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# Steam cracking and methane to olefins: Energy use, CO<sub>2</sub> emissions and production costs

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## Abstract

While most olefins (e.g., ethylene and propylene) are currently produced through steam cracking routes, they can also possibly be produced from natural gas (i.e., methane) via methanol and oxidative coupling routes. We reviewed recent data in the literature and then compared the energy use, CO<sub>2</sub> emissions and production costs of methane-based routes with those of steam cracking routes. We found that methane-based routes use more than twice as much process energy than state-of-the-art steam cracking routes do (the energy content of products is excluded). The 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 (LNG) may increase the prices of natural gas in these locations. Oxidative coupling routes are currently still immature due to low ethylene yields and other problems. While several possibilities for energy efficiency improvement do exist, none of the natural gas-based routes is likely to become more energy efficient or to lead to less CO<sub>2</sub> emissions than steam cracking routes do.

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## 1. Introduction

Light olefins (e.g., ethylene and propylene) are the most important basic petrochemicals, which are used to produce plastics, fibers and other chemicals. Most light olefins are produced by steam cracking. As the current global capacity for light olefin production has exceeded 150 million tons,<sup>1</sup> steam cracking is now the most energy consuming process in the chemical industry. Steam cracking accounted for about 3 EJ primary energy use (due to the combustion of fossil fuels and excluding the energy content of products) and nearly 200 million tons of CO<sub>2</sub> emissions (due to the combustion of fossil fuels) in 2000 [4,5].<sup>2</sup> The major

feedstocks used for steam cracking are naphtha and ethane. Alternatively, olefins can be produced from methane (about 90% of natural gas on the mass basis is methane) through the so-called C<sub>1</sub> routes (since methane contains one carbon). C<sub>1</sub> routes have been hailed as the “holy grail” of the chemical industry due to their potential to utilize methane in remote locations [6]. Recently, C<sub>1</sub> routes via methanol (methanol-related routes) have been demonstrated in pilot plants. Oxidative coupling of methane (OCM) for ethylene production is undergoing intensive R&D.

In view of these developments, the objective of this article is to compare several C<sub>1</sub> routes with steam cracking in terms of their energy use, CO<sub>2</sub> emissions and economics. A few studies that were conducted in the late 1980s and the early 1990s have estimated the energy use in C<sub>1</sub> routes [7–9]. However, an updated comparison of the cumulative process energy use (see definition later) and CO<sub>2</sub> emissions of the most recently developed C<sub>1</sub> routes and steam cracking is yet missing. Production costs of C<sub>1</sub> routes and steam cracking have been studied separately by a few licensors, consultancies and producers [10–13]. It is of

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<sup>1</sup>Our estimate is based on the recent production capacity and annual growth rate reported in Refs. [1,2].

<sup>2</sup>Three EJ is about 20% of the final energy use (including combusted fuels and electricity only; excluding the energy content of chemicals) in the global chemical industry while 200 million tons of CO<sub>2</sub> is about 30% of the total CO<sub>2</sub> emissions from the global chemical industry (mostly due to combustion of fossil fuels) [3,4].

interest to use the data contained in these sources for a comparative analysis of production costs of various routes.

Our research question is defined as: what are the cumulative process energy use, CO<sub>2</sub> emissions and production costs of natural gas-to-olefin routes in comparison with naphtha and ethane-based steam cracking routes?

The main research method used in this article is techno-economic analysis.<sup>3</sup> The technical and economic data used in the analysis were found in publicly available literature.<sup>4</sup> We chose datasets which we consider to be most reliable and up-to-date. These datasets were then subjected to crosschecking and to adaptations to make them comparable with regard to the underlying assumptions. See details in Section 3.

As part of our techno-economic analysis, we first describe the main process steps of the routes (Section 2). We then define the indicators used as the basis for comparison (Section 3). In the core section of this article (Section 4), we characterize the various routes in terms of their energy use and CO<sub>2</sub> emissions and identify several possibilities for energy efficiency improvement in the future. Finally, we analyze the production costs of these routes by using various assumptions (Section 5).

Energy use in the world-average steam crackers and state-of-the-art steam crackers processes (to be defined later) is used as the benchmark to study the C<sub>1</sub> 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.

There are two types of C<sub>1</sub> 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). In this paper, we focus on several *indirect* routes that are frequently discussed in the open literature: three designs of methanol-to-olefins (MTO) and two designs for OCM via ethane. Another indirect route is methane to olefins via Fischer–Tropsch (FT) liquids and then the subsequent conversion to high value chemicals (HVCs) by means of steam cracking. This route is not discussed in this paper, but we will study it in the future.

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 [14]. Today, the chemistry of the direct route remains one of the world's major scientific challenges while there are very few publications currently available on the topic [15]. The idea is over 60 years old, but there has been no commercialization so far [16].

Several C<sub>1</sub> technologies that are currently known as being extremely energy consuming<sup>5</sup> are rarely discussed in the current industrial research. Therefore, these technologies are excluded from this article.

## 2. Methanol and oxidative routes

The two routes to be discussed are as follows:

- *Methanol-related route.* First, methanol is produced and then is converted to olefins through MTO (methanol-to-olefins) processes. The recent development of methanol-related routes is summarized in Table 1. Research on methane routes started about 20–30 years ago and currently, two pilot plants in Norway are in operation. Plans for commercial-scale plants located in Africa have been announced (Table 1). We will discuss three major designs of methanol-related routes in Section 2.1.
- *Oxidative route.* OCM via ethane is sometimes called partial oxidation of methane via ethane to ethylene or catalytic oxidative dimerization of methane [24]. Table 1 lists a number of major companies involved in R&D for OCM. Since the pioneering work in the early 1980s, OCM has attracted much attention from both academia and industry [25]. The number of publications and patents reached a peak in 1988–1992 and then started to decrease [24]. Researchers in the Netherlands produced some optimistic studies in the early 1990s [8,26,27]. No breakthroughs for OCM are foreseen at this moment. No OCM pilot plants have been described in recent literature.

### 2.1. Methanol-related routes

The methanol-related route, as illustrated in Fig. 1, consists of three steps: methanol production (A), conversion of methanol-to-olefins and gasoline (B) and product recovery and separation (C).

- *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 H<sub>2</sub>/CO<sub>2</sub> ratio around 3–5). Pre-reforming reduces coking in the subsequent steps. Unreformed methane is further converted to syngas in the auto-thermal

<sup>5</sup>Some C<sub>1</sub> processes require extremely high temperatures, such as thermal pyrolysis (1000–1200 °C), oxy-pyrolysis (850–900 °C), and chloro-pyrolysis of natural gas (900 °C) [17]. Some of them, such as those via syngas [18,19], via syngas/methanol-derived ethanol [20] and methyl-chloride CH<sub>3</sub>Cl [21], have very low once-through yield. The catalytic conversion of CO<sub>2</sub> (captured from other processes or from air) and other gases (e.g., ethane, propane, etc.) to petrochemicals also has the problem of a low yield [22,23]. Low yield requires much recycling, which means large amount of energy use and capital investment. For these reasons, these processes will not be discussed in this article.

<sup>3</sup>A small number of personal communications with experts are also used as references.

<sup>4</sup>Most of the sources were found from the Internet, libraries and conferences and they belong to the following categories: journals (e.g., Oil and Gas Journal and Hydrocarbon Processing), US and European Patent Offices, conferences and seminar proceedings (e.g., European Petrochemical Technology Conference) and publications by producers and licensors (e.g., UOP and Lurgi).

Table 1  
Historical development in methanol-to-olefins and oxidative coupling of methane via ethane 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          | [77–79]                       |
| 1980–now    | ARCO, Akzo, BP, DSM, UOP LLC, ExxonMobil, etc.     | Oxidative coupling of methane to olefins via ethane  | R&D since 1980; approximately 20 patents were filed since 1986                  | Various          | [25,34,80]; BP [17]; DSM [12] |
| 90s–now     | S.C. ZECASIN                                       | ZECASIN (methanol-to-olefins)                        | In operation but information unavailable  | Romania          | [81]                          |
| 90s–now     | ExxonMobil and UOP LLC                             | Methanol-to-olefins and gasoline                     | Extensive R&D   | Various          | [70,74–76]                    |
| 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 | [28,31,82]                    |
| 2002–now    | Lurgi and Statoil                                  | Methanol-to-propylene                                | Capacity of a pilot plant undisclosed; offered for commercialization            | Norway           | [72,83]                       |
| 2003–now    | UOP LLC and Eurochem                               | Methanol-to-olefins (plus poly-olefin production)    | 800–1000 kt olefins per year (planned) <sup>a</sup>                             | Nigeria          | [84]                          |
| 2003–now    | UOP LLC and EATCO Suez                             | Methanol-to-olefins (plus poly-olefin production)    | 400–550 kt olefins per year (planned)   | Egypt            | [85,86]                       |

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

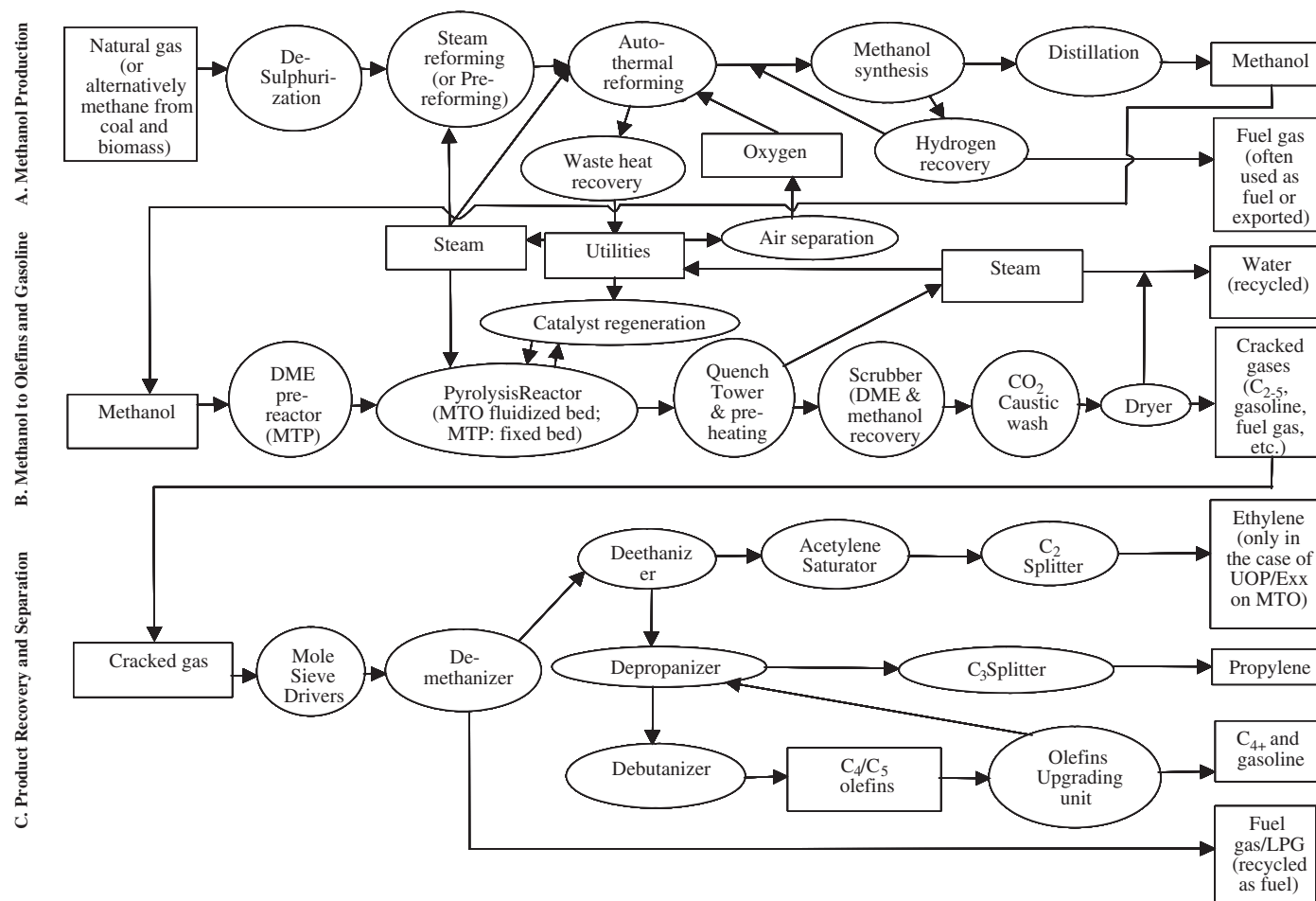


Fig. 1. Natural gas via methanol-to-olefins: Lurgi MegaMethanol, UOP MTO, Lurgi MTP and ExxonMobil MTO (section A is Lurgi MegaMethanol [45], sections B and C represent UOP MTO [71] and Lurgi MTP [72]. Section C includes UOP/total olefin upgrading [29,73]. See ExxonMobil MTO in Refs. [74–76]).

reforming reactor with oxygen used 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 5.4 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 to syngas. This is an endothermic reaction (about 30 GJ/t methane). After these two stages, syngas is converted to raw methanol (not yet dewatered) through an exothermic synthesis process at a temperature range of 200–280 °C.

- *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  $\text{CH}_3\text{OCH}_3$ ) and water. Then, DME is converted to olefins through olefin synthesis reactions. A fluidized or fixed bed reactor is used. Severity conditions are milder here than those in the case of steam cracking. Temperature is controlled to no higher than 600 °C as opposed to 750–900 °C in steam cracking. Pressure is about 1–3 bar. As in the steam cracking processes 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 [28]. 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  $\text{C}_4/\text{C}_5$ , the olefin upgrading (sometimes called olefin conversion) process converts  $\text{C}_4/\text{C}_5$  to ethylene and propylene [29]. 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 methanol-to-olefin routes discussed in this article:

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

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

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

## 2.2. Oxidative coupling of methane

Fig. 2 shows a generic OCM route diagram with integrated electricity cogeneration and air separation for oxygen production. Table 2 shows a summary of data on OCM routes. The processes in OCM 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 6 bar and very low temperatures (about  $-185^\circ\text{C}$ ). 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 and to reach desired selectivity to ethylene.
- *Oxidative coupling (petrochemicals production)*. A common oxidative coupling reactor design has a fluidized bed, though many other designs are also being considered. In the reactor, methane ( $\text{CH}_4$ ) and oxygen react over a catalyst to form water and a methyl radical ( $\text{CH}_3$ ). This reaction is called partial oxidation of methane. The methyl radicals combine to form a higher alkane, mostly ethane ( $\text{C}_2\text{H}_6$ ), which dehydrogenates into ethylene ( $\text{C}_2\text{H}_4$ ). The function of the catalysts is to control the activity of oxygen ions so that reactions can be kept on the desired path. Complete oxidation (rapid formation of  $\text{CO}_2$  before the radicals link up to form ethane and ethylene) is an undesired reaction. The catalysts used are mostly oxides of alkali, alkaline earth and other rare earth metals. Hydrogen and steam are sometimes added to reduce coking on catalysts. After one pass, roughly 80% of the total oxygen feed by mass is consumed [30]. Ideally, 100% is desired since oxygen is difficult to separate and can cause undesired combustion or even explosion [31]. The per-pass ethylene yield on a mass basis of methane is about 30% due to low conversion and poor selectivity to ethylene<sup>6</sup> [32,33].
- *Compression, separation and recovery (petrochemicals production)*. These processes are similar to those of ethane-based steam cracking except for the sections

<sup>6</sup>We calculated the final yield of ethylene from the OCM routes by dividing the weight of ethylene by the weight of methane (feedstock) on the yearly basis. This definition is used to compare the OCM routes with other processes.

Table 2

Summaries of natural gas-to-olefins routes (all yields are maximum yields and are given as the mass weights 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 <sup>a</sup>   | ExxonMobil MTO <sup>b</sup>         | Lurgi MTP <sup>c</sup>  | BP OCM <sup>d</sup>  |
| Intermediate           | Via methanol and DME   | Via methanol and DME                | Via methanol and DME  | Via ethane   |
| Desired reactions      | $\text{CH}_3\text{OH} \rightarrow \text{H}_3\text{COCH}_3 + \text{H}_2\text{O}$ ; $\text{H}_3\text{COCH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{C}_3\text{H}_6 + \text{H}_2\text{O}$ |                                     | $\text{CH}_3\text{OH} \rightarrow \text{H}_3\text{COCH}_3 + \text{H}_2\text{O}$ ; $\text{H}_3\text{COCH}_3 \rightarrow \text{C}_3\text{H}_6 + \text{H}_2\text{O}$ | $\text{CH}_4 + \text{O}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2\text{O}$ ; $\text{C}_2\text{H}_6 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$ |
| 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)   |
| Temperature (°C)       | 350–525  | 350–500                             | 400–450   | 650–850  |
| Ethylene yield         | 26% w/t C <sub>4–5</sub> upgrading   | 14%                                 | Negligible  | 50% per pass yield   |
| Propylene yield        | 33% w/t C <sub>4–5</sub> upgrading   | 18%                                 | 46%   | 7%   |
| C <sub>4–5</sub> yield | 9% (w/o upgrading)   | Negligible                          | Negligible  | 2%   |
| Gasoline yield         | Negligible   | 29%                                 | 20%   | Negligible   |
| Fuel gas yield         | 2%   | 0.1%                                | 6%  | H <sub>2</sub> 3% and others 7%  |
| Water yield            | 83%  | 81%                                 | 81%   | Water 180%; CO and CO <sub>2</sub> 70%   |
| Total HVCs yield       | 62%  | 45% (61% if gasoline weighted 100%) | 57% (65% if gasoline weighted 100%)   | Per pass 18%   |

<sup>a</sup>UOP MTO data is based on Refs. [87,88]. Olefin upgrading data is based on Refs. [29,73].<sup>b</sup>ExxonMobil MTO data is based on Refs. [16,89].<sup>c</sup>MTP data is based on Refs. [72,83,90].<sup>d</sup>BP OCM data is based on Ref. [32]. 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 and II have a conversion rate of 30% and a selectivity of 50% [12].

responsible for water/CO<sub>2</sub> removal and methanization. Ethylene-containing gas streams are compressed and water is condensed. Then, the gases pass through an acid gas removal system where CO<sub>2</sub> is removed. Additional water is removed in a refrigeration unit and then completely removed along with CO<sub>2</sub>. In the methanization section, CO, CO<sub>2</sub> and H<sub>2</sub> are converted to methane, which is recycled as feedstock to increase the total yield [12,34]. From the remaining stream, ethylene/ethane and propylene/propane are separated through C<sub>2</sub> and C<sub>3</sub> separation units, respectively.

Given the absence of OCM pilot plants, we base our analysis on two designs by G. Swanenberg in a DSM-sponsored feasibility study [12] (hereafter referred to as DSM OCM I and II in this article). Both DSM OCM I and II produce ethylene, water, CO<sub>2</sub> and heat. Heat is used for electricity co-generation. Oxygen required for the process 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 [12]. In DSM OCM II, all non-ethylene effluent (unconverted methane, propylene, 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<sub>e</sub>/t ethylene). About 2.3 t CO<sub>2</sub> per ton ethylene is also produced. In DSM OCM I,

a CO<sub>2</sub> separation unit is included so that CO<sub>2</sub> can be separated and be sold if a market exists [12]. However, DSM OCM II does not have a CO<sub>2</sub> separation unit. In order to make DSM OCM I and II comparable, energy used in the CO<sub>2</sub> separation unit in DSM OCM I is not considered in our analysis.

- The final products of DSM OCM II are ethylene and electricity (approximately 148 GJ<sub>e</sub>/t ethylene). About 15 t CO<sub>2</sub> 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. Definitions

#### 3.1. Primary energy use, feedstocks and energy supply

Primary energy use refers to the use of primary energy sources, such as crude oil and natural gas (electricity use is final energy use and not primary energy). Feedstocks refer to naphtha/ethane (for steam cracking), methanol (for MTO/MTP) and methane (for OCM routes).

All energy figures are reported in terms of primary energy (GJ or giga joule), unless otherwise specified (e.g., GJ<sub>e</sub> as electricity). In addition, these energy figures are given in terms of lower heating values (LHVs). Energy use and CO<sub>2</sub> emissions from the production of the catalysts and equipment is rather negligible and we have therefore excluded it from the analysis.

The heat required in a process is often supplied by external energy sources, such as fuels and steam. Alternatively, it is supplied by fuel-grade byproducts

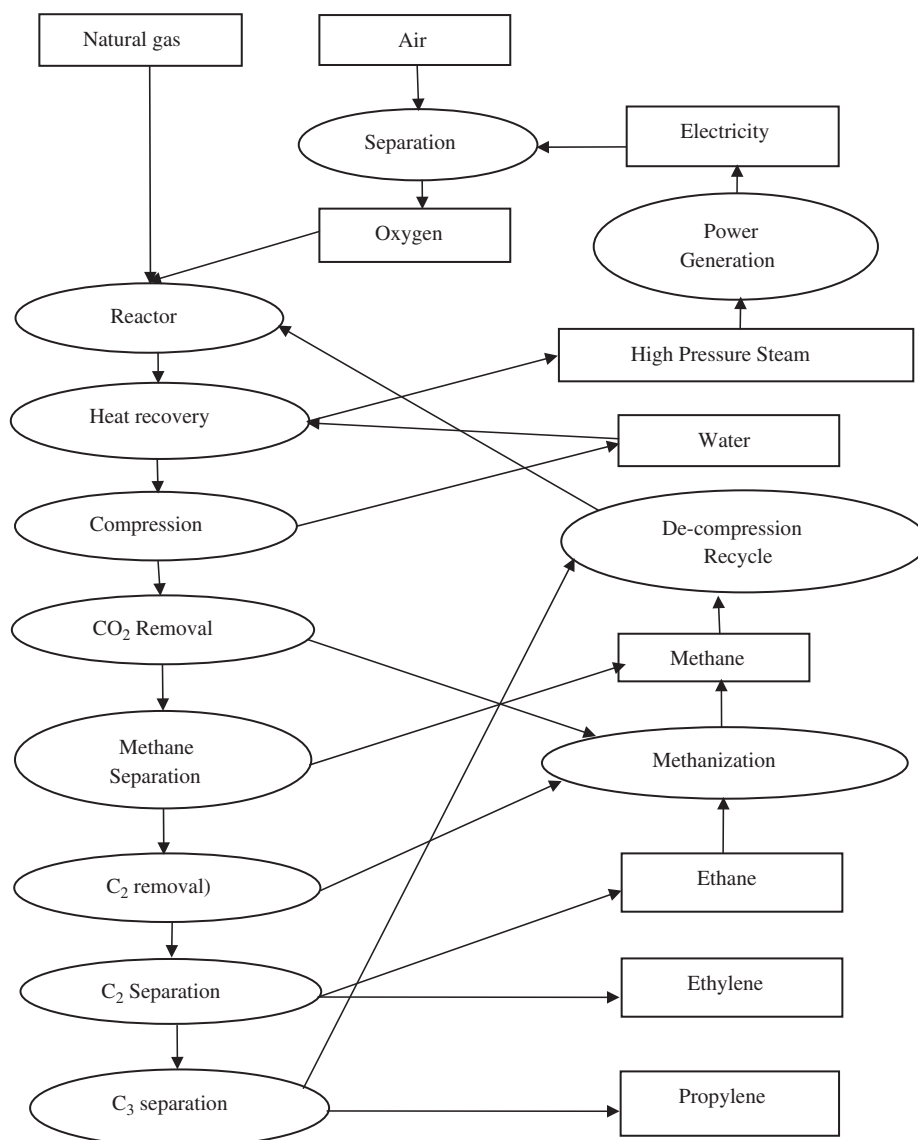


Fig. 2. Oxidative coupling of methane to olefins via ethane (this generic figure is based on Refs. [12,32]. Electricity cogeneration is based on Ref. [12]. CO<sub>2</sub> methanization is based on Ref. [34]).

(e.g., methane in the case of naphtha steam cracking). Oxygen is produced through air separation units with the use of electricity. Details on electricity will be given in Section 3.4.

### 3.2. Cumulative process energy use

The main indicator used for the energy analysis in this article is cumulative process energy use. It is the sum of the net energy use per ton of product in all steps of the process route from the extraction of primary energy to the petrochemicals.<sup>7</sup> It is also equivalent to the difference

<sup>7</sup>Since cumulative process energy use is expressed in primary energy terms in this article, it is approximately the same as cumulative process energy consumption. The concept of cumulative process energy use (in primary energy terms) originates from the concept of gross energy requirements discussed in Ref. [35] and from the concept of the cumulative

between the total energy input and the energy content of the final products per ton of product. The energy content of final products is not part of the cumulative process energy use. Cumulative process energy use consists of the net energy use per ton of product in *feedstock production* and *petrochemicals production*:

- Energy use in *feedstock production* refers to the net energy use for the conversion of primary energy sources to feedstocks (including also extraction, transportation and preprocessing of primary energy sources) and all the subsequent processes for the production of feedstocks.
- Energy use in *petrochemicals production* refers to the net energy use in the conversion of feedstocks to olefins and

(footnote continued)  
consumption of energy and cumulative exergy consumption discussed in Ref. [36].

all the subsequent processes (i.e., compression, recovery and separation of products).

The term specific energy consumption (SEC) is often used in the literature to express energy use per ton of product. However, it should be noted that SEC usually only refers to energy use in a single step in the process chain (e.g., steam cracking) and is therefore not the same as cumulative process energy use. See details in our previous paper [37].

### 3.3. High value chemicals (HVCs)

We now define the term HVCs. HVCs include light olefins and non-olefin chemicals. Light olefins are ethylene, propylene, butadiene and butylene. Non-olefin chemicals are mostly aromatics (and a small amount of  $C_{5+}$  hydrocarbons) in the case of steam cracking routes and mostly gasoline (and a small amount of butanes and  $C_{5+}$ ) in the case of  $C_1$  routes.

Backflows from naphtha steam cracking to the refinery (8–10% yield on a mass basis) are of very low economic value and are therefore not counted as HVCs.<sup>8</sup>

In this article, the yield of HVCs refers to the final yield (after separation, recycling, etc.). It is defined as a percentage of desired product output divided by hydrocarbon input on a mass basis.

### 3.4. Approaches to assess multiple product processes

Steam cracking is a multiple product process since it yields not only large olefins but also low-value products or co-products such as aromatics. In many studies on steam cracking processes, the total fuel use is allocated to ethylene alone, which means that all other products are produced “for free” in terms of energy use (likewise for emissions and for costs). However, this approach is particularly unsuitable to assess processes which lead to large amounts of co-products other than ethylene, such as propylene in the case of naphtha-based steam cracking and electricity in the case of DSM OCM I and II. In the current literature on energy, environmental and economic analysis, two approaches are commonly used in order to account for co-products [39]. These two approaches are explained as follows:

- *Allocation approach.* Using this approach, the energy use is allocated to the products on the basis of either their *mass values* (referring to the weight of the products) or their *economic values* (referring to market prices of the products).
- *Credit approach.* This approach involves two steps. First, the energy use of producing each of the

co-products (these are all products except for the main product) in a standalone process is identified. This is the amount of energy that would have been needed to produce these co-products if they have been produced individually (avoided energy use). Second, the sum of the energy use calculated in the first step is deducted from the total energy input. The result represents the energy use of the main product only. The deduction in the second step represents a credit, which gives the name to this approach.

In this article, we chose the *credit approach* to account for electricity co-generation in the case of DSM OCM I and II. Here electricity is assumed to be alternatively produced by a standalone, natural gas-fired power plant. However, the *credit approach* is not suitable for treating feedstocks and petrochemicals (e.g., aromatics). Unlike electricity, which is the only product of most power-generation technologies, none of feedstocks and petrochemicals is produced entirely alone and therefore they cannot be assumed to have been produced individually in a standalone plant (e.g., there is currently no standalone plant for the large-scale production of ethylene only). Therefore, we use the *allocation approach* when multiple chemical products are produced by a single process.

In this article, we apply the *allocation approach* on the basis of two values:

- *Economic value based.* We allocate energy use and  $CO_2$  emissions based on the economic values of olefins and non-olefin products. This means that we give 100% weight to the mass of olefins while giving 50% weight to the mass of non-olefin products (without backflows in the case of naphtha steam cracking). The reason is that the prices of non-olefin products are typically half as much as those of light olefins in the past 10 years [40–42]. This method is useful to compare routes that produce a variety of chemicals with very different yields and economic values. In this article, this method is actually only relevant to naphtha cracking, ExxonMobil MTO and Lurgi MTP because the yields of non-olefins from these routes are significant. For other routes, the yields of non-olefin products are negligible.
- *Mass value based.* We allocate energy use and  $CO_2$  emissions based on the mass of olefins and non-olefin products. This means that we give 100% weight both to the mass of olefins and non-olefins (without backflows). The mass value-based allocation approach was chosen in studies on “best available technologies” [6].

In our energy and emissions analysis, the *economic value-based allocation approach* is applied for all routes while the *credit approach* is only applied for those routes with electricity cogeneration, namely DSM OCM I and II. The *mass value-based allocation approach* has a subordinate role and is only used to test the sensitivity to the choice of the method. In our economic analysis, the mass value-based

<sup>8</sup>In our calculation, the weight of backflow has been subtracted from that of naphtha. As a result, the yields of high value chemicals become slightly higher than typical yields reported in Refs. [6,38]. For example, in Fig. 3 ethylene yield is 33% instead of a typical 30%.



allocation approach is not used; only the *economic value-based allocation approach* and the *credit approach* are used.

#### 4. Energy and emissions analysis

The data used to calculate the cumulative process energy use by C<sub>1</sub> and steam cracking routes are shown in Tables 3–5. The following three sections explain how the data were chosen and how the calculations are done for the energy and emissions analysis.

##### 4.1. Steam cracking routes

For steam cracking, naphtha and ethane are the most representative feedstocks since they are used to produce about 85% of olefins made in the world. Cumulative process energy use in steam cracking is the sum of energy use in naphtha and ethane production and in the conversion of these feedstocks to HVCs. Naphtha is produced in refineries and accounts for approximately 8% of oil refinery output on a mass basis [43]. Ethane is typically produced by separation of natural gas (on average 4–5% of wet gas<sup>9</sup> on the mass basis) and by recovery from refinery gases. Energy use for naphtha and ethane production is estimated to be approximately 8% of the energy content of crude oil and approximately 5% of the energy content of natural gas [4,44].

Data on energy use in naphtha and ethane-based steam cracking at the world average and state-of-the-art levels come from our previous study [37]. These data are presented in Table 3. CO<sub>2</sub> emissions from naphtha and ethane steam cracking are estimated based on emissions factors listed in Table 6.

##### 4.2. Methanol-related routes

Cumulative process energy use in the methanol-related routes is the sum of net energy use in methanol production and in the conversion of methanol-to-olefins. Energy use for methane production is assumed to be 5% of the energy content of natural gas (the same as in the case of ethane discussed above). For methanol production from natural gas, we assumed the Lurgi MegaMethanol technology, which has a SEC of 9 GJ/t methanol (including energy use in oxygen production and excluding the energy content of methanol, i.e., 20 GJ/t) [45]. If energy use for methane production is also included, then energy use in methanol production is 10 GJ/t methanol instead of 9 GJ/t (Table 4). Nine giga joules per ton methanol is slightly lower than that given by Topsoe (10 GJ/t methanol) and Syntex (10–14 GJ/t methanol) [46]. Lurgi, Syntex and Topsoe dominate the global market for methanol technology. The current world-average SEC for methanol production is approximately 15 GJ/t methanol [47].

<sup>9</sup>Wet gas is a type of natural gas, which contains more ethane, propane and heavier gases than dry gas, which is nearly pure methane.

The SEC for the conversion of methanol-to-olefins is in the range of 12–15 GJ/t ethylene (11.6 GJ/t ethylene [7], 12.3 GJ/t ethylene [8] and 14.5 GJ/t ethylene [32]). 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 [16]. The large difference between the SECs in the UOP MTO and the ExxonMobil MTO routes is the result of different product yields (see Table 2). Energy use in olefin upgrading processes used in UOP MTO is estimated to be approximately 0.5 GJ/t C<sub>4</sub> and C<sub>5</sub> byproducts [29].

##### 4.3. Oxidative coupling of methane

Cumulative process energy use in an OCM route is the sum of net energy use for methane and oxygen production and the conversion of methane to olefins. Energy use for methane production is the same as that for methanol-related routes. Primary energy use for production of high-purity oxygen (99%) with the use of electricity is approximately 3 GJ/t oxygen [48].

The original source on OCM processes assumed two internal efficiencies of electricity production: 56% for DSM OCM I and 53% for DSM OCM II [12]. To make them comparable, we assume that the electricity would otherwise have been produced by a stand-alone, state-of-the-art power plants with an energy efficiency of 55% (see the credit approach in Section 3.4). We also assumed 60% to test the sensitivity of DSM OCM I and II to different energy efficiencies. 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, respectively, for the energy efficiency at 55% and 60%.<sup>10</sup>

CO<sub>2</sub> emissions from conversion of methane to ethylene are allocated in the same way as the calculation of SEC. To calculate CO<sub>2</sub> emissions from electricity production in DSM OCM I and II, we also considered the same two power plants as mentioned above: one plant with an efficiency of 55% and CO<sub>2</sub> emissions of 0.102 t/GJ<sub>e</sub> while another with an efficiency of 60% and CO<sub>2</sub> emissions of 0.093 t/GJ<sub>e</sub>. These emissions are then deducted from the total emissions by DSM OCM I and II.

##### 4.4. Results

Our estimates for cumulative process energy use in terms of GJ/t HVCs in UOP MTO, ExxonMobil MTO and Lurgi MTP are presented in Tables 4 and 5. CO<sub>2</sub> emissions from

<sup>10</sup>Our estimates for energy use in DSM OCM I and II are much higher than two early studies on different designs of oxidative coupling [8,26]. 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.

Table 3  
Cumulative process energy use in steam cracking routes (the energy content 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           | 3 GJ/t naphtha <sup>a</sup> (state-of-the-art)<br>4 GJ/t naphtha (world average) | Naphtha 8% of crude oil <sup>b</sup>                                     | 5 (or 5) (state-of-the-art)<br>7 (or 7) (world average)     | Ethane production           | 2 GJ/t ethane <sup>c</sup>  | Ethane 1% of natural gas         | 3  |
| Naphtha to HVCs <sup>d</sup> | 12 GJ/t ethylene (state-of-the-art)<br>22 GJ/t ethylene (world average)          | Ethylene 33% and HVCs 60% of naphtha (or 63% if aromatics weighted 100%) | 7 (or 7) (state-of-the-art)<br>12 (or 12) (world average)   | Ethane to HVCs              | 10 GJ/t ethylene (state-of-the-art)<br>15 GJ/t ethylene (world average) | Ethylene 80%; HVCs 84% of ethane | 9 (state-of-the-art)<br>14 (world average)   |
| Total (GJ/HVCs)              | Not applicable   |  | 11 (or 11) (state-of-the-art)<br>19 (or 18) (world average) | Total (GJ/HVCs)             | Not applicable  |                                  | 12 (state-of-the-art)<br>18 (world average)  |

<sup>a</sup>Estimation is based on Ref. [91]. Crude oil extraction, transportation and pre-processing are included.

<sup>b</sup>Estimation is based on Ref. [43].

<sup>c</sup>Estimation is based on Ref. [92]. Natural gas extraction, transportation and pre-processing are included.

<sup>d</sup>All data on steam cracking are based on Ref. [37]. Endothermicity is not included as part of cumulative process energy use. Please see details in Ref. [37].

Table 4  
Cumulative process energy use in natural gas-to-olefins routes (Part I) (the energy content of feedstocks and HVCs is excluded from cumulative process energy use)

| Natural gas-to-olefins (UOP MTO)                            |                                    |   |  | Natural gas-to-olefins (ExxonMobil)         |                                    |   |   |
|---|------------------------------------|---|--|---|------------------------------------|---|---|
| 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 <sup>a</sup> | 10 GJ/t methanol                   | Methanol yield 145% of natural gas <sup>b</sup> | 23 <sup>c</sup>                              | 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 <sup>d</sup>      | Ethylene 26% and HVCs 62% of natural gas        | 5 <sup>d</sup>                               | Methanol to HVCs                            | 25 GJ/t ethylene <sup>e</sup>      | Ethylene 14% and HVCs 45% of natural gas (or 61% if gasoline weighted 100%) | 8 (or 6)                                  |
| Total (GJ/HVCs)   | Not applicable                     |   | 29   | Total (GJ/HVCs)                             | Not applicable                     |   | 40 (or 30)                                |

<sup>a</sup>Methanol data is based on Ref. [45]. Approximately 2 GJ/t natural gas is used for natural gas production [91]. Natural gas extraction, transportation and separation are included.

<sup>b</sup>Methanol yield is expressed by the weight of methanol divided by that of natural gas, which is larger than 100% because methanol contains oxygen [47].

<sup>c</sup>As an example, we present the calculation for this case: in the first step, 1 t of natural gas can be converted into 1.45 t 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 HVC) = 23 GJ/(t HVCs); 13 GJ/(t ethylene) × 26% ethylene yield/62% HVCs yield = 5 GJ/(t HVCs). The calculations for all other cases in Tables 4 and 5 are similar to this case.

<sup>d</sup>Estimation is based on Refs. [88,93]. Energy use in olefin upgrading, approximately 0.5 GJ/t C<sub>4-5</sub>, has been accounted for Ref. [29].

<sup>e</sup>Estimation is based on Ref. [16].

Table 5  
Cumulative process energy use in natural gas-to-olefins routes (Part II) (the energy content of feedstocks and HVCs is excluded from cumulative process energy use)

| Natural gas-to-olefins (Lurgi MTP)          |                                    |  |   | Natural gas-to-olefins (DSM OCM I and 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)  |
| Natural gas production, methanol production | 10 GJ/t methanol                   | Methanol yield 145% of natural gas   | 25 (or 22)                                | Natural gas production<br>Oxygen production                               | 2 GJ/t natural gas <sup>a</sup><br>3 GJ/t oxygen <sup>d</sup>   | Not applicable  | 4 <sup>b</sup> (DSM I)<br>13 <sup>c</sup> (DSM II)<br>13 <sup>c</sup> (DSM I)<br>11 <sup>f</sup> (DSM II) |
| Methanol to HVCs                            | 10 GJ/t propylene <sup>e</sup>     | Propylene 46% and HVCs 57% of natural gas (or 65% if gasoline weighted 100%) | 8 (or 7)                                  | Conversion to ethylene (electricity production efficiency of 55% and 60%) | 17 and 20 GJ/t ethylene <sup>h</sup><br>14 and 36 GJ/t ethylene | HVCs 50% of natural gas (DSM I)<br>HVCs 15% of natural gas (DSM II) | 17 and 20 (DSM I)<br>14 and 36 (DSM II)   |
| Total (GJ/HVCs)                             | Not applicable                     |  | 33 (or 30)                                | Total (GJ/HVCs)   | Not applicable  |   | 35 and 38 (DSM I)<br>38 and 61 (DSM II)   |

<sup>a</sup>For DSM I, 2.0 t of methane is needed as the total energy input to produce 1 t of ethylene [12]. For DSM II, 6.6 t of methane is needed to produce one of ethylene.

<sup>b</sup>DSM I: 2.0 t methane/ton ethylene × 2.0 GJ/t methane = 4 GJ/t ethylene.

<sup>c</sup>DSM II: 6.6 t methane/ton ethylene × 2.0 GJ/t methane = 13 GJ/t ethylene.

<sup>d</sup>Estimation is based on Ref. [48]. Methane/oxygen ratios in DSM OCM I and II on the mass basis are 1:2.2 and 1:0.56, respectively [12].

<sup>e</sup>DSM I: 2.0 t methane/ton ethylene × 2.2 t oxygen/ton methane × 3.0 GJ/t oxygen = 13 GJ/t ethylene.

<sup>f</sup>DSM II: 6.6 t methane/ton ethylene × 0.56 t oxygen/ton methane × 3.0 GJ/t oxygen = 11 GJ/t ethylene.

<sup>g</sup>Estimation is based on Refs. [47,83].

<sup>h</sup>Estimation for DSM OCM I and II is based on Ref. [12] but with an efficiency of 55% for power generation. Energy use in compression, recovery and separation is included and is clearly higher in the case of OCM I than in the case of OCM II.

these routes are calculated on the basis of emission factors listed in Table 6. The results of energy and emissions analysis in terms of HVCs are shown in Figs. 3 and 4. Our key findings are:

- Energy use and CO<sub>2</sub> emissions in all C<sub>1</sub> routes are much higher than those of steam cracking. Methane-based routes use more than twice as much process energy than state-of-the-art steam cracking routes do. Methane-based routes lead to 60–85% more CO<sub>2</sub> emission than the state-of-the-art ethane cracking.
- Among the methanol-related 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-related routes have similar energy use, but cause slightly higher CO<sub>2</sub> emissions than DSM OCM I and II do.
- Due to large amount of electricity cogeneration, DSM OCM II is highly sensitive to the assumed efficiencies of electricity cogeneration.

As shown in Fig. 3, most of energy use in methanol-related routes is caused by methanol production. The same

can be concluded about the CO<sub>2</sub> emissions from methanol-related routes.

Figs. 3 and 4 also show that much energy use and CO<sub>2</sub> emissions occur in the feedstock production (mostly for oxygen production) of DSM OCM I and II. The rest of energy use occurs mostly in recycling and separation processes (DSM OCM II has no recycling but has separation of ethylene and the rest). However, in the case of DSM OCM II, relatively less energy is used for oxygen production since most of the methane is combusted to produce electricity and therefore relatively less oxygen is required. The large amount of co-generated electricity is the reason why DSM OCM II is extremely sensitive to the assumed efficiencies of electricity cogeneration.

In the case of DSM OCM I and II, the share of CO<sub>2</sub> emissions from petrochemicals production within the total CO<sub>2</sub> emissions is relatively smaller than the share of energy use in petrochemicals production within the cumulative energy use (compare Figs. 3 and 4). It is because part of the energy used for electricity co-generation<sup>11</sup> comes from the

<sup>11</sup>The rest of the energy used for electricity co-generation comes from the complete oxidation of methane.

Table 6  
Emissions factors for steam cracking and natural gas-to-olefins routes (t CO<sub>2</sub> per GJ energy consumed)

| Naphtha-based steam cracking <sup>a</sup>                 | Ethane-based steam cracking <sup>b</sup>                | Natural gas-to-olefins  |   |  |
|---|---|---|---|--|
|   |   | UOP MTO, ExxonMobil MTO and Lurgi MTP   | DSM OCM I   | DSM OCM II   |
| <i>Feedstock production</i>                               |   |   |   |  |
| 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) <sup>c</sup>                                | 0.056 (combustion of natural gas for methane production)  |  |
|   |   | 0.042 (combustion of natural gas and partial oxidation of methane for methanol production) <sup>d</sup>         | 0.056 (combustion of natural gas for oxygen production)   |  |
| <i>Petro-chemicals production</i>                         |   |   |   |  |
| 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 for electricity production with an efficiency of 55% and 60%, respectively (combustion of all non-methane and non-ethylene byproducts) <sup>e</sup> | −0.004 and 0.033 for electricity production with an efficiency of 55% and 60%, respectively (combustion of all non-ethylene byproducts and methane) <sup>f</sup> |

<sup>a</sup>Data is based on Ref. [94]. Refinery gases have higher carbon content than natural gas.

<sup>b</sup>Data is based on Ref. [94]. The difference between CO<sub>2</sub> emission factors of naphtha and ethane cracking is due to different fuels used. Ethane cracking emits 6 kg CO<sub>2</sub>/GJ less than naphtha cracking because the hydrogen content in the fuel grade byproducts from ethane cracking is higher than that from naphtha cracking.

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

<sup>d</sup>Data is based on Ref. [94]. This emission factor is smaller than that of natural gas due to auto-thermal reforming, partial oxidative reaction and CO<sub>2</sub> recycling.

<sup>e</sup>Data is based on Ref. [12]. This is the result of partial oxidative, exothermic reactions in which thermal energy is released without producing CO<sub>2</sub> (See Table 2).

<sup>f</sup>Data is based on Ref. [12]. The emission factor of OCM II is higher than OCM I because of less recycling.

exothermic, partial oxidation reactions (see reaction equations in Table 2). These reactions, unlike complete oxidation of methane, do not produce CO<sub>2</sub>. CO<sub>2</sub> emissions from DSM OCM I and II come from undesired, complete oxidation of methane.

In Fig. 4, CO<sub>2</sub> emissions from petrochemicals production in the case of DSM OCM II are slightly negative because of the assumed efficiencies for electricity cogeneration used in our analysis. We used 55% and 60%, both of which are higher than 53% used in the original design of DSM OCM II [12]. If 53% is used, CO<sub>2</sub> emissions from DSM OCM II are very close to those from DSM OCM I.

#### 4.5. Further improvement

##### 4.5.1. Methanol-related routes

For methanol-related 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) [49–51].

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 [52]. Also, a so-called “sono-chemical” process can convert methane to methanol using

high-intensity ultrasound [53]. However, no energy use data is published on this process. Dry reforming instead of steam reforming<sup>12</sup> is reported to allow curbing CO<sub>2</sub> 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 reaction is approximately 3 GJ/t methanol [49,55] (for 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-related routes would be as efficient as the state-of-the-art naphtha steam cracking. It is therefore questionable whether methanol-related routes will ever be more energy efficient than the steam cracking routes.

<sup>12</sup>Mitsubishi has filed patents on a so-called oxo gas process, which recovers CO<sub>2</sub> from both flue gas and steam reforming [54]. The oxo process is also called dry reforming as opposed to steam reforming. The formula for the reaction is: CH<sub>4</sub> + CO<sub>2</sub> → 2CO + 2H<sub>2</sub>. Mitsubishi claims that this process has the potential to drastically reduce CO<sub>2</sub> emissions. Also, air can be used instead of pure oxygen and therefore CO<sub>2</sub> emissions from oxygen production are also avoided.

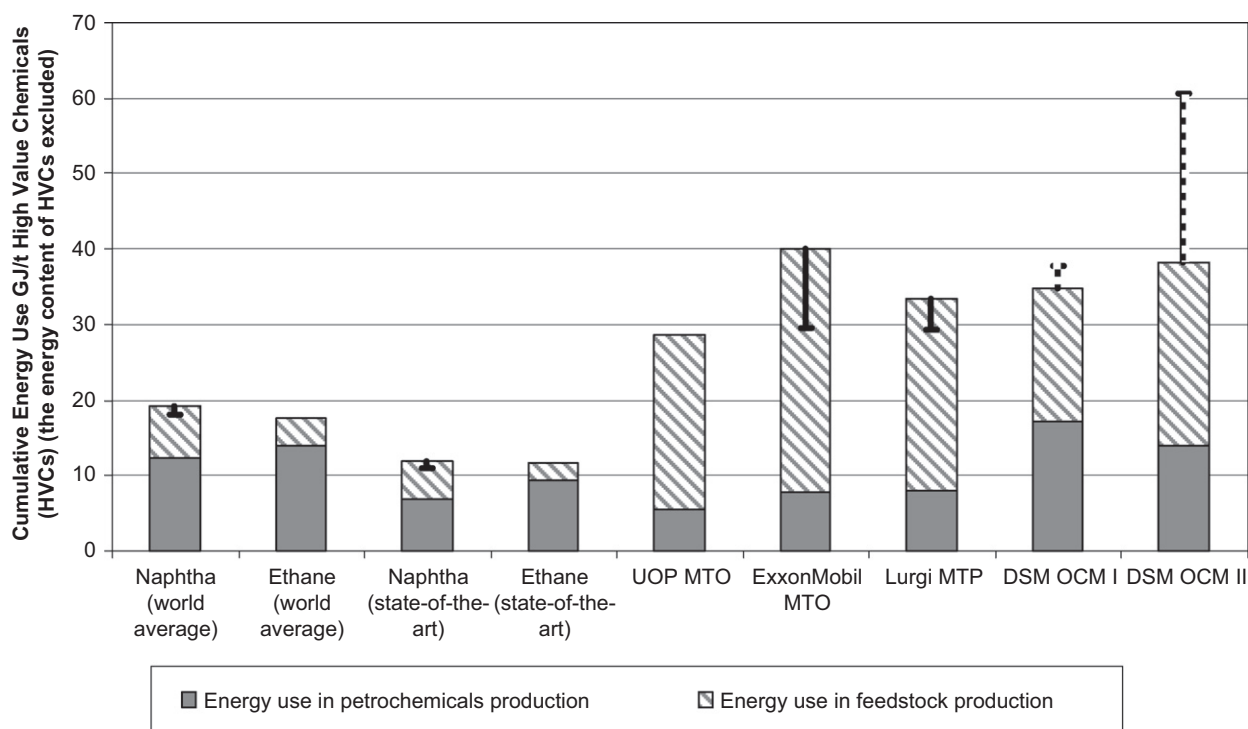


Fig. 3. Comparison of cumulative process energy use by steam cracking and C<sub>1</sub> routes with sensitivity analysis for different definitions of high values chemicals and power-generation efficiencies (the energy content of products excluded). Data come from Tables 3 to 5. HVCs have an energy content of approximately 50 GJ/t. The solid errors 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 OCM I and 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%.

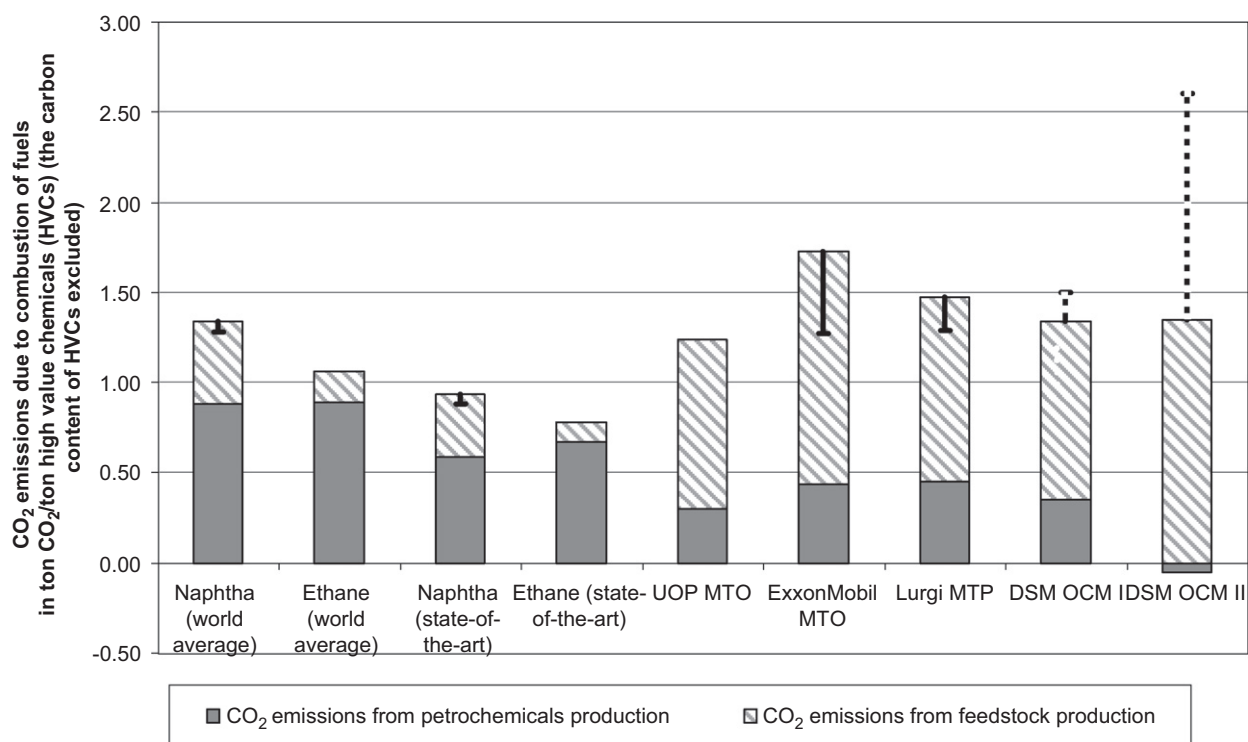


Fig. 4. Comparison of estimated CO<sub>2</sub> emissions in steam cracking and C<sub>1</sub> routes with sensitivity indication for different definitions of high values chemicals and electricity co-generation efficiencies. Data is based on data in Tables 3–6. The error bars represent the same sensitivity analyses as those in Fig. 3. Please note that CO<sub>2</sub> emissions from DSM OCM I and II are low as the result of a partial oxidative, exothermic reaction. See Table 6 for emission factors and more explanations.

#### 4.5.2. Oxidative coupling of methane

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 [56,57]. Under 600 °C, the rate of reaction is slow, but above 600 °C undesired oxidations dominate the reactions [55].
- *Separation.* Relatively high energy use in separation and recycling [56,58].
- *Catalysts.* Additional oxygen and hydrogen are required for reducing coking on catalysts [59,60]. High temperatures at 750–1000 °C require catalysts with high thermal stability [56].

Other issues concern safety (possible explosion due to the mixture of oxygen and hydrocarbons), environmental pollution (CO and CO<sub>2</sub> emissions, aromatic hydrocarbons, acid gas and organic acid), and operability [17].

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 [56,61]. Oxygen-permeable membrane reactors could eliminate the need for oxygen plants and enhance the selectivity to ethylene [62]. This could result in ethylene yields up to 50% [63] though the slow oxygen flux might require a large reactor, which implied higher investments [64]. If oxygen-permeable membrane reactors could be integrated with an OCM plant, they would allow approximately 20% (approximately 6.5 GJ/t ethylene) energy savings compared to a DSM OCM I plant (without membrane reactors) [64].
- *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 [33]. In addition, experiments are being conducted to try out several AgNO<sub>3</sub> sorbents for ethylene absorption [65].
- *Retrofitting.* OCM 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) [27,66–68]. However, some say that this is difficult because steam crackers have only limited capacities to process light gases [31].

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 CO<sub>2</sub> 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 CO<sub>2</sub> emissions than steam cracking routes do.

## 5. Production cost analysis

Our 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 prices in the case of DSM OCM I and II) dominate the results. We distinguish three sets of feedstock costs and electricity prices (Table 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 and the situation 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 in Russia) where natural gas is abundant and local gas consumption is low. Natural gas in these regions account 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, according to several sources [10,16,24,69]. However, due to the rapid development of liquefied natural gas (LNG),<sup>13</sup> 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 Fig. 5). Other variable costs include utilities (electricity, water, etc.). Fixed costs include labor, operation and maintenance. We assumed a lifetime of the plant to be 15 years and the discount rate for capital costs to be 10%. All values are given in US\$ of year 2000.

The production cost analysis follows the *economic value-based allocation approach* described in Section 3.4. For DSM OCM I and II, electricity sales are deducted from the total production costs. Assumptions for electricity price are shown in Table 7. These electricity prices are assumed to be strongly dependent on the prices of natural gas for electricity generation.

Fig. 5 shows that feedstock costs dominate production costs for these routes. We have made the following three observations:

- First, the high oil prices (\$60/bbl) and high gas prices (\$9/GJ) under the average situation in 2006 made the production costs of HVCs 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, C<sub>1</sub> routes can lower

<sup>13</sup>The LNG transportation cost from gas-rich countries to the US and Europe is currently about \$3–4/GJ natural gas [70].

Table 7  
Three sets of assumptions for feedstock costs and electricity prices (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 |
|--|--|---|--|
| <i>Crude oil</i>   | \$60/bbl (\$440/t) [95]                            | \$20/bbl (\$147/t) [95,96]  | Not applicable   |
| Naphtha (price in \$/t = 10 × oil prices in \$/bbl as a rule of thumb derived from Ref. [6])   | \$600/t  | \$200/t   |  |
| Ethane (price in \$/GJ = 1/6 × oil prices in \$/bbl as a rule of thumb derived from Ref. [95])   | \$10/GJ (or \$450/t)                               | \$3/GJ (or \$135/t)   |  |
| <i>Natural gas</i>   | \$400/t (or \$8/GJ) [95,97]                        | \$125/t (or \$2.5/GJ) [95,97]                                     | \$35/t (or \$0.75/GJ) [95,97]                            |
| Methanol (estimated on the basis of methanol production costs: other variables and fixed costs together at \$15/t and capital cost at \$40/t [52]) | \$355/t  | \$150/t   | \$75/t   |
| Electricity (estimated on the basis of Refs. [98,99])  | \$20/GJ <sub>e</sub> (\$0.08/kWh)                  | \$8/GJ <sub>e</sub> (\$0.03/kWh)                                  | \$5/GJ <sub>e</sub> (\$0.02/kWh)                         |
| Oxygen (estimated on the basis of oxygen production costs: 350 kWh/t plus fixed and capital costs together at \$50/t [48])                         | \$80/t   | \$60/t  | \$55/t   |

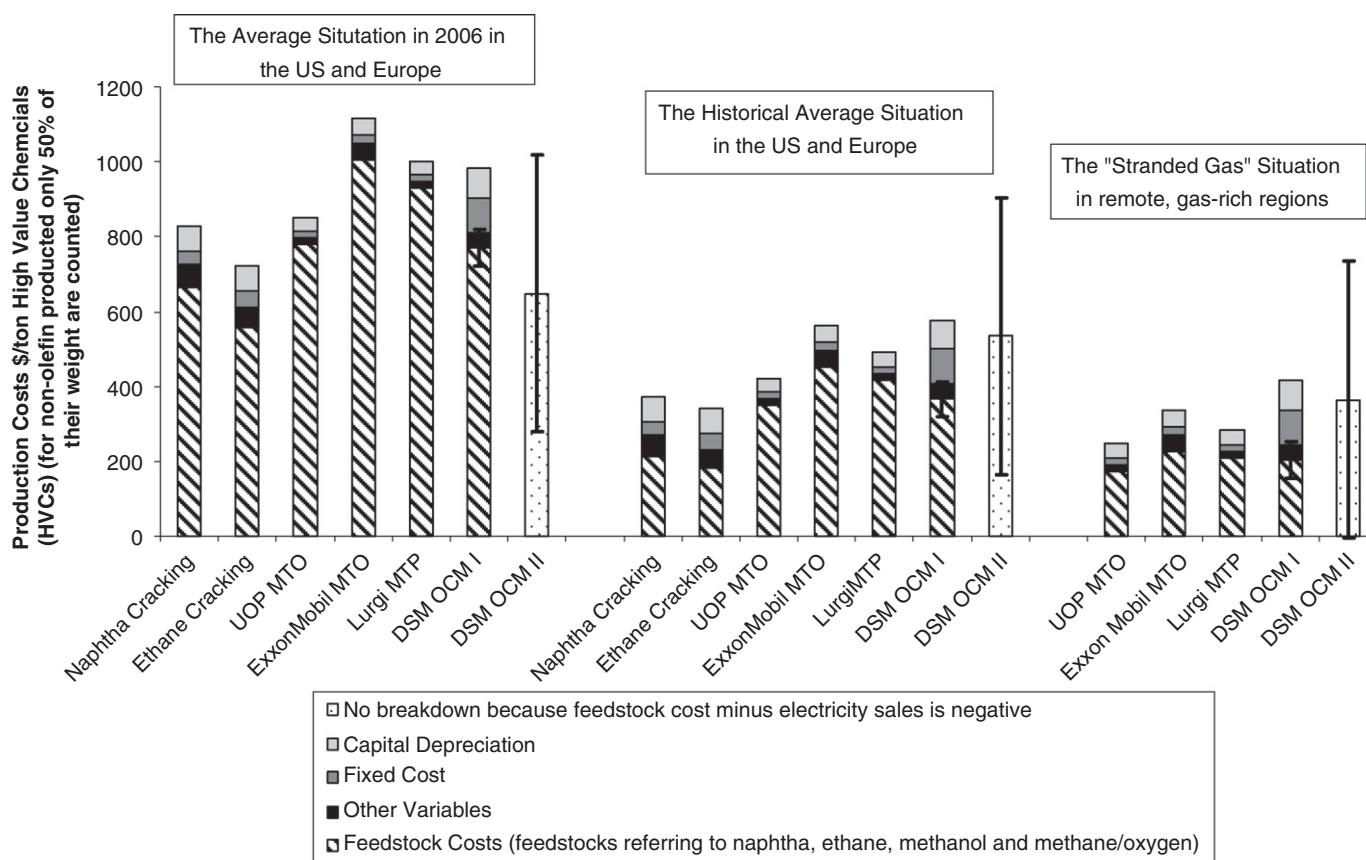


Fig. 5. Comparison of production costs by steam cracking and C<sub>1</sub> routes (based on Table 7; error bars showing the effect of electricity prices deviating ±\$0.01/kWh from the price assumptions in Table 7; all in US\$ of year 2000).

production costs to \$300–400/t HVCs. Clearly, the economics of C<sub>1</sub> routes are highly economically attractive in those remote, gas-rich regions.

- Third, production costs of DSM OCM II do not change in a similar way as other routes do when the prices of natural gas change. However, DSM OCM

II is very sensitive to the change of electricity prices: the errors bars in Fig. 5 show the effect of electricity prices when deviating ±\$0.01/kWh from the assumptions in Table 7. This shows once more that DSM OCM II is rather a power plant than a petrochemical plant.

However, the uncertainty of production costs for  $C_1$  routes is high because:

- Low production costs are only possible in very remote, gas-rich regions in the Middle East, Russia and other countries. However, as said 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.
- 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 OCM for ethylene production at large, commercial scale.

## 6. Conclusions

By conducting a comparative analysis of the energy use,  $CO_2$  emissions and production costs of  $C_1$  technologies and steam cracking, we found that methane-based routes use more than twice as much than process energy than state-of-the-art steam cracking routes do (the energy content of products is excluded). Oxidative coupling routes are currently still immature due to low ethylene yields and other problems. The 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 (or LNG) may increase the prices of natural gas in those locations. While several possibilities for energy efficiency improvement do exist, 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 do.

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## References

- [1] Nakamura D. Global ethylene capacity grows 4% in 2005. *Oil Gas J* 2006(March 27):44–56.
- [2] Chemical Market Associates Inc. (CMAI). World Petrochemical Feedstocks Analysis. Houston, TX: Chemical Market Associates Inc. and Purvin & Gertz, 2005. See also: <<http://www.cmaiglobal.com/apps/news/WPFA.pdf>>.
- [3] International Energy Agency (IEA). The reduction of greenhouse gas emissions from the oil refining and petrochemical industry (Report no. PH3/8). Cheltenham, UK: IEA Greenhouse Gas R&D Program, 1999.
- [4] 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* 2006; doi:10.1016/j.energy.2006.08.005 (in press).
- [5] Department of Energy (DOE). Ethylene process design optimization. Washington, DC: US Department of Energy (DOE), 2001. See also: <[www.oit.doe.gov/chemicals/factsheets](http://www.oit.doe.gov/chemicals/factsheets)>.
- [6] 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.
- [7] Stratton A, Hemming DF, Teper M. Ethylene production from oil, gas and coal-derived feedstock. London: Coal Research at International Energy Agency (IEA); 1983.
- [8] Geem P. Nieuwe routes naar etheen. *NPT ProcesTechnologie* 1992 (April):15–22 (in Dutch).
- [9] Geerts J. Ethylene from natural gas by direct oxidation (Report: EUR 1361 EN). Eindhoven, the Netherlands: Eindhoven University of Technology, 1991.
- [10] Burke B. Emerging technologies to develop stranded gas. In: 2001 annual meeting of NPRA (National Petroleum & Refinery Association) in New Orleans. New Orleans: NPRA, 2001.
- [11] Heber J. Economic comparison of naphtha cracking and MTO UOP/Norsk Hydro. In: The 3rd Asian olefins and polyolefins markets conference in Bangkok. Thailand, Singapore: Centre for Management Technology, 2000.
- [12] 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.
- [13] ChemSystems. Process Evaluation/Research Planning: PERP 2002/2003 Program. Houston, TX: ChemSystem/Nexant Inc., 2002.
- [14] Wang C, Xu L, Wang Q. Review of directly producing light olefins via co-hydrogenation. *J Nat Gas Chem* 2003;12(1):10–6.
- [15] Norwegian Institute for Energy Technology. The Gas Value Chain: technology strategy for competitive gas production and off-take. Oslo: Norwegian Institute for Energy Technology, 2003. See also: <[http://www.ife.no/media/1234\\_OG\\_21-2003-Gassverdikjeden.pdf](http://www.ife.no/media/1234_OG_21-2003-Gassverdikjeden.pdf)>.
- [16] Keep P. Comparison of remote gas conversion technologies. London: Syntex Inc., 1999. See also: <[www.syntex.com/methanol/pdfs/papers/imtof99-paper9\(59w\).pdf](http://www.syntex.com/methanol/pdfs/papers/imtof99-paper9(59w).pdf)>.
- [17] Zaman J. Oxidative processes in natural gas conversion. *Fuel Process Technol* 1999;58(2–3):61–81.
- [18] Murchison C, Murdick D. Using syngas for olefins feedstock. *Hydrocarbon Process* 1981(January).
- [19] US Patent Office. Process for the manufacture of unsaturated hydrocarbons (US Patent 5,546,642). Ruhrchemie Aktiengesellschaft, US Patent Office, 1986.
- [20] US Patent Office. Ethanol from methanol, hydrogen and carbon monoxide (US Patent 4,133,966 by W. Pretzer, T. Kobylinski, J. Bozik). Gulf Research & Development Company, US Patent Office, 1979.
- [21] US Patent Office. Conversion of methane (US Patent 4,199,533 by S. Bensen). University of Southern California, US Patent Office, 1980.
- [22] Inui T. Rapid catalytic reforming of methane with  $CO_2$  and its application to other reactions. *Appl Organomet Chem* 2001;15(2): 8794.
- [23] Hattori T. Catalytic reduction of carbon dioxide by lower alkanes. *Carbon Dioxide Chem (Environ Issues R Soc Chem)* 1994;153 (Special Publication):74–81.
- [24] Moiseev II, Plate NA, Tereshchenko GF. Ergochemical technologies: energy and bulk/basic chemicals in a single process. *Russ Chem Bull (Int Ed)* 2001;50(11):2015–9.
- [25] Keller GE, Bhasin MM. Synthesis of ethylene via oxidative coupling of methane. *J Catal* 1982;9(73):9–19.
- [26] Geerts J, Hoebink J, Wiele K. Ethylene from natural gas: proven and new technologies. In: Alibright L, Crynes B, Nowak S, editors. Novel production methods for ethylene, light hydrocarbons and aromatics. New York: Marcel Dekker; 1992. p. 207–37.



- [27] US Patent Office. Olefins process which combines hydrocarbon cracking with coupling methane (US Patent 5,254,781). Amoco Corporation, US Patent Office, 1993.
- [28] Barger P. UOP presentation. In: The IZA pre-conference school. Poitiers, France: The International Zeolite Association (IZA), 2001.
- [29] Gregor J. Meeting the changing needs of the olefins market by UOP LLC. In: The 5th EMEA petrochemical technology conference in Paris. London: Euro Petroleum Consultancy Ltd., 2003.
- [30] US Patent Office. Process for producing olefins from natural gas (US Patent 5,025,108). Institute Francais du Petrole, US Patent Office, 1991.
- [31] Bearden MD. Personal communication. Hydrocarbons & Energy Research, Dow Chemicals, Freeport, TX, 8 September 2006.
- [32] Gradassi M, Green N. Economics of natural gas conversion processes. *Fuel Process Technol* 1995;42(5):65–83.
- [33] 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 reactor. *Appl Catal* 1997;155:L1–7.
- [34] US Patent Office. Oxidative coupling of methane with carbon conservation (US Patent 6,096,934). UOP LLC, US Patent Office, 2000.
- [35] International Federation of Institutes for Advanced Study (IFIAS). Workshop report: energy analysis and economics. *Resour Energy* 1978;1(2):151–204.
- [36] Szargut J. Analysis of cumulative exergy consumption. *Energy Res* 1987;11(4):541–7.
- [37] Ren T, Patel M, Blok K. Olefins from conventional and heavy feedstocks: energy use in steam cracking and alternative processes. *Energy* 2006;31(4):425–51.
- [38] Chauvel A, Lefebvre G. Petrochemical processes. Part I: Synthesis gas derivatives and major hydrocarbons. Paris: Editions Technip; 1989.
- [39] Blok K. Introduction to energy analysis. Amsterdam: Technie Press; 2006.
- [40] Energy Information Administration. International Energy Price Information. Washington, DC: Energy Information Administration at the US Department of Energy, 2006. See also: <http://www.eia.doe.gov/emeu/international/prices.html>.
- [41] Pettman A. Europe and Middle East—an evolving relationship. In: Aspentech chemicals conference in Genval. Belgium, Houston: Aspentech Inc., 2002.
- [42] Chemical Market Associates Inc. (CMAI). Europe/Middle East reports on olefins & derivatives (various issues in 1995–2006). Houston: Chemical Market Associates Inc., 2006.
- [43] Hydrocarbon-Processing. Refining Processes 2002. Hydrocarbon Processing 2002 (November).
- [44] Hydrocarbon-Processing. Refining Processes 2002. November 2002.
- [45] Lurgi. Lurgi MegaMethanol brochure by engineering division of Lurgi Oel, Gas and chemie GmbH. Frankfurt: Lurgi GmbH; 2003.
- [46] Syntex. Methanol plant technology. Cleveland, England: Syntex Inc., 2004. See also: <http://www.jmcatalysts.com/pct/pdfs-uploaded/methanol/shortlcm.pdf>.
- [47] 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, CO: National Renewable Energy Laboratory (NREL) at the US Department of Energy (DOE); 2003.
- [48] van-Ree R. Air separation technologies: an inventory of technologies for pure oxygen production for pulverized coal combustion in a CO<sub>2</sub>(g)/O<sub>2</sub>(g) atmosphere. Petten, the Netherlands: Energy Research Center of the Netherlands (ECN); 1992 (in Dutch).
- [49] 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).
- [50] 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: ECN (Energy Research Center of the Netherlands); 2001.
- [51] Lunsford J. Catalytic conversion of methane to more useful chemicals and fuels: a challenge for the 21st century. *Catal Today* 2000;63(2):165–74.
- [52] Michel S. Methanol production costs, reports on science and technology 61/1999. Munich, Germany: Linde; 1999.
- [53] 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: [www.ttu.edu/~ottip/techlib/physical/0164.html](http://www.ttu.edu/~ottip/techlib/physical/0164.html).
- [54] International Energy Agency (IEA). Mitsubishi synthesis gas process for CO<sub>2</sub> emission free GTL plant. Paris: International Energy Agency (IEA/OECD), 2002. See also: [www.iea.org/textbase/work/2002/stavanger/mhi.pdf](http://www.iea.org/textbase/work/2002/stavanger/mhi.pdf).
- [55] Weissermel K, Arpe H. Industrial organic chemistry. Weinheim: Wiley-VCH GmbH & Co. KGaA; 2003.
- [56] Choudhary VR, Uphade BS. Oxidative conversion of methane/natural gas into higher hydrocarbons. *Catal Surveys Asia* 2004;8(1):15–25.
- [57] Lange JP, Schoonebeek RJ, Mercera PDL, van Breukelen FW. Oxycracking of hydrocarbons: chemistry, technology and economic potential. *Appl Catal A* 2005;283:243–53.
- [58] Gonzalez L. Conversion of natural gas into heavier hydrocarbons: a process scheme. In: The 78th annual convention of gas processors association. Nashville, TN: Gas Processors Association, 1999.
- [59] Maitra AM. Critical performance evaluation of catalysts and mechanistic implications for oxidative coupling of methane. *Appl Catal* 1993;104:11–59.
- [60] Lunsford J. The catalytic oxidative coupling of methane. *Angew Chem Int Ed* 1995;34(9):970–80.
- [61] Pyatnitskii Y. Contemporary methods for the direct catalytic conversion of methane. *Theor Exp Chem* 2003;39(4):201–18.
- [62] Lu Y. Oxygen-permeable dense membrane reactor for the oxidative coupling of methane. *J Membr Sci* 2000;170(1):27–34.
- [63] Lu Y, Dixon AG, Moser W, Ma YH. Analysis and optimization of cross-flow reactors for oxidative coupling of methane. *Ind Eng Chem Res* 1997;36(3):559–67.
- [64] Hugill J, Tillemans F, Dijkstra J, Spoelstra S. Feasibility study on the co-generation of ethylene and electricity through oxidative coupling of methane. *Appl Therm Eng* 2005;25(8–9):1259–71.
- [65] Kim J, Cho S, Park J, Han S. Comparison of AgNO<sub>3</sub>/Clay and AgNO<sub>3</sub>/ALSG Sorbent for Ethylene Separation. *Chem Mater Sci* 2005;11(1):145–9.
- [66] US Patent Office. Catalytic wall reactors and use of catalytic wall reactors for methane coupling and hydrocarbon cracking reactions (US Patent 5,599,510). Amoco Corporation, US Patent Office, 1997.
- [67] Hoebink H, Venderbosch H, Geem P. Economics of the oxidative coupling of methane as an add-on for naphtha cracking. *Chem Eng Technol* 1995;18(1):12–6.
- [68] 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. *J Chem Technol Biotechnol* 2004;79(2):182–6.
- [69] Roberto C, Lorenzo D, Nazareno V. Unlocking marginal gas reserves through technological innovation. In: The 17th World Energy Council Congress. London: World Energy Council, 1998.
- [70] Vora B. Personal communication. UOP LLC, Des Plaines, IL, 11 August 2004.
- [71] UOP. UOP/Hydro MTO process methanol to olefins conversion. Des Plaines: UOP LLC; 2003.
- [72] Liebner W. GTC-Gas to Chemicals Process Options for Venezuela by Lurgi Oel-Gas Chemie Engineering. In: PdVSA-EFO seminar. Caracas, Venezuela: Petróleos de Venezuela S.A., 2002.
- [73] Grootjans J, Vanrysselberghe V, Vermeiren W. Integration of total petrochemicals: UOP olefins conversion process into a naphtha steam cracker facility. *Catal Today* 2005;106(1–4):57–61.
- [74] US Patent Office. Catalytic production of olefins at high methanol partial pressures (US Patent application 20030109765). ExxonMobil, US Patent Office, 2003.

- [75] Kunii D, Levenspiel O. Free fall reactor. New York: Robert E. Krieger Publishing Co.; 1977.
- [76] Zenz FA, Othmo DF. Fluidization and fluid partial systems. New York: Reinhold Publishing Co.; 1960.
- [77] EPO. ICI olefins (European Patent application 40,015). ICI, European Patent Office, 1981.
- [78] US Patent Office. Conversion process by J.H. Brophy and R.P. Manning (US Patent 4,726,913). BP, US Patent Office, 1988.
- [79] US Patent Office. Production of light olefins (from methanol, etc.) (US Patent 4,499,327). Union Carbide Co., US Patent Office, 1985.
- [80] Addroulakis I, Reyes S. Optimal design and operation of methane oxidative coupling reaction systems for the production of higher hydrocarbons. In: Technical program at the annual meeting of the American Institute of Chemical Engineers (AIChE). Houston: American Institute of Chemical Engineers, 2000.
- [81] ChemSystems. 10-year proprietary report summaries. Houston: ChemSystems Inc.; 2003.
- [82] Pujado P, Greer D, Andersen J, Foley T, Bhirud V. The role of new technology in the light olefins industry. In: 2002 spring national meeting of the American Institute of Chemical Engineers (AIChE) in Houston. New York: American Institute of Chemical Engineers, 2002.
- [83] Koempel H, Liebne W, Wagner M. MTP—an economic route to dedicated propylene. In: The 2nd ICIS-LOR world olefins conference. Amsterdam: ICIS-LOR Inc., 2003.
- [84] Alperowicz N. Methanol-to-olefins complex planned for Nigeria. Chem Week 2002(October 2).
- [85] US Trade and Development Agency (USTDA). EATCO-Suez Petrochemicals Complex Gas to Polyolefin Project Final Report (Executive Summary). Washington, DC: US Trade and Development Agency, 2000.
- [86] Alperowicz N. Egyptian firm to build MTO complex. Chemical week. See also News report at [www.chemweek.com](http://www.chemweek.com) April 9, 2003.
- [87] Kvisle S, Nilsen HR. MTO: state of art and perspectives. In: DGMK conference: creating value from light olefins-production and conversion in Hamburg. Hamburg: German Society for Petroleum and Coal Science and Technology, 2001.
- [88] US Patent Office. Methanol to olefin process with increased selectivity to ethylene and propylene (US Patent 6,534,692). UOP LLC, US Patent Office, 2003.
- [89] US Patent Office. Production of light olefins from oxygenate using framework gallium-containing medium pore molecular sieve (US Patent application 20030018231). ExxonMobil Inc., US Patent Office, 2003.
- [90] Rothaemel M, Holtmann HD. MTP, methanol to propylene—Lurgi's way. In: DGMK conference “creating value from light olefins—production and conversion”. Hamburg: German Society for Petroleum and Coal Science and Technology, 2001.
- [91] Patel M. Cumulative energy demand and cumulative CO<sub>2</sub> emissions for products of the organic chemical industry. Energy 2003;28(7): 721–40.
- [92] Energetics. Energy and environmental profile of the US chemical industry. Columbia, MD: Energetics Inc. and the Office of Industrial Technology at the US Department of Energy; 2000.
- [93] US Patent Office. Two-stage quench tower for use with oxygenate conversion process (US Patent 6,459,009). UOP LLC, US Patent Office, 2002.
- [94] Neelis M, Patel M, Gielen D, Blok K. Modelling CO<sub>2</sub> emissions from non-energy use with the non-energy use emission accounting tables (NEAT) model. Resour Conservat Recycl 2005;45(3):226–50.
- [95] Energy Information Administration (EIA). International Energy Price Information. Washington, DC: Energy Information Administration at the US Department of Energy, 2007. See also <http://www.eia.doe.gov/emeu/international/prices.html>.
- [96] Energy Information Administration (EIA). Annual Energy Outlook 2006 with Projections to 2030 (Report number: DOE/EIA-0383). Washington, DC: Energy Information Administration at the US Department of Energy, 2006.
- [97] Department of Energy (DOE). Prices of natural gas for power generation in selected countries. Washington, DC: US Department of Energy, 2006. See also: <http://www.eia.doe.gov/emeu/international/ngasprie.html>.
- [98] Department of Energy (DOE). Prices of natural gas for power generation in selected countries. Washington, DC: US Department of Energy, 2000. See also: <http://www.eia.doe.gov/emeu/international/ngasprie.html>.
- [99] Intergovernmental Panel on Climate Change (IPCC). IPCC Special Report on Carbon Dioxide Capture and Storage. Geneva, Switzerland: Intergovernmental Panel on Climate Change (IPCC), 2005.