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Perspective

Future Feedstocks for the Chemical Industry—Where Will the Carbon Come From?

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Introduction

Future energy needs and their potential economic, environmental, and ultimately societal impacts have been the source of intense public debate. What has been discussed much less is that the chemical industry faces a similar challenge in identifying new feed sources to meet projected global growth. This growth, driven mainly by developments in Asia, will demand new feedstocks and technologies and will come with economic and environmental trade-offs. In this Perspective, we give a brief historical overview of the chemical industry and then outline possible new sources of carbon that could help us meet projected growth in the chemical industry. The positive and negative aspects of each of these feedstocks is described, along with any potential technology gaps. The goal of this Perspective is not to identify winners or losers but rather to give researchers new to the fields of energy and chemical production a foundational basis through which they can assess various feedstocks and ultimately identify new areas within this nexus where they can contribute.

The chemical industry has relied on many different sources for feedstocks since its inception.[1–3] Before the advent of the industrial revolution, the primary source of feedstocks was biobased. Examples of this include the soda ash industry and the manufacturing of dyes. Soda ash, before the development of the Leblanc process in 1790 and the subsequent Solvay processes in 1861, was predominantly made via plant matter.[2] However, growing market demand and increased environmental concerns over deforestation forced producers to develop processes that were more productive and alleviated these environmental impact concerns.[2]

The industrial revolution, which began around 1760 and extended into the mid-1800s, led the transition away from biobased fuels to coal. This adoption of a new energy source created feedstock opportunities for the chemical industry to use newly abundant waste byproducts resulting from the processing of coal. One such example was the development of artificial dyes in 1856 by Perkin from coal tar, a waste residue of coal gas and coke manufacturing.[3] Before the creation of these artificial dyes, all cloth was colored by natural plant and animal extracts. The creation of these dyes was often very labor intensive, and the dyes themselves often lacked color fastness (i.e., stability). It was not until the development of aniline dyes by Perkin that the issues of supply, cost, and stability were resolved.[3] The increased adoption of coal as the primary fuel source for both industrial and residential use allowed it to be further exploited as a feedstock for the chemical industry. The development of acetylene and synthesis gas chemistries are all derived from the use of coal.

By 1930, coal was the primary feedstock for the production of organic chemicals.[4] However, advances in petroleum refining technologies and the increased adoption of the internal combustion engine soon allowed a new source of energy to supplant coal as the primary choice for fuel. Once again, the chemical industry followed the lead of the energy industry's adoption of a new energy source and adapted to these newly available, low-cost alternative feedstocks. By taking those less desired cuts of petroleum and creating new chemical processes for the synthesis of chemicals, the industry was able to adapt and prosper. By 1960, petroleum had displaced coal as the primary feedstock in the production of organic chemicals,[4,5] although there are still some segments of the world where coal is used in the production of chemicals, for example, China.

The scale of the energy industry far exceeds that of the chemical industry. When measured by output (tons per year), the energy market is 14–20 times the size of the chemical industry.[6,7] As such, the chemical industry follows the dictates

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of the energy industry and reacts to actions taken by it. This is clearly evidenced by the aromatics (i.e., benzene) chemical feedstock markets.[8] Recent government regulations on the aromatic content in fuels have caused changes in the amount of benzene in fuels and the way in which refiners produce fuels for the energy market. These changes have impacted both the short- and long-term supply of benzene to the chemical industry.

Changes in regional production volumes of petroleum have also played a role in how and where chemicals are produced. The decline in U.S. petroleum production, which began around 1970 and extended until 2008, limited the supply of low-cost feedstocks and is an example of this.[9] The search for low-cost feeds has resulted in chemical producers moving offshore and the rise of new regional manufacturers, such as those in the Middle East. Those manufacturers that continued to produce in the United States had to adapt to whatever feeds were advantageous (i.e., cost and availability). An example of this is in the adaptability with which the U.S. manufacturers operated their steam crackers, using either light gas or naphtha feeds to supply their downstream needs.[10,11] The high-energy/feedstock price in the period between 2007 and 2014, combined with the increased scrutiny of the CO_2 footprint for industrial processes in general and chemicals manufacture in particular has led to the re-examination of biobased feedstocks for chemicals. This time, however, the criteria of the price and availability were evaluated along with the added metric of sustainability (i.e., carbon life cycle) of this renewable feed.

Since late 2014, oil prices have dropped more than 50%. This has caused some producers to both limit their production and curtail future investments. At the time of this writing (spring 2015), the impact of these production cuts have yet to be felt in the market; therefore, there is still downward pressure on oil prices being seen in the market. This drop in oil prices has the effects of making some sources of chemical feedstock less attractive in comparison and putting margin compression on those chemical producers using such feeds.

Shale gas is one of most obvious areas where these market gyrations have impacted production. However, the scale of estimated shale gas reserves means that its importance as a feedstock cannot be ignored. The main question is how and where this resource will be used. There are obvious outlets for shale gas products both in transportation fuels and in the chemical industry; however, it can also be used in the electrical power generation industry. The natural-gas-powered generation of electricity is now considered more economically attractive than other routes when capital expenditures and operating costs are taken into consideration.[9,12] This, combined with the reduction of CO_2 emissions of over 40 wt % versus coal, makes this a very attractive feed.[9] One can imagine, that as battery technology advances and electrically powered transportation becomes more widely adopted, natural gas consumption by this industry will become a more important consideration as a feed.

The chemical industry continues to grow to meet the increased demands of world markets, and as household incomes rise across the globe, this growth is expected to continue. Its manufacturing footprint is global in nature with production facilities being collocated near existing markets more and more as the size of these markets justify their own production facilities. The reason for this collocation is driven by the need to minimize expenses, such as transportation costs. The production of chemicals in regional markets, however, means that chemical producers must be more adaptable than ever to the varying regions' governmental policies, environmental concerns, and the economically advantaged feedstock of each region, all of which, when taken into consideration, can potentially alter one feedstock's favorability over another.

The purpose of this article is to give the reader a perspective and points for consideration of various carbon sources as potential feedstocks. The way we have chosen to benchmark these feedstocks is to look at the technical and economic viability of directly converting these feedstocks into three building block chemicals: methanol (oxygenates), ethylene (olefins/alkanes), and benzene (aromatics). We identify existing technologies, if available, and identify research challenges in the case where no viable technology exists. We also consider scale issues, feedstock availability, and related resource challenges, and as appropriate, political and environmental issues.

Economics

As with any business, the overall process economics determine the viability of any investment to be made. This fact is even more apparent for the chemical industry because the majority of this industry can be considered commoditized. Although there are certain segments of this industry that are not commodity in nature, their feedstock volume requirements are small by comparison and outside the scope of this article. Commodity chemical production typically requires a large capital investment and easy access to both raw material feedstocks and product markets. These capital investments are typically recouped over the course of the plant's operating life, which can span 2 or more decades. Because of the lifetime under which a plant will operate, the investor must take a calculated risk for the choice of technology, the size of investment (i.e., plant size/economies of scale), and the future feedstock supply and price for the region of manufacture under consideration.

The choices surrounding the manufacture of methanol illustrate this well. Methanol is a commodity chemical used in industries as varied as paints and plastics to fuel additives. Methanol is produced around the globe and can be sourced from virtually any common feedstock, including methane, coal, or biomass. In fact, initial methanol production was sourced from the destructive distillation of biomass (i.e., wood alcohol).[13] Today, however, it is mainly produced through catalytic processes, and that is the type of process considered.[13]

Large-scale methanol production is currently performed via a two-step process.[14] The first step converts the feedstock of choice into a synthesis gas containing H_2, CO, CO_2, and H_2O. This conversion typically involves the reaction of the feedstock with one or more oxidants: O_2, steam, and/or air. The goal of this process is to create a gas stream with an H_2/CO ratio that is able to be readily converted in the second step to methanol. The second step is the conversion of the synthesis gas to methanol followed by its separation and purification from the reactor effluent.

The production of methanol is very cost competitive, and this has driven producers to seek out both low-cost feeds and

Table 1. Economic Summary for a 5000-TPD Methanol Plant

Capital for a 5000 metric ton (MT)/day plant	$ MM
ISBL	\$600
Outside battery limits plus all other required capital	\$600
Total capital required	\$1200
Raw materials (feed and utilities)	**\$/MT CH_3OH**
Methane	22.46
Fuel	1.98
Process water	0.02
Electricity	23.10
Total materials costs	47.56
Total fixed costs	24.30
Total cash cost	71.86
Depreciation	53.99
Total production cost	125.85

economies of scale in production. Today's largest plants are the so-called mega methanol plants that produce approximately 1.7 million (MM) tons of methanol annually per plant in a single train.[14] This is the size of plant that we consider for illustration. The primary feedstocks for methanol are either natural gas (i.e., methane) or coal. Not surprisingly, the overall required plant capital, with either feed, are within 30–40% of one another.[15] Therefore, our analysis focuses on a plant with methane as a feedstock, with the assumption that the general conclusions drawn are common to all feeds.

The capital required for a 5000 ton per day (TPD) methanol plant (i.e., 1.7 MM tons/year) is approximately \$1.2 billion dollars.[14,16] This value encompasses the overall capital required for the investment and is based on literature values from early 2000. On the basis of this value and the cost estimates presented by Pellegrini et al.,[16] the following production costs, listed in Table 1, can be generated. The data in this table are based on the following set of assumptions. The capital required for inside the battery limit (ISBL) construction is 50% of the overall project capital. The raw materials and utilities are the same as those listed by Pellegrini et al.[16] The total fixed costs are 0.0675% of the ISBL costs, and the depreciation is 10% of the ISBL and 5% of the remaining capital requirements. Although a more rigorous analysis would be needed for investment decisions, the data in Table 1 can be used to illustrate the importance of feedstock price in commodity processes.

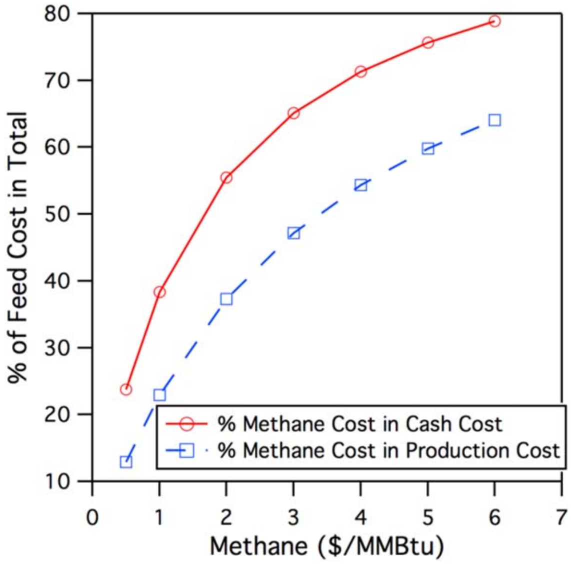


Figure 1. Plot showing the contribution of the methane cost to the cash cost and production cost in methanol production as a function of the methane price.

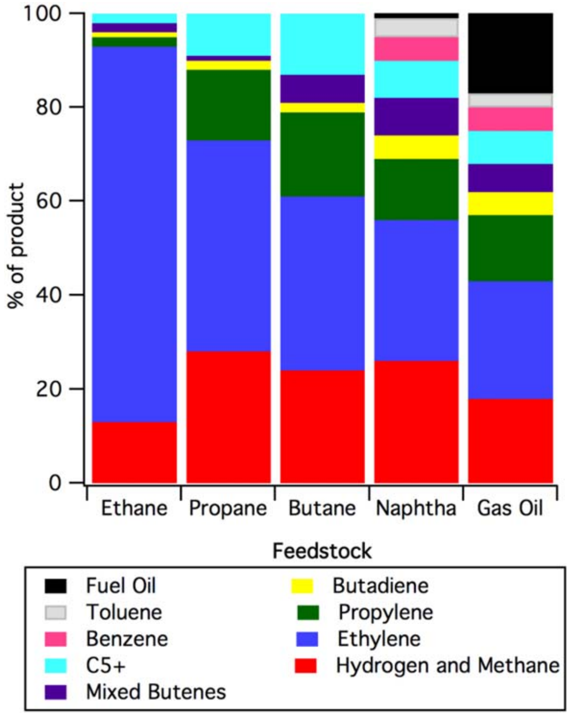


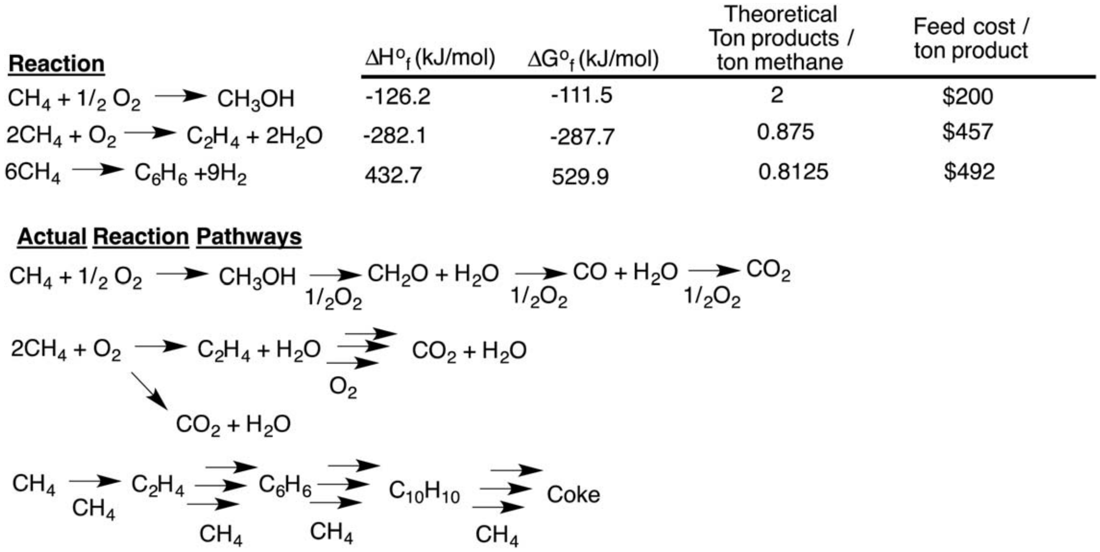
Figure 2. Product slate obtained from a steam cracker as a function of the feed. C5+ is aliphatics with carbon number of five or greater.

Figure 1 depicts the how the price of the feed can dominate the costs associated with producing methanol. The figure demonstrates the sensitivity of the plant economics to feedstock costs. This figure is intended to reinforce the message that the overall feed price and stability are major concerns to any commodity process.

In short, three key factors play a critical role in the economic viability of a commodity chemical process: (1) feedstock cost, (2) capital costs, and (3) sales price.

Oil and Gas

Petroleum and natural gas have been the primary feedstocks of the chemical industry for the past 50 years. If one looks at the major commodity chemical value chains, they are derived from two primary sources: (1) aromatics production from catalytic reforming in a refinery[17] and (2) olefin and aromatic production from steam cracking.[18] In the case of steam cracking, the product slate is highly feedstock-dependent. For instance, an ethane steam cracker makes predominantly ethylene, with minor amounts of methane and hydrogen and only a small amount of C3 and heavier compounds. However, as one goes to heavier feeds, such as butane and naphtha, the amount of heavier products, such as C4s and benzene/toluene/xylene,



Reaction	ΔH°$_f$ (kJ/mol)	ΔG°$_f$ (kJ/mol)	Theoretical Ton products / ton methane	Feed cost / ton product
$CH_4 + 1/2\ O_2 \rightarrow CH_3OH$	-126.2	-111.5	2	$200
$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$	-282.1	-287.7	0.875	$457
$6CH_4 \rightarrow C_6H_6 + 9H_2$	432.7	529.9	0.8125	$492

Figure 3. High-level overview of the possible direct routes to methanol, ethylene, and benzene from methane. The economic number assumes a $4.00/million Btu methane price at the theoretical yield.

becomes more significant at the expense of ethylene production. Figure 2 shows the relative product slate obtained from hydrocarbon steam cracking as a function of the feed.[19] The information in Figure 2 is significant given the construction of several ethane crackers in the United States over the next few years. These new projects will lead to an increase in U.S. ethylene production, which is estimated to be over 8 million metric tons per year.[19] However, there will also likely be tight markets in propylene and butadiene production given the product slate from ethane steam crackers. This offers opportunities for on-demand propylene or butadiene production technologies. To help benchmark the subsequent feedstocks considered, the cost of production for a ton of ethylene from a world-scale ($\sim$1000 kTa, kTa is kilotons per year) ethane steam cracker is approximately $920–1150/ton. The feed contribution to this is 60–70% of the production cost with the assumption of $330/ton ethane.[11]

Shale gas

The development and implementation of hydraulic fracturing in the United States will have a significant impact on the global chemical industry. It is important to remember that 15 years ago, the United States was at a severe feedstock disadvantage as compared to several other regions in the world, most notably the Middle East. A simple illustration of this was the construction of several U.S. liquified natural gas (LNG) import terminals in the early 2000s. These are now being retrofitted to serve as export terminals as discussions take place about the possibility of the United States becoming a LNG exporter.[20]

This Perspective, however, is not a shale gas review as there are other outstanding summaries of this topic from a variety of vantages.[21–23] Here, rather, we summarize how this will impact the chemical industry. Given that ethane and propane (and higher alkanes) can be readily converted into olefins and other high-value chemicals with well-established steam cracking technology, we limit our discussion of those molecules, as this has been well reviewed elsewhere. Most of our discussion will instead focus on the direct conversion of methane to methanol, benzene, and ethylene and highlight the competing forces with the energy sector (Figure 3).

Per the discussion in the Economics, methanol is produced by the steam reforming of hydrocarbons, preferably methane. Thus, given the current growth of methane production in the United States, there has been a resurgence of methanol plants, ammonia plants, and even preliminary announcements and speculation about Fischer-Tropsch plants. The methanol economics previously showed the driver for this: cost-advantaged feedstock. However, methanol plants are capital intensive; there has been and continues to be considerable efforts made to produce methanol directly from methane. The basic chemical properties of methane have been summarized elsewhere in several outstanding reviews and is not described here.[24–26] However, the key challenge in C1 chemistry is the ability to selectively activate the C—H bond in methane (bond energy [BE] $\approx$ 108 kcal/mol @ 298 K) while retaining the ability to stop the chemistry selectively along a reaction pathway as the target products of interest are (1) inevitably less stable than methane and (2) usually an intermediate in a series reaction scheme (Figure 3).

Methane to methanol. The direct partial oxidation of methane to methanol is significant. This has, in fact, been studied for many years.[27] The key challenge in this chemistry, like most oxidation processes, is that the intermediate product is much more reactive than the initial reactant. The vast majority of works to date have focused on the high-temperature ($>$500 K), gas-phase activation of methane. This leads to severe challenges in controlling the reaction pathways as overoxidation is ubiquitous. Most transition-metal oxides have been investigated as catalysts for this reaction. In these systems, the best yields to date of methanol have been in the 5% range; where, the yield is equal to the methane conversion times the selectivity to methanol. More recently, zeolites containing both iron and copper have been the subject of intense scrutiny.[28,29] Although some of these materials can activate methane at modest conditions, the details of which depend on the oxidant and metal identity, the desorption of the methoxide species to produce methanol is problematic, and often, this intermediate must be extracted from the zeolite. The great challenge is the ability to activate methane under conditions where the oxidation chemistry can be at least somewhat controlled, that is, achieving conversions above 10% without leading to nonselective combustion products. If, for instance, the reactivity of the Cu or Fe active sites in zeolites could be modified so desorption of the formed methoxide is facile, this would represent a significant breakthrough. An alternative view of this problem is that the ability to selectively activate oxygen under conditions that do not lead to nonselective oxidation is still lacking. In support of this is work showing that activating methane with a preactivated form of oxygen, such as hydrogen peroxide, is much more feasible at or near ambient conditions.

Many researchers in this field point to methane monooxygenase (MMO) and other biological systems for inspiration as these enzymes operate under ambient conditions and perform oxidation chemistry with very high selectivity, albeit low rates. With this in mind, there has been tremendous effort spent on identifying homogeneous catalysts that will achieve selective partial oxidation in the liquid phase with comparable success on the whole to gas-phase work. It is clear that work will continue in developing both molecular catalysts and extended solids that may be capable of both selectively activating C—H bonds and facilitating controlled oxygen activation and insertion at moderate temperatures.

Methane to ethylene. The thermal pyrolysis of methane to higher hydrocarbons, such as ethylene, is feasible. However, both the energy intensity and subsequent carbon inefficiencies of this process dictate the need for cheap, plentiful feedstock. Additionally, both energy recovery/integration and byproduct utilization will be required for the maximum economic benefit to be derived. Ideally, one would like to use a more selective process, such as the direct coupling of methane.

The direct oxidative coupling of methane (OCM) to form ethylene is perhaps the most heavily studied reaction in the field of heterogeneous catalysis.[30] This reaction, analogous to methane partial oxidation, suffers from selectivity challenges. The conditions under which this reaction has typically been investigated, that is, at temperatures higher than 500°C, leads to both overoxidation and significant gas-phase free-radical chemistry. Given that the amount of control one can exert over the homogeneous gas-phase chemistry is minimal, one approach going forward would appear to be the development of catalysts wherein more of the chemistry occurs on the surface, perhaps by operation at lower temperatures. Catalysts have been developed that can perform this chemistry with a yield of 20–25% ethylene per pass; this low per-pass conversion poses severe process engineering challenges. Large recycle streams not only lead to high capital expenses (CAPEX) costs but also prohibit the use of air as an oxidant because it is 80% diluent. This issue becomes even more pronounced as one considers an attempt to use OCM to displace ethane steam crackers, which typically produce 800–1000 kTa of ethylene.

In summary, both methane to methanol and OCM suffer from the same general challenges. Although they are thermodynamically downhill, the ability to selectively control the chemistry degrades rapidly as one begins to push conversions above 5% (methane to methanol) or 30–40% (OCM). Thus, a key breakthrough would be to develop catalysts with active sites that can activate methane and oxygen under conditions where side reactions such as overoxidation can be controlled. In the case of OCM, this would suggest performing more of the chemistry on the catalyst surface; in the case of methane to methanol, the need to minimize overoxidation is formidable.

Methane to benzene. Methane to benzene has been studied extensively with nonoxidative routes for nearly 30 years.[31] This chemistry suffers from two severe challenges. The first is thermodynamic, as the equilibrium conversion at 700°C is approximately 10%. Thus, one has severe constraints in terms of throughput that are imposed by thermodynamics. Also, one will need to burn on the order of 40% of the methane fed to the reactor to drive the highly endothermic reaction. The second is the chemical pathway. Upon inspection of this literature, it becomes clear that this is primarily a chemical pathway to coke formation and that benzene is just one intermediate along the pathway. Thus, one is not only fighting thermodynamics but also chemistry. Thus, in our eyes, this is not a catalyst problem; many materials have been shown to get to or very near the equilibrium conversion for this chemistry. Rather, we believe that this is a reaction engineering problem. For instance, an advance would be the development of a reaction engineering scheme where the heat generated during coke removal in a fluidized bed/cyclone configuration could be used to preheat the feed and drive this highly endothermic reaction so that its economic viability would improve. However, the thermodynamic constraints are intrinsic and pose severe challenges.

By contrast for C2 and higher feeds, there are no technology breakthroughs needed to use shale gas because of the mature efficient technologies around steam cracking. For completeness, Figure 4 shows part of the C2 value chain and helps to explain the excitement around shale gas use for chemical production. Estimates of new capital investments in ethylene projects vary, but a total value of $15 billion in investments on the gulf coast alone is conservative. The breakthroughs outlined previously would potentially transform methane to chemicals. However, it is important to remember that syngas production is a highly mature, optimized, and competitive route to methanol and other chemicals, especially with low feed costs. In fact, with proven methanol-to-olefin (MTO) and methanol-to-gasoline (MTG) technologies, it is possible to get to benzene and olefins from methane via syngas to methanol. However, this route has not historically proven sufficiently profitable in most places to justify the investment.

The technology to produce shale gas, hydraulic fracturing, has several challenges that have the potential to impact its

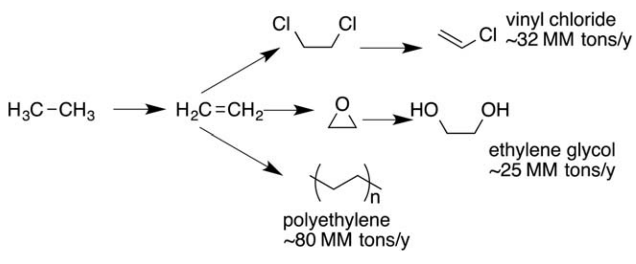


Figure 4. Some major products in the C2 value chain and their annual global production.

future supply. From an environmental viewpoint, there are a few major concerns. The first is possible fugitive methane emissions. Methane's greenhouse gas impact over a 100-year period is 20 times greater than that of CO_2. The contribution of hydraulic fracturing to methane fugitive emissions is a controversial issue, and many would argue one that is not totally resolved. However, it seems likely that more stringent monitoring requirements will be implemented in the coming years. The second issue is based around water: both the level of consumption and concerns of water contamination due to the use of chemical additives to water used in the fracturing process. On a relative basis, hydraulic fracturing is not as water intensive compared to agricultural usage or coal-based electricity production. Although ranges vary, the number typically cited is 3–5 million gallons of water per well. This is, in fact, quite modest compared to the estimated 130,000 million gallons per day used in the power-generation industry.[32] However, as water shortages continue in parts of the country, this will lead to increased efforts to reuse water, a trend already being observed in the sector.

Concerns around the previous two points coupled with land rights issues have restricted adoption of hydraulic fracturing methods in other countries. For instance, in China, many areas with shale gas reserves are remote with insufficient water resources. By contrast, in Europe, property/mineral rights coupled with environmental concerns have prevented hydraulic fracturing. Thus, at this point, hydraulic fracturing does not appear to be something that will necessarily get widespread adoption globally in the next 10–15 years.[33]

Beyond environmental concerns, there are also potential challenges around feedstock allocation and economics. The former is quite important for methane, where the chemical and electricity sectors will be in competition. Government policy in the form of what level of gas exports are allowed is also a potential challenge. Related to this is the so-called drip condensates, which are mainly C5+ cuts (aliphatic molecules with at least 5 carbons) that have not found their way into the chemical industry as a feedstock but can now potentially be exported after minimal refining.[34] Although most U.S. chemical producers are not in favor of exports, some energy producers are. This is a highly political issue with an uncertain outcome.

Coal

As mentioned in the Introduction, coal was the main feedstock in the early 20th century chemical industry. The calcium carbide process, where one forms acetylene from coal, was and still is a viable technology. From acetylene, one can form a wide variety of building block molecules and higher value products (e.g., butanediol, vinyl acetate monomer). There is perhaps no better example of this than the resurgence of coal to chemicals currently taking place in China. Coal, the primary indigenous feedstock in China, is being used to make a large variety of chemicals, including syngas, acetylene, and their subsequent downstream derivatives, such as methanol, butanediol, and vinyl acetate monomer (Figure 5). This is a case study of a nation trying to mitigate its reliance on imported feedstocks. As an example, coal can be converted to syngas, which is then upgraded to methanol. This methanol can then be converted to a variety of molecules, including olefins (MTO),[35] gasoline (MTG),[36] or other molecules, in the methanol value chain, for example, formaldehyde and acetic acid. The methanol-to-olefin process is finding increasing interest in China, as the Chinese chemical sector is one of the major consumers of olefins.

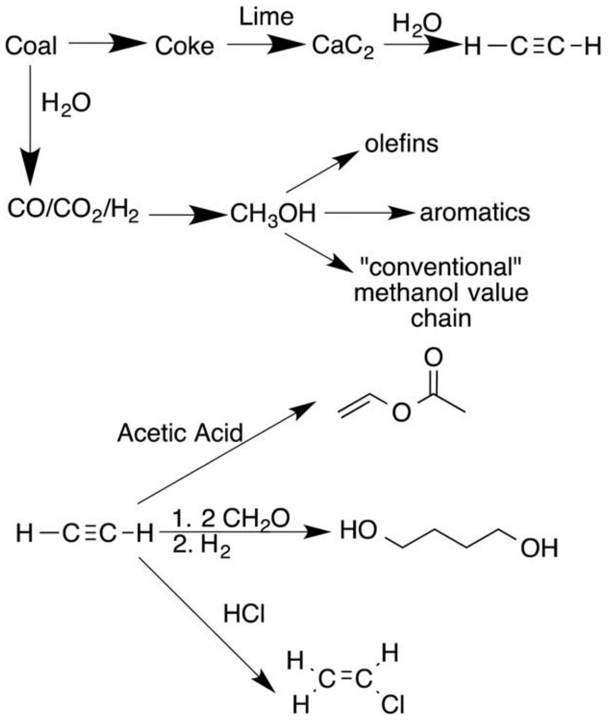


Figure 5. Established routes to chemicals from coal as a feedstock.

A key strength for coal as a feedstock is that the coal-to-chemical process is technologically mature. If coal is displaced as a feed for electricity generation by natural gas, this would be an economic driver for revisiting coal as a chemical feedstock. However, there are good reasons why the shift from coal to oil and gas was made in the first place. First, coal has a lower energy density (ca. 24 MJ/kg, depending on the coal rank) and is hydrogen deficient compared to gas and oil. Second, as a solid, it is more complicated (and more expensive) to process; this leaves it economically disadvantaged from a CAPEX vantage. For instance, comparably sized methanol plants (5000 TPD methanol) where coal is the feed will cost over $300 MM more to build than a methanol plant using natural gas as feed; this is, in no small part, due to the cost of the coal gasifiers.

So what would bring coal back into the competitive landscape on a cost-parity basis in a world of inexpensive natural gas? The best case scenario seems to be a breakthrough in gasification or liquefaction technology. The ability to generate synthesis gas from coal in a more efficient, less capital-intensive process would potentially broaden the scope of coal-to-chemical processes.

Biomass

Both academic and industrial labs have revisited biomass conversion to fuels and chemicals over the last 10 years. This effort has also drawn considerable attention in the mainstream media. Before our analysis begins, it is important to point out that the driver for this feedstock is not purely economic as it is in the case of shale gas. Sustainability and environmental

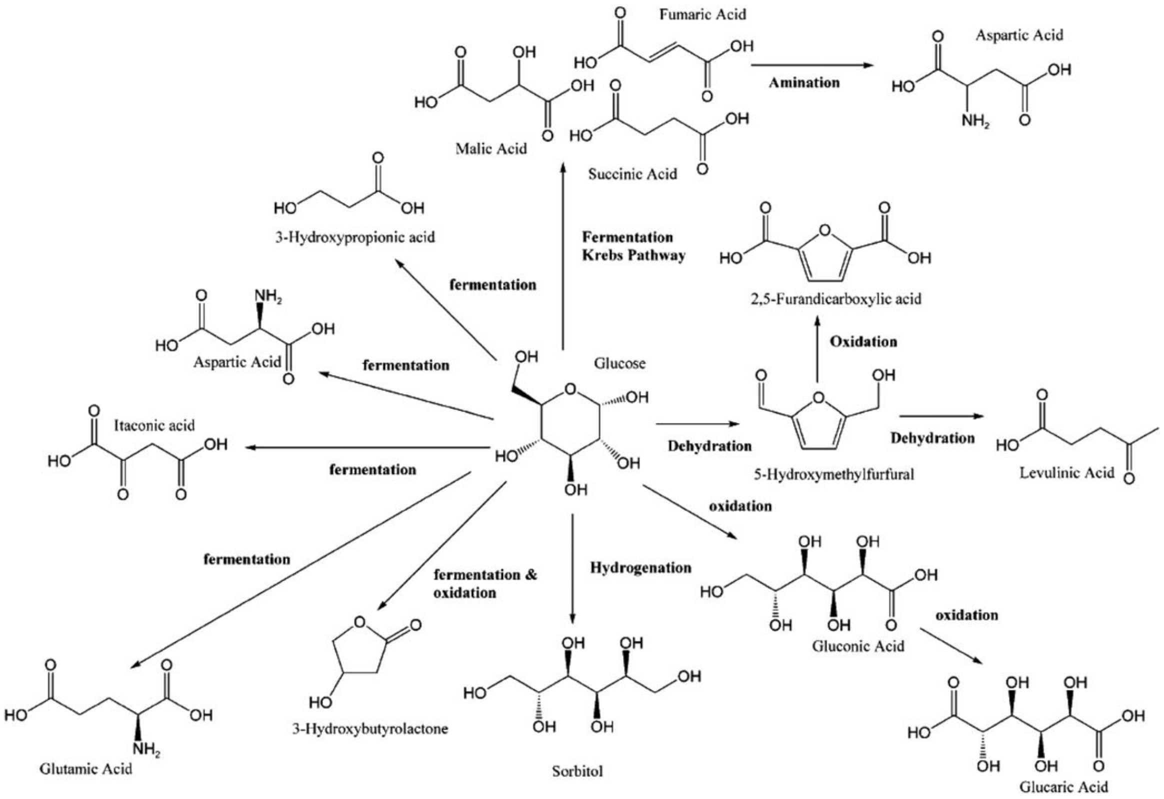


Figure 6. One possible set of chemistries achievable from biomass-derived glucose.[39]

concerns are two of the major drivers for this line of work. The sustainability factor is hard to quantify economically; thus, the discussion focuses primarily on feedstock costs.

There are innumerable reviews on the production of chemicals and fuels from biomass with a variety of approaches.[37,38] Conversion schemes can be conveniently, and perhaps simplistically, put into three categories: (1) biochemical processes, (2) thermal processes, and (3) catalytic processes. From the vantage of producing hydrocarbons, the basic challenge is that one is trying to go from $C_6H_{12}O_6$ to $C_xH_{2x}O_0$; that is, it is necessary to reject large amounts of oxygen. Thus far, there are two demonstrated ways of doing this: rejecting oxygen as CO_x or as H_2O. In the former case, one pays a price in carbon yield. In the latter case, one pays an energy price, where to date the energy is provided in the form of hydrogen. Both routes make it difficult for biomass-to-hydrocarbon-fuel processes to compete economically with petroleum; the cost of the hydrogen needed alone poses severe economic constraints. Figure 6 gives an example of one scheme for upgrading biomass.

Intrinsic challenges

Before outlining the technological advances needed for biomass-to-chemical processes, we outline a few of the intrinsic challenges biomass poses as a feedstock. The first is that its energy density is markedly lower than many other potential chemical/fuel feedstocks. Figure 7 illustrates succinctly the inherent uphill battle one is fighting when attempting to make fuel from biomass; that is, it is intrinsically inferior on an energy basis to hydrocarbons. At a mass energy density of 10–20 MJ/kg (versus 40–50 MJ/kg for liquid petroleum products), the economically viable shipping radius of biomass falls somewhere between 15 and 50 miles, depending on assumptions for the type of material, water content, and so on. This effectively limits the amount of biomass that can be used as a feedstock and, hence, limits the plant size. Thus, one clear

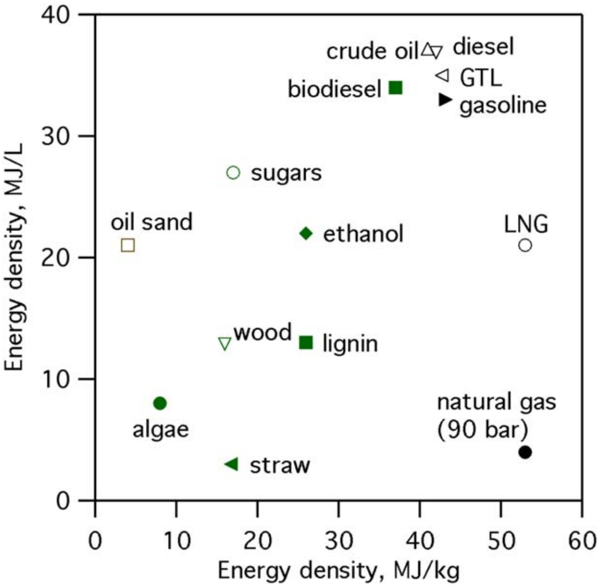


Figure 7. Gravimetric and volumetric energy densities of a variety of materials.[40]

Reaction	ΔH^o_f (kJ/mol)	ΔG^o_f (kJ/mol)	Theoretical Ton products / ton biomass	Biomass cost / ton product	Biomass + H_2 cost / ton product
$C_6H_{12}O_6 + 6H_2 \rightarrow 6CH_3OH$	63.8	-62	1.07	$315	$348
$C_6H_{12}O_6 + 6H_2 \rightarrow 3C_2H_4 + 6H_2O$	-25.3	-256.1	0.47	$720	$758
$C_6H_{12}O_6 + 3H_2 \rightarrow C_6H_6 + 6H_2O$	-99.9	-331.9	0.43	$775	$791

Figure 8. Thermodynamic analysis, theoretical yields, and feed cost per ton of product at theoretical yields.

breakthrough for removing this constraint would be a technology to couple harvesting with liquefaction.

The second challenge is oxygen rejection and its impact on yield. Whereas chemical feedstocks are historically oxygen deficient and carbon and hydrogen rich, the opposite is true of biomass. With these two points in mind, the section that follows (1) identifies possible ways to make methanol, benzene, and ethylene directly from biomass and (2) identifies research needs that would enable a best case scenario for economic competitiveness. In the analysis that follows, we assume that the biomass feedstock will have a nominal composition of $C_6H_{12}O_6$ and a feedstock cost comparable to sugars of $0.15/lb.

Biomass to methanol, ethylene, and benzene

Figure 8 lays out the overall reaction stoichiometry, with the assumption that all needed oxygen rejection is achieved in the form of H_2O to maximize the carbon yield. A few observations become clear immediately. First, to pursue this pathway, one will need large quantities of hydrogen, with increasing amounts as one goes to more reduced forms of carbon. Thus, the inclusion of this hydrogen production in the economics is essential for any meaningful analysis of producing chemicals from biomass. Second, on a yield basis, it becomes very clear that the production of hydrocarbons from biomass is unfavorable, as in the best case the yield will be 47%. This number assumes that all carbon from the feed ends up in the product and that all oxygen is selectively rejected. As an aside, this is one of the challenges faced by methanol-to-olefin and methanol-to-gasoline technologies and is, thus, not unique to biomass. So, clearly, one technological challenge is to develop catalytic materials that will selectively remove oxygen biomass while maximizing the carbon yield. To date, the community has done this with large quantities of hydrogen; this is likely not practical on any sort of scale.

The limiting case is the desire to reject oxygen in the form of molecular oxygen (i.e., O_2). Although attractive from a yield vantage, it appears to be unrealistic from a preliminary thermodynamic analysis. When one rejects oxygen as O_2, there is a large thermodynamic penalty, as one is no longer making water, which has a large favorable contribution to the Gibb's free energy (~ -285 kJ/mol). In other words, the reduction of biomass is thermodynamically favored because of the concomitant oxidation of hydrogen to water when oxygen is rejected with H_2. Although from an intellectual vantage the ability to design catalysts to remove oxygen in the form of O_2 would be a significant scientific advance, it is unclear if this would be the true technological game-changer envisioned by some.

To summarize, to reach toward the best possible case scenario for hydrocarbon production from biomass, one will need to reject oxygen at a very high efficiency. Using a fairly expensive energy source/reductant such as hydrogen will economically disadvantage such a process. Thus, a key breakthrough for this field would be the development of a lower cost reductant, which could possibly be generated *in situ* and which does not come at the expense of a lower carbon yield. This might imply a coconversion process, where for instance a much more highly reduced and low-value form of carbon is cofed and used to upgrade the biomass.

From a yield perspective, biomass offers more potential as a feedstock for the production of oxygenates. For instance, it can be seen that from a yield basis, the synthesis of methanol is favorable. Along this line, there have been many efforts to develop biorenewable-based platform molecules. An early example was DuPont's effort in making 1,3-propanediol.[41] In contrast to making hydrocarbons economically from biomass, companies that have looked at making more highly functionalized molecules, that is, oxygenates, appear to be having more success in the market. One recent example is BASF's announcement of making polytetrahydrofuran (poly-THF) from a biorenewable feedstock.[42] Another example is Rennovia, which is now offering a variety of C_6-based molecules, such as adipic acid, from biorenewable feedstocks. This perhaps in retrospect is not surprising, as one way to improve the yield is to make molecules that are compositionally similar to the feed. In other words, because process economics are highly dictated by the feed cost, the need for less feed to produce a unit of product effectively lowers the feedstock cost. One very large but yet to be realized prize in this space is economically competitive biomass-based terephthalic acid.[43,44] This is a large space (with an estimated global consumption of 66 million tons in 2020), and as one moves more into consumer products from bulk commodity chemicals, the green differentiation might have true market value at cost parity. Consistent with these observations, real scientific advances have been made in both the use and understanding of how solid Lewis acids, such as tin zeolites, facilitate the interconversion of small model biomass compounds, such as glucose, fructose, and hydroxymethylfurfural.[45,46]

In summary, this is a highly active space. Clearly, the optimism around rapid implementation of economically viable transportation fuels from biomass was misplaced. However, the science is advancing; like any emerging sector, there are clear business examples of successes and failures. For now, biomass is not economically competitive enough to displace petroleum for transportation fuel production. However, a large uncertainty around all of this is how future political factors around carbon taxes and other sustainability issues will factor.

Biomass, however, appears to have more potential as a feedstock for highly oxygenated molecules. The first successes will likely be in specialty and smaller (by commodity chemical standards) volume niches, where the target molecules are compositionally similar to the biomass feedstock.

Recycling and Reuse Versus Feed

In contrast to the feedstocks considered previously, here two other possible feeds are described, which fall under the theme of recycling and reuse: carbon dioxide and recycled plastics. This differentiation is appropriate, as both of these potential feeds are waste products. As outlined later, whereas both have strong drivers for use from a sustainability vantage, both face severe but very different challenges for utilization.

Carbon dioxide

One train of thought to deal with rising atmospheric carbon dioxide levels is the use of carbon dioxide as a feedstock with the admirable goal of closing the carbon cycle completely. However, the production of hydrocarbons from carbon dioxide is problematic not from a chemistry viewpoint but rather an energy vantage. To quantify this, the standard-state Gibbs free energies of carbon dioxide and methane are -394.4 and -50.5 kJ/mol, respectively, a difference of 344 kJ/mol on a carbon basis. If the goal of using carbon dioxide to make fuels is to reduce CO_2 emissions and levels, this energy will need to come from a fossil-fuel free source. If one had such quantities of renewable energy, it would likely be used for other things, for example, electricity generation. Another challenge is the yield issue; if the goal is to make nonoxygenated molecules from CO_2, that is, C_nH_{2n+2}, the best one can do is to use 12/44 of the molecule on a weight basis if one removes all the oxygen; that is, intrinsic best case yield is 27 wt %. In short, the conversion of carbon dioxide to hydrocarbons is less of a chemistry problem (see later) and more intrinsically of a yield and energy problem.

All of the challenges of converting biomass to hydrocarbons are present in a much more severe form, that is, when going from C_1O_2 to C_1H_2. There seem to be two feasible approaches. The first option is to react carbon dioxide with something highly unstable; this will leave some or all of the oxygen in the product molecule. The second option is adding energy to reduce the carbon dioxide via oxygen rejection. Currently, hydrogen is mainly used as the energy source. Thus, it would seem that the real question to answer is if we have the ability to make hydrogen renewably on a large scale and do not want to transport or use it in the form of H_2, is carbon dioxide the best molecule to use to store the energy from hydrogen? It is a virtual certainty that the answer to this question would be varied.

This said, the problem does have a silver lining: there are existing technologies wherein carbon dioxide is the active molecule, most notably methanol synthesis.[47–49] Thus, it is possible at present to, for instance, shift the CO/CO_2 feed ratio in a methanol plant. The price is, of course, lower methanol yields because of equilibrium constraints. Another topic that has drawn considerable attention is dry reforming:[25]

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$$

Here is a direct route to the production of hydrogen-lean syngas. However, there is an energetic penalty in replacing water (for dry reforming) with carbon dioxide that must be paid. Thus, it becomes clear quickly that unless one has energy from a non-fossil-fuel source, none of these processes are net carbon dioxide consumers. These observations lead to the conclusion that these types of processes are intrinsically disadvantaged relative to existing technologies. However, it should also be clearly noted that there are many materials that very efficiently catalyze the conversion of carbon dioxide to value-added chemicals. Thus, in contrast to methane utilization for chemicals, carbon dioxide utilization is an energy problem not a chemistry problem. Given sufficient amounts of energy, it is possible with current technologies to make chemicals with carbon dioxide as a feed source. At present, the financial incentives are not present to justify such processes.

A different approach to this problem is the use of solar photoreduction schemes. This field is in its infancy. Advancing the scientific understanding of how to capture solar energy and store it in chemical bonds is worth pursuing. This work is on a different timescale for implementation compared to the other topics described here. This review does not focus on this topic, as the review literature in this field is recent and abundant.

Recycled plastics

Another possible feedstock, with very different challenges than those outlined previously for carbon dioxide, is recycled (i.e., depolymerized) plastics. The driver for this is simple: the chemical industry produces huge quantities of polymers. If one considers just the plastics with recycling numbers, such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), and polyvinyl chloride (PVC), these five polymers alone represent over 200 million tons per year, with that of PE alone being over 80 million tons per year. This is a large carbon source. Put in a different context, approximately 37.5 million metric tons of carbon are used per year in global methanol production, whereas approximately 68.6 million metric tons of carbon are used in global polyethylene production. The comparison shows both the scale of polymer production and the potential allure of using recycled plastics as a feedstock.

Beyond the previous reasons, there are two major reasons for considering recycled plastics as carbon feedstocks. The first is sustainability. Currently, the majority of polymers are disposed of in landfills after a single use. In 2009, less than 10% of all plastics in the United States were recycled; however, that number is rising, particularly around plastic bottles (with a 28% recycling rate in 2009). Nonetheless, huge quantities of polymers are landfilled. The second rationale is chemistry driven. The polymers listed previously are much closer compositionally to the desired products in the chemical industry than biomass, coal, or carbon dioxide. Thus, in principle, it should be possible to take, for instance polyethylene, and deconstruct it back into smaller units for subsequent reprocessing into chemicals.

There are two major barriers to the use of recycled plastics as chemical feedstocks. The first is that recycled plastics tend be diffuse, and so, concentrating these at the scale needed for a commodity chemical plant feedstocks, hundreds of thousands of tons a year, is nontrivial. This will necessitate stronger interactions between chemical producers, the waste handling industry, and even end users. These interactions are starting to appear. Alternatively, this could be accelerated via political forces; it is no accident that countries with much higher population densities and minimal access to local feedstocks (e.g., Japan) have much higher recycling rates than those with much lower population densities (e.g., the United States). The second challenge is that plastics contain much more than polymers. Pigments, fillers, modifiers, and so on lead to the final plastic material being highly complex. These two points have, by and large, led to waste plastics being used as fuels or being made into syngas for subsequent upgrading. Thus, it is clear there that is an opportunity for the industry. To date these waste plastics have been used, by and large, for only their heating and fuel value. For recycled plastics to be reconverted into higher value products, a clear technological need is the development of better separation schemes to remove pigments, fillers, and additives in thermoplastics.

Conclusions

We live in an era where the fuel and commodity chemical sectors are built on very mature technology based on oil and gas. For a variety of reasons, there is interest in expanding these sectors to feedstocks beyond oil and gas. However, the competition will be fierce; the sector did not arrive at the choice of petroleum and gas and feedstocks by accident. They are high-energy-density materials and relatively inexpensive (cf. the price of a gallon of fuel to a gallon of bottled water), and there is an amazingly integrated infrastructure in these sectors that wastes nothing. Thus, the bar is high in displacing them. The hope of this Perspective is to give the reader a basis for thinking about different feedstocks, the challenges they face, and thus under what set of circumstances they would fill targeted needs.

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