

Shale Gas Revolution: An Opportunity for the Production of Biobased Chemicals?*

Pieter C. A. Bruijninx* and Bert M. Weckhuysen*

aromatics · biomass · butadiene · catalysis · shale gas

The Shale Gas Revolution

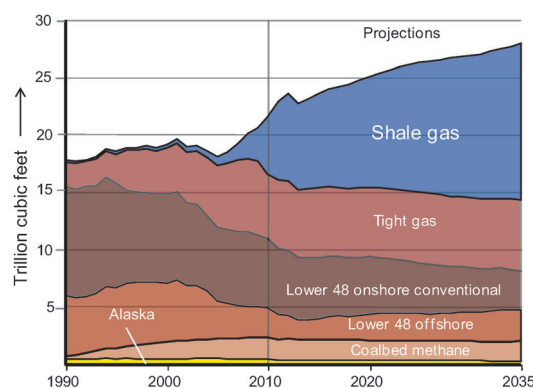
The current shale gas revolution is causing much excitement because it is leading to job creation, economic growth, and projected energy independence. Yet, at the same time, it causes concerns about the environmental impact, industrial competitiveness, and the resulting geopolitical changes. In the Netherlands and elsewhere, the topic features prominently in the media and political discussions, with pros and cons being extensively debated. Most of those involved do agree on one thing: the potential of the large-scale exploration of shale gas, and of related resources, such as shale and tight oil, to become a game changer for the chemical industry. Indeed, companies are rapidly adjusting to the change in energy flows, trying to take advantage of the cheap resources that now flow abundantly, at least in certain places on earth.

The shale gas revolution, in essence the (local) availability of cheap natural gas as a nonconventional fossil fuel (Figure 1a), might adversely influence another nascent revolution, that is, the necessary transition from a fossil resources-based society to one that produces its energy carriers, chemicals, and materials in a more sustainable manner. Actually, the shale gas revolution is often seen as a direct threat to the many current efforts aimed at the renewable fuels and chemicals production, or more generally put, the desired transition towards a biobased economy. While cheap and abundant, shale gas might indeed pose a considerable threat to biofuels production, we would like to argue here that rather than a threat, it provides exciting new opportunities for the production of a selection of biobased chemicals. Indeed, the shale gas revolution might actually enable the large-scale production and implementation of the first wave of biobased bulk chemicals, such as butadiene and aromatics.

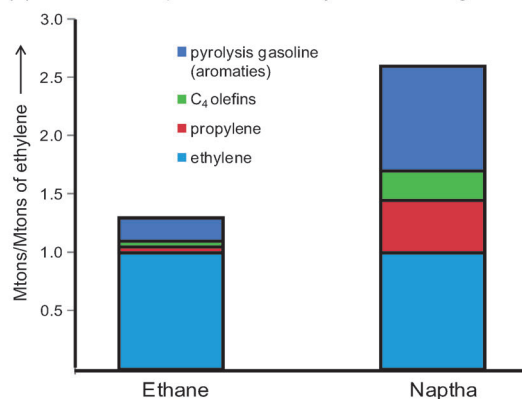
[*] Dr. P. C. A. Bruijninx, Prof. Dr. B. M. Weckhuysen
Inorganic Chemistry and Catalysis
Debye Institute for Nanomaterials Science, Utrecht University
Universiteitsweg 99, 3584 CG Utrecht (The Netherlands)
E-mail: p.c.a.bruijninx@uu.nl
b.m.weckhuysen@uu.nl
Homepage: <http://www.anorg.chem.uu.nl>

[**] P.C.A.B. acknowledges the Netherlands Organization for Scientific Research (NWO) for a Vernieuwingsimpuls Veni Grant. B.M.W. acknowledges the European Research Council (Advanced ERC grant), NWO (Top research grant) and the CatchBio program for funding.

(a) Natural gas production in the US by source



(b) Feedstock-dependent cracker yield of building blocks



(c) US olefin production from steam crackers

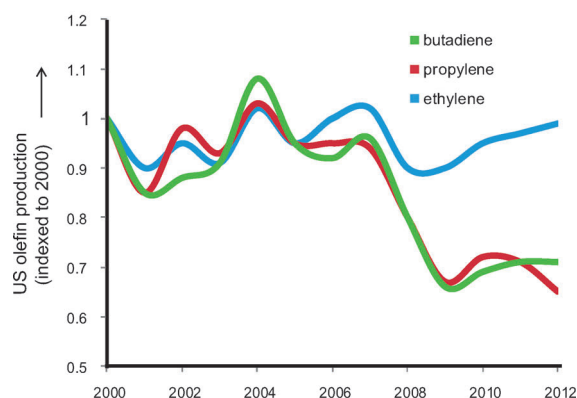


Figure 1. Setting the scene: The increased production of shale gas (a) will have consequences for the product output of ethylene crackers (b). The impact is exemplified by the decoupling and drops in propylene and butadiene production from ethylene (c). Adapted from the Annual Energy Outlook 2012 (<http://www.eia.gov>).

A Threat to Biofuels Production?

Even though the volume of the shale gas reserves and the economics of their exploration are still hotly debated,^[1,2] the extraordinary recent growth in US shale gas production, which might be complemented in the (near) future with exploration and production in European countries, such as Poland, China, Australia and other places, is already having a profound influence on global energy flows. According to the “World Energy Outlook” of the International Energy Agency (IEA), shale gas exploration is expected to turn the US into a net natural gas exporter by 2020.^[3] This remarkable shift is already evidenced, for instance, by the retrofitting of storage facilities in the Gulf of Mexico region originally constructed for incoming fossil fuel supplies, but now intended to store liquefied natural gas meant for export. The IEA also projected a net export of oil in 2030, making the US self-sufficient in terms of net energy use, but this prediction has been questioned.^[2]

Such large changes in the composition of the energy mix of the largest economy on earth will inevitably have a profound impact on the global efforts to replace fossil resources with renewable ones, a transition that is ultimately aimed at reducing carbon emissions and mitigating the adverse effects of climate change. The economic viability of the renewable liquid transportation fuels that are currently being developed, often aided by government subsidies and mandates, will clearly be impacted. The IEA report indeed warns that fossil fuels will continue to dominate the global energy mix, further complicating the global efforts to make our energy consumption more sustainable.^[3,4]



Pieter C. A. Bruijninx, born in 1979 in Roosendaal, The Netherlands, obtained his Master's degree from Utrecht University (The Netherlands) in 2002 and his Ph.D. degree in 2007. He then moved to the University of Warwick (UK) to work as a postdoctoral research fellow in the group of Prof. Peter Sadler on an NWO Rubicon grant. In 2009, he joined the Weckhuysen group as an Assistant Professor to work on the catalytic conversion of biomass and renewables for the production of bulk and fine chemicals. He is the recipient of an NWO Veni grant.



Bert M. Weckhuysen, born in 1968 in Aarschot, Belgium, received his Master's degree from Leuven University (Belgium) in 1991 and his Ph.D. degree in 1995 under the supervision of Prof. Schoonheydt. He was a postdoctoral fellow with Prof. Wachs (Lehigh University) and Prof. Lunsford (Texas A&M University). He has been Full Professor of Inorganic Chemistry and Catalysis at Utrecht University since 2000. He has received several awards including the Paul H. Emmett Award in Fundamental Catalysis in 2011, the International Catalysis Award in 2012, and the Bourke and Spinoza Awards in 2013.

Typically four arguments are presented for necessity of alternative technology development to alleviate our dependence on fossil resources: dwindling supply, rising prices, political instability in the areas where the more conventional fossil resources are located and, arguably most importantly, the concerns regarding climate change that are associated with their use. While the shale gas boom will mitigate the importance of the first three, it does not reduce, but rather increases the urgency of the fourth argument. With the prospect of economic growth and energy independence, it seems unlikely that shale gas exploration will be limited or regulated, despite the concerns regarding its potential environmental impact. In particular groundwater contamination has been regarded as a source of concern, with a recent study linking methane in drinking water to shale gas extraction.^[5]

A telling example is the current lobby to amend the US Renewable Fuel Standard (RFS), originally intended to provide a trajectory for renewable fuels to enter the market, to include natural-gas-based fuels as a “domestic alternative”.^[6] The RFS mandates that only renewable feedstocks (e.g. corn or lignocellulosic material) can be used for ethanol production and has so far mainly benefited corn farmers, with cellulosic ethanol production still lagging behind its projected production volumes. Ethanol can also be produced, however, from cheap shale gas in a process that is proposed, for instance, by Celanese Corp. to be more than cost-competitive. This alternative, yet clearly nonrenewable technology for ethanol production, marketed by emphasizing drought resistance and independence of food prices, might improve energy independence, but defeats the purpose, of course, of mandating the use of renewable fuels to lower carbon emissions. To urge lawmakers to include such alternative, US-based, yet nonrenewable fuels in the RFS is questionable and provides a threat to cellulosic ethanol production. These developments show the difficulties that are faced by the biofuels production processes, in particular the development of new technology to produce second- or third-generation transportation fuels that would have better fuel properties than bioethanol. The fact that coal-fired plants have to file for bankruptcy and cannot compete for energy generation might not bode well for the less-developed, biomass-based energy generation technologies.

It has also been argued, however, that as advanced biofuels producers often require hydrogen for the hydrodeoxygenation and hydroprocessing of biomass feeds to produce liquid transportation fuels, they might be able to take advantage of the drop in natural gas prices. As hydrogen is produced mainly from natural gas, the various commercial-scale biorefineries worldwide that are operational or planned and heavily use hydrogen (e.g. by (catalytic) fast pyrolysis processes), will become cheaper to operate.^[7] To consider shale gas as a partial enabler for advanced biofuels production seems a bit counterintuitive, but the cheap natural gas might help the biofuels producers gain a firmer footing and enter the market, after which technologies that produce hydrogen from sustainable sources could take over.

In any case, the influence of shale gas on biofuels production will ultimately depend on proven production capacity and (fluctuations in) the price of the nonconven-

tional resource, on the legislation and mandates steering the composition of the energy mix, and on the speed with which scientific and technological breakthroughs for efficient renewable fuel production are developed and implemented. It should be noted in this sense, that biofuels were never expected to fulfill the entire global energy demand, but are rather a transition solution to ultimately arrive at a diverse, sustainable energy mix in which biomass-derived liquid transportation fuels are complemented with renewable energy captured from the sun (be it as electricity generated by wind or tidal changes or as solar fuel energy vectors, for instance in a “solar refinery”).^[8] While the shale gas revolution may be a few years too late to really stop the production of biofuels, or more generally the biobased economy, in its tracks, it is certainly expected to influence the scale on which biofuels will be produced and it might narrow the window of opportunity in which advanced biofuels can play their important transitional role to a more sustainable society.

An Opportunity for the Production of Biobased Chemicals?

The shale gas revolution might have a silver lining, however, if we consider its impact on the production of biobased chemicals. Indeed, increased reliance on (nonconventional) natural gas as a feedstock for the petrochemical industry will actually lead to a shortage of key building blocks for the chemical industry (Figure 1b,c). This provides a clear opportunity for biobased alternatives. Rather than focusing solely on the production of biofuels, such as cellulosic ethanol, advanced biofuel producers are expected to diversify and, analogous to current petrochemical refineries, evolve to fully fledged biorefineries that show the integrated production of a slate of products, including both drop-in (i.e. molecularly identical) biobased fuels as well as drop-in biobased commodities and specialty chemicals. The necessity of the co-production of base and fine chemicals as well as materials in addition to biofuels for a biorefinery to be more economically viable has been advocated.^[9,10]

The impact of shale gas on chemical production is felt in different ways. First, as a result of the large differences in natural gas price, refineries outside of the US, in particular in Europe and Japan, will find it increasingly difficult to compete with the American ones. Over the period 2005–2012 natural gas prices rose 35 % in the EU and dropped 66 % in the USA,^[11] and the cost of making petrochemicals is down 50 % in the USA and up 20 % in Europe compared to five years ago.^[12] These developments have led the largest German chemical manufacturers, BASF and Bayer, to voice their concerns, emphasizing the real threat to conventional, petrochemical manufacturing capabilities in Europe.^[13] Sabic also recently shut down some of its manufacturing capacity in Europe, again citing the stiff competition from US based, shale-fueled producers. Locally, the shale gas revolution thus directly threatens the economic viability of traditional manufacturers, and as a consequence, job security and economic prosperity.

A few cautionary comments should be made here regarding the influence of possible price fluctuations of natural gas on the impact of chemical production. Indeed, as shale gas prices are decoupled from the price of petroleum in the US but not elsewhere, US oil and gas companies are lining up to sell the shale gas bounty abroad.^[14] More than 20 natural gas exporting facilities are now being built or have been proposed, in particular in the Gulf of Mexico region, sufficient to export over a third of the domestic liquefied natural gas (LNG) consumption. If and how much should be exported is currently being debated, as oil/gas companies argue that exporting shale gas as LNG will have little impact on domestic (US) prices, US-based chemical companies on the other hand are afraid that large export volumes will undercut their international competitiveness and that the abundant supply of natural gas would be better used to further manufacturing domestically.^[14] As a rule of thumb, US chemical producers need a ratio higher than six to one for the price of a barrel of oil to 1000 cubic feet of natural gas for domestic manufacturing investments to be competitive. The current, very favorable ratio is in the high twenties, but might fall if large volumes of gas are exported. LNG exports are thus becoming a contentious issue, with Dow Chemical even leaving the National Association of Manufacturers advocacy group (the largest US industrial trade organization) for the latter's support of LNG exports and has joined another advocacy group, America's Energy Advantage, which aims to limit export licenses for LNG. Issues on the production side might also lead to increases in the price of natural gas. Indeed, maintaining supply levels requires ever-increasing drilling of new wells (with the low-hanging fruit, the “sweet spots”, already being exploited). In this light, it has been argued that the large investments in infrastructure needed to maintain the supply actually are not covered by the sales price of natural gas, requiring prices to go up to remain economically viable.^[2] While some price increase might therefore be expected, chemical producers in the US are still expected to have a significant advantage over, for instance, chemical manufacturers based in Europe and Japan.

The second consequence of the shale gas revolution will impact us all in the same way, however, as it could lead to a tight global supply of key commodity chemicals. This projected scarcity is largely related to changes in the production of ethylene. Ethylene is predominantly produced by steam cracking facilities, which were typically fed with the naphtha fraction of crude oil. These installations are now increasingly being retrofitted, or even newly built, to convert lighter, shale-derived feeds to ethylene. Ethylene is not the only product of a naphtha cracker, however, as propylene, butadiene as well as the aromatics benzene, toluene, and xylenes (BTX) are obtained as valuable co-products in the process. Figure 1b shows the change in product composition per unit of ethylene produced from either ethane (i.e. shale-gas-derived feed) or naphtha. It is clear that new on-purpose production routes, ones that are not coupled to ethylene production, are needed to make up the shortages in C₃/C₄ olefins and aromatics and the value chains that are connected to these building blocks.

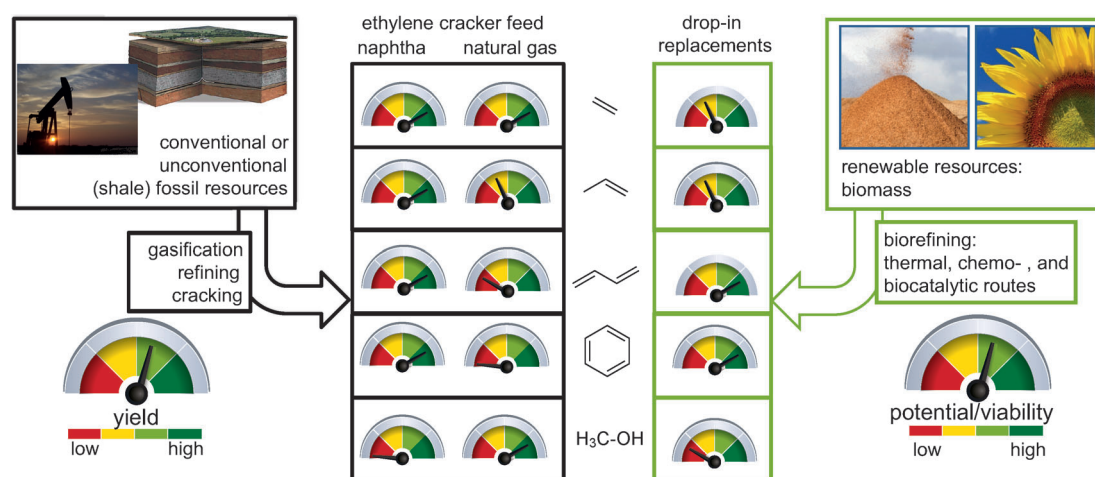


Figure 2. A typical petrochemical refinery produces five major building blocks. A shift to lighter feeds, such as shale gas, will strongly impact the availability of propylene, butadiene, and aromatics (BTX, benzene, toluene, and xylene). Methanol, predominantly produced from syngas, will not be affected much. On-purpose renewable-based production routes for butadiene, BTX, and, to a lesser extent, propylene have the potential to address shale-gas-related scarcity of these building blocks and as a result make the chemical industry more sustainable.

While tight or shale oil might also be able to replace heavy naphtha as feedstock for naphtha crackers in some cases, it should be noted that forecasted production volumes are still unclear,^[2] and that the tight oils seem to be more paraffinic and lighter than the traditional sources of crude oil. Indeed, as argued below, biomass-based routes seem very well suited for the on-purpose production of these bulk chemicals. As the biobased chemicals need to be able to compete in price, availability and cost of the renewable feedstock are very important for economic viability. For example, for fossil BTX, about 60 % of the price is accounted for by feedstock costs. Of the various types of biomass feedstock, wood (chips) seems to be very attractive in this regard. A telling sign of its cheap availability is that currently wood pellets are being shipped from Canada to the Netherlands to be used for energy generation. Surely, if this is a viable option for fuel production, higher value products, such as base and fine chemicals, should be able to make use of this source as well.

In this essay, we highlight the many opportunities for the production of biobased commodity chemicals in view of the recent shale gas revolution (Figure 2). It is important to note that this article is by no means intended to provide a comprehensive review, but rather to show the current trends by a selected number of approaches, that is, developments in industry and routes explored by academia.

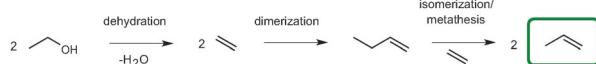
Opportunity 1: Olefins. As a result of cheap ethylene production from light feeds, such as tight oil, global propylene and butadiene production capacity will become increasingly tight and eventually fall short of demand (Figure 1c). For example, naphtha-fed and ethylene-fed crackers produce about 16–18 tons and two tons of butadiene per 100 tons of ethylene, respectively. Indeed, US production of crude C₄ olefins has dropped 20 % since 2007, with butadiene prices more than doubling as a result. On-purpose production routes for propylene are desired,^[15] but for this particular chemical shale gas exploration actually offers a solution, as the large increase in propane that is recovered from underground reservoirs allows for the production of propylene by propane

dehydrogenation instead. The announcement of Clariant, for instance, to expand its capacity for the manufacturing of its Houdry dehydrogenation catalysts, aimed at propane and butane dehydrogenation to propylene and butadiene, illustrates the increased importance of this conversion.

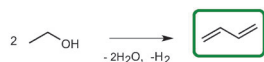
Large propane dehydrogenation plants are now being operated or are announced, for instance by Petrologistics and Dow Chemical. Other dedicated propylene production routes include Sinopec's deep catalytic cracking of gas oil, a zeolite-catalyzed process that can be run in conventional fluid catalytic cracking (FCC) reactors, but produces more propylene and less gasoline than a conventional cracking process. The use of syngas, which can be obtained by gasification of coal, natural gas, and biomass, has also received much attention in this respect. Direct routes such as Fischer–Tropsch-to-olefins^[16] and indirect, methanol-based routes such as methanol-to-propylene (MTP)^[15] are being explored in particular in China, which has abundant reserves of coal but limited supplies of naphtha or natural gas, with the world's first commercial MTP plant being operated at Shenhua Baotou.

The efforts aimed at producing renewable propylene, derived from biomass-derived building blocks, are quite limited and process maturity is still quite low. Braskem, for instance, is constructing a plant for sugar ethanol-based polypropylene that involves a process in which ethanol-derived ethylene is dimerized to (ultimately) 2-butene, which is subsequently converted to propylene and ethylene by olefin metathesis (Figure 3). The latter metathesis step of the process is mature technology (e.g. the Lummus process) and considered an economically attractive production route for propylene if use can be made of the economy-of-scale. A biotechnological glucose-to-propylene route has been proposed by Global Bioenergies, using the same artificial metabolic pathway that is used by the company for the production of bio-isobutene. While petrochemical propylene production will most likely be more competitive in the short term, sugar fermentation-based routes that use price-advan-

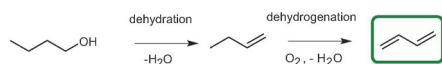
a) ethanol-to-propylene:



b) ethanol-to-butadiene:



c) 1-butanol-to-butadiene:



d) tetritol-to-butadiene:

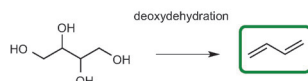


Figure 3. Selected examples of renewables-based routes for the production of propylene and butadiene.

tagged feedstocks (i.e. lignocelluloses) are thought to be able to compete for the long term.^[17]

As with propylene, the increase in butadiene price might be bad for business and consumers (car tires have for instance become considerably more expensive partly as a result of the shale gas revolution^[18]), but will also encourage the development of on-purpose production technologies, which might also be sustainable and renewables-based. Butadiene production actually used to be a rather green process: the ethanol-to-butadiene Ostromislenskiy and Lebedev processes were developed in the first half of the 20th century and commercially operated (Figure 3), with larger volumes of butadiene being produced in the US in 1944 from ethanol than from petroleum.^[19] In the second half of the 20th century, this route lost its economic competitiveness to butadiene production by steam cracking. Nonetheless, as a result of the availability of low-cost ethanol and the changes in ethylene production, the ethanol-to-butadiene process is currently experiencing a renaissance with efforts aimed at improving the chemocatalytic conversion efficiency of the process.^[19] This development is part of a more general trend, in which bioethanol is not only considered a biofuel but also a potential biobased building block for the chemical industry. If sustainably produced by second- or higher-generation technologies, preliminary techno-economic sustainability assessments show bioethanol can become a major renewable resource with butadiene and diethyl ether production holding the most promise, followed by the production of ethylene, propylene, acetaldehyde, ethylene oxide, and ethyl acetate.^[20]

Alternatively, butadiene can also be obtained from various routes that involve butene as the key intermediate. For instance, 1-butanol, which is produced through sugar fermentation by companies, such as Gevo and Cobalt, can be dehydrated in an acid-catalyzed step to 1-butene, followed by (oxidative) dehydrogenation to yield 1,3-butadiene (Figure 3). The latter step is known technology and the process was operated at more than one million tons per year under the tradename Oxo-D in 1960–1980s. Currently, butene dehydrogenation accounts for only 5% of the butadiene production,

but depending on the availability of *n*-butanol and price increases of steam cracker-derived butadiene the process might become more competitive again.^[21] It should be noted though that 1-butanol in itself is also a valuable chemical and that its conversion to butene is a step back in the value chain. Plans for butane-based routes have also been announced, for instance by the TPC group (the biggest converter of crude C₄ olefin to butadiene in the US today) who aim to combine a butane-to-butene step with the previously practiced Oxo-D butene-to-butadiene process.

Another approach to butadiene production from renewable resources would be by butanediol dehydration. 2,3-Butanediol is an intermediate that can be produced by fermentation and its dehydration using thorium oxide as the catalyst was explored in World War II as an alternative route to synthetic rubber production.^[22] A recent collaboration between the nylon-producer Invista and the biotech firm Lanzatech is aimed at the production of 2,3-butanediol by fermentation from the industrial waste gas CO, followed by conversion to bio-butadiene in a two-step process. Alternatively, Genomatica reported the production of butadiene by dehydration of 1,4-butanediol, which is again obtained by fermentation. However, the difficult and costly separation of the diols from the fermentation broths might hamper the economic feasibility of these routes. Also, Shiramizu and Toste recently showed that sugars and sugar alcohols could be readily deoxygenated in a rhenium-catalyzed deoxydehydration reaction, including an example of the conversion of tetritols to butadiene (Figure 3).^[23]

Isoprene, another major component of rubbers and elastomers, is typically produced in 2–5% yield as a byproduct of ethylene production by naphtha or gas oil cracking. Similar to the butanol-to-butadiene conversion, Gevo has also proposed the production of the C₅-diene isoprene from pentanol again by a combination of bio- and chemocatalytic processes, including fermentation, dehydration, and dehydrogenation steps. It is claimed, as an additional advantage, that the butadiene and isoprene obtained are substantially purer than those obtained by petrochemical processes.^[24] As with bio-butadiene production, the desire of major rubber users for biobased synthetic rubbers is also driving the manufacture of bio-isoprene. Indeed, various combinations of producers/end users, for example, Ajinomoto/Bridgestone and Dupont/Goodyear, have developed (fermentative) routes for bio-based isoprene. Amyris and Michelin have also announced plans for the microbial production of renewable isoprene from Brazilian sugarcane, to be used in synthetic rubber and specialty chemical applications such as adhesives, coatings, and sealants. Chemocatalytic routes to bio-isoprene can be based on isobutene, obtained by fermentation,^[25] and involve, for instance, the condensation with formaldehyde in the Prins process.

Opportunity 2: Aromatics. In addition to the olefins ethylene, propylene, and butadiene, the aromatics benzene, toluene, and xylenes (BTX) constitute the other main class of building blocks for the chemical industry. The shift in cracker feedstock also greatly impacts the production of these aromatics, as the major BTX production routes are connected to naphtha and its conversion by either steam cracking or by

catalytic reforming. Some estimates suggest that aromatic cracker output is already down by some 20% in the US. At the same time, the demand for aromatics is expected to rise by 5–10% annually.

Various alternative routes for on-purpose BTX production are being explored, of which a few are renewable-based. Compared to the olefins discussed above, most of the processes studied still seem to be in the early stages of research, however. For instance, a new route has recently been reported that produces *p*-xylene using only ethylene, which can of course be obtained both from shale gas as well as from bioethanol. The multistep conversion process consists of Cr catalyzed ethylene trimerization, Ir catalyzed transfer dehydrogenation, Diels–Alder reaction of the diene with ethylene, and finally dehydrogenation of the Diels–Alder adduct over a platinum-based catalyst to give *p*-xylene (Figure 4).^[26] Although so far only a proof-of-principle has been reported, this elegant route might be of interest given the cheap availability of ethylene.

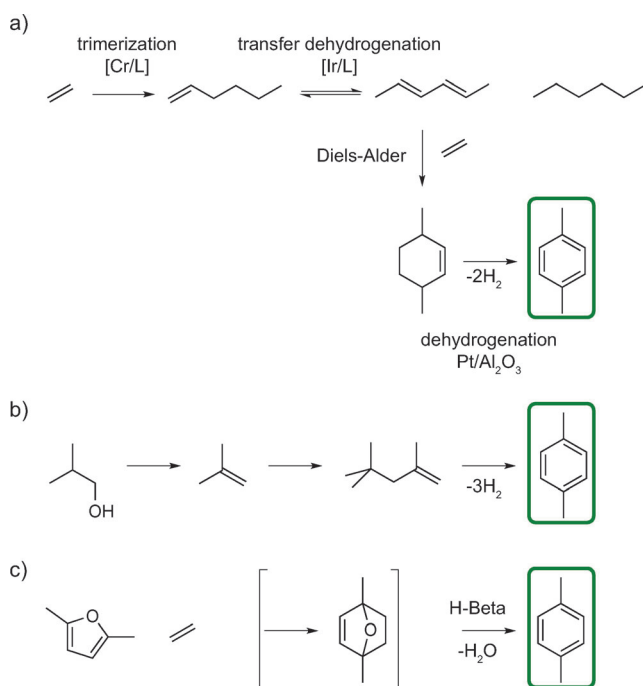


Figure 4. Three different routes to potentially renewable-based *p*-xylene: a) ethylene-to-*p*-xylene route reported by Brookhart and co-workers;^[26] b) isobutanol-to-*p*-xylene route operated at pilot-plant scale by Gevo; c) Diels–Alder aromatization of dimethylfuran and ethylene as reported by Dauenhauer and co-workers.^[32]

The different approaches taken in the few notable examples of renewable aromatics production processes that have already been brought closer to commercialization can be illustrated with one of the biggest challenges in the plastics industry: to come up with a fully renewable polyester for soft drink bottles. The largest obstacle to this is replacing the terephthalic acid used nowadays in PET bottles with a renewably sourced alternative, be it a drop-in one (i.e. bio-terephthalic acid) or a functional replacement. Many differ-

ent approaches are currently being explored, with Coca-Cola having identified three partners with attractive technologies.^[27] Gevo and Virent both aim at the production of a drop-in replacement by producing *p*-xylene, the petrochemical precursor to terephthalic acid (see, for example, press releases by both companies). Gevo uses a yeast-based fermentation process that converts lignocellulosic sugars into isobutanol, which is converted to isobutylene, dimerized to isooctane, and subsequently dehydroaromatized to aromatics containing more than 90% *p*-xylene (Figure 4). Alternatively, Virent converts water-soluble sugars by aqueous phase processing to a hydrocarbon mixture that is very similar to the reformates that are now produced by petrochemical refining. The mixture, formed in Virent's bioforming process, is claimed to contain about 65% aromatics. This mixture can be further refined and converted with the current infrastructure and processes. Avantium's approach is rather different, as it targets the replacement of terephthalic acid by 2,5-furandicarboxylic acid, which is produced by chemocatalytic conversion of C_6 -sugars such as glucose or fructose.^[28] The resulting polyethylene furanoate (PEF) is said to have gas-barrier and thermal properties that are superior to PET. Of course, introducing new products or building blocks to the plastics market comes with considerable challenges, but if such new products do indeed show improved performance they will have considerable potential to become the next-generation polyester.

Furanics, such as 5-hydroxymethylfurfural or furfural, which can be obtained from the hexose and pentose sugars in lignocellulosic biomass, are expected to become important biobased molecules and their production and further conversion to renewable chemicals and fuels are being extensively studied.^[29,30] A particularly interesting route is the further conversion of these furans to traditional drop-in aromatics, such as toluene, *p*-xylene, or more highly functionalized aromatics. An attractive route is the Diels–Alder addition/aromatization of the various furanics, for instance using ethylene as the dienophile. UOP recently claimed the production of *p*-xylene by a Diels–Alder/aromatization reaction of 2,5-dimethylfuran and ethylene (Figure 4).^[31] For the same reaction, Dauenhauer and co-workers recently showed that the use of the zeolite H-Beta as catalyst leads to very selective *p*-xylene formation, obtaining a yield of 90%.^[32] Shiramizu and Toste also reported on a sequence of reactions involving the Diels–Alder aromatization of dimethylfuran and acrolein (rather than ethylene) as a key step for the production of biobased *p*-xylene.^[33] The Diels–Alder approach thus constitutes an elegant and attractive pathway to renewable aromatics, but the *p*-xylene routes probably need to be further improved to become economically viable.^[28]

It should be noted that the processes aimed at renewable aromatics mentioned above are all based on the sugar fraction of biomass. The lignin fraction of lignocellulose might, however, be a more obvious source of renewable aromatics. The production of cellulosic ethanol, which also produces large amounts of lignin as waste, has led to significant research directed at lignin-to-aromatics conversion and chemocatalytic,^[34] biocatalytic,^[35] and thermochemical^[36]

routes for its depolymerization to aromatics are being extensively studied. Lignin's recalcitrant nature and the difficulties encountered in lignin depolymerization have, however, severely hampered its conversion into drop-in aromatics (leading to the too often-heard, and by now somewhat stale joke "you can make anything out of lignin, but money"). While the commercial production of the specialty chemical vanillin from lignin by Borregaard is an example of a successful lignin valorization process, lignin-derived BTX production processes are still in their infancy.

While most state-of-the-art depolymerization processes still typically show limited yields of often complicated mixtures of monoaromatics (10–20%), some recent examples report much improved yields, with nickel-based catalysts even yielding close to 50% of the monomeric aromatics propylguaiacol and propylsyringol.^[37] The products obtained are still highly oxygenated though and further deoxygenation to BTX is required. Be it by catalytic pyrolysis followed by upgrading of the lignin-derived bio-oil, by direct depolymerization/deoxygenation, or by stepwise reduction of molecular weight and oxygen content, steps are being made in the development of chemocatalytic lignin conversion processes and as with the sugars, pilot-scale commercial activities might be expected in the next ten years or so.

Finally, rather than converting either the sugar or lignin fraction, whole biomass can also be used for the production of aromatics. Promising approaches are based on thermochemical, catalytic fast pyrolysis processes. Anellotech, for instance, uses technology developed by Huber and co-workers (then at the University of Massachusetts, Amherst)^[38] to obtain aromatics from pyrolysis oils in a zeolite-catalyzed process or directly from biomass in a one-step process. Catalytic fast pyrolysis is also behind the production of biobased BTX from low-value biomass streams, for which a Dutch consortium named BioBTX is currently operating a kilogram-scale pilot plant. These recent developments illustrate the potential of lignin as a viable and renewable resource for the production of BTX.

Shale Gas as a Game Changer

One of the major consequences of the advent of shale gas production is that chemical producers are looking for feedstock diversification to keep up the production of their main building blocks. The projected scarcity of some of these key chemicals provides an excellent window of opportunity to further develop and encourage the switch to biobased commodity chemical production. Importantly, this transition would now not only be driven by the advocated necessity of producing biobased chemicals for reasons related to sustainability and environmental concerns, but will also be propelled by economic incentives. Government policies should aim to align and support these market forces, with legislation that can find justification in increased current consumer preference for renewable energy and biobased products. Many opportunities exist for the development of routes to biobased building blocks and materials.^[10,39,40] Given their large volume, the production of drop-in biobased olefins and aromatics

will nonetheless have the biggest impact and could lead the first wave of sustainable chemicals to be produced on a large scale. The many current efforts in this direction, some of which are highlighted above, show that impressive advances have already been made, often based on combinations of fermentative and chemocatalytic technology. Further technological advances are now required, particularly in the production of biobased BTX, to lead to breakthrough science and technology that can selectively valorize the various types of biomass.

Importantly, drop-in biobased bulk chemicals need to be able to compete on price (in contrast to new renewable building blocks, which can also compete on performance). A key challenge here might not be so much the availability of the feedstock, but rather its costs. Lignocellulosic biomass, including agricultural and wood-waste streams, should therefore be viewed as the end-goal feedstock.^[4] To drive down costs, improvements in growth, harvesting and distribution, as well as (energy) efficiency and selectivity of the pretreatment and bio- or chemocatalytic conversion are now required. With respect to the catalytic conversions, this means more robust and productive microorganisms for fermentation, and chemocatalysts specifically developed for the demanding conditions of selective conversion of a highly polar, highly oxygenated feed carrying various impurities that is often converted into the liquid phase. In addition to being on par economically, the production of biobased chemicals should also bring a clear environmental benefit (i.e. an improved footprint in terms of sustainability). Sustainability of new routes should always be compared with the petrochemical route by a careful technological and socio-economical analysis.

It is often said that the Stone Age did not end because we ran out of stones^[4] and that the age of oil will not end because we run out of fossil fuels. Ironically, one might indeed even think that the large-scale utilization of an unconventional fossil resource, such as shale gas, may usher in a new era of a more sustainable chemical industry that produces—at least in part—some of its main bulk chemicals from biomass. The future will tell if the described scenario may indeed come true. The answer to this question will, however, depend on the breakthroughs academia and industry can generate to effectively produce olefins and aromatics from biomass.

Received: June 12, 2013

Revised: July 13, 2013

Published online: October 18, 2013

[1] The proven and estimated reserves vary, as do the estimates at which price shale gas can be economically extracted. Price increases are expected, but on the short to medium term, cheap natural gas will still provide US-based manufacturers with a distinct advantage. Whether shale gas is a real long-term game changer, its impact on commodity chemicals production is already clearly felt. See also Ref. [2].

[2] J. D. Hughes, *Nature* **2013**, 494, 307.

[3] World Energy Outlook **2012**, <http://www.worldenergyoutlook.org>.

[4] S. Chu, A. Majumdar, *Nature* **2012**, 488, 294.

- [5] R. B. Jackson, A. Vengosh, T. H. Darrah, N. R. Warner, A. Down, R. J. Poreda, S. G. Osborn, K. Zhao, *Proc. Natl. Acad. Sci. USA* **2013**, *110*, 11250.
- [6] *Chem. Eng. News* **2012**, *90*(50), 6.
- [7] M. M. Wright, Y. Roman-Leshkov, W. H. Green, *Biofuels Bioprod. Biorefin.* **2012**, *6*, 503.
- [8] R. Schlögl, *Angew. Chem.* **2011**, *123*, 6550; *Angew. Chem. Int. Ed.* **2011**, *50*, 6424.
- [9] J. J. Bozell, G. R. Petersen, *Green Chem.* **2012**, *12*, 539.
- [10] E. De Jong, A. Higson, P. Walsh, M. Wellisch, *Biofuels Bioprod. Biorefin.* **2012**, *6*, 606.
- [11] http://ec.europa.eu/europe2020/pdf/energy3_en.pdf.
- [12] *Chem. Eng. News* **2013**, *91*(14), 28.
- [13] Financial Times, 9. Nov. **2012**; <http://www.ft.com/intl/cms/s/0/c7ff93d0-28ef-11e2-b92c-00144feabdc0.html#axzz2Sbwf3dmx>.
- [14] *Chem. Eng. News* **2013**, *91*(9), 9.
- [15] J. Ding, W. Hua, *Chem. Eng. Technol.* **2013**, *36*, 83.
- [16] H. M. Torres Galvis, J. H. Bitter, C. B. Khare, M. Ruitenbeek, A. I. Dugulan, K. P. de Jong, *Science* **2012**, *335*, 835.
- [17] Green propylene, report PERP07/08S11, Nexant Inc.
- [18] *Chem. Eng. News* **2013**, *91*(18), 24.
- [19] C. Angelici, B. M. Weckhuysen, P. C. A. Bruijninx, *ChemSusChem* **2013**, *6*, 1595.
- [20] J. A. Posada, A. D. Patel, A. Roes, K. Blok, A. P. C. Faaij, M. K. Patel, *Bioresour. Technol.* **2013**, *135*, 490.
- [21] M. Mascal, *Biofuels Bioprod. Biorefin.* **2012**, *6*, 483.
- [22] M. J. Syu, *Appl. Microbiol. Biotechnol.* **2001**, *55*, 10.
- [23] M. Shiramizu, D. F. Toste, *Angew. Chem.* **2012**, *124*, 8206; *Angew. Chem. Int. Ed.* **2012**, *51*, 8082.
- [24] M. Peters, J. Taylor, D. A. Henton, L. E. Manzer, WO2010099201A1, **2010**.
- [25] B. N. M. van Leeuwen, A. M. Wulp, I. Duijnste, A. J. A. van Maris, A. J. J. Straathof, *Appl. Microbiol. Biotechnol.* **2012**, *93*, 1377.
- [26] T. W. Lyons, D. Guironnet, M. Findlater, M. Brookhart, *J. Am. Chem. Soc.* **2012**, *134*, 15708.
- [27] *Chem. Eng. News* **2012**, *90*(4), 19.
- [28] M. A. Dam, G. J. M. Gruter, L. Sipos, E. De Jong, D. Den Ouden in *Society of Plastics Engineers—EUROTEC 2011 Conference Proceedings*.
- [29] L. Hu, G. Zhao, W. Hao, X. Tang, Y. Sun, L. Lin, S. Liu, *RSC Adv.* **2012**, *2*, 11184.
- [30] R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres, J. G. de Vries, *Chem. Rev.* **2013**, *113*, 1499.
- [31] T. A. Brandvold, US 2010/0331568A1, **2010**.
- [32] C.-C. Chang, S. K. Green, C. L. Williams, P. J. Dauenhauer, W. Fan, *Green Chem.* **2013**, DOI: 10.1039/C3GC40740C.
- [33] M. Shiramizu, D. F. Toste, *Chem. Eur. J.* **2011**, *17*, 12452.
- [34] J. Zakzeski, P. C. A. Bruijninx, A. L. Jongerius, B. M. Weckhuysen, *Chem. Rev.* **2010**, *110*, 3552.
- [35] T. D. H. Bugg, M. Ahmad, E. M. Hardiman, R. Rahmanpour, *Nat. Prod. Rep.* **2011**, *28*, 1883.
- [36] M. P. Pandey, C. S. Kim, *Chem. Eng. Technol.* **2011**, *34*, 29.
- [37] Q. Song, F. Wang, J. Cai, Y. Wang, J. Zhang, W. Yu, J. Xu, *Energy Environ. Sci.* **2013**, *6*, 994.
- [38] T. R. Carlson, Y.-T. Cheng, J. Jae, G. W. Huber, *Energy Environ. Sci.* **2011**, *4*, 145.
- [39] A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411.
- [40] C. O. Tuck, E. Perez, I. T. Horvath, R. A. Sheldon, M. Poliakoff, *Science* **2012**, *337*, 695.