



Research
Smart Process Manufacturing—Perspective

New Trends in Olefin Production

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ABSTRACT

Most olefins (e.g., ethylene and propylene) will continue to be produced through steam cracking (SC) of hydrocarbons in the coming decade. In an uncertain commodity market, the chemical industry is investing very little in alternative technologies and feedstocks because of their current lack of economic viability, despite decreasing crude oil reserves and the recognition of global warming. In this perspective, some of the most promising alternatives are compared with the conventional SC process, and the major bottlenecks of each of the competing processes are highlighted. These technologies emerge especially from the abundance of cheap propane, ethane, and methane from shale gas and stranded gas. From an economic point of view, methane is an interesting starting material, if chemicals can be produced from it. The huge availability of crude oil and the expected substantial decline in the demand for fuels imply that the future for proven technologies such as Fischer-Tropsch synthesis (FTS) or methanol to gasoline is not bright. The abundance of cheap ethane and the large availability of crude oil, on the other hand, have caused the SC industry to shift to these two extremes, making room for the on-purpose production of light olefins, such as by the catalytic dehydrogenation of propane.

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1. Introduction

Olefins are considered to be key components of the chemical industry. Ethylene and propylene are the most important olefins, with an annual production of roughly 1.5×10^8 t and 8×10^7 t, respectively [1]. These production rates are expected to increase as a result of an increasing global population combined with rising living standards [2]. Light olefins are the mainstay of modern life, as many different derivatives used in our daily lives are produced from these building blocks. Traditionally, olefin production depends mainly on natural gas processing products or crude oil fractions. The current leading technology for olefin production is steam cracking (SC). In this process, hydrocarbons that primarily originate from fossil resources are cracked at elevated temperatures in tubular reactors suspended in a gas-fired furnace. In recent decades, this process has been highly optimized and its capacities have been increased, resulting in a well-established technology whose economics can hardly be challenged. Declining crude oil reserves and increasing social awareness

of the human impact on the environment have had very little impact on the petrochemical industry. Investments in alternative processes and feedstocks are still to come; the lack of economic viability of such processes in an uncertain commodity market threatens their large-scale implementation. However, some exceptional cases have showed economic viability as a result of limited supply, or have benefited from favorable policies. A continuing search for alternative—and preferably also more sustainable—processes and feedstocks will eventually be required in order to fulfill the future demand for commodity chemicals. Potential alternative feedstocks are coal, natural gas, biomass, waste streams, and their derivatives.

Thanks to technological advancements and refinements in fracking, the methane supply has increased enormously since 2008 and the price of methane has dropped significantly [3,4]. This makes shale gas a game changer and an interesting cost-competitive feedstock. The large availability of shale gas has reinforced the interest in routes for valorizing methane in the form of olefins and higher hydrocarbons, either directly or indirectly. These methane-conversion

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processes could be an excellent way to valorize large amounts of methane from stranded gas rather than from shale gas. Although the growth of shale gas has triggered increasing research into methane-upgrading processes, methane from shale gas is relatively expensive due to stringent specifications on maximum ethane content. This has caused the price of ethane to drop significantly, falling even below its calorific value. The abundance of cheap ethane created by shale gas exploitation has enabled cheap low-olefin production via SC and has had a profound impact on the local US olefin market [5–7]. Many newly built crackers are ethane based, and many existing liquid crackers are retrofitted to lighter gaseous feeds, as such feeds offer an economic advantage when accessible. New ethane steam crackers are expected to come online soon and to add 1×10^7 t of ethylene capacity by 2020 in the United States. Globally, ethylene producers will experience a substantial capacity expansion in the next five years, with an annual increase from 1.76×10^8 t to 2.18×10^8 t and with investments of nearly \$45 billion USD in upcoming projects. These large investments suggest that SC of hydrocarbons will remain the main pathway in the production of light olefins. Ethane cracking is highly selective toward ethylene; hence, few or no other olefins are coproduced. Therefore, the shift toward lighter feedstocks has resulted in increasing interest in developing on-purpose production routes toward propylene and higher olefins [5,8].

On the other hand, direct SC of crude oil is also gaining importance. Using this process, petrochemical producers can skip the refining step and thus reduce their production cost [9]. In 2014, Exxon-Mobil commissioned a world-scale facility in Singapore—the first of its kind—that produces 1×10^6 t·a⁻¹ of ethylene directly from crude oil. An announcement was also made regarding a joint venture by Sabic and Saudi Aramco [9]. The use of coal as feedstock for chemicals or fuels is discouraged from an environmental point of view. The conversion of coal typically has very low carbon efficiencies and hence results in huge emissions of carbon dioxide (CO₂). Furthermore, the enormous scale of the current production and conversion facilities suggest that, in the near future, renewables and waste streams will be used to complement rather than to completely replace fossil resources. However, the need for cleaner air and water and for environmental protection will eventually lead to the exploration of sustainable production possibilities, accelerated and activated by political decisions. Researchers and engineers are expending considerable efforts to explore and optimize these alternative production possibilities, in an attempt to increase both efficiency and profitability. Nevertheless, still more effort is absolutely necessary in order to take full advantage of sustainable or alternative feedstocks and technologies. Reliable fundamental multi-scale models need to be developed and enhanced in order to explore unprecedented levels of efficiency, increase process maturity, and address major bottlenecks. In this respect, fast implementation at a lower risk can be made possible. Aside from obtaining a fundamental understanding of the new processes, the end-goal of these efforts is to face the fact that environmental resources are limited and to secure future needs in terms of energy and chemicals. However, the use of fossil feedstocks as a fuel or for the production of chemicals will remain dominant in the near future. This contribution focuses on promising olefin-production technologies that are most likely to challenge the current leading technology. Each of these alternative olefin-production pathways benefits from the abundance of propane, ethane, and methane that is available from shale gas and stranded gas. Furthermore, the relevance of each pathway could be enlarged, as the shift toward lighter feedstock utilization in the SC of hydrocarbons results in the decreased production of important co-products. Pathways that adopt renewables or waste streams [10–13] will not be addressed in this perspective because they are believed to have rather low significance for the total quantity of olefins produced in the near future. The following technologies are of

interest: the catalytic dehydrogenation of light alkanes, the oxidative coupling of methane (OCM), and syngas-based routes such as the Fischer-Tropsch synthesis (FTS) and methanol synthesis followed by methanol to olefins (MTO).

2. Steam cracking

Ethylene and propylene production will continue to proceed mainly by the SC of hydrocarbons. The SC of hydrocarbons is both one of the most important and one of the most energy-intensive processes in the petrochemical industry. It is the leading technology for light olefin production, and is a well-established technology. In this process, a hydrocarbon feedstock is mixed with steam and cracked at elevated temperatures in a tubular reactor. In order to attain these elevated temperatures, and hence initiate the thermochemical conversion, the reactors are suspended in a gas-fired furnace. The feedstock ranges from light alkanes such as ethane and propane to complex mixtures such as naphthas and gas oils [14]. Since the first commercial steam cracker, the capacity of this process has grown; up to 1.5×10^6 t of ethylene is now produced by this process annually, taking full advantage of the economy of scale [1]. A steam cracker unit can be roughly divided into two distinct parts—namely, a hot and a cold section. In the latter, the reactor effluent is separated into different products, usually at high purity as required for polymer production. Ethane crackers have a less-intensive separation train than liquid crackers, and hence a lower capital investment cost. The choice of the feedstock is mainly based on availability and profitability. An ethane cracker is preferred when the feedstock is available in sufficient amounts; otherwise, a liquid cracker is more beneficial, as the transportation of gases is relatively costly. The global steam cracker portfolio is dominated by naphtha crackers. As a result of shale gas developments in the United States, ethane cracking has become more attractive due to its low cost [15]. The abundance of ethane has widened the ethane cracking margins [16]. Therefore, there is a strong push to minimize liquid feedstocks and, preferably, even to fully replace them with ethane. There is a high abundance of ethane in shale gas, and more ethane is produced than US ethane crackers can consume. This excess opens the doors for ethane export, as many ethylene producers outside of the United States want to take advantage of the low ethane price. The margins are large enough that even shipping ethane and converting it to ethylene becomes profitable [17]. Pipelines and export terminals are ready for the future export of ethane, as depicted in Fig. 1 [18]. Projections estimate that 8×10^6 t of ethane will be exported by 2022. Ethylene producers located mainly in India, Brazil, Canada, and several European countries will import ethane to feed their crackers. To date, no shipment to China has been confirmed. Olefin production in China still mainly depends on naphtha cracking; hence, shifting toward ethane could increase China's competitiveness. China is undergoing two significant developments that are driven by a fast-growing dependence on imported oil: coal-based chemical production and propane dehydrogenation (PDH). These developments affect not only the domestic Chinese chemical market but the global market as well. By 2018, ethylene and propylene capacity from coal to olefins (CTO), MTO, and PDH plants will account for nearly 40% of the country's olefin capacity [19]. However naphtha crackers will produce the largest fraction of the total ethylene production capacity. Increasing ethane cracking has led to a decline in the production volumes of some co-products such as propylene, as shown in Fig. 2 [20]. Liquid crackers have the opportunity to diversify these kinds of by-products and hence sustain their margins [16]. In addition, revamping SC facilities from liquid to ethane cracking is not always straightforward. Steam crackers are not standalone units but are highly integrated with downstream production units and the downstream demand for a range of cracker products. Furthermore,

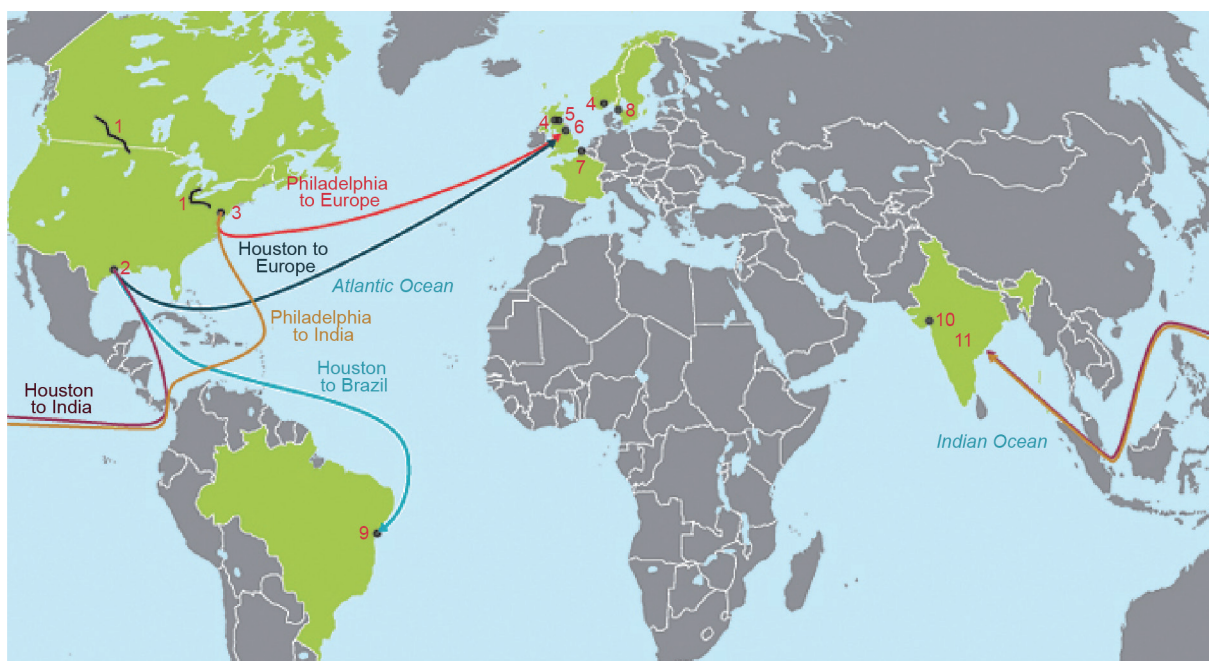


Fig. 1. Pipelines and shipping routes for the export of ethane to ethylene-producing facilities outside of the United States [18].

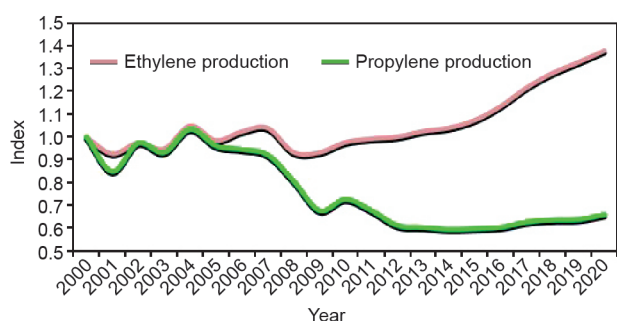


Fig. 2. North America's olefin production from steam crackers [20]. Index 1.0 = North America's olefin production from steam crackers in 2010.

the separation trains for liquid and gaseous feedstocks differ considerably. Completely switching the feed will lead to a different reactor effluent, whose effect will put pressure on different downstream units such as, for example, the methane refrigerant cycle, the performances of the columns, and the cracked gas compressor. Hence, the opportunity to take advantage of the low ethane price will be highly dependent on the downstream offtake and logistics of the plant. On the other hand, the large availability of crude oil has increased the interest in using it directly as feedstock for the production of chemicals. This interest has led to the first world-scale facility that feeds crude oil into a steam cracker, with a production capacity of 1×10^6 t of ethylene. The driving force is production cost savings. In this way, the refinery costs are omitted and the cost savings have been estimated to be as high as $\$200 \text{ USD} \cdot \text{t}^{-1}$ of ethylene [9]. The steam cracker includes a flash pot between the convective and radiant sections of the furnaces [9]. This modification allows the removal of the heavier component, prior to sending it to the radiant coils.

3. Alternative feedstocks

Since the discovery and exploitation of big oil fields, the world has been supplied with cheap crude-oil-based fuels and chemicals. Crude oil is a fossil fuel and hence, by definition, is limited. Crude oil reserves will eventually be depleted, or their exploitation will

become too costly. This opens doors for the use of alternative and cost-competitive feedstocks for the production of olefins. Since all feedstocks are limited, it is necessary to consider their best use and hence aim at the highest efficiencies. In addition, our common challenge to cut carbon emissions is an equally important criterion. CO_2 emission leads to global warming, and more effort must be made to reduce emissions and mitigate the adverse effects of climate change. In this respect, biomass and waste streams are believed to be important for future use in the production of chemicals. Biomass is a carbon-rich material that is mainly generated by photosynthesis, and is widely available at a relatively low cost. In contrast to fossil feedstocks, biomass can be considered to be virtually inexhaustible since it can be supplemented within a reasonable timescale. During photosynthesis, CO_2 is captured from the atmosphere; hence, if collection and processing is done in a sustainable manner, the use of this CO_2 will virtually not contribute to the increasing amounts of CO_2 in the atmosphere. Furthermore, waste streams such as plastic solid waste or municipal waste need to be better managed in order to protect scarce environmental resources and prevent pollution. The amount of waste will grow as a result of the increasing global population and higher living standards; hence, waste is a potential feedstock to be used [10,11]. Energy recovery for the production of heat and energy is the current focus, although chemical recycling is gaining momentum [10,11,21,22]. These feedstocks are of great benefit to the environment. Nevertheless, the enormous scale of current olefin-production facilities and the availability of biomass resources suggest that, in the near future, renewables will be used to complement rather than to completely replace fossil resources. Furthermore, the commercialization of technologies that convert these streams is limited by their poor economic viability. In addition, a large number of projects that primarily use classical SC are coming online in the coming decade, and will probably put a halt to the importance of biomass or waste streams for the production of olefins. Therefore, inexpensive fossil feedstocks such as coal, natural gas, and shale condensates remain an important source of energy and chemicals, and will remain dominant in the petrochemical industry. Thanks to technological advancements, shale gas has become a promising resource, causing its exploitation to increase exponentially since 2008 [3]. Also, cheap methane from stranded gas reserves will

have an important role in the future. From an economic point of view, methane is an interesting starting material for the production of chemicals.

4. Alternative technologies

The abundance of cheap propane, ethane, and methane from shale gas and stranded gas will facilitate cost-competitive paths in the production of light olefins (Fig. 3). In particular, the on-purpose production of propylene has grown as more and more steam crackers shift from naphtha feed to lighter shale condensates. This is especially true in the United States, where shale gas exploitation has grown exponentially [5,6], amplifying the issue of supply due to the strong growth in propylene demand compared with that of ethylene. Steam cracker units cannot fill this gap due to the low propylene/ethylene ratio. In this respect, other production routes could be profiled as an interesting alternative to overcome this issue. Furthermore, technologies emerging from the possibility of valorizing methane into higher hydrocarbons or chemicals are promising, especially due to low methane prices and huge methane availability [23]. However, high capital costs, low efficiencies, and low reliability of complex process sequences make commercialization very challenging and risky. In addition, some of these promising technologies still have room for improvement. To be industrially relevant, these technologies should be economically comparable to current steam cracker units and production capacities.

5. Methanol to olefins

MTO is one of the technologies that can produce basic petrochemicals. Methanol is produced mainly catalytically via syngas, which is a valuable gas mixture of hydrogen and carbon monoxide [24,25]. Methanol is used in large volumes for the production of a wide variety of commodity chemicals [24]. Syngas can be obtained from different carbonaceous resources through the gasification of natural gas, coal, or biomass. Hence, this process presents a suitable alternative in order to produce base chemicals from resources other than crude oil. However, the lowest production costs of syngas and the highest carbon efficiencies are based on methane [26]. Biomass and coal yield hydrogen-deficient syngas, introducing the need for a water gas shift facility, which has a negative impact on the overall carbon efficiency and produces immense carbon emissions. MTO was introduced in the late 1970s by ExxonMobil scientists [27] and was later patented by different companies: ExxonMobil and UOP/Hydro [28]. The process itself converts methanol to hydrocarbons over a zeolite containing active acid sites. In the MTO process of Exxon-

Mobil, zeolite socony mobil (ZSM)-5 is used as a catalyst; in contrast, in the UOP/Hydro process, silico-alumino phosphate (SAPO)-34 is used. Research has been performed on this process since its discovery, leading to significant progress in our understanding of the reaction and of catalyst design; this progress has led to significant improvement in process performance. By taking advantage of shape selectivity and the lower acidity of the SAPO-34 catalyst, a 75%–80% carbon selectivity toward ethylene and propylene has been reported [29]. In addition, the process conditions can be altered to favor propylene formation. The ethylene-to-propylene ratio can be varied between 0.5 and 1.5 [29]. Furthermore, by integrating MTO with the olefin-cracking process that is based on a technology developed and demonstrated by Total Petrochemicals and UOP, the light olefin yield can be increased and a higher flexibility to anticipate on the olefin market can be offered [29]. The MTO technology has been well developed and demonstrated in China, which has led to the successful construction and commissioning of the world's first CTO plant [30]. China's CTO production capacities have grown from $1.1 \times 10^6 \text{ t}\cdot\text{a}^{-1}$ in 2010 to the current rate of $1.55 \times 10^7 \text{ t}\cdot\text{a}^{-1}$, mainly due to favorable government policies. CTO requires high capital investment due to its complexity. Furthermore, the hydrogen deficiency of the syngas results in very low carbon efficiency and high water consumption. The CO_2 emissions of these plants are estimated to be between 6 t and 10 t per produced ton of olefin, compared with 1 t for the SC of hydrocarbons. When efforts toward reducing CO_2 emissions are performed globally, the trend of the large-scale development of coal-based olefin production under favorable governmental policies is highly questionable.

In order to improve the MTO process, some efforts are still required to face the main challenge of the process—namely, the rapid deactivation of the catalyst. The use of zeolites in catalytic reactions often includes side reactions leading toward coke deposits. This is known to be the major cause of deactivation, affecting both activity and selectivity [25,30,31]. A more fundamental understanding of the formation of these carbonaceous deposits and the reaction mechanism is a basis for improving the process, and much research effort has been focused on improving the stability of the catalyst [31].

6. Fischer-Tropsch synthesis

FTS is another technology that converts syngas into basic petrochemicals and mainly fuel-range hydrocarbons. Like MTO, it offers the possibility of market diversification to remote natural gas resource holders. Syngas is catalytically converted into a broad range of products that mainly consists of linear alkanes, 1-alkenes, and a small amount of oxygenates (alcohols, ketones, and aldehydes) [26,32].

Iron (Fe)- and cobalt (Co)-based catalysts are mainly used as the industrially relevant catalysts. In the mid-1920s, Franz Fischer and Hans Tropsch reported the catalytic formation of higher hydrocarbons and other organic compounds from syngas mixtures on a nickel (Ni) and Co catalyst [33]. The process itself has been shown to be a satisfying alternative for the production of fuels in regions where crude oil is scarce while other carbonaceous sources are abundant. Today, FTS is industrially operated in only a few countries. Sasol operates four plants in South Africa, and Shell has one operational plant in Malaysia. Two plants are operational in Qatar: One, the Oryx GTL (gas to liquids), is a joint venture between Qatar Petroleum and Sasol, while the other, the Pearl GTL, is a joint venture between Qatar Petroleum and Shell. The latter is the largest FTS plant in the world, with a capacity of 140 000 barrels per day and a total investment cost of \$18 billion USD—which was a much higher cost than initially estimated [34]. This emphasizes the rather high investment cost of the technology and project cost risks [34]. In addition, the viability of the FTS process is highly dependent on both oil and gas

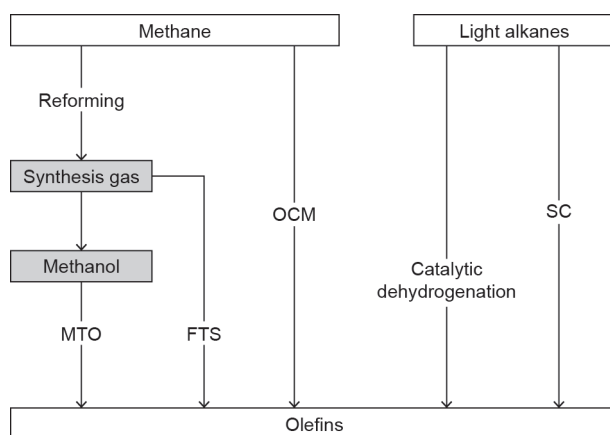


Fig. 3. Different technologies of interest for the production of light olefins from methane and light alkanes.

price fluctuations. FTS is clearly a mature technology and is typically operated at two distinct operational modes, as described by Dry [35]: the low-temperature and the high-temperature mode. The product spectrum depends mostly on the temperature mode. At a low temperature, the product distribution is shifted toward high-molecular linear waxes; at a higher temperature, the average molecular weight is less and larger amounts of 1-alkenes are formed, which is of interest for the production of light olefins. For the lower temperature mode, a supported Co-catalyst is more suitable, as it has higher activity [35,36]. The main design specification for a Fischer-Tropsch (FT) reactor is heat removal, as the occurring reaction is highly exothermic. Four reactor technologies have been designed and commercially used: the circulating fluidized-bed (CFB) reactor, the fixed-fluidized-bed (FFB) reactor, the multi-tubular fixed-bed reactor, and the slurry phase reactor [24]. Process intensification has led to the Sasol advanced synthol-FFB reactors, which replaced the older CFB reactor configuration. The reaction section is bigger and has a higher heat-removal capacity; in addition, lower pressure drops and higher throughputs are possible without affecting the isothermal operation of the reactor. This reactor technology is used for high-temperature FTS. The most advanced reactor design is the slurry bed. This reactor is designed to operate at low temperatures, which increases the selectivity to longer hydrocarbons and suppresses high methane yields [26,35,37]. Although the FT technology has been around since its discovery, it is still a challenge to improve selectivity [38,39]. The selectivity is rather low and the product spectra cover a broad carbon range, as described by the Anderson-Schulz-Flory distribution [33,35]. As a result, further upstream processing and refining are essential. For process improvement, a better fundamental understanding is required in order to improve the catalyst design and, in particular, to increase the poor resistance to sulfur poisoning.

7. Oxidative coupling of methane

A strong economic interest exists in developing processes that allow methane conversion into more valuable products [40,41]. The above technologies (MTO and FTS) can be used to convert methane to higher hydrocarbons, but only in an indirect way; that is, they require the production of syngas as a first step. This initial step to produce syngas represents an inherent inefficiency. On the other hand, the direct activation of methane and its conversion into other useful products remain one of the most challenging topics facing the catalysis community today [42].

In this regard, the OCM is one of the most promising direct routes to convert methane into ethylene and higher hydrocarbons. Ever since the pioneering work of Keller and Bhasin [43], OCM has attracted both industrial and academic interest. Although the benefits of OCM have been known for over 30 years, the issue of finding a viable catalyst with the necessary performance for the commercialization of the process is still crucial among researchers [44]. Furthermore, the low yields of ethylene and the strong exothermicity of this reaction need to be addressed in an appropriate reactor technology before OCM can be used as an alternative to SC for the production of ethylene and higher olefins [45,46]. The main challenges for OCM to be economically successful are hence twofold, with catalyst development on the one hand and a novel reactor design on the other [23,47].

In earlier research, the selectivity and catalyst stability at elevated temperatures were considered to be the most attractive features of a potential OCM catalyst. Considerable literature can be found on OCM catalysts that are based on La_2O_3 doped with alkaline earth metals (Sr, Mg, and Ca) [48–50], on Li/MgO [51–54], and on a catalyst generally represented by $\text{Mn}/\text{Na}_2\text{WO}_4/\text{SiO}_2$ [55–57]. Recently, however, the research focus shifted to OCM catalysts that enable low-temperature performance. It was found that not only does the

metal composition have an influence on catalyst activity, but the particle size and morphology do as well [23,58–60]. Specifically, by using nanostructured catalysts (nanofibers, nanowire, and nanorods), methane can be activated at lower temperatures and a better OCM performance can be obtained compared with the powder-form catalysts. The development of nanostructured catalysts has played a major role in the evolution of the OCM technology. Siluria Technologies, Inc. (Siluria for short) [61] recently announced the first commercial OCM process, in which a series of so-called “nanowire catalysts” are reported to operate at process temperatures below 600 °C. Although Siluria’s patent application reveals that the single-pass C_2 yield does not meet the target of 25%, the catalysts are durable over long periods of operation at low process temperatures [62].

At the moment, catalytic packed-bed reactors constitute the majority of all laboratory-scale OCM reactors; these are also used in Siluria’s demonstration plant [47]. Because of the high exothermicity of the OCM reaction, thermal control of the reactor is an important issue. Most laboratory-scale experimental setups use small-diameter tubes and run with very dilute mixtures and low methane conversions [63–65]. Of course, this is not practical for an actual large-scale process. According to a recent review on process intensification for natural gas conversion [23], thermal control in OCM reactors may follow three approaches. Microchannel reactors, membrane reactors, and staged reactors are listed as possible options, while combinations of these are possible in more innovative designs. Different authors [45,46,66,67] designated the fluidized-bed reactor as the best reactor concept for OCM. This is mainly because the beneficial heat-transfer characteristics in fluidized-bed reactors cannot be achieved in any type of packed-bed reactor.

Based on the abovementioned considerations, it is clear that some effort is still required before OCM can be considered as an alternative to SC for the production of ethylene and other olefins. Although the door toward successful commercialization has already been opened by Siluria, further investigation to enhance ethylene yields is still necessary. Catalyst design and the development of novel reactor technologies are important to this purpose.

8. Catalytic dehydrogenation of light alkanes

The shift from naphtha toward light feeds that are derived from tight oil, for the production of ethylene in steam crackers, has impacted the global propylene and crude C_4 production capacity. Therefore, routes for the on-purpose production of light olefins have received considerable interest [5]. Catalytic dehydrogenation provides the possibility of high selectivity to a single olefin product—much higher than can be expected from SC alone. Given the relatively high abundance of cheap light alkanes from shale gas, this option is worth considering [68]. The amount of propylene produced by dehydrogenation was 5×10^6 t in 2014 and is expected to increase, as it has been announced that a dozen new PDH plants are to be built worldwide [4,5]. The profitability of this process is emphasized by the rather low prices of propane, compared with those of propylene. Two patented industrial processes for the dehydrogenation of alkanes are currently in commercial use—namely, the Oleflex (UOP) and the Catofin (Lummus) technologies. Both technologies use an alumina-supported catalyst: $\text{Pt-Sn}/\text{Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ for Oleflex and Catofin, respectively. The occurring reaction is highly endothermic and equilibrium-limited, so high temperatures and low pressures are favored. These high temperatures hamper high selectivity and favor side reactions such as coke deposition, introducing the need for a regeneration step; however, this step is not fully reversible at this point, thus affecting the activity of the catalyst [4]. The catalysts and technologies are available and the process can run continuously for several years [4]. Although the process has been successfully commercialized, there is room for improvement. Further

advances with respect to catalyst design, such as lower noble metal loading and increased stability, are essential. Further improvements are still possible by increasing the energy efficiency of the hydrogenation process and overcoming the biggest drawback—namely, the limited equilibrium conversion and the occurrence of side reactions at relatively high temperature. It is notable that the reaction equilibrium could be shifted toward the product. Different strategies are already applied in industry, such as lowering the partial pressure or the selective *in situ* combustion of hydrogen. The latter is of great interest, as the combustion heat promotes the dehydrogenation step. A third strategy is to remove hydrogen from the reacting system by using membranes; nevertheless, thermal stability remains an issue [4].

9. CO₂ emissions

Novel technologies for olefin production need to be viable from an environmental perspective as well as from a technical one. In this regard, it is important to evaluate the CO₂ emissions associated with the different technologies discussed above. Fig. 4 [69] shows the total CO₂ emissions per ton of high-value chemicals (HVC) such as ethylene, propylene, and aromatics. These data were taken partly from a recent review by Ren et al. [69] and partly from various figures published by the International Energy Agency (IEA). A distinction is made between the CO₂ emission resulting from the energy requirement of the process (i.e., fuel combustion) and the chemical CO₂ that is produced in the reaction. It is clear from the figure that SC is still the best-performing technology, even in terms of CO₂ emissions. The process produces almost no chemical CO₂, and the energy efficiency of the process has been optimized in such a way that the energy CO₂ is very low in comparison with those of the other techniques. OCM looks very promising as well, as it has the lowest energy CO₂. However, because of the relatively low ethylene selectivity, the chemical CO₂ for this technology is still quite high. As expected, the coal-based techniques are major producers of CO₂, both energetically and chemically.

Carbon capture and storage or utilization techniques are a promising way to further cut the carbon emissions from light-olefin production technologies. Ethylene producers, which are considered to be large industrial emitters, will have to deal with the requirement (activated by political decisions) to reduce CO₂ emissions in the near future. These techniques are currently under rapid development; they are becoming promising methods to reduce carbon emissions, and are therefore a crucial aspect in meeting CO₂ emission-

reduction targets [70,71]. In this context, it is important to distinguish between chemical-related and energy-related (process-related) emissions, in that the latter is inherent to the nature of the process. The use of coal as feedstock comes with high chemical carbon emissions. This CO₂ stream is already separated; therefore, it could be further prepared for storage or utilization. However, this processing step comes at a higher cost and energy efficiency penalty, because the CO₂ needs to be compressed and maintained within the supercritical envelope for storage [71]. On the other hand, energy-related emissions are the result of the fuel-combustion process for heat or power generation. Hence, the applicability of these carbon capture techniques is highly dependent on the process layout. In the particular case of SC furnaces, two different carbon capture techniques are of interest—namely, oxyfuel combustion and the post-combustion process, both because of the high firing duty in the furnace [72]. The latter can be seen as an add-on solution, with low changes to the cracking furnace itself, and thus a lower associated implementation cost. However, the low CO₂ concentration in the flue gas leads to a high load to the processing unit. Oxyfuel combustion is based on separating oxygen from the air, leading to a more concentrated CO₂ stream, and resulting in less-intensive post-processing steps. In addition, higher thermal efficiency in the radiant section can be expected and there is no emission of thermal NO_x. A challenge remains regarding the cost of separating oxygen from air. According to Weikl and Schmidt [72], a penalty on CO₂ emission of \$85 USD·t⁻¹ would be necessary in order to arrive at a break-even point for the application of this carbon capture technique. Such a penalty would result in a higher ethylene production cost, estimated at roughly \$130 USD·t⁻¹ of ethylene [72].

10. Conclusions

This perspective discussed some of the most promising alternative technologies and feedstocks for olefin production. Alternative feedstocks mainly arise from the abundance of cheap propane, ethane, and methane from shale gas and stranded gas. Although biomass and waste streams were also mentioned here, they are believed to be useful as a complement to rather than a complete replacement for fossil resources in the near future. Coal, natural gas, shale condensates, and crude oil will remain dominant in the petrochemical industry. However, the use of coal as feedstock for chemicals is rather questionable from an environmental point of view, as it has very low carbon efficiencies and hence huge CO₂ emissions. Therefore, recent developments of coal as feedstock for the production

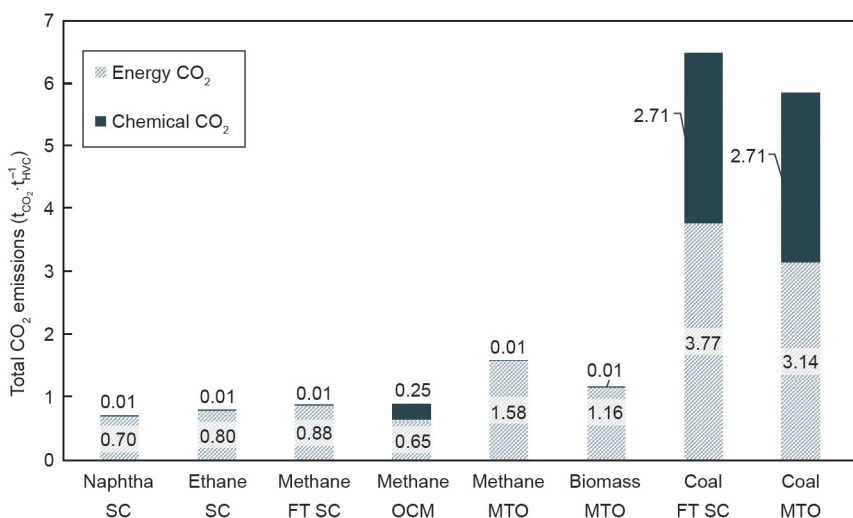


Fig. 4. Total CO₂ emissions per ton of high-value chemicals (tCO₂-t_{HVC}⁻¹) for different technologies [69].

of chemicals are debatable. As a response to low ethane prices and large ethane availability, the SC feedstock portfolio is making a shift to ethane feedstocks. Shipping and transport via pipes of ethane has become advantageous and allows ethylene producers outside of the United States to take advantage of the local low ethane prices. On the other hand, the large availability of crude oil has caused ethylene producers to shift toward this extreme as well. ExxonMobil was the first to commission a large-scale plant that uses crude oil to produce olefins.

Recent investments and the huge capital in current production facilities suggest that SC of hydrocarbons will remain the leading technology for the production of ethylene. The large number of projects coming online will lead to a substantial capacity expansion for ethylene producers. As a result, biomass and waste stream conversion technologies will have to become even more competitive than before, or else their focus should be on olefin complexes. Nevertheless, it will eventually be necessary to deploy biomass and waste streams, although this shift will need to be pushed by world governmental regulatory bodies, because the contribution of these streams in the coming lustrum will remain marginal. Drop-in feedstocks for the current generation of steam crackers would be a first step. However, the change in the global steam cracker portfolio—that is, the significant lighter feedstocks—creates the need to develop routes for the on-purpose production of propylene and other light olefins. The catalytic dehydrogenation of light alkanes is a well-established process that accomplishes this goal. The main improvements that are possible here are related to energy efficiency and catalyst deactivation.

Furthermore, the abundance of methane has caused an increased interest in developing processes to valorize methane to higher hydrocarbons or chemicals. Several of these processes were identified as potential alternatives for the SC process: FTS, MTO, and OCM. Both the FTS and the MTO processes are proven technologies, with some plants already operational worldwide. Despite the maturity of these technologies, both are inherently inefficient due to the syngas production step. In addition, FTS is not selective enough to solely produce light olefins, and produces a considerable amount of fuel-range hydrocarbons. However, improvements to these processes are still possible, especially with regard to catalyst design. For OCM, major efforts are still required before it can be considered as an alternative to SC. Catalyst design and the development of a reactor technology that is able to deal with the strong exothermicity of this reaction are mandatory.

In the near future, SC will still be the predominant process for the production of olefins, albeit with a mainly lighter feedstock. The alternative technologies discussed in this perspective are promising, provided that the bottlenecks in their process efficiency and CO₂ footprint are resolved.

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Compliance with ethics guidelines

Ismaël Amghizar, Laurien A. Vandewalle, Kevin M. Van Geem, and Guy B. Marin declare that they have no conflict of interest or financial conflicts to disclose.

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