The Shale Gas Revolution: A Methane-to-Organic Chemicals Renaissance?

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INTRODUCTION

The ever increasing availability of domestic shale oil and gas has resulted in a return-to-profitability for the United States chemical industry, and is spurring 148 projects and $100 billion dollars in new capital investment spread over the next ten years (American Chemistry Council 2014). The significant feature of current major US shale gas plays, e.g. Bakken and Eagle Ford, is that they have large relative quantities of condensate or wet natural gas that contain ethane and propane fractions. Ethylene and propylene, the primary olefin feedstocks of the modern organic chemical industry, are derived from these fractions. Ethylene, increasingly derived in the United States from the steam cracking of ethane (SCE), is the dominant organic chemical in the world with a world production capacity of 123,000 kilotonnes per year (kta). The US produces 24,000 kta of ethylene with a 10,000 kta increase in capacity announced over the next 10 years: A 50% increase (Devanney 2011). The US-produced ethane increase starting in 2007 is visible from Figure 1, and this increased market supply is lowering the relative price to where ethane is now trading at fuel (methane) value. The net current effect is increasing relative profits for chemical producers after conversion of ethane to ethylene and then to polymers and derivatives. Additionally, the relative pricing of US ethane to global naphtha, which trades at the price of oil, is driving both the US competitive advantage for chemicals production investment and the current US trend towards cracking a lighter feedstock to produce US ethylene supply. Additional US investment is garnered from announced capital and processes to directly address the decreasing amounts of heavier industry feedstocks such as propylene and C_4's that result from decreased naphtha cracking. The continued viability of these US chemical industry trends is based on the future pricing of ethane relative other potential fungible feedstocks such as naphtha, and is a complex function of production and global import/export dynamics.

Society places a premium value on chemical derivatives over fuel. This is apparent in the price we pay for energy versus plastic, e.g. polyethylene. The chemical industry exists to upgrade potential fuels, like ethane, to ethylene and derivatives. While wet shale sources rich in ethane are providing this US boom, Figure 1 also clearly shows the majority of all sources of natural gas is dry gas, or methane. The inset chart in Figure 2 shows that most methane is used as a fuel or for electricity generation. The chemical industry currently derives some chemical value from methane, in the form of both ammonia and methanol, but mostly the chemical industry uses methane as a fuel. Methane has long held unrealized feedstock potential for organic chemical producers as it has typically traded below the cost of many potential feedstocks. The increasing availability of domestic methane will inevitably once again raise questions as to the viability of producing higher value ethylene and propylene derivatives from this most abundant of natural gas resources. However, throughout the modern chemical industry, the direct use of methane as feedstock for derivatives remains an economically tantalizing and elusive challenge. To date, and not for lack of effort, no process that directly utilizes methane to produce olefins economically operates in the US. After decades of research a burning question remains for the chemical industry: Is methane a fuel or feedstock?

Ethylene Production

The desired use of methane as an organic chemical feedstock unfortunately converges with certain technological and economic realities regarding how the world currently produces ethylene. The incumbent technology for ethylene production is the hydrocarbon steam cracker. In the US this is increasingly becoming the ethane steam cracker, a mature and successful technology, fundamentally consisting of two parts: a reaction plant and a separations plant (Cesar 2003, Sundaram*, et al.* 2000, van Goethem*,* 2006, Zimmermann*, et al.* 2000). The reaction plant is a natural gas (methane) fired furnace where steam and ethane are reacted inside high-alloy metal tubes at residence times of less than 1 second to produce a mixture of unreacted ethane, ethylene, propane, propylene, hydrogen, methane, and a small amount of heavier hydrocarbons. This cracked gas mixture is water-quenched and treated to remove impurities such as CO_2 and H_2S. Also removed are alkynes, e.g. acetylene, which are hydrogenated before downstream separations. The separations plant uses high pressure steam generated during energy cross-exchange from the cracker furnace effluent to drive compression turbines, liquefying the cracking products for separation by a series of cryogenic distillations of component pairs (olefin-paraffin) that have very similar relative volatilities. The steam cracker is akin to a small power generation plant where fuel (methane) is used to generate electricity (ethylene). This technology is practiced at tremendous scales in a single plant, with single train capacities now approaching 1500 kta of ethylene, or around 175,000 kilograms of olefins processed every hour. The size of these complexes continues to increase as individual ethylene producers seek to capitalize on SCE production scaling laws that are less than unity, extracting maximum profitability for capital invested. The use of methane as a feedstock for ethylene, or the displacement of any part of conventional technology, will require market risk that is only justified if the capital and variable cost intensity of any conceived methane process is significantly lower than conventional technology to justify that risk. If there is no feedstock variable cost advantage, such as what we now see with methane and ethane trading at parity, any US-build methane-to-ethylene process, with or without required oxidants, will likely require a huge capital reduction relative to the SCE process for legitimate attention (Lange 2005).

Methane-to-Ethylene

The chemistry industry currently makes a significant amount of “inorganic” chemicals from methane including refinery hydrogen, ammonia, methanol, and liquids (fuels) via Fischer-Tropsch synthesis. These chemicals share a common derivation from synthesis gas (CO, H_2) that is readily made from the partial oxidation (POX) of methane. Routes for methane-to-ethylene have been envisioned and investigated at varied scale, but have been historically disadvantaged by fixed capital and/or variable costs economics in geographies with direct access to sufficient ethane. The utilization of a methane derivative, methanol, to produce olefins via the methanol-to-olefins (MTO) process is taking root in currently ethane-poor China, where regionally-advantaged cheap and abundant coal resources outweigh the increased process complexity of MTO relative to SCE. MTO has a current advantage in potential methane-to-ethylene processes because its methanol feedstock is already a world-fungible commodity that can be decoupled from olefin synthesis, reducing risk to those producers only interested in olefins and derivatives. This technology, in effect, cheats the direct methane-to-ethylene challenge by first forming in succession the metastable products synthesis gas and methanol. Increased capital relative for MTO relative to SCE is one penalty for the cheating.

In contrast to MTO, direct methane conversion technologies, such as the oxidative coupling of methane (OCM) or methane pyrolysis (MP), both suffer from product selectivity losses as methane conversion increases. Process flowsheets for these processes can be found in Figure 2. In OCM, the product ethane has C-H bonds more reactive toward oxygen than those of methane, decreasing useful selectivity as conversion is increased to economic levels. The resulting CO_2 must be rejected as lost carbon. In MP, the high temperatures needed to overcome the reaction free-energy hurdle favor carbon-carbon bond scission, forming soot, instead of the desired products acetylene, ethylene, and H_2. Selectivity loss can be partially overcome with unique burner design, using substoichiometric amounts of oxygen to provide necessary enthalpy while preserving more carbon product, but significant CO_2 rejection remains necessary. Despite these challenges, both OCM and MP are possible at large scale. With generic polyethylene trading at a current equivalent of \$42/MMBtu (2014), over 8x the current value of methane, why is SCE still the preferred method for the manufacture of ethylene in most geographies?

The most important answer to this question is evident from Figure 3 when considering relative capital intensity, or the size of the pies. Despite using methane fuel to power endothermic ethane-to-ethylene chemistry, the steam cracker and its separation train have been remarkably energy integrated over the technology lifetime, resulting in an ethane utilization efficiency of over 85%, resulting in a total carbon efficiency (methane + ethane) from the plant of nearly 60%. Favorable SCE capacity scaling-laws per unit product currently give it total fixed capital and variable cost advantages relative to MTO, OCM, and MP in world geographies with access to cheap methane and ethane. Processes with higher capital costs for equivalently sized methane-to-ethylene plants cannot economically complete at the current valuation of ethylene derivatives in the marketplace. Despite the success of SCE, Figure 3 also suggests that an ultimate potential liability of SCE in a carbon-tax world is its overall thermodynamic efficiency of less than 20%. This efficiency is significantly less than the 50-60% efficiency at which combined-cycle power plants can generate electricity from natural gas. Clearly the equivalent retail value of electricity (\$29/MMBtu) relative to generic polyethylene (\$42/MMBtu) shows the value society places on ethylene derivatives. Chemical producers are currently willing, and able, to trade lower energy efficiency, and higher greenhouse gas emissions (primarily CO_2), to deliver this product to market.

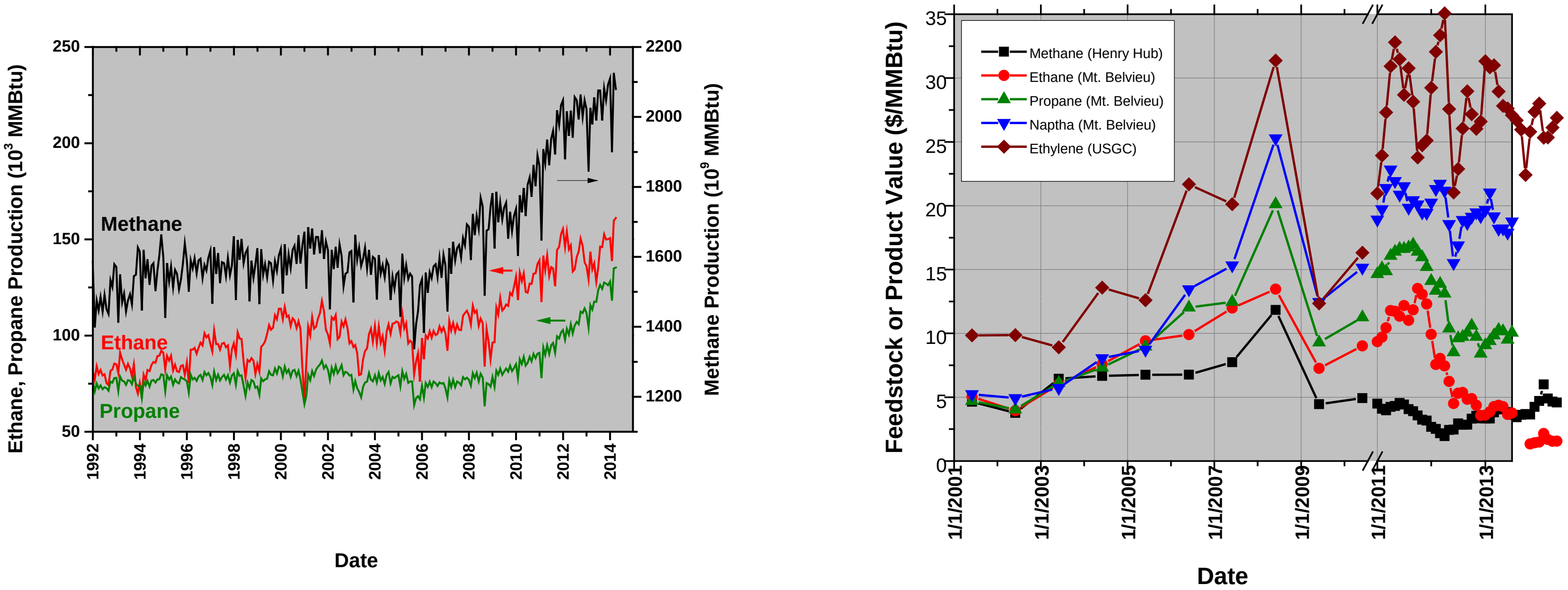
For chemical industry engineers, increasing the sustainability of chemicals and chemical processes is often at the forefront of our current challenges. The term sustainability can have many meanings, but in the chemical industry one could define it as choosing our chemical feedstocks such that our derived chemical processes are the most efficient from both 1st and 2nd thermodynamic law perspectives as well from other socioeconomic factors such as the ultimate cost of those products (International Energy Agency 2013, Banholzer and Jones 2013). For most of historic and US Gulf Coast chemical production, what SCE lacks in energy efficiency is compensated for by the lower risk of return on borrowed capital for plant construction and depreciation. Figure 3, however, does provide us an answer to our previous question: Is methane fuel or feedstock? There is obvious value in methane as a sustainable feedstock, and not a just fuel. Both MTO and OCM have the potential to be more carbon and thermodynamically efficient than SCE. Methane pyrolysis as it is currently envisioned seems to fall behind. The overall reactions for SCE and MP are strongly endothermic, and methane must be burned to provide energy for these plants, whereas the overall exothermic reactions for MTO, and particularly OCM, take advantage of the naturally higher energy density of methane itself to drive the relevant reactions in one vessel, albeit with the help of an oxidant. At the current valuation of ethylene relative to methane fuel, our choices of oxidant appear limited to oxygen (Lange 2005).

Engineering challenges for sustainable methane-to-ethylene

So what challenges remain which, if solved, would allow for increased monetization of our natural methane resources to higher derivatives? First overall methane-to-ethylene capital must be reduced. The reasons for the higher cost of capital are evident in the trade-offs for each chemistry: the multiple world-scale unit complexity of MTO, the low per-pass methane conversion with large CO_2-scrubbing units of OCM, and the multiple reactor capital units in MP of pyrolysis, acetylene hydrogenation, and COx hydrogenation needed to boost carbon selectivity. However, all of these processes share a common thread with SCE. The capital distributions shown in Figure 3 suggest that nearly 50% of the total fixed capital resources are tied to the separation and purification of the product ethylene, and not the reaction step. While reaction section capital improvements in the form of catalysts or novel reactor design may impact reaction capital, one cannot tackle the problem of significantly reducing overall methane-to-ethylene capital without holistically addressing both the reaction and separations section.

The primary method of ethylene purification in all cases is cryogenic distillation. The low relative volatility difference between olefin and paraffin, and inherent low boiling point of C_1 and C_2 hydrocarbons make compression and distillation a significant cost contributor to any methane/ethane conversion process that does not have 100% olefin selectivity. The ability of distillation to scale relatively economically, despite its high energy requirement for separation, makes it the industry separation method of choice (Neelis*, et al.* 2008). Replacement of distillation by lower capital and energy usage options is the second challenge. The incumbency of distillation for ethylene production demonstrates the technical and economic deficiencies of potentially less energy-intensive technologies employing mass-separating agents or membranes to perform the needed separations at scale. Figure 4 makes clear that heat transfer loss and separations require the majority of energy for these processes. It is also well known that capital intensity scales with increasing needs of heat transfer duties (Lange 2001). Figure 4 also shows that on a relative basis, the operators and innovators of SCE processes have made energy integration a priority, and the energy usage of SCE is low relative to alternatives despite the fact that 80% of the specific heat generated in the SCE process must be utilized for heat transfer and separation even after discounting for reaction enthalpy. This SCE efficiency complicates the replacement challenge. Innovations from multiple disciplines will be required for a solution:

chemists/chemical engineers for design of new catalysts and integrated chemical processes, materials engineers for development of new separation materials, computer and information engineers for new ways to control complex chemical processes, and executive entrepreneurs who are willing to be the first to take on the risk.



(a) (b)

Figure 1. (a) Production levels of dry methane to ethane and propane from US gas wells. (b) Value of various potential fuels relative to ethylene on the US Gulf Coast. Data before the plot break (symbol and line) are plotted as the June average value for that year, whereas data after the plot break is plotted weekly. Sources: Sources: U.S. Energy Information Administration 2014, Reed Business Information Limited 2014.

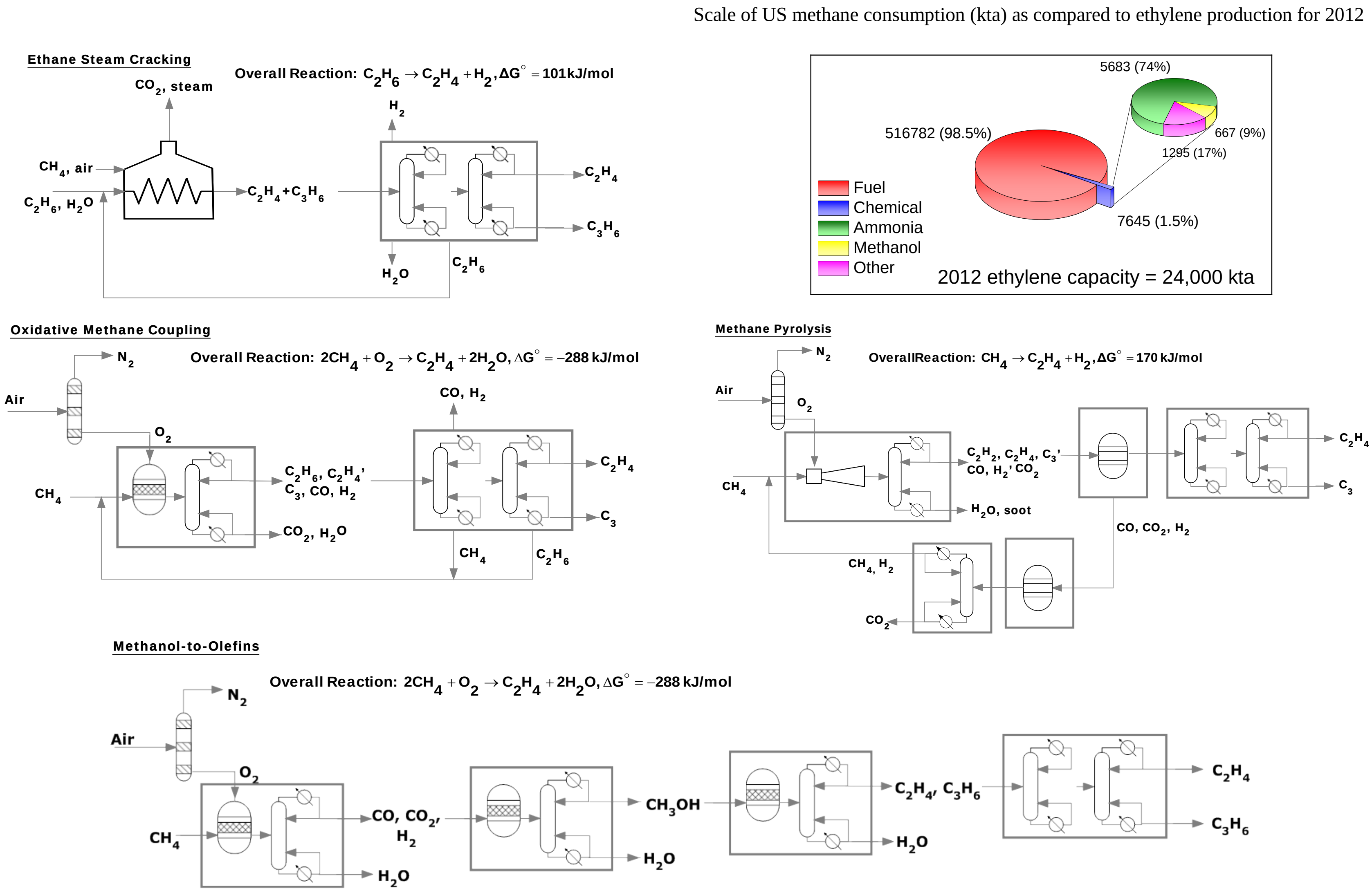


Figure 2. Simplified flow sheets showing for an ethane steam cracker along with some of the known processes that could produce ethylene from methane resources. Inset pie charts give addition information on the size of current methane-to-chemical streams as compared to the fuels market. Reactor and separations sections (represented by distillation columns) are meant to show types of grouped unit operations and are not meant to represent the complexity of each section.

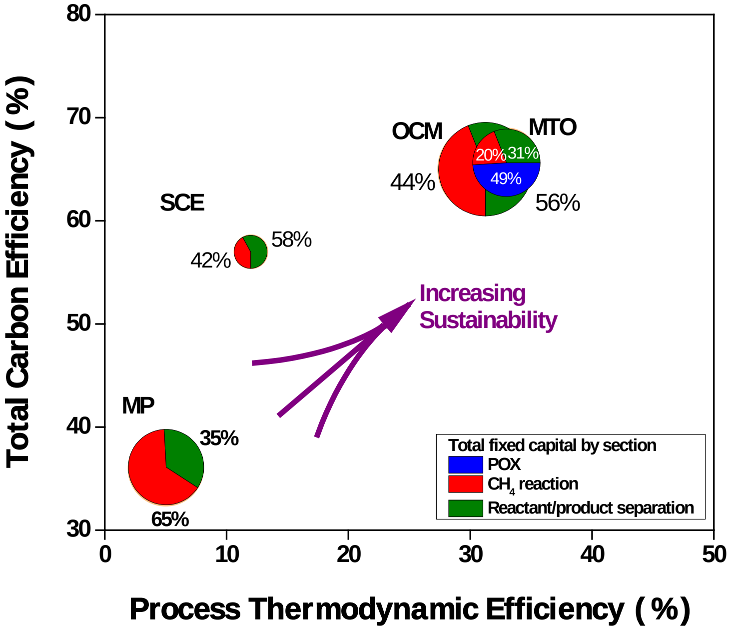


Figure 3. Comparison of methane-to-ethylene processes relative to ethane steam cracking in terms of total carbon efficiency (including methane fuel usage) and 2nd law thermodynamic process efficiency. Process thermodynamic efficiency was estimated by the ratio of the estimated process Gibbs free energy change relative to the change for primary methane reaction and separation of pure reactants and products at 298 K. The size of each pie is proportional to the total fixed capital for each process. The pie is further divided by the percentage of fixed capital in the POX, methane/syn gas reaction, and olefin separation sections. Economics and thermodynamics have been derived from the relevant SRI or Nexant process economic reports, scaled to a 1000 kta olefin capacity. For the MTO case, the scaling basis was 66-33% ethylene and propylene mix at 1000 kta and for OCM it was 86-14% ethylene and propylene mix at 1000 kta. In all processes, steam was rejected at 413 K for thermodynamic analysis. Sources: SRI Consulting 1994, Cesar 2003, Wan 2007, Nexant 2009.

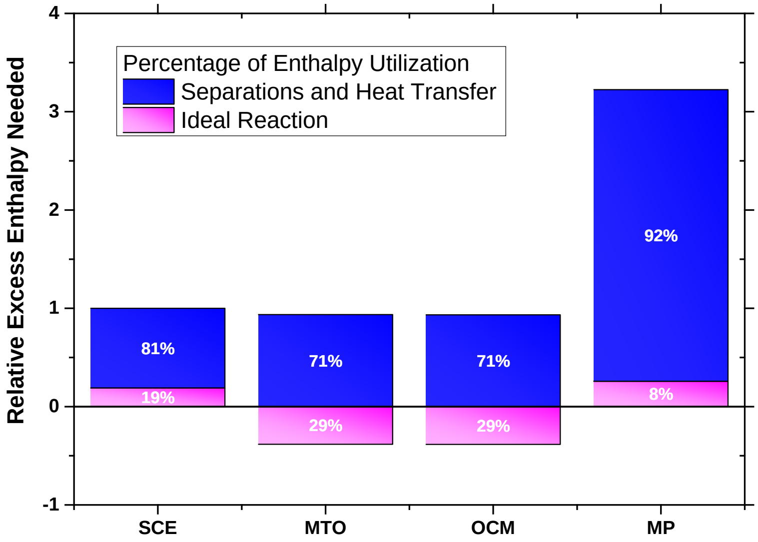


Figure 4. **Relative energy usage for the separations and reaction sections of methane-to-ethylene processes as compared to ethane steam cracking. Typical energy usage for ethane steam cracking used for analysis was 14440 Btu/lb-ethylene. A positive value represents specific heat needed in addition to any that can be recovered from the primary exothermic chemistry in the cases of OCM and MTO (SRI Consulting 1994, Cesar 2003, Wan 2007, Nexant 2009).**

American Chemical Council, 2014. U.S. Chemical Investment Linked to Shale Gas Reaches $100 Billion, http://www.americanchemistry.com/Media/PressReleasesTranscripts/ACC-news-releases/US-Chemical-Investment-Linked-to-Shale-Gas-Reaches-100-Billion.html, February 20, 2014.

Banholzer WF and Jones ME, 2013. Chemical engineers must focus on practical solutions, AIChE J. 59(8):2708-2720.

CEH Marketing Research Report, 2011. Ethylene, Chemical Engineering Handbook, SRI Consulting.

Chemsystems PERP Program, 2009. Gas to Ethylene, Nexant.

ICIS Pricing Report, 2014. Ethylene (US Gulf), http://www.icispricing.com, Accessed Reed Business Information Limited.

ICIS Pricing Report, 2014. Feedstocks Report, http://www.icispricing.com, Reed Business Information Limited.

ICIS Pricing Report, 2014. Polyethylene (USA), http://www.icispricing.com, Reed Business Information Limited.

International Energy Agency, 2013. Technology Roadmap: Energy and GHG Reductions in the Chemical Industry via Catalytic Processes, http://www.iea.org/publications/freepublications/publication/technology-roadmap-chemical-industry-via-catalytic-processes.html.

Lange J-P, 2001. Economics of Alkane Conversion, Sustainable Strategies for the Upgrading of Natural Gas: Fundamentals, Challenges, and Opportunities, Springer.

Lange J-P, 2005. Fuels and Chemical Manufacturing. Guidelines for Minimizing the Production Costs, CATTECH 5(2):82-95, Springer.

Neelis M, Worrell E and Masanet E, 2008. Energy Efficiency Improvment and Cost Savings Opportunities for the Petrochemical Industry, LBNL-964E, Ernest Orlando Lawrence Berkeley National Laboratory.

Process Economics Program, 1994. Ethylene from Methane, SRI Consulting.

Process Economics Program, 2003. Steam Cracking for Olefins Production, SRI Consulting.

Process Economics Program, 2007. Methanol to Olefins, SRI Consulting.Sundaram KM, Shreehan MM and Olszewski EF, 2000. Ethylene, Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Inc.

U.S. Energy Information Administration, 2014. Natural Gas Plant Field Production http://www.eia.gov/naturalgas/.

U.S. Energy Information Administration, 2014. Natural Gas Pricing, http://www.eia.gov/naturalgas/.

U.S. Energy Information Administration, 2014. U.S. Natural Gas Monthly Supply and Disposition Balance http://www.eia.gov/naturalgas/.

Van Goethem MWM, Barendregt S, Grievink J, Moulijn JA and Verheijen PJT, 2006. Ideal Chemical Conversion Concept for the Industrial Production of Ethene from Hydrocarbons, Industrial & Engineering Chemistry Research 46(12):4045-4062.

Zimmermann H and Walzl R, 2000. Ethylene, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA.