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# What role for the bioeconomy in an electrified transportation sector?

Tristan R. Brown

*State University of New York College of Environmental Science and Forestry*

Robert C. Brown

*Iowa State University, rcbrown3@iastate.edu*

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# What role for the bioeconomy in an electrified transportation sector?

## **Abstract**

The growth of the bioeconomy has recently been slowed by over production of petroleum and natural gas from unconventional domestic reserves, which has reduced demand for biofuels. In the longer term, liquid transportation fuels, both petroleum- and bio-based, are threatened by electrification of the transportation sector, which will benefit from the use of low-cost natural gas to generate electricity for battery electric vehicles. Low-cost natural gas in the USA is attractive for other applications as well, including the production of certain petrochemicals. On the other hand, natural gas is not suitable for producing many high molecular weight petrochemicals. Cost-competitive biorenewable versions of these products will need to be commercialized if petroleum is to be displaced without causing substantial economic distortions. This article reviews the available bio-based pathways and the current state of research on their technical and, where available, economic feasibility.

## **Disciplines**

Energy Systems | Mechanical Engineering | Oil, Gas, and Energy | Other Economics

## **Comments**

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## **What Role for the Bioeconomy in an Electrified Transportation Sector?**

**Tristan R. Brown**, Department of Forest and Natural Resources Management, SUNY-ESF, Syracuse, NY 13210<sup>1</sup>

**Robert C. Brown**, Department of Mechanical Engineering, Bioeconomy Institute, Iowa State University, Ames, IA 50011

### **KEYWORDS**

Natural gas; biobased products; bioeconomy; petroleum refining; petrochemicals

### **ABSTRACT**

The growth of the bioeconomy has recently been slowed by over production of petroleum and natural gas from unconventional domestic reserves, which has reduced demand for biofuels. In the longer term, liquid transportation fuels, both petroleum- and biobased, are threatened by electrification of the transportation sector, which will benefit from the use of low cost natural gas to generate electricity for battery electric vehicles. Low cost natural gas in the U.S. is attractive for other applications as well, including the production of certain petrochemicals. On the other hand, natural gas is not suitable for producing many high molecular weight petrochemicals. Cost-competitive biorenewable versions of these products will need to be commercialized if petroleum is to be displaced without causing substantial economic distortions. This article reviews the available biobased pathways and the current state of research on their technical and, where available, economic feasibility.

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<sup>1</sup> Correspondence to: Tristan R. Brown, SUNY-ESF, 320 Bray Hall, 1 Forestry Drive, Syracuse, NY. Phone: 315-565-3003. Email: trbro100@esf.edu.

## 1. INTRODUCTION

The bioeconomy was originally premised on wide-scale replacement of petroleum-based transportation fuels with biofuels to improve energy security and environmental quality.<sup>1</sup> In the past decade, rapid advances in technologies for the extraction of fossil fuels and the manufacture of electric vehicles have challenged this premise, requiring a reassessment of the role of the bioeconomy in meeting national goals.

The most immediate threat to the bioeconomy has been the development of new fossil fuel extraction techniques such as hydraulic fracturing, which has caused the U.S. to become a major producer and exporter of both natural gas and petroleum. These new supplies of unconventional gas and petroleum have placed competitive pressure on producers of conventional petroleum, who have responded by increasing production, resulting in a glut of petroleum in world markets.<sup>2,3</sup> Rising fuel consumption in response to recent low prices has supported demand for 1<sup>st</sup>-generation biofuels such as starch ethanol and biodiesel by increasing the volume allowed by the 10 vol% blend wall, albeit at the expense of economic competitiveness.<sup>4</sup> However, oversupply has weakened the energy security argument that originally justified domestic biofuels production, prompting criticism about continuing biofuels mandates.<sup>5,6</sup>

The current oversupply of petroleum is a transient event as world demand is expected to grow significantly in the coming decades, eventually outstripping supply.<sup>7</sup> Higher future petroleum prices will also be necessary to support national budgets in major producers such as Saudi Arabia, while low current prices could prompt underinvestment and future supply shortages. Furthermore, continuing dependence of the transportation section on petroleum exacerbates the

problem of reducing greenhouse gas emissions into the atmosphere.<sup>7</sup> In the long term, more challenging to the aspirations of the bioeconomy is the rise of electric vehicles.

## **2. ELECTRIFICATION OF THE ELECTRIC SECTOR**

A longer term challenge to the role of the bioeconomy in the transportation sector has been improvements in battery-electric vehicles (BEV). As recently as 2012 a McKinsey & Company analysis concluded that BEVs were not cost-competitive with internal combustion engine vehicles (ICEV) despite the presence of relatively high fuel prices (\$13.25-\$15.14/liter) due to the high costs of lithium-ion battery packs (\$525-\$625/kWh).<sup>8</sup> Since then lithium-ion battery prices have fallen by an annual rate of 8% as BEVs have achieved commercial-scale production.<sup>9</sup> Large BEV companies such as Tesla and GM have recently stated that their lithium-ion battery packs now cost less than \$200/kWh.<sup>10</sup> In the next 9-14 years BEVs could become fully competitive with ICEVs on an unsubsidized basis if the current cost reduction trajectory is maintained (U.S. BEV purchasers currently receive federal and state tax credits while ICEV drivers must pay an excise tax on fuel purchases).<sup>11,12</sup>

Widespread vehicle electrification will have substantial impacts on the U.S. transportation energy landscape. The country's transportation infrastructure has historically been characterized by the consumption of refined petroleum products in light and heavy vehicles. Gasoline made up 54 vol% of the country's finished petroleum products in 2015, followed by diesel fuel at 23 vol% and jet fuel at 9 vol%.<sup>13</sup> Vehicle electrification will reduce demand for gasoline by either improving the fuel economy of light passenger vehicles in the case of hybrid-electric vehicles (HEV) or completely eliminating the need for gasoline in the case of BEVs.

The rise of inexpensive natural gas in the U.S. has resulted in its growing use in electric power generation, raising the prospect that natural gas will become a major contributor to the U.S. transportation sector's energy needs. The price of natural gas in the U.S. declined by 70% between 2008 and 2015<sup>14</sup> as domestic production increased by 36%.<sup>15</sup> These shifts coincided with a decline in the share of total U.S. electricity generation provided by coal from 48% in 2008 to 33% in 2015 and an increase in the share provided by natural gas from 21% to 33% over the same period.<sup>16</sup> The U.S. Energy Information Administration (EIA) forecasts the shares of total generation from coal and natural gas to be 20% and 36%, respectively, in 2040,<sup>7</sup> with the latter generating more electricity than any single other source.

Hybrid-electric heavy-duty vehicles (HDV) have also attracted interest from both federal policymakers<sup>17</sup> and the private sector<sup>18</sup> as a means of increasing HDV fuel economy and reducing diesel fuel consumption. NASA is pushing the technology still further by developing hybrid-electric and battery-electric passenger aircraft capable of achieving better fuel economies than conventional aircraft.<sup>19</sup> Even in the event that the electrification of HDVs and passenger aircraft does not significantly reduce demand for diesel fuel and jet fuel, however, the technology for producing and/or displacing both fuels with natural gas on a commercial scale has existed for several decades. Natural gas can be converted to synthetic diesel and jet fuels via the Fischer-Tropsch pathway. Alternatively, HDVs can be modified to be fueled by compressed natural gas and liquefied natural gas. The EIA forecasts the use of natural gas by the U.S. transportation sector to increase by 9.8% annually through 2040, greatly exceeding the electric power sector's forecast annual natural gas consumption growth rate of 0.9% over the same period.<sup>7</sup>

Whether electrification of the transportation sector contributes toward a reduction in greenhouse gas emissions depends upon the primary source of energy for both electric power generation and

transportation fuel.<sup>20</sup> Charging BEVs with electricity from coal-fired power stations would have net greenhouse gas (GHG) emissions that are comparable to ICEVs powered by gasoline or diesel.<sup>21</sup> Ideally, electricity for BEVs would come from solar or wind power. However, electricity from natural gas-fired stations is an attractive alternative until the price of renewable power becomes more attractive. Greenhouse gas emission reductions are especially large when renewable natural gas in the forms of biogas and/or biomethane is employed as feedstock for electric power generation<sup>22</sup> or as fuel in compressed natural gas vehicles.<sup>23</sup> Biogas produced from lignocellulosic biomass has become a major contributor to the U.S. revised Renewable Fuel Standard (RFS2): of the 142.2 million gallons-equivalent of cellulosic biofuels produced under the program in 2015, over 98.5% took the form of compressed and liquefied renewable natural gas.<sup>24</sup>

The low cost of natural gas in the U.S. makes it an attractive option for other applications as well, including the production of petrochemicals. Substitution of natural gas for petroleum in the production of organic commodity chemicals highlights possible opportunities for biorenewable resources.

### **3. NATURAL GAS SUBSTITUTION IN THE PETROCHEMICAL INDUSTRY**

Naphtha, which is produced in a petroleum refinery's distillation unit, has historically been used as feedstock in steam crackers to produce ethylene, propylene, aromatics, and other olefins, all of which are important building blocks in the petrochemical industry. U.S. consumption of naphtha as a petrochemical feedstock reached 0.4 million barrels per day (MMBPD) in 2004. Ethane, which is a major component of natural gas, has steadily replaced naphtha as steam cracker feedstock as domestic natural gas prices have declined relative to petroleum prices, however.<sup>25</sup>

U.S. consumption of naphtha as a petrochemical feedstock declined by 43% between 2004 and 2015 while consumption of ethane for the same purpose increased by 50% over the same period to 1.1 MMBPD.<sup>13</sup> U.S. ethane production has actually reached a state of oversupply, resulting in the export of substantial volumes for the first time in 2014.

So much naphtha consumption has been displaced by ethane that the U.S. is expected to be the world's largest exporter of light naphtha by 2020.<sup>26</sup> The shift from naphtha to ethane for domestic steam cracker feedstock has impacted product volumes due to yield differences between the two feedstocks. While both produce large yields of ethylene, naphtha produces much larger yields of propylene, aromatics, and low molecular weight olefins (see Figure 1).<sup>27</sup> Alternative fossil pathways have not always offset falling output of these products from steam crackers: for example, U.S. benzene production declined by roughly 30% between 2004 and 2015, resulting in a growing production shortfall relative to demand.<sup>28</sup>

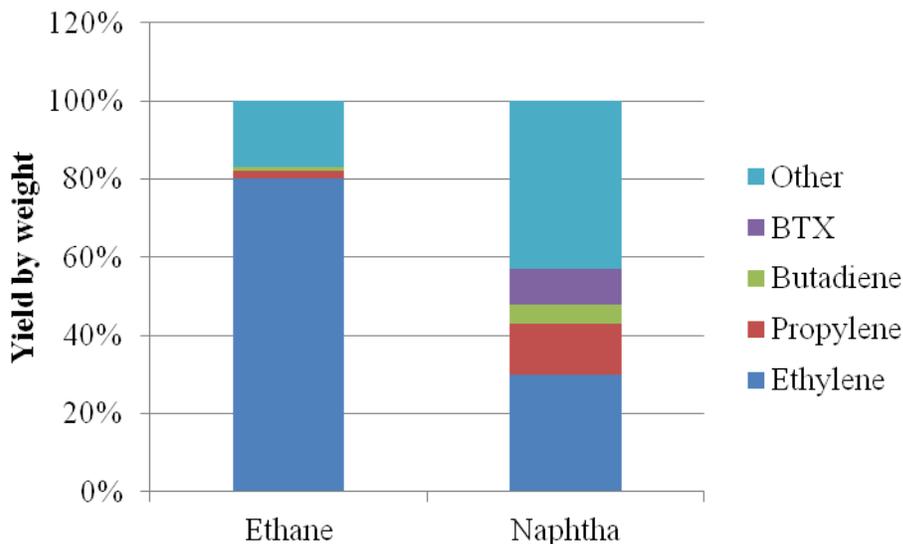


Figure 1. Steam cracker yields by feedstock.<sup>27</sup>

Natural gas has already displaced or is expected to displace increasing volumes of demand for major refining products such as gasoline, diesel fuel, jet fuel, and naphtha in the coming decades. It cannot completely replace petroleum, though, since the U.S. economy relies heavily on several petroleum refining co-products that natural gas and electricity (either fossil- or renewable-based) are unlikely to serve as adequate substitutes for due to reasons of economics and/or chemistry. Asphaltenes, aromatics (benzene, toluene, and xylene, or BTX), industrial lubricants, petroleum coke, and waxes are all co-products of petroleum refining that the U.S. economy has become reliant upon. U.S. output of these important co-products has declined over the last decade (see Figure 2) even as demand for them has remained stable or increased because of reduced demand for petroleum-derived fuels. This has caused co-product prices to increase relative to petroleum (see Figure 3) <sup>29,30</sup> since refineries cannot inexpensively shift product mixes (i.e., converting gasoline-range hydrocarbons to asphalt) in response to changing demand patterns. A similar effect has been observed with U.S. gasoline prices as ethanol's share of total gasoline consumption has reached 10 vol%.<sup>31</sup>

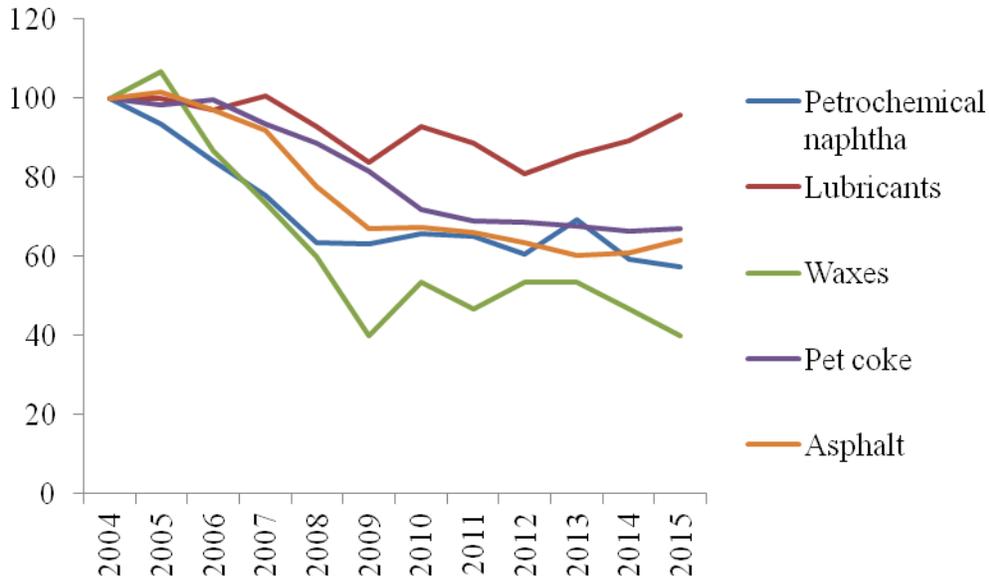


Figure 2. Change in select refining co-product volume indices since 2004. 2004 = 100.<sup>13</sup>

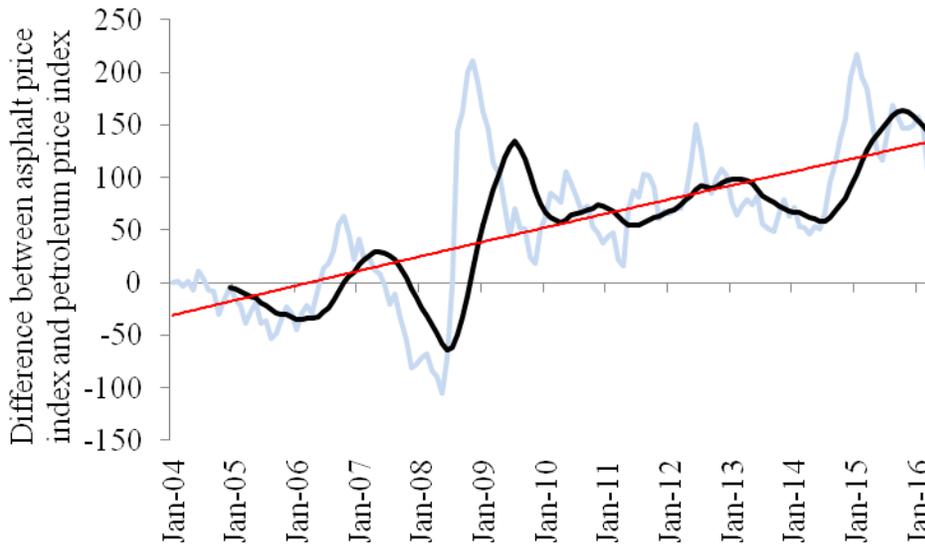


Figure 3. Difference between asphalt price index and petroleum price index (light blue) with 12-month average (black) and 2nd-order polynomial trendline (red).<sup>32,33</sup>

It is increasingly important for the U.S. to identify cost-competitive alternative pathways for the production of these refining co-products as petroleum consumption undergoes a long-term

decline in response to rising biofuel mandates, emission restrictions, and fuel economy standards. Declining retail fuel consumption due to widespread vehicle electrification would also cause fuel excise tax receipts to fall, much as they did between 2007 and 2014, making it still more difficult for the U.S. government to continue to finance infrastructure investments from the existing receipts in a rising price environment. Unlike natural gas and electricity, however, biomass can serve as feedstock for the production of these refined co-products via biorenewable pathways. Increased U.S. natural gas production and vehicle electrification will cause refining co-product prices to become still more expensive relative to petroleum unless biorenewable pathways for the production of these non-fuel outputs are commercialized here.

#### **4. OPPORTUNITIES FOR BIOBASED PRODUCTS**

There are two primary approaches to the development of biobased products that have been employed to date.<sup>34</sup> The first approach focuses on the development of biobased products that are similar but not identical to a refinery's co-products. The second approach focuses instead on the development of biobased "drop-in" products that perform as well as or better than those from a refinery. A disadvantage with the first approach is that the alternatives can struggle to gain industry and consumer acceptance even when performance characteristic differences are manageable. Biobased ethanol consumption driven by the revised Renewable Fuel Standard was initially expected by U.S. policymakers to reach as high as a quarter of gasoline consumption by 2022. Refiners, fuel retailers, and consumers have broadly resisted the adoption of ethanol blended with gasoline at rates exceeding 10 vol%. As a result, the EPA has acted to prevent the RFS2 from requiring biofuel blending in excess of 10 vol% since 2013, and growth in U.S. ethanol consumption has slowed greatly since 2010.<sup>4</sup> Drop-in biobased products do not suffer from this disadvantage to the extent that they can utilize the existing end-use infrastructure.

While many pathways are capable of producing both fuel and non-fuel biobased products, those that achieve high yields of non-fuel products are of particular interest since they are most likely to experience high demand if vehicle electrification becomes widespread. High yields are especially important for biobased product pathways in order to overcome the high capital costs that they incur. A review of small pioneer advanced biorefineries found capital costs ranging from \$200 million to \$500 million, or roughly \$3/liter installed capacity.<sup>35</sup> Techno-economic analyses of nth-plant advanced biorefineries have calculated similar costs on an installed capacity basis.<sup>36</sup> The next section reviews recent research advances into drop-in non-fuel biobased products (see Table 1) and also discusses their economic feasibility as replacements when techno-economic data is available in the refereed literature.

Table 1. Summary of biobased non-fuel refining products.

| <b>Refined Product</b> | <b>Alternative or drop-in?</b> | <b>Biobased pathways</b>                | <b>Feedstock</b>       |
|------------------------|--------------------------------|---|------------------------|
| Aromatics              | Drop-in                        | Pyrolysis                               | Lignocellulose         |
| Asphaltenes            | Both                           | Pyrolysis                               | Lignocellulose         |
| Lubricants             | Both                           | Esterification, gasification, pyrolysis | Lignocellulose, lipids |
| Petcoke                | Drop-in                        | Pyrolysis                               | Lignocellulose         |
| Waxes                  | Both                           | Gasification, hydrogenation             | Lignocellulose, lipids |

#### **4.1 Aromatics (benzene-toluene-xylene)**

Aromatics in the form of BTX are a critical building block within the chemicals industry. Polystyrene, epoxy, polyethylene terephthalate, polyurethane, and nylon are all examples of products that are derived from BTX. While aromatics can be used in gasoline, concerns over the carcinogenic properties of benzene in particular have caused them to be increasingly removed

from fuel streams and sold as petrochemical feedstock instead. BTX is produced by steam cracking from both naphtha and ethane feedstocks, although the yield from the latter is only a small percentage of the former.<sup>25</sup> The shift among U.S. chemical producers away from naphtha as feedstock in favor of ethane in 2011 and 2012 caused BTX prices to rise sharply relative to petroleum, although they declined again in 2014 in response to increased domestic petroleum production.<sup>37</sup>

Fast pyrolysis of lignocellulosic biomass has been the subject of research as a pathway for the production of hydrocarbon-based biofuels.<sup>35</sup> Fast pyrolysis yields liquid (bio-oil), solid (biochar), and gaseous (syngas) products. The bio-oil can be catalytically cracked into fuel-range hydrocarbons, although this process yields large amounts of coke and low hydrocarbon yields compared to petroleum refining. Vispute et al.<sup>38</sup> describe a process called Integrated Catalytic Processing in which the bio-oil is reacted with hydrogen (hydrotreating) prior to undergoing catalytic cracking. This process reduces coke yields by 46% while increasing yields of aromatics as well as olefins by up to 36% compared to catalytic cracking alone. Subsequent analyses determined that the Integrated Catalytic Processing pathway yields positive 20-year net present values under higher yield scenarios despite incurring high capital costs<sup>39</sup> while also achieving negative carbon emissions.<sup>40</sup> Sharifzadeh et al.<sup>41</sup> calculate that higher BTX yields are achieved via the cracking of hydrotreated bio-oil than via naphtha or ethane cracking. This suggests that it is possible to achieve higher aromatics yields from biomass than from conventional petroleum refining, although the ability to achieve similar yields at the commercial scale is uncertain.

Catalytic fast pyrolysis of biomass potentially eliminates the need for bio-oil hydrotreating at the expense of high coke yields compared to aromatics yields, reducing the pathway's economic feasibility.<sup>42,43</sup> Zeolite catalysts have been found to generate the highest yields of aromatics.<sup>44,45</sup>

Catalytic co-pyrolysis of lignocellulosic biomass with polymers is proposed as one method of cost-effectively increasing the pathway's aromatics yields and reducing coke yields.<sup>46</sup> Methanol has also been identified as a biomass co-pyrolysis feedstock capable of increasing aromatics yields.<sup>47</sup>

As one of the three primary fractions of lignocellulosic biomass, the U.S. supply of lignin is potentially large. At present it is used as a low-value boiler fuel or disposed of as a waste stream by the paper and advanced biofuel industries. The fact that lignin is rich in aromatics suggests its use for production of renewable benzene and toluene. The reaction of model compounds with various bimetallic catalysts has been found to produce a variety of yields of these two chemicals as well as derivatives such as cyclohexane.<sup>48</sup> Similar results have been obtained from lignin feedstocks.<sup>49,50</sup> A major advantage of using lignin rather than cellulose and/or hemicellulose as feedstock for biobased BTX production is that it allows the carbohydrate fractions to be used as substrates for fermentation of biofuels and other chemicals.<sup>51</sup> A biorefinery yielding both fuels and BTX would more closely resemble a petroleum refinery in terms of output, minimizing the economic disruption from a shift to biobased products and increasing product diversity.<sup>52,53</sup> A recent analysis calculates that a biomass fast pyrolysis and hydroprocessing pathway yielding biobased fuel oil, aromatics, and olefins has a much smaller 30-year NPV uncertainty range ( $\pm$ \$30.1 million) than pathways yielding fewer products ( $\pm$ \$268.9 million).<sup>54</sup>

Despite its lack of lignin content, microalgae has been identified as a potential feedstock for thermochemical production of BTX. Wang et al.<sup>55</sup> report BTX as the highest-yielding products achieved from the catalytic pyrolysis of low-lipid microalgae. Thilakaratne et al.<sup>56</sup> further show that similarly-high yields of BTX can be obtained from the catalytic pyrolysis of defatted microalgae, a co-product from an algal lipid biorefinery. However, even assuming that an

inexpensive waste stream is used as feedstock, the pathway's high capital costs incurred prevent the pathway from being competitive with petroleum refining. The use of dried distillers grains and solubles (DDGS) has also been employed as catalytic pyrolysis feedstock to yield relatively large amounts of BTX (44.5% carbon yield).<sup>57</sup> The ability to "bolt-on" this process to existing starch ethanol facilities provides it with substantial economic advantages in the form of 2% lower annual operating costs and 131% higher annual revenues compared to standalone catalytic pyrolysis facilities.<sup>58</sup>

## **4.2 Asphaltenes**

Asphaltenes are polyaromatic hydrocarbon compounds that are found in heavy residues generated by a refinery's vacuum distillation unit. They are difficult to distill, having boiling points in excess of 500 °C. They are also difficult to handle because of their high viscosity at ambient temperatures. Asphaltenes primarily take the form of asphalt when produced by a petroleum refinery. Asphalt's high viscosity makes it suitable as road surfacing material after being mixed with aggregate. Asphalt is also used to manufacture roofing shingles and as waterproofing agent. Finally, it can be converted to synfuels, although the high energy requirements and expense have discouraged this application.

Asphalt demand is correlated with economic growth rates due to its widespread use as an infrastructure material.<sup>59</sup> Its rising price relative to petroleum has coincided with concerns that reduced government tax receipts in many countries around the world are insufficient to meet required infrastructure investment, resulting in diminished government purchasing power for infrastructure purposes. For example, the American Society of Civil Engineers estimated in 2013 that an additional \$79 billion of annual investment, or an increase of 87%, was needed just to

“significantly improve” the country’s road infrastructure<sup>60</sup>. U.S. asphalt demand is forecast to increase 3.3% annually to 26.8 million tons in 2019 as rebounding economic growth drives infrastructure repairs.<sup>61</sup>

Research into biobased replacements for asphalt has focused on two different routes: binder replacements and additive replacements. Liquid biobased binders produced via thermochemical processing of biomass have also been investigated as an alternative rather than additive for petroleum-based asphalt binders. Swine manure, corn stover, wood pellets, and Miscanthus have all been successfully tested as feedstocks for liquid biobased asphalt binders,<sup>62-65</sup> although reported performance characteristics vary by feedstock. The fast pyrolysis product bio-oil in particular has been investigated as a biobased asphalt binder, with laboratory test results finding that its addition can reduce mixing temperatures and improves high temperature performance<sup>66</sup> while reducing low temperature performance.<sup>67</sup> The reduced low temperature performance is offset by the ability to introduce a higher reclaimed asphalt pavement content into asphalt containing bio-oil.<sup>68</sup> Bio-oils derived from corn stover,<sup>69</sup> waste wood,<sup>67</sup> switchgrass,<sup>70</sup> and oak<sup>71</sup> have all been identified as having performance properties that are similar to and comparable with petroleum-based asphalt binders.

It is also possible to replace conventional asphalt additives with higher-quality biobased versions that improve the asphalt’s performance and lifespan, thereby reducing demand by mitigating the need for maintenance and replacement. For example, biochar, a co-product from the pyrolysis of biomass, added to hot-mix asphalt improves the product’s performance by reducing its temperature susceptibility.<sup>72,73</sup> Other biobased additives such as isosorbide distillation bottoms have also been found to improve the low temperature performance of asphalt, suggesting that further performance improvements are possible with newly-developed biobased additives<sup>74</sup>.

Initial techno-economic analyses of biobased asphalt production indicate that it could be competitive with asphalt produced by a petroleum refinery. Fini et al.<sup>75</sup> estimate that biobased asphalt binder possessing similar performance properties as petroleum-based asphalt binder can be produced via the hydrothermal liquefaction of swine manure for \$0.13/liter compared to an asphalt market price of \$0.53/liter. It is important to note that the study doesn't actually model the hydrothermal liquefaction process but instead utilizes estimated costs for a sugar beet pulp biorefinery. A more recent analysis calculates a positive 30-year NPV for a fast pyrolysis pathway yielding biobased asphalt binder in addition to biobased cement and asphalt, with a 100% chance that the NPV will be positive when considered under uncertainty.<sup>54</sup>

### **4.3 Industrial lubricants**

Lubricants are widely employed across industries for a number of purposes, including engine and motor grease, chain grease, hydraulic fluids, gas seals, and a various other mechanical applications. While lubricants comprise only a small fraction of total refining products, most modern machinery relies on them for cooling, corrosion resistance, wear prevention, power transmission, and friction reduction. The base stock for petroleum-based lubricants is derived from the straight-run refining residue that remains after asphaltene, aromatics, and waxes have been removed.<sup>76</sup> It can also be synthesized from ethylene via polymerization to branched-chain paraffins rather than from straight-run crude. However, the higher costs incurred by the additional processing steps cause synthetic lubricants to primarily be used under severe conditions (such as in a jet engine).<sup>76</sup>

Concerns about the persistence of conventional lubricants in the environment have prompted the development of biodegradable lubricants derived from biomass. Vegetable oil is commonly used

as a biobased lubricant due to the abundance of oilseed crops in both developed and developing economies. Its high viscosity and low volatility are attractive attributes, although these are offset by poor oxidative stability and poor low- and high-temperature performance. Modified vegetable oils avoid many of these disadvantages. Oilseed crops can be genetically modified to improve oxidative stability.<sup>77</sup> A more direct approach modifies the vegetable oil so as to improve its performance characteristics. Soybean oil has been chemically modified via a process in which it is reacted with acid anhydrides to yield diesters at its unsaturated points.<sup>78</sup> The resulting modified soybean oil has cold-flow and oxidative properties that are comparable to petroleum-based lubricant. An alternative process thermally polymerizes soybean oil to increase its viscosity, then blends it with a combination of synthetic base stocks, antioxidant additives, and pour point depressants.<sup>79</sup> The resulting blend has performance characteristics that are equal or superior to petroleum-based lubricants with the exception of thermal oxidation, although this too falls within an acceptable range.

Pathways for the production of biobased synthetic lubricants have also been developed.

Polyalphaolefins (PAO) are synthetic lubricants possessing excellent low-temperature and high-pressure performance characteristics.<sup>77</sup> They are commonly produced via the oligomerization of ethylene to yield 1-decene, which is then polymerized to form a PAO. While ethylene is usually derived from naphtha and ethane in the U.S., it can also be produced via biomass catalytic fast pyrolysis<sup>80</sup> or biomass fast pyrolysis with Integrated Catalytic Processing.<sup>38</sup> Biomass gasification yields syngas that, when reacted over catalysts, forms ethylene and propylene via the methanol-to-olefin pathway. Finally, fermentation also provides possible routes for the production of lubricants from biomass. The dehydration of ethanol, whether produced via gasification/mixed alcohols synthesis or sugar fermentation, yields ethylene. Alternatively, the fermentation of

biomass-derived sugars with *Clostridia* strains and subsequent synthesis and hydrodeoxygenation yields biobased synthetic lubricants.<sup>81</sup>

#### **4.4 Petroleum coke**

Petroleum coke is a solid byproduct that remains after petroleum is cracked into lighter products.

Petroleum coke is a carbonaceous solid of low ash content, providing it with a higher heating content than most types of coal. These characteristics made it attractive as an energy source before greenhouse gas emissions from high carbon fuels was a concern. Worldwide, approximately 80% of petroleum coke production was used as a source of fuel in refineries, cement kilns, and electric power plants.<sup>82</sup> Calcined petroleum coke has a higher carbon purity than thermal petroleum coke, and it is suitable for use in aluminum smelting anodes<sup>83</sup> and microbial fuel cell electrode materials.<sup>84</sup>

Bio-oil that undergoes an atmospheric distillation followed by a vacuum distillation yields distillates and coke bottoms.<sup>83</sup> The latter product can be calcined in a manner similar to petroleum coke to produce biobased calcined coke. The resulting biobased product has been characterized as being superior to calcined petroleum coke due to its lower sulfur and trace metal content, making it a potential high-value substitute for petroleum coke.<sup>83</sup>

Calcined petroleum coke is also employed in the production of granular activated carbon and synthetic graphite granules. These materials are used in the construction of microbial fuel cells that are employed for the production of energy, biochemicals, and disinfectants, as well as wastewater treatment.<sup>84</sup> Biochar produced via wood pyrolysis has been utilized in laboratory experiments as microbial fuel cell electrodes and found to have performance characteristics comparable to petroleum coke-derived electrodes. Biochar electrodes produced from waste

products was further found to have lower production costs, energy requirements, and GHG emissions than the petroleum coke versions.<sup>84</sup>

#### **4.5 Petroleum waxes**

Petroleum waxes are long-chained hydrocarbons that are solid at room temperature but liquid at higher temperatures. They are produced from refined heavy distillates during the production of petroleum lubricants. Two types of petroleum waxes are produced by refineries. The most common type is paraffin wax, which is comprised of unbranched alkanes. The attractive electric resistivity and specific heat capacity characteristics of paraffin wax make it popular in the production of electrical insulators and heat storage materials. It is also used in a variety of other applications ranging from candle-making to food additives to water-proofing. The second type, microcrystalline wax, contains a larger percentage of branched and naphthenic hydrocarbons. It has a higher molecular weight and melting point than paraffinic wax, two characteristics that make it useful in more specialized applications in the cosmetics, personal care, and jewelry industries.

Chemically-modified vegetable oil has found use as a biobased wax in certain applications. The vegetable oil is partially- or fully-hydrogenated over a catalyst to form saturated compounds that are solid at room temperature. Soybean oil is a popular feedstock in this process due to its carbon-chain length and the resulting wax has similar performance characteristics as paraffin wax. Vegetable oil-derived waxes contain a number of defects, however, including a greasy surface texture, brittle structure, and reduced hardness compared to paraffin wax.<sup>85</sup> The blending of different vegetable oils or use of acid- or alcohol-catalyzed reactions can improve these characteristics.

Synthetic biobased waxes can also be produced from lignocellulosic biomass via gasification/Fischer-Tropsch synthesis. Biomass is converted to syngas which is then reacted over an iron catalyst to form straight-chain alkanes, including waxes. The wax yield is the largest product by yield for lower-temperature processes and can be produced as one of several biobased refining products as part of a biorefining process.<sup>86</sup> Biobased waxes produced via this pathway are calculated to be competitive with petroleum-derived products at a petroleum price above \$146/barrel.<sup>86</sup>

## **5. CONCLUSION**

Abundant domestic reserves of natural gas in the U.S. have resulted in its wide-spread displacement of coal and its use in the production of certain petrochemicals. Vehicle electrification, by reducing demand for petroleum, could reduce the supply of petrochemicals. Several refined products cannot be easily and cost-effectively replaced by natural gas, including aromatics, asphaltenes, industrial lubricants, petroleum coke, and petroleum waxes. These petroleum-derived products are used for a wide variety of purposes throughout the economy. Replacements will need to be found if natural gas and electric vehicles displace a large fraction of future petroleum demand. Replacements or substitutes for these refined products can be derived from biomass. The various biobased products are at early stages of research, however, and the economic feasibility relative to petroleum-based products has been assessed for only a few bioproducts. More research is needed to determine which biobased products are capable of serving as cost-effective replacements for petroleum versions at scale while also achieving reduced or even net positive environmental impacts.

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