Potential synergies of drop-in biofuel production with further co-processing at oil refineries

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Abstract: Drop-in biofuels have been defined as functionally equivalent to petroleum-based transportation fuels and are fully compatible with the existing petroleum infrastructure. They will be essential in sectors such as aviation if we are to achieve emission reduction and climate mitigation goals. Currently, 'conventional' drop-in biofuels, which are primarily based on upgrading of lipids / oleochemicals, are the only significant source of commercial volumes of drop-in biofuels. However, the necessary increased, future volumes will likely come from 'advanced' drop-in biofuels based on biomass feedstocks such as forest and agriculture residues. Biocrudes / bio-oils produced from lignocellulosic feedstocks using thermochemical technologies such as gasification, pyrolysis, and hydrothermal liquefaction need to be further upgraded to drop-in biofuels. However, advanced drop-in biofuels have been slow to reach commercial maturity due to significant technical challenges, high capital costs, and the challenge of generally lower oil prices. It is likely that the co-processing of drop-in biofuels with conventional petroleum refining could considerably reduce capital costs. Initially, co-processing is likely to be established through the upgrading of conventional / oleochemical feedstocks (lipids). Lipids are readily available in large volumes (global production in 2017 was ~185 million metric tonnes) and can be more easily integrated into oil-refinery processes. In contrast, lignocellulose-derived biocrudes / bio-oils are not yet available in significant volumes and are more complex to co-process in a refinery. The likely strategies for co-processing of oleochemicals (lipids) and bio-oil and biocrude feedstocks based on different insertion points within the refinery infrastructure are discussed. © 2019 The Authors. *Biofuels, Bioproducts, and Biorefining* published by Society of Chemical Industry and John Wiley & Sons, Ltd.

Keywords: co-processing; drop-in biofuels; fluid catalytic cracker (FCC); hydrotreater; lipids / oleochemicals; pyrolysis bio-oils / biocrudes

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Introduction

The development of biofuels that can contribute to the decarbonization of long-distance transport, specifically drop-in biofuels, which are functionally equivalent to petroleum fuels and fully compatible with existing infrastructure, are becoming increasingly interesting to sectors such as aviation, marine, rail, and long-distance trucking.[1] The vast majority of current biofuels are oxygen-containing bioethanols and fatty acid methyl ester (FAME) biodiesels, which are not typically defined as drop-in biofuels. However, renewable diesel (also known as green diesel, hydrotreated / hydrogenated vegetable oil (HVO), hydrotreated / hydroprocessed ester and fatty acid (HEFA), hydrotreated biodiesel, or hydrogenation-derived renewable diesel (HDRD)) can be considered to be a drop-in biofuel and is likely to be used increasingly by sectors such as marine and rail and as one route to biojet fuel production. Although this fuel has been used primarily as a diesel substitute,[2,3] significant volumes of drop-in biofuels, potentially as high as 426 million tonnes, will be required by a sector such as aviation where there is no other low carbon alternative such as electrification to meet climate goals.[4]

Currently, the only drop-in biofuel that is produced at a commercial scale is based on the hydrotreatment of lipids (the oleochemical pathway), primarily to make renewable diesel and biogasoline but also providing smaller volumes of biojet fuels by companies such as World Energy in California.[5] To date, vegetable oils have been predominantly used as the feedstocks as they are available in relatively high volumes, have a relatively high energy density, and can be readily transported in large quantities. Used cooking oil and tallow have also been utilized by companies such as Neste at their large-scale renewable diesel facilities in Rotterdam, Finland, and Singapore.[6]

However, it is recognized that the supply of oleochemical feedstocks is constrained relative to the demands of the world's long-distance transport sectors.[3,7] Thus it is probable, building on the pioneering supply chains established by the production and upgrading of conventional / oleochemical-based drop-in biofuels, that complementary and still-evolving advanced drop-in biofuel technologies, based on lignocellulosic feedstocks, will be required to meet market demands for drop-in biofuels. As summarized in earlier reports,[3] it is likely that initial upgrading based on thermochemical-based technologies will use pyrolysis / hydrothermal liquefaction (HTL) platforms as gasification / Fischer–Tropsch-based technologies are challenged with issues such as economies of scale, gas clean up, etc. As wil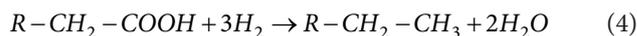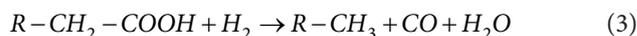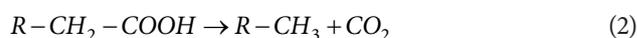l be described in more detail, the co-location of these facilities with oil refineries should be an attractive option as processes such as catalytic cracking and hydrotreating / hydrocracking will be used to upgrade the biocrudes to fractions such as biojet fuel, renewable diesel, and biogasoline. Refinery integration will also facilitate both increased access to hydrogen, where the refinery already has the existing infrastructure, and co-processing, through the insertion of biobased feedstocks at suitable points within the refinery.

It is also likely that refinery integration will improve the economics of drop-in biofuel production as, using a co-processing strategy, biocrudes could serve as an intermediate commodity that could be sold to refineries where further processing to finished fuels can be carried out. This review discusses the potential of near-term lipid-based (conventional) and longer term lignocellulose-based (advanced) 'biocrudes' to provide drop-in biofuels, their probable upgrading requirements and the possible refinery integration strategies that will likely be adopted to fully commercialize drop-in biofuels production.

Drop-in biofuel production – Oxygen removal and implications

As mentioned earlier,[3] one of the greatest challenges of upgrading lipids / biomass to drop-in biofuels is the removal of oxygen. Although other heteroatoms such as nitrogen may be present, oxygen is the most prominent and it reduces the energy density of the fuel. Oxygen-containing biofuels are limited to low blending volumes, and oxygen-containing functional groups also attract water, which can lead to an increased risk of corrosion to pipes and storage containers.[3] Typically, the removal of oxygen takes place through three types of reactions, decarboxylation (oxygen removed as CO_2), decarbonylation (oxygen removed as CO), and hydrodeoxygenation (oxygen removed as H_2O).[8–10]

These reactions are summarized below:[8,11]

$$C_6H_{12}O_6 \rightarrow aC_xH_{2x+2}O_y + bCO_2 + cH_2O + dCO + eC \quad (1)$$

$$R-CH_2-COOH \rightarrow R-CH_3 + CO_2 \quad (2)$$

$$R-CH_2-COOH + H_2 \rightarrow R-CH_3 + CO + H_2O \quad (3)$$

$$R-CH_2-COOH + 3H_2 \rightarrow R-CH_2-CH_3 + 2H_2O \quad (4)$$

The removal of oxygen, typically as CO and CO_2 reduces the yield of fuel products, as carbon is 'lost' to these gases rather than captured in valuable liquid reaction products (reactions 2 and 3). In contrast, hydrodeoxygenation requires an external source of hydrogen (reaction 4).

Earlier work ranked the various likely lipid / biomass feedstocks on a staircase based on their effective H/C ratio (Fig. 1).[3] This served as an indicator of the extent of upgrading that will usually be required to produce a deoxygenated drop-in biofuel. It also provided an indication of the increased demand for hydrogen during upgrading, as the oxygen content in biomass increases.[3] Related work by Talmadge *et al.*[10] also showed that higher H/C ratio feedstocks were easier to upgrade than lower H/C ratio feedstocks and that other factors such as increased coking, were often observed with low H/C feedstocks.[10]

Although deoxygenation in the presence of hydrogen promotes the hydrodeoxygenation reaction, the extent of hydrodeoxygenation is also influenced by reaction conditions such as pressure, temperature and the type of catalyst used.[12–14] This is in addition to economic considerations such as the cost of hydrogen and availability of supply.[15] In practice, all three reactions (Eqns (2)–(4)) take place during oxygen removal and all three byproducts are formed in various quantities. This is regardless of whether hydrogen is supplied or not, as it has been shown that hydrogen transfer takes place between molecules to facilitate hydrodeoxygenation.[16] Supplying external hydrogen will be costly and its source will impact the life cycle analysis of a biofuel. Thus, the extent and control of hydrodeoxygenation is important. The type of catalyst used also has an impact on reaction selectivity.[17,18]

The CO_2, CO, and H_2O formed as a result of deoxygenation are different from the gaseous products that are typically formed during upgrading of fossil crude, where a heteroatom such as sulfur is removed as hydrogen sulfide. In addition, depending on the proportion of biobased feedstock inserted into the refinery and its oxygen content, the volumes of gaseous products produced may be significantly higher. This will likely present engineering challenges, related to pressure buildup and the treatment capacity of gaseous products, while co-produced water may damage alumina supported catalysts and impact subsequent downstream processing.[19]

During oxygen removal, the control of temperature in a reactor is important due to the relationship between hydrogen consumption and increases in temperature due to the exothermic nature of hydrodeoxygenation.[20] The consumption of hydrogen was shown to be highest when using biogenic feedstocks, when the degree of feedstock unsaturation is greatest and when using higher temperatures.[12,21] It has been shown that elevated temperatures can cause damage to some catalysts while also potentially resulting in unwanted secondary reactions, such as the formation of CH_4 from CO. This diverts hydrogen away from the final fuel, increases hydrogen consumption, and results in a higher yield of single-ring aromatics.[22]

Although refinery operations such as hydrotreating and hydrocracking routinely use hydrogen for removal of heteroatoms such as sulfur and nitrogen, the concentration of these contaminants is typically very low (average 1.8% S, 0.1% N in typical crude oil) when compared to the oxygen levels in biobased feedstocks (~10% in vegetable oil and up to 40% in bio-oil).[23] Thus, within the broader scope of heteroatom removal, the high levels of oxygen in bio-based feedstocks and the complex reactions taking place during oxygen removal pose an ongoing challenge during upgrading of biobased intermediates. Not only the concentration of oxygen but also the nature of oxygen-containing functional groups (hydroxyl, carboxyl, aldehyde, ketone, ester, ether) and their reactivity at different temperatures can help predict the likely behavior of biofeeds during processing.[8,10,24,25]

As well as high pressures, high amounts of hydrogen may be required to complete upgrading, the hydrogen consumption varying with different processes.[26] The source of the hydrogen, which will likely be from the steam reforming of natural gas in the short term, will also have an impact on the life cycle analysis with subsequent carbon intensity of the biofuel probably influencing the economics of upgrading.[10]

Potential refinery integration points

Many oil refineries have different configurations and product profiles, including fuels, chemicals, and asphalt. Consequently, they may be more-or-less suitable for insertion of bio-intermediates, depending on the nature of the intermediate and the desired products. A basic, hypothetical refinery configuration is depicted in Fig. 2.
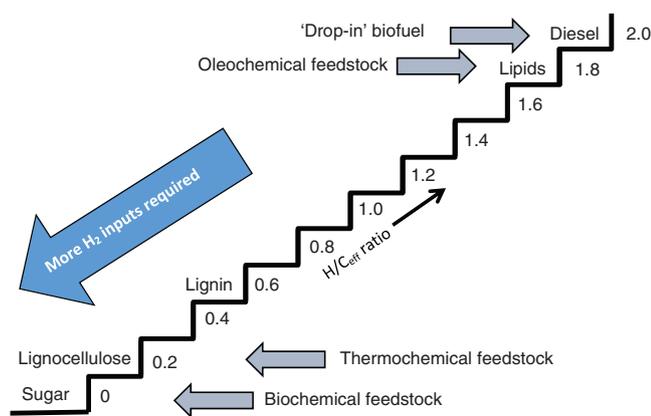

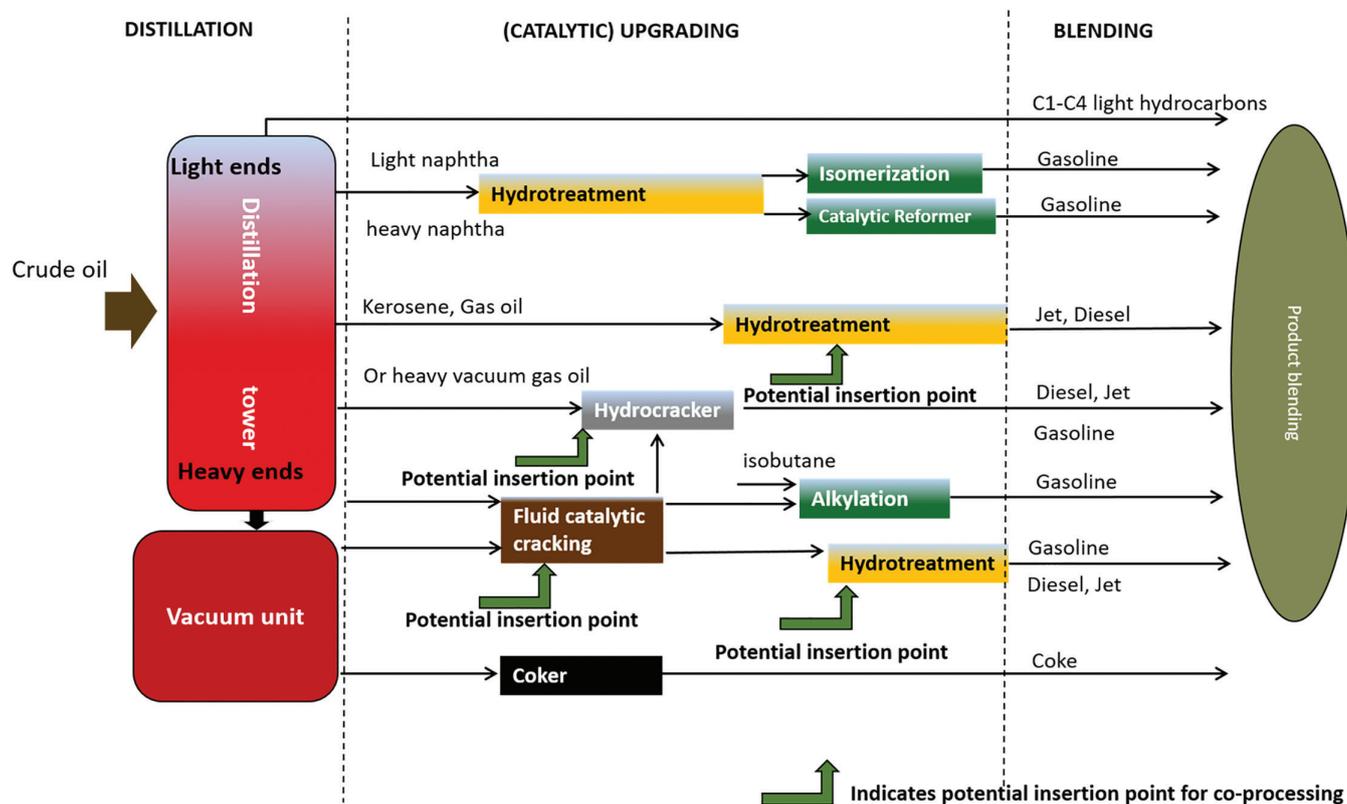Figure 1. The effective hydrogen to carbon ratio 'staircase' for feedstocks (adapted from references).[1,3]

Figure 2. Simplified diagram of an oil refinery.[1,15]

It is probable that many of the biocrudes that might be upgraded at a refinery will contain larger molecules composed of phenols, catechols, guaiacols, and syringols.[25] Consequently, some form of cracking will be required to create shorter molecules that comply with the specifications for specific fuels. This could take place in one or more of the three processing units of, the fluid catalytic cracker, the hydrocracker, or the delayed coker (thermal cracking). Typically, hetero-atoms are removed through hydrotreating, whereas processes such as isomerization, catalytic reforming and alkylation are usually used for any final polishing steps.

A recent review by PNNL describes the US refineries that could be well suited to 'biorefinery integration', based on configuration.[27] It was apparent that two characteristics are important in a refinery integrated with biobased intermediates, namely processes that convert large molecules into smaller molecules (cracking, with or without hydrogen) and processes that remove oxygen, primarily through hydrotreating. Earlier work has suggested that refineries that have no hydrotreating facilities are not suited for upgrading bio-feedstocks unless oxygen removal is carried out prior to insertion.[27]

In the following section, different potential insertion points were evaluated. As it is likely that potential processing needs will be determined based on the desired products, some of the key upgrading needs for different feedstocks and technologies are summarized in Table 1.

Evaluation of insertion points

The potential risk to the refiner will play a significant role in the final selection of the biocrude insertion point. Blending of biobased fuels with petroleum fuels as finished fuels represents the lowest risk for a refiner, while insertion at the predistillation phase poses the greatest risk. A number of potential refinery processes are briefly described below, as are the potential insertion points for bio-intermediates (Fig. 3).

Distillation as an insertion point for biobased intermediates

Unless the biobased intermediates are functionally equivalent to crude oil, several problems can arise when trying to upgrade them by insertion at the distillation stage. For example, a biobased intermediate that contains

Table 1. Characteristics of different bio-intermediates and main refinery requirements.[1,28–32]		
	Characteristics	Refinery needs
Vegetable oils	Triglycerides and free fatty acids Some heterogeneity with respect to chain length of fatty acids, but chemically quite homogenous Lipids in diesel range 11% oxygen, 1.8 H/effC ratio Waste oils have higher free fatty acids which affects the acidity. Waste oils also have other contaminants Metals/inorganic compounds	Removal of oxygen Some cracking may be required for specific products such as jet fuel as lipids in diesel range Isomerization / branching to improve cold-flow properties (biojet) Needs the least upgrading Fractionation may be required after cracking
Pyrolysis bio-oils	Up to 400 different components High oxygen levels over 40% Variable aromatic content from degradation of lignin Water content Catalytic pyrolysis oils or partially hydrotreated pyrolysis bio-oils have lower oxygen levels than bio-oil (for catalytic pyrolysis oil, the oxygen content is generally between 18 and 24 wt%)	Removal of oxygen Thermal or catalytic cracking of large molecules into smaller molecules Potential hydrocracking of aromatics Fractionation into different products after upgrading
HTL biocrudes	Lower oxygen content (range: 6–18%) Lower water content	Oxygen removal Cracking of larger molecules Hydrocracking of aromatics
Fischer-Tropsch (FT) liquids	High temperature FT creates smaller molecules suitable for gasoline Low temperature FT creates longer molecules in the diesel range	Fractionation required May require cracking Isomerization
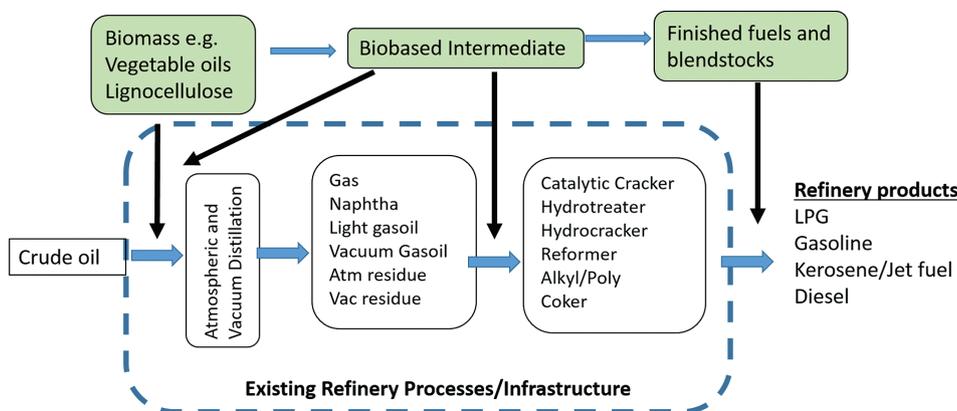
Figure 3. Potential refinery insertion points for bio-intermediates (based on Holladay[26]).

contaminants could result in the contamination being distributed throughout the refinery. Any biobased intermediates that are inserted at this stage of the refinery will have to be virtually free of oxygen and free of possible contaminating and reactive species such as olefins, carbonyls, alcohols, and aldehydes. An additional problem is the unstable nature of biobased intermediates at increased temperatures, with heating resulting in an increase in polymerization as the compounds react with each other, leading to increased viscosity and increased residue formation. Many bio-oils / biocrudes also contain significant amounts of non-volatile compounds such as sugars and oligomeric phenolics and are not suitable for distillation.

Fluid Catalytic Cracker (FCC) as insertion point

The fluid catalytic cracking (FCC) unit is typically used to 'crack' heavy molecules (the usual feed is heavy gas oil, vacuum gas oil, or residues), and is the main process for production of gasoline (50%) and propylene.[33] The FCC insertion point should be economically attractive as no external hydrogen is required and FCC catalysts are more tolerant than hydroprocessing catalysts of higher oxygen levels in the biofeeds.[34] The FCC catalysts, usually zeolite catalysts in a silica or alumina matrix, are continuously regenerated on site by burning off any coke deposits in a

regenerator attached to the FCC unit before recirculating the catalyst. The regeneration and combustion of coke produces heat, which can be used in the refinery. However, excess coke production resulting from the insertion of biobased feeds could cause unacceptable increases in temperature that could cause damage to the FCC catalyst, posing a challenge to maintain an appropriate heat balance.[10,35,36] It is also recognized that acid-catalyzed cracking occurs in the FCC, with additional thermal cracking of larger molecules taking place outside the catalyst due to the high temperatures that are generated. The general characteristics of catalytic cracking are that the largest molecules are cracked first, olefins are formed, and the alkyl chains attached to aromatic rings are then cleaved off if they have three or more carbons.[20] Secondary reactions, involving polymerization and condensation, also take place and these contribute to the formation of coke. It should be noted that aromatics do not undergo any cracking in an FCC and insertion of pyrolysis bio-oils into the FCC usually results in a greater aromatic content in the products.[16] The removal of oxygen from the bio oils in the FCC results in the consumption of hydrogen from the hydrocarbon feedstock and, consequentially, more olefins are produced as well as aromatics.[10]

A key consideration when assessing catalytic cracking as a possible co-processing insertion point is the experimental set-up, as it may not be truly representative of what might actually be carried out in a more realistic bio-oil co-processing approach.[15] Various configurations including the micro activity test (MAT) reactor, advanced catalyst evaluation (ACE), laboratory-scale micro-risers and a laboratory-scale two-stage riser fluid catalytic cracking unit, as well as pilot plants. Many of these options have been used for both catalyst evaluation and to assess reactor behavior and product formation based on different feedstocks. However, the authors pointed out several shortcomings of these options, such as the fixed bed MAT reactors not being steady-state processes. The contact time between catalyst and feedstock is also 10–100 s whereas in commercial FCCs it would be 1 s. This enhances hydrogen transfer reactions and has an impact on the products formed.[15] In related work by de Rezende Pinho *et al.*,[16,37] these experimental setups generally resulted in higher coke formation than in more realistic setups, which mimic commercial-scale FCCs. These workers concluded that these experimental set-ups helped us better understand the possible co-processing of bio feedstocks but they also confirmed the challenge in accurately predicting product distribution (coke versus liquid products).

As fluid catalytic cracking capacity is closely linked with the demand for gasoline, it is more common in refineries in North America where there is a higher demand for gasoline. In contrast, refineries in Europe have a higher demand for diesel, which is typically produced through hydrotreating / hydrocracking.[38,39]

The Hydrotreater as an insertion point

Hydrotreating is primarily used in petroleum refineries to remove heteroatoms from petroleum product streams. The process involves high temperatures and pressures as well as specialized catalysts. Hydrocracking is more severe and requires specialized bifunctional catalysts.[20,40] Hydrotreating reactions will generally proceed in the following order, (organometallic) metals removal, olefin saturation, sulfur removal, nitrogen removal, oxygen removal and finally halide removal.[20] Although some aromatic saturation will take place, this will be limited as ring opening requires special catalysts and higher operating pressures.

Hydrotreating reactors are mostly fixed catalyst beds, with cobalt and molybdenum sulfide on alumina catalysts most often used. Other catalysts that have been used include nickel sulfide, nickel thiomolybdate, tungsten and nickel sulfides, and vanadium oxide.[1] Typically, catalysts are regenerated at an off-site facility after months or years (cycle can be 12 months to 60 months) of operation as replacement of catalyst can be costly.[41] The absence of *in situ* regeneration, as occurs with the FCC catalysts, means that the hydrotreater is less tolerant to contaminants. Thus, deactivation and the risks associated with insertion of unknown feeds are much greater.

Hydrotreating is an exothermic reaction, with heat release proportional to the consumption of hydrogen.[20,21,24] Thus, as discussed earlier, oxygen removal generates significant heat and temperature in the reactor and has to be controlled to prevent unwanted reactions taking place. This could lead to increased coking, a decrease in pressure, or poor liquid flow distribution. As a result, modified cooling systems will be required to prevent uncontrolled increases in temperature.[19,42] It should be noted that sulfur and nitrogen occur at relatively low concentrations in crude oil as compared to the potential high concentration of oxygen in biobased intermediates (see Table 2 for a comparison between composition of different biobased feedstocks compared with crude oil).

Consequently, although the processes for removal of sulfur, nitrogen,. and oxygen are similar, the conditions will have to be adjusted. More hydrogen will be required to remove the oxygen while the catalysts that are most

Table 2. Comparison of typical composition of various biobased feedstocks with crude oil.[23,43–45]

	Vegetable oil[a]	Fast pyrolysis[b]	Catalytic fast pyrolysis[c]	Hydrothermal liquefaction[d]	Crude oil[b]
C, wt%	77.6	55–65	72	81.4	83–86
O, wt%	10.4	28–40	21.5	9.8	<1
H, wt%	11.7	5–7	6.4	8.7	11–14
S, wt%	0.0006	<0.05	—	0.01	<4
N, wt%	0.0011	<0.4	0.02	0.095	

[a]Data taken from Holmgren *et al.*[23] using soybean oil.
[b]Data taken from Mortensen *et al.*[43]
[c]Data taken from Passikallio.[44]
[d]Data taken from Jensen *et al.*[45]

suitable for removing sulfur and nitrogen may not be optimal for removing oxygen. Even at high hydrogen pressures the removal of oxygen will not exclusively proceed through hydrogen addition as CO and CO_2 will also be formed. These products can also cause inhibition of catalysts and, as regeneration does not take place *in situ*, can cause significant problems for the refinery.

Hydrocracking as an insertion point

Hydrocracking involves the reduction of large molecular weight compounds into lower molecular weight products, while adding hydrogen and carrying out similar reactions as described for hydrotreating. This is done in the presence of hydrogen and at high pressures (around 2000 psig/14 MPa).[1] Although hydrocracking is costly, the resulting products require less downstream processing. It should be noted that hydrocracking reactors are not suitable for feedstocks containing oxygen or other impurities unless the feeds have first been hydrotreated. The high cost of catalyst and offsite generation make this process very sensitive to any contamination, particularly when the hydrocracking catalysts contain noble metals such as palladium (Pd) or platinum (Pt) which are expensive to replace.[41] Thus, hydrocracking may be used as a second step in upgrading of biobased feedstocks where size reduction is still required.

Refinery co-processing of vegetable oils and lipids

The oleochemical (conventional) route to producing drop-in biofuels is the best developed and commercialized process, producing more than 4 billion liters in multiple facilities around the world.[3] The vast majority of current production takes place in freestanding facilities, some based on repurposed oil-refinery infrastructure. Co-processing of lipids has been primarily investigated based on insertion

in the hydrotreater with limited work published on co-processing of lipids in fluid catalytic crackers.[8,9,15]

As a variety of sources of oleochemicals / lipids can be used to produce drop-in biofuels the differences in the chemical characteristics of the feedstock have to be considered, including chain length of fatty acids, degree of unsaturation, free fatty acid content and the possible presence of contaminants. Processes such as hydrotreating are more flexible with respect to the free fatty acid content than is the traditional production of biodiesel (fatty acid methyl esters). The main consideration from an engineering perspective is the acid or total acid number (TAN) levels of the feedstock with feedstocks with a high free fatty acid content, likely requiring more expensive metallurgy to prevent corrosion.[46]

So-called waste feedstocks, such as brown grease and used cooking oil, could potentially improve the economics and LCA of oleochemical based drop-in biofuel production as these types of lower cost oleaginous feedstocks can be used with appropriate pretreatment. Another oleaginous feedstock that has been used successfully is tall oil, which is a waste product from the pulp sector. For example, Preem is using esterified tall oil in a co-processing strategy to make drop-in renewable diesel.[19,42,47]

Possible insertion of lipids in the hydrotreater

The upgrading of triglycerides takes place in multiple stages with the double bonds on the fatty acid chains first hydrogenated, followed by the formation of fatty acids and propylene. The propylene is converted to propane, using hydrogen and high pressures. This is finally followed by the deoxygenation of the fatty acids through hydrodeoxygenation, decarboxylation, and decarbonylation.[21] As described earlier, hydrotreating of vegetable oils results in the formation of CO, CO_2 and H_2O, thus one potential concern with co-processing vegetable oils with petroleum

liquids is how it might impact desulfurization, as greater volumes of hydrogen will likely be required.[48,49]

Conflicting reports in the literature indicate that this is not a simple matter, as reduced hydrodesulfurization and hydrodenitrogenation was found for conventional CoMo-type catalysts, but not for NiMo catalysts.[13,42] Other workers also showed that hydrocracking was inhibited when vacuum gas oil and sunflower oil were co-processed.[50] However, some studies have shown that hydrotreating of vegetable oils with a petroleum-based feed did not impact hydrodesulfurization and improved the yield of alkanes when compared to hydrotreatment of vegetable oils alone.[11,18,51]

Recently, Bezergianni *et al.*[15] suggested that these variable results were partly due to the specific fossil feedstock used during co-processing, as well as the nature of the renewable feedstock (chain length, degree of saturation), blending level, reactor conditions, etc. For example, the presence of double bonds (unsaturated) in the feedstock means more hydrogen consumption, thus the more exothermic reaction will require additional cooling to prevent catalyst deactivation in the fixed-bed hydrotreaters.[19] However, the more saturated the lipids are, the more likely it is that they will be in a solid or semi solid state at room temperature. This is the case with feedstocks such as tallow and palm, which typically need to be heated to make them liquefied and more easily transported.

Some general trends highlighted by Bezergianni *et al.* include:[50]

- Low-quality feedstocks containing water and a high fatty acid content may require pretreatment prior to insertion into the hydrotreater.
- Above a 15% feed, lower liquid yield and sulfur removal resulted. An optimum ratio of 10% vegetable oils was recommended.
- Higher H_2 pressures are required for co-processing of vegetable oils. However this could cause some cracking to take place.
- Some studies indicate that saturated lipids could be hydrotreated at lower temperatures (320–340°C) than unsaturated lipids (over 340°C).
- A higher H_2 to oil ratio favors saturation and heteroatom removal. However, this depends on the saturation level of the bio-feedstock (palm oil and tallow are more saturated).
- Compared to CoMo and NiW catalysts, NiMo catalysts are usually better for lipid co-processing as they show lower deactivation rates while the hydrodesulfurization and hydrodenitrogenation reactions are not affected.[13,18,51]

Despite these challenges, hydroprocessing is the only type of co-processing that has reached full commercial scale, as demonstrated by Preem, Cepsa, Repsol and Kern Oil.[7,52] However, co-hydroprocessing using oleochemical feedstocks will likely remain challenging. Standalone hydroprocessing units co-located at existing refineries might be more attractive, even though the initial capital costs are higher.[7,9] This is because the purer, higher value products (renewable diesel, renewable jet, renewable gasoline, and renewable propane) provide the refiner with increased flexibility to either blend with other low-grade streams or sell them directly as drop-in biofuels.[7]

Although co-hydroprocessing of oleochemicals may not be suitable for every refiner, as additional equipment may be needed and operational cost will probably be higher, as discussed below, it is still likely that this is where co-processing of biocrudes will first be developed at a commercial level.

Insertion of lipids in the fluid catalytic cracker

As most studies have focused on co-processing in the hydrotreater or via standalone hydrotreatment, only limited information has been published on the co-processing of vegetable oils and lipids in the fluid catalytic cracker (FCC). However, it is likely that co-processing of lipids in the FCC will be advantageous as potential synergies between the lipids and the fossil feed can result in increased conversion and increased octane number of the products, as well as oxidative stability.[15,53] In contrast, other studies have suggested that no or little synergistic action took place, illustrating the complexity of the subject and the limited data available.[54–56] It should be noted that lipids are generally considered to be easier to co-process than biocrudes/bio-oils as they are completely miscible with the fossil feed and are easily cracked under reactor conditions.

Although earlier work by Melero *et al.*[57] showed that increased coking resulted with the addition of vegetable oils to a FCC feed,[57] this study was carried out in a MAT reactor which does not provide a realistic simulation of reactions in an FCC. These researchers also observed an increase in the formation of aromatic compounds when the percentage vegetable oil was increased in the FCC feed. However, more recently, Bezergianni *et al.*[15] suggested that decreased aromatics and decreased sulfur levels could be expected.[15] Thus, it is apparent that the type of lipids/vegetable oils and the saturation levels of the fatty acids will have an impact on the products formed as olefinic bonds are more reactive.

It is likely that co-processing oils and fats in the FCC will be the least risky strategy because the fluidized FCC is designed to increase the value of heavy fraction of the crude with the catalysts regenerated onsite. However, only limited information has been reported on any commercial-scale work.[58] Although Petrobras catalytically cracked soybean oil in the 1980s, to produce gasoline with higher octane number and lower sulfur and nitrogen levels, the large scale of the FCC made the co-processing possible only at low blending levels.[59] This early work also identified that access to large volumes of inexpensive, lipid feedstock will be an ongoing challenge.

Refinery co-processing of thermochemical liquefaction platforms

Although all types of biomass can be potential feedstocks for the thermochemical liquefaction platform, to date, slurries such as algae and sewage sludge have proven easier to process. Thermochemical liquefaction of biomass feedstocks via pyrolysis or hydrothermal liquefaction results in the formation of complex mixtures of hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids and phenolics compounds.[60] Many of these are very reactive species that make biocrudes/bio-oils unstable at higher temperatures. Significant variability also results from both the different processing strategies, such as fast pyrolysis, catalytic pyrolysis, hydropyrolysis or hydrothermal liquefaction and the nature of the biomass feedstock (wood, bark, agricultural residues, sludge, wet/dry, size, etc.).[43,61,62] Most of the co-processing studies reported to date focus on bio-oil produced by fast pyrolysis processing. While some general conclusions can be made, these observations cannot be automatically extrapolated to all bio-oils / biocrudes, as biocrudes derived via hydrothermal liquefaction have already been deoxygenated to an oxygen content of around 10% whereas fast pyrolysis oils still have an oxygen content of around 40%. In addition, the characteristics of the fossil feed that will be used during co-processing will also have a significant impact on the final product characteristics.[63]

Fast pyrolysis bio-oils generally have a high oxygen and water content, are highly acidic (high TAN level), and neat pyrolysis oils are not miscible with hydrophobic fossil feeds unless additives are used.[10,60,64] The miscibility of the bio-oil with fossil feed is important if using a co-feeding strategy but it is less important if a separate feed strategy is used.

The two main goals in successfully upgrading bio-oils are the removal of oxygen and reducing chain length of the carbon molecules (cracking). Cracking in an oil refinery is achieved by thermal cracking in the coker, catalytic cracking in the FCC or hydrocracking in the hydrocracker. The approach chosen will depend on the specific refinery configuration, desired products required and the characteristics of the biofeed. As mentioned earlier, hydrocracking reactors are very sensitive to contamination and catalyst inhibition. Biofeeds that require significant upgrading will therefore not be attractive.

Dry biomass, such as wood, typically contains 40–44% oxygen.[65] Thus, any pyrolysis oils produced by fast pyrolysis will have a similar oxygen content.[10] As the target for effective drop-in biofuel use is for it to be virtually oxygen free, significant oxygen removal has to take place. Early work found that co-processing of pyrolysis oils resulted in reactor plugging and high coke formation due to polymerization.[50,66–68] As a result, it was concluded that fast pyrolysis oil (FPO) should not be co-processed in an unhydrotreated form and, instead, should first be hydrotreated (hydrodeoxygenated pyrolysis oil HDO; or hydrotreated pyrolysis oil HPO) to substantially reduce its oxygen content prior to co-processing. As mentioned earlier, untreated fast pyrolysis oils (FPO) typically contain water, making them immiscible with fossil feeds for co-processing. Miscibility is required for co-hydrotreating and, while additives such as isopropanol or glycol have been used to facilitate miscibility, reducing the oxygen content of the biofeed will also improve miscibility.[66,69] However, the extent of oxygen reduction that is required in order to achieve miscibility is unclear. Arbogast *et al.*[70] have argued that refiner requirements for oxygen-free pyrolysis oil have forced pyrolysis oil producers to add 'miniature refining facilities' to their plants.[70] These authors also highlight yield loss and excessive high hydrogen consumption, which made complete deoxygenation of pyrolysis oil prior to co-processing inefficient.[70] The authors thus suggested that more relaxed oxygen levels for pyrolysis oil intermediates should be adopted by refineries, for co-processing purposes, to make biofuel production cost competitive. However, they also concluded that a significant amount of additional data will be required to determine the target oxygen levels that make the most economic sense.[71] Earlier work has argued that a 10% oxygen content was lower than required and that only the most reactive compounds and functional groups needed to be stabilized.[72]

More recently Bezergianni *et al.*[15] have suggested that catalytic pyrolysis oil (CPO) would be a far better intermediate for co-processing because much lower oxygen levels are achieved during pyrolysis, so there may not be a need

for hydrotreatment.[15] This might be correct from a technical perspective but the economics of catalytic pyrolysis oil production have also to be considered. Most of the past catalytic pyrolysis oil work used acidic zeolites, particularly HZSM-5.[44] However, this catalyst has been shown to deactivate quickly and often needs frequent replacement due to the contaminants like ash in the biomass.[25,44] This adds significant costs to the process and is thought to be one of the major technical difficulties encountered by KiOR who failed to commercialize this technology.[44]

Insertion of bio-oils / biocrudes in the fluid catalytic cracker

Recently Stefanidis *et al.*[73] discussed the possible insertion of bio-oil / biocrudes in the fluid catalytic cracker.[73] These authors suggested that increased coking and reactor plugging due to char and coke formation made raw bio-oil unsuitable for co-processing unless the bio-oil was first upgraded through hydrotreatment to remove oxygen. However, they also indicated that these findings were a result of the experimental set-up as the conditions did not resemble a real FCC, as different conclusions were obtained when using a pilot-scale FCC under more realistic conditions. In related work, de Rezende Pinho *et al.*[16,37] looked at the co-processing of bio-oil in the FCC after appropriate reactor modifications,[16,37] including separate injection of bio-oil. However, other workers have argued that only the most reactive compounds and functional groups needed to be stabilized. Thus, up to a 28 wt% oxygen could be tolerated.[72]

Despite these differences in opinion, there seems to be a general consensus that partial deoxygenation of bio-oil is probably required before insertion, if potential suppliers are to meet the minimum requirements of the refinery. However, complete deoxygenation of bio-oil is expensive because deoxygenation becomes disproportionately costlier when approaching an oxygen-free status.[24,70,74] Catalytic pyrolysis bio-oils and biocrudes from hydrothermal liquefaction are already partially deoxygenated and could potentially bypass intermediate steps prior to catalytic cracking. However, many partially deoxygenated bio-oils and HTL biocrudes have very high viscosities, making pumping difficult.[24,75,76]

Earlier FCC-based trials, which looked at co-processing bio-oil in blends with vacuum gas oil (VGO), demonstrated that lower H/C ratio products were produced when compared to processing VGO alone.[50,77] It was also concluded that heavier (coke and tar) and lighter (gasoline and gases) fractions were produced at the expense of mid-

dle distillates while the gasoline produced was generally poorer in saturates and richer in aromatics.[50]

In a related study, a mixture of 20% HDO bio-oil (at 20% oxygen) was co-processed in an FCC with petroleum VGO,[78] while in similar approach de Miguel Mercader *et al.*[72] co-processed an HDO bio-oil (28% oxygen) with a long residue heavy petroleum feed.[72] Both of these studies reported a decrease in the coking propensity of HDO bio-oils when they were blended as compared to fossil feeds catalytic cracking. This was attributed to the transfer of hydrogen from the petroleum to the biomass feed during co-processing.

In more recent work, where FCC co-processing of raw bio-oils with a 51% oxygen content was tested,[16,37] the oxygen was primarily removed as H_2O, while CO yields were higher than CO_2 yields. Co-processing resulted in gasoline and diesel products with some renewable content, as determined by ^{14}C isotopic measurement. A 10 wt% blend of bio-oil resulted in a 2% renewable content in the total liquid product.[16] It was also concluded that oxygen removal took place through hydrogen transfer from the fossil-feed molecules. This resulted in a higher aromatic content in the final products, with higher levels of phenolics found in the naphtha product. It is important to note the experimental set-up for this FCC demonstration study, in contrast to the many previous laboratory / pilot scale tests, featured a circulating rizer with different feed nozzles. This allowed the separate insertion of the bio-oil (below 50 °C) at a lower point in the rizer to be cracked at higher temperatures and catalyst to oil ratios, when compared with the temperature of the VGO at 220–280 °C. It also resulted in lower coke formation than the FCC labscale test using Micro Activity Testing (MAT) where the feed was blended and heated prior to insertion into the reactor. Thus, de Rezende Pinho *et al.*[16] concluded that lab-scale testing was not adequately able to predict the behavior of co-processing of bioblends in an FCC,[16] as it was difficult to replicate real reactor conditions. Bezergianni *et al.* came to a similar conclusion,[15] although they thought the observation was mostly applicable to raw bio-oil cracking. However, in earlier work, Bryden *et al.*[79] noted increased coke formation in spite of using a pilot-scale circulating rizer reactor and modified feed delivery system.[79] This was similar to the subsequent results reported by Zacher *et al.*[80] where changes in the product yields were also reported, specifically a reduced gasoline yield.[80]

Other related work has suggested that the co-processing of hydrogen deficient bio-oils with hydrogen-rich petroleum feeds can have a positive synergistic effect in mitigating the production of solid by-products.[73] This indicated

that the characteristics of the fossil feed will impact potential synergy, as hydrogen transfer between the fossil feed and bio-components takes place.

In summary, catalytic cracking of raw pyrolysis oil is possible when certain modifications are made to overcome miscibility problems, but the processing of hydrodeoxygenated oils (HDO) and catalytic pyrolysis oils (CPO) is usually easier.[73]

Insertion of bio-oils / biocrudes into the hydrotreater

The lack of miscibility of bio-oils with the fossil feed is a key problem as hydrotreating cannot take place unless mixing takes place. However, most studies on co-processed hydrotreatment have used model compound and the results have therefore been difficult to apply to real bio-oils.[15]

As mentioned earlier, hydrotreatment units are sensitive to oxygen and unlikely to be used to process bio-oils with an oxygen content that exceeds 5%, at blending ratios of less than 10%.[81] Depending on the molecular weight distribution of the bio-oil, cracking of molecules may be required, although this is not usually carried out in the hydrotreater as mild conditions are used. However, hydrocracking typically follows hydrotreating in an oil refinery and it is even less tolerant to oxygen than hydrotreatment (due to higher pressures and temperatures).

It should be noted that there is limited experimental data on co-feeding of real bio-oils with petroleum feeds in hydrotreating units. This is expected as problems such as increased coking and catalyst deactivation, increased hydrogen demand and potential irregular hydrogen pressure drops inside the reactor can be anticipated.[82]

Fate of renewable carbon and tracking of renewable content in fuel products

Policies such as British Columbia's low carbon fuel standard,[83] which helps promotes biofuels consumption, need to account for the renewable content of the fuel to determine its carbon intensity. These types of policies will play an increasingly important role in promoting the willingness of refineries to co-process bio-oils/biocrudes. However, it also means that we will have to better determine the carbon intensity of a fuel using tools such as life cycle assessment (LCA).

At this time, the California Air Resources Board (CARB) is considering including co-processing pathways within their Low Carbon Fuel Standard.[84] One of the key issues

that is under consideration is how to quantify the renewable content of a fuel and the corresponding credits that can be earned by obligated parties. The methods under consideration include the ^{14}C isotopic method, mass balance based on observed yields, and the carbon mass balance method.[85,86]

To date the ^{14}C isotopic approach has been the predominant research method used to track renewable content.[16,37,87,88] However, it is expensive and time-consuming and there are ongoing concerns related to the absolute error of the methodology, especially for low percentage co-processing.[84] Existing biofuel producers such as the Renewable Energy Group (REG) and those represented by the national biodiesel board have indicated that both the mass balance method, based on observed yields, and the carbon mass balance method are inadequate, as neither provides verifiable quantification that could be used to ensure renewable content in the fuels.[89,90]

While the focus of this review is on liquid fuels, 'renewable content' may also end up in solid or gaseous products. Consequently, consideration should also be given to how decarbonization of these products might also be included. For example, using renewable coke products to generate heat may reduce the emissions related to fuel production (as opposed to combustion where a baseline value for a fuel is used).

Another impact of co-processing is the regulatory environment around fuels and fuel specifications, which will have to be adapted to accommodate the inclusion of renewables. This has particular significance for the aviation sector as biojet fuels go through a lengthy and expensive process to become certified under ASTM D7655. The insertion of biobased intermediates in a refinery producing jet fuel as part of their product slate will result in renewable content in the jet fuel. Thus, unless an ASTM standard has been approved for co-processed jet fuel, it will not meet specifications. Currently, an application for certification of co-processed vegetable oil jet fuel has been approved based on 5 vol% insertion of vegetable oil with middle distillates in hydroprocessing. The certification is based on compliance with D7566 (of HEFA) and is further explained in the latest standard specification for aviation turbine fuels (D1655-18a).[91]

Conclusions

Drop-in biofuels, which are functionally equivalent to petroleum fuels and fully compatible with existing infrastructure, will be essential if the world is to achieve significant emission reductions in long-distance transport

sectors such as aviation, marine, rail, and long-distance trucking. However, drop-in biofuels have been slow to commercialize and, currently, the only commercial drop-in biofuels available are based on the upgrading of oleochemical feedstocks such as virgin and waste vegetable oils, fats, and greases (so-called 'conventional' drop-in biofuels). Lipids / oleochemicals are readily available, supply chains are already in place and they have relatively low oxygen levels compared to other bio-based feedstocks and are easy to upgrade to drop-in biofuels. However, supposedly inexpensive lipids, such as used cooking oil, are in short supply and other oleochemical feedstocks, such as palm and canola, are likely to be costly and come with sustainability concerns. The development of advanced drop-in biofuels from what should be cheaper and more abundant lignocellulosic feedstocks via thermochemical processes therefore remains of high interest. At this time there are numerous researchers and companies pursing the production of so-called biocrudes via processes such as fast pyrolysis, catalytic fast pyrolysis and hydrothermal liquefaction (HTL). Although full commercialization of these technologies is proceeding slowly, for various reasons, the integration of drop-in biofuel production with oil refineries is one potential way to enhance their development. An obvious benefit would be helping oil refineries decarbonize and likely make the production of drop-in biofuels more economical.

As detailed in the main body of this review, bio-based intermediates are quite distinct from crude oils as they have a higher oxygen content and more reactive chemistry, which will impact refinery operations. Bio-based intermediates will also display significant variations depending on the feedstock and technology platform used for their production. However, different refinery processing units could be potential insertion points. Thus, final selection will depend on the refinery configuration and the desired products, as well as the characteristics of the bio-based intermediate and economic considerations (value propositions).

To date, most co-processing research has focused on hydrotreaters or fluid catalytic crackers (FCCs) as potential insertion points. The FCC is the most flexible processing unit as it is able to tolerate a variety of feedstocks plus the catalyst is regenerated *in situ*. Although an FCC is able to crack large molecules into smaller ones, it is primarily used to produce gasoline rather than jet fuel range products and many refineries do not have an FCC. In contrast, hydrotreaters generally use expensive catalysts that are regenerated off site every few years. They are typically not used to crack large molecules into smaller molecules but rather as processing units for producing finished fuels (fuel blendstocks). Thus it is likely that refinery co-processing will initially be based on fluid catalytic crackers that offer an 'easier-and-less-risky' insertion point in existing petroleum refineries.

It is probable that initial supply chains / markets for drop-in biofuels will be based on the 'conventional / oleochemical' route where hydrotreaters have already been used to co-process / upgrade the lipid feedstocks. Lipids have a relatively lower oxygen content (11%), when compared to biomass, and are chemically quite similar to one another, making upgrading to drop-in biofuels significantly easier. In contrast, the biocrudes produced by pyrolysis and HTL routes generate more variable and complex bio-intermediate feedstocks that will likely initially need to be inserted / upgraded via fluid catalytic crackers.

Although both conventional and advanced routes to drop-in biofuel production have been demonstrated, with the former already at a commercial scale, ongoing research is still required to elucidate the behavior of different biobased feedstocks in different reactors (chemistry and reactions) and the impacts on the product characteristics. Equally important is the need to better determine the fate of the renewable carbon which will be distributed into the various product fractions, i.e., kerosene, gasoline, diesel, etc., produced during normal refinery operation. Techno-economic assessments of the different feedstock / reactor co-processing combinations will also be required to better determine the economic viability of refinery integration.

The extent to which 'pretreatment / preliminary upgrading' of biocrudes will be needed prior to insertion into a refinery unit is also a key issue that has yet to be resolved. However, once it this has been achieved, it should allow biobased intermediates to become commodity petroleum refinery feedstocks and allow faster commercialization of co-processing. In parallel, supportive policies and other incentives will be required to encourage refineries to study and advance such co-processing technologies.

Acknowledgements

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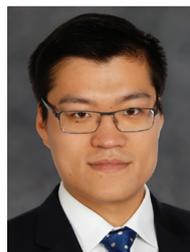
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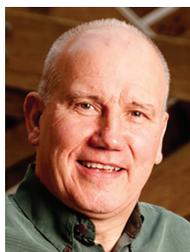
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