Upgrading Bio-oil: Catalysis and Refinery

Robert M. Baldwin

1 Introduction

Fast pyrolysis (FP) is a biomass conversion technology that can produce feedstocks for upgrading to renewable drop-in transportation fuels and blendstocks for petroleum refineries (Richards 2013; Urbanchuk 2012; Green Goods and Services 2013; Production Statistics 2012). Fast pyrolysis is characterized by high throughput at short residence time (1–2 s) under moderate temperatures (400–650 °C) and pressures (c.a. 1 atm), which allows for compact reactors constructed with relatively inexpensive materials and utilizing mature reactor technology such as circulating and bubbling fluidized beds. The yields of organic liquids from FP can be as high as 75 wt%, allowing for high utilization of the renewable carbon (Bridgwater 2003). Some of the remaining light gases and char can be used for plant heat, and the char may be valuable as a soil amendment or for producing high-value coproducts such as bio-graphite and carbon nanotubes ($10–$20/kg).

The liquid produced by FP (pyrolysis oil or bio-oil) has a number of undesirable properties such as high viscosity, reactivity, immiscibility in hydrocarbons, and corrosivity (Oasmaa et al. 1997; Oasmaa and Peacocke 2001, 2010), which are largely due to the high oxygen content (~40 wt%). To address this barrier, a great deal of research has been conducted to develop upgrading processes to remove the oxygen either from the pyrolysis vapors or from the condensed liquids.

In one upgrading strategy known as catalytic fast pyrolysis (CFP), catalysts are employed to upgrade the bio-oil vapors (prior to condensation) with the optional addition of hydrogen to enhance yields. Two modes of operation are possible: in situ CFP where the catalyst is in contact with biomass in the pyrolysis reactor and ex situ CFP where pyrolysis vapors are catalytically upgraded in a separate reactor downstream from the primary pyrolysis reactor. A common application of CFP uses

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zeolite catalysts such as HZSM-5, which produces primarily olefins and aromatic molecules. Mono-ring aromatics (principally benzene, toluene, and xylenes or BTX) from this process can be used as a gasoline blendstock or as replacements for fossil-derived BTX, but the yields of low-oxygen hydrocarbon products from CFP are generally poor (Oasmaa et al. 1997), which results in unfavorable economics when compared to yields from fossil feedstocks. In addition, this approach does not form a significant amount of hydrocarbons that are suitable for diesel and jet fuels, which are considered better targets for advanced biofuels due to projections for future fuel usage (US Energy Information Administration 2016). As a result, alternative approaches to producing "drop-in" hydrocarbon fuels from biomass are being investigated, including the use of metal-based catalysts and adding hydrogen during CFP (Murugappan et al. 2016; Nolte et al. 2016; Venkatakrishnan et al. 2015). Although CFP may significantly reduce the amount of oxygen in the product, liquid-phase hydrotreating may still be required to meet specifications for introduction into a refinery or use as an intermediate or final fuel blendstock.

Hydrotreating of crude bio-oil is a viable strategy for producing hydrocarbon fuels (Jones et al. 2013), but the reactivity of the oil often leads to catalyst fouling and reactor plugging. This can be addressed with multistage upgrading, in which the oil is first catalytically stabilized by hydrotreating at a lower severity and then hydrotreated at higher severity to produce hydrocarbons (Wang et al. 2016). The hydrotreating stage needs to be conducted in two steps with increasing severity to prevent coke formation and to improve hydrogen utilization. The stabilization step targets the removal of reactive components, such as carbohydrates and carbonyl compounds, which can lead to gelation and solid formation. This stabilization step may not be required if the pyrolysis vapors are catalytically upgraded before they are condensed (Wang et al. 2016).

In this chapter we will first review fast pyrolysis for production of bio-oil and the properties of the resulting liquids. This will be followed by a review of options for upgrading bio-oil using catalysts and for integrating pyrolysis oil into a standard petroleum refinery.

1.1 Biomass Pyrolysis and Composition of Pyrolysis Oil

Biomass is composed of three main biopolymers, cellulose, hemicellulose, and lignin, and the decomposition of these three materials is largely responsible for the observed solid, liquid, and gaseous products during pyrolysis. As can be seen (Fig. 1), these biopolymers contain a significant amount of oxygen, which translates into 30–60 wt% oxygen (including oxygen in water) in the oil. Cellulose is a linear polymer consisting of repeat units of cellobiose with a degree of polymerization (dp) often exceeding 2000.

The organization of these polymers in cell walls is the subject of intense research, but it is clear that cellulose microfibrils form what appears to be a mat that provides the structure and strength for plant cell walls and the hemicellulose and lignin are

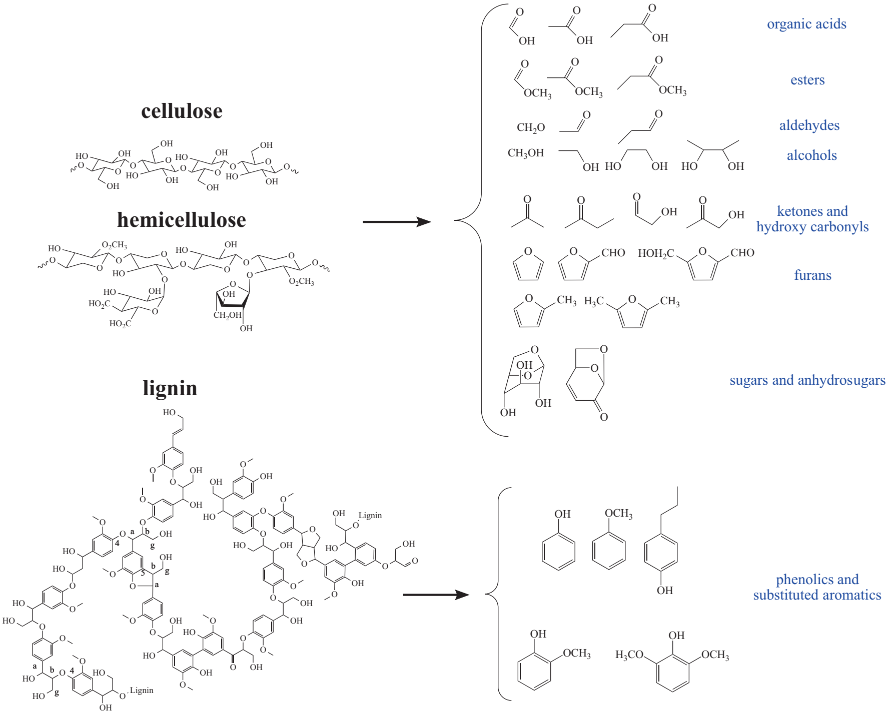

Fig. 1 Typical products formed from the pyrolysis of the biopolymers in plant cell walls

Table 1 Typical biomass composition[a]

Species	Extractives	Ash	Lignin	Hemicellulose	Cellulose
Hybrid poplar (Agblevor et al. 1992)	3.6	0.9	23.3 (24.6)	27.8 (29.3)	43.7 (46.1)
Monterey pine (Wiselogel et al. 1996)	2.7	0.3	25.9 (28.6)	23.0 (25.4)	41.7 (46.0)
Switchgrass (Johnson et al. 1993)	17.0	5.8	17.4 (23.1)	27.3 (36.1)	30.8 (40.8)
Corn stover (Qu et al. 2011)	7.6	6.8	17.2 (21.1)	26.3 (32.5)	37.8 (46.4)

[a] wt% values in parenthesis are ash- and extractive-free

intimately intertwined with the cellulose microfibrils. Although these biopolymers in biomass largely determine the yields and composition of the observed products in biomass pyrolysis oil, small levels of inorganic constituents also affect the product yields (Evans and Milne 1987; Oasmaa et al. 2010a; Patwardhan et al. 2010).

The composition of biomass varies significantly from woody to herbaceous materials; data on the composition of several potential feedstocks for biofuel manufacture is available at the US Department of Energy's Alternative Fuels Data

Table 2 Products from the fast pyrolysis of select biopolymers at 500 °C (Qu et al. 2011)

Yields	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Gas	20	26	13
Char	18	23	47
Liquid	62	50	40
Products in gas			
CO_2	48	60	32
CO	47	30	25
CH_4	4	7	42

Center.[1] Typical compositions are shown in Table 1 for some species including hard- and softwoods (poplar and pine), energy crops (switch grass), and agricultural residue (corn stover). Woody materials typically have lower ash, extractives, and hemicellulose and more lignin than the herbaceous species. The extractives, materials that can be removed from the biomass using solvents, consist of fatty acids, lipids, fatty alcohols, terpenes, resin acids, and terpenoids (Oasmaa et al. 2003a) for woody materials and free sugars, sugar oligomers, alditols, organic acids, and inorganic ions (Chen et al. 2007, 2010) for herbaceous feedstocks. Extractives can have a major influence on the properties of pyrolysis oil (Oasmaa et al. 2003a, b; Oasmaa and Kuoppala 2003), and pretreatment of the biomass can often impact these components resulting in changes in bio-oil composition.

During fast pyrolysis, the biopolymers found in plant cell walls are converted into non-condensable gases, liquids, and solid char. The gases are primarily CO_2, CO, H_2, and some light hydrocarbons (C_1–C_4). The liquids contain 15–30% water in an emulsion with hydrophobic and hydrophilic organic compounds, some suspended solid material, and alkali and alkaline earth metal compounds that are present as inorganic matter in the feed biomass. Depending upon the temperature of pyrolysis, the char is primarily carbon (significant amounts of inorganics are present in the char), which can be used for processing heat or for upgrading to value-added coproducts. The organic compounds in the bio-oil typically contain a wide variety of oxygen functional groups, which impart undesirable physical and chemical properties to the oil.

Determining the yields of char, gas, and liquid is very important for assessing the viability of different feedstocks for production of bio-oil. As shown in Table 2, carbohydrates make up roughly 70% of the biopolymers and have liquid yields of 50–60%, while lignin makes up 20–30% of the biopolymers and only produces 40% liquid. Thus, the carbohydrates contribute 3–4 times as much liquid as does lignin in biomass pyrolysis.

The presence of inorganic materials—especially alkali and alkaline earth metals—in biomass also impacts yields. Oasmaa et al. measured the pyrolysis yields for several feedstocks and showed that the organic materials in the liquids were directly related to the amount of ash in the feedstock. Alkali metals present in

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[1] (http://www.afdc.energy.gov/biomass/progs/search1.cgi)

the ash are known to increase the yields of char, water, and gases during pyrolysis (Patwardhan et al. 2010; Abdullah and Gerhauser 2008; Abdullah et al. 2010; Hayes and Hayes 2009; Nowakowski et al. 2007; Diebold et al. 1995; Baldwin and Feik 2013), and this could lead to lower yields of liquid organic compounds; potassium is known to be particularly active (Davidsson et al. 2002; Jensen et al. 2000; Knudsen et al. 2004; Wei et al. 2005; Oasmaa and Meier 2005).

Oxygen Content Organic oxygen in bio-oil is responsible for some of the physical and chemical properties that make it problematic for direct use or a refinery feedstock. There are a significant number of studies that report on the elemental composition of biomass fast pyrolysis oils; some of these data are shown in Table 3. In this table, the elemental composition is reported on a water-free basis (water makes up roughly 20% of the bio-oil). As can be seen, the amount of oxygen varies from 32 to 48 wt%, and significant variations are found both between and within each feedstock grouping. Organic sulfur and nitrogen levels are generally very low, which is a potential advantage since fuel standards require low levels of sulfur in finished fuels and both organic N and S compounds can be catalyst poisons. Potassium, sodium, and chloride can all be catalyst poisons; chloride can also contribute to corrosion.

Molecular Composition The chemical composition of bio-oils produced from process conditions that maximize liquid yields is very complex, and complete analysis of those oils requires the combined use of several analytical techniques. A precise description of bio-oil composition has not yet been achieved, and even with considerable analytical efforts, about 20% of the composition still remains unknown. Water is the single most abundant component of bio-oil, accounting for 15–30 wt% of the whole oil (Meier 1999). Major organic compound classes identified in bio-oil are hydroxy aldehydes, hydroxy ketones, sugars, carboxylic acids, and phenolics (Piskorz et al. 1988), with most of the phenolic compounds present as oligomers with molecular weights ranging from 900 to 2500 AMU (Meier and Scholtze 1997). GC/MS analysis has been used extensively to identify and quantify the volatile components of bio-oils (Garcìa-Pérez et al. 2007; Azeez et al. 2010). The most abundant organic components of bio-oils that have been reported studies are generally hydroxyacetaldehyde, acetic acid, formic acid, acetol, glyoxal, levoglucosan, and cellobiosan. Information on bio-oil composition from ^{13}C NMR analysis is shown in Table 4 for several bio-oils produced in an auger pyrolyzer (Ingram et al. 2008).

Two-dimensional gas chromatography coupled with time of flight mass spectrometry (2D GCxGC/TOFMS) and two-dimensional flame ionization detection (2D GCxGC/FID) has been recently applied to more comprehensively characterize bio-oil (Talmadge et al. 2014). Figure 2 presents information on major functional groups have been identified in crude bio-oil.

Table 3 Elemental composition of fast pyrolysis oil on a dry basis

	Weight %					ppm	
Feedstock	C	H	O^{a}	N	S^{b}	K-Na^{b}	Cl^{b}
Pine							
VTT (Oasmaa and Peacocke 2010)	55.8	5.8	38.2	0.1	0.02	20	30
Dynamotive (Oasmaa and Peacocke 2010)	52.6	7.53	39.52	0.09	0.0197		
BTG (Oasmaa and Peacocke 2010)	53.7	6.0	40.0	0.3			
Fortum (Oasmaa and Peacocke 2010)	57.1	6.4	36.4	0.1			
PNNL (Elliott 1994)	51.2	7.5	41.1	0.1		10	
PNNL (Elliott et al. 2012)	53.0	6.4	40.5	0.1	0.003		
Poplar							
NREL (NREL poplar bio-oil composition n.d.)	57.3	6.3	36.2	0.18	0.02	10	8
NREL (NREL poplar bio-oil composition n.d.)	60.5	6.7	32.6	0.23	0.02	12	8
Waterloo (Scott et al. 1985)	54.7	6.7	38.3				
Waterloo (Scott and Piskorz 1982)	51.8	6.7	41.3				
Waterloo (Scott and Piskorz 1984)	57.3	6.29	36.4				
Oak							
Dynamotive (Oasmaa and Peacocke 2010)	47.2	4.5	48.0	0.12	0.022		
PNNL (Oasmaa and Peacocke 2010)	56.0	6.8	37.2			57	
NREL (Baldwin and Feik 2013)	59.6	6.0	34.2	0.11	0.01	100	
Corn stover							
UMinn (Yu et al. 2007)	60.66	7.70		2.2	0.15		
USDA (Mullen et al. 2010)	53.97	6.92	37.94	1.18			
Iowa St (Shah et al. 2012)	58.4	5.2	30.9	0.5			
Straw							
VTT (Oasmaa and Peacocke 2010)	55.3	6.6	37.7	0.4	0.05	2	330
Waterloo (Scott and Piskorz 1984)	55.55	6.39					
Switchgrass							

Feedstock	Weight %					ppm	
	C	H	O[a]	N	S[b]	K-Na[b]	Cl[b]
NREL (Oasmaa and Peacocke 2010; Scott and Piskorz 1984)	55.8	6.9	36.3	0.79	0.03	128	1900
PNNL (Elliott 1994)	46.6	8.0	45.4			165	
USDA (Boateng et al. 2007)	46.0	6.7	42.6	0.3			

[a] By difference

[b] Some of the studies did not report sulfur, alkali, and chloride

Physicochemical Properties of Oils Table 5 shows specifics for pyrolysis oil properties that are relevant to catalytic upgrading and/or introduction into a refinery (Talmadge et al. 2014); these properties are discussed in more detail below.

2 Catalytic Upgrading of Bio-oil

2.1 Vapor-Phase Upgrading

CFP of biomass has been studied for nearly 30 years using biomass, biopolymers, and model compounds from the microscale up to pilot scale (Diebold et al. 1988; Evans et al. 1988; Horne and Williams 1995). Use of commercial-scale CFP to produce hydrocarbon fuels was recently attempted in the United States, and Anellotech, Inc. is currently scaling up in situ CFP technology for production of BTX from biomass (Anthrop 2013). In addition, the development and scale-up of the two-stage catalytic hydropyrolysis IH^2 technology is ongoing (Turriff 2014).

Table 4 Distribution in bio-oils produced in an auger reactor (Ingram et al. 2008)

	Carbon content (% of all bio-oil carbon)			
Type of carbon	Pine wood oil	Pine bark oil	Oak wood oil	Oak bark oil
Carbonyl	11.8	0.5	18.1	2.4
Aromatic	48.4	43.9	40.1	35.3
Carbohydrate	5.8	1.4	10.3	2.1
Methoxy/hydroxy	16.1	20.8	16.1	12.5
Alkyl	17.9	33.4	15.5	47.7

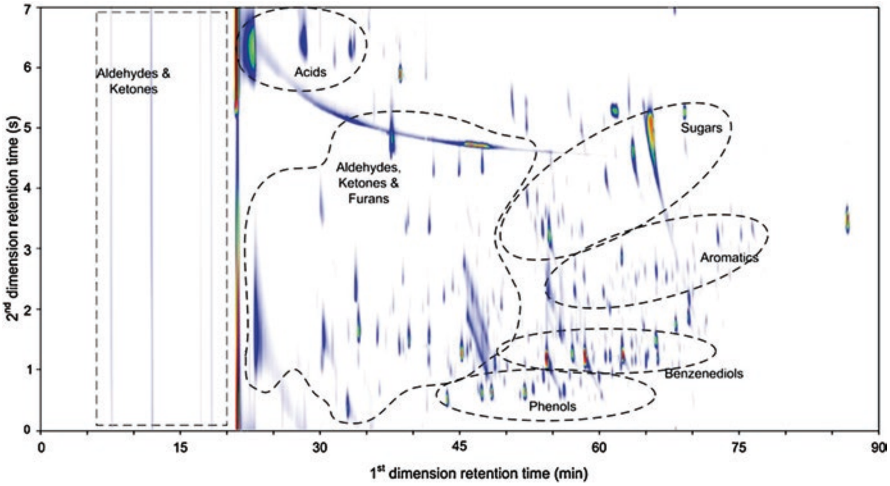

Fig. 2 Group-type analysis of the crude bio-oil by two-dimensional GCxGC

There have been several recent reviews of CFP (Liu et al. 2014; Martín-Aranda and Čejka 2010; Ruddy et al. 2014; Perego and Bosetti 2011; Taarning et al. 2011; Bulushev and Ross 2011; Asadieraghi et al. 2015; Rezaei et al. 2014); some aspects of advances in technology are highlighted in the following section.

Upgrading Using HZSM-5 HZSM-5 has been the most extensively used zeolite catalyst for CFP and is effective for removing oxygen from pyrolysis vapors, at a cost of reduced carbon yields for condensed organic oil. Typical product distributions from CFP of woody biomass with HZSM-5 compared to FP are shown in Table 6. As can be seen, the oxygen content of the oil can be significantly reduced from close to 40% for FP to 4% in one instance for CFP (Iisa et al. 2017). Oxygen reduction is accompanied by a decrease in the organic oil yield, which has a strong negative impact on the cost of fuel production; total liquid yields (including water) are reduced from ~70 wt% for FP to less than 55 wt% for CFP. FP oil typically is an emulsion with 15–30 wt% water (Czernik and Bridgwater 2004), while CFP oil

Table 5 Properties of biomass pyrolysis oil

Property	Notes
Water	15–30 wt%
Viscosity	13–80 cSt @ 50 °C
Solids content	0.01–1 wt%
Miscibility in organic solvents	Poor
Stability	Oil components polymerize, particularly at elevated temperatures
Corrosivity	pH 2.0–3.7, TAN 50–200
Distillation	30–50% residue
Density	1.2 g cm^{-3}

Table 6 Product distributions (g/g feed, %) from CFP over HZSM-5

	CFP[a]	CFP[a]	CFP[b]	CFP[c]	CFP[d]	CFP[e]	FP[f]
Liquids	**32**	**33**	**52**	**45**	**43**	**51**	**67**
Organic	9	11	28	26		32	
Aqueous	27	22	24	19		19	
Gas	**34**	**33**	**29**	**36**	**40**	**21**	**18**
Solids	**19**	**16**	**19**	**25**	**18**	**27**	**12**
Oxygen, wt%[g]	4	14	18		19	22	36
Bio:Cat, g/g	0.5	1.5	0.06	0.17	3.0		

[a] Iisa et al. (2017), ex situ, pine, 500 °C
[b] Vasalos et al. (2016) in situ, beechwood, 482 °C
[c] Jae et al. (2011), in situ, pine, 500 °C
[d] Mante and Agblevor (2014), in situ, pine, 550 °C
[e] Paasikallio et al. (2014) (VTT), in situ, pine, 520 °C
[f] Howe et al. (2015), pine, 500 °C; note that in some cases liquids are single-phase, hence no separate organic and aqueous fractions
[g] Oxygen content in the oil on a dry basis

typically has a separate aqueous layer, which is 20–25 wt% of the biomass, and the organic liquid yield is low (9–32 wt%; water-free basis). Lower organic yield in CFP is concomitant with higher gas and solid (i.e., coke) formation.

The chemical composition of condensable products from CFP with HZSM-5 shows a strong dependence on the ratio of the mass of the pyrolysis vapor processed to the mass of the catalyst. Direct measurements of the compositional change of CFP oil as a function of biomass-to-catalyst ratio (B:C) show that the oxygenated species increase with B:C (Iisa et al. 2017; Czernik and Bridgwater 2004; Mukarakate et al. 2014; Lappas et al. 2002). Figure 3 shows that increasing B:C leads to increased selectivity for phenols, indenols, naphthols, methoxyphenols, levoglucosan, acids, and carbonyls; these compounds are intermediates formed by incomplete deoxygenation and not simply due to breakthrough of raw pyrolysis products. These compounds are largely responsible for the corrosivity of bio-oils and fouling problems during hydrotreating but can be greatly reduced by application of CFP.

Microscale experiments have been conducted as a function of B:C and show that at low B:C the products from CFP with HZSM-5 are almost exclusively oxygen-free aromatics and olefins (Mukarakate et al. 2014). As shown in Fig. 4, increasing B:C leads to the formation of oxygenated intermediates (primarily phenols and other hydroxylated aromatic molecules and furans) followed by the breakthrough of the oxygenated molecules found in the raw pyrolysis vapors at higher B:C. This change in product composition is likely due to the buildup of carbon on the catalyst, which reduces deoxygenation reactions and deactivates the catalyst. The difference

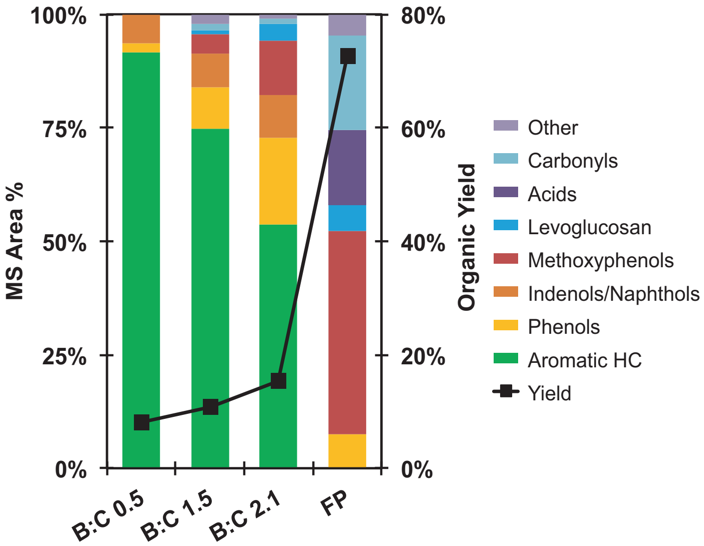

Fig. 3 Measured composition of fast pyrolysis (FP) oil and the organic oils from CFP at different biomass-to-catalyst ratios (B:C) (Knudsen et al. 2004)

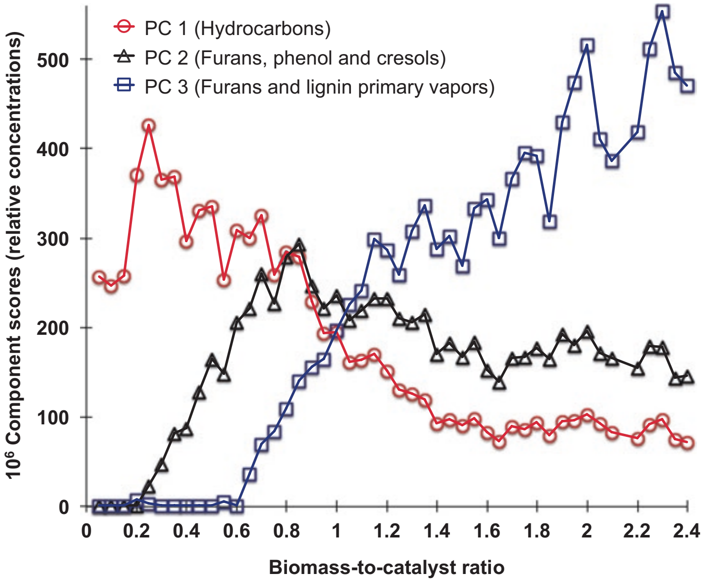

Fig. 4 Deactivation of HZSM-5 as a function of the amount of biomass vapors introduced into a fixed bed (Mukarakate et al. 2014). The mass spectra at each point were analyzed using multivariate analysis, and the red trace (PC1) is the principal component (PC) containing aromatic hydrocarbons, the blue trace (PC3) is the principal component containing the molecules of raw pyrolysis vapor, and the black trace (PC2) is the principal component containing oxygenated intermediates, primarily phenols

in chemical composition of CFP oils relative to the raw FP oils is marked by lower carbonyls and acids and explains why CFP oils are amenable to distillation (Agblevor et al. 2010) and do not require a stabilization step needed for hydrotreating raw pyrolysis oils (Agblevor et al. 2016).

Other Zeolites Other zeolites used for CFP show a similar product suite as HZSM-5 but are typically not as efficient and often lead to enhanced coke formation (Mullen and Boateng 2013). This is likely due to the micropore size and shape; smaller pores cannot pass aromatic molecules, while larger pores produce more coke (Carlson et al. 2009).

Amorphous Silicates Amorphous silicates such as MCM-41 or SBA-15 are highly structured silica materials with regular mesopores and amorphous silica walls (Ciesla and Schuth 1999). These have been studied as catalysts for vapor-phase upgrading—their weak acid sites enable greater selectivity toward oxygenated products than HZSM-5. There are a number of microscale experiments that suggest these weak acid sites contribute to the formation of oxygenated intermediates, such as furans, phenols, and ketones (Antonakou et al. 2006; Suzuki et al. 2008).

Metals Oxides of metals such as Ti, Sn, Zr, Ce, and Mo have acid and reducible metal sites that can deoxygenate biomass pyrolysis vapor when used in either the in situ or ex situ CFP mode. Many microscale studies have been conducted that show high conversion and the formation of oxygenates, such as furans, phenols, and ketones, which can be separated for chemicals or coupled to produce diesel range renewable fuels (Nolte et al. 2016; Agblevor et al. 2010; Doornkamp and Ponec 2000; Lu et al. 2010, 2009; Budhi et al. 2015; Donar and Sınağ 2016; Mante et al. 2015).

Deoxygenation by metal oxides can be facilitated with added H_2 as shown by a number of model compound studies (Prasomsri et al. 2013, 2014; Shetty et al. 2015). One microscale study of pine pyrolysis vapors using MoO_3 supported on TiO_2 and ZrO_2 at 500 °C with low pressure (c.a. 1 atm) H_2 (Ruddy et al. 2014) reported completely deoxygenated pine vapors until a biomass-to-catalyst ratio of 1, after which furans and phenols were formed. A separate study (Zhou et al. 2016) collected oil from the upgrading of lignin and wood using MoO_3. The organic phases from these studies consisted of furans and alkyl furans, ketones, cyclopentanones, phenol and alkyl phenols, naphthols, and indenols. Similar oxygenated species such as furan and alkyl furans, C_4–C_5 ketones, and cyclopentanone were also observed in the aqueous phase.

Another approach for upgrading biomass pyrolysis vapors in the presence of added hydrogen is to promote breaking of C–O bonds over C–C bonds and to reject oxygen as water. Catalysts used for this purpose have both metal sites for hydrogenation and, depending upon the support, acid sites that facilitate hydrodeoxygenation (HDO) and other reactions catalyzed by solid acids. Pd/SiO_2 was used for upgrading of *m*-cresol to form 3-methylcyclohexanone with 65% selectivity, toluene with 27% selectivity, and 3-methylcyclohexanol with 8% selectivity (de Souza et al. 2014). Similar results were also observed with Pt/SiO_2 and metals (e.g., Pt) supported on carbon, which also has low acidity (Gao et al. 2014). Upgrading of guaiacol using Ru/SiO_2 was found to favor formation of phenol by hydrogenation, while Ru/Al_2O_3 favored formation of catechol by HDO (Boonyasuwat et al. 2013). Recently there has been significant interest in carbide catalysts for ex situ CFP (Lee et al. 2014, 2015; Sullivan and Bhan 2016; Sullivan et al. 2015). Mo_2C has both metallike sites for hydrogenation and acid sites to facilitate HDO (Sullivan et al. 2016).

3 Bio-oil Hydrotreating

Hydroprocessing Hydrotreating of bio-oils takes place in the presence of a catalyst at high hydrogen partial pressures (500–2000 psi). Oxygen removal may take place by HDO, decarboxylation, decarbonylation, or dehydration reactions; other reactions such as saturation of aromatic and C–C double bonds, cracking of molecules into smaller ones, and repolymerization take place simultaneously. The literature on catalytic hydrotreating of FP bio-oil is very extensive, and several reviews of hydrotreating of pyrolysis oils have been published on both the process and catalysts (Elliott 2007; Zacher et al. 2014; Wang et al. 2013a, b; He and Wang 2012; Ma and van Bokhoven 2014; Furimsky 2000).

The main technical barrier to hydrotreating of pyrolysis oils is fouling of the hydrotreating catalyst due to carbonaceous deposits from thermally induced polymerization of reactive components such as aldehydes and sugars. At low temperatures, these compounds can be hydrogenated, but at the higher temperatures required for HDO of less reactive components, they rapidly form cross-linked polymers. A two-stage hydrotreating process with a first stage operating at a low temperature to prevent coking followed by a second, higher-temperature stage was developed early on to combat polymerization issues (Baker and Elliott 1988; de Miguel Mercader et al. 2011). More recently, a third stabilizer stage has been added to the process such that a total proposed process consists of a low-temperature stabilizer followed by two-stage hydrotreating (Jones et al. 2013). Reduction of sugars and hydrogenation of aldehydes during the stabilization step have been shown to lead to improved hydrotreating performance (Olarte et al. 2016); however, some deactivation of the stabilization catalyst was still observed, and poisoning of the catalyst by sulfur-containing species was identified as the major cause for deactivation. Recently, 1000 h of FP hydrotreating has been demonstrated (Abdullah n.d.). The FP oil was ion exchanged and filtered to remove heteroatoms responsible for deactivation of the stabilization catalyst, and coke from the stabilization stage was removed by solvent rinse.

Traditional sulfided CoMo and NiMo catalysts have been found to be efficient for hydrotreating of pyrolysis oils. Precious metal catalysts on carbon support are another group of catalysts that have been assessed for pyrolysis oil hydrotreating (French et al. 2014; Elliott et al. 2014), and sulfided Ru/C has been used for the first stage of hydrotreating in several studies (Olarte et al. 2016; Bui et al. 2011).

For deoxygenation of compounds such as phenols, the traditional sulfided Mo-based catalysts have been reported to favor direct deoxygenation by removal of the hydroxyl group without ring hydrogenation (Ma and van Bokhoven 2014; Wang et al. 2013b). In contrast, noble metal catalysts are efficient for hydrogenation and favor first hydrogenating the aromatic ring, followed by deoxygenation. Direct deoxygenation is preferable because of the lower hydrogen consumption. Therefore, sulfided CoMo and NiMo have been the catalyst of choice for the second hydrotreating stage (de Miguel Mercader et al. 2011). Sulfided NiMo and CoMo catalysts are typically supported on Al_2O_3, whereas the noble metal catalysts are usually supported on carbon. Al_2O_3 may not be a good support due to poor hydrothermal stability and resistance to organic acids, and other, more stable supports have been tested, including carbon extrudates, TiO_2, and ZrO_2 (Zacher et al. 2014).

Hydrotreating CFP Oil CFP oils are partially upgraded, but they still contain oxygen in significant quantities and may require hydrotreating if the objective is to produce finished transportation fuels or refinery blendstocks. CFP oils contain a variety of oxygenates including phenols, which are of low reactivity; hence, it can be expected that the final temperature required for hydrotreating is similar to that for hydrotreating of non-catalytic FP oils that have been stabilized. CFP may, however, remove the more reactive oxygenated compounds, such as aldehydes and ketones which are responsible for catalyst bed plugging during FP oil hydrotreating and hence require multiple hydrotreating stages at increasing severity for FP oils.

There is limited information on hydrotreating of CFP oils, but CFP oil with oxygen content as high as 25 wt% has been successfully hydrotreated in a single stage (Agblevor et al. 2016). Table 7 highlights differences in CFP oil and FP oil hydrotreating. As shown, CFP oils could be hydrotreated in a single stage for times on stream exceeding 300 h, whereas the two FP oils hydrotreated in the same equipment as the first CFP oil led to bed plugging or lost catalyst activity in less than 100 h. Limited or no catalyst deactivation was observed with the CFP oil hydrotreated at 400 °C, but the catalyst tested at 290 °C deactivated rapidly, and the oil oxygen contents increased significantly during the experiment. The yields of the hydrocarbon product are significantly higher for CFP oils than for FP oils, and oil carbon yields can exceed 90% (French et al. 2014). The higher yields are partially a direct consequence of the initially lower oxygen contents but also of the types of oxygen functional groups remaining in the CFP oil, e.g., phenols, which are likely to lose oxygen via dehydration as opposed to the release of CO and CO_2, which lead to mass and carbon losses.

The composition of the CFP oil impacts the hydrotreating. Figure 5 shows GCMS analysis of the product oils from hydrotreating of CFP oils with different oxygen contents produced over ZSM-5. Phenols were the most persistent oxygenates and were detected at low levels in all hydrotreated CFP oils (Iisa et al. 2017). In addition, low quantities of methoxy groups and carbonyls were detected in the product oils with higher oxygen contents. Aromatic hydrocarbons became partially

Table 7 Comparison of hydrotreating FP and CFP bio-oil

	FP[a]	FP[a]	CFP[b]	CFP[c]
Feed oil O, wt% dry basis	40.5	40.5	24.8	19.5
Temperature, °C	170/400	170/400	–/400	–/290
Catalyst	Sulfided Ru/C/ sulfided NiMo	Sulfided Ru/C/ sulfided CoMo/C	Sulfided $CoMo/ZrO_2$	Sulfided HDO catalyst
Pressure, bar	138	138	138	138
Oil yield, g/g dry feed oil	35–45%	35–43%	67–79%	68–83%
Normalized C yield, g C in product/g C in feed oil	~82%	~82%	87–96%	80–93%
Product oil O, wt% dry basis	0.2–0.3	0.3–2.7	1.0–1.2	0.5–11
H_2 consumption, g H_2/g feed oil	0.043–0.050	0.025–0.044	0.067–0.074	0.069–0.073
Time on stream (h)	90	90–100	>300	>300

[a] Elliott et al. (2014)
[b] Agblevor et al. (2016)
[c] Mante et al. (2015)

saturated; one-ring aromatics had relatively low conversions (up to 15%) to cyclohexanes; multiring compounds typically retained one aromatic ring and consisted, for example, of tetrahydronaphthalenes. The degree of saturation of the aromatic bonds decreased as hydrotreating temperature was increased, which can be attributed to thermodynamic limitations.

Even though the oxygen contents and H:C molar ratios in the products from hydrotreating of FP and CFP oils may be similar, differences in the chemical composition of the product oils can be expected. Upgrading of pyrolysis vapors during CFP in most cases results in cracking of the heavier molecules; consequently, both the CFP oils and the hydrotreated CFP oils will likely be of lower molecular weight than the corresponding FP oils. Simulated distillation (SIMDIST) analysis of hydrotreated CFP and FP oils has indeed shown higher gasoline fraction for the hydrotreated CFP oil (Agblevor et al. 2010). Many CFP catalysts, such as HZSM-5, produce aromatic rings, including monoaromatics (e.g., BTX) and bi- and multiring compounds.

The monoaromatic compounds in CFP oils have high octane numbers and can provide high-quality gasoline. For both hydrotreated FP and CFP oils, low levels of oxygen remaining in the products will be mainly in the form of phenols, but the molecular weights and side chains are likely different.

An advantage for CFP oils is separation of the liquid products into organic and aqueous phases. Only the organic fraction will be hydrotreated, which reduces the volume of the liquid to be processed and thus reduces cost. In addition, the water content of the CFP organic phase is lower than that of FP oils (generally <5 wt%), and this may enable the use of catalyst supports that are less hydrothermally stable.

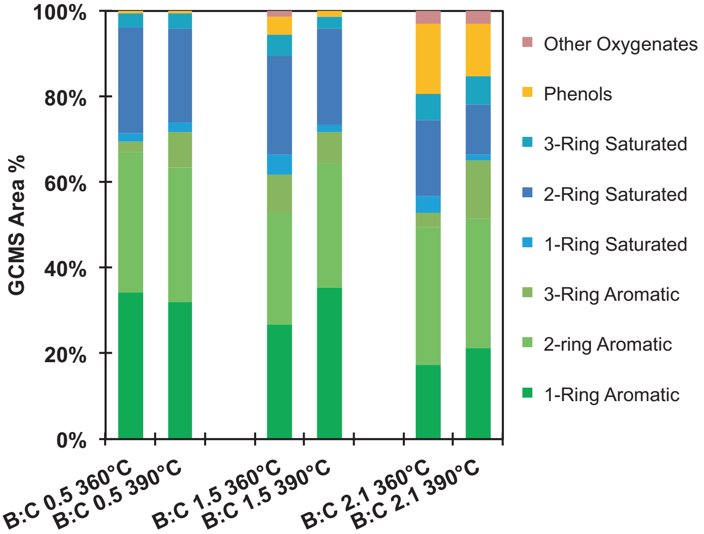

Fig. 5 Measured composition of hydrotreated CFP oils prepared at different biomass-to-catalyst ratios (B:C) and hydrotreated at either 360 or 390 °C over sulfided CoMo/Al_2O_3 (Iisa et al. 2017). The CFP oil prior to hydrotreating had oxygen contents of 4, 14, and 18% (dry basis)

4 Refinery Integration

4.1 Integrating Pyrolysis Oil into Standard Refineries

A potentially very attractive option for introducing biomass-derived materials into the fuel marketplace would be to use bio-oil or bio-crude (derived via hydrothermal liquefaction) as a feedstock and/or blendstock in a standard petroleum refinery, either replacing or supplementing fossil-derived materials with biomass-derived materials (Fig. 6). This would, in principle, facilitate the introduction of renewable carbon into the fuel infrastructure and would economically advantage the biofuel industry by using the multitrillion-dollar refining and distribution infrastructure already in place. Simultaneous processing of bio-oil with fractions from fossil petroleum in existing refinery unit operations is known as co-processing; a recent review article summarizes opportunities (Bezergianni et al. 2018). From the refiner's perspective when evaluating potential refinery feedstocks, important properties include the boiling range distribution obtained from the main crude oil fractionator and the hydrocarbon types (PONA) and heteroatom (sulfur, nitrogen, oxygen) contents of each of the resulting primary distillation and process-derived intermediate fractions. The boiling range distribution from the main fractionator impacts all of the major downstream unit operations, which are in turn designed to optimize the refinery product slate to produce the most profit per barrel of feedstock.

Using bio-oil as a refinery blendstock and/or feedstock introduces several potential problems due to differences in physicochemical properties of bio-oil relative to petroleum crude oil. Important properties of bio-oil as they relate to refinery feedstocks include the following, all of which represent significant barriers to utilization of bio-oil in a conventional petroleum refinery:

Miscibility Due to its high organic oxygen content and the presence of highly polar oxygenates, raw or non-upgraded bio-oil is largely immiscible in aliphatic and aromatic hydrocarbons typical of petroleum-derived crude oil and crude oil fractions. This problem can be mitigated by catalytic upgrading of the bio-oil to reduce oxygen and improve miscibility (French et al. 2014).

Water Content Bio-oil produced by non-catalytic FP can contain as much as 30 wt% H_2O—which results from water in the biomass feedstock and water formed during pyrolysis by dehydration reactions of carbohydrates. At these levels pyrolysis oil generally will not separate into aqueous and oil phases but remains as a single-phase pseudo-emulsion. The oxygen-containing functional groups on the bio-oil can form hydrogen bonds to water molecules and hence facilitate the formation of a stable emulsion. Imaging (Garcìa-Pérez et al. 2006) has shown that 5–10 μm aqueous droplets are found in these emulsions. At water loadings greater than 30%, separation of water and oil into two distinct phases can take place. The impact of water content on downstream upgrading and refinery operations is a key issue that impacts use as a refinery feedstock. Water will decrease the viscosity of

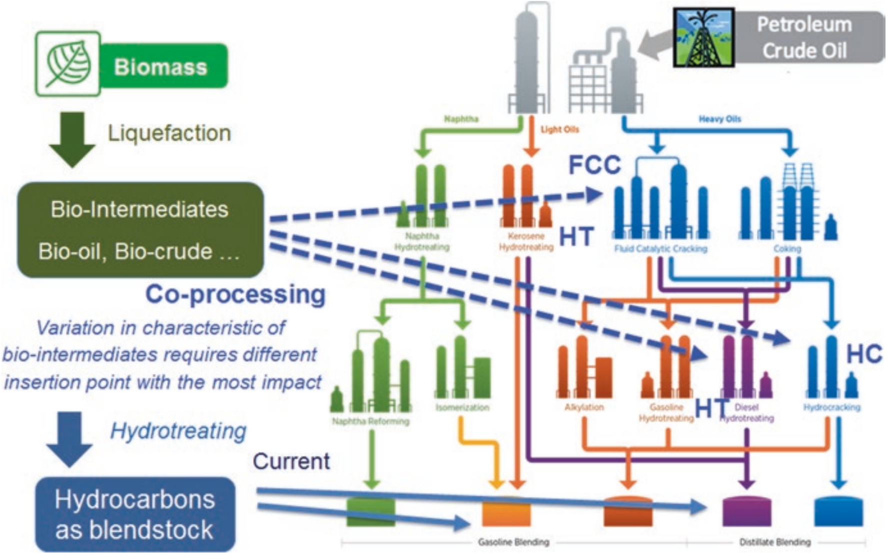

Fig. 6 Schematic biorefinery

bio-oil, but the presence of water can be damaging to some catalysts used in the downstream unit operations that lack hydrothermal stability. Production of a partially upgraded bio-oil by either in situ or ex situ catalytic fast pyrolysis normally results in a two-phase product with an organic phase that is much lower in water content than raw pyrolysis oil.

Stability and Aging Fast pyrolysis reaction conditions of rapid heating and quenching produce a bio-oil condensate that is not at thermodynamic equilibrium at ambient conditions. During storage, the chemical composition of the bio-oil shifts toward thermodynamic equilibrium resulting in changes in the viscosity, molecular weight, and co-solubility of its many compounds. Aging of biomass pyrolysis oil has been extensively studied; investigations have shown that chemical reactions in the oil lead to increased water content, the evolution of light gases, greater tendency toward phase separation, increased molecular weight, and increased viscosity. The rate of aging is strongly dependent upon temperature (Oasmaa and Sipilä 1996; Czernik 1994) which also has important implications for introduction into refinery unit operations. Studies have found viscosity increases by roughly 50% in 80 days at 37 °C, while the viscosity doubles in 15 h at 90 °C. The associated increase in molecular weight suggests that polymerization reactions are occurring during aging. The reactions that occur in pyrolysis oil during storage at ambient conditions largely involve the oxygen functionalities, including:

- Esterification: The reaction of organic acids with alcohols to form esters and water

- Condensation reactions involving aldehydes and ketones and water or alcohols
- Condensation reactions of aldehydes with phenols
- Condensation reactions involving furfurals

Many of these reactions can be catalyzed by solid material in the bio-oil, such as inorganics from the biomass. Studies where the solids are filtered out show much slower changes in viscosity (Meier and Scholtze 1997). The reactivity of pyrolysis oil can be particularly problematic for distillation operations. Polymerization and molecular weight growth during distillation lead to the formation of very high molecular weight solid residue. This can result in up to 50% of the starting material remaining as solid residue (Oasmaa and Meier 1999).

Viscosity The viscosity of bio-oil as produced (measured at 40 °C) can vary from as low as 25 cP to as high as 1000 cP or more depending on the feedstock, the water content of the oil, the amount of light ends, and the extent to which the oil has aged. Other researchers have found that polymerization reactions that lead to viscosity increases are accelerated at higher storage temperatures, and it has been shown that the rate of change in viscosity can increase from 0.009 cP/day when stored at −20 °C to more than 300 cP/day at 90 °C (Diebold 2000). Bio-oil is more viscous than crude oil at room temperature; however, its viscosity is very similar to that of crude oil in a temperature range of 35–45 °C. To transport bio-oil in pipelines, the temperature of the pipeline should be maintained in the range of 35–45 °C to keep the viscosity similar to that of crude oil (Pootakham and Kumar 2010).

Simple methods such as adding polar solvents and diesel or other fuels can address some of these undesirable bio-oil physicochemical characteristics. Polar solvents, such as methanol or ethanol, can improve the volatility and heating value and decrease the viscosity and acidity (Zheng and Kong 2010), while blending diesel or other fuels can positively impact oil viscosity. Finally, application of hot gas filtration prior to condensation offers a relatively simple method to produce a bio-oil with low particulate content (essentially zero ash) and improved stability with respect to increases in viscosity (Baldwin and Feik 2013).

Acidity The acidity of petroleum crude oil is usually very low, and acidic components present in crude oil generally represent naphthenic acids. These components are corrosive to mild steel at high temperatures. The refining industry has long since determined mechanisms[2] for mitigating the impact of corrosion imparted by naphthenic acids including blending (industry standard is that the TAN of the blend must be <0.6 (Marker 2005)), use of corrosion inhibitors, and upgraded materials of construction. The corrosivity of pyrolysis oil is primarily due to its acidity, which is derived mainly from strong acids (carboxylic acids) and weak acids (phenolic compounds). Measurements of total acid number (TAN) of bio-oil samples show that TAN values in the 90–100 range are fairly common, with a pH typically in the range 2–3; TAN values of 150–200 are not uncommon. Other groups of compounds in fast

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[2] http://www.setlaboratories.com/nac/tabid/79/Default.aspx

pyrolysis liquids that influence acidity include phenolics (5–10%) and fatty and resin acids (<5%) (Oasmaa et al. 2010b).

This level of acidity has been shown to cause corrosion problems for many materials. In particular, high corrosion rates for carbon steel (AISI01) have been observed (Oasmaa and Peacocke 2010)—this is particularly problematic as many refinery unit operations are constructed from carbon steel. Further, corrosivity increases significantly at higher temperatures (Aubin and Roy 1980). Measured corrosion rates for carbon steel alloys were much more than could be tolerated in any system that was expected to last for years. Several metal and polymer materials have been tested (Das et al. 2004; Fuleki 1999; Soltes and Lin 1984; Jay et al. 1995; Darmstadt et al. 2004; Keiser 2013) for resistance to corrosivity from bio-oil. Stainless steel specimens showed minimal weight change. Hydroprocessing can address the high acidity problem; however this requires significant CAPEX investment and normally is accompanied by substantial yield losses of distillate-range product (up to 50%). Torrefying biomass has resulted in 25% less acetic acid in the produced oil; however torrefaction also results in a loss of carbon efficiency.

Organic Oxygenates Most crude oils contain very small amounts of organic oxygen, in general less than 1 wt% and often less than 0.1 wt% (Speight 1991). Accordingly, catalysts and processes used in the refinery unit operations for hydroprocessing intermediates and upgrading fossil petroleum to finished fuels are not designed to effectively process or utilize oxygen-containing molecules. The presence of organic oxygenates and oxygen functional groups can impart very different properties to feedstocks in the refinery when compared to streams that are predominately hydrocarbon. Physical properties such as density, viscosity, and storage stability can be altered, and oxygenates can also degrade elastomers used in engine parts. The presence of organic oxygen leads to changes in volatility, which impacts unit operations used for separating intermediates or producing final products such as distillation. Chemical properties are also altered by the presence of organic oxygen, which can influence the reaction chemistry of important conversion and fuel synthesis processes. Catalysts, which are effective for converting crude fractions in the absence of oxygenates, may function entirely differently when oxygenated compounds are present, leading to changes in catalyst activity and selectivity.

Alkali and Alkaline Earth Metals and Other Particulates in the Oil Crude oil has a very small inorganic content, which is generally comprised of salt and porphyrins of vanadium and nickel. Salts and suspended solids in crude oil are readily removed in a desalting unit operation prior to the initial fractionation. Refiners have developed strategies to mitigate and/or passivate the impact of vanadium and nickel contamination on refining catalysts, but introducing bio-oil brings a new suite of potential catalyst poisons from silicon, calcium, potassium, and other alkali and alkaline earth metals. These metals could act as poisons for cracking and hydrotreating catalysts, leading to changes in selectivity and/or permanent activity loss. Particulate matter is generated by pyrolysis, and in spite of attempts to filter this material with cyclones, some of the solid material is often carried into the pyrolysis oil (Garcìa-Pérez et al. 2006). In addition, there is evidence that particulate matter—ranging in size from a few nanometers to micrometers—is formed during bio-oil condensation and aging of pyrolysis oil (Oasmaa and Peacocke 2001). The solids could be from char formed during pyrolysis, sand or other heat transfer material, polymerized pyrolysis products, or inorganic material from the biomass. Studies by the National Renewable Energy Laboratory (NREL) have shown that application of hot gas filtration to pyrolysis vapors prior to condensation is effective for producing a bio-oil with very low particulate content and with very low concentrations of alkali and alkaline earth metals (Diebold et al. 1995; Baldwin and Feik 2013). As these metals are known to catalyze condensation reactions, the stability of the hot gas filtered oil was also found to be greatly improved when compared to unfiltered oil (Baldwin and Feik 2013).

4.2 Refinery Integration Studies: Co-processing

In a comprehensive investigation on incorporation of bio-renewables into the petroleum refinery, Marker (Marker 2005) examined several opportunities for including bio-oil into standard petroleum refinery unit operations. In addition to an examination of utilizing waste fats and greases as refinery feedstocks and hydrogen production from the aqueous fraction of bio-oil, this study looked at:

- Hydroprocessing pyrolytic lignin to produce aromatics and gasoline
- Co-processing bio-oil with vacuum gas oil (VGO) in the fluid catalytic cracker (FCC)

In these studies, co-processing whole raw bio-oil and pyrolytic lignin in a laboratory ACE system was carried out for blends of up to 20 wt% raw bio-oil. These experiments were accompanied by tests on the catalytic cracking of a hydrotreated whole bio-oil and for VGO alone. Results showed that all three biomass-derived oils gave greatly increased yields of coke (16 and 27 wt% for the bio-oil/VGO blends) when compared to catalytic cracking of VGO alone. The bio-oil/VGO blends were found to increase the "crackability" of the feedstock when compared to VGO alone and to increase the yields for light-end products, which is potentially an economically attractive outcome.

A comprehensive investigation of opportunities for incorporating biomass-derived materials in the petroleum refinery was carried out under the auspices of the BIOCOUP project (BIOCOUP 2011). This study concluded that the best strategy for co-processing bio-oil was the FCC using a partially deoxygenated bio-oil containing up to 20% organic oxygen as the feedstock.

A study was conducted by a team with members from NREL, PNNL, GEMI, and Valero (Christensen et al. 2011a; Arbogast et al. 2017a, b) on the impact of hydroprocessing on several of the important refinery-relevant properties of bio-oil. These properties included acidity, boiling range distribution, elemental composition (including total oxygen), and hydrocarbon and oxygenate types in streams that represent important refinery intermediates. These data were correlated with hydroprocessing severity (principally temperature, pressure, liquid hourly space velocity or LHSV) and total oxygen content of the upgraded oil. Three levels of hydroprocessing severity were analyzed, consisting of reaction conditions required to produce an oil with low oxygen content (LOC; organic oxygen = 0.4 wt% on a water-free basis), medium oxygen content (MOC; water-free organic oxygen = 4.9 wt%), and high oxygen content (HOC; water-free organic oxygen = 8.2 wt%). Information on the distillate fractions and elemental analysis of the upgraded bio-oil fractions are shown in Table 8. As can be seen, hydrotreating results in a gradual shift of the distillate product slate toward lighter fractions (naphtha + light ends) with a reduction primarily in the gas oil fraction as hydroprocessing severity increases. For the HOC and MOC oils, an additional 10 wt% of the starting oil comprised a nonvolatile residue. These data show that organic oxygen is concentrated in the lighter cuts for the HOC oil, while the opposite trend is found for the MOC oil with organic oxygen concentrated in the heavier fractions. For the LOC oil, the organic carbon content of all fractions was basically the same.

In addition to elemental composition and boiling fraction distribution, the acidity of the fractions is extremely important to the refiner. Table 9 presents data on the relationship between acidity and hydroprocessing severity for each distillate fraction obtained from this study.

These acidity data are presented in terms of total acid number (TAN) and carboxylic acid number (CAN). The intent here was to indicate the relative proportion of strong acids (carboxylic acids) in the TAN, as corrosion issues associated with carboxylic acids are anticipated to be quite problematic. As shown, for the HOC oil, TAN is still very high, and most of the total acids consist of carboxylic acids, indicating that the weak acids (phenolics) have been removed by hydrotreating. At higher hydrotreating severities, the TAN and CAN are both significantly reduced.

A paraffin, olefin, naphthene, aromatic (PONA) analysis of the LOC, MOC, and HOC fractions is shown in Table 10. Oxygenated compounds were present in all of the HOC fractions. In the light ends and naphtha fractions, these were primarily C_5, C_6, and C_7 cyclic and noncyclic ketones, esters of C_6 and shorter carboxylic acids, methyl-substituted tetrahydrofurans, and aliphatic alcohols. Some acetic acid was present in these fractions. In the jet fraction, oxygenates were primarily methyl- and ethyl-substituted phenols, with some methoxy phenols and C_6 and C_7 cyclic ketones. Ketones in the jet fraction were less than in the lighter fractions, but phenols were much greater in this fraction. The MOC fractions contained much lower levels of oxygenates compared to the HOC fractions; detected compounds consisted primarily of alkyl phenols and aryl ethers. Fractions from the LOC oil contained no oxygenates in the lights and naphtha (below detection limits), with a small amount of alkyl-substituted phenols in the jet fraction.

Results for the PONA analysis showed increasing hydroprocessing severity decreased aromatics and increased paraffins and naphthenes in the light and naphtha fractions. For the LOC fraction, the data indicate low aromatic content and moderate isoparaffin content leading to the relatively low research octane number (RON) and motor octane number (MON) for these fractions. Benzene content in the light and naphtha fractions was found to be below the limits set by the EPA for motor gasoline in all fractions analyzed. While it is clear from this study that hydropro-

Table 8 Elemental analysis of boiling range fractions (Christensen et al. 2011a)

Oil sample	Fraction	Distillate fraction, % w/w	C, % w/w	H, % w/w	N, % w/w	S, ppm	O, % w/w
HOC	Lights	5.3	72.8	11.9	0.01	25	14.2
	Naphtha	19.7	73.7	11.5	0.01	19	14.4
	Jet	18.7	77.8	11.0	0.03	23	11.9
	Diesel	17.2	82.4	10.7	0.09	101	7.5
	Gasoil	30.3	84.6	10.4	0.14	354	5.3
MOC	Lights	4.6	85.6	13.6	0.02	8	0.5
	Naphtha	17.7	84.5	11.9	0.05	8	3.9
	Jet	23.1	83.9	10.1	0.14	12	6.6
	Diesel	18.3	85.7	10.2	0.32	21	4.4
	Gasoil	32.6	87.8	9.9	0.40	116	2.5
LOC	Lights	13.9	85.9	14.6	0.01	2	0.3
	Naphtha	30.2	86.3	13.3	0.02	2	0.3
	Jet	22.0	87.0	12.3	0.02	12	0.7
	Diesel	20.6	88.4	11.4	0.02	310	0.5
	Gasoil	13.5	88.6	11.5	0.03	243	0.4

Table 9 Acidity of hydrotreated fractions (Christensen et al. 2011a)

	HOC		MOC		LOC	
mg KOH/g	CAN[a]	TAN[b]	CAN	TAN	CAN	TAN
Lights	102	102	BD	14	BD	BD
Naphtha	123	123	BD	100	BD	2
Jet	67	154	BD	199	BD	14
Diesel	20	20	BD	0.3	0.1	0.1
Gasoil	9	9	BD	BD	0.4	0.4

BD below detection limit
[a] Carboxylic acid number (strong acids)
[b] Total acid number (strong plus weak acids)

cessing is very effective in improving the quality of bio-oil, the CAPEX and OPEX associated with oxygen removal to low levels (<1%) remain a significant challenge.

Integration of Bio-oil in the FCC The FCC is the single most important unit operation in the modern petroleum refinery that has been optimized for producing motor gasoline; accordingly, a great deal of interest has been focused on processing bio-oil in the FCC—either by itself or as a blend with petroleum-derived gas oil/vacuum gas oil (co-processing). It has been speculated that decarboxylation via FCC could provide a more cost-effective route for producing transportation fuels from biomass when compared to deoxygenation by hydroprocessing (Butler et al. 2011). Further, the FCC is a flexible refinery unit operation that can, in principle, be readily tuned to accommodate different feedstocks by modifying catalysts and/or operating conditions. Several potentially viable strategies exist for integrating bio-oil into the fluid catalytic cracking unit of an existing petroleum refinery.

Co-processing Whole Bio-oil in the FCC A simple and straightforward method for integrating bio-oil into an existing refinery would be to use whole bio-oil without pre-treatment or fractionation as a blendstock with petroleum-derived GO or VGO and direct feed the blend to the FCC (Watkins et al. 2008). In one study, mixtures of model compound oxygenates (acetone, acetic acid, 2-propanol) and isooctane as a surrogate for gas oil were cracked over an industrial equilibrium catalyst (E-cat) in a fixed-bed laboratory reactor (Domine et al. 2008). In general, selectivity to light gases and olefins was reduced, and coke was found to be dramatically increased by adding oxygenates. In a different study, blends of model oxygenates such as acetic acid, hydroxyacetone, and phenol with petroleum-derived gas oil were processed under standard FCC conditions in a lab-scale reactor using both an E-cat and a mixture of E-cat and ZSM-5 (Graca et al. 2009). Adding the oxygenates increased overall conversion, reduced the coke yield, and increased the yield of fuel gas, LPG, and gasoline. Overall conversion of the gas oil was not significantly altered.

Fluid catalytic cracking mixtures of petroleum-derived gas oil with whole bio-oil has been reported by Fogassy et al., who investigated co-processing VGO and whole bio-oil over a standard FCC catalyst, H-Y zeolite, and HZSM-5 in a laboratory reactor. These studies found that introducing bio-oil resulted in lower rates for formation of cracked products except for coke and aromatics (Fogassy et al. 2011). These researchers also investigated partitioning fossil carbon and biomass-derived carbon in products from co-processing bio-oil with petroleum gas oil. Using carbon-14, they were able to determine that both coke and light gases were richer in ^{14}C than the gasoline from the FCC, suggesting that biomass-derived components react preferentially to undesirable products under cat cracking conditions (Fogassy et al. 2012). In a laboratory cracking reactor (ACE system), Agblevor et al. (2012) were able to produce fuel-range products by co-processing bio-oil with gas oil in a ratio of 15/85 (wt/wt). The product yields were almost identical to that for cracking gas oil alone, and the products were found to contain negligible amounts of oxygen. Similar results were reported for co-processing a mixture of 10 wt% bio-oil and 90 wt% vacuum gas oil using an E-cat in a laboratory ACE system (De Almeida

Table 10 PONA analysis of the distillate fractions as a function of hydrotreating severity (Christensen et al. 2011a)

	LOC		MOC	HOC	
Vol %	Lights	Naphtha	Lights	Lights	Naphtha
Paraffins	28.3	15.4	13.6	7.9	5.9
Isoparaffins	14.9	26.8	25.9	32.8	38.8
Naphthenes	51.3	46	47.8	31.8	20.3
Aromatics	5.6	11.8	5.2	10.9	27.0
Olefins	0.07	0.01	7.54	16.7	8.3
Benzene	0.5	0.4	0.6	0.3	0.8
RON	64	71	73	79	88
MON	61	68	72	77	87

2008); however in this case, up to 1500 ppm phenols were found in the liquid products. In a recent pioneering pilot-scale study by NREL and Petrobras, co-processing 10 wt% bio-oil and 90 wt% vacuum gas oil indicated substantial differences in the yields of coke and liquid products, and the products contained significant organic oxygen content (Pinho et al. 2017). Similar findings were reported by these same researchers when cracking a feedstock containing 100% bio-oil in a laboratory ACE unit.

Co-processing whole bio-oil with hydrogen-rich materials other than petroleum has been studied (Bezergianni et al. 2018; Chang et al. 1976; Chen et al. 1988). These investigations found that mixing bio-oil (a hydrogen-deficient material with a low effective hydrogen index or EHI) with a hydrogen-rich material (such as methanol) dramatically improved the conversion of bio-oil to hydrocarbons during catalytic cracking in the vapor phase over HZSM-5. It was reported that a mixture with a combined EHI of 1.0 or greater resulted in a greater than 300% increase in C5+ hydrocarbon yield accompanied by a 32 wt% reduction in coke-on-catalyst (water-free basis) when compared to vapor-phase cracking of whole bio-oil alone. Petrobras has applied this concept to the catalytic cracking of petroleum-derived hydrocarbons with ethanol to produce ethylene in high yields (Pinho et al. 2011).

Findings from these studies show that whole bio-oil and model compounds representing the major oxygenated compounds in whole bio-oil produce large amounts of coke and light gases when processed over acid catalysts typical of those used in a conventional FCC unit. Catalyst deactivation was found to be rapid, and alkali and alkaline earth metals present in the whole oil caused severe and irreversible poisoning of the catalysts. Other factors, including the acidity and high water content of whole bio-oil, make whole bio-oil a particularly difficult feedstock for the cat cracker. FCC units are generally not made from high alloy steel, and the corrosivity of whole bio-oil would present severe operational difficulties. Similarly, the high water content of whole bio-oil is deleterious to catalyst integrity in the FCC unit. Finally, it is unlikely that production facilities for bio-oil will be able to supply sufficient quantities of product. Typical modern petroleum refineries process upward of 200,000 barrels/day of crude; a significant fraction of that amount is fed to the FCC. Single biorefineries based on pyrolysis will initially produce bio-oils at a rate of only about 8000 BBL/D,[3] which is insufficient to satisfy the demand for the FCC in even one small- to medium-sized refinery. Accordingly, integration strategies based on processing whole bio-oil without blending with refinery feedstocks and/or intermediates do not appear to be technically or commercially feasible (Diebold et al. 1995). A blend of up to 10 wt% whole (untreated) bio-oil was suggested to be a suitable feed for the FCC unit in a conventional petroleum refinery (Melero et al. 2012). Problems associated with co-processing whole bio-oil can be partially addressed by upgrading the whole oil prior to blending with gas oil. Thermal and catalytic hydrotreating of FP pyrolysis oil and use of in situ and ex situ catalytic fast pyrolysis (CFP) have all been investigated as upgrading strategies to improve properties with respect to co-processing of bio-oil in the FCC. Both low-severity thermal

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[3] Assuming a single biorefinery processing 2000 metric tons/day lignocellulosic biomass.

(e.g., non-catalytic) hydrotreating and catalytic hydrotreating have been investigated (Samolada et al. 1998); it was found that the heavy fraction from thermal hydrotreating could be successfully co-processed with light cycle oil in the FCC. Co-processing hydrotreated bio-oil in the FCC has been studied by several investigators (Lappas et al. 2009; Mercader et al. 2010; Fogassy et al. 2010). Using a laboratory FCC system, Mercader et al. found that co-processing HDO bio-oil in the FCC with long residue and light cycle oil produced products that were almost free of organic oxygen without excessive coke formation. Fogassy et al. found that blending HDO bio-oil and VGO at a level as high as 20% gave comparable yields for the gasoline fraction when compared to cracking VGO alone. A common thread in many of these studies is that removing oxygen in the FCC consumes hydrogen from the hydrocarbon feedstock, resulting in the production of more olefins and aromatics in the products.

Co-processing partially upgraded bio-oil produced by catalytic fast pyrolysis (CFP) has been compared to co-processing an HDO bio-oil by Thegarid et al. (2014). This study showed that product distributions were similar but that the CFP oil could eliminate the need for upstream hydrodeoxygenation. Organic carbon efficiency of the CFP/FCC strategy was found to be significantly better than the HDO/FCC strategy. Co-processing upgraded bio-oil in the FCC provides a technical solution to some of the more problematic issues associated with using biomass-derived liquids in the refinery. However, the economics of these strategies are dominated by the high capital and operating costs associated with hydroprocessing. These costs are present, in part, because the strategies being employed involve high-severity hydrodeoxygenation and then co-processing the whole bio-oil. This results in high CAPEX due to large reactor volumes and high OPEX due to the hydrogen demand for hydroprocessing/deoxygenation of the whole oil. A different strategy, which in principle could circumvent some of these problems, is shown in Fig. 7. This scheme involves first *mildly* deoxygenating the whole bio-oil to the point where the oil can be distilled followed by fractionation. This mild deoxygenation step could be done either by hydrotreating, or by generating the bio-oil using catalytic fast pyrolysis. Conditions could be adjusted to allow for water removal as a separate phase during this initial step as mild hydrotreating has been shown to be effective in facilitating this separation (Fogassy et al. 2011). Depending on distillation characteristics and boiling range, the bio-derived fractions could then be sent to the appropriate unit operation in the refinery (e.g., bio-naphtha to the reformer hydrotreater, bio-diesel to the diesel hydrotreater) for blending with petroleum-derived material and further processing into finished fuels.

In this scheme, high severity hydroprocessing associated with the HDO step would be reserved for that fraction of the bio-oil that requires more severe processing to reduce acidity and improve miscibility. This would result in improved hydrogen utilization efficiency and savings in both capital and operating costs when compared to the whole-oil strategies discussed above. This strategy of selective hydrotreating also applies when the bio-oil is available from CFP. In the context of the scheme shown above, CFP is used to provide a partially upgraded bio-oil that can be fractionated, perhaps removing the need for hydrotreating the whole oil prior to fractionation and improving the overall economics and carbon efficiency accordingly. Conditions and catalysts for CFP required to produce a bio-oil that can be fractionated have not been widely investigated to date.

Strategies for optimizing bio-oil deoxygenation for CFP vs. hydrotreating have been recently proposed (Iisa et al. 2018). As shown in Fig. 8, the carbon efficiency of hydrotreating is high at low bio-oil oxygen levels, while CFP evidences high carbon efficiencies at high bio-oil oxygen contents. The dashed green line represents the efficiency of the combined process; the shaded zone indicates the target bio-oil oxygen content to maximize the synergy between the two deoxygenation strategies.

Co-processing in Hydrotreaters Co-processing bio-oil with petroleum-derived materials in hydrotreaters has not been extensively investigated to date but is a very important component in overall strategies for refinery utilization of bio-oil or bio-crude. Bui et al. (2009) investigated co-processing straight-run gas oil with guaiacol as the surrogate for bio-oil in a laboratory hydrodesulfurization (HDS) reactor using a standard CoMo/Al_2O_3 HDS catalyst and found a competition existed between HDS and HDO with a decrease in HDS activity under certain conditions. Pinheiro et al. (2009) used model oxygenates blended with straight-run gas oil (SRGO) to investigate the impact of bio-oil on HDS, HDN, and aromatic ring saturation. These studies showed no impact of 2-propanol, cyclopentanone, anisole, and guaiacol on HDS, HDN, or ring saturation; propanoic acid and ethyldecanoate were found to inhibit all three hydrotreating functions. In a separate study (Pinheiro et al. 2011), these same investigators found that CO and CO_2 formed during hydropro-

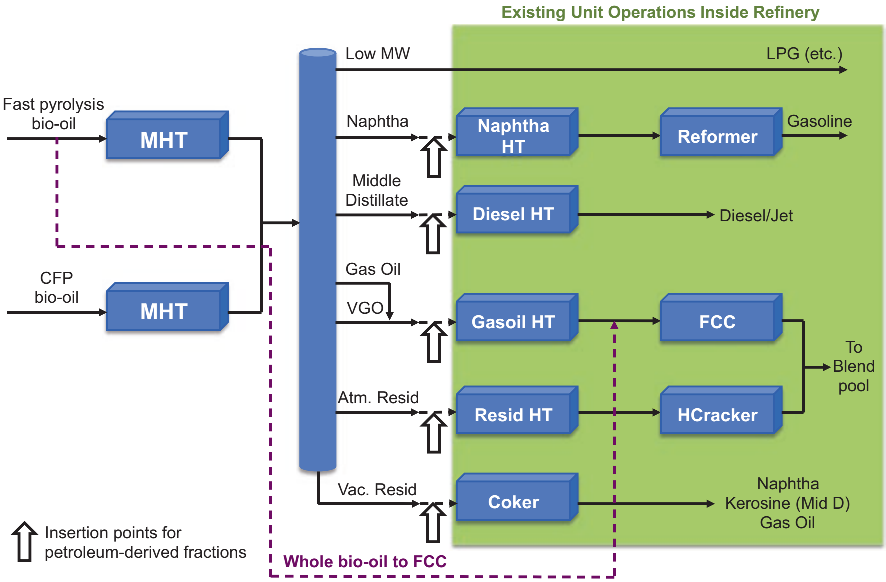


Fig. 7 Alternate refinery integration schemes

cessing also inhibited HDS and HDN for hydrotreating SRGO. One of the few studies of co-processing authentic bio-oil with petroleum-derived material in a hydrotreater was conducted by Mercader et al. (2011). These investigators processed HDO bio-oil with SRGO under typical HDS conditions and also found competition between HDS and HDO; the product from co-processing contained substantially higher levels of sulfur when compared to HDS of the SRGO alone. Catalyst activity for HDS was not reduced by co-processing with bio-oil as indicated by a return to the original low sulfur levels in the product when the bio-derived material was removed from the feed. Product yields were the same for SRGO and when SRGO was co-processed with bio-oil.

4.3 Co-processing in Other Refinery Unit Operations: Coker

Advanced pyrolysis approaches such as fast pyrolysis and catalytic fast pyrolysis can be used to produce feedstocks for transportation fuels and bio-based chemicals, but the high molecular weight fraction is difficult and costly to convert and thus represents a low value stream. An alternate approach to valorizing this material is to remove the "heavies" via fractional distillation and then upgrade the remaining bio-oil to fuel feedstocks and/or blendstocks. When bio-oil is used for co-processing in the refinery, removal of heavy fractions provides an upgraded distillate material that contains fewer coke precursors and hence represents a premium feedstock for refinery co-processing applications such as fluid catalytic cracking.

A portion of these heavy materials can be used to produce functional replacements for high-value carbon and graphite that are traditionally made from petroleum coke, coal tar, and natural mineral graphite. An especially important application

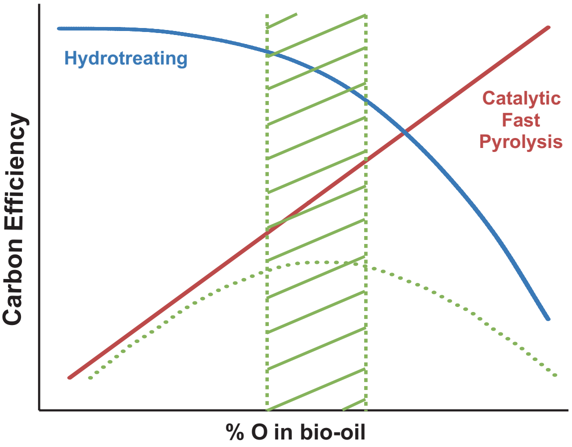


Fig. 8 Hydrotreating and CFP carbon efficiencies as a function of bio-oil oxygen content (Iisa et al. 2018)

for this material is for advanced energy storage devices such as lithium-ion batteries or carbon capacitors. Current pathways for production of anode-grade graphite depend on upgrading of mineral or petroleum-derived materials, which contain significant amounts of contaminants that must be reduced or eliminated. These processes are very energy intensive and environmentally unfriendly. Replacing fossil graphite with bio-graphite will provide a less energy-intensive pathway to a renewable and sustainable source for these and similar materials. Alternate strategies for valorizing bio-oil residuum are shown in Fig. 9.

4.4 Biomass-Derived Oxygenates in Finished Fuels

Because of the high oxygen content of bio-oils, there is a strong economic incentive to leave much of this oxygen in the finished fuel product to the extent that government regulations and product quality standards will allow. Arbogast et al. (2017a) have highlighted the high hydrotreating costs required to reduce oxygen content to the 2–3 wt% range. These costs increase exponentially as the oxygen content goes below approximately 2 wt%. Accordingly, it is important to investigate the potential for oxygenates in bio-oil to become components of drop-in fuels.

As described above, the three components of biomass (cellulose, hemicellulose, and lignin) produce different oxygenated products during pyrolysis. Cellulose and hemicellulose form low molecular weight (C_4 and smaller) ketones, aldehydes, acids, esters, ethers, and alcohols that cannot easily be directly incorporated into gasoline or diesel fuel. Hydrogenation of these compounds leads to low molecular weight hydrocarbons, suggesting that some form of oligomerization to increase molecular weight is necessary if this bio-derived carbon is to be incorporated into fuel. Cellulose and hemicellulose can also produce furanic compounds such as furfural, furfuryl alcohol, and furoic acid that, upon hydrogenation, can yield methyl furans because of the relative recalcitrance of the furan ring structure (Grange et al. 1996). Sugars and anhydrosugars have also been observed in the pyrolysis products, with hydrogenation producing 5- and 6-carbon alcohols. Pyrolysis of lignin, on the other hand, produces phenols and alkyl phenols, methyl aryl ethers, and guaiacols. Ethers are generally converted to phenolics by hydrotreating at adequately severe conditions.

The actual oxygenate composition of an upgraded pyrolysis oil is highly dependent upon the degree of upgrading, either by hydroprocessing or some advanced pyrolysis technology such as CFP (Iisa et al. 2018). Hydroprocessing to 8–10 wt% oxygen yields distillate fractions containing carboxylic acids, carbonyls, phenols, and ethers. Increasing the hydroprocessing severity eliminates carbonyl and carboxyl compounds and converts aryl ethers to phenols, consistent with model compound studies (Grange et al. 1996). The oxygen present also varies with distillate fraction. At roughly 8–10 wt% oxygen, the light and naphtha fractions will primarily contain carbonyl, carboxyl, and ether groups. The jet and diesel fractions will contain these functional groups at lower levels but will also contain phenolic compounds. Upgrading further, under more severe conditions, to roughly 5% oxygen leads to fractions containing almost exclusively phenolic compounds which may be acceptable in gasoline and diesel fuel but would never be accepted (under current standards) in jet fuel.

4.4.1 Properties of Biomass-Derived Oxygenates

With the exception of jet fuel, certain oxygen functional groups present in bio-oil are unlikely to be acceptable in fuel products. While carboxylic acids are used in fuels as corrosion inhibitors at very low levels (Peyton 2002), at higher levels, they cause corrosion and are potentially poorly soluble in hydrocarbons at cold temperatures. Aldehydes and ketones may undergo condensation reactions leading to the formation of gums. Esters, ethers, and alcohols have all been used successfully in fuels (biodiesel, methyl tert-butyl ether or MTBE, and ethanol, respectively)—with the caveat that MTBE's poor biodegradability in groundwater ultimately led to its removal from the US market (McCarthy and Tiemann 2006). Table 11 shows property data for a number of oxygenated compounds that have been observed in raw and upgraded pyrolysis oils. For gasoline, the boiling point must be between about 25 and the 225 °C; the end point limit is set in standard specifications (ASTM D4814). Additionally, the 90% volume boiling point is limited to 185 or 190 °C, depending on volatility class (time of year). Therefore, only limited amounts of compounds boiling above about 185 °C can be blended. Examination of the data in Table 11 indicates that the furans, as well as anisole and methyl anisole, boil in the acceptable range and also have high octane number and very low water solubility. Christensen et al. (2011b) have described the properties of dimethyl furan and 2-methyl furan blends with gasoline; and these oxygenates have many desirable properties, including little effect on vapor pressure. Singerman described the use of methyl aryl ethers as gasoline blend components in the early 1980s (Singerman

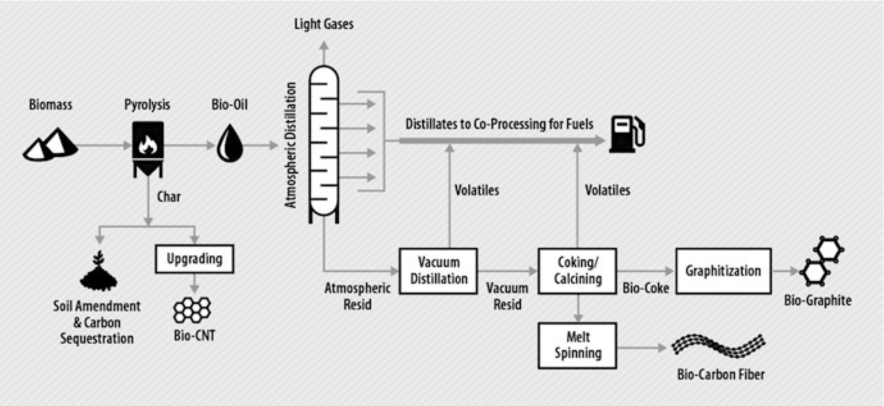
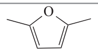
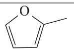
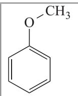
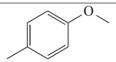
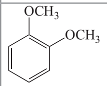
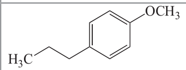
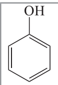
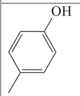
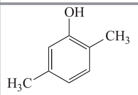
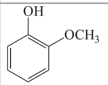
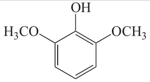
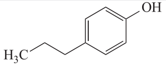
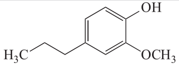


Fig. 9 Strategies for valorizing bio-oil residuum

Table 11 Properties of model biomass-derived oxygenates

Compound class/name	Molecular structure	Research and motor octane numbers	Boiling point (°C)	Solubility in water at 20 °C (wt%)	Solubility in hydrocarbon
Furans					
2,5-Dimethylfuran		153, 109	94	0.26	Miscible
2-Methylfuran		155, 92	65	0.3	Miscible
Ethers					
Anisole		Unknown	154	Insoluble	Miscible
4-Methylanisole		166,148	174	Insoluble	Miscible
1,2 Dimethoxybenzene (veratrole)		Unknown	206	Insoluble	Miscible
Propylanisole		Unknown	215	Insoluble	Miscible
Phenols					
Phenol		Unknown	181.7	8.3	Soluble, not miscible
p-Cresol		153, 149	202	1.9	Miscible

Compound class/name	Molecular structure	Research and motor octane numbers	Boiling point (°C)	Solubility in water at 20 °C (wt%)	Solubility in hydrocarbon
2,4-Xylenol		140, 113	211	0.5	Miscible
Guaiacol		Unknown	205	1.7	Soluble, not miscible
Syringol		Unknown	261	1.7	Soluble, not miscible
4-Propylphenol		Unknown	232	Insoluble	Miscible
4-Propylguaiacol		Unknown	250	Insoluble	Miscible

1981) and reported that these compounds improved octane number without degrading other gasoline properties. An important caveat is that gasoline aromatics have been linked to fine particle emissions for emerging gasoline direct injection engines (Khalek and Jetter 2012) and to the formation of secondary organic aerosol in the atmosphere (von Stackelberg et al. 2013). Both types of fine particles have been shown to have negative health effects. The US Environmental Protection Agency currently limits benzene in gasoline to an average of 0.62 vol%, not to exceed a maximum of 1.30 vol% (US Environmental Protection Agency 2007). It is unknown if furans or aryl ethers show the same effect on atmospheric fine particles. Phenol also has a boiling point just in the acceptable range; however, it also has high water solubility and poor solubility in hydrocarbon at cold temperatures and is corrosive. Other ethers and phenols have boiling points too high to be used in gasoline as blend components, although low residual levels (below roughly 1000 ppm oxygen) may be tolerable.

Diesel fuels boil between either 200 and 350 °C (No. 2 Grade) or 145–300 °C (No. 1 Grade). No. 1 grade or blends of No. 1 and No. 2 are used predominantly in cold climate, wintertime environments. Thus, the oxygenates in Table 23 that boil at too high a temperature for use in gasoline could be used in diesel fuels based on boiling point. Additionally, as C/O ratio increases, the phenolics become less soluble in water and more soluble in hydrocarbon. However, because these oxygenates are all aromatic compounds, they have a very low cetane number, significantly limiting the amount that could be economically blended. Their impact on precipitate formation at cold temperatures is also unknown. Potentially, these oxygenates could be tolerated in diesel fuels as residual components up to an oxygen content of roughly 1000 ppm. Very little research has been published on the potential for biomass-derived oxygenates to be present in fuels at these low levels.

Jet engine fuels boil between 180 and 300 °C and have a freezing point below −40 °C. However, quality standards and regulatory requirements for jet engine fuels are necessarily more strict. Jet engines require clean, low-soot formation combustion, and so the sooting tendency of jet fuels (measured as smoke number) is limited in ASTM standard D1655. The presence of aromatic compounds can lead to high sooting tendency, and so the standard also limits aromatics to 25 vol%. Oxygenated compounds other than specifically approved fuel additives are not permitted. Given these requirements, pyrolysis oil components will need to be fully hydrogenated to alkanes before their use in jet fuel could be considered.

4.4.2 Regulatory and Commercial Requirements

New transportation fuels cannot simply be produced and then introduced into the fuel marketplace. There are many federal and state regulatory, commercial, and consequent testing requirements that must be met. The exact requirements will depend on the chemical makeup of the new fuel. If it is demonstrably hydrocarbon (primarily hydrogen and carbon with less than perhaps 1000 ppm of sulfur, nitrogen, and oxygen), then requirements for market introduction are likely to be less than if the fuel is an oxygenate (such as ethanol, butanol, or biodiesel). Compliance with the

Clean Air Act is mandatory for fuels sold in the United States. If new fuels are to be used in existing engines designed for gasoline or diesel, the Environmental Protection Agency (EPA) will require demonstration that the emission performance of existing engines/vehicles is not degraded for the full useful life of the engine/vehicle (120,000 mi for a car, as much as 435,000 mi for a heavy duty truck). Potentially, this could involve testing many vehicles.

Since most, if not all, new fuels will be blended with petroleum fuels and utilized in existing engines, acceptance of the new fuel by the petroleum and auto/engine industries is critical. If the petroleum distribution industry refuses to distribute the blended fuel because they are uncomfortable handling it for safety or environmental reasons, because it cannot be obtained with consistent quality, or because they feel they accept too much liability for engine operating problems, then the new fuel will not be distributed. While these requirements are not directly legislated, they are an important aspect of consumer protection. Primarily, this involves developing data to show that the new material can be safely handled and that it is compatible with existing engines and vehicles. This compatibility is different than the emission performance mandated by the Clean Air Act. The primary way that this is accomplished is through development of an ASTM specification for the new fuel, which may take the form of a blendstock specification (such as exists for ethanol and biodiesel), adding the new fuel to existing specifications (such as those for gasoline or diesel fuel), or a new specification for a blended fuel (such as that for B6 to B20 blends). ASTM specification development requires data on a variety of issues, and what testing must be done ultimately depends on the properties of the new fuel. But it should be clear that this is a nontrivial requirement and may take 2–5 years to complete.

5 Summary

Bio-oil is currently being produced and sold as a boiler fuel and is increasingly finding niche markets for use as a transportation fuel. Use of bio-oil as a refinery feedstock for co-processing applications is expanding, with a number of demonstration projects either completed or planned. While upgrading of bio-oil to a drop-in replacement for fossil gasoline and diesel fuel remains economically challenging, introducing biomass pyrolysis oils into existing petroleum refineries offers an opportunity to accelerate the use of lignocellulosic bio-oils for production of renewable biofuels. Because raw pyrolysis oils have physical and chemical properties that make direct insertion into refinery unit operations challenging, technology development is currently underway for co-processing strategies that circumvent some of these issues by either blending or partial upgrading to reduce oxygen and water content. Finally, research and development on valorizing “the bottom of the barrel” could lead to entirely new concepts that could economically advantage pyrolysis-derived bio-oils either as refinery feedstocks or as products from stand-alone bio-refineries.

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