Annual Review of Chemical and Biomolecular Engineering

Shale Gas Implications for C_2-C_3 Olefin Production: Incumbent and Future Technology

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Annu. Rev. Chem. Biomol. Eng. 2018. 9:341–64

First published as a Review in Advance on March 29, 2018

The *Annual Review of Chemical and Biomolecular Engineering* is online at chembioeng.annualreviews.org

https://doi.org/10.1146/annurev-chembioeng-060817-084345

Keywords

shale gas, ethylene, propylene, economics, steam cracking, dehydrogenation

Abstract

Substantial natural gas liquids recovery from tight shale formations has produced a significant boon for the US chemical industry. As fracking technology improves, shale liquids may represent the same for other geographies. As with any major industry disruption, the advent of shale resources permits both the chemical industry and the community an excellent opportunity to have open, foundational discussions on how both public and private institutions should research, develop, and utilize these resources most sustainably. This review summarizes current chemical industry processes that use ethane and propane from shale gas liquids to produce the two primary chemical olefins of the industry: ethylene and propylene. It also discusses simplified techno-economics related to olefins production from an industry perspective, attempting to provide a mutually beneficial context in which to discuss the next generation of sustainable olefin process development.

INTRODUCTION

The US shale gas revolution, which is now approximately 10 years old, has already had a profound impact on the US energy and chemical sectors. The US chemical industry had seen a slow demise from the late 1990s to the turn of the last decade as rising US natural gas and oil prices, driven in part by decreased supply, adversely affected the competitiveness of US plants to produce basic olefins (ethylene and propylene) and downstream derivatives (1). The choice of feedstock for chemical production is highly regional, and local raw material feedstock [natural gas liquids (NGLs) versus naphtha] economics significantly influence geographical competitiveness (2). The introduction of this US "Golden Age of Natural Gas" has meant a complete turnaround for the US chemical sector, and as of March 2017, 294 capital projects cumulatively valued at $179 billion are either completed or under construction, with a projected direct, indirect, and payroll-induced impact to the US economy totaling about 820,000 jobs and $234 billion (3). The US chemical industry is undergoing a change inconceivable just 15 years ago, and massive-scale steam ethane cracking with subsequent derivatives production is now contemplated in areas even outside of the US Gulf Coast (USGC) related to the Marcellus (4) or Bakken (5) shale formations. Methanol, made from US natural gas, with export to the Far East for olefins production has been speculated for the Pacific Northwest (6). Although not all of these projects may reach fruition, even these announcements are a remarkable reversal of media coverage (7).

Hydrocarbon resources, after refinement, can be used as fuels (energy) or transformed into chemicals. Each has a different value for society based on their needs. Increasingly, the United States is not the only region to recognize the increased value that hydrocarbon resources, shale or otherwise, gain through upgrading to chemicals and derivatives relative to their use as basic fuels and power (8). This is exemplified by an analysis of the US marketplace value of polyethylene [$41.4/one million Btu (MMBtu)] (9) versus that of the average retail gasoline ($14.2/MMBtu) and electricity ($9.5/MMBtu) prices (10). The lower value of fuels and power is due in part to the many potential options, including shale-derived hydrocarbons, from which they are sourced, but it also indicates that there is significant value to be gained for any region that monetizes its hydrocarbon resources in a manner that sustainably gains the most potential GDP value for the benefit of its people and society. With this in mind, it is useful to occasionally revisit and question the metrics that help guide the appropriate technology decisions if chemical upgrading is the intent.

A 2006 report by the National Research Council has defined sustainability as a "path forward that allows humanity to meet current environmental and human health, economic, and societal needs without compromising the progress and success of future generations." They further define sustainable processes as ones that are "economically competitive and [do] not cause harm to the environment and human health" (11, p. 2). If a society believes that environmentally safe chemical derivatives enhance quality of life by satisfying societal needs, and therefore deserve continued growth and use in all portions of the developed and developing world, as an extension to how energy generation can be viewed (12) we can suggest that sustainable organic chemical production and processes should have the maximum return on carbon (feedstock and fuel) investment at the lowest cost to make them carbon responsible but at the same time economically available to the most people. For any societal region that wishes to valorize their hydrocarbon natural resources as chemicals for economic growth, making sustainable chemical derivatives means that regional investment and long-term cost-competitiveness of billion-dollar chemical plants must be weighed against the risks of competing in a global chemical market with other players that may have different or evolving definitions of sustainability. This delicate balance has implications for new technology selection.

A critical survey of shale gas chemical investment in the United States shows that at this time the chemical industry is choosing mature, not new, chemical technologies for shale liquid upgrading to C_2 and C_3 olefins while continuing to recognize the commitment to sustainable chemicals production (11). One reason for the choice of mature technology investment is that potential new chemical technologies, and any other sustainable advantages that may be derived from those technologies, are not yet sufficient to warrant positive economic return over decades, the lifetime of chemical plants, even if there is still some recognized potential for improved carbon efficiency (13). The relative economic predictability, experience in long-term reliability, and safety record of operation for mature, tested technology are significant steadying factors for investment when billions of dollars are at stake. Although incremental improvements in carbon selectivity and energy usage, in even the most mature technologies, are necessary to drive small margin advantages in the competitive chemical derivatives space, during the current phase of chemical industry expansion the shale gas revolution is one of cheap feedstocks and not revolutionary new chemical process and unit operations.

With these thoughts in mind, this review covers the basics of the chemical industry's two primary olefin building blocks, ethylene and propylene, for which the 2014 world demand was 137 MM tonnes/year and 87 MM tonnes/year, respectively (14). It discusses why the increased supply of shale gas liquids, primarily ethane and propane as the preferred feedstocks for ethylene and propylene, respectively, have had profound effects on US chemical investment, but not necessarily through new technology. Although much of the article focuses on the situation in the United States, where the most profound shale NGL effects have been noted to date, the techno-economic conclusions are meant to be broadly applicable and certainly have been made before (15). I have chosen to not focus this review merely on a survey of mature ethylene and propylene technologies, although some background is necessary for discussion, and I refer readers to a few of the excellent available resources where they can educate themselves on these existing technologies for the conversion of ethane and propane (14, 16–23). Although methane is part of the shale gas story, its use as a chemical feedstock as a replacement for coal in methanol-to-olefins (MTO) technology in China (24), or potential oxidative coupling (**http://www.siluria.com**), is not a focus here, and the reader is referred to the most recent review of this topic by Carl Mesters (25). The author's hope is that this review stimulates productive discussion around new technology adoption requirements for current and future sustainable chemical upgrading of NGLs.

SHALE GAS AND CHEMICAL INDUSTRY FEEDSTOCKS

The shale gas revolution has been described as one not just of geology but of technology: fracking (2). Although this has had profound implications for the US chemical industry, the primary market for fracked shale hydrocarbons is the energy and fuel sectors. According to 2010 data, the US chemical industry uses approximately 19%, or 8 exajoules (eJ)/year, of the worldwide 42 eJ/year of hydrocarbon resources used in chemical production (13). However, of this 8 eJ, approximately 5 eJ ends up directly in chemical products, a 62% efficiency. A survey of US energy flow charts from Lawrence Livermore National Laboratory suggests that even in 2010, 8 eJ made up only 12% of the 65 eJ of potential feedstock natural gas and petroleum that is extracted to generate electricity, fuel, and heat for the residential, commercial, industrial, and transportation sectors (26). The transportation sector itself consumes nearly 27 eJ of petroleum. This means that 88% of the total hydrocarbon resources available in the United States end up in energy and fuel; it is this volume that drives the hydrocarbon market. **Figure 1** shows the fundamental change in US supply for hydrocarbons at the advent of the shale revolution in the late 2000s. Although one notes specifically the huge volume of associated shale oil and natural gas that is driving the fundamental economics, **Figure 1** also shows the concomitant and opportunistic rise in ethane and propane

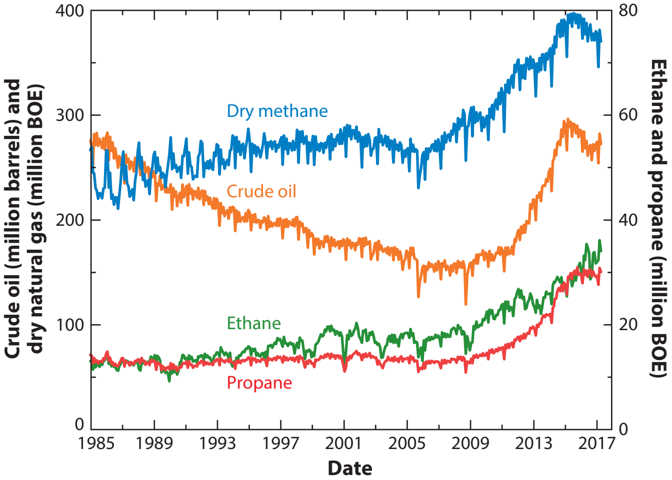

Figure 1

US production of crude oil, dry methane, and the natural gas liquids ethane and propane, since 1985, presented in equivalent barrels (BOE) of crude oil (146). One BOE is equal to 5.8 MMBtu.

supply due to the wet nature of the tight shale formations. **Figure 2** demonstrates the current relevant outcome of the US shale gas revolution for the chemical industry: Increased shale gas ethane and propane supplies have resulted in significant price decreases for these NGLs and a decoupling of their pricing from now more expensive oil derivatives (naphtha). At times in the last two years, ethane has traded at a cost below that of methane, complicating the contemplated use of methane as a chemical feedstock for olefins. The US chemical industry has once again become the recipient of shifting cheap feedstock sourcing and is moving to respond (27).

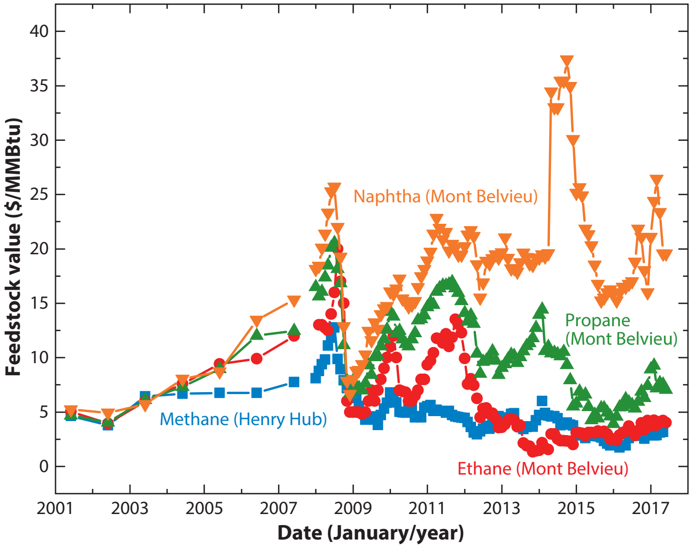

Figure 2

Dry methane (147) and olefin (148) feedstock values since 2001 for the US Gulf Coast. Data are plotted at the mid-year average until 2008 and plotted at the monthly average thereafter.

Why are cheap ethane and propane supplies important? Although the products of the chemical industry are often fungible, the feedstocks are less so (2). Many feedstocks can be used to produce ethylene and propylene, but each feedstock produces a different slate of olefins and by-products, and so each feedstock has a different value for ethylene and propylene derivative producers depending on their desired product mix. Although 50% of the world's ethylene is still derived from petroleum (naphtha) sources, those with direct access to ethane are able to increase their relative yields to ethylene for use in downstream derivatives versus those who source ethylene from naphtha (14). Access to cheap ethane is a significant advantage for predominantly polyethylene producers. On-purpose propane dehydrogenation (PDH) provides a similar advantage for propylene. Since 2012, the US chemical industry alone has committed capacity increases of 7–9 MM tonnes/year of ethylene and 2 MM tonnes/year of propylene by PDH (28). The public does not directly consume these olefins; in 2016 the largest-volume derivatives, polyethylene and polypropylene, accounted for approximately 93 and 63 MM tonnes of thermoplastic, with world average annual growth rates of 3.9% (29) and 4.6% (30), respectively.

Table 1 demonstrates the aforementioned lighter crack and dehydrogenation advantage for ethylene and propylene derivative producers by calculating the potential margin that can be obtained by using various feedstocks and processes to produce ethylene and propylene. The hypothetical product margin for olefins production starting from either ethane, propane, naphtha, or methanol is here defined as product (ethylene + propylene) price minus raw material cost. This simple analysis does not consider conversion cost, the value of by-products (which would be significant in the case of naphtha), the cost of capital recovery, or the shifting dynamics of feedstock pricing, but it does demonstrate reasons for shifting feedstock preferences.

Table 1 Prices and margins of ethylene and propylene from feedstock materials

Feedstock and process	Feedstock price[a] ($/kmol)	Ethylene unit ratio[b] (kmol/kmol)	Propylene unit ratio[b] (kmol/kmol)	Product margin[c] ($/kmol)
Steam ethane cracking[d]	5.40	1.17	100	7.80
Steam propane cracking[d]	13.60	1.52	6.36	1.84
Steam naphtha cracking [d]	34.80	1.06	3.33	(9.96)
Propane dehydrogenation[e]	13.60	–	1.14	17.8
Methanol-to-olefins[f]	9.00	2	3	5.60
	12.00	2	3	(9.40)
Ethylene/butene metathesis[g]	14.90/36.50	0.50	0.54[h]	20.00
Ethylene dimerization/ metathesis[i]	14.90	1.77	NA	9.32

[a] US Gulf Coast (USGC) feedstock pricing as of August 2017 (148). Methanol at two prices was considered: \$12.00/kmol for USGC and \$9.00/kmol in Asia. Ethylene is valued at \$14.90/kmol ethylene, whereas propylene is \$35.70/kmol propylene. Naphtha is treated as *n*-hexane for the purposes of unit ratio calculations.

[b] Ethylene or propylene unit ratio is defined as kmol feedstock per kmol ethylene or kmol propylene, respectively.

[c] Product margin is defined as the total value of ethylene and propylene produced per kmol of feedstock minus the cost of that feedstock in $/kmol.

[d] Cracking selectivities (unit ratios) are derived from Reference 14.

[e] Dehydrogenation selectivity (unit ratio) is derived from Reference 20.

[f] Here the methanol-to-olefins process calculation assumes that five methanol molecules yield a 50:50 molar selectivity for ethylene and propylene with no other mass lost. In practice, this value can be manipulated by the practitioner. Multiple feedstock prices are shown to demonstrate the sensitivity of methanol price to potential product margin.

[g] Unit ratio data derived from Reference 22.

[h] Unit ratio in kmol butenes/kmol propylene.

[i] Unit ratio derived from Reference 23.

For primarily ethylene producers, the potential product margin using ethane as feedstock to produce ethylene and propylene is greater than that of using pure propane, and it greatly exceeds that of naphtha cracking. However, often ethylene producers like some propylene, and ethane cracking leaves that producer short on propylene. Propane cracking does not result in substantially high selectivity to propylene but primarily makes ethylene (14). For this reason, some level of propane is often cracked simultaneously with ethane to supplement propylene yield for those who desire both ethylene and propylene feedstocks. Although a naphtha cracking practitioner has a greater quantity of propylene than either the ethane or propane cracker, they must also install additional capital to process the C_{4+} cracked fraction to recover value. This is indeed done (and **Table 1** makes it clear that there could be significant value for technologies, such as metathesis to convert 1,3-butadiene-depleted C_4-raffinate streams to more valuable propylene through the installation of appropriate capital). Other components of this C_{4+} stream are important in their own right as chemical feedstock (16, 17) but are increasingly in short supply as the world continues to crack lighter feedstocks (2). For those chemical producers who increasingly choose not to crack naphtha, PDH technology is the emerging choice for those in NGLs-rich regions who desire significant propylene. Potential access to cheap shale methane has prompted consideration of foreign investment to export methanol manufactured in the US Pacific Northwest to Chinese MTO plants for use in the production of ethylene and propylene. **Table 1** perhaps suggests the rationale for such considerations, that being methanol's better profit potential relative to naphtha in some geographies, and better carbon economy relative to coal, for ethylene/propylene mixes using MTO technology. It is also clear, from the two different methanol price points shown in **Table 1**, that since two methanol molecules are required for every carbon-carbon bond, the economics of MTO can be very sensitive to local methanol pricing and desired product slate. MTO practitioners also have the additional ability to tune ethylene/propylene ratios for their benefit (31–33).

Figure 3 shows that despite a continued decrease in the USGC price of ethane and propane, the product margin to ethylene and propylene remains the same, or even decreases, in the same

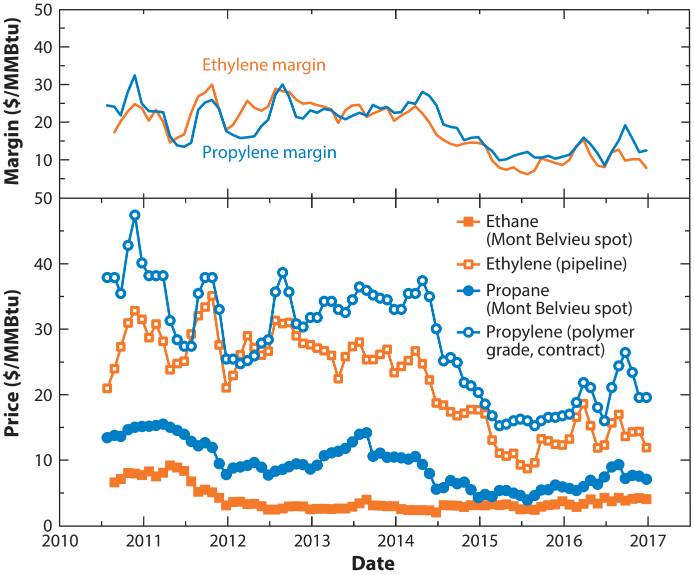

Figure 3

Pricing of ethylene and propylene (148) compared to the feedstock cost, along with the calculated product margin based on raw material cost.

time frame. There are significant economies of scale for the construction of chemical plants. In times of increased cheap feedstock supply (lower feedstock prices), manufacturers rush to take advantage, and the large incremental increases in ethylene and propylene can upset demand, resulting in downward pressure on margins. The first manufacturer to market may see the most profitable returns; this encourages rapid deployment of mature, safe technology. So despite the feedstock advantages that shale NGLs provide US chemical companies and investors, there is always significant pressure for derivatives producers to increase their economic efficiency relative to competition. But given the speed at which chemical investment takes place, this often does not encourage the deployment of new and potentially more sustainable, but also potentially risky and economically unproven, technologies. These market and investment realities have direct implications for technology selection to monetize the increasing shale gas NGL supply.

ECONOMICS OF ETHYLENE PRODUCTION TECHNOLOGY

The primary means to generate olefins from light alkanes is steam cracking. Ethylene from steam cracking (pyrolysis) technology is very mature, having been practiced for more than 60 years with continual improvements (19). Despite its maturity, to maintain competitive advantages on margin, research still occurs in areas such as process kinetic modeling for influencing product distribution (34–44), metallurgy (45–50), and additives to increase coil life and decrease coking rates (51–55). Because all cracking furnaces must have their coils decoked at some frequency, limiting downtime (56, 57) is of great value to the olefin producer when one considers that at a production rate of 1,500 kta (kilotonnes per annum) ethylene an ethylene manufacturer will lose ~$2 MM of potential revenue per day of downtime at current ethylene prices.

As previously noted, chemical producers responsible for the current increase in US construction projects have almost exclusively relied on existing, mature technology despite an extensive research history in alternative technology development. This continues to be true for even the second round of USGC investment (58). The choice of mature technology is borne out of rational economic analysis. To understand how these choices are made, it is instructive to review how the industry views the economics of new plant (greenfield) construction and how that provides limitations for new technology introduction. This is a complex and varied topic that is chemical and process dependent, but for the purpose of this review we limit analysis to ethylene technology and tackle the topics of energy use, feedstock cost, capital, and total production costs.

Energy Usage and Efficiency

It is true that ethane stream cracking is energy intensive, but often the tenor taken in publications is that energy-intensive technology is somehow not energy efficient, and that newer, less energy-intensive technology is poised to overtake ethane steam cracking in the next wave of ethylene investment. Van Goethem et al. (59) evaluated the energy efficiency of various ethane-to-ethylene conversion technologies in a 2007 paper. Using the pinch technique on black box models to evaluate simple thermodynamic energy requirements, they conclude there is no perfect thermodynamic process. However, it is evident from their comparative minimum heating and cooling requirements for the various processes that conventional (or potentially ceramic/adapted firing) furnace steam ethane cracking enjoys the least energy input of current or potential ethane-to-ethylene conversion processes. This results from the high degree of heat and energy integration both possible and practiced in ethane steam cracking. The other considered processes do not produce the right kinds of energy (energy at the right temperatures and steam pressures) amenable for use in the downstream distillation unit operations that are common to all considered ethane-to-ethylene processes. The inherent scalability of distillation has not been displaced as the sole means for

Table 2 Production normalized energy losses for olefins and other select processes (13)

Chemical process	Energy loss (eJ/year)	Productivity (kt/year)	Normalized energy loss (MJ/kt)
Propylene oxide	0.20	6,600	20.1
Ammonia (natural gas)	0.49	48,000	10.2
Methanol (natural gas)	0.20	28,000	7.2
Polyethylene	0.50	73,000	6.9
Polypropylene	0.30	49,000	6.2
Ethylene oxide	0.13	21,000	6.1
Olefins (naphtha)	0.72	123,000	5.9
Olefins (ethane)	0.34	82,000	4.1

olefin–paraffin separations, although it has been rightly deemed one of the separation challenges that if solved correctly might change the world (60). The commonality of separation schemes for the considered technology thus disadvantages the energy efficiency of alternative ethylene technology considered in van Goethem et al.'s study.

The energy efficiency of steam cracking, despite its intensity, is further confirmed by a joint International Energy Agency (IEA)/International Council of Chemical Associations/Gesellschaft für Chemische Technik und Biotechnologie (DECHEMA) technology roadmap for energy and greenhouse gas reductions in the chemical process industries (13). The 2010 energy loss estimates for several important industrial chemicals from the IEA report Annexes are recalculated as the normalized loss for a given production capacity, ignoring any selectivity losses. The result is shown in **Table 2** and again demonstrates the high-energy integration of ethane steam cracking processes, it having the lowest normalized energy loss in this subset of the largest-volume commodity organic chemicals. In fact, ammonia and methanol (both methane-derived chemicals) and propylene oxide (a chemical produced from propylene derived largely through coproduct processes or from electrons) are significantly higher in energy loss per productivity unit. In conclusion, although ethane steam cracking is energy intensive, it is nowhere near a model of energy inefficiency. Future research may yet provide energy reduction in this process, but in the absence of mandated carbon (CO_2) taxes, arguments for the implementation of new ethylene technology based solely on energy efficiency have not yet demonstrated sufficient economic potential to overcome the implementation risk.

Capital and Production Costs

Ethylene production is practiced at massive scale, and as a result it is also capital intensive. Consequently, there are huge economy-of-scale implications to be a competitive producer. With this in mind, it is instructive to review how to calculate total production cost assessments that combine our previous discussion of energy intensity with both raw material and capital costs. There are many sources to prepare one for such calculations (61, 62). **Table 3** shows a hypothetical and simplified total production cost calculation for a greenfield 1,500-kta ethane steam cracking plant based on an ethane price of \$0.10/lb and a typical value of ethylene crack selectivity (85%), including a credit for by-products (e.g., propylene). The total fixed capital for this steam cracker is about \$2.2 billion (14), and the capital cost enters the total production cost of ethylene as both straight-line depreciation of 10% per year and a desired yearly return on capital investment of 15%. Although these capital charges may vary dramatically between ethane cracking practitioners, these values are representative.

Table 3 **Hypothetical calculation of total production cost (TPC) for ethylene based on greenfield construction of a 1,500-kta ethane steam cracker**

Costs	\$/lb ethylene[a]	Percentage of TPC (%)
(*a*) Raw materials and credits		–
Ethane[b]	0.125	–
Catalysts and additives	0.007	–
Propylene and fuel credit	(0.034)	–
(*b*) Utilities	(0.025)	–
(*c*) Direct and indirect costs	0.041	–
Total cash cost (sum $a + b + c$)	0.114	41
(*d*) Depreciation (10%)	0.067	24
(*e*) Return-on-capital (15%)	0.100	35
TPC (sum total cash cost $+ d + e$)	0.281	100

[a] Data estimates for propylene and fuel credit, utilities, direct and indirect costs, and capital were estimated from Reference 14 based on a 1,500-kta ethane steam cracker excluding capital and related costs for high-purity H_2 recovery. H_2 is instead burned as fuel.

[b] The total cost of ethane needed, per pound of ethylene, is calculated from the price of ethane, \$0.10/lb, and the unit ratio, or selectivity (lb/lb), here equal to 1.25.

Table 3 suggests that the hypothetical ethylene producer must recover at least \$0.28/lb ethylene produced to break even for new capital investment. Ethane feedstock pricing contributes 42% to the total production cost after by-product credit for propylene. The utilities cost is also represented as a credit, as in this example sufficient H_2 is burned concomitantly with make-up natural gas to make the process a net energy (steam) exporter. In reality, the plant does not need to operate as a net exporter, and fuel gas make-up can be corrected to produce an energy-balanced plant. This would make the utilities cost slightly positive as per the original analysis (14). A thermodynamic analysis tells us that burning approximately 60% of the H_2 is sufficient to provide the needed energy for the endothermic cracking, and the remaining H_2 and supplemental methane are burned to provide the energy needed for separations and to overcome thermal inefficiencies. The remaining 58% of the total ethylene production cost is directly related to the cost of borrowing money for capital and the decreasing time value of those assets. Comparison of a \$0.28/lb ethylene total production cost to the spot prices and margins of pipeline ethylene from **Figure 3** demonstrates that this new plant has ethylene product already overpriced in the USGC marketplace, but it is the higher value of downstream ethylene derivatives over the entire plant lifetime (>20 years) that drives investment. Long-term access to cheap feedstocks is an important part of this investment equation.

The importance of feedstock price to the overall production economics of ethylene is further demonstrated by performing a Monte Carlo (MC) simulation using a subset of **Table 3** variables: ethane price, total capital, and ethylene selectivity (unit ratio). **Figure 4** shows the Pearson correlation coefficient (63) for this simulation demonstrating the extremely strong correlation of ethane price to the final production cost with the lesser, but nearly equal, dependencies of capital and ethane selectivity. Even though capital charges are 58% of the total production cost, because total capital contributes only 25% of its value to the total production cost, it is less sensitive relative to the direct cost of feedstock. This analysis is further extended in **Figure 5**, which plots the MC simulation results as a pair of contour plots showing the total ethylene production cost as a function of both capital and olefin selectivity at two different fixed ethane prices, \$0.05/lb and

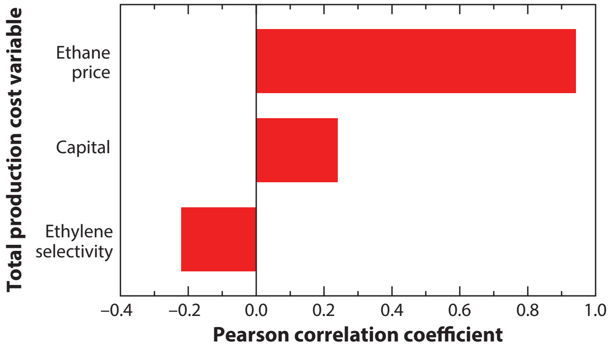

Figure 4

Sensitivity analysis of ethane price, total fixed capital, and ethylene selectivity on a hypothetical total ethylene production cost of a 1,500-kta ethane steam cracker.

$0.15/lb. As per our caveat for **Table 3**, although this analysis is highly simplified, it demonstrates the following truths about ethylene technology investment:

1. Ethane price largely dictates ethylene production economics, and so investment occurs where cheap feedstocks, increasingly ethane, are available.
2. At relatively low ethane prices ($0.05/lb), the span of the **Figure 5*a*** capital axis suggests that a 20% savings in capital results in a 14% cost savings for ethylene. The total production savings is relatively insensitive to small improvements or declines in ethylene selectivity relative to steam cracking.
3. At relatively high ethane prices ($0.15/lb), the span of the **Figure 5*b*** capital axis suggests a 20% savings in capital results in a 10% cost savings for ethylene. Total production cost is much more sensitive to selectivity losses, which makes the high–ethane price case much more sensitive to alternative technology consideration, such as ethane oxidative dehydrogenation,

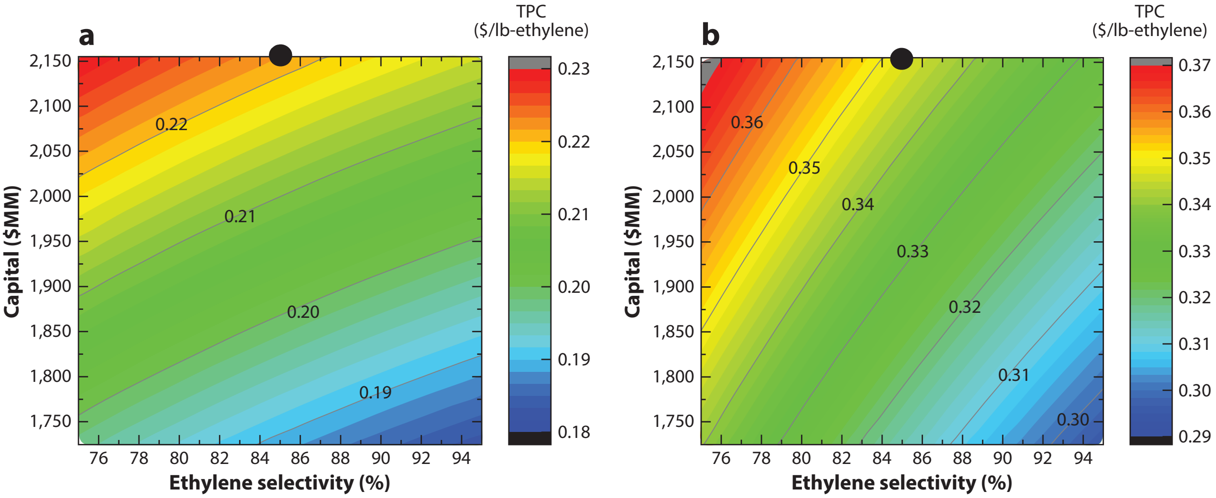

Figure 5

Contour plots representing a hypothetical ethylene total production cost (TPC) surface as a function of total fixed capital and ethylene selectivity for an ethane feedstock price of (*a*) $0.05/lb and (*b*) $0.15/lb. The black dot indicates the relative capital and selectivity graph position for the hypothetical ethane steam cracker in **Table 3** with its TPC of $0.28/lb for an ethane price of $0.10/lb.

which results in destruction of C_2 value to carbon oxides: \$0.01/lb higher cost for every 2.5% selectivity points lost relative to steam cracking.

4. At high ethane prices (\$0.15/lb), a capital reduction of 20% does not reduce the total production cost to levels that can be achieved by finding ethane available at \$0.05/lb—or even at \$0.10/lb (see **Table 3**).

Although **Figure 5** plots a capital axis to assume a potential 20% capital reduction, in reality reducing capital cost by 20% on any mature technology is a Herculean task: Technology would not be mature if this level of savings were available. To achieve a 20% capital savings, new, radically different technology is necessary. In the absence of radically different technology, feedstock cost drives the decisions, and if feedstocks are cheap enough, small continual improvement in ethylene crack efficiency can provide margin. As local feedstock prices increase, new technology that introduces capital savings advantages might gain traction, as long as feedstock prices do not become so high as to completely overwhelm any production cost capital savings advantage, but typically, moving mature technology to an area of advantaged feedstock is the choice.

NEXT-GENERATION ETHYLENE PRODUCTION TECHNOLOGY REQUIREMENTS

So what does the preceding analysis indicate about the potential for new sustainable ethylene production technology? Is there a proverbial carrot to chase? This has already been the subject of workshops (2). Mature technology investment with cheap and abundant feedstock has been the choice over the last two decades first in the Middle East (64) and now in the United States. Current investment in the United States may also be advantaged by relatively cheap oil prices that limit the role that shipping costs can have on geography selection. But if all chemical companies and investors flock to geographical regions with available low-cost feedstocks, eventually the increased production also puts continual downward pressure on the price of both the derived olefins and their derivatives. This in turn incentivizes ethylene and propylene producers to manufacture as efficiently and as cheaply as possible relative to their competition. Better, and new, technology can be part of that equation. Every olefins producer must calculate their total production cost based on their internal economic standards and requirements, and this does vary between companies; however, the preceding analysis shows that the unifying features of new ethylene technology include availing the use of cheaper feedstocks, increasing ethylene selectivity (reducing energy consumption and therefore CO_2), or reducing the capital charge required for new plant investment. Any new technology development has significant costs in terms of time and resources in research, development, pilot demonstration, design, and construction of new technology, and each company (and for publicly traded companies, their shareholders) will expect significant positive return on investment for their risk in funding this effort. These risks can be rationalized as both monetary and scientific (technology failure at scale). At this level of monetary investment, the risk for new technology at this scale is substantial, and to those who control the investment resources, new technology options that produce only small total production cost savings relative to the more assured economics of mature technology do not provide a sufficient carrot. These investors can simply build mature, less-risky technology in locations of substantially lower-cost feedstocks to turn profit.

High prices of local feedstocks and energy have driven new technology and nonconventional feedstock considerations. Absent petroleum, abundant coal has fueled Chinese chemical growth (2), but through known syngas technologies. The most obvious, usually available, nonconventional feedstock is low-cost methane, and certainly development in methane-to-ethylene technology continues (**http://www.siluria.com**; 25). Ethanol dehydration is viable (65–67), and at one time before the US shale boom, Brazilian cellulosic ethanol dehydration was regionally in play, but it is now on hold (68). Polyethylene pyrolysis to regenerate cracking feedstock has been contemplated (69, 70). But no routes, other than known syngas routes, have seen widespread commercialization. Often, cheap chemical feedstocks mean cheap energy, and therefore ethylene production utility costs in a world without a carbon tax often make up an inconsequential portion of total ethylene production costs. **Figure 5** suggests that if feedstock is cheap, total production cost variation with selectivity is somewhat insensitive. If a producer is already back-integrated into cheap feedstock, the only means left to substantially reduce production cost, and therefore technology risk, is to substantially reduce the capital of any new technology for ethylene investment. He & You (71) suggest that traditional production of ethylene concomitant with natural gas processing, for instance at the Bakken formation, can result in substantially increased net present values for a relatively small amount of additional installed capital relative to the capital of giant ethylene complexes. The analysis in this review suggests that with credit for sales gas and other liquids, the ethylene-ethane margin is consistent with **Figure 3** of this review, but a remaining open question is the cost of transport or otherwise processing of this ethylene into derivatives for effective transport from remote shale locations.

The challenge for researchers pursuing capital reduction relative to mature ethane cracking technology via alternative reaction technology is apparent from analysis of where capital is distributed in ethane steam cracking: 30–40% is associated with the cracking furnaces (reaction), whereas 60–70% of the capital investment is located in the separation train (14). Research efforts focused solely on the reaction of ethane to ethylene, regardless of selectivity, at less than near 100% feedstock conversion, may not address the majority source of capital, limiting the ability to significantly reduce the cost of new ethylene technology. Published results from perhaps the most researched of the alternative ethylene production technologies, ethane oxydehydrogenation (ODH), provide examples of this challenge.

Relevant reviews of ethane ODH from a catalyst and process commercialization perspective already exist (see 2, 72, 73). The ODH reaction is exothermic, through removal of H_2, and therefore does not have the thermodynamic conversion limits of ethane steam cracking. For this reason, it is quite attractive. However, even when interesting overall ethylene yields are observed in open literature, the results often receive tepid industrial responses due to the conditions of the experiments. **Table 4** assembles the reactant/product feed composition (partial pressure) from figure 8 of Reference 72 for all ethane ODH examples of ethylene yield above that of conventional ethane steam cracking (55%). No ODH results have an outlet ethylene partial pressure as high as steam cracking; the closest, short–contact time ethane ODH in the presence of H_2 (74), is a factor of two lower. The results of a ceramic membrane reactor (75), which has scaling challenges, and Li-promoted rare-earth oxide catalyst that demonstrates substantial deactivation (76) are a factor of three lower. All others are nearly an order of magnitude lower. This lower outlet pressure will drive up separation costs. Similar catalyst performances to **Table 4** at higher reactant/partial pressures would be quite relevant, but caution is warranted as to not operate the reactor at oxygen concentrations that are at any time within the flammable or explosive regimes. In industrial operation, flammability concerns practically limit the oxygen concentrations (77), and restricted oxygen concentration will limit single-pass conversion in ODH by mere stoichiometry. Significant alkane recycle is thus necessary; this also does not represent a cost savings in separation capital. Increasing oxygen partial pressure in ODH is also likely to cause additional carbon selectivity loss (78–81), challenge heat management (82, 83), and result in further capital considerations to remove the CO_2 or other oxygenates formed during reaction. All these facts challenge the overall ability of ODH to significantly reduce the total production capital.

Others have attempted to avoid ODH challenges such as overoxidation, heat management, or safe operation at high per-pass ethane conversions using unique process designs such as cyclic

Table 4 Experimental operating pressures for oxydehydrogenation results above 60% ethylene yield[a]

Experimental reactor type	Conversion (%)	Selectivity (%)	Yield (%)	Ethane feed (mbar)	Oxygen feed (mbar)	Outlet ethylene (mbar)	Reference
Fixed bed–flow	93	83	77	100	100	77	151
Fixed bed–flow	83	91	76	70	70	53	152
Membrane–flow	90	83	75	250	∼0[b]	187	75
Fixed bed–pulse	80	92	74	100	100	NC[c]	153
Fixed bed–flow	95	71	68	100	100	68	151
Fixed bed–flow	82	78	64	118	59	76	76
Fixed bed–flow	82	77	63	80	80	51	154
Fixed bed–flow	81	76	62	290	290	179	155
Fixed monolith–flow	73	83	61	480	240	291	74
Radiant coils–flow	65	85	55	∼1,000	0	∼550	14

[a] Based on figure 8 from Reference 72, as compared to ethane steam cracking. Results are arranged in decreasing order of observed ethylene yield.
[b] Here it is assumed the oxygen reacts quickly once it emerges from the membrane so that the effective concentration is low.
[c] Experiment uses reactive pulses, so there is no continuous (NC) exit concentration.

schemes, in which alkane reduction is performed in a separate step or reactor relative to catalyst reoxidation (84–87), through the use of microchannel reactors to improve heat transfer and minimize the potential for explosion (88, 89), or oxygen membranes to control overoxidation through the use of controlled oxygen flux to the catalyst (90–92). Straight gas-phase oxycracking of hydrocarbons in conventional and shock tubes has been investigated (93–95), suggesting marginal economic advantage relative to steam cracking (96). Comments on the use of alternative oxidants for ODH is reserved for the propylene discussion later in this review.

Although ODH has been specifically used here as an example of the challenges to new ethylene technology introduction, the recognized performance gap for many alternatives is not new (15, 73, 97). Technology and catalysts, however, are always under improvement, and each ethylene manufacturer has its own threshold of total production cost reduction required to overcome market risk for new technology. Until this threshold is breached, chasing low-cost feedstocks is the most assured path for further capacity expansion. Given the aforementioned capital reduction challenges, the next generation of ethylene production technologies likely requires a holistic research approach to reactor and separations technology (98, 99).

PROPYLENE PRODUCTION TECHNOLOGY

Once described as ethylene's ugly stepsister (16), propylene has spent much of the last 20 years growing in volume faster than ethylene (14), as its primary use, polypropylene, has replaced other polymers, such as polystyrene, in select applications (100). In addition to its sourcing as a product of either ethylene, naphtha, or other alkane cracking, a historically important source of propylene has been as a by-product of petroleum refining, especially fluidized catalytic cracking (FCC) (30). Sources of propylene due to MTO are increasing (30). Equilibrium-driven metathesis reactions to form propylene from ethylene and butenes have been practiced since the 1960s (101). The continued world trend of cracking lighter feedstocks combined with price increases for naphtha feedstocks has driven propylene margins extremely high, which when combined with the advent of fungible and cheap shale gas propane has seemed to focus the propylene-producing community on PDH technology: Since 2011, 40 new PDH plants have been announced worldwide, with 22 units now in operation (2).

Propane Dehydrogenation

The previous discussion of **Table 1** revealed that propane steam cracking is not particularly selective to propylene, no doubt a result of the high rates of methyl radical scission from $C_3H_7\cdot$ radicals after their formation (102). Many ethane steam crackers are designed to concomitantly crack propane with ethane to enhance the propylene yield (14). Naphtha cracking is more propylene rich, but the unit ratios from **Table 1** clearly indicate that catalytic PDH is the best yield option from a single feedstock. Propane has not historically been available at advantaged prices for economic catalytic dehydrogenation, and this caused propylene production to lag behind demand for some time, with an increased reliance on FCC propylene (i.e., oil feedstock) to meet the demand (103).

PDH is not new technology, and at least six named dehydrogenation processes are available for license (16, 20). Process options run the gamut from multiple fixed beds to circulating catalyst beds to fluidized beds, and all have different catalysts that are optimized for different operating conditions. One process now includes an option for ODH in adiabatic reactors, in addition to primary dehydrogenation, that partially burns H_2 to recover heat and facilitate additional propane conversion (21), although it is unclear if this option has even been implemented (104). New dehydrogenation processes are currently under development (105). PDH is highly endothermic and has thermodynamically limited conversions, similar to steam cracking, and catalysts and reactors are developed to handle the required high temperatures and to facilitate heat transfer. Despite the extreme conditions, propylene selectivities are upward of 90% (106). The high operation temperatures inevitably result in catalyst deactivation, by coking or metal sintering, and all PDH processes must design for rapid catalyst deactivation by employing online regeneration schemes (107). This increases the complexity of the reactor systems required for PDH relative to the fired tubes of steam cracking. Despite this complexity, catalyst and process development has been so successful in this area that current dehydrogenation processes are limited by heat transfer and not catalyst performance (2). Research continues into means with which to effectively heat integrate these processes to improve process thermal efficiency (106) or, similarly to ethane, combine PDH and membranes to increase conversion (108). Additional reviews of catalyst and process technology for dehydrogenation are available (109, 110) and are not discussed further in this review.

Alternative Oxidants for Propane Oxidative Dehydrogenation

The heat-transfer limitations and catalyst deactivation management complexities of PDH have also spurred interest in alternative propylene technologies. The rise in US propane availability due to shale NGLs, and the growing opportunity for on-purpose propylene production to meet rising demand, will no doubt spur interest in new research to advantage this resource. Many ideas for new propylene technologies have direct parallels to the alternative ethylene routes previously discussed in this review. This includes propane ODH technology, but in this case the lower bond strength and therefore high reactivity of the allylic hydrogen of propylene, versus the vinyl hydrogen of ethylene (111), result in significantly lower olefin yields relative to ethane (73). There continues to be significant catalyst research in the area of ODH using molecularly derived atomic oxygen, with oxygen either in the gas phase (112–119) or exclusively from the catalyst (120–122).

The higher reactivity of propane/propylene relative to ethane/ethylene in oxidative environments leads to both the formation of oxygenates and greater selectivity to CO_x. In fact, many catalysts used for propane ODH can be made to selectively produce C_3 oxygenates (123) and nitriles (124, 125). Recently reported novel catalysts demonstrate the continued interest in finding new catalysts that can fundamentally improve catalyst selectivity and lifetime at relevant conversion (126, 127). Despite considerable research, the performance of propane ODH catalyst is insufficient for commercialization (73, 128).

Alternative oxidants attempt to improve the selectivity and yield of the propane ODH. Specifically, but not exclusively, these include CO_2 (129–133), N_2O (134–139), and H_2S (140). In the case of CO_2, one oxygen molecule can be transferred to the lattice to complete a catalytic cycle, forming CO, or dehydrogenation equilibrium is influenced through water-gas-shift catalysis, which reacts H_2 to water. This exploits Le Chatelier's principle to further the conversion extent for the equilibrium-limited dehydrogenation. The use of N_2O provides an oxygen molecule in a more reactive form, and this generally results in improved selectivity. H_2S similarly serves as a soft oxidant. However, all of these oxidants have a raw material price that is greater than that of O_2. The simple use of O_2 itself in ODH is an added raw material cost relative to straight PDH. It is instructive to evaluate, similarly to our analysis for new ethylene technology, the required economic trade-off between increased raw material and capital costs that might displace growing PDH options.

Alternative Oxidant Economic Analysis

As was the case for the discussion of new ethylene technology, to overcome risk barriers for the introduction of new propylene technology, the total production cost of any new technology should be significantly lower than that for existing process technology. Modern greenfield PDH processes cost an estimated \$1 billion in total fixed capital (1,000 kta propylene basis), with approximately 40–50% of that capital tied to the cryogenic separation train (21). We should expect that if we ignore minor variation in impurity profiles—ODH processes might expect to have small levels of oxygenates as by-products—any new propylene ODH process technology that employs a distillation train for olefin/paraffin separation will have a similar percentage of its capital tied to this train, assuming less than 100% propane conversion. This leaves approximately 50%, or \$500 MM, of associated capital cost available and ripe for capital reduction with new catalyst and reactor process development. As was the case for ethylene, propane cost contributes significantly to the total production cost of propylene, and utilities will contribute but slightly. However, in our propane ODH example, one must also consider the added cost of the oxidant as part of the process. We can perform a paper analysis to understand the implications of increased raw material costs similarly to how we analyzed the total production cost for ethylene in **Table 3**.

Figure 6 plots the USGC olefin margin and oxidant prices for O_2, CO_2, and N_2O since 2011. Prices and margins are plotted in kilomoles of olefin, or per mole of atomic oxygen, for ease of comparing prices with reference to needed stoichiometry (i.e., one mole of CO_2 or N_2O is needed for every H_2 removed during ODH, but only half a mole of O_2 is needed). USGC variations in prices and margin, defined as the olefin minus corresponding alkane price, shown in **Figure 6** (and of course in **Figure 3**), are the result of constant changes in supply and demand for olefins due to many factors, including global operating rates, global demand, and changes in feedstock supply. Since olefin margins are set by supply and demand, and are agnostic of the technology used to produce the olefin, the desire for any new technology would be to provide margin relief, i.e., to increase a producer's margin relative to market dynamics. This necessitates that the production

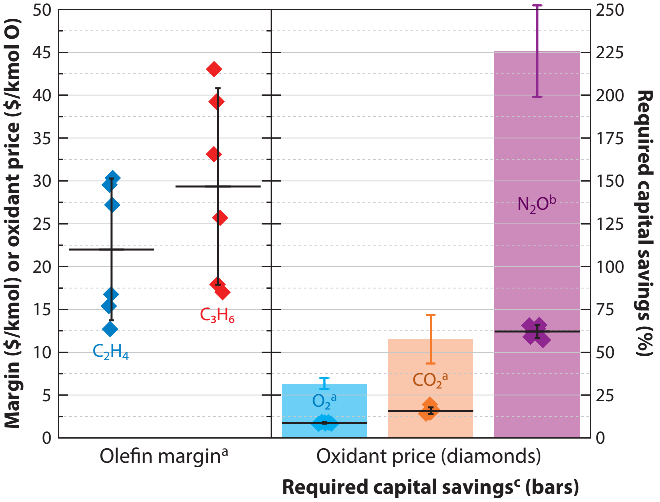

Figure 6

The last six years of data for current olefin margin and oxidant prices (based on raw material and product value) plotted as a yearly average (*diamonds*) along with the overall six-year average and 95% confidence interval (CI). Bars (with 95% CI) represent the required percent capital reduction of an oxidative process, relative to a 1,000-kta propane dehydrogenation (PDH) reactor section, to offset the oxidant raw material cost, assuming a similar propylene selectivity to PDH of 90%.

[a] Margins and prices derived from Reference 149.

[b] Price and variation estimated using the last six-year data for NH_3 and O_2 (149), assuming the total production cost worksheet found in Reference 150.

[c] Required capital savings percentage is calculated assuming that 25% of the total fixed capital savings resides in the total production cost calculation, and this reduced capital charge must offset the total increase in oxidant raw material cost assuming a zero sum. Error bars are derived from the variability in the feedstock price.

cost for a new technology adopter should decrease. If propane ODH is to be considered as the new technology, the increase in raw material cost of using an oxidant for propane ODH relative to straight PDH must be compensated for by either a significant decrease in utilities or a decrease in capital. Of our oxidant choices in **Figure 6**, oxygen is the cheapest. Large quantities of CO_2 are potentially available as a low-cost by-product of methane steam reforming combined with ammonia synthesis (141), but it is slightly more expensive than O_2. N_2O is relatively the most expensive, and in fact already reduces any potential olefin margin advantage by nearly half, creating a significant challenge to implementation.

The plotted bars in **Figure 6** show the required percent capital savings necessary for a propane ODH process, relative to the $500 MM of capital assumed to be in play for the reactor section, to offset the increased raw material price of the oxidant assuming 100% stoichiometric conversion of H_2. Under this hypothetical analysis, the added capital required for both the on-purpose production of N_2O combined with propane ODH would require an untenable negative total plant capital, whereas O_2 and CO_2 require about 30% and 60% reactor capital savings. Although once again this is a simplified analysis, it demonstrates for propylene and ethylene ODH technology the constraints that oxidant raw material costs put on the economic viability of new technology for olefin production. The large percentage of capital reduction required even for relatively inexpensive oxidants demonstrates that the capital reduction challenge for new olefin technology is made more challenging if concomitant separation capital reduction is not considered.

SUMMARY

Extraction of the NGLs ethane and propane from tight shale formations in the United States has increased their supply and lowered costs, resulting in a resurgence of investment for the ethylene and propylene feedstocks that form the backbone of basic chemical manufacturing. For ethylene manufacturing, this has meant construction of mature ethane steam cracking, whereas for propylene there is increasing reliance on accepted on-purpose PDH technology. A significant fraction of the economic cost of greenfield olefins production is related to basic feedstock cost, and so although these plants are capital intensive, the use of mature and demonstrated technology with cheap feedstocks allows chemical producers to make a profit with the least possible economic risk. Incremental changes in mature technology are pursued to keep competitive advantage, but economic risk due to the high capital outlay discourages radically different technology implementation for the manufacture of ethylene and propylene. To overcome incumbent market risk, any new technology offering must significantly lower the total production cost through reduction in total capital; otherwise, new plant investment will follow low-cost feedstocks. In a carbon tax–free environment, although these processes use large amounts of energy, they are highly energy integrated, and utilities contribute only slightly to the total production cost; cheap energy, such as that available with increased shale gas methane supplies, diminishes the effects of energy savings as a substantial driver for new technology. Since the separation trains for these olefin plants contribute significantly to the overall capital, new technology research focused only on the reactor section has a significantly higher hurdle to surmount if the goal is to reduce the overall capital cost.

Although the preceding discussion defines the substantial and daunting challenges for those who perform research in potential new olefin technology, there is no better time to have a robust discussion of new technology, given the advantages offered by increased supply from any number of world shale sources. However, it should be incumbent on this generation, and the next generation, of researchers and technology practitioners to honestly and objectively debate the truly sustainable options, both environmentally and economically, for chemicals production (142). Practically for C_2 and C_3 olefins, this does mean both energy and cost reduction, although it is often difficult to get both at the same time (143), which is the crux of the challenge. Sometimes the solution is found not in direct olefin production but in integrated processes that start from alkanes and produce C_2 and C_3 derivatives without the requirements of olefin recovery (144, 145).

DISCLOSURE STATEMENT

The author is not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

ACKNOWLEDGMENTS

Cathy L. Tway is acknowledged for reading and commenting on advanced copies of this draft. Ive Hermans is acknowledged for providing a link to the useful graphical abstract from Carrero et al. (128). EES acknowledges the reviewer who provided valuable comments and references for inclusion.

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