(Hemi)cellulosic Lubricant Base Oils via Catalytic Coupling and Deoxygenation Pathways

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Complete List of Authors:	Saha, Basudeb; RiKarbon, Inc, R&D; University of Delaware, Delaware Energy Institute Vlachos, Dion; Univ. of Delaware,

(Hemi)cellulosic Lubricant Base Oils *via* Catalytic Coupling and Deoxygenation Pathways

Basudeb Saha*[1,2] and Dionisios G. Vlachos[1,3]

[1]Catalysis Center for Energy Innovation, 221 Academy St., University of Delaware, Newark, Delaware 19716, United States

[2]RiKarbon, Inc., 550 S. South College Ave, Newark, Delaware 19716, USA.

[3]Department of Chemical & Biomolecular Engineering, 150 Academy St., University of Delaware, Newark, Delaware 19716, United States

ABSTRACT

The past decade has witnessed a significant growth in bioproducts development due to the strong interest in creating a more diverse energy supply, environmental sustainability, and a carbon neutral bioeconomy. The initial biorefinery strategy, focused mainly on the production of low carbon number drop-in bioproducts, has recently shifted to one focusing on production of high carbon number and high performance bioproducts with unique properties and value propositions. One such product is lubricant base oil (LBO) which represents over $150 billion global lubricant market and used for various industrial, automotive, marine, metal-working, consumer, and specialized applications. The application landscape of lubricants has changed significantly over the past decade because of environmental regulations, and the growing demand for sustainable lubricants to mitigate regulatory challenges and improve carbon footprint. Currently, only 3% LBOs are produced from bio-based triglyceride/fatty acid. Because of low oxidation stability and high hydrolytic susceptibility, these bio-based LBOs have narrow applications. Thus, research & development and commercialization efforts for (hemi)cellulosic LBOs to meet the market demand have received momentum over the past few years. This review describes strategies to produce (hemi)cellulosic LBOs, *via* carbon–carbon coupling and hydrodeoxygenation chemistries. We emphasize the coupling strategies to create LBOs with branched architecture to surrogate petroleum-based poly-α-olefins. A structure-property relationship for tuning key specifications of LBOs as a function of molecular architecture is illustrated. Mechanistic understanding and molecular interactions of multi-furan substrates with the active sites of complex multifunctional catalysts are described. Furthermore, techno-economic and life-cycle analysis are summarized along with standing challenges and future opportunities.

1. INTRODUCTION

The vast majority of chemicals, lubricants, fuels, and polymers are produced from petroleum, which impart a significant environmental footprint and large price-volatility due to global trade and policy uncertainties. The introduction of renewable alternatives, with similar or better properties and competitive cost, is vital to overcoming these concerns. Lignocellulose, the most abundant form of biomass, is a natural and waste feedstock for sustainable alternatives. Societal demand for sustainable alternatives has driven the development of catalytic and biological conversion technologies of lignocellulose to various cellulosic chemicals and fuels.[1-4] The refinery industries produce cuts of varying molecular weight *via* distillation, and the heavy residue is upgraded by C–C cleavage in fluid catalytic crackers. In contrast, lignocellulose consists of biopolymers; cellulose and hemicellulose account for approximately 70 to 85% of dry biomass, with the remaining being lignin.[5] Upon breaking down the biopolymers, the carbohydrate building blocks of lignocellulose contain C_5-C_6 carbons that are ideal for C_2-C_6 bioproducts, such as ethanol, propanol, xylenes, benzene, toluene, furan derivatives, various C_3-C_6 diols, butadiene, phenols, succinic acid, levulinic acid, and short chain alkanes for gasoline.[6]

Recently, the focus of biorefineries has shifted towards high carbon number products due to their higher value. Such bioproducts include surfactants, lubricants, flavors, fragrances, pharmaceutical ingredients, and antioxidants. Upgrading low carbon number biomass substrates into high carbon number products demands C–C coupling and deoxygenation strategies. This article reviews recent advances in catalytic conversion technologies to produce (hemi)cellulosic lubricant base oils (LBOs) from low carbon number biomass substrates (Figure 1) because of its large market size (US$146 billion/year[7]) and market demand to meet sustainability goals by industries. The current technology and market landscape of lubricants are introduced first. Then (hemi)cellulosic LBO production *via* selected C–C coupling chemistries to build high carbon number precursors and their hydrodeoxygenation (HDO) is discussed. Techno-economic and life-cycle analyses are also discussed. The review concludes with standing challenges and future opportunities.

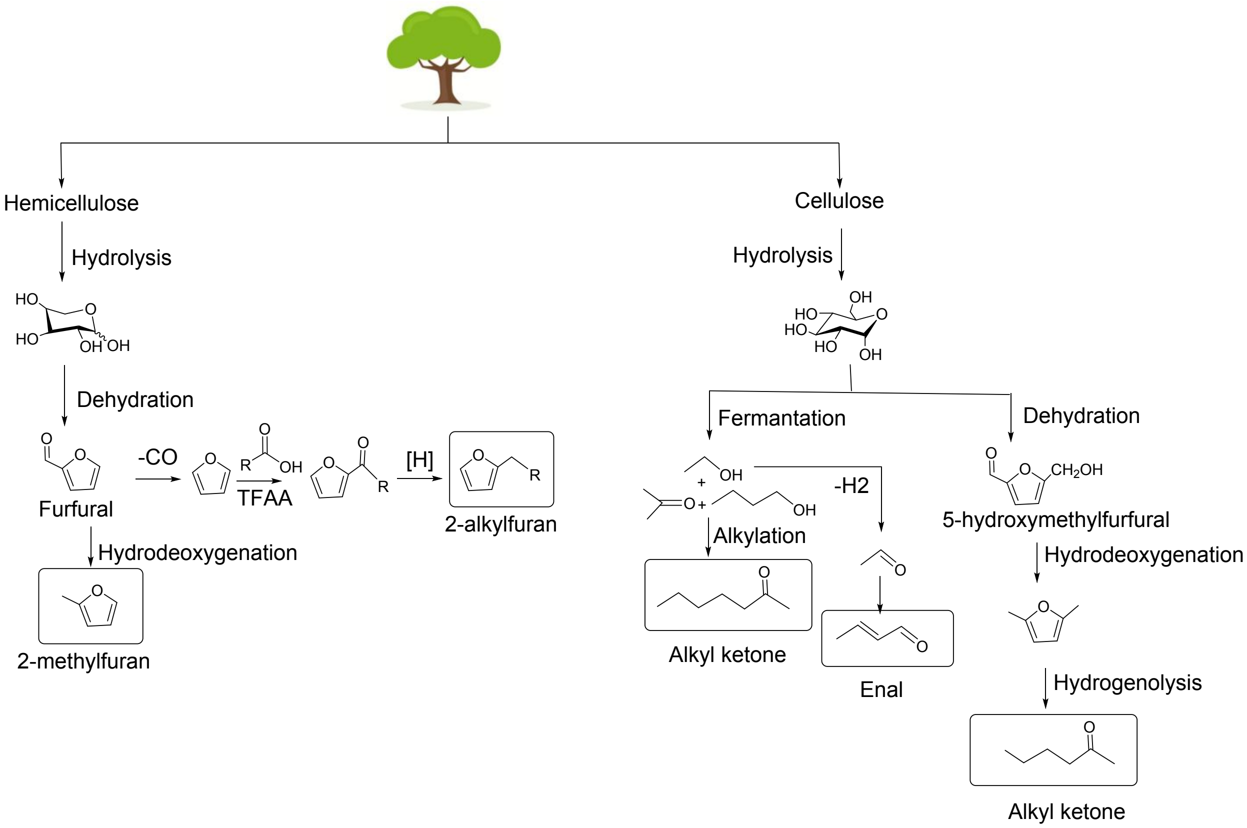


Figure 1. Key steps to convert biomass to precursors for (hemi)cellulosic LBOs shown in Figure 3. TFAA =trifluoroacetic acid. [H] = hydrogenation.

2. LUBRICANT MARKET LANDSCAPE

Lubricants contain up to 97% high carbon number alkanes, commercially known as LBOs. Up to 30% different chemical additives are added to LBOs in formulated lubricants to achieve desired specifications (viscosity, viscosity index, pour point, oxidative stability, acid number, rust prevention and corrosion, friction, etc.) for various applications. The global lubricant market size is projected to reach $166 billion by 2023 with a compound annual growth rate (CAGR) of 2.6%.[7] Figure 2a depicts the global lubricant market by application.

Conventional lubricants are of two types, mineral and synthetic, depending on the LBOs used in formulation. Mineral and synthetic lubricants account for about 78% and 18% of total market size (Figure 2c). The application landscape of lubricants has changed significantly over the past decade because of environmental regulations, *e.g.*, Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) in Europe and VGP (Vessel General Permit) in USA, and the growing demand for high-performance lubricants by consumers and OEMs (Original Equipment manufacturers) to mitigate regulatory challenges and improve carbon footprint. Fast paced technological advancement towards transformative modular equipment and engine design for improved energy efficiency, fuel economy, and environmental sustainability are also major drivers for this change. In order to accommodate the market needs, research and commercialization efforts for bio-based synthetic lubricants have received momentum in the past decade. Thus, the CAGRs of synthetic and bio-based lubricants are higher than their mineral analogues (Figure 2b).[7]

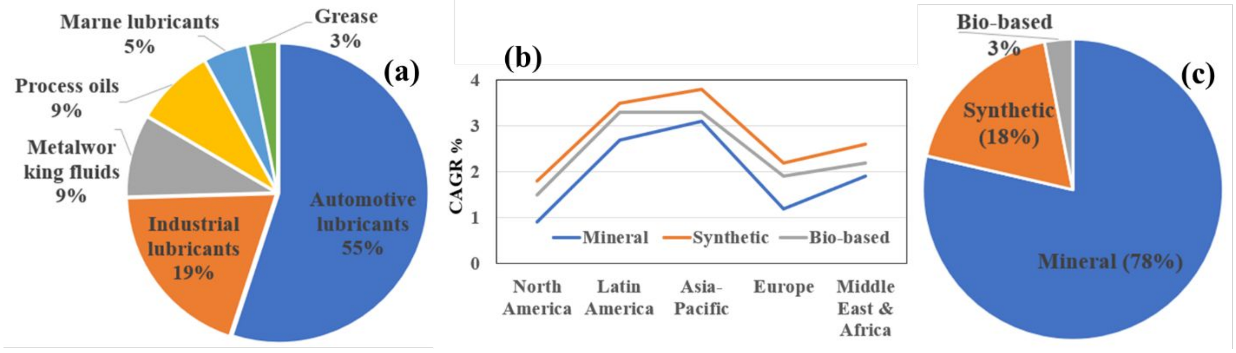


Figure 2. Global lubricant market by application (a) and type (c). (b) CAGR of global lubricant market by type and region.

Currently, bio-based lubricants represent over 3% of the total global lubricant market size (about \$5 billion) (Figure 2c)[7] and have significantly penetrated into the market because of their bio-preferred qualification and regulation compliance. The majority of current bio-based LBOs, produced from triglycerides and fatty acids *via* esterification/ transesterification,[8] acyloxylation,[9] epoxidation[10] and hydrogenation (section 3),[11] have poor oxidation stability for most industrial applications operating at high temperatures. To mitigate the challenges, science and technology innovations have evolved over the past few years to produce LBOs from biomass, which have similar structures to current petroleum-derived synthetic analogues and compatible oxidation stability at conditions encountered in turbines, engines, and machinery.

3. CURRENT STATE OF BIO-BASED LBOs FROM TRIGLYCERIDES

Current state of bio-based LBOs production is primarily limited to chemical modifications of fatty acids and natural-oils. Chemical modifications of triglycerides to produce LBOs have been extensively reported in the past decade via esterification and transesterification, estolides formation, epoxidation, hydrogenation and other reactions. The development of this chemistry (bio-based LBOs from triglyceride and fatty acid) has been extensively captured in several review articles.[12-17 8, 15, 16, 18-22]. These review articles also elaborated efforts to improve bio-based LBOs properties. For example, acid and base catalyzed transesterification/esterification of triglycerides with an alcohol (e.g. pentaerythritol, 1,3-propanediol, trimethylolpropane, 2-ethyl-1-hexanol, long chain alcohols (C>8), neopentyl glycol, pentaerythritol) formed LBOs with improved viscosity properties (50-199 cSt).[23-27] Acid catalyzed estolides, an interaction of carboxylic acid group of a fatty acid with the double bond of another fatty acid molecule,[9] formation of fatty acids have been performed to tune LBOs viscosities and cold flow properties.[28-33] Epoxidation of double bonds of triglycerides with H_2O_2 in the presence of homogeneous and heterogeneous acid catalysts[10, 34-37] followed by epoxide transformation to an ester with an alcohol is another way to improve vocosities, cold flow properties and oxidation stability of derived LBOs.[38-42] However, pour points, ranging between -18 to -36 °C, are still low for certain applications, e.g., aviation. In addition, this reaction requires multiple steps. Selective hydrogenation of double bonds of triglycerides or fatty acids using noble and non-nobel metal catalysts have been attempted to improve oxidative stability of fatty acids.[12], [11, 43-46] Other methods (hydroformylation,[47] alkylation and acylation,[48] ene-reaction,[49-51] and acyloxylation[52] have been reported for adding branches and functionalities to the derived products. Table 1 summarizes key properties for representative LBOs derived from triglyceride and fatty acid.

Table 1. Properties of bio-based LBOs from triglyceride and fatty acid.

Feedstock	**LBOs**	**KV40 (cSt)**	**VI**	**PP (°C)**	**Ref**
High oleic palm methylesters	Triesters	46-51	183-200	-37 to -9	12
Jatropha	Triesters	44	180	-6	31
Oleic acid	Pentaerythritol tetraoleate ester	63	190	-24	31
Rubber methylester	Triesters	23–63	206–222	-15 to- 3	11
Castor biodiesel	Triester	22	127	-	36
Soybean oil	n-alcohol-esters	10–433	45-195	-	24
Waste cooking oil	Trimethylolpropane Fatty acid triester	37	204	-8	18
Oleic acid, caprilic acid	Triesters	46.5	188	-27	21
Sunflower oil	Estolide	102-425	153-185	-	44
Olive oil	Estolide	272-519	168-188	-	44
Pennycress fatty acid	Estolide	494-497	134-163	-15 to -6	41
Saturated lesquerella fatty acid	Saturated estolide	37-46	187-196	-12 to 6	43

Saturated castor fatty acid	Saturated estolide	44-68	178-186	-36 to 6	43
Unsaturated castor fatty acid ester and capping FA	Unsaturated estolide	29-71	164-196	-54 to 23	43
Epoxidized canola oil	Epoxidized canola oil ester	-	-	-9	62
Epoxidized soybean oil	Ring opened product	60-74	96-135	-36 to -27	61
Epoxidized soybean oil	Ring opened product	195-23	86-113	-18	61
Epoxidized oleic acid	9-Hydroxy-10-Acyloxyoctadecanoic acid	-	71.2-232.1	-43 to -20	56
9-Hydroxy-10-acyloxyoctadecanoic acid	Octyl 9-hydroxy-10- acyloxyoctade-canoate	-	85.32-183.15	-44 to -21	56
Epoxidized oleic acid	Alkyl 9-alkyloxy-10-hydroxyoctade-canoate	-	95-215	-28 to -11	63
Epoxidized canola oil	Diacetylated ring opened product	-	-	-9	57
Epoxidized canola oil	Diacetylated ring opened product	116	-	-18	57
Epoxidized canola oil	Ring opened product	252	-	-5	58
Epoxidized canola oil	Ring opened product	191	-	-8	58
Epoxidized canola oil	Ring opened product	86	-	-15	58
Epoxidized castor oil, oleic acid	Polyoleate ester	95	189	<-36	69
Epoxidized linseed oil, oleic acid	Polyoleate ester	10ec	179	-15	69
Epoxidized sunflower oil, oleic acid	Polyoleate ester	45	180	-9	69
Epoxidized fatty acid waste cooking oil methyl esters	Epoxidized branched ester	16	157	-15	14
Epoxidized fatty acid waste cooking oil methyl esters	Epoxidized branched ester	25	142	-20	14
Epoxidized fatty acid waste cooking oil methyl esters	Epoxidized branched ester	44	135	-24	14

Ring opened epoxidized soybean oil	Acetylated, transesterified, ring opened product	36-42	137-149	-42 to -27	[61]
Ring opened epoxidized soybean oil	Acetylated, ring opened product	74-103	136-152	-27 to -33	[61]

KV40 = kinematic viscosity at 40 °C. VI =viscosity index. PP = pour point.

4 (HEMI)CELLULOSIC LBOs PRODUCTION TECHNOLOGY

4.1. Overview of this article. This article focuses catalytic production technologies of (hemi)cellulosic LBOs with branched carbon chains, which have structural similarly to petroleum-derived poly-α-olefins (PAOs). It involves two catalytic conversion steps. First, cellulosic sugar-derived alkylfurans,[53] furfural,[54] 5-hydroxymethylfurfural (HMF),[55] and other carbonyl compounds[56, 57] are C–C coupled to branch chain LBO precursors or furan-LBOs *via* hydroxyalkylation/alkylation (HAA) condensation,[56, 58] combination of aldol condensation (AC)[59-61] and hydrogenation, combination of aldol and Michael addition,[62] combination of conjugate addition (CA) and HAA, or others (Figure 3). Next, catalytic HDO converts these precursors to deoxygenated branch chain alkane LBOs. The Bell group reported aldol condensation/hydrogenation/HDO strategy to produce LBOs from biomass-derived alkyl ketones.[63] Thus, this article emphasizes other coupling strategies for LBO precursors. Synergistic effects between the active sites of the catalysts and molecular sizes of LBO precursors containing multiple furan rings are elaborated.

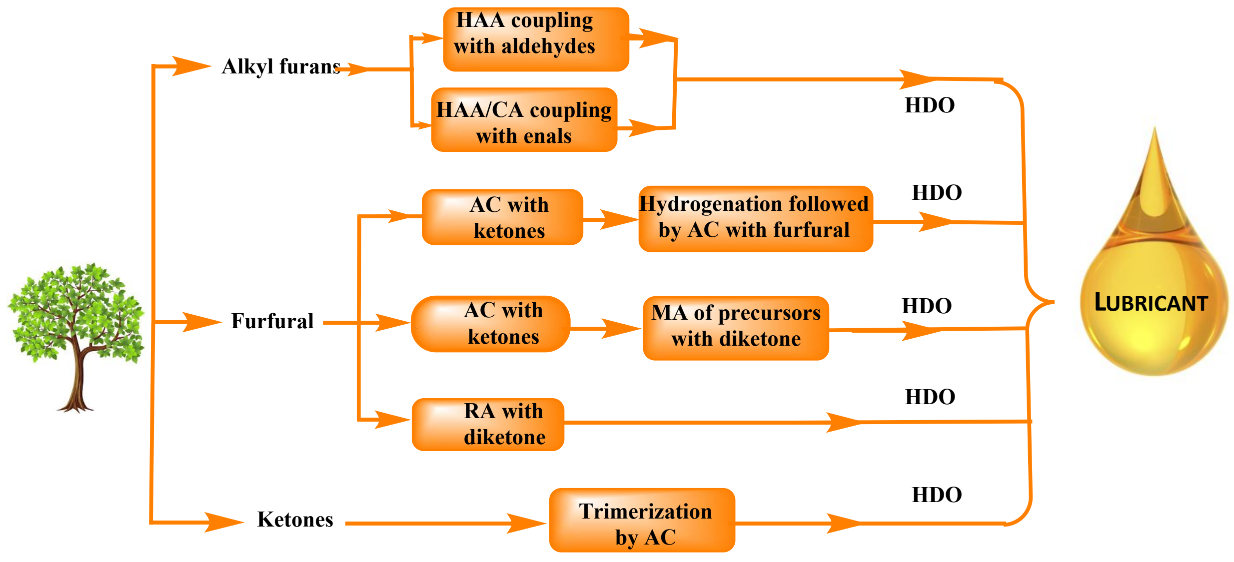


Figure 3. Pathways to produce LBOs from biomass feedstock. HAA = hydroxyalkylation/alkylation, CA = Conjugate addition, AC = Aldol condensation, HDO = hydrodeoxygenation, MA = Michael addition, RA = Robinson Annulation.

4.2. C-C coupling chemistry to produce furan-LBOs or LBO precursors

4.2.1. HAA coupling. The Corma group is one of the first that exploited the HAA chemistry to synthesize C_{11}-C_{15} multi-furan products, primarily for jet fuels, from (hemi)cellulosic 2-methylfuran (2MF) and a biomass-derived carbonyl compound (*e.g*., furfural, HMF, acetaldehyde, propanal, butanal, acetol).[64-66] Other groups have further exploited this chemistry using various catalysts (H_2SO_4,[67] USY, Beta, MCM-41, ITQ-2[64], Nafion-115, Amberlyst-15, Amberlyst-36[68], Nafion-212[69]) to produce C_{10}-C_{15} products (Figure 4A). Recently, we discovered that carbonaceous catalysts, improved graphene oxide (IGO) and graphene sponge, were effective to produce C_{12}-C_{21} condensation products with yields and selectivity up to 95% (compounds 1, 3, 5, 9-11; Figure 4A).[56, 70] IGO, decorated with surface oxygen functional groups and defects, exhibited superior yields and turnover frequencies over common zeolites and resins.

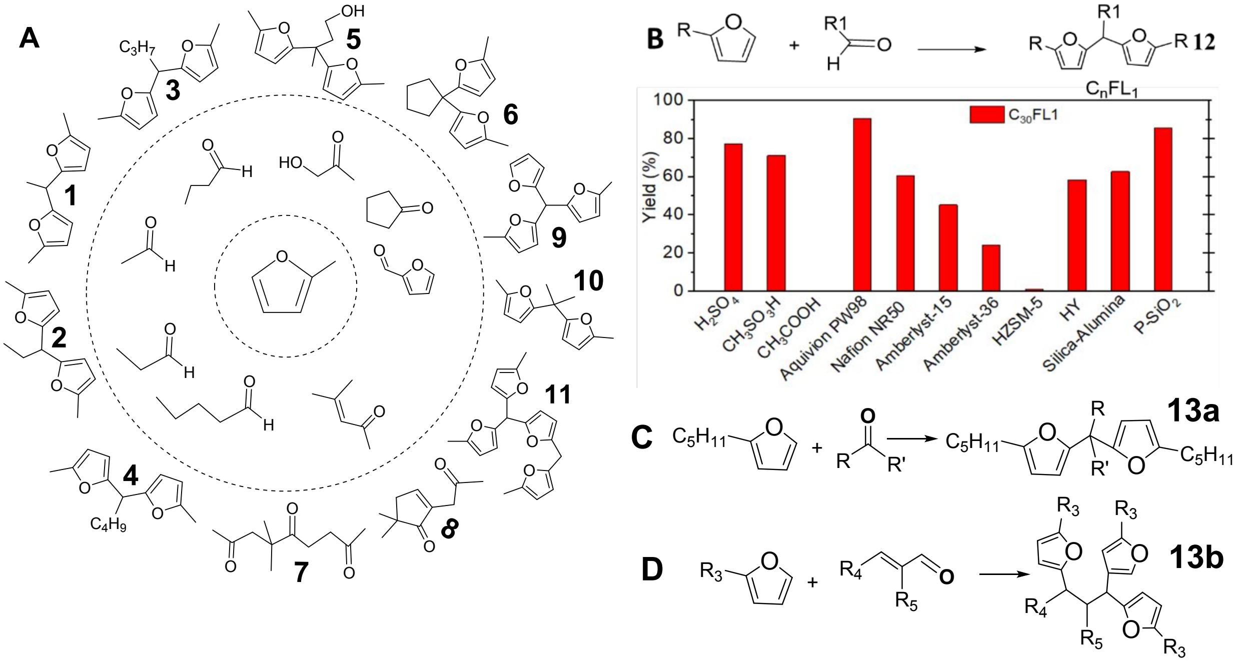


Figure 4. (A) Representative multi-furan products *via* HAA coupling reactions. (B) Synthesis of various C_nFL_1 LBO precursors or furan LBOs, where R and R1 carbon numbers are 1-5 and 1-12, respectively, and n is 22-34.[71] Bar graph compares the yield of a $C_{30}FL_1$ precursor using various acid catalyst. (C) Furan LBOs or LBO precursors of type C_nFL_2 from ketones and alkylfurans,

where n = 24-29, R = 1-5, and R' = 5-9.[72] (D) CA-HAA coupling strategy to produce LBO precursors or furan LBOs of type C_nFL_2 where n = 25-31.[73]

We expanded the HAA chemistry to produce LBO precursors for the first time[71] from lignocellulose-derived 2-alkylfurans[74] and biomass/fatty acid derived aldehydes.[75, 76] We produced C_{22}-C_{34} LBO precursors, referred hereto as C_nFL_m, where n is the carbon number and m is the number of branch carbon chains.[71] Homogeneous mineral acids produce up to 80% $C_{30}FL_1$ from 2-pentylfuran and dodecanal. Acidic resin catalysts (Aquivion PW98, Nafion NR50, Amberlyst-15, Amberlyst-36) exhibit moderate to high activity (Figure 4B) depending on the Brønsted acid strength. Aquivion PW98, a perfluorinated sulfonic acid resin with a strong deprotonation ability, achieved 90% yield of C_{30}FL1 with >98% selectivity at neat conditions and low temperature (65 °C).[71] Microporous zeolites pose diffusion limitations for larger size precursors, resulting in low yields. Mesoporous zeolites, especially a P-SiO_2 catalyst (P = phosphoric acid based active sites), is an effective catalyst for this chemistry. P-zeosils have recently been reported to be effective for the production of bio *p*-xylene[77] and butadiene.[78] The formation rate of C_nFL_1 was found to decrease with increasing carbon number of substrates and products,[71] possibly due to steric effects.

Mechanistic studies suggested that aldehyde, *e.g.* furfural, first interacts with the surface in a perpendicular configuration and creates an electrophilic carbenium ion.[56] The resulting ions then readily react with the adsorbed alkylfuran after the formation of a carbanion at the ω-position and formed a furanic dimer with an alcohol group as a linker. The alcohol group in the dimer dehydrates and forms a carbenium ion, which then reacts with another alkylfuran carbanion to produce LBO precursors.

Recently, we adapted the HAA chemistry to produce aromatic LBOs from (hemi)cellulosic ketones and 2-alkylfurans (Figure 4C; compounds of general structure 13a)[72] to complement commercial alkylnaphthaelene LBOs. Thiols promoted the reaction to achieve optimal yields, which varied on the basis of the molecular sizes of 2-alkylfurans and ketones. The yields decreased from 90% for $C_{24}FL_2$ LBOs to 72% for $C_{29}FL_2$. Without thiols, the reaction rates were slow. DFT calculation indicated that the promotion effect of thiol results from reduced barriers of the rate-limiting dehydration step during the condensation.[72]

Tandem HAA condensation of alkylfurans by carbonyl compounds is catalyzed by the Brønsted acid sites through a typical electrophilic aromatic substitution mechanism[58, 79] (Figure

5). The reaction is initiated by protonation of the carbonyl reactant. The protonated carbonyl group then adds preferentially to the 5-position of the furan ring on account of the electron donating group (EDG) in the 2-position, yielding a carbinol derivative intermediate in the hydroxyalkylation step. In the alkylation step, the carbinol derivative undergoes water elimination, while the resulting carbocation intermediate adds to a second furan molecule. The rate-limiting step of this tandem reaction is the hydroxyalkylation step.[80] DFT calculations suggested the reaction is preferred in perpendicular adsorption of alkylfurans on the surface of acid catalysts, for example, graphene oxide, over tilted conformation.[56]

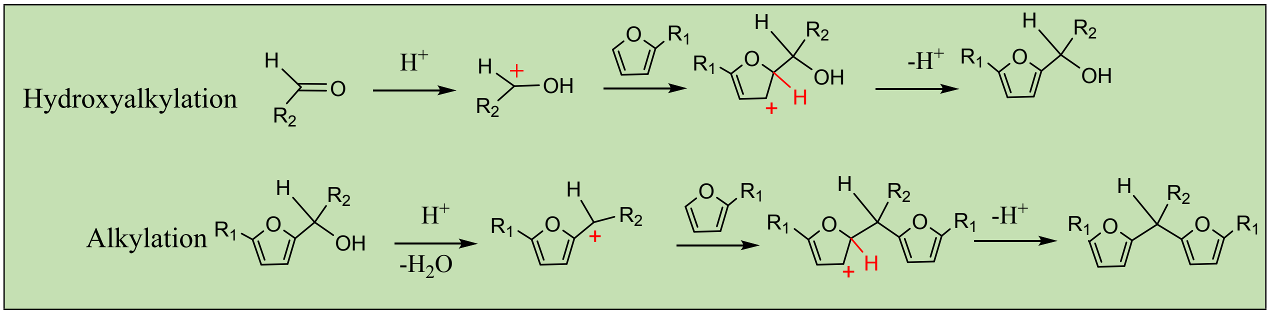


Figure 5. HAA condensation mechanism.

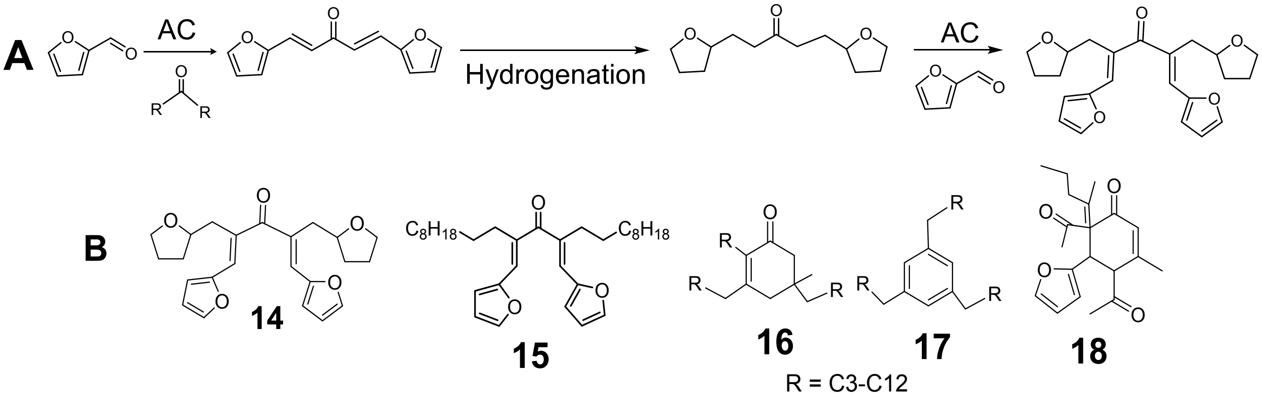
4.2.2. Conjugate addition-HAA reaction strategy. Tandem CA and HAA reaction between 2-alkylfurans and biomass-derived enals[81] produces LBO precursors of type C_nFL_2 with two branched carbon chains (Figure 4D; compounds of general structure 13b).[73] LBOs with higher branching exhibit lower pour points (PP) and are used for extreme cold temperature applications. We found Aquivion PW98 was effective for the one-step CA-HAA reaction.[73] The yields depend on the molecular size of enals. For example, the CA-HAA reaction between crotanaldehyde and 2-alkylfurans, with the alkyl group being *n*-propyl, *n*-butyl or *n*-pentyl, yielded 71-73% C_nFL_2, where n = 25-31. When accounting for all detected condensation products of n>20 (suitable for LBOs), the total yields are 77-84%.[73] Noteworthy, use of a larger size enal, 2-methyl-2-pentanal, lowers the selectivity to the desired precursor $C_{33}FL_3$ because of steric effects (Table 2) . The reaction profile suggested that CA takes place first with one molecule of alkylfuran bonded to the unsaturated carbon bond of enal. The resulting intermediate concomitantly undergoes HAA condensation with two molecules of alkylfuran to produce desired precursors. Self-condensation of alkylfuran and ring-opening of furan rings of the condensation products formed lower carbon number products.[73]

Table 2. Synthesis of C_nFL2 and C_nFL3 from enals and alkylfurans. Total yields represent C_{20}-C_{33} products (compounds of type 13b).[73]

Alkylfurans	Enals				Total
R3	R4	R5	Product	Yield (%)	yield (%)
n-Propyl	Methyl	H	$C_{25}FL2$	72	82
n-Butyl	Methyl	H	$C_{28}FL2$	73	84
n-Pentyl	Methyl	H	$C_{31}FL2$	71	82
n-Pentyl	H	H	$C_{30}FL2$	72	77
n-Pentyl	Ethyl	Methyl	$C_{33}FL3$	59	73

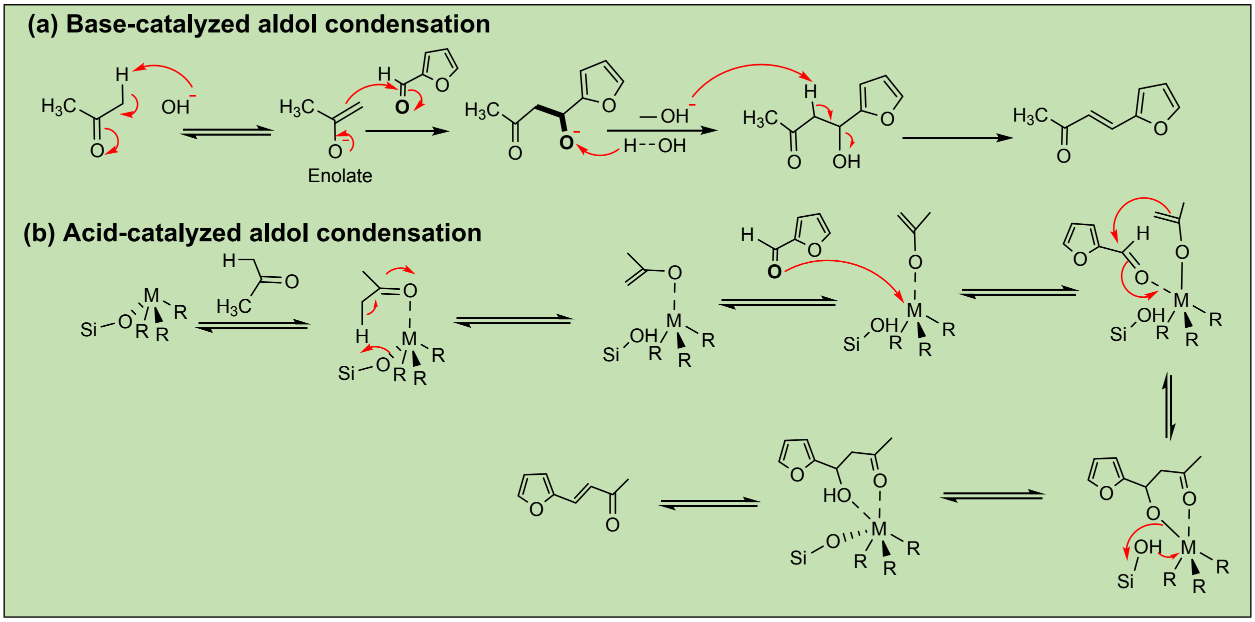
The number following 'FL' indicates the number of branches.

4.2.3. Aldol condensation and hydrogenation reactions strategy. A sequential four step strategy involving AC and hydrogenation reactions (Scheme 1) produces LBO precursors. For example, AC of a ketone, *e.g.* acetone, with furfural forms a C_{13} intermediate, which upon hydrogenation and another aldol step with furfural at the α-carbon of the ketonic group of the hydrogenated C_{13} intermediate produces a C_{23} LBO precursor (compound 14) with 50% yield.[82] Following this strategy, we reported the synthesis of a C_{33} LBO precursor (compound 15) from a C_{12}-tricosanone, obtained from ketonic decarboxylation of carboxylic acid. Up to 94% yield is obtained in methanol at optimized reaction conditions.[83] A profound effect of solvent was found, which contradicts prior work.[82] For example, non-polar solvents were ineffective because of limited solubility of the reactants while water formed degradation products. Alcoholic solvents, *e.g.* methanol, achieved the best performance.



Scheme 1. (A) Sequential AC and hydrogenation reactions to produce LBO precursors. (B) Structures of other LBO precursors.

Aldol condensation is catalyzed by a base or a Lewis acid. The base-catalyzed aldol reaction initiates by α-H abstraction of the carbonyl group of ketones, for example, acetone, and enolization.[84] Concurrent reaction of the nucleophilic enolates with the electrophilic carbonyl groups of furfural or HMF, followed by protonation of the adduct by the resultant water from the first step forms an aldol product (Figure 6a). The enolization step also occurs in the Lewis acid-catalyzed aldol condensation, for example, Sn-beta (Figure 6b).[85] Spectroscopic studies and DFT calculations suggested a direct adsorption of carbonyl reactants on the Lewis acid sites (Sn^{4+}) of the catalyst and abstraction of an α-H by the framework Si−O−Sn fragment, forming a Si−OH group and a metal-coordinated enolate, which then undergone C−C coupling with another carbonyl molecule. Over Zr-beta and Ti-beta, a concerted single-step mechanism involving co-adsorption of two carbonyl molecules at the Lewis acid sites and a proton transfer between the adsorbates likely occurred.


(a) Base-catalyzed aldol condensation

(b) Acid-catalyzed aldol condensation

Figure 6. Aldol condensation mechanism.

4.2.4. Other condensation strategies. Synthesis of LBO precursors has also been reported *via* other coupling reactions. For example, the Bell group reported base or acid catalyzed self-condensation of biomass-derived *n*-alkyl- or furyl-ketones to produce C_{24}-C_{45} LBO precursors (compounds 16,17).[57] The combination of ketones and catalysts (acidic or basic) dictate the structure and carbon number of the produced cyclic trimer precursors. For example, the base catalyzed self-condensation forms alicyclic trimers, with one double bond in the six-member cyclic ring (compound 16). In contrast, the acid catalyzed reaction predominantly forms aromatic precursors (compound 17) because of dehydration by the acid sites. Quantitative yields of precursors can be achieved at 230 °C for 24 h. Similar alicyclic precursors can also be synthesized *via* the Robinson Annulation condensation. First, AC of furfural and 2,4-pentanedione produced a C_{15} adduct first with 90% yield at 120 °C and 20 h using a $CoCl_2.6H_2O$ catalyst.[62] Subsequent intramolecular aldol reaction of the adduct with another molecule of pentanedione produced a small fraction of a C_{20} precursor (compound 18) with three structural conformations.

4.3. Hydrodeoxygenation to produce deoxygenated LBOs

Early research by the Corma group employing physically mixed catalysts (*e.g.*, Pt/C-Pt/TiO_2, Pt/C-Pt/Al_2O_3)[64-66] or single metal catalysts (*e.g.*, Pd/C, Pt/C, Pt/Al_2O_3) resulted in a significant C-C creaking of C_{12}-C_{15} multi-furan substrates (Figure 4A) in the vapor phase HDO reaction. SiO_2, Nb_2O_3, and SiO_2-Al_2O_3 supported Pt,[80] commercial Pd/C,[86] Ni/ZSM5,[87] and bimetallic Pd-FeOx/SiO_2[88] catalysts also caused similar C–C cracking. The literature reports point to the fact that HDO of multi-furan substrates requires high temperatures at which the acid support and/or the metal lead to significant cracking. Specific metal/metal oxides can be suitable candidates for this. Ir-ReOx/SiO_2 and other metal-metal oxide catalysts have been used for HDO of low carbon biomass substrates and single ring furans, *e.g.*, furfural, HMF, 2,5-dimethylfuran (DMF)[89] [70] but their effectiveness for multi-furan substrates had not been exploited until recently.

We reported that an Ir-ReOx/SiO_2 (Re/Ir molar ratio = 2) catalyst achieved up to 96% selectivity to C_{12}-C_{15} branched alkanes from HDO of compounds 2, 3 and 9 at lower temperature (170 °C) and quantitative conversion.[70] A comparison of HDO performance of compound 9 with various reported catalysts (Figure 7) indicates an excellent activity of Ir-ReOx/SiO_2 at comparatively lower temperature, which is due to the site cooperativity of its metal (Ir) and acid (ReOx) sites. The reaction profile showed that ring-opening of fully or partially hydrogenated furan rings, formed over Ir sites, occurred by either Lewis acid sites of partially reduced ReO_x or Brønsted acid sites, generated *via* a synergy between Ir and ReOx.[70] Oxygenated intermediates, carbonyls and/or hydroxyls form, are sequentially hydrogenated, dehydrated to olefinic species, and finally hydrogenated to branched alkanes.[70]

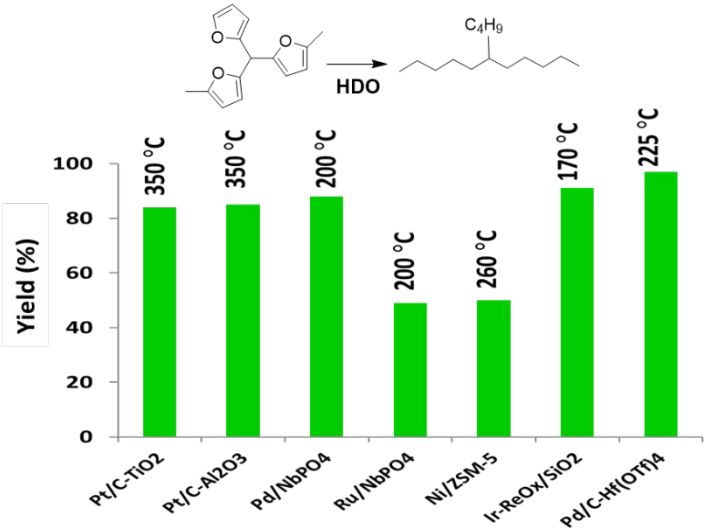
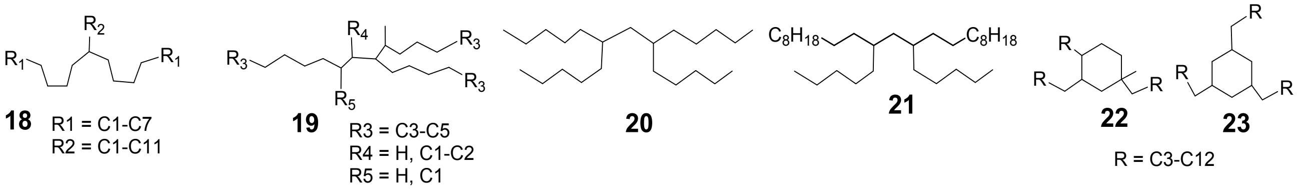


Figure 7. Catalytic performance of various catalysts for HDO of compound 9. Pt/C-TiO_2 (ref[64]), Pt/C-Al_2O_3 (ref [64]), Pd/$NbOPO_4$, Pd/$NbOPO_4$ (ref [90]), Ni/ZSM5 (ref[87]), Ir-ReOx/SiO_2 (ref[70]), and Pd/C-Hf(OTf)$_4$ (ref[91]). The yields in the bar graph also include C–C cleaved alkanes.

HDO of C_nFL_1 and C_nFL_2 LBO precursors was also effective over metal/metal oxide catalysts.[71, 73, 83, 92] HDO of $C_{30}FL_1$ over Ir-ReOx/SiO_2 (Re/Ir molar ratio = 2) was selective.[71] A maximum 87% yield of $C_{30}BA_1$ (BA and 1 refer to branched alkane and number of branch carbon chain) was achieved at 170 °C and 12 h.[71] Other C_nFL_1 precursors (n ~22-34) gave 83-91% yields of the corresponding branched alkanes (compounds of structure 18, Scheme 2).[71, 93] Ir-MeOx/SiO_2 exhibited similar HDO performance for $C_{20}FL_1$ and $C_{30}FL_2$ precursors.[92] A slight variation in the yields of LBOs is noted, which can be attributed to the difference in the molecular size of the LBO precursors, likely arising from steric effects in competitive absorption of furan rings on the catalyst surface.



Scheme 2. Structures of various branched alkanes (BA) as LBOs.

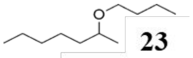
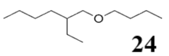
The molecular structure has a more pronounced effect for C_nFL_2 LBO precursors containing three furan rings (compounds 13b). For example, HDO of C_{25}-C_{31} C_nFL_2 precursors achieved 68-

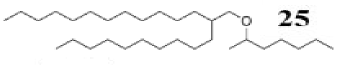
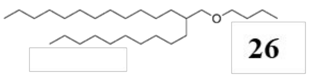
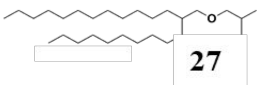
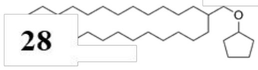
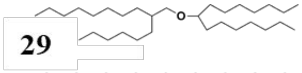
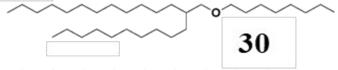
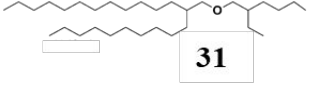
73% yield of the corresponding branched alkanes (compounds of structure 19, Scheme 2) with 4-20% C−C cracking over $ReOx/SiO_2$.[73] HDO of $C_{31}FL_2$ achieved the best yield of total LBO (88%) containing 68% $C_{31}BA_2$ (structure 19, where R_3, R_4, and R_5 are n-pentyl, methyl, and H, respectively). Noteworthy, HDO of $C_{33}FL_3$, a precursor containing three branches, formed only 31% $C_{33}BA_3$ (structure 19) and ~39% C−C cracking, indicating promoted C−C cleavage of tertiary carbons *via* a carbocation-based mechanism. A longer reaction time enhanced C−C cleavage.

The effect of molecular size of furan precursors is also evident in the HDO of compounds 14 and 15. Compound 14 produced 75% C_{23} alkane (compound 20) with two branches over $Pd/NbOPO_4$ at 175 °C for 24 h.[82] A C_{33} LBO precursor (compound 15) gave only 61% yield of compound 21 over $Ir\text{-}ReOx/SiO_2$.[83] While the HDO catalysts of compounds 14 and 15 are different, comparative analysis (Figure 7) suggests that $Ir\text{-}ReOx/SiO_2$ is more effective and selective than $Pd/NbOPO_4$ for HDO of compound 9. Thus, the lower yield and selectivity to compound 21 from compound 15 is likely stemming from molecular size effects discussed above.

The Bell group hydrodeoxygenated[57, 63] compounds 16-17 with different substituents to the corresponding alicyclic alkanes (compounds 22-23). To minimize C−C cleavage of high carbon precursors, especially at furan moieties, they followed a two-step sequential hydrogenation and HDO over Pd/C and Pd/NbOPO4, respectively.[57] While the yields of the resulting alicyclic alkanes were not disclosed, the resulting products containing a mixture of alkanes have suitable specifications for LBOs, as discussed below. The Bell group also reported the synthesis of a range of ether LBOs from biomass derived synthones (aldehydes, ketones) and alcohols via reductive etherification/reductive O-alkylation over Pd/C and an acid catalyst (silica-supported 4-ethylbenzenesulfonic acid ($EBSA/SiO_2$)) (Table 3).[94]

Table 3. The yields of ether-LBOs from biomass substrates.[94]

Carbonyl compound	Alcohol	Ether	$EBSA/SiO_2$ (mol%)*	Conversion of limiting substrate [%]	Yield [%]
2-heptanone	1-butanol	 23	2.5	100	88
2-ethylhexanal	1-butanol	 24	2.5	100	85
2-heptanone	2-decyl-1-tetradecanol		10/10	100/72	91/48

butanal	2-decyl-1-tetradecanol	 **25**	5	97	88
isobutanal	2-decyl-1-tetradecanol	 **26**	5	100	86
cyclopentanone	2-decyl-1-tetradecanol	 **27**		100	87
8-pentadecanone	2-hexyl-1-decanol	 **28**		93	88
octanal	2-decyl-1-tetradecanol	 **29**	5	94	59
		 **30**			
2-ethylhexanal	2-decyl-1-tetradecanol	 **31**	5	79	51

EBSA = 4-ethylbenzenesulfonic acid. Pd/C (2.5 mol%) was also used.

5. STRUCTURE-PROPERTY RELARIONSHIP OF LBOs

LBOs are typically assessed in terms of multiple properties. This section summarizes the properties of furan-based and fully deoxygenated LBOs. Key properties include kinetic viscosities at 100 °C and 40 °C (KV_{100}, KV_{40}), viscosity index (VI), PP, oxidation stability, and volatility. Desired specifications of formulated lubricants used in engines, compressors, gears, hydraulic systems, turbines, and others are achieved by adding various additives. Additives are often expensive and have an environmental impact. Improved properties of LBOs can minimize additives use, improving overall production cost and environmental impact.

Table 4 illustrates that the properties of LBOs largely depend on their molecular structure and carbon number. For example, $C_{30}FL_1$,[71] possessing aromatic character, has comparable VI as the

Table 4. Properties of (hemi)cellulosic LBOs compared with select commercial analogues.

LBOs	KV_{100}[a] (cSt)	KV_{40}[a] (cSt)	VI[b]	PP[c] (°C)	Noack Volatility[d] / wt%	DSC oxidation onset T[e] / °C
C_{30}FL1[f]	3.14	12.91	105	-63	10	170
C_{30}BA1[f]	3.19	11.84	140	-21	13.8	201
C_{31}BA2[g]	3.47	13.58	138	-48	17.2	181
C_{24}FL2[h]	2.85	13.3	31	<-60	49	145

C29FL2[h]	3.95	19.2	99	-60	16.9	142
Compounds 22+23 R = *n*-pentyl[i]	3.35	17.01	40	-69	58	224
Compounds 22+23 R = *n*-hexyl[i]	4.07	21.19	82	-66	21.6	224
Compounds 22+23 R = *n*-heptyl[i]	4.87	26.06	109	-72	7.5	226
Compounds 22+23 R = *n*-octyl[i]	5.72	31.57	123	-69	2.6	226
Compounds 22+23 R = *n*-nonyl[i]	6.55	37.18	131	-60	1.2	225
Compounds 22+23 R = *n*-dodecyl[i]	9.64	59.48	146	-9	0	229
Compounds 22+23 R = 2-ethylhexyl[i]	7.09	59.74	66	-54	22.5	212
Compounds 22+23 R = 2-pentylheptyl[i]	11.49	106.46	94	-51	1.7	212
Compound 25[j]	3.1	10	150	-60	6	186
Compound 26[j]	3.1	11.1	143	-21	11.9	210
Compound 27[j]	3.3	12.2	142	-12	11.5	210
Compound 28[j]	3.6	14.2	147	-30	10.8	189
Compound 29[j]	2.7	9.6	123	-18	12.9	195
Compound 30[j]	3.3	11.9	146	-27	3.9	213
Compound 31[j]	3.5	12	145	-36	5.1	206
ExxonMobil PAO4	4.1	19.0	126	-66	18.8	221
Group II (150N)[i]	5.3	30.6	106	-13	14.5	N/A

[a]KV100 and KV40 are kinematic viscosities at 100 ^{o}C and 40 ^{o}C, respectively (ASTM D445). [b]VI (viscosity index) calculated from KV100 and KV40 (ASTM D2270). [c]PP (pour point) measured by ASTM D97 method. [d]Volatility measured by ASTM D6375 method. [e]Oxidation stability measured by ASTM E2009, method B, 500 pis O_2. [f]ref [71], [g]ref [73], [h]ref[72], [i]ref [57], [i]Mineral group II base oil, [j]ref[94]

commercial Group II lubricants, but its branched backbone leads to an improved PP. The viscosities and VI of C_nFL_m increased while the Noack volatility decreased with an increase in the carbon number. This can be explained by the larger London dispersion forces increase with the molecular size. However, the oxidation stability of C_nFL_m is lower than that the Group II or PAOs because of the furan moieties. Thus, furan LBOs are suitable for low temperature applications. Deoxygenation of the furan base oil precursors to $C_{30}BA_1$, structurally similar to commercial

C_{30}PAO, results in significantly improved VI and stability but lower PP due to having one branch carbon chain. The PP can be improved by adding additional branches*, e.g.*, $C_{31}BA_2$,[73] without significantly affecting other properties. Alicyclic LBOs containing different substituent carbon chains possess viscosity profiles that largely depend on the structure and carbon number.[57, 94] Thus, tuning of LBOs properties by tailoring their molecular structure is desirable and feasible. This tuning of properties can bypass or minimize use of additives and bring unparallel opportunities to future biorefineries. Advancement in molecular simulations, *e.g.*, molecular dynamic (MD), to predict the base oil structure for desirable properties, a glimpse of which was published recently,[71] can further fuel scientific and technological advancement in this area.

6. CELLULOSIC ADDITIVES FOR LIBRICANTS FORMULATION

Cellulose esters have been used as additives for formulation of bio-based LBOs. For example, ethylcellulose has been used as viscosity modifiers to the vegetable oil-based lubricants.[95] Methylcellulose and ethylcellulose have been evaluated as thickening agents in the formulation of castor oil.[95] The esterification of microcrystalline cellulose with different molar ratios of lauryl chloride was performed to evaluate their effect as additives on the wear scar diameter of the spherical specimen and average coefficient of friction of formulated lubricants.[95] The results indicated that the wear scar diameter and average friction coefficient decreased as the concentrations of these ester additives increased in base oils. Similarly, cellulose palmitate esters with different degree of substitution exhibited good lubricity properties, in terms of wear scar diameter and friction coefficient, in formulated lubricants.[96] Cellulose derivations such as non-ionic hydroxyethyl cellulose and anionic sodium carboxymethyl cellulose have been evaluated as gelators in the formulation of gel lubricants with a mixture of water and poly(ethyleneglycol)200 as a base fluid.[97] The thermal, rheological and the tribological properties of the formulated gel lubricants indicated that the ionic and non-ionic cellulose gelators are effective additives to reduce wear, stabilize friction coefficient and enhance the thermal stability of the formulated gel lubricants.

7. TECHNO-ECONOMIC AND LIFE-CYCLE ANALYSIS

This section summarizes techno-economic and life cycle analyses from limited number of reported articles to evaluate commercial viability as well as environmental impact for (hemi)cellulosic LBOs.[71, 98, 99]

We have recently reported TEA for $C_{30}BA_1$ production.[99] The process flow simulation and economic analysis used Aspen Plus V8.8. Two potential scenarios were assumed. For scenario 1, an integrated process to LBO along with *p*-xylene was considered. C_6 sugar of lignocellulose was used to produce *p*-xylene *via* sugar dehydration to HMF, HDO of HMF to DMF and DMF cycloaddition with ethylene. TEA for *p*-xylene was recently published.[100] Lignocellulose derived furfural was used for LBO production. The analysis assumed back-integration of the process to produce 2-pentylfuran, instead of purchasing it. The process steps are: (1) furfural decarbonylation to furan over Pd/Al_2O_3 at 250 °C,[101] (2) furan acylation over an Al-SPP catalyst with an anhydride, produced from trifluoracetic acid catalyzed reaction of valeric acid, and then HDO of the acylated intermediate to 2-pentylfuran over a CuCrO4 catalyst,[53] (3) HAA condensation of 2-pentylfuran and lauraldehyde over $P\text{-}SiO_2$[71] to produce $C_{30}FL_1$, and (4) HDO of $C_{30}FL_1$ over $Ir\text{-}ReOx/SiO_2$[71] to produce $C_{30}BA_1$. The production target of $C_{30}BA_1$ was 98,945 ton per year with 97% purity. In scenario 2, furfural was appropriately allocated to produce four downstream bioproducts, butadiene (6,495 ton), jet furls (3.6 million gallons), $C_{30}BA_1$ (24,385 ton) and surfactant (43,969 ton),[99] along with *p*-xylene from C_6 sugar.

For scenario 1, the CapEx and total operating costs estimated as \$363.3 million and \$458 million, respectively. For scenario 2, these values were \$456.6 million and \$302 million, respectively.[71, 99] The operating costs included raw materials and solvents, catalysts, utilities, labor, maintenance, plant overhead, general and administration costs, and others. The main contributor to the operating cost is the cost of raw materials. In scenario 1, the minimum selling price is \$4,037/ton. The price of petroleum derived PAO LBO is ~\$4,000-4500/ton. For scenario 2, the variable cost for LBO is \$3,649/metric ton and the contribution margins keeping the aforementioned selling price is \$388/ton.

In a different scenario, when furfural is purchased from the market, the model estimated the minimum selling price of LBO as \$4,570/ton. This represents an increase of ~ 13% in the minimum selling price. The above examples indicate the combinatorial nature of scenarios underscore the need for a more integrated and holistic systems engineering approach.

Life-cycle analysis (LCA) was performed using the SimaPro® [100] software and a cradle-to-gate system boundary.[99] A process flow diagram is shown in Figure 8. Furfural was considered as the starting material for both products. Steam heating, generated by natural gas and heavy oil, water cooling from unspecified natural origin with 99% being recycled, and waste heat emit into atmosphere were assumed. Impact categories (climate change, water depletion, land occupation, and fossil depletion) were calculated using ReCiPe midpoint method.[102] The total emissions for each impact category for per ton LBO production were 8119 kg CO_2 eq., 321 m^3, 1133 kg oil eq. and 5667 m^2a, respectively. The main contributor for all the impact categories was the requirement of biomass production for furfural. Other small contributions stem from use of steam for heat and electricity.

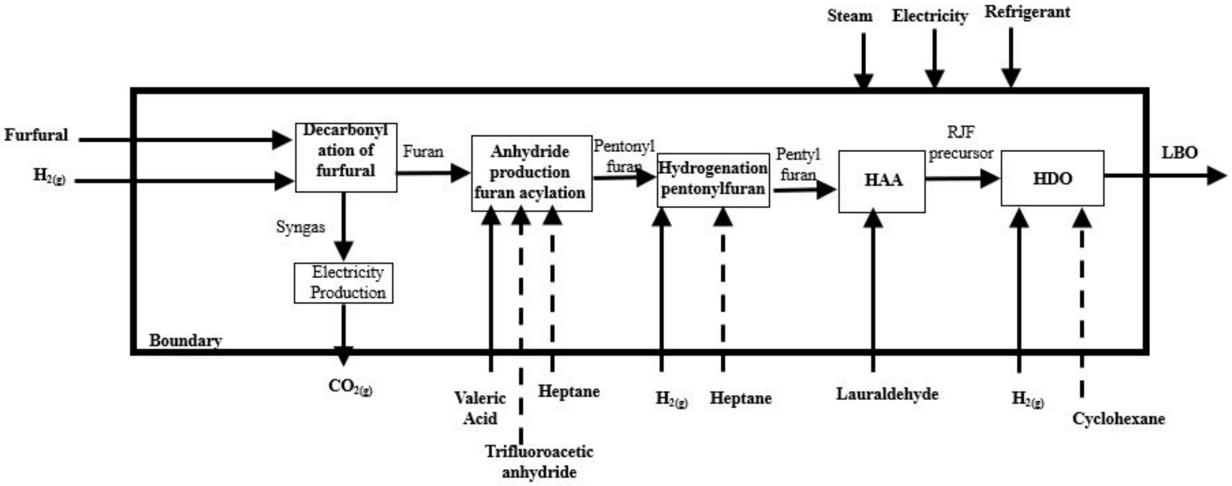


Figure 8. Scope definition of life-cycle analysis for production of LBO. The solid lines are the component streams which are consumed while the dashed lines represent the streams that are recycled. HDO = hydrodeoxygenation. HAA= hydroxyalkylation/alkylation.

8. CHALLENGES AND FUTURE OPPORTUNITIES

The structural complexity of oxygenated large molecules derived from biomass require multifunctional catalysts for their effective conversion, and hierarchical material structures consisting of fairly large pores for accessing the active sites and reducing diffusion limitations but also micropores to impart selectivity. Single metal catalysts and solid acids are neither as active nor as selective. Active site cooperativity and molecular interactions with the catalysts control the HDO rates of LBO precursors containing multiple furan rings and the selectivity to branched alkanes. Highly oxygenated environments, arising from furan rings and water co-product, make the reaction more complex, and unselective. While significant experimental and computational efforts have been dedicated to understanding the deoxygenation paths for single furan substrates and small molecules, such fundamental studies for multi-furan substrates are currently lacking. Emphasis should be placed on (1) elucidating the reaction mechanisms and large molecule/catalyst interactions, (2) developing kinetic and process models for reactor design and flow-sheeting, (3) developing design principles for multifunctional, hierarchical catalysts to further enhance product selectivity and avoid C-C cleavage, (4) developing cascade of reactions to minimize capital cost and to improve process economics, and (5) novel reactors for in situ removal of water to drive the reaction equilibrium to the product side and improve energy efficiency. Advances in these areas also will facilitate the development of other high carbon number downstream bioproducts such as polyols, cosmetic ingredients, and food additives.

Another challenge is lack of established and reliable supply chain of feedstocks. Production of LBO precursors requires 2MF, alkylfurans, ketones, aldehydes, and others. Currently, commercialization of LBOs *via* the chemistry described herein is inhibited because of lack of supply of these upstream biomass substrates. Such biomass substrates are also necessary to produce other high value bioproducts, such as surfactants, polyols, and ingredients for cosmetics, fragrances and food flavorings. The feedstock supply chain as well as process chemistries and separation technologies for petroleum-based refinery have been developed over the past century. Development of a similar supply chain for the biorefinery will require time and also need unparallel investment commitment from public-private entities. Efforts have been initiated in the past decade to commercialize some upstream feedstocks. However, this focus has significantly weakened in recent years because of lack of investment. Consequently, early stage biorefineries involved in the commercialization and development of supply chain for biorefinery feedstocks have either declared bankruptcy or diversified their product portfolio. Developing better routes to produce the necessary precursors and exploit other waste streams in the bigger picture of a circular economy are strongly encouraged.

Long term cohesive policy among stakeholders, *e.g.*, funding agencies, private investors, policy makers, industries, and research institutions, is necessary to render biorefineries sustainable. For example, industries could focus on scale up, commercialization and supply chain development while academic research institutes could focus on scientific advances, mechanistic understanding, and materials and conceptual process development. The research institutes should work alongside with industries to mitigate risks.

Detailed LEA and LCA profiles are currently missing for many bioproducts including LBOs. While research groups have chosen specific bioproducts synthesis, more comprehensive TEA/LCA are necessary to guide future directions regarding feedstock availability, commercial practicality, and environmental impact.

9. CONCLUSIONS

We highlighted novel C-C coupling and deoxygenation strategies to produce (hemi)cellulosic LBOs with varying carbon number and branching from (hemi)cellulosic biomass substrates. This review focused on HAA, combination of aldol and Michael addition and conjugate addition-HAA coupling strategies to produce furan-LBOs or LBO precursors with branched architecture using homogeneous and heterogeneous acid catalysts. Catalytic HDO of these precursors to the branched alkanes for LBOs was also described. LBOs from triglyceride and fatty acid and their properties were concisely summarized. Key properties of LBOs underscore the importance of structure on dictating their properties. The specificity of C–C coupling using oxygenated precursors enables tailoring of base oil's molecular structure and thus of desirable properties. Techno-economic and life-cycle analyses for reported systems under different production scenarios were described. The best scenario calculated comparable price for (hemi)cellulosic LBO to the petroleum analogue. A significantly higher selling price for LBO was estimated when using commercially procured furfural, underscoring the need for a more integrated approach for a sustainable cellulosic biorefinery. Finally, standing challenges for biorefinery and possible future directions to mitigate such challenges were outlined.

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