the dual challenges of climate change and security of energy supply. Therefore, it is of interest for energy researchers and policymakers as well as chemical engineers to gain a greater understanding of both the potential of energy efficiency improvement and the options of using alternative primary energy sources (e.g. methane, coal or biomass) for the production of basic petrochemicals.

Besides the state-of-the-art technologies that utilize the conventional primary energy sources crude oil and natural gas, there are a number of more energy efficient technologies for basic petrochemicals production. In addition, there are several innovative technologies that use alternative primary energy sources to produce feedstocks for basic petrochemicals. Methodologies for assessing these technologies, such as energy analysis, are readily available. However, so far there have been no comprehensive studies in which these methodologies have been applied to cross-compare the technologies mentioned above and to explore their future prospects.

Given this knowledge gap, we defined the central research question as: *What are the prospects of improved and new technologies for basic petrochemicals production in comparison with conventional state-of-the-art technologies?* Subsequently, three sub-questions can be derived from the central research question:

- *Environment* What is the environmental effect in terms of energy use and CO₂ emissions of improved technologies and innovative technologies utilizing alternative primary energy sources in comparison with conventional technologies?
- *Economics* What is the economic potential in terms of production costs of innovative technologies utilizing alternative primary energy sources in comparison with conventional technologies?
- *Innovation* Which drivers, barriers and strategies influence the innovation process of improved and new process technologies?

The main methodologies used in this thesis are literature research and quantitative analysis of energy use and production costs. Interviews with experts in the oil, gas and petrochemical industry were also conducted.

Regarding the *environmental* aspects, we first reviewed the literature on energy analysis of the steam cracking processes¹ based on naphtha derived from crude oil and ethane derived from natural gas (see Chapter 2). The basis for the comparison of energy use is the specific energy consumption in gigajoule (GJ) per ton of high value chemicals (light olefin value equivalent), or GJ/t HVCs. The specific energy consumption is expressed as lower heating value of fuels combusted during the production process (excluding the calorific value of high value chemicals).

The main findings are:

- The specific energy consumption in state-of-the-art naphtha steam cracking technologies is about 11 GJ/t HVCs, of which roughly 4-5 GJ/t HVCs becomes part of the calorific value of the final products (due to the endothermicity effect²).
- An overview of the state-of-the-art naphtha steam cracking technologies shows that savings of approximately 20% are possible compared to the current world average energy use in steam cracking.

¹ Following the first step feedstock production (i.e. refinery for naphtha production and natural gas processing for ethane production), steam cracking is the second step of the conventional routes for the production of petrochemicals.

² This means that 4-5 GJ/t HVCs is not lost, but embedded in the final products. The remaining 6-7 GJ/t HVCs is the actual energy use (which is part of the cumulative process energy use, a term used in Chapter 3 and Chapter 4).

- In the naphtha steam cracking process, the pyrolysis section consumes 50-65% of the energy use. Advanced naphtha steam cracking technologies in the pyrolysis section, such as advanced coil and furnace materials, together can lead to savings of up to about 20% compared to the energy use in state-of-the-art naphtha steam cracking technologies. Together with the potential improvements in the compression and separation sections, savings of up to 30% are possible compared to the energy use in state-of-the-art naphtha steam cracking technologies.
- Alternative processes utilizing low-cost, crude oil-derived heavy feedstocks, i.e. catalytic olefin technologies, can lead to savings of up to about 20% compared to the energy use in state-of-the-art naphtha steam cracking technologies.

As a petrochemicals production process, steam cracking is part of a route from primary energy sources to petrochemicals (a route consists of feedstock production and petrochemicals production). In Chapter 3 and Chapter 4, we compared three conventional and 21 alternative routes. The basis for comparison is: *total energy use* (the sum of cumulative process energy use and the calorific value of the high value chemicals) and *total CO₂ emissions* (the sum of cumulative process CO₂ emissions and the carbon content of HVCs). The main findings are:

- *Total energy use* The most energy efficient routes are the state-of-the-art conventional technologies that utilize naphtha and heavy feedstocks derived from crude oil and ethane derived from natural gas. Their total energy use is about 60 GJ/t HVCs, of which 10 GJ/t HVCs is the cumulative process energy use (in feedstock production and petrochemicals production) and 50 GJ/t HVCs is the calorific value of HVCs. The total energy use of methane-based routes is 30% higher and that of the coal and biomass-based routes is about 60-150% higher than that of the conventional routes (see Chapter 3 and Chapter 4);
- *Total CO₂ emissions* The total CO₂ emissions of conventional and methane-based routes are similar (4-5 ton CO₂/t HVCs). The total CO₂ emissions of coal-based routes are by far the highest (8-11 CO₂/t HVCs), with an exception of a coal-based route with CO₂ capture and storage whose CO₂ emissions are similar to those of the

conventional routes. It is technically possible to add CO₂ capture and storage to any of the routes mentioned. The total CO₂ emissions of biomass-based routes range from 2 ton CO₂/t HVCs (a maize-based ethanol related route) to 4 ton of *avoided* CO₂/t HVCs (a lignocellulosic biomass-based Fischer-Tropsch route). Avoided CO₂ emissions are due to electricity cogeneration and the use of biomass-derived energy.

Regarding the *economic* aspects, we performed an economic analysis of the 24 routes mentioned above (see Chapter 5). The basis for comparison is production costs in \$/t HVCs. According to various energy and policies scenarios found in the literature, energy prices in 2030-2050 are projected to be:

- oil \$26-60/bbl;
- natural gas \$4-8/GJ;
- coal \$37-57/t;
- biomass \$1-5/GJ;
- plastic waste \$120-220/t;
- electricity production costs \$0.03-0.05/kWh.

Using these assumptions, we calculated a range of production costs for each of the 24 routes. Then, we used a Monte Carlo analysis method to rank production costs in the future. For the analysis, 10,000 trials of energy prices were conducted based on the correlations between energy prices derived from historical and projected trends. The effect of CO₂ emissions costs was also tested (randomly varying from \$0/t to \$100/t CO₂; these are the cradle-to-grave or total CO₂ emissions, which means that the carbon content of products is included). The main findings are:

- *Range* While the costs of crude oil and natural gas-based routes are mostly within \$500-900/t HVCs, those of coal and biomass-based routes are mostly within \$400-800/t HVCs. Production costs of coal and biomass-based routes are quite similar to each other.

- *Ranking* Among the top seven most expensive routes, six are crude oil and natural gas-based. Among the top seven least expensive routes, six are coal and biomass-based.
- The effect of CO₂ emissions costs was tested and was found to be strong on coal-based routes and also quite significant on biomass-based routes. The effect on other routes was found to be relatively small or moderate. If the current CO₂ related policies are assumed for 2030-2050 (meaning that the carbon content of products from all routes is excluded from the calculation of CO₂ emissions costs described above), the ranking of coal-based routes improves most and that of the oil and natural gas-based routes improves least. The ranking of biomass-based routes worsens if the carbon content of products is excluded from the calculation of CO₂ emissions costs. However, the general findings do not change.
- In a separate analysis, the effect of energy prices at the level of prices seen in the first three quarters of 2008 was tested (these prices were much higher than those projected for 2030-2050). Most of the coal-based routes and biomass-based routes (in particular the sugar cane-based route) were found to have significantly lower production costs than oil and gas-based routes, even if international freight costs are added.
- Under specific conditions, the supply of oil and natural gas will possibly not be sufficient for making petrochemicals and therefore 15-30% of the demand in 2030-2050 will have to be met by coal and biomass. These specific conditions are: 1) oil production stagnates at a plateau of 125 mbpd (million barrels per day) in 2030-2050; 2) the same percentage of crude oil and natural gas (i.e. ethane and natural gas liquids) is used for petrochemicals as in the past; 3) the annual growth rate for petrochemicals demand is 3% in the period of 2008-2050.

Regarding the *innovation* aspects, we first looked at the innovators/networks and procedures of innovation in basic petrochemical processes to gain insight into current innovation activities. Subsequently, over 30 interviews were conducted with experts from the refinery and petrochemical industries. A number of drivers and barriers to energy efficiency improvement

and innovation in basic petrochemical processes were identified (see Chapter 6). The main findings are:

- For different types of innovation activities, there are different drivers and barriers. For improving existing processes (conventional routes), the main drivers are energy cost savings, tight supply of gas feedstocks and personal commitment of individuals. The main barriers are staff and time shortages, competition from other prioritized projects and existing process configurations.
- For developing new processes (alternative routes), the main drivers are the use of low-cost feedstocks (derived from alternative primary energy sources) for producing high-value chemicals, competition among firms and the wish to broaden the application of existing knowledge. The main barriers are unfavorable economic situations, insufficient modeling tools and concerns for job security.
- The basic differences between these drivers and barriers can be understood in terms of different levels of knowledge and uncertainties regarding reward-to-risk ratios. Improving existing processes involves lower risks and much better known innovations than developing new processes.
- As far as improving existing processes is concerned, energy efficiency improvement is usually carried out as a routine activity to improve operational performance. Although energy efficiency is always a highly desirable outcome of improving existing processes, in itself it is not of strategic importance.
- As far as developing new processes is concerned, energy efficiency is always a relevant issue, but feedstock economics are of strategic importance. New processes are in fact strategic innovations. Therefore, the relevance of energy efficiency for innovation in basic petrochemical processes is determined by the specific technological and economic context. This explains the strategic importance of new processes even if they are often less energy efficient than the existing processes.

The findings on the three aspects described above (i.e. environment, economics and innovation) are the answers to the central research question. Based on these findings, we conclude that the innovative technologies discussed in this thesis have the technical and economic potential for the petrochemical industry to deal with the dual challenges it faces, i.e. climate change and the security of energy supply. We also conclude that there are complex barriers and drivers related to energy efficiency and strategic innovations. These barriers and drivers need further consideration by policymakers. The following proposals may serve as a starting point:

- First, given the importance of utilizing alternative primary energy sources as a strategic innovation for the petrochemicals industry, policymakers can expect methane, coal or biomass—alongside the conventional crude oil—to be used for at least part of basic petrochemicals production in the future. Therefore, policies are needed to steer the development of methane, coal and biomass-based process technologies so that they will become both economically and environmentally sustainable.
- Second, given the significant differences between conventional routes and alternative routes on energy efficiency, CO₂ emissions and production costs, policy incentives are necessary to encourage R&D on energy efficiency improvement of biomass-based routes, especially those based on lignocellulosic biomass with electricity cogeneration. The development of coal-based routes should only be encouraged if CO₂ capture and storage is applied in an environmentally sound and socially responsible way.
- Third, given the strong effect of policy certainty on the long-term strategic scenario planning in many large chemical firms, a level playing field (a global biomass market within a global CO₂ emissions trading system) is needed to promote the construction and development of biomass-related infrastructure. Clear direction in this policy area will enable the global petrochemical industry to make long-term investment decisions and to take full advantage of the immense business opportunities offered by the current market for environmentally friendly technologies and petrochemical products.

Samenvatting en conclusies

Allerlei stoffen, zoals plastic en rubber, die wij dagelijks gebruiken, worden geproduceerd uit petrochemische stoffen, die ook wel de bouwstenen van de chemische industrie worden genoemd. De belangrijkste petrochemische stoffen zijn olefinen (bv. etheen en propaan) en aromaten. De petrochemische productie is de eerste stap in de chemische industrie. Petrochemische stoffen worden tegenwoordig geproduceerd uit de grondstoffen aardolie en aardgas door middel van conventionele technologieën zoals destillatie en stoomkraken. In 2004 waren petrochemische stoffen verantwoordelijk voor meer energiegebruik (drie exajoule) en CO₂ emissie (twee honderden miljoen tonnen) dan andere soorten chemicaliën. De petrochemische industrie wordt geconfronteerd met twee uitdagingen: klimaatverandering en energievoorzieningszekerheid. Vele chemische bedrijven, onderzoekers en beleidsmakers zijn dus zeer geïnteresseerd in innovatieve routes waarbij de energie-efficiëntie verhoogd wordt of waarbij andere energiebronnen gebruikt worden voor de petrochemische productie (bv. methaan, steenkolen of biomassa).

Deze innovatieve technologieën staan beschreven in de literatuur. Hoewel er wel methodes bekend zijn om de productieroutes te vergelijken van petrochemische stoffen vanuit de belangrijkste primaire energiebronnen (bv. aardolie, aardgas, kolen en biomassa), zoals energieanalyse, ontbreekt er tot op heden een alomvattende studie waarbij deze vergelijking wordt gemaakt.

Met het oog op deze lacune hebben we de onderzoeksvraag als volgt gedefinieerd: wat zijn de mogelijkheden voor de verbeterde en nieuwe productieprocessen van petrochemische stoffen, in vergelijking met de conventionele productieprocessen? Uit deze vraag komen drie aspecten naar voren:

- *Milieu* Wat zijn, in termen van energieverbruik en CO₂ emissie, de milieueffecten van de productieprocessen die alternatieve grondstoffen gebruiken vergeleken met de conventionele productieprocessen?
- *Economie* Wat is het economisch potentieel van de productieprocessen die alternatieve grondstoffen gebruiken, in termen van productiekosten?

- *Innovatie* Welke barrières en stimulansen hebben invloed op het innovatieproces van de verbeterde en nieuwe productieprocessen van petrochemische stoffen?

Deze drie aspecten zijn bestudeerd door middel van literatuuronderzoek, kwantitatieve analyse van energiegebruik en productiekosten, interviews met deskundigen uit de olie, gas- en petrochemische industrie.

Vanuit het *milieu* perspectief hebben we eerst een literatuuronderzoek gedaan en vervolgens een energieanalyse uitgevoerd voor het energieverbruik van het meest geavanceerde stoomkraakproces¹ op basis van nafta uit aardolie (hoofdstuk 2). De vergelijking vindt plaats op basis van het specifieke energiegebruik in gigajoule per ton van hoogwaardige chemicaliën, of GJ/t HVCs (bv. olefinen zoals ethyleen). Dit is hetzelfde als de energie-inhoud van de brandstof die gebruikt wordt tijdens het productieproces (dus exclusief de energie-inhoud van de chemicaliën). Er kunnen vier conclusies worden getrokken:

- Het specifieke energiegebruik van het meeste geavanceerde stoomkraakproces op basis van nafta is ongeveer 11 GJ/t HVCs, waarvan ongeveer 4 à 5 GJ/t HVCs deel uitmaakt van de calorische waarde van de chemicaliën (i.v.m. het zogenoemde endotherme effect²).
- Het specifieke energiegebruik van het meeste geavanceerde stoomkraakproces op basis van nafta is 20% minder dan het gemiddelde stoomkraakproces.
- Bij het stoomkraakproces op basis van nafta verbruikt de pyrolyse reeds 50-65% van het totale specifieke energiegebruik. Ongeveer 20% van het energieverbruik kan bespaard worden door het gebruik van verbeterde materialen voor het kraakproces. Samen met de verbetering bij de compressie en scheidingprocessen is een energiebesparing mogelijk van in totaal 30%.

¹ Stoomkraken is de tweede stap van de conventionele productieroute (destillatie is de eerste stap).

² Dit betekent dat 4-5 GJ/t HVCs niet verloren gaat, maar deel uitmaakt van het uiteindelijke product. De rest, 6-7 GJ/t HVCs, is het werkelijke energiegebruik (een deel van het cumulatieve energiegebruik; zie hoofdstuk 3 en 4).

- Ongeveer 20% van het energieverbruik van het meeste geavanceerde stoomkraakproces kan bespaard worden door het gebruik van katalytische olefine-technologieën gebaseerd op laagwaardige bijproducten van de olieraffinaderij.

Vervolgens hebben wij het energiegebruik van drie conventionele productieroutes en 21 alternatieve routes vergeleken (hoofdstuk 3 en 4). Deze vergelijking vond plaats op basis van het totale energiegebruik per ton hoogwaardige chemicaliën (inclusief het cumulatieve procesenergiegebruik en de energie-inhoud van chemicaliën) en de totale CO₂-emissie (inclusief cumulatieve proces CO₂-emissie en de koolstofinhoud van chemicaliën). De conclusies zijn:

- *Energieverbruik* De meest energie-efficiënte routes zijn de conventionele routes waarbij nafta en laagwaardige bijproducten uit raffinaderijen en ethaan worden gebruikt. Het totale energiegebruik van de conventionele routes is ongeveer 60 GJ/t HVCs, waarbij het cumulatieve proces-energiegebruik verantwoordelijk is voor 10 GJ/t HVCs en 50 GJ/t HVCs voor rekening komt van de energie-inhoud van de HVCs. Het totale energiegebruik van de methaan-productieroutes is 30% hoger en dat van steenkolen en biomassa routes is 60-150% hoger dan dat van de conventionele routes (zie hoofdstuk 3 en 4).
- *CO₂-emissie* De totale CO₂-emissie van de conventionele routes en van de methaanroutes zijn bijna hetzelfde (4 à 5 ton CO₂ per ton HVCs). De totale CO₂-emissie van de steenkolenroutes is het hoogst (8 à 11 ton CO₂ per ton HVCs). De totale CO₂-emissie van een steenkolenroute met CO₂-opvang en-opslag (CCS) is 4 ton CO₂ per ton HVCs. CCS is technisch mogelijk voor alle routes. De totale CO₂-emissie van de biomassa-routes is tussen 2 ton CO₂ per ton HVCs (voor een maïs-ethanol route) en -4 ton CO₂ per ton HVCs (voor een lignocellulose Fischer-Tropsch route). Een negatieve CO₂-emissie kan het gevolg zijn van de coproductie van elektriciteit of van het gebruik van biomassa als grondstof.

Vanuit *economisch* perspectief hebben we een economische analyse gemaakt voor de productiekosten van 24 routes waarbij primaire energiebronnen (bv. aardolie, aardgas, steenkolen en biomassa) omgezet worden in petrochemische stoffen (zie hoofdstuk 5). We

hebben eerst de verwachte prijzen verzameld van primaire energiebronnen voor de periode 2030-2050, afkomstig uit verschillende energiescenario's. De verwachte kosten komen uit op:

- aardolie \$26-60/bbl;
- aardgas \$4-8/GJ;
- steenkolen \$37-57/t;
- biomassa \$1-5/GJ;
- plastic afval \$120-220/t;
- elektriciteit \$0.03-0.05/kWh.

Op basis van deze energiekosten hebben wij de productiekosten van de 24 routes berekend. Vervolgens hebben wij een Monte Carlo-analyse gebruikt om de effecten in te schatten van de energiekosten (met een bepaalde correlatie) en de kosten van CO₂-emissie (\$0-100/t CO₂) op het concurrerend vermogen van deze routes. Hierbij wordt rekening gehouden met de totale CO₂-emissie. Verder worden in een aparte analyse de hoge energie prijzen van 2008 (veel hoger dan de verwachte prijzen in 2030-2050) getest. We zijn tot vijf conclusies gekomen:

- *Bandbreedte* Terwijl de kosten van olie en gas routes meestal tussen \$500-900/t HVCs liggen, liggen die van steenkolen en biomassa routes tussen \$400-800/t HVCs. De kosten van steenkolen en biomassa routes zijn vergelijkbaar.
- *Concurrentie* Zes van de zeven duurste routes zijn routes op basis van aardolie en aardgas, terwijl zes van de zeven goedkoopste routes op basis zijn van steenkolen en biomassa.
- *Kosten van CO₂-emissie* De kosten van CO₂-emissie kunnen leiden tot verhoogde productiekosten voor de steenkolenroutes. Bij andere routes is dit effect niet groot. Als wordt aangenomen dat het huidige CO₂-beleid ook voor 2030-2050 geldt (en er de koolstofinhoud van de chemicaliën buiten beschouwing blijft), worden de steenkolenroutes goedkoper (de olie- en gasroutes ook, maar minder), terwijl de biomassa-routes duurder worden. Op hoofdlijnen blijven resultaten hetzelfde.

- Het effect van de hoge energie prijzen in januari tot augustus 2008 werden getest. De productiekosten van de meeste steenkolen- en biomassa-routes (vooral de route op basis van suikerriet) zijn veel lager dan de olie- en gasroutes—ook als de vervoerkosten voor steenkolen en suikerriet (of chemicaliën) worden meegerekend.
- Als ervan wordt uitgegaan dat de olieproductie stagneert op een plateau van 125 mvpd (miljoen vatten per dag) in de periode 2030-2050, hetzelfde percentage van aardolie en aardgas (zoals ethaan) als vroeger wordt gebruikt voor de petrochemische productie, en de verwachte jaarlijkse groei voor de marktbehoefte aan chemicaliën wordt aangenomen voor de periode 2008-2050 3% is, dan kunnen de olie- en gasroutes niet voldoen aan de marktbehoefte aan chemicaliën in de periode 2030-2050. Ongeveer 15-30% van de globale capaciteit van de petrochemische productie zou dan van de steenkolen- en biomassa-routes moeten komen.

Vanuit het perspectief van innovatie, hebben wij eerst het netwerk, de bedrijven en de procedures van de innovatie van de petrochemische processen bekeken om een beter begrip te ontwikkelen van de innovatieve activiteiten in de petrochemische industrie. Vervolgens hebben we 30 interviews gehouden met deskundigen uit de petrochemische industrie om inzicht te verkrijgen in de strategieën, barrières en stimulansen voor het verbeteren van de energie-efficiëntie en innovatie in petrochemische processen (hoofdstuk 6). We zijn tot de volgende conclusies gekomen:

- Verschillende barrières en stimulansen horen bij verschillende innovatieve activiteiten. Voor het verbeteren van bestaande processen (conventionele routes) zijn energie- en kostenbesparingen, een krappe aanvoer van gasgrondstoffen en persoonlijke betrokkenheid van individuen belangrijke drijfveren. De belangrijkste obstakels zijn een tekort aan medewerkers en tijdgebrek, andere projecten die meer prioriteit krijgen en reeds bestaande procesconfiguraties.
- De belangrijkste drijfveren voor het ontwikkelen van nieuwe processen zijn het verbruik van laagwaardige grondstoffen waaruit hoogwaardige chemicaliën vervaardigd kunnen geproduceerd worden, concurrentie tussen bedrijven en de wens om de huidige kennis

meer toe te passen. De belangrijkste obstakels zijn het ongunstige economische klimaat, onvoldoende mogelijkheden voor het vervaardigen van modellen en bezorgdheid over arbeidsplaatsen.

- De verschillen tussen deze drijfveren en obstakels komen voort uit de verschillende kennisniveaus en uit de onzekere verhoudingen tussen winst en risico.
- Het verbeteren van de energie-efficiëntie in bestaande processen wordt in de meeste bedrijven niet als strategische innovatie gezien, maar vormt een onderdeel van de operationele activiteiten. Desalniettemin is het verbeteren van energie-efficiëntie altijd een zeer wenselijke uitkomst van het verbeteren van bestaande processen. Het verbeteren van bestaande processen betreft innovaties die veel beter bekend zijn en dus veel lagere risico's vertegenwoordigen dan het ontwikkelen van nieuwe processen.
- Voor het ontwikkelen van nieuwe processen wordt energie-efficiëntie altijd als relevant beschouwd, maar van strategisch belang zijn vooral de kosten en de verkrijgbaarheid van grondstoffen. Daarom zijn nieuwe processen een kwestie van strategische innovatie. Daarom wordt de relevantie van energie-efficiëntie bij de innovatie in chemische processen bepaald door de specifieke technische en economische context. Dit verklaart het strategische belang van nieuwe processen zelfs als zij vaak veel minder energie-efficiënt zijn dan de bestaande processen.

De bevindingen over de drie hierboven beschreven aspecten (milieu, economie en innovatie) zijn de antwoorden op de centrale onderzoeksvraag. Gebaseerd op deze bevindingen concluderen wij dat de innovatieve technologieën die in dit proefschrift worden onderzocht het technische en economische potentieel hebben om de dubbele uitdagingen voor de petrochemische industrie, namelijk klimaatverandering en de veiligheid van energievoorziening, het hoofd te bieden. Wij concluderen ook dat er complexe barrières en stimulansen met betrekking tot energie efficiëntie en strategische innovaties zijn. Met deze barrières en stimulansen moet rekening gehouden worden bij de beleidsvorming. De volgende voorstellen kunnen als uitgangspunt dienen:

- Allereerst, vanwege het belang van alternatieve primaire energiebronnen als strategische innovatie voor de petrochemische industrie, kunnen de beleidsmakers er vanuit gaan dat

methaan, steenkolen of biomassa in de toekomst gebruikt zal worden voor tenminste een deel van petrochemische productie. Daarom is er specifiek beleid nodig om de ontwikkeling te sturen van procestechnologieën op basis van methaan, steenkolen en biomassa, zodat zij zowel economisch duurzaam als milieuvriendelijk zullen worden.

- Ten tweede, gezien de significante verschillen tussen de conventionele en alternatieve routes op het gebied van energie-efficiëntie, CO₂-emissies en productiekosten, zijn beleidsinspanningen noodzakelijk om onderzoek en ontwikkeling te stimuleren op het gebied van verbetering van energie-efficiëntie van biomassa-routes, vooral de routes op basis van lignocellulose-biomassa met coproductie van elektriciteit. De ontwikkeling van routes op basis van steenkolen zou slechts moeten worden gestimuleerd op voorwaarde dat CO₂-afvang en -opslag op een milieuvriendelijke en sociaal verantwoordelijke manier gebeurt.
- Ten derde, aangezien beleidszekerheid in vele grote chemische bedrijven een sterk effect heeft op de strategische scenarioplanning op lange termijn, is een op het rechtvaardigheidsprincipe (level playing field) gebaseerde globale biomassamarkt nodig binnen een globaal handelssysteem in CO₂-emissies om de ontwikkeling te bevorderen van een infrastructuur voor biomassa. Een duidelijke richting in dit beleidsgebied zal het mogelijk maken voor de wereldwijde petrochemische industrie om te besluiten tot lange-termijn investeringen. Zo kan volledig gebruik worden gemaakt van de immense bedrijfskansen die de huidige markt voor milieuvriendelijke technologieën en petrochemische producten biedt.

摘要

传统的化工生产途径是先把原料从原油和天然气提炼出来，然后通过蒸汽裂化过程转化为乙烯，丙烯，芳族等基本化工产品，最后再把这些产品加工成其它化学产品(比如塑料等等)。这种蒸汽裂化过程是现代石油化工产业的构建中枢。但是，这个生产途径也是当今所有化工生产中消耗能量最高的环节。2004年因此消耗能量高达3EJ而且排放的二氧化碳高达200万吨。传统的化工生产途径并不是的生产化工产品的唯一途径。新型的化工生产途径可以利用其它能源(如甲烷，煤炭，废弃塑料和生物质能)来替代传统的原油和天然气来生产乙烯，丙烯，芳族等基本化工产品。另外，用改良的生产技术来高效率地利用能源也是可能的。能源多元化和能源高效率利用对于目前我们面临的全球气候变化和能源供给问题来讲，具有深远的经济和环境意义。因此，现在研发的改良的和新型的化工生产技术很可能成为未来的一个可持续发展的化工产业需要的战略性的技术创新。

当前，利用甲烷(天然气的主要成分)，煤炭或生物质能为替代能源来生产运输燃料的技术途径已经是重点研究的领域。但是，这些新型的技术途径在化工生产上的应用还未受到应有的关注。迄今为止，关于化工生产的科技文献仍然很缺乏对能源多元化和能源高效率利用方面的全面深入的比较性分析。为了填补这个知识空缺，本文从科技、经济和创新三个角度上来阐述改良的和新型的基本化工产品生产途径。从技术角度上，本文将对利用多种能源的，不同的基本化工产品生产途径的能量消耗和二氧化碳排放量进行比较分析；从经济角度上，本文将集中讨论这些生产途径的生产成本和在未来的设定情形下的可行性和竞争力；从创新角度上，本文将涉及战略性创新中遇到的阻碍和推动力量。

从技术角度上，我们首先对最具有代表性的石脑油蒸汽裂化技术进行能量消耗分析¹。最具有代表性的石脑油蒸汽裂化技术当今使用燃料(不含化工产品自身的能量)约11GJ/吨HVCs(HVCs指相当于乙烯和丙烯的高价值化工产品)，但其中4-5GJ/吨HVCs转化为化工产品中化学能²。这比世界平均石脑油蒸汽裂化的能量消耗低20%。我们发现，在熔炉内的高温蒸汽裂化这一过程大约占据了总过程能量消耗的50到65%。通过利用改进的熔炉材料可以节约总过程能量消耗的20%。加上在压缩和分离部位的改进，总能量消耗可以节约高达30%。另外，新型的催化裂化反应比最具有代表性的石脑油蒸汽裂化技术能量消耗要低20%。之后，我们又对24个利用多种能源的(原油、天然气、煤炭、生物质能以及废弃塑料)，不同的基本化工产品生产途径进行了能量消耗和二氧化碳排放分析。我们发现，就总能量消耗而言(含化工产品自身的能量)，在众多的途径中，能量消耗最低的生产途径是利用新型的催化裂化反应技术以及把最具有代表性的石脑油和乙烷蒸汽裂化技术，大约60GJ/吨HVCs(其中含总积累能量消耗10GJ/吨HVCs和化工产品自身的能量50GJ/吨HVCs)。生产同样的产品，用甲烷的途径要比以上提到的几个途径多消耗30%的能量，而用煤炭和生物质能的途径比以上提到的几个途径多消耗60-150%的能量(请看第三章和第四章)。以上提到的几个途径和用甲烷的途径排放大约相等量的二氧化碳(含使用燃料排放出来的二氧化碳和化工产品中

¹ 第二章只对石脑油蒸汽裂化技术进行能量消耗分析，而第三章包括对裂化技术的上游步骤(炼油)的能量消耗。

² 4-5 GJ/吨 HVCs 并未消耗掉。其余的 6-7 GJ/吨 HVCs 才是真正消耗掉的能量(这些消耗的能量是总积累能量消耗的一部分;请看第二章)。

的碳成分), 4-5吨/吨HVCs. 用煤炭的几个途径排放二氧化碳大约8-11吨/吨HVCs. 有一个用煤炭的途径配备了二氧化碳的收集和埋藏技术, 所以排放二氧化碳只有4吨/吨HVCs. 二氧化碳的收集和埋藏实际上对所有途径都技术上讲可行. 用生物质能的途径排放二氧化碳最高达到2吨/吨HVCs(使用玉米做原料以酒精为中间产品), 最低可以避免二氧化碳排放4吨/吨HVCs(使用木质纤维做原料和人工气化技术). 由于木质纤维可以提供大部份在工艺途径中消耗的能量并且同步生产出电能, 这些利用生物质能的途径可以避免大量的化石能源的消耗以及二氧化碳排放。

从经济的角度上, 我们首先对以上提到的把主要能源转化为基础石化产品的24种生产途径的生产成本以及它们相互之间的竞争力进行了分析。根据已知文献, 主要能源在2030到2050年的预期价格如下: 原油\$26-60/桶; 天然气\$4-8/GJ, 煤炭\$37-57/吨; 生物质能\$1-5/GJ; 废弃塑料\$120-220/吨; 电能\$0.03-0.05/千瓦时。用这些价格我们可以计算那些生产途径的生产成本所在的范围。另外, 我们用蒙特卡罗分析法来考虑这些生产途径相互之间的竞争力。我们也在这些计算中考虑了二氧化碳的排放成本(\$0-100/吨二氧化碳)可能带来的影响。比较结果发现, 用石油与天然气的生产途径的生产成本大约有\$500-900/吨HVCs, 然而很多用煤炭与生物质能的生产途径的生产成本只有\$400-800/吨HVCs. 7个最低成本的途径中, 6个是用煤炭与生物质能的生产途径. 7个最高成本的途径中, 6个是用石油与天然气的生产途径. 所以, 用煤炭与生物质能的生产途径相对于用石油与天然气的生产途径来讲有很强的竞争力。二氧化碳的排放成本可能对用煤炭的生产途径的相对竞争力有严重负面影响(用石油与天然气的生产途径影响相对很小), 但对用生物质能的生产途径得正面影响不太显著。如果当今的欧洲气候政策在2030-2050中仍然适用的话(化工产品中的碳成分无论化石还是生物质能都不考虑), 用煤炭的生产途径的相对竞争力帮助最大, 用石油与天然气的生产途径帮助不大, 而对用生物质能的生产途径的相对竞争力的有负作用. 我们用2008年的高能源价格计算了各个途径的生产成本, 发现用多数煤炭与生物质能的生产途径(特别是用甘蔗做原料以酒精为中间产品的途径)仍然低于用石油和天然气的途径. 考虑到2030-2050年间全球石油生产可能达到停滞的水平, 我们估计取代油气化工产品途径的用煤炭与生物质能的生产途径在所有化工生产的占有率在2030-2050年间可能会达到大约15-30%。

从创新的角度上, 我们需要了解基础化工领域提高能源使用效率以及能源多元化方面技术创新的推动与阻碍因素。我们查看了统计资料, 然后与30多位化工工业专家们进行了会谈。不同的技术创新有不同的推动与阻碍因素。对于改进已存在的生产技术来讲, 主要的推动因素是生产资源和成本的节约、天然气的供应紧张以及个人的敬业投入。主要的阻碍因素则是劳动力和时间的不足、来自其他高利润项目的竞争以及当前已存在的生产配置。对于发展新型的生产技术来讲, 主要的推动因素是廉价原料的增值潜力, 企业间的强烈竞争以及追求利用已有知识的最大价值。主要的阻碍因素则是不利的商业环境, 模拟工具的不足和缺乏以及决策人对个人工作保障的担忧。这些推动与阻碍因素的基本区别是可以从两方面理解: 对处在不同发展阶段的技术的认识和有关技术创新的风险回报比率不确定性。对于有关改进已存在的生产技术讲, 任何技术创新在认识和风险回报比率两方面, 都比起有关发展新型的生产技术的技术创新已有很多已知的情况而且风险要低得多. 对于改进

已存在的生产技术来讲，减少能源消耗对改进企业的生产业绩是很需要的，但其本身却并不是一个战略性的创新。对于发展新型的生产技术来讲，减少能源消耗也总是相关的，但对企业更重要的是利用廉价的生产给料可达到的增值。新型的生产技术实际上是一种战略性的创新。因此，能源使用效率对技术创新的相关程度必须由技术与经济两方面来决定。这就是为什么即使用甲烷，煤炭和生物质能的生产途径能源使用效率不如最具有代表性的石脑油和乙烷蒸汽裂化技术，但是有关它们的创新却很重要。

基于以上三个角度得到的认识，我们认为，本文所阐述的化工工业技术完全有经济和技术的潜力来对付与化工行业相关的气候变化和能源供给问题。另外，与创新相关的推动与阻碍因素不容忽视。因此，我们给政策制定者提出以下三点建议，以供参考。

首先，由于利用基本能源多元化途径的创新对企业有战略性重要意义，政策制定者可以期待用甲烷，煤炭和生物质能的生产途径将在一定程度上在未来被使用。所以，相对应的能源和化工政策需要对这些技术途径的创新进行引导，确保它们达到经济和环境两方面的可持续性发展。

其次，由于各个途径的能源使用效率和二氧化碳排放差别巨大，就需要政策来鼓励对在用生物质能的生产途径的研展，特别是那些用木质纤维并同步生产电能的技术。用煤炭生产途径应该配备了二氧化碳的收集和埋藏技术才可以继续发展。

再次，由于政策不确定性对石化工业的长期战略计划的重大影响，一个平等竞争的平台以及一个全球温室气体交易的市场是鼓励大规模生物质能基础设施建设和发展必需的。在这些方面明确的政策方向能够使化工行业放心地进行长期投资，从而充分利用在环境技术和清洁能源市场上已有的大量商业机会。

List of Figures

- Figure 1-1 Two Process Steps in Basic Petrochemicals Routes 7
- Figure 2-1 Typical Flow Diagram for a Naphtha Steam Cracker [22, 48] 23
- Figure 2-2 Energy Flow in a Typical Naphtha Steam Cracker with Fuel Use of 25 GJ/t Ethylene (fuel use is the energy loss plus endothermicity; one ton ethylene is produced) [10]27
- Figure 3-1 Natural Gas via Methanol to Olefins Based on Lurgi MegaMethanol, UOP MTO, Lurgi MTP and ExxonMobil MTO (Section A is Lurgi MegaMethanol [148]; Section B and C represents UOP MTO [149] and Lurgi MTP [144]; Section C includes UOP/Total Olefin Upgrading Unit [97, 150]; see ExxonMobil MTO in [138-140]) 52
- Figure 3-2 Oxidative Coupling of Methane to Olefins (based on [116, 155]. Electricity cogeneration based on [116]. CO₂ methanization based on [135]) 56
- Figure 3-3 Comparison of Cumulative Process Energy Use in Steam Cracking and C₁ Routes with Sensitivity Analysis for Different Definitions of High Values Chemicals and Power Generation Efficiencies (the calorific value of HVCs excluded. Data come from Tables 3-3, 3-4 and 3-5. HVCs have a calorific value of approximately 50 GJ/t. The solid error bars for naphtha cracking, ExxonMobil MTO and Lurgi MTP are the results if 100% (weight) of aromatics and gasoline is counted as HVCs. The dotted error bars for DSM OCM I & II are the results when a power generation efficiency of 60% is used. In the default bars, the results are based on a power generation efficiency of 55%) 64
- Figure 3-4 Comparison of Cumulative Process CO₂ Emissions in Steam Cracking and C₁ Routes with Sensitivity Indication for Different Definitions of High Values Chemicals and Electricity Cogeneration Efficiencies (Data is based on data in Table 3-3 to Table 3-6. The error bars represent the same sensitivity analyses as those in Figure 3-3. See Table 3-6 for emission factors. 65
- Figure 3-5 Comparison of Production Costs by Steam Cracking and C₁ Routes (based on Table 3-7; error bars showing the effect of electricity production costs deviating +/- \$0.01/kWh from the price assumptions in Table 3-7; all in US\$ of year 2000) 73
- Figure 4-1 Naphtha Related Conventional and Alternative Routes to Basic Petrochemicals (solid lines refer to technologies that are already commercialized; dashed lines refer to

technologies that are not yet commercialized; the oil sands route only briefly discussed) 80

Figure 4-2 Ethane, Methanol and Ethanol Related Routes to Basic Petrochemicals (solid lines refer to technologies that are already commercialized; dashed lines refer to technologies that are not yet commercialized) 81

Figure 4-3 Total Energy Use in Various Routes to High-Value Chemicals (HVCs) (both fossil and biomass-derived energy; error bars represent the result of using an economic value-based allocation approach to allocate the total energy use to electricity and HVCs)95

Figure 4-4 Cumulative Process CO₂ Emissions (Cradle-to-factory gate) in Various Routes for Production of High-Value Chemicals (HVCs) (CO₂ emissions from feedstock production and petrochemicals productions; the carbon content of HVCs for fossil-based routes is excluded; the carbon content of HVCs for biomass-based routes originates from the atmosphere and is sequestered in HVCs) 96

Figure 4-5 Total CO₂ Emissions (Cradle-to-grave) in Various Routes for Production of High-Value Chemicals (HVCs) (including the CO₂ emissions from feedstock production and petrochemicals productions as well as the carbon content of HVCs; dotted bars represent fossil carbon physically embodied in HVCs; the carbon content of HVCs from biomass-based routes is zero since it originates from the atmosphere) 97

Figure 4-6 Land Use for Growing Various Type of Biomass for Biomass-based Routes to High-Value Chemicals (HVCs) (the default is large round dots; the distance between two large round dots for each route represents a possible range of land use if the total energy use is allocated to HVCs only; the distance between the ends of error bars represents the land use if an economic value-based allocation approach is used to allocate the total energy use to both electricity and HVCs; see Section 4.5.1) 98

Figure 4-7 Total Energy Use in Various Routes to High-Value Chemicals (HVCs) (both fossil and biomass-derived energy; the upper and lower ends of the error bars represent respectively the results of using the energy efficiency of 60% and 40% for electricity production in coal and biomass-based routes) 99

Figure 5-1 Range of Production Costs Based on Various Energy Prices in January-August of 2008 and in 2030-2050 (US\$ of the year 2000; CO ₂ costs are calculated on the basis of cradle-to-grave CO ₂ emissions).....	122
Figure 5-2 Ranking of Production Costs of Basic Petrochemical Routes through Comparing Their Production Costs with Each Other by Using Projected Energy Prices in 2030-2050 (US\$ of the year 2000; CO ₂ costs are calculated on the basis of cradle-to-grave CO ₂ emissions).....	123
Figure 6-1 Innovators and Networks for Innovation in Petrochemical Processes (based on various interviews).....	142
Figure 6-2 Objectives of Innovation in the European Chemical Industry [263]	144
Figure 6-3 A Simplified Procedure for Innovation in Petrochemical Processes (based on interviews; feedbacks between various steps omitted).....	145
Figure 6-4 an Example of Strategic Scenario Planning in a Petrochemical Firm	163

List of Tables

Table 2-1 Estimated Global Energy Use and CO ₂ Emissions in Olefins Production in 2004	21
Table 2-2 Characteristics of Ethane and Naphtha-based Steam Cracking Processes.....	29
Table 2-3 Breakdown of Specific Energy Consumption (SEC) and Exergy Losses in a Steam Cracker	30
Table 2-4 Licensors for State-of-the-Art Naphtha Steam Cracking Technologies.....	34
Table 2-5 Catalytic and Other Olefin Technologies Using Conventional and Other Petroleum Feedstocks	39
Table 3-1 Historical Development in Methanol to Olefins and Oxidative Coupling of Methane Routes.....	51
Table 3-2 Summary of Natural Gas-to-Olefins Routes (All yields are maximum yields and are given as the mass of products divided by that of natural gas).....	53
Table 3-3 Cumulative Process Energy Use in Steam Cracking Routes (the calorific value of feedstocks and HVCs is excluded from cumulative process energy use)	60
Table 3-4 Cumulative Process Energy Use in Natural Gas-to-Olefins Routes - UOP MTO and ExxonMobil MTO (the calorific value of feedstocks and HVCs is excluded from cumulative process energy use).....	61
Table 3-5 Cumulative Process Energy Use in Natural Gas-to-Olefins Routes – Lurgi MTP and DSM OCM I & II (the calorific value of feedstocks and HVCs is excluded from cumulative process energy use).....	62
Table 3-6 Emission Factors for Steam Cracking and Natural Gas-to-Olefins Routes (ton CO ₂ per GJ energy used)	63
Table 3-7 Three Sets of Assumptions for Energy/Feedstock and Electricity Production Costs (all values in US\$ of 2000).....	72
Table 4-1 Overview of Primary Energy Sources, Feedstocks and High Value Chemicals (HVCs) On a Dry Basis.....	88
Table 4-2 Feedstock Production in Crude Oil and Natural Gas-based Routes (the 1 st step of a route)	89

Table 4-3 Feedstock Production in Coal-based Routes (the 1st step of a route)..... 90

Table 4-4 Feedstock Production in Biomass-based Routes (the 1st step of a route)..... 91

Table 4-5 Petrochemicals Production in Crude Oil and Natural Gas-based Routes (the 2nd step of a route)..... 92

Table 4-6 Petrochemicals Production in Coal-based Routes (the 2nd step of a route)..... 93

Table 4-7 Petrochemicals Production in Biomass-based Routes (the 2nd step of a route and a summary of both steps) 94

Table 5-1 Technical Data for Routes from Crude Oil and Natural Gas to Basic Petrochemicals (energy efficiency for electricity production at 55%; calorific value and carbon content of HVCs excluded; details on calculations can be found in Chapters 2, 3 and 4)..... 117

Table 5-2 Technical Data for Routes from Coal and Biomass to Basic Petrochemicals (energy efficiency for electricity production at 55%; calorific value and carbon content of HVCs excluded; details can be found in Chapters 2, 3 and 4)..... 118

Table 5-3 Assumptions for Calculating Production Costs of Routes that Convert Crude Oil and Natural Gas into Basic Petrochemicals (yield of feedstock as % of primary energy sources and yield of HVCs as % of feedstocks shown in Table 5-1)..... 119

Table 5-4 Assumptions for Calculating Production Costs of Routes that Convert Coal and Biomass into Basic Petrochemicals (yield of feedstock as % of primary energy sources and yield of HVCs as % of feedstocks shown in Table 5-2)..... 120

Table 5-5 A Summary of Energy and Policy Scenarios for 2030-2050 (expressed in US\$ of the year 2000)..... 121

Table 6-1 Definitions of Basic Chemicals and Non-basic Chemicals: Definitions Used in this Chapter and in [260, 261]..... 137

Table 6-2 Major Firms Involved In Petrochemicals Production and Processes (based on [270-272] and various annual reports)..... 143

Table 6-3 Drivers and Barriers to Improving Existing Processes and Developing New Processes 150

Glossary

BTX: Benzene, toluene and xylene

°C: Centigrade

C₁: Methane and syngas (mixture of CO and H₂ or synthetic gases)

C₂: Ethylene and ethane

C₃: Propylene and propane

C₄: Butadiene, butylenes and other C₄ hydrocarbons

C₅₋₆: Light naphtha

C₇₋₉: Heavy naphtha

CPP: Catalytic pyrolysis process

CC: Catalytic cracking

CCS: Carbon capture and storage

CHP: Combined Heat and Power generation

CTL: Coal to liquids

EJ: Exa or quintillion (10¹⁸) joules

ETE: Ethanol to ethylene via dehydration

FCC: Fluidized Catalytic Cracking

FOB: Free on Board

FT: Fischer-Tropsch

GJ: Giga or billion (10⁹) joules (there is also GJ_e for measuring electricity)

GTL: Gas to liquids

Ha: Hectare

HIDiC: Heat Integrated Distillation Column

HVCs: High Value Chemicals (value equivalent to ethylene and propylene)

LHV: Lower heating value

LPG: Liquefied petroleum gases

LNG: Liquefied natural gas

NGL: Natural gas liquids (mostly LPG and light naphtha)

M: Mega or million (10^6)

MTO: Methanol to olefins (i.e. ethylene, propylene, etc.)

MTP: Methanol to propylene

mm: Millimeter

Mha: million hectares

MVR: Mechanical vapor recompression

OCM: oxidative coupling of methane

P/E: Propylene/ethylene (used as an indicator of severity)

R&D: Research and development

SC: steam cracking

SEC: Specific Energy Consumption (expressed in GJ/t HVCs)

T.: Temperature

t (or ton): Tonne or metric ton of 1,000 kg

TLE: Transfer Line Exchangers

VSA: Vacuum Swing Adsorption

Wh: Watt hour for measuring electricity (e.g. KWh, MWh and GWh)

Wt.: Weight or mass basis

References

- [1] IEA. Tracking Industrial Energy Efficiency and CO₂ Emissions. Paris: International Energy Agency (IEA) and Organization for Economic Co-operation and Development (OECD), 2007.
- [2] Neelis M, Patel M, Blok K, Haije W, Bach P. Approximation of theoretical energy-saving potentials for the petrochemical industry using energy balances for 68 key processes. *Energy* 2007; 32(7): 1104-1123.
- [3] IPCC. Climate Change 2001: Mitigation (The Third Assessment Report). Geneva, Switzerland: Intergovernmental Panel on Climate Change (IPCC), 2001. See also at: <http://www.ipcc.ch/pub/reports.htm>.
- [4] USGS. USGS World Petroleum Assessment 2000. Reston, Virginia: US Geological Survey National Center (USGS), 2000.
- [5] DOE. Strategic Significance of America's Oil Shale Resource. Washington DC: Office of Naval Petroleum and Oil Shale Reserves at the US Department of Energy (DOE), 2004. See also at: www.fe.doe.gov/programs/reserves/publications/Pubs-NPR/npr_strategic.
- [6] BP. Putting energy in the spotlight: BP Statistical Review of World Energy 2005. London, UK: BP, 2005.
- [7] IEA. World Energy Outlook 2005. Paris: International Energy Agency (IEA) and Organization for Economic Co-operation and Development (OECD), 2005.
- [8] EC. EU-15 Energy and Transport Outlook to 2030. Luxembourg: DG Energy and Transport of European Commission and Office for official publications of the European Communities (EC), 2003.
- [9] Neelis M, Patel M, Bach P, Haije M. Analysis of energy use and carbon losses in the chemical and refinery industries (report number ECN-05--008). The Netherlands: Department of Science, Technology and Society at Utrecht University and Energy Research Center of the Netherlands (ECN), 2005.
- [10] Neelis M, Patel M, Blok K, Haije W, Bach P. Approximation of theoretical energy-saving potentials for the petrochemical industry using energy balances for 68 key processes. *Energy* 2007; 32(7): 1104-1123.
- [11] IEA. Energy Balances and Energy Statistics (energy balances and statistics in OECD countries 2002-2003 and energy statistics of Non-OECD Countries 2002-2003). Paris: International Energy Agency (IEA) and Organization for Economic Co-operation and Development (OECD), 2005.
- [12] PEMRG. Business Data and Charts 2006. Düsseldorf, Germany: PlasticsEurope Market Research Group (PEMRG), 2007. See also at: <http://www.unipetrol.cz/docs/Business%20Data%20and%20Charts%20PIEurope.pdf>.
- [13] OGJ. Industry Survey of Ethylene from Steam Crackers. *Oil & Gas Journal (OGJ)*, March 27, 2006.
- [14] CEFIC. Facts and Figures: The European Chemical Industry in a Worldwide Perspective. National Chemical Federation, Eurostat and European Chemical Industry Council (CEFIC), 2004. See also at: http://www.cefic.be/Files/Publications/FF_032004b.pdf.

- [15] Nakamura D. Global ethylene capacity grows 4% in 2005. *Oil & Gas Journal*, March 27, 2006.
- [16] CMAI. World Petrochemical Feedstocks Analysis. Houston, Texas: Chemical Market Associates Inc. and Purvin & Gertz, 2005. See also at: <http://www.cmaiglobal.com/apps/news/WPFA.pdf>.
- [17] CEFIC. Horizon 2015: Perspectives for the European Chemical Industry. Executive Summary of Chemical Industry 2015: Roads to the Future. Brussels: European Chemical Industry Council (CEFIC), 2004. See also at: <http://www.cefic.org/files/Publications/Scenarios2.pdf>.
- [18] CMAI. World Propylene Supply Study. Houston: Chemical Market Associates, Inc. (CMAI), 2001.
- [19] Stobaugh R. Innovation and competition: the global management of petrochemical products. Boston: Harvard Business School Press, 1988.
- [20] Quintella R. The Strategic Management of Technology in the Chemical and Petrochemical Industry. London: Pinter Publishers, 1993.
- [21] Arni V. Emerging Petrochemicals Technology: Implications for Developing Countries UNIDO/IS.350 code 35.10. Vienna: United Nations Industrial Development Organization (UNIDO), 1982.
- [22] EC-BREF. Integrated pollution prevention and control (IPPC) Reference Document on Best Available Techniques in the Large Volume Organic Chemical Industry, Lower Olefins Process. Seville: Institute for Prospective Technological Studies (Technologies for sustainable development) at the European IPPC Bureau, 2002.
- [23] Gartside R, McCall T, Wagner E, Whitney M. Emerging Technologies for Olefins Production. Proceedings of the 12th Ethylene Producers Conference of AIChE Spring Meeting on March 5-9, 2000, Atlanta: New York: American Institute of Chemical Engineers (AIChE), 2000.
- [24] Stratton A, Hemming DF, Teper M. Ethylene production from oil, gas and coal-derived feedstock. London: Coal Research at International Energy Agency (IEA), 1983.
- [25] Spath P, Dayton D. Preliminary Screening: Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas. Golden, Colorado: National Renewable Energy Laboratory (NREL) at the US Department of Energy (DOE), 2003.
- [26] Joosten L. The Industrial Metabolism of Plastics: Analysis of Material Flows, Energy Consumption and CO₂ Emissions in the Lifecycle of Plastics (PhD thesis). Utrecht, The Netherlands: Department of Science, Technology and Society, Utrecht University, 2001.
- [27] Patel M, Crank M, Dornburg V, Hermann B, Roes L, Hüsing B, Overbeek L, Terragni F, Recchia E. Medium and long-term opportunities and risks of the biotechnological production of bulk chemicals from renewable resources (The BREW Project). Utrecht, The Netherlands: Department of Science, Technology and Society at the Utrecht University, 2005. See also at: http://www.chem.uu.nl/brew/BREW_Final_Report_September_2006.pdf.
- [28] Fagerberg J, Nowery DC, Nelson RR. The Oxford Handbook of Innovation. Oxford: Oxford University Press, 2005.

- [29] Albach H, Audretsch D, Fleischer M, Breb R, Hofs E, Roller L, Schulz I. Innovation in the European Chemical Industry. Final report and discussion paper (FS IV 92-26) prepared by Research Area Market Processes and Corporate Development for the European Commission DG XXIII-D-4, "Innovation and Technology Transfer": Wissenschaftszentrum Berlin, 1996.
- [30] Blok K. Introduction to Energy Analysis. Amsterdam: Techne Press, 2006.
- [31] CMAI. Europe/Middle East Reports on olefins & derivatives (various issues in 1995-2006). Houston: Chemical Market Associates Inc. (CMAI), 2006.
- [32] Shell. Gas to liquids: Shell Middle Distillate Synthesis Processes and Products. Amsterdam: Shell Gas & Power, 2002.
- [33] Dancuar L, Mayer J, Tallman M, Adams J. Performance of the Sasol SPD naphtha as steam cracking feedstock. Preprints of American Chemical Society (Division of Petroleum Chemistry) 2003;48(2):132-138.
- [34] Nakamura D. Special report: ethylene capacity rising, margins continue to suffer. Oil & Gas Journal, March 11, 2002.
- [35] Zinger S. Where is the most value for ethylene and olefin byproducts? Proceedings of Spring Meeting of American Institute of Chemical Engineers (AIChE) and the 12th Ethylene Producers Conference Technology Session in Houston, Texas, New York: AIChE, 2001.
- [36] EIA. International Energy Price Information. Washington DC: Energy Information Administration (EIA) at the US Department of Energy, 2006. See also at: <http://www.eia.doe.gov/emeu/international/prices.html>.
- [37] Pettman A. Europe and Middle East--an Evolving Relationship. Aspentech Chemicals Conference in Genval, Belgium, Houston: Aspentech Inc., 2002.
- [38] IEA. Statistics on energy prices and taxes. Paris: International Energy Agency (IEA) and Organization for Economic Co-operation and Development (OECD), 2004.
- [39] Solomon. Worldwide Olefins Plant Performance Analysis 1995, quoted in "Energy efficiency improvement in ethylene and other petrochemical production" by D. Phylipsen, et. al., Report NW&S 99085 (1999), Department of Science, Technology and Society at Utrecht University, Utrecht in the Netherlands. Windsor: Solomon Associates Ltd., 1995.
- [40] van Ree R. Air separation technologies: an inventory of technologies for pure oxygen production for pulverized coal combustion in a CO₂ (g)/O₂(g) atmosphere. Petten, The Netherlands: Energy Research Center of The Netherlands (ECN), 1992 (in Dutch).
- [41] IFIAS. International Federation of Institutes for Advanced Study (IFIAS) workshop report: energy analysis and economics. Resources and Energy 1978;1(2):151-204.
- [42] Szargut J. Analysis of cumulative exergy consumption. Energy Research 1987;11(4):541-547.
- [43] IEA/NEA. Projected costs of generating electricity. Paris: International Energy Agency (IEA), Organization for Economic Co-operation and Development (OECD) and Nuclear Energy Agency (NEA), 2005. See also at: <http://www.iea.org/textbase/nppdf/free/2005/ElecCost.pdf>.
- [44] Albright LF, Crynes BL, Nowak S. Novel production methods for ethylene, light hydrocarbons and aromatics. New York: Marcel Dekker, 1992.

- [45] Worrell E, Beer JD, Faaij A, Blok K. Potential energy savings in the production route for plastics. *Energy Conservation and Management* 1994;35(12):1073-7085.
- [46] Weissermel K, Arpe H. *Industrial Organic Chemistry*. Weinheim: Wiley-Vch GmbH & Co. KGaA, 2003.
- [47] Bailey K. Optimize heat exchanger operations by minimizing fouling. *Hydrocarbon Processing*, June of 1999.
- [48] Jennings C. Adding value through growth and innovation: NAFTA region olefins complex. Houston: Houston: BASF, 2001.
- [49] Bearden MD. Personal communication. Freeport, Texas: Hydrocarbons & Energy Research, Dow Chemicals, 2006.
- [50] Smedt P. Personal communication. Feluy, Belgium: Total Petrochemicals Research, 2006.
- [51] Patel M. Cumulative energy demand and cumulative CO₂ emissions for products of the organic chemical industry. *Energy* 2003;28(7):721-740.
- [52] Hydrocarbon-Processing. *Petrochemical Processes* 2003, 2003. See also at: www.hydrocarbonprocessing.com.
- [53] Yabe A, Ohmori T, Okuma K, Nonoichi Y, Hijikata K. Energy and Exergy Analysis of High Temperature Naphtha Cracking Process in an Ethylene Center. *International Symposium on Advanced Energy Conversion System and Related Technologies*, Nagoya, Japan: The Japanese Society of Chemical Engineers, 1995.
- [54] Chang H. Exergy Analysis and Exergoeconomic Analysis of an Ethylene Process. *Tamkang Journal of Science and Engineering (Department of Chemical Engineering, Tamkang University, Taiwan)* 2001;4(2):95-104. See also at: www2.tku.edu.tw/~tkjse/4-2/4-2-3.pdf.
- [55] Szargut J, Morris, D. R. and Steward, F. R. *Exergy analysis of thermal, chemical and metallurgical processes*. New York: Hemisphere Publishing Co., 1988.
- [56] Matthews R. Personal communications with Dr. Martin Patel from Department of Science, Technology and Society at the Utrecht University in the first half of 2002. London: Guthrie-Matthews Consulting Limited, 2002.
- [57] Energetics. *Energy and Environmental Profile of the U.S. Chemical Industry*. Columbia, Maryland: Energetics Inc. and the Office of Industrial Technology at the US Department of Energy (DOE), 2000.
- [58] Neelis M, Patel M, Feber MD. Improvement of CO₂ emission estimation from the non-energy use of fossil fuels in The Netherlands (Report nr. NW&S E-2003-10 prepared for NOVEM & VROM). Utrecht, The Netherlands: Utrecht University, 2003.
- [59] Hydrocarbon-Processing. *Petrochemical Processes* 2003. 2003.
- [60] Chauvel A, Lefebvre G. *Petrochemical processes, Part I: Synthesis gas derivatives and major hydrocarbons*. Paris: Technip, 1989.
- [61] Brown HL. *Energy Analysis of 108 Industrial Processes*. Washington, D. C.: US Department of Energy (DOE), 1985.
- [62] Chang H. Personal communication on exergy analysis of separation processes in steam cracking several times in April of 2003. Taipei, Taiwan: Department of Chemical Engineering at the Tamkang University, 2003.

- [63] Kaiser V, Cintio D, Picciotti R. Ethylene plant energy analysis. Proceedings of Spring National Meeting of American Institute of Chemical Engineers, Houston: New York: American Institute of Chemical Engineers (AIChE), 1993.
- [64] Cole D. Olefin Economics: Impact of the Technology Supplier. Proceedings of 1995 Annual Ethylene Producers Conference and Spring Meeting of American Institute of Chemical Engineers (AIChE), Houston, Texas: New York: AIChE, 1995.
- [65] Albano J, Olszewski E, Fukushima T. Gas turbine integration reduces ethylene plant's energy needs. *Oil & Gas Journal*, February 10, 1992.
- [66] Buffenoir MH. Mega Crackers Mean Mega Challenges by Technip-Coflexip. Proceedings of the 5th EMEA Petrochemical Technology Conference in Paris on June 23-26, 2003, London: Euro Petroleum Consultancy Ltd., 2003.
- [67] KBR. Changing world of global ethylene business. 2000 Global super project conference in Dubai, Saudi Arabia, Norcross, Georgia: World Development Federation, 2000.
- [68] Picciotti M. Novel ethylene technologies developing, but steam cracking remains king. *Oil & Gas Journal*, June 23, 1997.
- [69] Nieuwlaar E. Personal communications with experts in the olefin industry quoted in "Sector Study for the Chemical Industry" (Report Nr. NWS-E-2001-19). Utrecht, The Netherlands: Utrecht University, 2001.
- [70] DOE. Membrane Separation Recovers Olefins (Chemicals project fact sheets). Washington DC: Office of Industrial Technologies at U.S. Department of Energy (DOE), 2003. See also at: www.oit.doe.gov/chemicals/factsheets.
- [71] Kolmetz K. Advances in Cracking Furnace Technologies. Proceedings of Refinery Technology Conference on 12-14 December in Dubai, Saudi Arabia, London: European Refinery Technology Conference (ETRC), 2002.
- [72] DOE. Fabrication and testing of a prototype ceramic furnace coil for chemical and petrochemical processing. Washington DC: Office of Industrial Technology at the US Department of Energy (DOE), 2003. See also at: www.oit.doe.gov/chemicals/factsheets.
- [73] IDEE. Industriële Databank voor Energie Efficiency, Versie 7. Utrecht, The Netherlands: NOVEM of the Dutch Ministry of Economic Affairs, 2000 (in Dutch).
- [74] Heida B, Bohner G, Kindler K. Consider divided-wall technology for butadiene extraction. *Hydrocarbon Processing*, 2002.
- [75] Vaartjes J. Integrated Distillation Column. *Energietechniek*, October 10, 2002 (in Dutch).
- [76] Hydrocarbon-Processing. Refining Processes 2002. 2002.
- [77] Staudt-Bickel C, Koros W. Olefin/paraffin gas separations with 6 FDA-based polyimide membranes. *Journal of Membrane Science* 2000 (170):205-214.
- [78] Bernadardo P, Criscuoli A. Application of membrane unit operations in ethylene process. *Clean Technology and Environmental Policy* 2004 (6):78-95.
- [79] Smit R, Beer J, Worrel E, Blok K. Styrene: Long term industry energy efficiency importance. Technology description. Report Nr. 94076. Department of Science, Technology and Society at Utrecht University, The Netherlands, 1994.
- [80] Ameringer GE. The gas/ethylene plant: concept and integration. *Gas Technology* 2000;5(2):119.
- [81] Pujado P, Greer D, Andersen J, Foley T, Bhirud V. The role of new technology in the light olefins industry. Proceedings of Spring National Meeting of the American Institute of

- Chemical Engineers (AIChE) in Houston, New York: American Institute of Chemical Engineers, 2002.
- [82] Knowlen E. Petrochemical pyrolysis with shock waves (AIAA Paper 95-0402). Reston, VA: American Institute of Aeronautics and Astronautics (AIAA), 1995.
- [83] IDEE. Kraakscherpteregeling voor betere selectiviteitsbeheering in etheenfabriek. Utrecht, The Netherlands: NOVEM of the Dutch Ministry of Economic Affairs, 2000 (in Dutch).
- [84] USPTO. Catalytic oxidative dehydrogenation process (US patent 6,452,061). US Patent Office (USPTO): Regents of the University of Minnesota, 2003.
- [85] Huff M, Schmidt LD. Ethylene Formation by Oxidative Dehydrogenation of Ethane over Monoliths at very short contact times. *Journal of Physical Chemistry* 1993 (November):118150-11822.
- [86] Sud-Chemie. Catofin propane dehydrogenation for propylene. Munich, Germany: Sud-Chemie, 2003. See also at: http://www.sud-chemieinc.com/houdry_propane.shtml.
- [87] Uhde. The Uhde Star Process: oxydehydrogenation of light paraffins to olefins. Dortmund, Germany: Uhde GmbH, 2003. See also at: www.uhde.biz/cgi-bin/download.cgi/pdf/broschueren/Oil_Gas_Refinery/The_Uhde_STAR_Process.pdf.
- [88] Han SS, Kim JN, Lee CW, Park YK. Catalytic Cracking of Heavy Naphtha and Olefin Separation in Atmospheric Temperature. Seoul, Korea: Advanced Chemical Technology Division, KRICT Co., 2002.
- [89] Park Y, Jeon JY, Han SY, Kim JR, Lee CW. Catalytic Cracking of Naphtha Into Light Olefins. *Hwahak Konghak* 2003;41(5):549-557 (in Korean and partially in English).
- [90] Jeong SM, Chae JH. Catalytic pyrolysis of naphtha on the KVO₃ based catalyst. *Catalysis Today* 2002:257-264.
- [91] ChemicalWeek. LG Develops Catalytic Naphtha Cracking Process. *Chemical Week*, May 22, 2002.
- [92] Yoshimura Y, Murata K, Mizukami F. Catalytic cracking of naphtha to light olefins. *Catalysis Surveys of Japan* 2001;4(2):157-169.
- [93] SRI. Abstract of Process Economics Program Report 248: Steam Cracking For Olefins Production. Menlo Park, California: SRI International Consulting Co., 2003.
- [94] VNIIOS. Catalytic pyrolysis of petroleum fractions to produce ethylene and propylene. Moscow: VNIIOS, 2003. See also at: <http://www.vniios.ru/english/index.htm#0>.
- [95] Taniewski M. Personal communication in May of 2003 and February of 2004. Gliwice, Poland: Silesian Technical University, 2004.
- [96] Tallman M. KBR's Superflex process to upgrade F-T liquids at Sasol. Proceedings of 5th EMEA Petrochemical Technology Conference on June 23-26, 2003 in Paris, London: Euro Petroleum Consultancy Ltd., 2003.
- [97] Gregor J. Meeting the changing needs of the olefins market by UOP LLC. Proceedings of the 5th EMEA Petrochemical Technology Conference in Paris, London: Euro Petroleum Consultancy Ltd., 2003.
- [98] Stanley SJ, Kukandar K. Improving Ethylene Plant Economics with Metathesis. Proceedings of the 15th Ethylene Producer Conference in New Orleans, New York: American Institute of Chemical Engineers (AIChE), 2001.

- [99] USPTO. Process for production of ethylene and propylene by catalytic pyrolysis of heavy hydrocarbons (US Patent 6,210,562). US Patent Office (USPTO): China Petrochemical Corporation and RIPP, 2001.
- [100] Xie C, Wang X. Commercial trial of catalytic pyrolysis process for manufacturing ethylene and propylene. Proceedings of the 17th World Petroleum Congress on September 1-5, 2002 in Rio de Janeiro, Brazil, London: World Petroleum Council, 2002.
- [101] Bowen C, Reid JA. Emerging Olefins Technology. Proceedings of 2002 Spring National Meeting of American Institute of Chemical Engineers (AIChE) in New Orleans, New York: American Institute of Chemical Engineers, 2002.
- [102] Deng R, Wei F, Jin Y, Zhang Q, Jin Y. Downer Catalytic Pyrolysis (DCP): a novel process for light olefins production. Chemical Engineering Technology 2002 (25):711-716.
- [103] Mattick T. Personal communications on shockwave technology in January of 2003. Seattle, Washington: University of Washington, 2003.
- [104] Siddall J. Catalytic Autothermal Partial Oxidation (internal report). Houston: Dow Chemical, 2000.
- [105] Dautzenberg F, Mukherjee M. Process intensification using multifunctional reactors. Chemical Engineering Science 2001(56):251.
- [106] USPTO. Hybrid catalyst for deep catalytic cracking of petroleum naphthas and other hydrocarbon feedstocks (US Patent application 20040014593). US Patent Office (USPTO): Concordia University, 2004.
- [107] UYSEG. FCC Cracking Saves Energy. York, UK: The University York Science Education Group, 2004. See also at: http://www.uyseg.org/catalysis/pages/cat_frames.htm.
- [108] Laszlo L. Oxidative conversion of lower alkanes to olefins (PhD thesis). University of Twente, 2002.
- [109] USPTO. Production of naphtha and light olefins (US Patent application number 20020063082). US Patent Office (USPTO): ExxonMobil Inc., 2002.
- [110] UNDP. World Energy Assessment - Overview. New York: United Nations Development Programme, United Nations Department of Economic and Social Affairs, World Energy Council, 2000.
- [111] Rogner H. An Assessment of World Hydrocarbon Resources. Annual Review of Energy and Environment 1997 (22):217-262.
- [112] Geem P. Nieuwe routes naar etheen. NPT ProcesTechnologie 1992 (April):15-22 (in Dutch).
- [113] Geerts J. Ethylene from natural gas by direct oxidation (Report: EUR 1361 EN). Eindhoven, The Netherlands: Eindhoven University of Technology, 1991.
- [114] Burke B. Emerging Technologies to Develop Stranded Gas. Proceedings of 2001 Annual Meeting of National Petroleum & Refinery Association (NPRA), New Orleans: NPRA, 2001.
- [115] Heber J. Economic comparison of naphtha cracking and MTO UOP/Norsk Hydro. Proceedings of the 3rd Asian Olefins and Polyolefins Markets Conference in Bangkok, Thailand, Singapore: Centre for Management Technology, 2000.
- [116] Swanenberg G. Cogeneration of ethylene and electricity with oxidative methane coupling: a study of technical feasibility and economic merit conducted for DSM, Sparqle

- International and SEP. Eindhoven, The Netherlands: Eindhoven University of Technology, 1998.
- [117] ChemSystems. Process Evaluation/Research Planning: PERP 2002/2003 Program. Houston, Texas: ChemSystem/Nexant Inc., 2002.
- [118] Zaman J. Oxidative processes in natural gas conversion. *Fuel Processing Technology* 1999;58(2-3):61-81.
- [119] Murchison C, Murdick D. Using syngas for olefins feedstock. *Hydrocarbon Processing*, January of 1981, 1981.
- [120] USPTO. Process for the manufacture of unsaturated hydrocarbons (US patent 5,546,642). US Patent Office (USPTO): Ruhrchemie Aktiengesellschaft, 1986.
- [121] USPTO. Ethanol from methanol, hydrogen and carbon monoxide (US patent 4,133,966). US Patent Office (USPTO): Gulf Research & Development Company, 1979.
- [122] USPTO. Conversion of methane (US patent 4,199,533). US Patent Office (USPTO): University of Southern California, 1980.
- [123] Inui T. Rapid catalytic reforming of methane with CO₂ and its application to other reactions. *Applied Organometallic Chemistry* 2001;15(2):8794.
- [124] Hattori T. Catalytic reduction of carbon dioxide by lower alkanes. *Carbon Dioxide Chemistry (Environment Issues by Royal Society of Chemistry; Special Publication)* 1994 (153):74-81.
- [125] Wang C, Xu L, Wang Q. Review of directly producing light olefins via co-hydrogenation. *Journal of Natural Gas Chemistry* 2003;12(1):10-16.
- [126] IFE. The Gas Value Chain: technology strategy for competitive gas production and off-take. Oslo: Norwegian Institute for Energy Technology (IFE), 2003. See also at: http://www.ife.no/media/1234_OG_21-2003-Gassverdikjeden.pdf.
- [127] Keep P. Comparison of remote gas conversion technologies. London: Syntex Inc., 1999. See also at: [www.syntex.com/methanol/pdfs/papers/imtof99-paper9\(59w\).pdf](http://www.syntex.com/methanol/pdfs/papers/imtof99-paper9(59w).pdf).
- [128] Moiseev II, Plate NA, Tereshchenko GF. Energochemical Technologies: energy and bulk/basic chemicals in a single process. *Russian Chemical Bulletin (International Edition)* 2001;50(11):2015-1019.
- [129] Geerts J, Hoebink J, Wiele K. Ethylene from natural gas: proven and new technologies. In: *Novel Production Methods for Ethylene, Light Hydrocarbons and Aromatics*. L. Albright, B. Crynes and S. Nowaks. New York: Marcel Dekker, 1992.
- [130] USPTO. Olefins process which combines hydrocarbon cracking with coupling methane (US Patent 5,254,781). US Patent Office (USPTO): Amoco Corporation, 1993.
- [131] Keller GE, Bhasin MM. Synthesis of Ethylene via Oxidative Coupling of Methane. *Journal of Catalysis* 1982;9(73):9-19.
- [132] EPO. ICI Olefins (European Patent Application 40,015). European Patent Office (EPO): ICI, 1981.
- [133] USPTO. Conversion process by J. H. Brophy and R. P. Manning (US Patent 4,726,913). US Patent Office (USPTO): BP, 1988.
- [134] USPTO. Production of Light olefins (from methanol, etc.) (US Patent 4,499,327). US Patent Office (USPTO): Union Carbide Co., 1985.
- [135] USPTO. Oxidative Coupling of methane with carbon conservation (US Patent 6,096,934). US Patent Office (USPTO): UOP LLC, 2000.

- [136] Addroulakis I, Reyes S. Optimal design and operation of methane oxidative coupling reaction systems for the production of higher hydrocarbons. Technical Program at the Annual Meeting of the American Institute of Chemical Engineers (AIChE), Houston: American Institute of Chemical Engineers, 2000.
- [137] ChemSystems. 10-year Proprietary Report Summaries. Houston: ChemSystems Inc., 2003.
- [138] USPTO. Catalytic Production of olefins at high methanol partial pressures (US Patent application 20030109765). US Patent Office (USPTO): ExxonMobil, 2003.
- [139] Kunii D, Levenspiel O. Free Fall Reactor. New York: Robert E. Krieger Publishing Co., 1977.
- [140] Zenz FA, Othmo DF. Fluidization and Fluid Partial Systems. New York: Reinhold Publishing Co., 1960.
- [141] Vora B. Personal communication. Des Plaines, Illinois: UOP LLC, 2004.
- [142] Barger P. UOP Presentation. The IZA Pre-conference School, Poitiers, France: The International Zeolite Association (IZA), 2001.
- [143] Koempel H, Liebne W, Wagner M. MTP--An economic route to dedicated propylene. Proceedings of the 2nd ICIS-LOR World Olefins Conference, Amsterdam: ICIS-LOR Inc., 2003.
- [144] Liebner W. GTC-Gas to Chemicals Process Options for Venezuela by Lurgi Oel-Gas Chemie Engineering. Proceedings of the PdVSA-EFO Seminar, Caracas, Venezuela: Petróleos de Venezuela S.A., 2002.
- [145] Alperowicz N. Methanol-to-Olefins Complex Planned for Nigeria. Chemical Week, October 2, 2002.
- [146] USTDA. EATCO-Suez Petrochemicals Complex Gas to Polyolefin Project Final Report (Executive Summary). Washington DC: US Trade and Development Agency, 2000.
- [147] Alperowicz N. Egyptian Firm to Build MTO Complex. Chemical Week, April 9, 2003. See also at: www.chemweek.com.
- [148] Lurgi. Lurgi MegaMethanol brochure by engineering division of Lurgi Oel, Gas and Chemie GmbH. Frankfurt: Lurgi GmbH, 2003.
- [149] UOP. UOP/Hydro MTO Process Methanol to Olefins Conversion. Des Plaines: UOP LLC, 2003.
- [150] Grootjans J, Vanrysselberghe V, Vermeiren W. Integration of Total Petrochemicals: UOP olefins conversion process into a naphtha steam cracker facility. Catalysis Today 2005;106(1-4):57-61.
- [151] Kvisle S, Nilsen HR. MTO: state of art and perspectives. DGMK-Conference: creating value from light olefins-production and conversion in Hamburg, Hamburg: German Society for Petroleum and Coal Science and Technology, 2001.
- [152] USPTO. Methanol to Olefin process with increased selectivity to ethylene and propylene (US Patent 6,534,692). US Patent Office (USPTO): UOP LLC, 2003.
- [153] USPTO. Production of light olefins from oxygenate using framework gallium-containing medium pore molecular sieve (US Patent application 20030018231). US Patent Office (USPTO): ExxonMobil Inc., 2003.

- [154] Rothaemel M, Holtmann HD. MTP, Methanol to Propylene--Lurgi's Way. DGMK Conference "Creating Value from Light Olefins--Production and Conversion", Hamburg: German Society for Petroleum and Coal Science and Technology, 2001.
- [155] Gradassi M, Green N. Economics of natural gas conversion processes. *Fuel Processing Technology* 1995;42(5):65-83.
- [156] USPTO. Process for producing olefins from natural gas (US Patent 5,025,108). US Patent Office (USPTO): Institute Francais du Petrole, 1991.
- [157] Pyatnitskii Y. Contemporary methods for the direct catalytic conversion of methane. *Theoretical and Experimental Chemistry* 2003;39(4):201-218.
- [158] Cordi E, Pak S, Rosynek M, Lunsford H. Steady-state production of olefins in height yields during the oxidative coupling of methane: utilization of a membrane contractor. *Applied Catalysis* 1997(155):L1-L7.
- [159] BUWAL. Bundesamt fur Umwelt, Wald und Landschaft. Bern: Vergleichende ökologische Bewertung von Anstrichstoffen im Baubereich. Band 2. Daten Scheriftenreihe Umwelt Nr. 23 1995 (in German).
- [160] Bonnekamp P, Mannaert H. Protocol Monitoring Energiebesparing (ECN-C-120, RIVM 408137005). Petten, The Netherlands: Energy Research Center of The Netherlands (ECN) and CPB/Novem/RIVM, 2001 (in Dutch).
- [161] Dermaut J, Geeraert B. A better understanding of greenhouse gas emissions for different energy vectors and applications. Proceedings of the 17th World Energy Council Congress in Houston, London: The World Energy Council, 1998.
- [162] Machado G, Schaeffer R, Worrell E. Analysis: energy and carbon embodied in the international trade of Brazil: an input-output approach. *Ecological Economics* 2001;39(3):409-424.
- [163] Costanza R, Herendeen R. Embodied energy and economic value in the US economy: 1963, 1967 and 1972. *Resources and Energy* 1984;6(22):129-163.
- [164] Syntex. Methanol plant technology. Cleveland, England: Syntex Inc., 2004. See also at: <http://www.jmcatalysts.com/pct/pdfs-uploaded/methanol/shortlcm.pdf>.
- [165] Hydrocarbon-Processing. Refining Processes 2002. Hydrocarbon Processing, November of 2002.
- [166] USPTO. Two-stage quench tower for use with oxygenate conversion process (US Patent 6,459,009). US Patent Office (USPTO): UOP LLC, 2002.
- [167] Neelis M, Patel M, Gielen D, Blok K. Modeling CO₂ emissions from non-energy use with the non-energy use emission accounting tables (NEAT) model. *Resources, Conservation & Recycling* 2005;45(3):226-250.
- [168] Machida S, Yagi J, Akiyama T. Exergy analysis of methanol production system. Tokyo, Japan: New Energy and Industrial Technology Development Organization (NEDO) 1998 (in Japanese).
- [169] Hugill J, Overbeek J, Spoelstra S. A comparison of the eco-efficiency of two production routes for methanol (ECN-I-01-003). Petten, The Netherlands: Energy Research Center of the Netherlands (ECN), 2001.
- [170] Lunsford J. Catalytic conversion of methane to more useful chemicals and fuels: a challenge for the 21st century. *Catalysis Today* 2000;63(2):165-174.

- [171] Michel S. Methanol Production Costs, Reports on Science and Technology 61/1999. Munich, Germany: Linde, 1999.
- [172] Casadonte D, Donahue M. Oxidative Sonochemical Production of Methanol from Methane (file TTU D-0164). Austin: Office of technology transfer and Intellectual property, Texas Tech University System, 2001. See also at: www.ttu.edu/~ottip/techlib/physical/0164.html.
- [173] IEA. Mitsubishi synthesis gas process for CO₂ emission free GTL plant. Paris: International Energy Agency (IEA) and Organization for Economic Co-operation and Development (OECD), 2002. See also at: www.iea.org/textbase/work/2002/stavanger/mhi.pdf.
- [174] Choudhary VR, Uphade BS. Oxidative conversion of methane/natural gas into higher hydrocarbons. Catalysis Surveys from Asia 2004;8(1):15-25.
- [175] Lange JP, Schoonebeek RJ, Mercera PDL, van Breukelen FW. Oxycracking of hydrocarbons: chemistry, technology and economic potential. Applied Catalysis A General 2005 (283):243-253.
- [176] Gonzalez L. Conversion of natural gas into heavier hydrocarbons: a process scheme. Proceedings of the 78th Annual Convention of Gas Processors Association, Nashville, Tennessee: Gas Processors Association, 1999.
- [177] Maitra AM. Critical Performance Evaluation of Catalysts and Mechanistic Implications for Oxidative Coupling of Methane. Applied Catalysis 1993 (104):11-59.
- [178] Lunsford J. The Catalytic Oxidative Coupling of Methane. Angewandte Chemie International Edition 1995;34(9):970-980.
- [179] Lu Y. Oxygen-permeable dense membrane reactor for the oxidative coupling of methane. Journal of Membrane Science 2000;170(1):27-34.
- [180] Lu Y, Dixon AG, Moser W, Ma YH. Analysis and optimization of cross-flow reactors for oxidative coupling of methane. Industrial Engineering Chemistry Research 1997;36(3):559-567.
- [181] Hugill J, Tillemans F, Dijkstra J, Spoelstra S. Feasibility study on the co-generation of ethylene and electricity through oxidative coupling of methane. Applied Thermal Engineering 2005;25(8-9):1259-1271.
- [182] Kim J, Cho S, Park J, Han S. Comparison of AgNO₃/Clay and AgNO₃/ALSG Sorbent for Ethylene Separation. Chemistry and Materials Science 2005;11(1):145-149.
- [183] USPTO. Catalytic wall reactors and use of catalytic wall reactors for methane coupling and hydrocarbon cracking reactions (US patent 5,599,510). US Patent Office (USPTO): Amoco Corporation, 1997.
- [184] Hoebink H, Venderbosch H, Geem P. Economics of the oxidative coupling of methane as an add-on for naphtha cracking. Chemical Engineering and Technology 1995;18(1):12-16.
- [185] Czechowicz D, Skutil K, Torz A, Taniewski M. An Integrated process of oxidative coupling of methane and pyrolysis of naphtha in a scaled-up unit. Journal of Chemical Technology and Biotechnology 2004;79(2):182-186.
- [186] Roberto C, Lorenzo D, Nazareno V. Unlocking Marginal Gas Reserves through Technological Innovation. Proceedings of the 17th World Energy Council Congress, London: World Energy Council, 1998.

- [187] EIA. International Energy Price Information. Washington DC: Energy Information Administration (EIA) at the US Department of Energy (EOE), 2007. See also at: <http://www.eia.doe.gov/emeu/international/prices.html>.
- [188] EIA. Annual Energy Outlook 2006 with Projections to 2030 (Report number:DOE/EIA-0383). Washington DC: Energy Information Administration (EIA) of the US Department of Energy, 2006.
- [189] DOE. Prices of natural gas for power generation in selected countries. Washington DC: US Department of Energy (DOE), 2006. See also at: <http://www.eia.doe.gov/emeu/international/ngasprie.html>.
- [190] Gielen D, Yagita H. The long-term impact of GHG reduction policies on global trade: a case study for the petrochemical industry. *European Journal of Operational Research* 2002;139(2002):665-681.
- [191] Williams R. Climate-Compatible Synthetic Liquid Fuels from Coal and Biomass with CO₂ Capture and Storage. Sacramento, California: California Energy Commission, 2005. See also at: www.climatechange.ca.gov/publications/others/2005-12-19_WILLIAMS.PDF.
- [192] Navqvi S. Opportunities for gas-to-liquid technologies (Supplement C Process Economics Program). Menlo Park, California: SRI, 2000.
- [193] Smith R. New Developments in Gas to Liquids Technologies. Proceedings of CERI 2006 Petrochemical Conference, Alberta: Canadian Energy Research Institute (CERI), 2004. See also at: <http://www.sriconsulting.com/SRIC/Public/>.
- [194] Heyde M, Kremer M. Recycling and recovery of plastics from packaging in domestic waste. LCA-type analyses of different strategies (LCA documents vol. 5 by Fraunhofer Institut für Verfahrenstechnik und Verpackung IVV). Freising, Germany: Eco-Infoma Press, 1999. See also at: http://www.scientificjournals.com/sj/lca_documents/volumes.
- [195] ECN. MARKAL MATTER Model Database 4.2. Input Data Technologies and Processes. Petten, The Netherlands: Policy Study Unit, Energy Research Center of The Netherlands (ECN), 2000.
- [196] Williams R, Larson E. A comparison of direct and indirect liquefaction technologies for making fluid fuel from coal. *Energy for Sustainable Development* 2003;7(4):103-129.
- [197] Zhang Y. Shenhua Coal Conversion Technology and Industry Development. Global Climate and Energy Project International Workshop on Exploring the Opportunities for Research to Integrate Advanced Coal Technologies with CO₂ Capture and Storage in China in Beijing, China, Palo Alto: Stanford University, 2005. See also at: http://gcep.stanford.edu/events/workshops_coal_08_05.html.
- [198] Bechtel. Gasification plant cost and performance optimization, Task 2 Topical Report: coke/coal gasification with liquids co-production (prepared by Bechtel Co., Global Energy Inc. and Nexant Inc. for the US National Energy Technology Laboratory of US Department of Energy under Contract No. DE-AC26-99FT40342). Washington DC: US Department of Energy (DOE), 2003.
- [199] DTI. Technology Status Report 010: Coal Liquefaction (Cleaner Coal Technology Program). London: Department of Trade and Industry (UK), 1999.
- [200] Nelson R. The Karrick LTC Process. Jean, Nevada: ReX Research, 2000.
- [201] van Steen H. Personal communication. The Hague: ABB Lummus, 2006.

- [202] Gray D. Producing Liquid Fuels from Coal. Proceedings of the National Research Council Board on Energy and Environmental Systems Workshop on Trends in Oil Supply and Demand on 20-21 October, 2005, Washington DC: US National Academy of Sciences, 2005.
- [203] Williams RH, Larson ED, Jin H. F-T Liquids Production from Coal and Coal + Biomass with Capture and Alternative Storage Options: Aquifer CO₂ storage vs CO₂-Enhanced Oil Recovery. Princeton, New Jersey: Princeton Environmental Institute, Princeton University, 2006. See also at: www.colorado.edu/law/eesi/Background_Paper.pdf.
- [204] Hamelinck C. Outlook for Advanced Biofuels (PhD thesis). Utrecht, The Netherlands: Utrecht University, 2004.
- [205] Larson E, Ren T. Synthetic fuel production by indirect coal liquefaction. *Energy for Sustainable Development* 2003;7(4):79-102.
- [206] Schut J. What is ahead for green plastics: look for more supply, more varieties, better properties. Cincinnati, Ohio: Gardner Publications, Inc., 2008. See also at <http://www.ptonline.com/articles/200802fa1.html>.
- [207] PRW. Dow links up with Brazilian ethanol major. See also at: http://www.prw.com/homePBP_NADetail_UP.aspx?ID_Site=8. *Plastics Industry News*, 2007.
- [208] Braskem. Braskem has the first certified green polyethylene in the world. San Paulo, Brazil: Braskem, 2007. See also at: http://www.braskem.com.br/site/portal_braskem/en/sala_de_imprensa/sala_de_imprensa_detalhes_6062.aspx.
- [209] Sunopta. Sunopta Updates Current Cellulosic Ethanol Projects. Brampton, Ontario: Sunopta Inc., 2007. See also at: <http://phx.corporate-ir.net/phoenix.zhtml?c=82712&p=irol-newsArticle&t=Regular&id=951516&>.
- [210] IPCC. IPCC Guidelines for National Greenhouse Gas Inventories. Geneva, Switzerland: Intergovernmental Panel on Climate Change (IPCC), 2006. See also at: <http://www.ipcc-nggip.iges.or.jp/>.
- [211] IEA. Energy Statistics Manual. Paris: International Energy Agency (IEA) and Organization for Economic Co-operation and Development (OECD), 2004.
- [212] Patel M, Crank M, Dornburg V, Hermann B, Roes L, Hüsing B, Overbeek L, Terragni F, Recchia E. Medium and long-term opportunities and risks of the biotechnological production of bulk chemicals from renewable resources (The BREW Project: European Commission Community Research 5th Framework Program). Utrecht, The Netherlands: Department of Science, Technology and Society at the Utrecht University, 2006. See also at: http://www.chem.uu.nl/brew/BREW_Final_Report_September_2006.pdf.
- [213] Ogden JM, Williams RH, Larson ED. Societal lifecycle costs of cars with alternative fuels/engines. *Energy Policy* 2004;32(2004):7-27.
- [214] IPCC. IPCC Special Report on Carbon Dioxide Capture and Storage. Geneva, Switzerland: Intergovernmental Panel on Climate Change (IPCC), 2005.
- [215] Klass D. Biomass for renewable, energy, fuels and chemicals. San Diego: Academic Press, 1998.
- [216] Farrell A, Plevin R, Turner B, Jones A, O'Hare M, Kammen D. Ethanol can contribute to Energy and Environmental Goals. *Science* 2006 (January): 311.

- [217] USDA. The Energy Balance of Corn Ethanol: An Update (Agricultural Economic Report Number AER-814). Washington DC: Office of Energy Policy and New Uses at the US Department of Agriculture, 2002.
- [218] Hoogwijk M. On the global and regional potential of renewable energy sources (PhD thesis). Utrecht, The Netherlands: Utrecht University, 2004.
- [219] Smeets E. Possibilities and Limitations for Sustainable Bioenergy Production Systems (PhD thesis). Utrecht, The Netherlands: Utrecht University, 2008.
- [220] Crank M, Patel M, Marscheider-Weidemann F, Schleich J, Hüsing B, Angerer G, Wolf O. Techno-economic Feasibility of Large-scale Production of Bio-based Polymers in Europe. Utrecht, The Netherlands: Department of Science, Technology and Society, Utrecht University, 2005. See also at: <http://ipts.jrc.ec.europa.eu/publications/pub.cfm?prs=1343>.
- [221] Hildebrandt D, Glasser D, Patel B, Hausberger B. A New Fischer-Tropsch Technology for China. Proceedings of 2006 Spring Meeting of American Institute of Chemical Engineers (AIChE) in Orlando, Florida, New York: AIChE, 2006.
- [222] Syncrude. Sustainability Report 2004 Fort McMurray, Alberta: Syncrude Canada Ltd., 2006. See also at: www.syncrude.com.
- [223] Plessis D, Laureshen C. Transformation of Heavy Gas Oils Derived from Oil Sands to Petrochemical Feedstocks. Proceedings of 2006 Spring Meeting of American Institute of Chemical Engineers (AIChE), Orlando, Florida: AIChE, 2006.
- [224] Coskata. Energy Positive Process. Warrenville, Illinois: Coskata Inc., 2008. See also at <http://www.coskata.com/EthanolEnergyPositive.asp>.
- [225] BRI. Gasification-Fermentation Pilot Facility in Arkansas. Fayetteville, Arkansas: BRO Energy LLC and Bioengineering Resources, Inc., 2005. See also at: www.brienergy.com.
- [226] Rangefuels. Our First Plant. Broomfield, Colorado: Range Fuels, 2008. See also at <http://www.rangefuels.com/our-first-plant>.
- [227] TSS. Gridley Ethanol Demonstration Project Utilizing Biomass Gasification Technology: Pilot Plant Gasifier and Syngas Conversion Testing for the City of Gridley, California: August 2002-June 2004 (subcontract report NREL/SR-510-37581); updates posted at <http://programreview.biomass.govtools.us/%5Cdocuments%5Cd2a1c5aa-f92a-4eab-a67d-fe84150c33ac.ppt>. Golden, Colorado: TSS Consultants and US National Renewable Energy Laboratory (NREL), 2005.
- [228] Steinberg M, Dang V. Production of synthetic methanol from air and water using controlled thermonuclear reactor power (I technology and energy requirement and II capital investment and production costs). *Energy Conservation* 1977;17(2-4):97-140.
- [229] Aldewereld C, Dautzenberg B, Guldemond M, Wijers J. Back from the Future: the petrochemical industry in the Rhine-Scheldt Delta in 2030 (a winning report presented for a national competition "Back from the Future", which Delft Technical University and Shell also took part; see also at http://wwwtest.iri.tudelft.nl/~klooster/reports/back_from_the_future.pdf). Eindhoven, The Netherlands: Eindhoven Technical University, 2006.
- [230] Abdel-Aal HK, Shalabi MA. Non-petroleum routes to petrochemicals. *International Journal of Hydrogen Energy* 1992;17(5):359-367.
- [231] Ruth M, Amato A, Davidsdottir B. Carbon Emissions from US Ethylene Production under Climate Change Policies. *Environmental Science & Technology* 2002;35(2):119-124.

- [232] Energy-Portal. Energy Prices for Industrial Users. Brussels: Energy Portal, 2008. See also at: <http://www.energy.eu/#industrial>.
- [233] EIA. Short-Term energy outlook (published on September 9, 2008). Washington DC: US Energy Information Administration (EIA), 2008. See also at: <http://www.eia.doe.gov/emeu/steo/pub/sep08.pdf>.
- [234] EIA. International Energy Outlook 2006. Washington DC: Energy Information Administration (EIA) of US Department of Energy (DOE), 2006.
- [235] CPB. Four Futures of Europe. The Hague: Netherlands Bureau for Economic Policy Analysis (CPB), 2003. See also at: <http://www.cpb.nl/nl/pub/bijzonder/49/>.
- [236] OECD. Improving recycling markets. Paris: Working Group on Waste Prevention and Recycling, Environment Directorate and Environment Policy Committee of OECD (Organization for Economic Co-operation and Development), 2005. See also at: <http://www.oecd.org/dataoecd/24/14/35582045.pdf>.
- [237] IEA. World Energy Outlook 2006. Paris: International Energy Agency (IEA) and Organization for Economic Co-operation and Development (OECD), 2006.
- [238] Petak K. Oil and gas prices: will they stay linked? Proceedings of 2006 EIA energy outlook and modeling conference in Washington DC, Arlington, Virginia: Energy and Environmental Analysis, Inc., 2006.
- [239] EPA. Guiding Principles for Monte Carlo Analysis (EPA/630/R-97/001). Washington DC: US Environmental Protection Agency (EPA), 1997. See also at: <http://www.epa.gov/ncea/pdfs/montcarl.pdf>.
- [240] D'Auria J. The Role of Innovation in USGC Competitiveness. UH-GEMI Conference on The Future of the Gulf Coast Petrochemical Industry, Houston: Global Energy Management Institute (UH-GEMI) at the University of Houston, 2005.
- [241] IPCC. IPCC Special Report on Emissions Scenarios. Cambridge: Cambridge University Press, 2000.
- [242] IndexMundi. Commodity Price Indices. Original sources include International Monetary Fund, Central Intelligence Agency, etc. Unknown location: Webmaster Miguel Barrientos, 2008. See also at: <http://indexmundi.com/commodities>.
- [243] IEA. Oil market report. Paris: International Energy Agency (IEA) and Organization for Economic Co-operation and Development (OECD), 2008. See also at: <http://omrpublic.iea.org/currentissues/full.pdf>.
- [244] Letsrecycle. Plastics Prices Archive 2008. London: letsrecycle.com, 2008. See also at: <http://www.letsrecycle.com/prices/plasticsArchive2008.jsp>.
- [245] WRI. Wood Resource Quarterly (1st Quarter and 2nd Quarter of 2008). Bothell, Washington: Wood Resources International (WRI), 2008. See also at: <http://www.woodprices.com/>.
- [246] EIA. International Energy Price Information. Washington DC: Energy Information Administration (EIA) at the US Department of Energy (DOE), 2008. See also at: <http://www.eia.doe.gov/emeu/international/prices.html>.
- [247] Platts. Coal trader international. London: The MacGraw-Hill Company, 2008. See also at: <http://www.platts.com/Content/Coal/Newsletters%20&%20Reports/Coal%20Trader%20International/See%20A%20Sample/index.pdf>.

- [248] EWG. Crude oil: the supply outlook. Ottobrunn, Germany: Energy Watch Group and Ludwig-Bölkow-Stiftung, 2007. See also at: http://www.energywatchgroup.org/fileadmin/global/pdf/EWG_Oilreport_10-2007.pdf.
- [249] Bruggink J. The Next 50 years: Four European Energy Futures. Petten: Netherlands Energy Research Center (ECN), 2005.
- [250] Poten. Naphtha Prognosis 2002-2012. Middle East Economic Survey 2005;68(10).
- [251] EIA. International Energy Outlook 2005. Washington DC: Energy Information Administration (EIA) of US Department of Energy (DOE), 2005.
- [252] IEA. Energy Statistics, 2004 Edition (containing Energy Statistics in OECD countries 2001/2002 and Energy Statistics of Non-OECD Countries 2001/2002). Paris: International Energy Agency (IEA) and Organization for Economic Co-operation and Development (OECD), 2004.
- [253] CMAI. World Methanol Analysis. Houston, Texas: Chemical Market Associates, Inc. (CMAI), 2008.
- [254] OECD. OECD Environmental Outlook for the Chemical Industry. Paris: OECD Environment Directorate (Organization for Economic Co-operation and Development), 2001. See also at: www.oecd.org/ehs.
- [255] Shell. Energy needs, choices and possibilities: scenarios to 2050. The Hague: Shell International, 2001. See also at: <http://www.shell.com/scenarios>.
- [256] Korevaar G. Sustainable chemical processes and products (PhD thesis). Delft, The Netherlands: Delft Technical University, 2004.
- [257] Dijkema G. Process system innovation by design: towards a sustainable petrochemical industry (PhD thesis). Delft: Delft Technical University, 2004.
- [258] OECD. Oslo Manual: Proposed Guidelines for Collecting and Interpreting Technological Innovation, 2nd Edition. Paris: OECD (Organization for Economic Co-operation and Development)/Eurostat 1997.
- [259] Latour B. Science in Action: How to Follow Scientists and Engineers Through Society. Milton Keynes, UK: Open University Press, 1987.
- [260] USCB. Standard Industrial Classification (SIC) and North American Industry Classification System (NAICS). Washington DC: US Census Bureau, 2002.
- [261] UN. International Standard Industrial Classification of all Economic Activities, Third Revision, Statistical Papers Series M No. 4, Rev. 3. New York: Statistical Office of the United Nations, (UN) 1990.
- [262] Fagerberg J. Innovation: A guide to the literature. In: The Oxford Handbook of Innovation. J. Fagerberg, D. Mowery and R. Nelsons. Oxford: Oxford University Press, 2004.
- [263] Eurostat. Statistics on Innovation in Europe (data 1996-1997): Results from Community Innovation Survey (CIS II). Luxembourg: Eurostat and Enterprise DG European Commission, 2001.
- [264] Eurostat. Innovation in Europe (data 1998-2000): Community Innovation Survey (CIS III) Results for EU, Iceland and Norway. Luxembourg: Eurostat and Enterprise DG European Commission, 2004.
- [265] Freeman C, Perez C. The Economics of Industrial Innovation. London: Pinter, 1997.

- [266] Colombo U. A viewpoint on innovation in the chemical industry. *Research Policy* 1980;9(3):205-231.
- [267] Arora A. Patents, licensing and market structure in the chemical industry. *Research Policy* 1997;26 (4):391-403.
- [268] Madden J. Personal communication. Houston, Texas: Vice President of Chemical Marketing Resources, 2005.
- [269] Walthie T. Creating Advantage. Proceedings of 2004 Dow Institutional Investors Meeting, Location Undisclosed: 2004. See also at: http://www.corporate-ir.net/ireye/ir_site.zhtml?ticker=DOW&script=11983&item_id='092304test.htm').
- [270] CEN. Global top 50 chemical producers. *Chemical & Engineering News* 2004;82(29).
- [271] Arora A, Fosfuri A, Gambardella A. Market for Technology: why do we see them, why don't we see more of them and why we should care. Madrid: Universidad Carlos III, Working Paper No. 99-17(4), 1999.
- [272] Bowonder B. Innovation and convergence: expanding boundaries of the chemical industry. *Interdisciplinary Science Reviews* 2001;26(1):43-55.
- [273] Strohrman M. Personal communication. Ludwigshaven, Germany: BASF, 2005.
- [274] Kopytowski J, Pejewski P. Invention to innovative process bridge: heuristic rules. Proceedings of the IUPAC (International Union of Pure and Applied Chemistry) CHEMRAWN XVI conference on "innovation in the chemical industry: the way from pure to applied chemistry", Ottawa: Chemistry International, 2003.
- [275] CEFIC. R&TD and Innovation in the EU. Economic Bulletin of European Chemical Industry Council (CEFIC) published in June of 1997, 1997.
- [276] Slawinski M. Innovation as a business strategy for Atofina Polyolefins. Proceedings of the 25th Annual AIChE European Benelux Section Colloquium "Innovation in the Chemical Industry" in The Hague, New York: AIChE, 2004.
- [277] Stinger D. Personal communication. Houston, Texas: WOW Energy Inc., 2005.
- [278] Butler P, Berendes R, Elliott B. Cyclicity: Trying to Manage the Unmanageable (McKinsey & Company). In: Value Creation: Strategies for the Chemical Industry. F. Budde, f. Farha, H. Frankemolle, D. Hoffmeister and K. Kramers. Weinheim, Germany: Wiley-Vch, 2001.
- [279] Deason D. Personal communication. Baytown, Texas: ExxonMobil, 2005.
- [280] Anonymous-2. Personal communication. Baytown, Texas: Process control engineers at a major petrochemical company in the US Gulf Coast, 2005.
- [281] Theising T. Personal communication. Freeport, Texas: BASF, 2005.
- [282] Burchmore S, Ayscough N, Gendebien A. Techno-Economic Study on the Reduction Methods, Based on BAT of Industrial Emissions (Air, Water, Wastes) from the Basic Petrochemical Industry. European Commission, 1993.
- [283] Anonymous-1. Personal communication. Houston, Texas: R&D Department of a major petrochemical company located in the Westhollow Technology Center, 2005.
- [284] Burchmore S, Ayscough N, Gendebien A. Techno-Economic Study on the Reduction Measures based on BAT of Industrial Emissions (Air, Water, Wastes) from the Basic Petrochemical Industry. Brussels: European Commission, 1993.

- [285] Cagnolatti C. Global Ethylene Plant Performance Comparison. Proceedings of 2005 AIChE Spring National Meeting and 17th Annual Ethylene Producers Conference in Atlanta, New York: American Institute of Chemical Engineers (AIChE), 2005.
- [286] Ferland K. Personal communication. Austin, Texas: Texas Industries of the Future at the University of Texas, 2005.
- [287] Zarker K. Personal communication. Austin, Texas: Pollution Prevention and Industry Assistance at Texas Commission for Environmental Quality, 2005.
- [288] CEN. Employment: Another Decline. Chemical & Engineering News (CEN), July 11, 2005.
- [289] Tallman M. Personal communication. Houston, Texas: KBR, 2005.
- [290] Thornley S. Personal communication. Houston, Texas: ABB Lummus, 2005.
- [291] ExxonMobil. Annual Report 2004 of ExxonMobil Chemical. 2005. See also at: www.exxonmobil.com/corporate/files/corporate/ar_2004_chemical.pdf.
- [292] Herzog C. Personal communication. Atlanta, Georgia: Mustang, 2005.
- [293] Blom H. Personal communication. Amsterdam: Shell Global Solutions, 2005.
- [294] Calis H. Personal communication. Amsterdam, The Netherlands: Shell Gas & Power, 2005.
- [295] Gartside R, Stanley S. ABB's Olefin Vision 2010. Proceedings of Spring Meeting of American Institute of Chemical Engineers (AIChE), New Orleans: New York: AIChE, 2002.
- [296] Laghate A. Personal communication. Zoetermeer, The Netherlands: Technip, 2005.
- [297] Vora B. Personal communication. Des Plaines, Illinois: UOP LLC, 2005.
- [298] SRI. The Chemical Industry and Technology Opportunities in China. Proceedings of the 9th Annual China Chemical Industry Conference in Shanghai, China, Menlo Park, California: SRI International Consulting Co., 2003.
- [299] Richman P. Personal communication. Houston, Texas: UOP LLC, 2005.
- [300] Rothel T, Faha G, Hoffmeister D. Managing Commodity Portfolios (McKinsey & Company). Weinheim, Germany: Wiley-Vch, 2001.
- [301] EIA. Performance Profiles of Major Energy Producers. Washington DC: Energy Information Administration (EIA) at the US Department of Energy (DOE), 2004. See also at: <http://www.eia.doe.gov/emeu/perfpro/>.
- [302] Anonymous-3. Personal communication. Amsterdam, Netherlands: Research and Technology Center of a major petrochemical company, 2005.
- [303] Arbogast S. Conference Report. Proceedings of 2005 Conference on the Future of the Gulf Coast Petrochemical Industry, Houston: University of Houston, 2005. See also at: www.bauer.uh.edu/gemi/events/GCPI-Conference%20Paper.doc.
- [304] Schoemaker P. Profiting from uncertainty. New York: The Free Press, 2002.
- [305] Fiato R, Sibal P. ExxonMobil's advanced Gas-to-Liquids technology ABC21. Proceedings of Middle East Oil & Gas Show and Conference on March 12-15, 2005 in Bahrain, Houston: ExxonMobil, 2005.
- [306] Hall K. Personal communication. College Station, Texas: Professor, Department of Chemical Engineering at A&M University, 2005.

- [307] Clark W. Internal Growth and Risk Taking in the Chemical Industry. R&D Meets M&A, Proceedings of 2003 Conference on Innovation and Creativity in Chemical R&D, Philadelphia: Chemical Heritage Press, 2004.
- [308] Sharpe WF. Portfolio Theory and Capital Markets. New York: McGraw-Hill, 1999.
- [309] Ringland G. Scenario Planning: Managing for the Future. Chichester: John Wiley & Sons, 1998.
- [310] Heijden K. Scenario, Strategies and the Strategy Process. Breukelen, The Netherlands: Nijenrode University Press, 1997.
- [311] Schoemaker P. Using Scenarios in Strategic Planning. Philadelphia: Chemical Heritage Press, 2003.
- [312] Irvin J, Martin B. Foresight in Science: Picking the Winners. London: Pinter Publishers, 1984.
- [313] Imanari M. Innovation in the Japanese Chemical Industry. Proceedings of the IUPAC (International Union of Pure and Applied Chemistry) CHEMRAWN XVI conference on innovation in the chemical industry: the way from pure to applied chemistry, Ottawa: Chemistry International, 2003.
- [314] CEN. Global Top 50. Chemical & Engineering News (CEN), July 18, 2005. See also at: www.cen-online.org.
- [315] Tsouris C, Porcelli J. Process Intensification--has its time finally come? Proceedings of Spring Meeting of American Institute of Chemical Engineers (AIChE), Topical Conference and Workshop sponsored by AIChE's Sustainable Engineering Forum and Institute for Sustainability with support from the US Department of Energy in New Orleans, New York: AIChE, 2003.
- [316] Achilladelis B, Schwarzkorf A, Cines M. The dynamics of technological innovation: The case of the chemical industry. Research Policy 1990;19(1):1-34.
- [317] Fleischer M, Kelm S, Palm D. Regulations and Innovation in the Chemical Industry. The Impact of EU Regulation on Innovation of European Industry. Seville: Institute for Prospective Technological Studies at the European Commission DG Joint Research Center, 2000.
- [318] Roveda C, Vercesi P, Lindblom J. Case Sector Report: Basic Industrial Chemicals, European Commission's Futman Project--the Future of Manufacturing in Europe 2015-2020: the Challenge for Sustainability. Milano: Fondazione Rosselli, 2004.
- [319] EIA. US Manufacturing Consumption Energy Survey. Energy Information Administration (EIA) of US Department of Energy (DOE), 1998. See also at: www.eia.doe.gov/emeu/mecs/iab98/chemicals/index.html.
- [320] Stankiewicz A, Moulijn J. Process Intensification. Industrial Engineering and Chemical Research 2002;41(8):1920-1924.
- [321] EC. Green Paper on Energy Efficiency or Doing More with Less. Brussels: European Commission (EC), 2005. See also at: http://europa.eu.int/comm/energy/efficiency/doc/2005_06_green_paper_text_en.pdf.
- [322] Eder P, Sotoudeh M. Innovation and cleaner technologies as a key to sustainable development: the case of the chemical industry. Seville: Institute for Prospective Technological Studies at the European Commission DG Joint Research Center (JRC), 2000.

Acknowledgements

The author wishes to express his appreciation of the Policy Study unit of Netherlands Energy Research Center of the Netherlands (ECN) and the Utrecht Energy Research Center (UCE) for financing this project. The author thanks his supervisors, Martin Patel and Kornelis Blok, for their criticisms and patience through the years. Special thanks go to Ton van Dril, Bert Daniels and Gerrit-Jan Schaeffer from ECN for providing supervision at various stages. Thanks to the review committee for their time.

Many thanks go to all interviewees and contact persons in the industry, academia and government bodies for their valuable contributions. Without their input, this thesis would not have been possible. Please note that their contributions are purely personal opinions and do not represent the positions of the companies they are associated with. Special thanks to those who spent much time reading and commenting on early drafts: M. Bearden and M. Steijns at Dow, E. Forkink at Shell and P. Smedt at Total. Thanks to the following individuals who have either commented on early drafts, have been interviewed or have assisted in this research: P. Lewellen, G. Koot, A. Grondman, H. Blom, M. Wilfried, HP Calis, C. Gomez, J. Lange, F. Niele, J. Harmsen and R. Bos at Shell, M. Braber and D. Zanten at Verificatiebureau Benchmarking, M. Stromann at BASF, K. Ferland at U. of Texas in Austin, K. Zarker at Texas TCEQ, H. Steen and S. Thornley at ABB Lummus, P. Pujado, P. Richman and B. Vora at UOP, M. Brau and D. Stinger at WOW Energies, G. Beck at Eco-Holdings, J. Madden at CMR, T. Theising at BASF, D. Deason at ExxonMobil, J. Siddall, K. Tannenbaum and M. Steijns at Dow, M. Maggio and J. Merrit at ChevronPhilips, A. Laghate, S. Barendregt, V. Kaiser and S. Singare at Technip, Prof. H. Rahier at Vrije Universiteit Brussel, Prof. dr. C. Vandecasteele at Katholieke Universiteit Leuven, G. Dijkema and J. Moulijn at Delft Technical University, P. O'Connor at Bio^cCon, C. Bull and S. Warren at Hamworthy, T. Mattick at U. of Washington, Prof. A. Rayford en K. Hall at Texas A&M University, C. Herzog at Mustang V. Partington and C. Bowen at Stone & Webster, M. Tallman at KBR, A. Victor at Aspentech, M. Dr. Liebner at Lurgi, B. Beloff and D. Tanzil at Bridges Consultancy, J. Venselaar and C. Montalvo at TNO, G. Roukens at CO₂ Global Norway, Prof. H. Chang at Tamkang University (Taiwan), Prof. M. Taniewski at Silesian

Polytechnical University (Poland), Prof. X. Chaogang and W. Xuefeng at SINOPEC (China), S. Cho at KIER (Korea), S. Han and Y. Park at KRICT (Korea) and A. Yabe at MITI (Japan). Thanks also to those interviewees who helped the author but preferred to remain anonymous. The author owes gratitude to Peter Alderliesten, Pieter Bach, Piet Bonenkamp, Jos Bruggink, Arend de Groot, Jim Hugill, Pieter Kroon, Ruth Mourik, Gerard Stienstra and Simon Spoelstra at ECN for useful comments. Thanks to Detlef van Vuuren and Bert de Vries at MNP for stimulating conversations.

The author also wants to pay tribute to all of his colleagues and former colleagues at Utrecht University. The thesis has been built upon work by Veronica Dornburg, Carlo Hamelink, Barbara Hermann, Monique Hoogwijk, Esther Luiten, Maarten Neelis (especially for the concept of endothermicity), Dian Phylipsen, Louis Joosten and Ernst Worrell. The author owes great gratitude to Pita Verwij for her support and counseling. Siham Belarbi, Mirjam van Deutekom, Aisha Elfring and Cosy Harpe should be thanked for the administrative support. Thanks also go to the following individuals for the inspiring conversations: Manuela Crank, Kay Damen, Martijn van Rietbergen, Andre Faaij, Carlo Hamelinck, Marko Hekkert, Krijn de Jong, Wim Turkenburg, Martin Junginger, Corry de Keizer, Erik Lysen, Enrico Marsilli, Evert Nieuwlaar, Vlasis Oikonomou, Andrea Rameriz, Oscar van Vliet and Martin Weiss.

The author is forever indebted for receiving teachings and friendship from the following individuals: J. Allgaier, C. Bear, L. Box, A. Sarra, C. Oversteegen, I. Olaussen, J. Ulmanen, M. Joosten, R. Wang and S. Hong. Thanks to his lovely friends and paranimfs: Felix van Vugt and Marijn Kuijper. The author is thankful for the support of all his friends in China who can always make him laugh. Thanks to Frank Peters and Martha Kets for lessons in the impossible Dutch language. Thanks to Junying Chang for helping with the Chinese translation. Ex-colleagues and friends at EcoSecurites Group PLC worldwide, E. Cyhlarova in Oxford and Albert Fischer at Yellow & Blue are thanked for their encouraging words.

Finally, the author's most special thanks go to Morna Isaac and the extended families (the Rens and the Xiaos in China as well as the Isaacs in The Netherlands and Israel) for their love, support and understanding throughout these years.

About the Author

Tao Ren was born on June 2, 1974 in Urumqi, the capital city of Xinjiang Uyghur Autonomous Region located in Northwest China. He received an associate's degree in International Trade Statistics from Nankai University in China in 1994, a bachelor's degree in Business Management from the University of North Dakota in the USA in 1998 and a master's degree in Science and Technology Studies from Maastricht University in the Netherlands in 2002. He did his PhD research project at the Department of Science, Technology and Society and Copernicus Institute at Utrecht University in the Netherlands in 2002-2006. He then worked for EcoSecurities Group PLC in the UK, where he specialized in Clean Development Mechanism projects as a Project Manager. These projects aim to reduce greenhouse gas emissions and to improve energy efficiency in developing countries. He is currently a Business Analyst at Yellow & Blue Clean Energy Investments BV in Utrecht, where he helps in bringing renewable energy and energy efficiency related technologies into the global clean tech market.