



Summary of IEA Bioenergy Task 39 report:

“The potential and challenges of drop-in biofuels”

A Report by IEA Bioenergy Task 39

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Introduction

The main report that this compressed summary refers to was commissioned by IEA Bioenergy Task 39 with the goal of providing a background to the topic of so-called “drop-in” biofuels, an assessment of technical approaches being developed and an overview of anticipated challenges to large scale commercialization of “drop-in” biofuels technologies. The main report can be accessed at the Task 39 [website](#). For the purposes of this report, “drop-in” biofuels are defined as “liquid bio-hydrocarbons that are functionally equivalent to petroleum fuels and are fully compatible with existing petroleum infrastructure”.

There is considerable interest in developing advanced biofuels that can be readily integrated in the existing petroleum fuel infrastructure in a “drop-in” fashion, particularly by sectors such as aviation where there are no real alternatives to sustainably produced biofuels for low carbon emitting fuel sources. Although the production of ethanol and biodiesel is well established, these biofuels are not fully compatible with the substantial inventory of existing vehicle engines or the overall liquid transportation fuel refining and distribution infrastructure.

Drop-in biofuels are attractive from both an infrastructure and a fuel market perspective. Trillions of dollars’ worth of petroleum infrastructure (refineries, pipelines, blending terminals, fuel pumps) has already been built that is not fully compatible with either ethanol or biodiesel production and

distribution, whereas drop-in biofuels by definition should be fully fungible and compatible with, and thus able to leverage, this large existing “petroleum-based” infrastructure. At the same time, the ongoing “dieselification” of the global transportation fleet implies that ethanol, which is primarily used as a gasoline blendstock, is becoming increasingly constrained as a global liquid fuel source as compared to biodiesel and jet fuels.

Overview of Drop-in Biofuel Technologies and Challenges

There are several ways to produce drop-in biofuels that are functionally equivalent to petroleum-derived transportation fuel blendstocks. These are discussed within three major sections of the full report and include: oleochemical processes, such as the hydroprocessing of lipid feedstocks obtained from oilseed crops, algae or tallow; thermochemical processes, such as the thermochemical conversion of biomass to fluid intermediates (gas or oil) followed by catalytic upgrading and hydroprocessing to hydrocarbon fuels; and biochemical processes, such as the biological conversion of biomass (sugars, starches or lignocellulose-derived feedstocks) to longer chain alcohols and hydrocarbons. A fourth category is also briefly described that includes “hybrid” thermochemical/biochemical technologies such as fermentation of synthesis gas and catalytic reforming of sugars/carbohydrates.

One challenge that the development of drop-in biofuels shares with the global petroleum industry is the requirement for increasing amounts of molecular hydrogen (H_2). In the case of petroleum, more hydrogen will be needed to upgrade crude oil feedstocks of declining quality (i.e., increasingly heavier and more sour, as in the case of heavy oils being sourced from Venezuela and Canada). Similarly, greater amounts of hydrogen are generally needed to produce more energy dense and highly reduced drop-in biofuels. For the foreseeable future, much of this increased demand for hydrogen is likely to be met using hydrogen derived from natural gas.

Oil refineries use hydrogen to upgrade low-grade crude oil, both to remove problematic sulfur and other heteroatom impurities (hydrotreating) and to “crack” longer carbon chain molecules to shorter chain molecules while also enriching them with hydrogen (hydrocracking). One result of these hydrogen-consuming processes (collectively known as hydroprocessing) is to elevate the hydrogen to carbon ratio of low grade crude oils. The hydrogen to carbon ratio is a good indicator of petroleum feedstock quality since a high sulfur content or the presence of long, condensed carbon chains (e.g., in coal) reduce the H/C ratio. As detailed in the main body of the report, the H/C ratio can be visualized as a staircase (see Figure 1 below). In this simplified staircase analogy, the more “steps” that have to be climbed up the “H/C staircase” to achieve an H/C ratio suitable for liquid gasoline, diesel and jet transportation fuel

applications, the more hydrogen inputs and processing efforts are required. Non-hydrogen-consuming processes such as catalytic or thermal cracking can also be used to increase the H/C ratio of petroleum feedstocks by removing carbon in the form of tars and char (coke). However, this approach consumes feedstock and reduces yields and so is generally avoided, particularly when prices for crude oil feedstocks are high.

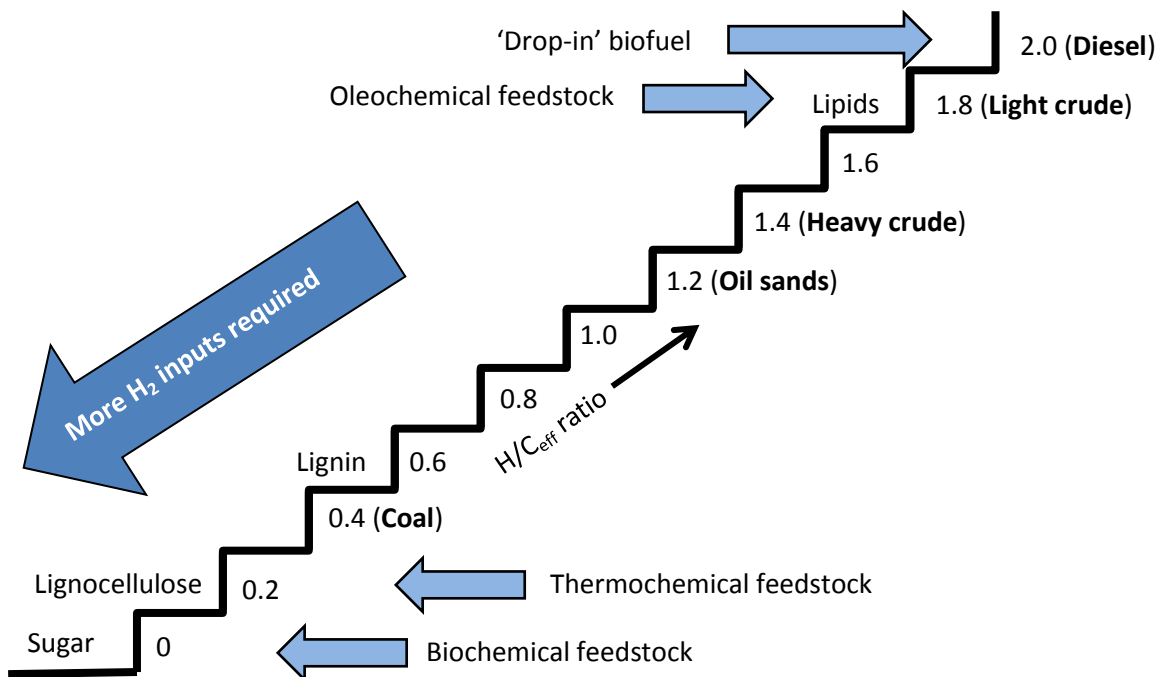


Figure 1: The increase in effective Hydrogen to Carbon ratio represented as a “staircase.” (Fossil feedstocks in brackets and bold)

It is also evident that a majority of evolving drop-in biofuel technologies require hydrogen (H₂) inputs or other chemical reduction processes to upgrade oxygen-rich carbohydrate, lignin or lipid feedstocks to hydrogen-rich hydrocarbons that are functionally equivalent to petroleum-derived liquid fuels. As detailed in the main report, some type of hydroprocessing step will likely be required for most drop-in biofuel technology platforms, with imported hydrogen used to remove oxygen (in the form of H₂O) from oxygenated lignocellulose intermediates or lipid feedstocks. Alternatively, non-hydrogen consuming processes (whether chemical or biological) will have to oxidize significant amounts of feedstock carbon in order to produce the required hydrogen or alternative reducing power carriers (such as NADPH used in biological processes). However, as is the case for petroleum feedstocks, these alternative routes to

deoxygenation will reduce yields by consuming a portion of the feedstock and thus are generally less attractive than hydroprocessing using imported hydrogen.

An effective hydrogen to carbon ratio, H_{eff}/C , can also be defined for biomass feedstocks (see Figure 1 above) by adjusting for their significant oxygen content (compared to fossil fuel-based feedstocks), and constitutes a relevant metric for understanding and comparing the techno-economic challenges for drop-in biofuel processes using different types of biomass feedstocks. Highly oxygenated biomass feedstocks such as sugar molecules have a H_{eff}/C ratio of 0 whereas the target ratio for drop-in biofuels is approximately 2, similar to the H/C ratio of diesel. Most biomass feedstocks (sugars, cellulose, lignocellulosic biomass, lignin) have a H_{eff}/C ratio near zero, much lower than petroleum feedstocks, and are positioned at or near the bottom steps of the H/C staircase. Biomass feedstocks thus need to “climb” more steps than fossil feedstocks to reach a chemically reduced state similar to diesel, jet and gasoline fuels. Even low grade fossil feedstocks such as coal ($H/C = 0.5$) contain a substantially higher H_{eff}/C ratio than most biomass feedstocks. A notable exception are the biomass-derived lipids and other oleochemical types of biomass feedstocks, which contain much lower levels of oxygen than other biomass feedstock types and have an H_{eff}/C ratio of about 1.8. These types of oleochemical feedstocks start much farther up the H/C staircase and are thus more readily suited for conversion to drop-in biofuels than other types of biomass feedstocks.

Stoichiometrically, an equivalent amount of hydrogen is required to remove oxygen atoms from biomass (in the form of H_2O) as is required to remove sulfur atoms from low grade petroleum (in the form of H_2S). In reality, a lot more hydrogen is required to upgrade biomass feeds than petroleum feeds because biomass contains much more oxygen (approximately 10 wt% oxygen in vegetable oils and 40 wt% oxygen in lignocellulosics) than high sulfur petroleum (up to 3 wt% sulfur in high sulfur petroleum). It should also be noted that the performance of petroleum desulfurization processes has been optimised for decades and is thus at a significantly more advanced stage of development than biomass deoxygenation processes.

Technologies for Oleochemical Feedstocks

Current commercial drop-in biofuel production represents a small percentage (<4%) of total global biofuel markets with the vast majority of drop-in biofuels derived via the oleochemical platform which uses feedstocks such as palm oil, used cooking oil and tallow. These “fat-derived” or “oleochemical-

derived” drop-in biofuels are often referred to as hydrotreated esters and fatty acids (HEFA) and represent a subcategory of hydrotreated vegetable oil (HVO) biofuels. HVOs are notably distinct to fatty acid methyl ester (FAME) biodiesels which retain an oxygen ester and are therefore too oxygenated to be a drop-in biofuel.

Vegetable oils contain about 10 wt% oxygen and this oxygen has to be removed to produce drop-in HVO biofuels. Hydrotreating to remove this oxygen typically consumes about 3 wt% hydrogen on vegetable oil. Alternative deoxygenation processes that require less hydrogen, or even no hydrogen, can be used to remove oxygen in whole or in part as carbon oxides (CO and CO₂). However, these types of “decarboxylation” processes achieve lower fuel yields due to these carbon losses. Hydrotreated vegetable oil (HVO) biofuels can also be produced by co-processing oleochemical feeds with petroleum feeds in modern oil refineries and there have been a variety of commercial demonstration trials. The work already performed on combined processing of oleochemical and petroleum feeds has shown that there are significant opportunities to further improve hydrotreating catalysts for such applications. In particular, current hydrotreating catalysts need to be adapted to the oxygenated and often more “waxy” nature of vegetable oils compared to crude oil, and companies active in catalyst development such as Haldor Topsoe and UOP Honeywell are making considerable R&D investments in this area. In addition, hydrotreating units processing oleochemical feedstocks have about an order of magnitude higher hydrogen demand than those processing conventional petroleum feeds. Even at low biofeed blending levels, this disparity in hydrogen requirements can lead to problems in co-processing biofeeds with petroleum feeds. Reported difficulties include hydrogen starvation and excessive pressure drops within hydrotreating units, as well as poor desulfurization (of the petroleum feed fraction) through coking and deactivation of hydrotreating catalysts. As a consequence of these issues, HVO biofuels are currently produced in commercially significant volumes in stand-alone facilities using specialised conditions and catalysts. Examples are Neste Oil’s three major HVO facilities which convert palm and other vegetable oils to 46,000 barrels of HVO biofuels per day.

Drop-in oleochemical biofuels contain no aromatics (tall oil diesel is an exception). While this may be beneficial in terms of reducing the toxicity of emissions from fuel combustion, it means additional blending of aromatic components will be needed in applications where aromatics are required (e.g., for swelling elastomer parts in jet engines).

The vast majority of aviation trials using drop-in biofuels have used HVO biofuels because they are already commercially available and are ASTM approved. However, the price of HVO biofuels remains relatively high and in the absence of incentives to produce these biofuels, vegetable oils will most likely be converted to conventional FAME biodiesel as it costs considerably less to produce than drop-in HVO biofuels. Typically, increasing the fraction of jet fuel range products being produced from oleochemical feedstocks requires higher hydrogen inputs (more extensive hydrocracking) and these extra costs must be considered when designing strategies to promote greater production of aviation drop-in biofuels.

One of the major reasons why there has not yet been more extensive deployment of HVO biofuel technologies is that the selling price of the vegetable oil feedstocks has historically been higher than the selling price of diesel and jet fuels. Vegetable oils such as palm and rapeseed are, at the time writing, priced in the range of USD \$500-\$1200/t (or \$12-30/GJ) [compared to approximately USD \$75-\$125/t (oven dry basis, or \$4-6/GJ) for lignocellulosic biomass] and their supply is often limited by competition from other value-added markets (e.g., food and cosmetics industries). Another reason is that vegetable oil feedstocks are quite land-intensive to produce in comparison to other feedstocks types (e.g., algae, lignocellulosic biomass). However, not all oleochemical feedstocks are created equal and there is ongoing research focussed on developing oleochemical feedstocks that can be sustainably sourced and which have a fatty acid composition better suited for fuel as opposed to food/feed applications. Algae and non-food crops such as camelina are examples of such oleochemical feedstocks that are being targeted for further improvement by major aviation biofuels development programs such as the USDAs “farm-to-fly” initiative, the USDOE’s NAABB consortium and the European “flightpath” programs.

Thermochemical Technologies for Lignocellulosic Feedstocks

The various thermochemical methods currently being assessed for biofuel production have their origins in the ancient process of “burning” biomass in the absence of oxygen to make charcoal, a high energy content product. The major challenges of thermochemical conversion are less about feedstock and more about conversion process efficiency and the technology risks involved. Thermochemical processing conditions for lignocellulosic feedstocks can be optimized to influence the ratio of the three main products of bio-oil, synthesis gas and char. The two main routes to drop-in biofuels are through pyrolysis and gasification.

Fast Pyrolysis

Fast pyrolysis has been studied in detail since the early 1980s and it essentially exposes small biomass particles (ca. 3 mm) at a temperature of about 500 °C for a few seconds to produce a “bio-oil” (up to 75

wt% yield) at relatively low cost (estimated at ca. \$10 USD/GJ based on a USD \$83/t (oven dry basis) feedstock). Although there are a few, niche high value markets for bio-oil components, such as food flavouring (barbeque flavour), today pyrolysis liquids are primarily considered for use in stationary power generating facilities such as Pyrogrot's proposed 720 tpd facility in Sweden.

Pyrolysis bio-oils contain up to 40% oxygen and need to be extensively upgraded to produce deoxygenated hydrocarbon drop-in biofuel blendstocks. This upgrading is typically achieved through hydroprocessing and it represents a large proportion of equipment and production costs including significant hydrogen gas (H₂) inputs (Jones et al., 2009). It is estimated that current US refinery hydrogen-generating capacity of 3 billion standard cubic feet per day, would need to be tripled to meet the 2022 US RFS cellulosic advanced biofuel mandate of 15 billion gallons (57 billion L) using pyrolysis platform-derived diesel/gasoline blendstock. While hydrogen can be generated from the biomass feedstock itself, this process is costly from both capital and operating cost perspectives compared to externally sourcing less expensive hydrogen derived from natural gas.

Pyrolysis platform approaches also have great potential to leverage existing oil refinery infrastructure to reduce biofuels production capital and operating costs. Major savings are possible in part by sourcing hydrogen from the oil refinery directly and in the longer term through the ability to use existing processing units. However, although existing hydroprocessing units (downstream in a refinery) can theoretically be used to co-process petroleum and hydrotreated pyrolysis oils (HPO), this practice is not yet commercial and it comes with challenges related to adapting hydrotreating catalysts to be able to perform well on blends of two disparate feedstocks (HPO and petroleum). Performance trials carried out by Haldor Topsoe (the world's largest manufacturer of petroleum refining catalysts) on industrial hydrocrackers using various biofeeds identified several challenges to catalytic "co-processing" of biofeed blends with petroleum. Although insertion points for biofeeds have been suggested upstream of hydrocrackers, such as at the vacuum distillation tower, it is likely such strategies could only be used with minimally processed pyrolysis oils which presumably would still contain large amounts of undesirable refinery contaminants such as oxygen and inorganics. Thus, two of the major challenges constraining development of pyrolysis-derived drop-in biofuels are the limited availability of low cost sustainable hydrogen and the need to develop hydrotreating catalysts that can accommodate bio-oil feedstocks. A variety of companies such as Canada's ENSYN have operated pyrolysis pilot plants for several years and KiOR recently completed a 13 million gallon (49 million L) per year commercial facility

in the US (However, note that this facility did not reach full production capacity as KiOR entered into financial difficulties recently).

As already described, the catalysts involved in upgrading bio-oils to drop-in biofuels represent a major performance and cost sensitivity of the pyrolysis platform. The lifespan of current hydrotreating catalysts, for example, is limited by their sensitivity to oxygen, water and coking, which are features commonly associated with processing bio-oils. Bio-oil hydrotreating catalysts with a lifespan exceeding 200 hours have not yet been demonstrated at scale (for comparison, the lifespan of current petroleum hydrotreating catalysts routinely exceeds 6 months). Identifying alternative catalyst formulations that are better able to tolerate challenging bio-oil feedstocks is an active area of R&D. It has already been shown that catalysts incorporating precious metals such as platinum and ruthenium are less prone to coking and more selective towards desirable hydrodeoxygenation reactions. However, such precious metals are orders of magnitude more expensive than conventional cobalt and molybdenum-based hydrotreating catalysts and further progress is needed to realize economic formulations. Aside from catalyst improvements, hydrotreatment process optimization options are also being investigated as a means of reducing the cost of pyrolysis-based drop-in biofuels. For example, due to the compositional complexity of bio-oils, it has been suggested that a two-step hydrotreatment process might be a more cost effective approach to bio-oil upgrading (Elliott, 2007; Jones et al., 2009; Jones et al., 2013). The first step would stabilize the bio-oil by selectively hydrotreating its most reactive (unstable) organic species and, once stabilized in this manner, a second step would be used to complete hydrotreatment. This two-step approach lends itself to a spoke and hub processing model where the first stabilization step is performed at many smaller scale facilities located near feedstock supplies and the second final upgrading step is performed at a few larger centralized facilities – perhaps petroleum refineries – where greater economies of scale are possible and existing capital assets, if available, can be used.

The cost of pyrolysis-based biofuel processes can be significantly reduced (both CAPEX and OPEX) if existing petroleum refinery infrastructure can be used. Although it has been suggested that pyrolysis oils can be inserted at any point throughout the refining process, the present analysis concludes that there are two particularly favourable insertion points for pyrolysis oils, namely before either a refinery's Fluid Catalytic Cracking (FCC) units or its hydroprocessing (hydrotreating and hydrocracking) units. The rationale is that FCC units have a similar configuration to the fluidized bed reactors used for pyrolysis. These units are at the heart of an oil refinery and are mainly used to crack heavy petroleum cuts and maximise production of lighter cuts such as gasoline blendstocks. As gasoline consumption continues to

decrease relative to diesel consumption within global fuel markets (the ‘dieselification’ trend described earlier), many refinery FCC units are becoming underutilized. In the US, fully 20% of FCC units were idle in 2013 and more are expected to be idle over the next decade or so. Inserting minimally upgraded pyrolysis oils into FCCs (e.g., in blends with vacuum gas oil) provides a strategy to put these “stranded” assets into productive use while also providing a “green credit” to a refinery’s product slate. The FCC insertion point for pyrolysis oils represents a “workhorse” approach where little hydrogen is used and the bio-oils are minimally preprocessed and then co-processed with heavy vacuum gas oils to produce a relatively low value hydrocarbon intermediate and large amounts of renewable power (i.e., from burning the ample coke and gaseous byproducts resulting from FCC processing). Recent studies under the European BIOCOUP program indicated that the insertion of bio-oil containing 20 wt% oxygen for co-processing with heavy (petroleum-based) oils in FCCs has potential as one strategy for upgrading bio-oils within an oil refinery.

The second, more “boutique” insertion point for bio-oils in a refinery is before the refinery’s hydroprocessing unit operations. Hydroprocessing is more sensitive to oxygen and impurities than FCC units and unlike the FCC insertion, hydroprocessing insertion of pyrolysis oils relies on substantial hydrogen inputs (e.g., 800 litres H₂ per kg of bio-oil processed, including pre-refinery hydrotreatment processing), much costlier catalysts (e.g., ruthenium-based vs ZSM5-based) and requires extensively pre-processed bio-oils (e.g., de-oxygenated to contain only 3-5 wt% oxygen). The co-hydroprocessing of lower oxygen content bio-oils with petroleum feeds generates similar, but likely more pronounced, problems as those seen when co-hydroprocessing vegetable oils inside oil refineries. Such problems include hydrogen starvation, increased pressure drops, accelerated catalyst deactivation and poorer desulfurization of the co-processed petroleum liquids. While the strategy of inserting before hydroprocessing is clearly more costly, it produces increased yields of higher value middle distillates such as diesel and jet fuels than the FCC insertion strategy. In contrast, the cheaper FCC insertion strategy generally favours the production of lower value light and especially heavy hydrocarbons such as gasoline and bunker fuels, respectively, as well as the generation of coke and gaseous byproducts (that can be used as “green” fuels for process heat and power generation). Both these refinery insertion strategies are synergistically beneficial but remain more technically challenging than is generally acknowledged by bio-oil commercialization companies and related stakeholder organizations.

Another important role that refineries can play is to generate hydrogen for pyrolysis and other drop-in biofuel facilities. Access to low cost hydrogen is important to achieving favourable drop-in biofuel

economics and makes co-locating drop-in biofuel facilities with oil refineries synergistically beneficial even when no actual co-processing is performed at the refinery. While hydrogen can be generated from the biomass feedstock itself, as already discussed this process is inefficient when compared to sourcing hydrogen from an external source such as a refinery (which usually makes hydrogen from natural gas or petroleum gases).

Once the hydrogen sourcing and catalyst issues are resolved, the pyrolysis platform holds great potential since it can effectively utilize a range of biomass feedstocks and has relatively low capital costs (compared to gasification), particularly if it can be developed to leverage the substantial existing petroleum refining infrastructure. It is also interesting to note that, unlike HVOs and most other drop-in biofuel platforms, pyrolysis-derived biofuels contain aromatics produced from the conversion of the phenolics in the lignin component of biomass.

Gasification

The other major thermochemical route to drop-in biofuels is through gasification. Gasification of biomass or bio-oil produces synthesis gas (“syngas”, comprised of mostly H₂ and CO), which is primarily used to fuel stationary heat and power facilities such as the 8 MW bio-power station in Gussing, Austria. Syngas can also be upgraded (catalytically condensed) to drop-in liquid biofuels via the Fischer-Tropsch process (FT), which has its origins in Germany during the 1920’s when access to oil was problematic. Building on this earlier work, South Africa’s Sasol has converted coal syngas into diesel at its Ctl Secunda facility since the 1980’s. This facility has a current capacity of 160,000 barrels of diesel per day. Another variation of the FT process is used in the world’s largest natural gas-to-liquids facility (Shell’s Pearl GTL facility in Qatar, completed in 2011) to produce 140,000 barrels of diesel per day. However, biomass-derived syngas is less energy dense than natural gas and it contains more impurities and a lower H/C ratio. As a result, biomass syngas needs to be enriched in hydrogen and cleaned of the impurities such as tars, nitrogen and other heteroatoms that can deactivate synthesis catalysts. Hydrogen is typically produced from the syngas itself by a process known as the “water-gas shift” reaction. However, this reaction consumes feedstock carbon and thus reduces the overall biomass-to-fuel yields. Alternatively, as is being proposed by companies such as Sundrop Biofuels in the US, the hydrogen can be derived from natural gas. Generally, gasification technologies entail high capital costs to both gasify the biomass and convert the resulting syngas to Fischer-Tropsch liquids or partially oxygenated liquid hydrocarbon products such as mixed alcohols. To benefit from economies of scale, these types of facilities usually have to be constructed at a large scale. The capital cost estimates for a first-of-its-kind commercial (2000

tonnes of biomass (dry basis) per day) gasification-based facility are in the region of USD \$600-900 million. Several companies are pursuing gasification platform routes to drop-in biofuels such as UPM-Kymmene's (Finland) proposed 32 million gallons (120 million L) per year (MGPY) facility in Stracel, France and Forest BtL Oy (Finland), which has licensed Choren's Carbo-V technology and hopes to complete a 34 MGPY (130 million L) by 2016.

Leveraging the facilities of oil refineries

The capital costs of both the oleochemical and thermochemical processes could be reduced significantly by leveraging existing process units available in petroleum refineries. Oil refineries are complex facilities comprised of the many unit operations needed to fractionate and upgrade diverse crude oil feedstocks. Upgrading entails a number of intertwined processes such as cracking (breaking heavy hydrocarbon chains to lighter ones), naphtha reforming (creating aromatic molecules necessary for gasoline blends) and hydrotreatment (mainly used to remove sulfur before fuel blendstock finishing). The dilemma in trying to identify refinery insertion points for renewable feedstock drop-in biofuel intermediates is to what extent should the intermediate be upgraded (deoxygenated) prior to insertion and to what extent should the refinery be adapted to accept less-upgraded, oxygen-containing biofeed intermediates. The challenges of processing biofeeds in an oil refinery are significant, as has been demonstrated by previous industrial trials using less problematic renewable feedstocks such as fatty acids containing relatively low amounts of oxygen (11% oxygen). The oxygen content of biofeeds translates to corrosion of metallurgy and extensive coking of catalyst surfaces as well as downstream contamination risks and requirements for venting of oxygenated gases (CO, CO₂ and H₂O). Strategies to mitigate these challenges include limiting the blending rate of biofeeds in petroleum feeds and favouring insertion points towards the end of refinery processing, both of which lower the risk of downstream contamination with biomass oxygenates, inorganics and tars. Hydrocracking units situated at the end of the oil refining process are suitable for drop-in biofuel leveraging. All of the drop-in biofuel processes proposed to date entail some form or degree of capital intensive and hydrogen-consuming hydroprocessing (especially pyrolysis and hydrotreated ester and fatty acids (HEFA) platforms). Refineries can be leveraged by drop-in biofuel facilities in order to utilize existing hydroprocessing facilities and also to source low cost fossil feedstock derived hydrogen. Still, even with this lower risk co-location strategy, there are significant challenges that need to be resolved such as matching the scale, siting and catalyst design for two distinctly different feedstocks (bulky and reactive solid biomass versus relatively inert petroleum liquids (crude oil)).

Biochemical technologies

Alternative biological routes have been proposed as a third *biochemical* technology platform for producing drop-in biofuels where the capital costs should be significantly lower than those projected for thermochemical routes. In contrast to the traditional fermentation of sugar to ethanol, these “advanced” biological routes convert sugars to less oxygenated, more energy-dense molecules such as longer chain alcohols (butanol, butanediol) or even larger hydrocarbon molecules such as isoprenoids and fatty acids. Although butanol, n-butanol and isobutanol, are oxygenated and thus cannot be considered to be fully “drop-in” biofuels, they are less oxygenated and hydrophilic than ethanol and companies such as Butamax, Cobalt and Gevo are currently assessing their suitability as intermediates for drop-in biofuel production. Other companies such as Solazyme, using heterotrophic algae, and Amyris and LS9, using genetically engineered yeasts and bacteria (*E. coli*) respectively, are trying to convert sugars directly to renewable hydrocarbons. One of the attractive characteristics of these technologies is the potential to “piggy-back” onto existing ethanol facilities by simply switching the ethanol producing yeast with alternative microorganisms that would instead make the drop-in intermediate. As some of the biological intermediates, such as farnesene, are quite hydrophobic, they should, in theory, be more readily recoverable from the aqueous fermentation broths. However, the recovery of these molecules from the fermentation broth has proven to be more challenging than anticipated due to several factors, such as intracellular expression of hydrophobic metabolites or, as in the case of butanol, fermentation titers typically well below the concentration that induces phase separation (70 - 80 g/L butanol).

Depending on the microorganism used, the “biochemical drop-in pathways” can produce highly reduced biohydrocarbon molecules such as sesquiterpenes and fatty acids thus minimizing the degree of final hydroprocessing needed to bring the biofuel product up to diesel, gasoline or jet fuel specifications. However, most of these advanced biological pathways require more energy and carbon intensive metabolic processes to “reduce” feedstock sugars to saturated hydrocarbons than is required for conventional ethanol production. These metabolic pathways are typically activated under conditions of stress, thus industrial stability of these biological systems can be problematic. The reducing power needed to perform this biological deoxygenation of sugars is usually generated by the microorganism in the form of hydrogen carriers such as NADPH. This reducing power is typically generated at the expense of feedstock (e.g., sugar) carbon, which gets oxidized (“burned” to CO₂) and thereby reduces the overall yields of these processes. For example, fatty acid biosynthesis requires a significant portion of the

feedstock carbon to be consumed to produce the energy required to drive fatty acid elongation. Each elongation cycle requires one reducing NADPH molecule to drive biosynthesis, such that one molecule of a C16 fatty acid (i.e., palmitic acid) requires 7 repetition cycles and thus 7 NADPH molecules, which are usually generated by oxidizing feedstock carbon at the expense of product yield. The demonstrated volumetric productivities and product yields for such advanced biological production (“fermentation”) processes are currently about an order of magnitude lower than what is now achieved by conventional ethanologenic yeast fermentations. As was described previously for thermochemical processes, the use of hydrogen (H₂) from an outside source can improve the yields and volumetric productivities of advanced biological processes. For example, Lanzatech intends to use natural gas derived hydrogen in order to convert CO₂ to biofuel using their proprietary bacteria. Biochemical based drop-in platforms should have one advantage over thermochemical based processes in that relatively pure and functionalized long carbon chain molecules should typically be produced.

However, it should be noted that drop-in biofuels might not be the best value proposition for the biochemical processing of biomass and sugars. Biochemical platform routes, due to fewer processing steps and lower NADPH requirements (or hydrogen consumption), are already well suited to make oxygenated products such as carboxylic acids, alcohols and polyols that can generate substantially higher revenues in the rapidly growing bio-based chemicals markets. Less oxygenated microbial metabolites with potential to be drop-in biofuel intermediates such as Amyris’s farnesene and Gevo or Butamax’s butanol are already being sold in the value added chemicals and cosmetics markets. Thus, market competition for biochemical drop-in products will be significant and likely grow as markets for biobased chemicals continue to expand. Estimates are that these markets will reach 10-50 million tonnes per year by 2020, equal to the current market size for biofuels (Lux Research, 2010; Higson, 2011; Bomgardner, 2012). Until these value-added markets are saturated, there is little economic incentive for the biochemical platform companies to focus on drop-in fuels.

Hybrid technologies

Several hybrid platforms for drop-in biofuel are also under active commercial development, including catalytic aqueous phase reforming (APR) (e.g., Virent), alcohol-to-jet (ATJ) (e.g., Cobalt, Gevo), acid-to-alcohol (e.g., Zechem) and syngas fermentation (e.g., INEOS Bio, LanzaTech). Based on the limited information in the public domain, each of these approaches appears to have both distinct advantages and significant challenges. For example, the APR process can produce drop-in fuel blendstocks but relies

on new catalysts that have not, as yet, been proven at an industrial scale or over prolonged operation when processing highly oxidized (hydrogen-deficient) renewable feeds. Similarly, although syngas fermentation offers the potential to convert higher proportions of feedstock carbon to product, the limited solubility of the CO gas in the aqueous solutions makes scale-up difficult while the need to cool the syngas from over 700 °C to below 50 °C for fermentation hinders process thermal efficiency. However, two hybrid platform companies that are using syngas fermentation technology -- INEOS Bio and LanzaTech – have built and are operating large demonstration/small commercial scale facilities. It should be noted that although ATJ and acid-to-alcohol technologies are technically proven, the drop-in intermediates and many of the proposed feedstocks, such as ethanol, acetic acid, ethyl acetate, etc., are typically more valuable (on an energy basis) as chemicals than as jet or alcohol fuel products. However, as jet fuels from alcohols are expected to acquire ASTM certification in 2014, there is a possibility that ATJ drop-in jet fuels could become commercially attractive in countries such as Brazil and the US where ethanol is currently available at relatively low cost.

Future Outlook

While tremendous technical progress and commercialization activity have taken place over the past several years, only relatively small amounts of drop-in biofuels that are “functionally equivalent to petroleum-derived transportation fuels” are commercially available today. In the same way conventional (so-called “first generation”) bioethanol from sugar and starch was used to establish the infrastructure and “rules” for subsequent production and use of advanced (so-called “second generation”) bioethanol, it is likely that oleochemical derived drop-in biofuels will initially be used to establish the markets and procedures for use of drop-in biofuels. This is exemplified by the many HVO-based biofuel flight trials and refinery processing trials that have been undertaken over the last few years and by the recent ASTM approval of oleochemical derived jet fuel blendstocks. However, the further expansion of the oleochemical platform will be limited by the cost, availability and sustainability of food grade (vegetable oil) or animal oil/fat based feedstocks.

This likely evolution of emerging thermochemical based drop-in technologies piggy-backing on the development of oleochemical based drop-in biofuels is analogous to what is happening in the commercialisation of cellulosic ethanol, where the use of more plentiful, cheaper, non-food lignocellulosic feedstock typically entails larger technology risks and higher capital costs for the processing of the feedstock than sugar and starch-based ethanol production processes but also offer the

potential to greatly expand the level of production and minimize concerns about potential food versus fuel issues. Although oleochemical based biofuels are helping to establish markets for drop-in biofuels, it is likely that, in the mid-to-long term, thermochemical based processes will account for a considerable amount of the growth in drop-in biofuels production. As biochemical and hybrid based processes typically provide lower yields of more oxygenated drop-in biofuels intermediates and these intermediate products often command higher prices as chemicals in the rapidly growing bio-based chemicals markets than they do as biofuels, it is likely that this is where their initial growth will occur, at least until the chemical markets are saturated.

While it is possible that future biorefineries will utilize biomass in much the same way that current petroleum refineries use crude oil (by converting the raw feedstock into a diverse range of fuels and chemical products in a single highly integrated facility), it is probable that larger sized thermochemical based facilities will primarily focus on converting biomass feedstocks to commodity scale drop-in biofuels and bioenergy products while somewhat smaller scale biochemical or algal platform based facilities will convert sugar, biomass or syngas feedstocks to specific higher value non-commodity products such as farnesene, butanediol, succinic acid, butanol or oils for use in more lucrative bio-based fine-chemicals markets (e.g., cosmetics, food additives, lubricants, etc.). Regardless of the specific technology, hydrogen sourcing will play a major role in future commercialization of drop-in biofuels.

Recommendations and future work

Due primarily to the significant processing and resource requirements (e.g., sufficient hydrogen supply and effective catalysts) needed to make drop-in biofuels as compared to “conventional” oxygenated alcohol and FAME biofuels, large scale production of cost-competitive drop-in biofuels will be challenging in the near-to-midterm. Thus, supportive policies will likely be needed to promote the development and commercialization of these fuels if they are to become significant contributors to global biofuels production. Currently, no policies (e.g., tax breaks, subsidies, etc.) differentiate new, more fungible and infrastructure ready drop-in type biofuels from less infrastructure compatible oxygenated biofuels. While some mandates distinguish between conventional and advanced biofuels in terms of their greenhouse gas emissions reduction potential (e.g., the US RFS), there are currently no such incentives to stimulate development and use of drop-in biofuels. While oleochemical platforms are commercial today, their future growth is constrained by the cost and availability of feedstocks. Although thermochemical based processes have considerable potential, further R&D support is required to help

resolve scale and catalyst issues. In the short term, biochemical based platform will likely focus on producing higher value chemicals while building the experience and capacity needed to be able to scale up drop-in biofuel production when bio-based chemicals markets become saturated. While tremendous technical progress has been made in developing and improving the various routes to drop-in fuels, supportive policies directed specifically towards the further development of drop-in biofuels will be needed to ensure their continued development and to hasten their future commercial success.

R&D focus areas that should have a significant impact on enhancing the commercial viability of drop-in biofuels:

- Development of economically viable processes to produce renewable industrial grade hydrogen;
- Establish more cost effective and area efficient terrestrial or aquatic based systems to produce oleochemical feedstocks;
- Improve the cost, performance, lifespan and recyclability of hydroprocessing catalysts for oxygenated biomass feedstocks;
- Create economically viable small scale gasification and syngas cleanup processes;
- Produce biofuel intermediates that are miscible and better able to be co-processed with petroleum feeds;
- Improve the productivity and product recovery methods of biochemical platforms;
- Develop the potential synergies of co-processing bio-oil and fossil liquids in thermochemical processes and in existing petroleum refineries.

Strategic/logistic recommendations:

- Use of pyrolysis oils as intermediates for gasification (logistics benefits);
- Utilize idle Fluid Catalytic Cracking (FCC) and hydrogen generating capacity located within current oil refineries;
- Incorporate value added chemicals in all drop in biofuel platforms, particularly in the case of biochemical platforms;
- Develop and implement policy measures that differentiate and enhance drop-in biofuels RD&D and reduce regulatory hurdles limiting the co-processing of bio-oils in oil refineries;
- Include and consult with the aviation sector in the development of drop-in biofuel promoting strategies (i.e. development of drop-in aviation biofuel mandates and tax incentives as well as transportation GHG reduction strategies such as those described in the EU ETS and the US RFS).

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