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ENERGY EFFICIENCY AND INNOVATIVE EMERGING TECHNOLOGIES FOR OLEFIN PRODUCTION

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ABSTRACT

Among the current IPPC installations, steam cracking for olefin production is the single most energy consuming process (ca. 30%) in the chemical industry, accounting for ca. 180 million tons of CO₂ worldwide. This paper reviews steam cracking and innovative emerging olefin technologies in terms of energy efficiency. Pyrolysis section alone consumes ca. 65% of the total energy use and ca. 75% of the total exergy loss. An overview of state-of-the-art naphtha cracking technologies shows that ca. 20% savings on the current average energy use are possible. Advanced naphtha steam cracking technologies in the pyrolysis section (e.g. advanced coil and furnace materials) may together lead to up to ca. 20% savings on the total energy use by state-of-the-art technologies. Improvements in the compression and separation sections may together lead to up to ca. 15% savings on the total energy use by state-of-the-art technologies. Catalytic olefin technologies could possibly save at least ca. 20% on the total energy use by the state-of-the-art naphtha steam cracking.

Keywords: energy efficiency, energy analysis, steam cracking, catalytic olefin technologies, ethylene and propylene

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1 Introduction

Among the current IPPC installations, olefin production is the most energy consuming processes in the chemical industry, accounting for ca. 30% of the sector’s total final energy use [1]. The core process for olefin production is steam cracking\(^1\), which converts hydrocarbon feedstocks (naphtha, ethane, etc.) to olefins (ethylene, propylene, etc.) and other products. Steam cracking accounts for ca. 2-3 EJ primary energy use and ca. 180 millions tons of CO\(_2\) emission worldwide (see Table 1). Reduction of this emission can help meet the emission targets set by Kyoto Protocol [2]. Energy cost is counted ca. 70% of production costs in typical ethane or naphtha based olefin plants [3, 4]. In addition, over 35% of the European crackers are over 25 years old. Therefore, energy management and re-investment are important considerations [5]. From both environmental and economic perspectives, it is therefore of interest to study energy losses in the existing processes as well as energy-saving potentials offered by recent improvements and alternative processes. Also, R&D priority setting and innovation policy studies may benefit from such characterization.

Many technical papers that describe alternative olefin processes with an emphasis on technical details on catalysis and engineering can be found in [6]. Interesting techno-economic studies for various ethylene processes have been done in the 1970s and 80s [7, 8]. A number of new olefin production technologies for short-term development were also reviewed by [9]. However, a thorough comparison of alternative olefin technologies and steam cracking that take into account energy allocation on byproducts and all feedstock production is still missing. It is interesting to study such olefin technologies, which might affect energy use in the next 20 to 30 years. Therefore, our research question is: what are possible technological developments in steam cracking and in alternative processes for the coming decade and how is their potential energy efficiency in comparison?

Our approach for energy analysis follows two stages. First, we try to understand the existing process and how energy is used. Then, we will make an inventory of new technologies and characterize them in terms of potential energy-efficiency improvement. This approach is similar to what has been used in [10]. This article is mostly based on data available in the public literature\(^2\). We limit ourselves to technologies that produce olefins from conventional (ethane, naphtha and propane) and heavy feedstock only. Also, due to its large share as a feedstock (Table 1), naphtha steam cracking is the main subject and ethane steam cracking is less discussed. Technologies involving other feedstocks, i.e. natural gas, biomass, coal, organic waste and CO\(_2\) will not be discussed in this paper\(^3\).

This paper first reviews background factors that affect energy use in olefin production in section 2. Section 3 gives a process description for naphtha steam cracking. Energy terms used in this article are defined in section 4. Section 5 presents

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\(^1\) It includes all production processes in a steam cracker, i.e. from pyrolysis to separation. See process description later.

\(^2\) The major sources are of four categories: government reports (e.g. by EU Joint Research Center and US Department of Energy), journals (e.g. Oil & Gas, Hydrocarbon Processing, Catalyst Today and Fuel Processing Technology), conference proceedings (e.g. Ethylene Producers Conference) and publications by producers and licensors (e.g. Stone & Webster, UOP, Shell, etc.) Interviews and correspondences with producers and licensors made also a limited amount of contributions.

\(^3\) We have completed an analysis of energy use, CO\(_2\) emission and production cost for natural gas to olefins (UOP LLC MTO, ExxonMobil MTO and Lurgi MTP) and oxidative coupling of methane via ethane. Our conclusion shows that these new processes are far less efficient than the state-of-the-art steam cracking.
the results of the energy analysis. Under section 6, state-of-the-art and advanced naphtha cracking technologies are described. Section 7 discusses further on catalytic olefin technologies.

2 Background Factors

We will first discuss three background factors that are relevant for further analysis. They are: the role of steam cracking in the industrial sectors, market growth and feedstocks. First, steam cracking and its products, in particular olefins, have a backbone status for many industrial sectors. The worldwide demand and production of olefins are higher than any other chemicals [5]. Daily goods ranging from computer parts to pharmaceuticals are primarily derivatives of steam cracking products. In Western Europe, 95% of ethylene and 70-75% of propylene are produced through steam cracking [5]. The rest of propylene comes from refinery fluidized catalytic cracking (FCC) units (28%) and propane dehydrogenation or metathesis (2%) [5], which will be discussed later. In general, steam cracking plays a dominant role in olefin production.

Global ethylene production in the late 1990s has grown at a very high rate of 7-8% per year [11]. This is largely due to the strong demand growth in East Asia, especially by China, while the current market growth in the US and Europe was rather moderate [11]. In the last 2-3 years, the annual growth rate of the global olefin market slowed down to 3-4%. The propylene market is growing faster than the ethylene market by (1-3%). Recently, large capacities are being built or planned in the Middle East, but most of them produce ethylene from ethane, which is available at very competitive prices ($0.8-1.3/GJ in Middle East as opposed to $4/GJ in Asia) [11]. This might increase the global share of ethane relative to naphtha in the coming years (see Table 1).

There are two categories of feedstocks for the current olefin production: one derived from crude oil (such as naphtha, gas oil, propane, etc.) and another derived from natural gas (ethane, propane, etc.) (see Table 1). Their availability depends on the composition of crude oil and natural gas and their production volumes. Generally speaking in terms of weight, ca. 10% of oil refinery output is naphtha while 1-14% of natural gas is ethane and 80-90% is methane. Natural gas from the Middle East and Norway usually has higher ethane content than that from Russia. These regions together have 80-90% of the world’s natural gas reserves [12].

3 Process Description of Naphtha Steam Cracking

Steam cracking typically refers to all processes inside the battery limits of a steam cracker. As Figure 1 shows, a steam cracker comprises the following three sections: pyrolysis (A), primary fractionation/compression (B) and product recovery/separation (C).

**Pyrolysis section (A)** This is the heart of a steam cracker. Naphtha first enters the convection section (where a series of heat exchangers are located) of a pyrolysis furnace and is preheated to 650 °C. Then, it is vaporized with superheated steam and is passed into long (12-25 meters), narrow (25-125 mm) tubes, which are made of chromium nickels alloys. Pyrolysis mainly takes place in the radiant section of the furnace where tubes are externally heated to 750-900 °C (up to 1100 °C) by fuel oil or gas fired burners [5]. Depending on the severity¹, naphtha is cracked into smaller

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. Low severity has the temperatures at lower than
molecules via free-radical mechanism in the absence of catalysts. The beta scission of the free radicals leads to the formation of light olefins in the gaseous state [14]. After leaving the furnace, the hot gas mixture is subsequently quenched in the transfer line exchangers (TLE) to 550-650 °C (or sometimes lower to 400 °C). TLE will then be followed by a series of heat exchangers and temperatures could drop down to 300 °C [13]. These heat-transfer activities avoid degradation by secondary reactions and at the same time generate high-pressure steam for driving compressors, etc. However, heat exchangers are prone to fouling\(^1\) and therefore have to be shut down, both scheduled and unscheduled.

**Primary fractionation/compression (B)** Primary fractionation applies to naphtha and gas oil feed only. In the primary fractionation section, gasoline and fuel oil streams (rich in aromatics) are condensed out and fractionated. While this liquid fraction is extracted, the gaseous fraction is de-superheated in the quench tower by a circulating oil or water stream. The gaseous fraction is then passed through four or five stages of gas compression (temperatures at ca. 15-100 °C), cooling and final cleanup to remove acid gases, carbon dioxide and water. Most of the dilution water steam are condensed, recovered and recycled. Fuel oil and BTX (aromatic gasoline which contains benzene, toluene and xylene.) are products from this section. A common problem with compression is fouling in the cracked gas compressors and after-coolers. The built up of polymers on the rotor and other internals results in energy losses as well as mechanical problems [16]. Wash oil and water are used to reduce fouling.

**Product recovery and fractionation (C)** It is essentially a separation process through distillation, refrigeration and extraction. Equipment includes chilling trains (chilling and refrigeration) and fractionation towers (de-methanizer, de-ethanizer and the rest in Figure 1). De-methanization requires very low temperatures (e.g. –114 °C). C\(_2\) (ethylene and ethane) separation often requires large distillation columns (splitters) with 120 to 180 trays and high reflux ratios [17]. Undesired acetylene will be removed through catalytic hydrogenation or extractive distillation. Similarly, in a C\(_3\) splitter, C\(_3\) (propane and propylene) are re-boiled with quench water at ca. 80 °C and separated. Ethylene and propylene refrigeration systems could be operated at low temperatures (within the range of –10 °C and -150 °C) for cooling and high pressure (200-450 psia) for compression [5, 18]. Ethane and propane are recycled as feedstock (not fully shown in Figure 1). Methane and hydrogen are separated at cryogenic temperatures. As fuel grade byproducts, they are often used as fuel gas in the pyrolysis process, but they can also be exported. Butadiene, other C\(_4\) and aromatic gasoline are separated in the end. The total products yields from naphtha cracking differ depending on the paraffin and aromatic content of naphtha (full range, light, etc.) and severities (high, moderate and low).

Generally, steam cracking of ethane and other feedstocks also requires three sections that are similar to those in the case of naphtha cracking process [5]. However,

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800 °C and ca. 1 second residence time [13]. 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 [5]. Severity is strongly restrained by metallurgy of the tubes and rapid coking tendency in the coils.

\(^1\) Fouling is a complex science and is still an unresolved problem in the process industry. Simply explained, it is the degradation in heat transfer (or increase in the thermal resistance) due to a buildup of polymers or coke on the heat transfer surface. It also leads to higher hydraulic resistances that result in higher energy use [15].
the processes differ depending on feedstock properties and design arrangement, which often concern fractionation and separation sections [19]. For instance, ethane cracking requires slightly higher temperature in the furnace, higher capacity of C₂ splitter but less infrastructure facilities. Storage tanks or recovery equipment for propylene, butadiene and BTX aromatics are not needed, but an ethane vaporizer and super-heater are required.

An additional issue is about coking. Regular decoking is required in various parts of the pyrolysis section. Before decoking, the furnace first has to be shut down. Then, high pressure steam and air (sometimes hydrogen) are fed to the furnace while 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 burned off, washed away with high pressure water or be removed mechanically. Decoking process can take 20-40 hours for a naphtha cracker [20]. Depending on the feedstocks, coil configuration and severity, decoking for steam cracking furnaces is required every 14-100 days in average [5]. Typically, a naphtha pyrolysis furnace is decoked every 15-40 days. Maximum cycle time is 60-100 days [5, 20]. Decoking is also required for quench towers, TLE and other sections.

4 Definitions

Energy indicators used in this article are defined as follows. The total energy use (per unit for a specific process) is our focus in this article. It does not exported energy (e.g. steam). The total energy use includes energy use in olefin processes and for additional imports (if applicable).

- Energy use in olefin process is the sum of fuel, steam and electricity in primary terms that are used for reactions (converting feedstock into olefins) and all the subsequent processes (e.g. compression and separation). This definition is referred to as “process energy use”. Process energy use is usually defined as the energy use in an industrial process. Process energy use in the case of naphtha/ethane steam cracking is the sum of energy loss and thermodynamic theoretical energy requirement. Process energy use is typically expressed in terms of specific energy consumption (SEC). These two terms are commonly used to measure the energy efficiency of ethane/naphtha steam crackers. In this article, the total energy use of steam cracking is the same as its process energy use or SEC, therefore, these three terms are used interchangeably only for steam cracking in this article.

- For several alternative, non-steam cracking processes (to be discussed later), however, energy use in olefin process is only part of the total energy use. Some of these processes import oxygen, hydrogen, electricity and/or steam. Primary energy uses in the production of these imports are also accounted as part of the total energy use. All of these energy uses are expressed in SEC as well.

1 Energy loss represents the difference between the total energy input and total energy output. Thermodynamic theoretical energy requirement is the minimum energy input requirement for converting naphtha to end products. It is the difference between the total calorific value of products and the calorific value of naphtha at ambient temperatures. The former is larger than the latter because the overall naphtha-based steam cracking reactions are endothermic. Thermodynamic theoretical energy requirement is needed to produce products at certain yields from a given feedstock and it can neither be changed nor avoided. Therefore, process energy use can only decrease by reducing energy loss. However, since feedstock and product yields vary from process to process, thermodynamic theoretical energy requirements vary as well. In order to compare energy efficiencies across different processes, we believe process energy use for steam cracking (thermodynamic theoretical energy requirements and energy loss together) can be used as a basis for comparing energy efficiency in this article. Its calculations for steam cracking will be explained later.
All energy figures are in terms of primary energy. Final energy figures for electricity and steam have been converted to primary energy using efficiency factors 40% and 85% respectively. Energy use in catalyst and equipment production is not included. Energy contents of products (or calorific values) are calculated based on their low heating value (LHVs) collected in [21].

The degree of energy efficiency is measured by the expression of SEC, GJ/t. This article uses several expressions of SEC, e.g. GJ/t feedstock, GJ/t ethylene or GJ/t high value chemicals (HVCs). In this paper, GJ/t ethylene means that all energy use is allocated to ethylene only and all other byproducts are hence produced “for free” in terms of energy use. This is not always the best indicator. For example, if ethane cracking is compared with naphtha cracking, it will not be fair to use GJ/t ethylene for comparison. Ethylene yield from ethane cracking is much higher than from naphtha cracking, but naphtha cracking also yields considerable amounts of other valuable byproducts (Table 2). For this reason, we believe GJ/t HVCs is a better indicator. HVCs include light olefins (ethylene, propylene and butadiene) and non-olefins. Non-olefins are aromatics and other C5+ in the case of steam cracking. While the mass of light olefins is fully taken into account, the mass of non-olefins is weighted with 50%\(^1\). The reason is that these non-olefin products are usually priced approximately half as much as light olefins\(^2\) [22]. Our estimates for energy savings refer to savings on total energy use in terms of GJ/t HVCs.

This paper presents an exergy analysis for naphtha-based steam cracking. Exergy of an energy carrier refers to the maximum amount of work that can be extracted from an energy carrier. It is instructive to study exergy losses here because exergy analysis can locate where energy savings for a process are possible. Exergy loss in the naphtha-based steam cracking is considered equal to energy content of combusted fuels at ambient temperature.

All CO\(_2\) emissions from the use of fuel-grade byproducts and external energy sources are counted. In this article, yield refers to final yield (after separation, recycling, etc.). It is defined as a percentage of desired products divided by hydrocarbon feedstock (oxygen not counted) on the mass basis, unless otherwise specified. Chemistry literature often uses per-pass yield on the mol basis. It will be noted where this definition is used in this paper.

5 Energy Analysis of naphtha/ethane steam cracking

Our energy analysis is aimed at searching for the areas for energy efficiency improvement. This section will first set a basis for further comparison of the total energy use in steam cracking, then it will show where energy and exergy are used in a typical naphtha steam cracker and finally it will discuss energy integration.

\(^1\) It is different from the definition of HVCs used in [5] where ethylene, propylene, butadiene, benzene and hydrogen are weighted with 100%. However, this does not lead to large differences in terms of SECs since the yield of non-olefins from steam cracking is small (e.g. aromatics yield max. 10%). Our definition of HVCs is useful to compare steam cracking with alternatives, e.g. catalytic cracking from which aromatics yield is high (15-30% see Table 5).

\(^2\) Aromatics (pyrolysis gasoline) market prices are ca. $190/t in 2002-2003 [3, 22].
5.1 Typical Specific Energy Consumption

It is a difficult task to identify a SEC (GJ/t HVCs or GJ/t ethylene) that represents current process energy use by a typical existing naphtha crackers. Most data available are in SECs in terms of GJ/t ethylene and do not give further data on yields and methodologies. They are rather old, incomplete or within a very wide range. The world average SECs (excluding Japan and Korea\(^1\)) in 1995 was ca. 30-36 GJ/t ethylene for naphtha crackers [23]. If we consider that an efficiency improvement rate is 1.7% per year for typical steam crackers in the past thirty years [5] and typical yields of HVCs in Table 2 are valid, then the SECs for a typical naphtha cracker should be approximately within the range of 26-31 GJ/t ethylene and 14-17 GJ/t HVCs.

Based on Table 2, calculations show that the thermodynamic theoretical energy requirement (see definition) for naphtha cracking is ca. 8 GJ/t ethylene or ca. 5 GJ/t HVCs. In the case of ethane steam cracking, this figure is ca. 5 GJ/t ethylene or ca. 5 GJ/t HVCs. Therefore, the SEC for a typical naphtha cracker is three times of the theoretical energy input needed to convert naphtha to final products. As earlier defined, SEC in the case of naphtha steam cracking is the sum of energy loss and thermodynamic theoretical energy requirement. So the energy loss in a typical naphtha-based steam cracking process is at least 17 GJ/t ethylene or 8 GJ/t HVCs. In this case, the energy loss is approximately equal to exergy loss since the energy discussed here is the energy content of fuel-grade byproducts combusted in the naphtha/ethane steam cracking.

5.2 Breakdown of SEC and Exergy Losses

Data for a breakdown of SEC and exergy losses found in literature are summarized in Table 3. For energy analysis, both thermodynamic theoretical energy requirement and energy loss are considered. Pyrolysis accounts for ca. 2/3 of the total SEC of naphtha crackers. The remaining third is consumed by compression and separation sections. The compression section (ca. 15% of the total energy use in naphtha cracking) uses slightly less energy than separation section (ca. 1/5 of the total energy use in naphtha cracking).

For exergy analysis, only exergy loss (17 GJ/t ethylene) due to fuel combustion is considered. With respect to exergy in pyrolysis section of naphtha crackers, ca. 75% of the total exergy losses are estimated to occur in the naphtha pyrolysis section. Fuel combustion is predictably 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 over seven mpa [25].

With respect to exergy use in the rest of sections in a naphtha cracker, the large losses occur in propylene refrigeration, de-ethanization/C\(_2\) splitter and compression. Exergy losses that occur in the compression and separation sections mainly are caused by the production of electricity used in refrigeration and compression. All these exergy losses are not surprising if the conditions in separation and compression sections are considered. As the process description has indicated, most of the conditions for

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\(^1\) The SECs of naphtha steam crackers in Japan and Korea in 1995 are exceptionally low, namely ca. 25 GJ/t ethylene [23]. About 40% of steam crackers in Europe have SECs at ca. 31-35 GJ/t ethylene [5]. Naphtha and gas oil steam crackers in the US have SECs at ca. 32 GJ/t [24].
refrigeration are very cryogenic: low temperatures (as low as \(-150\, ^\circ\text{C}\)) and high pressure (up to 450 psia).

Ethane cracking has a similar distribution of energy consumption. However, an important difference from naphtha cracking is that the contribution of SEC in the pyrolysis section of ethane cracking (ca.1/2) is less by percentage than that in the case of naphtha cracking (ca. 2/3). In turn, the contribution of SEC in compression and separation sections is slightly higher in the case of ethane cracking than in the case of naphtha cracking. The chiller that condenses and separates ethylene and ethane uses up to ca. 21% of the total energy consumption [26]. As our process description mentioned, ethylene and ethane have similar boiling points, which explains why this separation task is very energy consuming.

As mentioned in the process description of steam cracking, additional energy used in decoking/defouling, shutdowns/restarts and related maintenance for various sections of a steam cracker could consume up to ca. 1-2% of the total energy use in the existing processes [27]. This additional energy use in decoking and defouling is usually not counted as part of SEC in steam cracking. Shutdowns also directly lead to large monetary losses. Therefore, it is not surprising to hear that the greatest challenge for steam-cracker engineers today is to improve the on-stream factors (intervals between shutdowns) by reducing coke formation and to extend furnace life between tube replacements [28].

5.3 Energy Integration

In the case of naphtha cracking, process energy used in the pyrolysis section is provided through combustion of fuel gases, which are fuel-grade byproducts in significant volumes. These byproducts, together with flue gases (not fuel gases) and waste heat, can meet ca. 95% of process energy demand in naphtha steam crackers [24]. These fuel-grade byproducts amount to ca. 20-25% of the energy content of naphtha (ca. 10-12 GJ out of LHV 44 GJ/t naphtha). Energy needed for compression and separation sections is provided by steam, which can almost all be produced from heat exchangers, or so called Transfer Line Exchangers (TLEs). Typically, steam is in balance, which means that there is no net steam import or export. A small amount of electricity is provided from external sources [29]. Electricity is used primarily for running cooling water, quench oil pumps and sometimes methane compressors [24]. It amounts to ca. 1 GJ/t ethylene [24]. Backflows to refinery and energy export together can be up to ca. 9-10 GJ/t ethylene for naphtha cracking [24]. In contrast to naphtha cracking, ethane cracking is not self sufficient in terms of energy and therefore requires energy import (15% of the total SEC through various energy carriers) [30].

6 Latest Developments of Naphtha Steam Cracking

In search for alternatives, we draw a family portrait of olefin technologies sorted by feedstocks (Figure 2). We have chosen a number of the latest technologies based on the following criteria: using conventional or heavy 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 will be discussed in two categories: (6.1) state-of-the-art naphtha cracking processes (Table 4); (6.2) advanced technologies in specific sections of naphtha steam cracking.
6.1 State-of-the-Art Naphtha Steam Cracking

Table 4 is an attempt to summarize state-of-the-art technologies for naphtha steam cracking, which is sorted by licensors. These technologies are offered as the most standard, widely accepted processes to olefin producers if they want to build a new olefin plant today. Table 4 contains only limited, public available information. For the separation section, only information on the de-methanization for each licensor was available. Regarding pyrolysis furnaces, most technologies focus on optimization design of furnace coils, which are located in the radiant section where cracking occurs (see process description in section 4). The goal is to improve heat transfer, raise severity, minimize coking and maximize olefin yields. As Table 4 shows, small, double coils and double radiant cells seem to be common features. With respect to improvements in separation processes, front-end de-methanization reduces refrigeration needs and therefore energy demand. For example, ABB Lummus claims a 75% cut in refrigeration needs [31]. However, traditional energy-consuming refrigeration and distillation as the main separation method remain unchanged. Further, no significant changes in the subsequent sections (compression and C₂, C₃ and C₄ separation) are reported as part of state-of-the-art naphtha steam cracking technologies.

These processes in Table 4 could reach SECs in the range of ca. 18-25.2 GJ/t ethylene, which is equivalent to a saving of ca. 20% on current average SEC (26-31 GJ/t ethylene). Gas turbine mentioned in Table 4 is not being commonly offered by every licensor. It will be discussed again in the next section. Without considering gas turbine, we consider the average SECs for state-of-the-art naphtha steam cracking is ca. 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/HVCs) by state-of-the-art naphtha cracking technologies are still far more than the absolute thermodynamic theoretical energy requirement for naphtha to olefin conversion mentioned earlier (5 GJ/HVCs).

In addition to Table 4, we observed a trend that the sizes of state-of-the-art crackers are increasing. While the current average steam cracker is around 450,000-500,000 tons ethylene per year [5], new naphtha crackers can produce over one million tons of ethylene annually (tpa). Technip built a plant with ethylene capacity of over 1.2 million tpa in Iran [32]. KBR (Kellogg Brown & Root) claims that they are able to build a two-million tpa ethylene plant [33]. The same trend goes with ethane crackers as well. Stone & Webster built an ethane cracker for NOVA in Canada with ethylene capacity of 1.27 million tpa. Technip claims the SEC of their mega cracker is 20 GJ/t ethylene as opposed to the average 30 GJ/t ethylene³ [32].

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¹ State-of-the-art is technologies that would be used if a new plant is to be built nowadays. For example, those process introduced in the “petrochemical processes 2003” in [31], which are commonly offered by licensors.

² ABB Lummus’ steam cracking technology is said to be used by over 40% of the world’s olefin plants [31].

³ Technip also claims that their mega crackers have lower product losses (0.25% in comparison with the average 1%), lower CO₂ emission (half of the average 1.6 t/t ethylene in Table 2) and lower operational cost advantages because of economy of scale [32]. Technip also claims that the maximum capacity may have been reached mainly due to the limits of compressors.
6.2 *Advanced Naphtha Steam Cracking Technologies*

Advanced technologies in specific sections in a naphtha cracker are not being offered by major licensors as part of standard commercialized processes. In fact, some of them are commercially available, but due to high costs, most of them are not yet widely implemented. Others are new and their technical and economic feasibility have yet to be proven.

With respect to the pyrolysis section, there are a few significant innovations and all of them are aiming at improving heat transfer and raising severity. There are circulating solids/particles (such as sand, coke and other carriers), circulating beds [34], selective radiant coils (which allows better control of P/E ratio by adjusting combustion gas) [35], ceramic coated tubes/coils and other advanced furnace materials [28, 36]. Here we only discuss *Advanced furnace materials*. 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 (e.g. cast-fins) are coated with glass, ceramics (aqueous salt of IA/IIA metals, silicon and phosphorus compounds) and they do not need chemical treatment [28, 37, 38]. Coating can also have catalytic effects for olefins selectivity [39]. Also, coating could allow higher severity and thereby enhance ethylene yields. Sintered silicon carbide (SiC) ceramics, for instance, offer maximum skin temperature up to 1400 °C, high conductivity and low surface catalytic activity [40-42]. Conventional pyrolysis tubes made of Cr-Ni alloys allows the maximum skin temperature only up to 1100 °C [41]. It is estimated that these advanced materials could lead to up to ca. 10% savings on current average SEC, or ca. 2-3 GJ/t ethylene\(^1\).

An additional new technology is *gas turbine integration*. Gas turbine integration results in the export of both steam and electricity. Also, it produces hot combustion gas for feedstock heating in a pyrolysis furnace. It can possibly save 13% (ca. 3 GJ/t ethylene) on the SEC of state-of-the-art steam cracking technologies [43] [44]. If both advanced furnace materials and gas turbine are applied, ca. 20% energy saving (ca. 4 GJ/t ethylene) on the SEC of state-of-the-art naphtha steam cracking is possible.

With respect to 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 light olefin adsorption (such as ethylene and propylene) over paraffin (such as ethane and propane). MVR could be used in a conventional propane/propane splitter. It can lead to ca. 5% (ca. 1 GJ/t ethylene) saving on the SEC of state-of-the-art steam cracking [45].

*Advanced distillation column* technology has been studied since 1930s as thermally coupled column. One type of such columns is “divided-wall” distillation columns for butadiene extraction. It could save ca. 16% on the SEC in the conventional butadiene distillation section [46]. Another type of such advanced distillation column is Heat Integrated Distillation Column (HIDiC). Two variations of HIDiC developed in the Netherlands are called *Plate Fin* and *Concentric* [47]. These advanced columns improve heat transfer by building heat exchangers between stripping and rectifying sections. They can be applied in ethylene/ethane (E/E) splitter and propylene/propane (P/P) splitter. It is generally estimated that HIDiC saves ca. 60 to 90% energy (or 0.1-0.3 GJ/t ethylene) on the SEC of a conventional P/P distillation column, which is known for poor

\(^1\) This estimate is based on personal communications quoted in [35].
energy efficiency (ca. 20-30%) [47-49]. HIDiC is even possible to save ca. 50% (ca. 0.15 GJ/t ethylene) on the SEC in modern distillation columns with heat pumps [47].

Membrane is another long-known technology, but it is rarely applied in steam cracking. Membrane materials are often made of polymer (e.g. polypropylene) or inorganic materials. Membranes can be possibly applied in separation of olefin/paraffin \((C_2/C_3)\), gases (hydrogen recovery\(^1\), acids, etc.) and coke/water (water purification) [51]. Membranes could combine high selectivity with a high permeability. With regards to the membrane application in the \(C_2\) and \(C_3\) separation alone, ca. 8% (1.5 GJ/t ethylene) savings on process energy is expected [52]. However, membrane separation is widely believed as an immature technology because it is unable to withstand severe operating conditions and needs regular replacement (due to erosion, etc.). Therefore, membrane is not yet licensed by any steam cracking licensors.

Energy integration of a steam cracker with another industrial process can also possibly save energy. Combined refrigeration synchronizes the cryogenic natural gas liquid plant, natural gas liquid fractionation and ethylene plants into a single unit [53]. It is claimed that the total refrigeration requirement by an ethylene plant is reduced by 60-80%, or ca. 1 GJ/t ethylene can be saved [53].

Since some of the technologies mentioned above could be applied in the same process (e.g. HIDiC columns and membrane for \(C_2/C_3\) separation) and most of them are not yet mature, it is not possible to simply add up all the energy savings together. Considering the distribution of SEC described in Table 3, we roughly estimate that advanced steam cracking technologies altogether could lead to up to ca. 15% of energy savings (ca. 3 GJ/t ethylene) on the SEC of state-of-the-art steam cracking.

7 Catalytic and other Alternative Technologies

7.1 Energy Use

An alternative to conventional steam cracking comprises catalytic and other alternative olefin technologies, which can process conventional or heavy feedstock. Table 5 is a list of these technologies in the order of feedstock weight from light (left) to heavy (right). Note that technologies in Table 5 only differ 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. The first three technologies use gas feedstocks. Gas stream technologies use gases as heat carriers to provide enthalpy needed for pyrolysis [54, 55]. 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 [54]. It uses ca. 45% (primary energy use for steam production included) less than the SEC of the state-of-the-art steam cracking [56]. Olefin producers are very concerned about the overall system complexity that result from large requirement of steam (ca. 5-10 times the steam requirement by conventional steam cracking) and subsequent energy recovery from waste steam [54]. R&D on shockwave technology was stopped in 1998.

There are two oxidative dehydrogenation processes, both for processing gas feedstocks. Both processes require oxygen with high purity (ca. 90%). Ethane oxidative

\(^1\) Hydrogen recovery may have been among the first wide-scale commercial application of membrane [50].
$\text{dehydrogenation}$ has ca. 35% potential saving\(^1\) (primary energy use in oxygen production included) on the SEC by state-of-the-art ethane cracking [57]. Another process is $\text{propane oxidative dehydrogenation}$. This process produces little ethylene. Ethylene yield from steam cracking of propane is up to 45% and propylene yield is 12% [30]. Propane oxidative dehydrogenation has potential to lead to ca. 45% (primary energy use in oxygen production included) savings on the SEC by conventional propane steam cracking, which is 15-18 GJ/t HVCs.

The rest of technologies in Table 5 use naphtha or heavy feedstocks. SEC by $\text{catalytic cracking of naphtha}$ is estimated to be within 10-11 GJ/t HVCs. This is also ca. 10-20% less than the SEC by the state-of-the-art naphtha cracking (11-14 GJ/t HVCs). Some of these processes, developed by LG (a major Korea chemical company) and AIST (a Japanese research institute), are reported to be commercialized soon.

$\text{Hydro-pyrolysis}$ (non-catalytic) could save ca. 9% (primary energy use in hydrogen-methane fraction included) less than the SEC by the state-of-the-art naphtha cracking. The reasons for such energy savings include several factors: higher yields, lower temperature in the furnace (heat coefficient of hydrogen higher than methane or fuel oil), low coking and less steam requirement [59].

$\text{Byproduct upgrading}$ technologies produce olefins by processing the byproducts (ranging from $\text{C}_4$ to $\text{C}_9$) from conventional steam cracking or from refinery [22]. As an add-on process to naphtha cracking, byproduct upgrading technologies can raise the total propylene yield of naphtha cracking from the average 15% to 30%. This process has a potential saving of ca. 7-10% less than the SEC by the state-of-the-art naphtha cracking.

Using heavy feedstocks, such as crude oil, the $\text{catalytic pyrolysis process (CPP)}$ saves ca. 12% on the SEC of the state-of-the-art naphtha cracking. Because CPP feedstock can be crude oil and other heavy feedstock, energy use in naphtha production is avoided, which is about ca. 2-3 GJ/t naphtha [49] If this is taken into account in the comparison with naphtha steam cracking, the energy savings by CPP would be ca. 20%. Another important reason for energy saving is the mild reaction conditions in CPP. Its reaction temperatures are around 650-750 °C, which is 150-350 °C lower than steam cracking [60, 61].

The energy savings estimated here are due to improvement of energy efficiency in the pyrolysis section. If the advanced separation technologies (mentioned under 6.2) are also applied, then the energy savings by catalytic olefin technologies on the SEC by state-of-the-art naphtha cracking could be up to ca. 40%. Among the alternative olefin technologies discussed, gas stream and hydropyrolysis (non-catalytic) have not been actively pursued by the industry in recent years. However, catalytic olefin technologies are under intensive R&D, especially in China and Japan.

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\(^1\) However, if the CO\(_2\) emission from oxygen usage is included, the total CO\(_2\) emission by ethane oxidative dehydrogenation is 0.31 ton CO\(_2\) per ton ethylene produced. This is 15% higher than that from ethane cracking. Ethane cracking emits less due to combustion of hydrogen although it uses more energy per ton of ethylene than ethane oxidative dehydrogenation [57]. Oxygen production (if using electricity) requires primary energy ca. 3-4 GJ/t oxygen [58]. Its emission factor is assumed as 60 kg CO\(_2\)/GJ. In the future, this CO\(_2\) emission factor could be reduced by membrane or other efficient oxygen production processes.
7.2 Reactors and Catalysts

It is interesting to discuss further about possibilities for energy saving by these catalytic olefin technologies just mentioned\(^1\). The emergence of catalytic olefin technologies is in line with the recent discussion on energy saving through process intensification\(^2\). This is reflected by the reactors and catalysts used in catalytic olefin technologies. The reactors of new catalytic technologies\(^3\) in Table 5 often share similar reactor design with conventional FCC reactors used in refineries (fixed or fluidized bed catalytic cracking reactors). China’s SINOPEC has named its catalytic olefin technologies (e.g. CPP) as “FCC family techniques” [64]. FCC reactors are smaller than pyrolysis furnaces. Also, moving beds and catalysts used in FCC enable intensive contact between catalysts, reactors and feedstocks (by maximizing contact surface) and consequently, such intensity leads to efficient heat transfer. Unsurprisingly, FCC reactors\(^4\) are known for using less energy in terms of SEC/t feedstock (SEC ca. 2-3 GJ/t feedstock) [49] than steam cracking furnaces (SEC ca. 5-9 GJ/t ethane or naphtha) [49]. Because catalytic reactors usually operate under lower temperatures than those for steam cracking, it is possible to use recovered waste heat (combined with fuel combustion) as sources of process energy [25].

The use of catalysts is commonly known for energy saving. Zeolite FCC catalysts adopted by US refinery in 1977 have helped save 200 million barrels of crude oil (30 million tons) in the US alone [66]. Similarly, many of catalytic technologies mentioned in Table 5 use zeolite (other also use metal oxides) catalysts\(^5\). Figure 3 illustrates that catalytic olefin technologies can save activation energy use in conventional steam cracking. There are three reasons for such energy saving.

- 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 [14]. Also, most of the catalysts cannot withstand extremely high temperatures and pressures as in steam cracking (up to 1,100 °C and 75 mpa). Consequently, the temperatures for the new catalytic naphtha cracking processes are 150-250 °C lower than those for steam crackers (Table 5).

---

\(^1\) This is not to say all catalytic pyrolysis technologies for olefin production save energy in comparison with the state-of-the-art steam cracking. We limit our discussions only on those listed in Table 5 that are believed to have energy saving potentials.

\(^2\) The 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 [62].

\(^3\) Catalytic olefin technologies, there are basically two categories: acidic catalytic cracking and thermal catalytic pyrolysis [63]. Acidic cracking is associated with zeolite catalysts, FCC-like riser/bed reactors and heavy feedstocks. This technology is being developed by Sinopco/Stone & Webster (in commercial test), ABB Lummus, KRICT, LG, Asahi and AIST. 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. This technology is being developed by VNNIOS (in commercial test), Toyo, IIT, Stone & Webster, Idemitsu, KRICT and LG.

\(^4\) FCC reactors operate under low temperature: ca. 450-600 °C, which is 200-400 °C less than steam cracking [65]. However, it is commonly known that FCC ethylene yield usually only is 1-2% and propylene yield is 5% while naphtha yield is over 50% and cycle oil yield is 20% [49].

\(^5\) Zeolite catalysts are complex alumino-silicates and are large lattices of aluminum, silicon and oxygen atoms. In the case of FCC, zeolite catalysts lead to formation of carbonium ions. These ions then reorganize and lead to various FCC products. In the case of catalytic olefin technologies, the combined use of zeolite and other catalysts lead to formation of both carbonium-ions and free-radicals [64, 67]. They are then reorganized and eventually lead to light olefins, aromatics and other products [14].
• Second, catalysts improve selectivity to desired products, such as propylene [68]. Even if the same operating conditions as those of steam cracking are applied for catalytic cracking, the total olefin yield by LG’s catalytic pyrolysis technology is still enhanced by at least 15% [68].

• Third, coke formed during the cracking process is constantly removed by catalysts that are in turn de-coked through catalyst regeneration (or catalyst decoking). As said earlier, coke lowers energy efficiency by hindering heat transfer.

Earlier attempts to catalytically convert heavy hydrocarbons to light olefins often showed that the use of catalysts is often problematic because of thermodynamic equilibrium limitations, coking, low yields of olefins and high yield of low-value byproducts\(^1\) [64, 69]. The new catalytic technologies in Table 5 have made some progresses in solving these problems, but continuous improvement is still needed.

• First, regarding the problem with the equilibrium limitation, oxygen is used to drive the reaction toward 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 [65]. At the same time, oxygen can also burn off coke on the catalysts. Also, reactors using inorganic catalytic membranes could also separate oxygen, ethane/naphtha, hydrogen and other products (reducing undesired reactions) and improve the conversion of equilibrium limited reaction [70, 71].

• Second, older metal oxide catalysts were prone to coking and quickly deactivate. Therefore, high temperatures and short residence time were required to hinder coking. High temperatures (800 °C or above) and extremely short residence time (in milliseconds), however, are often very harsh on catalysts and result in quick deactivation of catalysts and short lifetime. Recently, new zeolites catalysts (e.g. metal, silica and hybrid) have shown to have less coking and to be more effective under higher temperatures [61, 72]. One recent patent on catalytic olefin technologies claims that new catalysts can reduce CO\(_2\) and methane contents in the air stream from catalyst regeneration by 90% and 50% respectively in comparison with the CO\(_2\) and methane content in the air stream from steam cracking [65].

• Third, older catalysts often show strong selectivity to aromatics and heavy hydrocarbons instead of light olefins. New catalysts, such as Ga-P zeolite, suppress aromatization and provide relatively high yield of ethylene and propylene [73].

### 7.3 Short and Long-Term Prospects

According to major worldwide licensors and research institutions we have contacted through 2002 to 2004, currently none of these catalytic olefin technologies listed in Table 5 are fully mature and economically competitive in comparison with state-of-the-art technologies.

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\(^1\) Coke can be significant even at high reaction temperature. It can currently only be burned through catalyst generation 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 to be separated. Other low-value byproducts, such as aromatic-rich gasoline is difficult to be used due to instability caused by olefins, but additional processing will lead to high costs [64].
steam cracking technologies. Nevertheless, it is of our interest to discuss the short and long-term prospects of catalytic olefin technologies.

In the short term, catalytic olefin technologies appear to be driven by two economic factors: strong demand for propylene and low cost feedstock [74, 75].

- First, propylene demand is an economic factor that is often discussed. The three catalytic technologies in the middle of Table 5 are devoted to produce propylene and are sometimes referred to as “propylene on purpose” [11]. For the same reason, conventional FCC used in refineries (cracking heavy feedstocks) also becomes attractive for R&D since it yields considerable amount of propylene (up to wt. 17%) and is likely to supplement propylene supply unfulfilled by steam cracking [74, 76].

- The second economic factor is feedstock. Heavy feedstocks (heavier than naphtha), such as gas oil and heavy residues indicated in the center of Table 5, are cheaper than naphtha and ethane and they can also yield multiple high value byproducts [65]. Such feedstocks are attracting much attention in the US, Europe and Asia. Cracking heavy feedstock can enhance competitiveness compared to ethane cracking in the Middle East. Therefore, the overall economics for upgrading heavy feedstock to high value olefin products (in particular propylene) looks quite attractive. Besides unsolved technical problems, whether the production volume by using these new technologies is able to increase further will be decided partially by propylene market pull and partially by cost competition between conventional and heavy feedstocks.

In the long term, more and more R&D can be expected to be devoted to catalytic olefin technologies because of their potentials in energy saving as well as upgrading low-value heavy feedstocks. Catalysis has brought tremendous progresses to many fields in the chemical industry, but unfortunately it has not been capitalized in light olefin production. Steam cracking essentially is a non-catalytic and non-selective process. Catalysts have never been widely used in the pyrolysis section in steam cracking to optimize energy efficiency. The application of catalysts in cracking naphtha and ethane has only become attractive since the beginning of 1990s. Beside those institutions in Korea, Japan and China (mentioned under Table 5), major licensors (e.g. Stone & Webster and ABB Lummus) and olefin producers (e.g. ExxonMobil and BP) are also filing patents on catalytic olefin technologies. Recently, catalytic processes developed by AIST, Sinopec/Stone & Webster and VNIIOS are said to be already under commercial tests [63]. Adoption of FCC-like catalytic olefin technologies has been expected since more than ten years ago [25]. Whether these new processes can replace steam cracking will depend on how well they mature both technically and economically in the next 20 to 30 years.

In a word, after reviewing alternative technologies in Table 5, we conclude that there is a strong rising interest in applying special reactors and catalysts to control yield and thereby to improve energy efficiency, but the future development of catalytic olefin technologies will be strongly affected by maturity of catalytic technologies, market pull and feedstock cost competition.

8 Conclusion

Issues concerning the reduction of energy use, costs and emissions by olefins production initiated this analysis of olefin technologies. The findings from our energy
analysis indicated the most important sections in terms of the energy use, e.g. pyrolysis section alone accounts for ca. 65% of total energy use and ca. 75% of the total exergy losses. This paper then discusses the latest olefin technologies that still use conventional feedstocks. An overview of state-of-the-art naphtha cracking technologies offered by licensors shows that ca. 20% savings on the current average energy use are possible. Advanced naphtha steam cracking technologies in the pyrolysis section (e.g. advanced coil and furnace materials) may together lead to up to ca. 20% savings on the energy use by state-of-the-art technologies. Improvements in the compression and separation sections may together lead to up to ca. 15% savings on the energy use by state-of-the-art technologies. Alternative olefin technologies apply special reactors, catalysts or additional materials (oxygen, hydrogen, etc.) to crack conventional and heavy feedstocks. In particular, catalytic olefin technologies can lead to higher yields of valuable chemicals (e.g. propylene) under lower reaction temperatures. Due to energy efficiency improvement in the pyrolysis section, catalytic naphtha cracking could possibly save up to ca. 20% on the energy use by the state-of-the-art naphtha steam cracking is possible.
Acknowledgement

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References


22


Figure 1 Typical Flow Diagram for a Naphtha Steam Cracker

A. Pyrolysis Section

- Naphtha
- Pyrolysis Furnace
- Transfer Line Exchange (producing steam)
- Cracked gas

B. Fractionation and Compression Section

- Oil/water quench tower and oil fractionator
- Multi-stage compressor, acid removal and caustic scrubbing
- Scrubbed products
- Drying, pre-cooling and refrigeration
- De-methanizer
- De-ethanizer acetylene hydrogenation (acetylene converter) and C2 splitter
- De-propanizer and C3 splitter
- De-butanizer and C4 extraction

C. Recovery and Separation Section

- Fuel gases
- Ethylene
- Propylene
- Butadiene
- BTX
- C4 raffinates, C8+ fraction and fuel oil

1 Figure was drawn based on [5, 77].
BATH: Bio acid acetone to hydrocarbons (such as olefins) [6];
CC: Catalytic Cracking or catalytic pyrolysis;
DCC: Deep catalytic cracking, etc. (see Table 5);
DH: Dehydration process (such as methanol to olefins, methanol to propylene and ethanol dehydration); [13, 78];
FM: Fermentation [79, 80];
FP: Flash pyrolysis, sometimes in the presence of methane [80];
FT: Fischer Tropsch synthesis (using syn-gas CO and H2 mixture to synthesize methanol or other products) [6];
GAS:  Gasification; LIQ: after gasification, then liquefaction [6, 79];
GS:  Gas stream reactor technologies, such as shockwave reactors (Table 5)
HG:  Hydrogenation [6, 79];
HP:  Hydro-pyrolysis (see Table 5);
HTUL: Hydro-Thermal Upgrading Liquefaction which produces naphtha from biomass feedstock [6, 79];
OC:  Oxidative coupling via ethane [6];
OD:  Oxidative dehydrogenation [6];
OM:  Olefin metathesis, e.g. ABB-Lummus Olefin Conversion Technology, IFP-CPC meta-4 [81];
OU:  Olefins Upgrading (conversion of C4- C10) to light olefins, such as Superflex [82], Propylur [83] and Olefins Cracking [22].
PD:  Propane dehydrogenation [84, 85];
RCY:  Re-CYcling pyrolysis using organic waste, such as discarded plastics, used rubber, etc.[6, 79];
REC:  Recovery of refinery off gases, which contains ethylene, propylene, etc.. [79];
REF:  Oil refinery process. Distillation produces naphtha and heavy oil. Catalytic cracking produces off gases. Cryogenic and absorption produces ethane and LPG;
SC:  Steam Cracking (conventional);
SEP:  Gas Separation Process which produces methane, ethane and propane;
SR:  Steam Reforming of natural gas, a process which in this case produces methanol
Figure 3 Simplified Energy Profile of Conventional Steam Cracking and Catalytic Olefin Technologies

Energy saving!
Table 1 Estimated Global Energy Use and CO\textsubscript{2} Emission by Current Olefin Production\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>World</th>
<th>US</th>
<th>Europe (including new EU member states and FSU)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total feedstock (Million tons)\textsuperscript{b}</strong></td>
<td>300</td>
<td>85</td>
<td>90</td>
</tr>
<tr>
<td><strong>Breakdown of</strong></td>
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<tr>
<td><strong>Feedstock (wt. %)</strong></td>
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<td></td>
</tr>
<tr>
<td>naphtha 55,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ethane 30,</td>
<td></td>
<td></td>
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<tr>
<td>LPG\textsuperscript{c} 10,</td>
<td></td>
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<td></td>
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<tr>
<td>gas oil 5</td>
<td></td>
<td></td>
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<tr>
<td>ethane 55,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>naphtha 23,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>propane15,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>gas oil 5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>naphtha 75,</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>LPG 10,</td>
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<td></td>
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<tr>
<td>gas oil 9,</td>
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<td></td>
</tr>
<tr>
<td>ethane 5</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td><strong>Ethylene capacity</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Million tons)</td>
<td>110-113</td>
<td>28-30</td>
<td>30-32 (23-24 by Western Europe)</td>
</tr>
<tr>
<td><strong>Propylene capacity</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Million tons)</td>
<td>53-55</td>
<td>16-17</td>
<td>17-18</td>
</tr>
<tr>
<td><strong>Total energy use</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(fuel combustion and utilities included) (EJ)\textsuperscript{d}</td>
<td>2-3</td>
<td>0.5-0.6</td>
<td>0.7-0.8</td>
</tr>
<tr>
<td><strong>Total CO\textsubscript{2} emission</strong>\textsuperscript{e}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(fuel combustion, decoking and utilities included) (Million tons)</td>
<td>180-200</td>
<td>43-45</td>
<td>53-55</td>
</tr>
</tbody>
</table>

\textsuperscript{a} We estimated energy use on the basis of current production level. The annual growth rate of olefin production for 2003-2004 is assumed at 3.5\% [11].

\textsuperscript{b} Feedstock, ethylene and propylene production data are based on [86, 87]; US figures come from [24].

\textsuperscript{c} LPG is a mixture of ethane, ethylene, propane, propylene, butane and butylenes.

\textsuperscript{d} Since the world production between 1994 and 2004 went up from 50 to over 110 million tons of ethylene per year, we estimated that global energy used in olefin production has more than doubled from 1EJ in 1994 [88]. US. Department of Energy put the global process energy used in ethylene production as 2.6 EJ when the global ethylene production is 93 million tons in 2000 [89].

\textsuperscript{e} CO\textsubscript{2} emission and process energy use are based on [5, 30]. Decoking is based on [36]. US figures are lower than those of Europe due the fact that heavy feedstock uses more energy use in total.
### Table 2 Overview of Two Currently Most Used Conventional Feedstocks in Olefins Production

<table>
<thead>
<tr>
<th></th>
<th>Ethane</th>
<th>Naphtha</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SEC (GJ/t ethylene)</strong></td>
<td>17-21 (typical)</td>
<td>26-31 (typical) and 20-40 (maximum)</td>
</tr>
<tr>
<td></td>
<td>15-25 (maximum)</td>
<td></td>
</tr>
<tr>
<td><strong>SEC (GJ/t HVCs)</strong></td>
<td>16-19 (typical)</td>
<td>14-17 (typical)</td>
</tr>
<tr>
<td><strong>CO₂ emission (t CO₂/t ethylene)</strong></td>
<td>1.0-1.2 (typical)</td>
<td>1.8-2.0 (typical)</td>
</tr>
<tr>
<td><strong>CO₂ emission (t CO₂/t HVCs)</strong></td>
<td>1.0-1.2</td>
<td>1.6-1.8</td>
</tr>
<tr>
<td><strong>Ethylene yield (wt. %)</strong></td>
<td>80-84%</td>
<td>29-34% (30% typical)</td>
</tr>
<tr>
<td><strong>Propylene yield (wt. %)</strong></td>
<td>1-1.6%</td>
<td>13-16%</td>
</tr>
<tr>
<td><strong>Butadiene yield (wt. %)</strong></td>
<td>1-1.4%</td>
<td>4-5%</td>
</tr>
<tr>
<td><strong>Aromatics and C4+ yield (wt. %)</strong></td>
<td>2-3%</td>
<td>10-16%</td>
</tr>
<tr>
<td><strong>HVCs yield (wt. %)</strong></td>
<td>82% (typical)</td>
<td>55% (typical)</td>
</tr>
<tr>
<td><strong>Methane yield (not counted as HVCs) (wt. %)</strong></td>
<td>4.2%</td>
<td>13-14%</td>
</tr>
<tr>
<td><strong>Hydrogen yield (not counted as HVCs) (wt. %)</strong></td>
<td>4.3%</td>
<td>1%</td>
</tr>
<tr>
<td><strong>Backflows to refinery (wt. %)</strong></td>
<td>0%</td>
<td>9-10%</td>
</tr>
<tr>
<td><strong>Losses (due to fouling, coking, etc.) (wt. %)</strong></td>
<td>1-2%</td>
<td>1-2%</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>a</em> Energy use is based on [24, 30]. SEC here only refers to process energy use in pyrolysis and separation.</td>
</tr>
<tr>
<td><em>b</em> Emission is calculated based on [30, 90]. Emission is a result of fuel combustion and utilities, both of which use fossil fuel. Ethane cracking results higher hydrogen and ethylene content, therefore less CO₂ emission per ton of ethylene, than naphtha cracking does.</td>
</tr>
<tr>
<td><em>c</em> Yield data is based on [30, 31]. Yields are on the mass basis and are all final yields.</td>
</tr>
<tr>
<td>Process</td>
</tr>
<tr>
<td>---------------------------------</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Heat of reaction</td>
</tr>
<tr>
<td>Fuel combustion and heat transfer to the furnace</td>
</tr>
<tr>
<td>Pyrolysis</td>
</tr>
<tr>
<td>Steam, heating &amp; losses</td>
</tr>
<tr>
<td>Fractionation and Compression</td>
</tr>
<tr>
<td>De-methanization</td>
</tr>
<tr>
<td>De-ethanizer and C&lt;sub&gt;2&lt;/sub&gt; splitter</td>
</tr>
<tr>
<td>C&lt;sub&gt;3&lt;/sub&gt; splitter</td>
</tr>
<tr>
<td>De-propanization/De-butanzation</td>
</tr>
<tr>
<td>Separation</td>
</tr>
<tr>
<td>Propylene refrigeration</td>
</tr>
<tr>
<td>Total process energy use</td>
</tr>
</tbody>
</table>

- **Ethane** and **Naphtha** columns represent specific energy consumption (SEC) and exergy losses, respectively, in the steam cracking process.
- **Our estimation** column provides our estimates on certain processes.
- **Total process energy use** refers to the total energy used in the process.
- **Total exergy losses** indicate the total exergy losses in the process.

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**Notes:**

- All energy figures in the table are in primary energy terms. Generally speaking, the contribution of electricity is very small (ca. 1 GJ/t ethylene) [24]. Steam is produced internally and in balance. Almost all process energy (including steam) originates from combustion of fuel-grade byproducts and extra fuel (only in case of ethane cracking). The distribution of byproduct/fuel energy contents is represented by the percentages in the table.
- Our estimate on the pyrolysis section is based on [25]. Our estimate on the compression and separation sections is based on [18, 91].
- Another figure for heat of reaction given in [8] is 21%. Energy use for "heat of reaction" refers to the energy used to convert feedstocks into desired products.
- Another figure for compression given in [8] is 16%.
- Another figure for compression given in [8] is 13%.
- Data on the exergy loss in fractionation and quench towers is not found. We roughly estimated the exergy loss here is below 0.2 GJ/t ethylene.
Table 4 State-of-the-Art Naphtha Steam cracking Technologies sorted by Licensorsa

<table>
<thead>
<tr>
<th>Licensor</th>
<th>Technip-Coflexipb</th>
<th>ABB Lummusc</th>
<th>Linde AGd</th>
<th>Stone &amp; Webstera</th>
<th>Kellogg &amp; Brown Rootf</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Coil related furnace features</strong></td>
<td>Radiant coils pretreated to reduce coking with a sulfur-silica mixture</td>
<td>Double pass radiant coil design; online decoking reduces emissions</td>
<td>Twin-radiant-cell design (single split) is 13m (shorter than the average length 25m)</td>
<td>Twin-radiant-cell design and quadra-cracking</td>
<td>Coil design (straight, small diameter), low reaction time; very high severity</td>
</tr>
<tr>
<td><strong>De-methanizer separation features</strong></td>
<td>Double de-methanizing stripping system</td>
<td>De-methanizer with low refrigeration demand</td>
<td>Front-end de-methanizer and hydrogenation</td>
<td>De-methanization simultaneous mass transfer and heat transfer</td>
<td>Absorption-based demethanization system with front-end design</td>
</tr>
<tr>
<td><strong>Gas Turbine</strong></td>
<td>N/a</td>
<td>Ca. 3 GJ/t ethylene saved</td>
<td>N/a</td>
<td>Offered but no data</td>
<td>N/a</td>
</tr>
<tr>
<td><strong>Ethylene Yield</strong></td>
<td>35%</td>
<td>34.4%</td>
<td>35%</td>
<td>N/a</td>
<td>38%</td>
</tr>
<tr>
<td><strong>SEC</strong></td>
<td>18.8-20 (best) or 21.6-25.2 (typical)</td>
<td>18 (with gas turbine); 21 (typical)</td>
<td>21 (best)</td>
<td>20-25</td>
<td>No data</td>
</tr>
</tbody>
</table>

a For the conventional naphtha steam cracking, ethylene yield is typically 30%. HVCs yield is typically 55%.
b Technip data come from [31, 92]. According to Technip, SECs vary depending on the processing scheme, extent of heat integration and climatic conditions [92].
c ABB data come from [31]; Other yields are 14.4%, butadiene 4.9% and aromatics 14%. The total HVCs yield is 60.7%. Gas turbine data based on [43].
d Linde data come from [31].
e Stone & Webster data come from [31, 93, 94];
f Kellogg & Brown Root come from [31, 95];
g The average SEC in the industry today is around 26-31 GJ/t ethylene for naphtha cracking.
### Table 5 Catalytic and Alternative Olefin Technologies Using Conventional and Heavy Feedstocks

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Gas Stream Technologies</th>
<th>Ethane Oxidative De-hydrogenation</th>
<th>Propane Oxidative dehydrogenation</th>
<th>Catalytic cracking of naphtha</th>
<th>Hydro-pyrolysis of naphtha</th>
<th>Byproduct upgrading (C4-9)</th>
<th>Catalytic Pyrolysis Process (CPP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane and other gas feedstock</td>
<td>Ethane and oxygen</td>
<td>Propane and oxygen</td>
<td>Naphtha</td>
<td>Naphtha</td>
<td>C4-C9 (from steam cracking, refinery, etc.)</td>
<td>Crude oil, refinery heavy oils, residues, atmospheric gas oil, vacuum gas oil</td>
<td></td>
</tr>
<tr>
<td>Olefins</td>
<td>Ethylene</td>
<td>Ethylene</td>
<td>Propylene</td>
<td>Ethylene/propylene</td>
<td>Ethylene</td>
<td>Propylene</td>
<td>Ethylene/propylene</td>
</tr>
<tr>
<td>Reactor</td>
<td>Shockwave, combustion gas; shift syngas; plasma; etc.</td>
<td>Alloy Catalyst Reactor with hydrogen co feed</td>
<td>Both a stem reformer and an (oxy-reactor); or, cyclic fixed-bed</td>
<td>Fluidized bed</td>
<td>Reactors with hydrogen co feed but less steam</td>
<td>Fixed or fluidized bed</td>
<td>Riser and transfer line reactor</td>
</tr>
<tr>
<td>Catalysts</td>
<td>N/a</td>
<td>Mordenite zeolite</td>
<td>Zinc and calcium aluminate based</td>
<td>Zeolite (or various metal oxides)</td>
<td>N/a</td>
<td>Zeolite</td>
<td>Acid zeolite</td>
</tr>
<tr>
<td>Total energy use</td>
<td>Shockwave: ca. 8-10 GJ/t ethylene/HVCs</td>
<td>Dow: ca. 10-12 GJ/t ethylene/HVCs</td>
<td>Uhde: ca. 8-10 GJ/t propylene; ca. 8-10 GJ/t HVCs</td>
<td>KRICT: ca. 19 GJ/t ethylene and ca. 10 GJ/t HVCs</td>
<td>Blachownia: ca. 16-20 GJ/t ethylene and ca. 10-13 GJ/t HVCs</td>
<td>N/a</td>
<td>CPP: ca. 35 GJ/t ethylene and ca. 12 GJ/t HVCs</td>
</tr>
<tr>
<td>Yield (wt. %)</td>
<td>Shockwave: highest ethylene yield ca. 90%</td>
<td>Dow: ethylene yield on the mass basis is ca. 80%</td>
<td>Uhde: propylene yield on the mass basis is ca. 84%</td>
<td>KRICT: ethylene 38%, propylene 17-20%, aromatics 30% and HVCs 73%</td>
<td>Blachownia: Ethylene yield 36-40% and HVCs yield 70%</td>
<td>UOP: propylene yield from steam cracking is 30% and HVCs yield 85%</td>
<td>CPP: ethylene 21%, propylene 18%, C4 15%, and HVCs yield 60%</td>
</tr>
<tr>
<td>Current status</td>
<td>Lab</td>
<td>Lab</td>
<td>Commerially available</td>
<td>Pilot plant</td>
<td>Commercially available</td>
<td>Commercially available</td>
<td>Lab and near commercialization</td>
</tr>
</tbody>
</table>

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

b Gas stream data come from [55]. Shockwave data come from [56]. Combustion gas could save 0.3 GJ/t ethylene [96].

c Per pass ethylene yield on the mol basis is typically ca. 30%. Data is based on [97, 98]. Oxygen production needs 3-4 GJ/t oxygen and this is accounted.

d Per-pass propylene yield on the mol basis is typically ca. 30-40%. Data is based on [84, 85]. Oxygen production needs 3-4 GJ/t oxygen and this is accounted. 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% [30]. Other similar processes include Oleflex by UOP, Catofin by ABB Lummus, etc.

e KRICT data is based on [63]. Also, LG claims ethylene up by 20% yield and propylene yield up by 10% and 10% energy savings on the current SECs of naphtha cracking in Korea [68, 99]. The SEC 7.5 GJ/t naphtha is assumed based on [67]. Other processes are: AIST ethylene/propylene yield together 60-70% and 20% energy savings per ton of ethylene and propylene is claimed [40, 67]. VNIIOS ethylene yield 30-34% and propylene yield 18-20% [100]; Asahi ethylene 22%, propylene 20-40% [34]. Hydro-pyrolysis was used in Blachownia Chemical Works in Poland, which claims a 20% increase of the average ethylene yield and ca. 30% less energy use [59]. The technology is not offered by major licensors.

f Olefins upgrading data is based on [82] and [22]. A similar industrial process is Metathesis [101]. Metathesis is an olefin conversion process, which in this case converts ethylene and butane-2 to propylene [13]. It is basically an extension of naphtha cracking to increase the yield of propylene.

g CPP data comes from [60, 61, 94]. The SEC 7.5 GJ/t feedstock is estimated. A review of several similar processes can be found in [64].

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

i Typically, ethane cracking has 81% ethylene yield. Naphtha cracking has 30% ethylene and 15% propylene yield.