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# Novel Strategies for the Production of Fuels, Lubricants, and Chemicals from Biomass

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CONSPECTUS: Growing concern with the environmental impact of CO_2 emissions produced by combustion of fuels derived from fossil-based carbon resources has stimulated the search for renewable sources of carbon. Much of this focus has been on the development of methods for producing transportation fuels, the major source of CO_2 emissions today, and to a lesser extent on the production of lubricants and chemicals. First-generation biofuels such as bioethanol, produced by the fermentation of sugar cane- or corn-based sugars, and biodiesel, produced by the transesterification reaction of triglycerides with alcohols to form a mixture of long-chain fatty esters, can be blended with traditional fuels in limited amounts and also arise in food versus fuel debates. Producing molecules that can be drop-in solutions for fossil-derived products used in the transportation sector allows for efficient use of the existing infrastructure and is therefore particularly interesting. In this context, the most viable source of renewable carbon is abundantly available lignocellulosic biomass, a complex mixture of lignin, hemicellulose, and cellulose. Conversion of the carbohydrate portion of biomass (hemicellulose and cellulose) to fuels requires considerable chemical restructuring of the component sugars in order to achieve the energy density and combustion properties required for transportation fuels—gasoline, diesel, and jet. A different set of constraints must be met for the conversion of biomass-sourced sugars to lubricants and chemicals. This Account describes strategies developed by us to utilize aldehydes, ketones, alcohols, furfurals, and carboxylic acids derived from C_5 and C_6 sugars, acetone−butanol−ethanol (ABE) fermentation mixtures, and various biomass-derived carboxylic acids and fatty acids to produce fuels, lubricants, and chemicals. Oxygen removal from these synthons is achieved by dehydration, decarboxylation, hydrogenolysis, and hydrodeoxygenation, whereas reactions such as aldol condensation, etherification, alkylation, and ketonization are used to build up the number of carbon atoms in the final product. We show that our strategies lead to high-octane components that can be blended into gasoline, C_9−C_{22} compounds that possess energy densities and properties required for diesel and jet fuels, and lubricants that are equivalent or superior to current synthetic lubricants. Replacing a fraction of the crude-oil-derived products with such renewable sources can mitigate the negative impact of the transportation sector on overall anthropogenic greenhouse gas (GHG) emissions and climate change potential. While ethanol is a well-known fuel additive, there is significant interest in using ethanol as a platform molecule to manufacture a variety of valuable chemicals. We show that bioethanol can be converted with high selectivity to butanol or 1,3-butadiene, providing interesting alternatives to the current production from petroleum. Finally, we report that several of the strategies developed have the potential to reduce GHG emissions by 55−80% relative to those for petroleum-based processes.
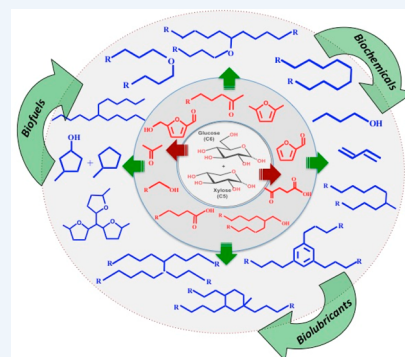
INTRODUCTION

Concerns over the impact of greenhouse gas (GHG) emissions on the climate have stimulated the search for long-term strategies for producing fuels, lubricants, and chemicals from renewable sources of carbon.[1,2] Most of these efforts have focused on finding alternatives to petroleum, since two-thirds of the total global GHG emissions (∼45 gigatons of CO_2 per year) is associated with the combustion of petroleum-based transportation fuels—gasoline, diesel, and jet.[3] While a significant part of these emission could be avoided by the use of battery-powered light-duty vehicles recharged from renewable electrical energy sources, such as wind and solar radiation, the balance of the transportation sector, which includes aircraft, long-haul trucks, and ships, will continue to require high-

energy-density hydrocarbon fuels. The fuel demand for these forms of transportation constitutes about 30% of the total current fuel demand.[2] To minimize the environmental impact associated with combustion of the fuels for these modes of transportation, they should be produced from a renewable carbon source such as biomass. It is notable that biomass-derived transportation fuels are already produced at the level of nearly 2 million barrels a day (mbd). and by 2030 this is expected to rise to about 6 mbd, representing nearly 6% of the total fuels used.[4−6] Estimates suggest that the United States could sustainably produce more than 1 billion tons of
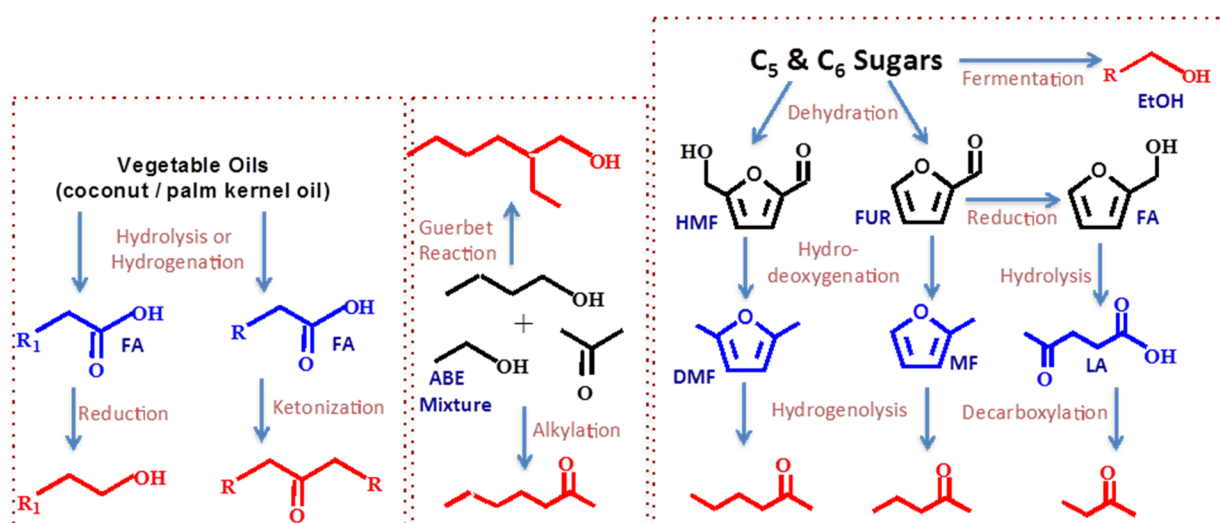
Figure 1. Chemical pathways to the production of furans, alcohols, Guerbet alcohols, ketones, fatty acids, and alkyl methyl ketones from vegetable oils, ABE mixture, and biomass sugars. The compounds shown in red are the alcohols and ketones produced by chemical pathways from various biomass sources (identified in black), and the boxes indicate three different approaches for producing the respective synthons from biomass.
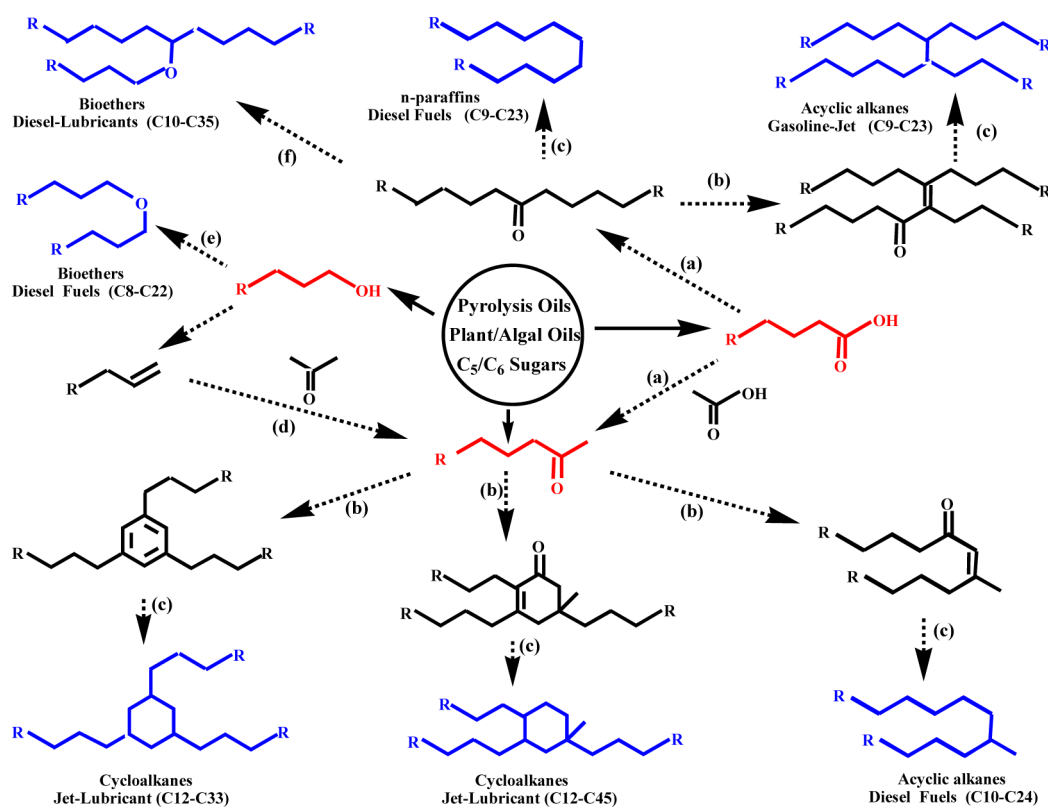

Figure 2. Formation of various synthons such as carbonyl compounds, alcohols, and carboxylic acids from biomass feed stocks (solid arrows) and their subsequent conversion to liquid transportation fuels and lubricants (dotted arrows) utilizing (a) self-cross-ketonization, (b) condensation, (c) hydrodeoxygenation, (d) alkylation, (e) direct etherification, and (f) reductive etherification reactions. Molecules appearing in red are biomass-derived synthons, whereas molecules shown in blue are products obtained from the respective synthons.

nonedible biomass per year, and these biofuels could replace more than one-third of the fossil fuels currently consumed by the transportation sector.[6] Therefore, it seems realistic to consider reducing the dependence on petroleum-based fuels and meeting the future demands for transportation fuels by a combination of renewable electricity and biofuels.[7−11] This Account discusses our efforts to develop efficient strategies for

converting biomass-derived sugars to fuels as well as to lubricants and selected chemicals.

To illustrate the motivation for our strategy, we begin with a short overview of the properties of biomass and those of the fuels one wishes to produce. Lignocellulosic biomass is composed of lignin, hemicellulose, and cellulose. The latter two components, which are carbohydrates, are polymers of C_5 and C_6 sugars. Neither the monosaccharides or disaccharides
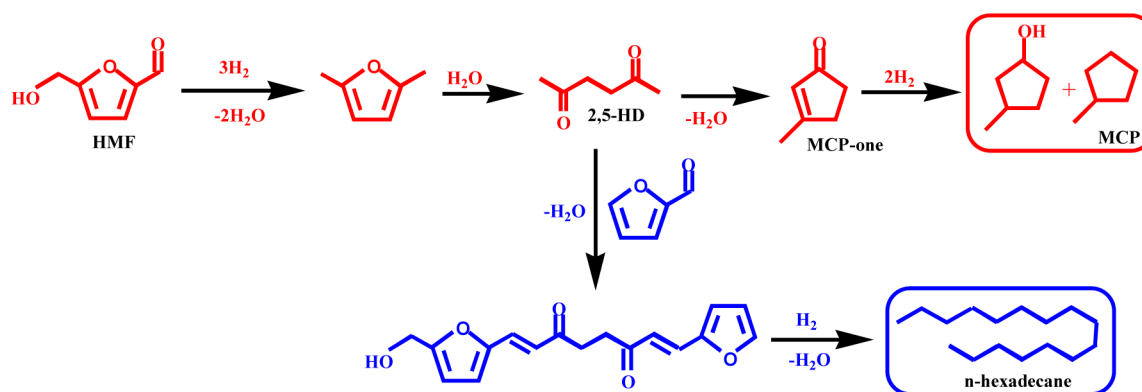
Figure 3. Pathways of HD utilization for the synthesis of gasoline additives and diesel compounds.[25] Reaction conditions: T = 453 K, 2,5-HD = 1.2 mmol, M_{Cat} = 50 mg, H_2O/toluene = 4 mL, P_{H_2} = 3 MPa, t = 2−5 h. The red color indicates pathways to gasoline additives, while blue color indicates the pathway to diesel.

produced by enzymatic or acid hydrolysis of biomass-derived carbohydrates are suitable as fuels because of their high oxygen content and low energy density (15−20 MJ kg^{-1} versus 42 MJ kg^{-1} for hydrocarbon fuels).[2,6] Moreover, transportation fuels require low volatility and suitable combustion characteristics, i.e., gasoline octane number and diesel cetane number and lubricity. Consequently, the conversion of biomass to fuels requires removal of most, if not all, of its oxygen content and the formation of molecules with five to 22 carbon atoms with either a branched (for gasoline) or linear (for diesel) backbone structure.[12−14] A further constraint on any process for the conversion of biomass to fuels is the overall H_2 demand for oxygen removal. Industrial processes rely upon steam reforming of methane, a fossil fuel for production of H_2, and while every CO_2 produced in the reforming reaction produces four moles of H_2,[2] the endothermicity of the reaction and the high pressure at which hydrogenations are generally conducted necessitate additional energy inputs from fossil sources.

We have developed a strategy for the synthesis of fuels based on two classes of biomass-derived synthons. The first class comprises ketones and alcohols derived from glucose and xylose. As shown in Figure 1, ketones can be produced by dehydration of C_5 and C_6 sugars followed by hydrogenolysis of the resulting furfural (FUR) and 5-hydroxymethylfurfural (5-HMF).[15,16] Alcohols including ethanol and butanol can be produced by fermentation of the C_5 and C_6 sugars, and the Guerbet reaction can be used to convert such alcohols to branched, higher-molecular-weight alcohols.[11] Sugars can also be fermented to yield a mixture of acetone, butanol, and ethanol (ABE), and condensation of these intermediates produces alkyl methyl ketones.[17] Another class of synthons comprises carboxylic acids that can be sourced from pyrolysis oils and fatty acids produced by hydrolysis or hydrogenation of triglycerides from plant, animal, algal, and tall oils.[18,19]

In the next sections of this Account, we show how we have been able to combine different catalytic reaction sequences to produce fuels and other value-added chemical feedstocks. As illustrated in Figure 2, a number of pathways can be used to convert low-molecular-weight oxygenates into hydrocarbons and cyclic and linear ethers with minimal consumption of hydrogen. The physical properties of the compounds produced are ideal as fuel blend stocks, fuel additives, and lubricants. We have also identified catalysts for the selective conversion of ethanol to n-butanol and 1,3-butadiene.

I. BIOMASS TO BIOFUELS AND FUEL ADDITIVES

As noted above, the physical properties of the bioderived fuels must closely match those of existing compounds.[20] The relevant fuel properties are the octane number or cetane number, the viscosity, the flash point, the pour point, the lubricity, and the energy density. Gasoline needs to be volatile with a low flash point (T_{flash} = −43 °C) so that it will ignite in a spark ignition (SI) engine, whereas diesel needs to be less volatile (T_{flash} ≥ 55 °C) and composed of heavier hydrocarbons that ignite at high temperatures under pressures in a compression ignition (CI) engine. The octane number (typical for gasoline) for SI engines is an empirical measure of the resistance of a fuel to autoignition on a scale of 0−100 compared with heptane and isooctane, respectively. In the U.S., gasoline uses a combined octane rating called the antiknock index (AKI), which is the average of the research octane number (RON) and motor octane number (MON) and is set at a minimum standard of 87. The cetane number for CI engines is defined by reference to the ignition properties of standard mixtures of hexadecane (cetane number 100) and 2,2,4,4,6,8,8-heptamethylnonane (cetane number 15) and determines how readily a fuel autoignites in a CI engine.[21] The minimum cetane number needed in the U.S. is 40, whereas in the European Union it is 51. Fuel volatility is another parameter that affects engine operation, safety, and handling and is closely linked with other fuel properties such as flash point, viscosity, and density. The flash point is the temperature at which the vapor of a liquid fuel forms an ignitable mixture with air at atmospheric pressure. This property is more critical in SI engines, as the fuel needs to be volatile enough to form ignitable fuel/air mixtures. Fuel viscosity also affects the overall fuel performance: high viscosity leads to incomplete combustion, increased engine deposits, and poor cold-temperature performance, whereas low viscosity leads to increased fuel consumption.[22] Because of increasing requirements for removal of sulfur-containing compounds from ultralow-sulfur diesel and the poor lubricity of alkanes, lubricity-enhancing additives are necessary to provide adequate lubrication in combustion engines. Recent studies suggest that among compounds containing −OH, −NH$_2$, and − SH groups, oxygen-containing compounds enhance the lubricity more than those containing nitrogen and sulfur. Furthermore, among oxygenates, lubricity enhancement increases in the order −COOH > −CHO > −OH > −COOCH$_3$ > −C−O > −C−O−C−.[23] Another relevant fuel property is the pour point (cloud point), which is

defined as the lowest temperature at which a fuel flows before it solidifies. The remainder of this section describes our efforts to synthesize compounds that meet or exceed most of these general fuel requirements.

Gasoline is a complex mixture of predominantly C_5–C_{13} hydrocarbons that has a high degree of branching and low flash point.[24] We have devised a pathway to gasoline-range products starting from HMF-derived 2,5-hexanedione (2,5-HD). This approach involves base-catalyzed intramolecular aldol condensation of 2,5-HD to produce 3-methylcyclopent-2-enone (MCP-one).[25] Screening studies show that calcined hydrotalcite (Mg(Al)O, Mg/Al = 3) is effective in catalyzing the intramolecular aldol condensation of 2,5-HD in the aqueous phase. Upon extraction of the product MCP-one into toluene, MCP-one yields close to 95% can be obtained at 453 K. As shown in Figure 3, hydrogenation of MCP-one over Ru/C produces a >90% yield of methylcyclopentane (MCP), a molecule that has an octane number of 103 and an energy density of 41 MJ/L. We have also found novel compounds suitable for use as diesel via cross-condensation of 2,5-HD with FUR over calcined hydrotalcite. Cross-condensation of 2,5-HD with FUR produces a C_{16} adduct that when subjected to hydrodeoxygenation over Pt-supported $NbOPO_4$ (Pt/$NbOPO_4$) produces n-hexadecane (Figure 3), a product with an exceptionally high cetane number (CN = 100).

Oxygenates in fuels are known to improve the combustion and lubricity of diesel. Therefore, we have explored the synthesis of furanic ethers and examined their suitability as diesel additives. While the energy density and lubricity of aromatic ethers produced through furan condensation of biomass-derived aldehydes with 2-methylfuran (Sylvan) meet the requirements for diesel, these products do not have a desirable cetane number and pour point (CN = 25, pour point = 11 °C) because of the presence of aromatic furan rings.[26] However, a novel class of products that fully meet or exceed most of the specifications for diesel can be produced by selective hydrogenation of aromatic furan rings to cyclic ether moieties (Figure 4). Ring saturation can be achieved with >95%
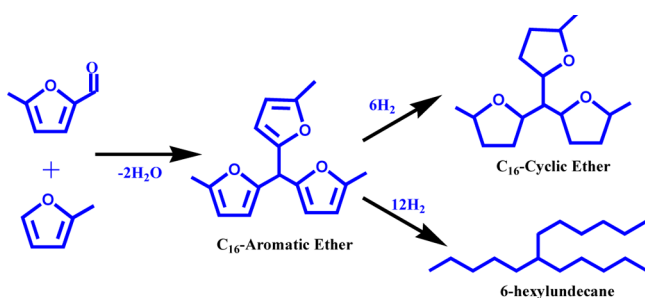

Figure 4. Branched alkanes and cyclic ethers produced via cross-condensation–hydrogenation and cross-condensation–hydrodeoxygenation of biomass-derived furans.[27] Reaction conditions: T = 348 K, $M_{Cat.}$ = 0.2 mol %, P_{H_2} = 2.1 MPa, t = 10 h.

selectivity without ring opening using Pd nanoparticles supported on ionic-liquid-modified SiO_2. This process is attractive because it requires nearly 50% less hydrogen compared with the complete hydrodeoxygenation of the furan rings to form the 6-alkylundecane. We have also found that the cyclic ethers have excellent lubricity and freezing point, >6% higher volumetric energy density than commercial U.S. #2

diesel (~35.8 MJ/L vs 33.6 MJ/L), and a significantly higher cetane number as well (60 vs 41).[27]

From an industrial perspective, isolating furanic intermediates from biomass is a challenge because of their high solubility and low vapor pressure. Therefore, we have focused our attention on precursors that can be obtained by other routes, such as fermentation (Figure 1), and are relatively easy to separate from aqueous solution. An example of such a strategy involves using alkyl methyl ketones, which possess electrophilic and nucleophilic functionality, making them good synthons for producing acyclic and cyclic alkanes that could be used for jet fuels or diesel blendstocks. Aldol-type condensation provides an excellent means for increasing the carbon chain length and decreasing the O/C ratio of alkyl methyl ketones, thereby producing compounds that can readily be converted to higher alkanes. For example, we have found that secondary alkyl amines grafted on silica–alumina particles can promote the selective dimerization of biomass-derived C_4–C_{11} alkyl methyl ketones to α,β-unsaturated enones, which after hydrodeoxygenation over Pt/$NbOPO_4$ produce C_8–C_{22} acyclic alkanes in high yields. The final products can be blended into diesel without any further modification.[28]

In contrast to gasoline and diesel, commercial jet fuel has an energy density of 42.80 MJ/kg and requires a minimum C/O ratio of 13:1.[20] Jet fuel must also have excellent cold-flow properties, and consequently, a higher degree of branching or aromatic/cyclic content compared with diesel is desirable to prevent wax formation. In an effort to achieve such properties, we have investigated the trimerization of C_4–C_7 alkyl methyl ketones over calcined hydrotalcite (Mg(Al)O). Individual ketones or a mixture of multiple ketones was condensed selectively via the aldol condensation of two methyl ketone molecules followed by the slower Michael addition of a third molecule of methyl ketone to produce a range of cyclic enone trimers (Figure 5). The water formed in the process tends to deactivate the hydrotalcite catalyst, so commercialization of such a process poses a major challenge. In the laboratory we solved this issue by using a Dean–Stark apparatus to distill off water in the form of an azeotrope with toluene. On an industrial scale the same could be achieved using reactive distillation in order to obtain condensed ketones as the product from the distillation bottoms. The condensates were hydrodeoxygenated over Pt/$NbOPO_4$ to produce cyclic alkanes with carbon numbers of C_{12}–C_{21} in >95% yield. We found that calcined hydrotalcite and the Pt/$NbOPO_4$ could be reused multiple times with minimal loss in activity.[29] Fuel properties, such as boiling point distribution, cold-flow properties, energy density, and derived cetane number (DCN), were evaluated for C_{12}–C_{21} cyclic alkanes synthesized through the condensation–hydrodeoxygenation of C_4–C_7 methyl ketones. The resulting product mixtures exhibit excellent cloud, pour, and freezing points (below −100 °C), and the boiling point distribution of the C_{12}–C_{18} alkanes closely matches that of commercial Jet-A. We also note that the C_{12}–C_{18} product has a 6% higher energy density than commercially available jet fuel. Additionally, the DCN of C_{12}–C_{21} alkanes is 48.6, which is well above the U.S. requirement for diesel. Combined with its similarity in volatility to traditional diesel, this blend is a promising diesel fuel blendstock, especially for cold weather conditions given its exceptionally low cloud and freeze points (below −54 °C and −100 °C, respectively).[29,30]

We have recently reported another approach for converting light carboxylic acids (C_2–C_6) to drop-in transportation fuels.
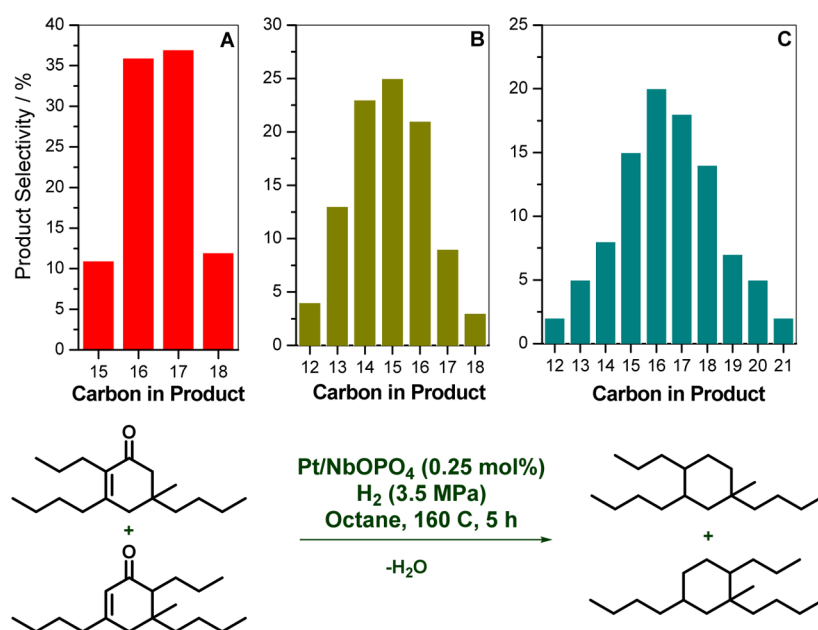
Figure 5. Mg(Al)O-catalyzed cross-condensation of mixed ketones to cyclic enones and its subsequent hydrodeoxygenation to cycloalkane derivatives.[29] Reaction conditions: mixture of C_4–C_7 methyl ketones = 2 mmol, Mg(Al)O = 200 mg, toluene = 3 mL, T = 433 K, t = 5 h. (A) 2-C_5:2-C_6 = 1:1; (B) 2-C_4:2-C_5:2-C_6 = 1:1:1; (C) 2-C_4:2-C_5:2-C_6:2-C_7 = 1:1:1:1. Abbreviations: 2-C_4 = 2-butanone, 2-C_5 = 2-pentanone, 2-C_6 = 2-hexanone, 2-C_7 = 2-heptanone.

Ketonic decarboxylation was used to synthesize symmetrical and unsymmetrical ketones with various chain lengths by self- and cross-ketonic decarboxylation of carboxylic acids over a tetragonal zirconia catalyst. In this process, two molecules of carboxylic acid condense to produce a linear ketone with $2n - 1$ carbon atoms, together with CO_2 and H_2O.[31] The product ketone can then undergo self-condensation over an acid–base catalyst to produce a mixture of acyclic and cyclic enones, which after hydrodeoxygenation over Pt/NbOPO$_4$ produce acyclic and cyclic alkanes that could be used as drop-in replacements for jet fuel (Figure 2). In a similar way, C_8–C_{16} fatty acids are converted to linear high-cetane (CN > 80) alkanes suitable as diesel by a ketonic decarboxylation–hydrodeoxygenation reaction pathway. Thus, carboxylic acids, which are known to have high solubility in water, low energy density, and high acidity, can be converted to drop-in linear and branched alkanes that are compatible with existing transportation fuels.

II. BIOMASS TO BIOLUBRICANTS

Since lubricant base oils are high-value, moderate-volume products, we explored options for producing such compounds from biomass. While some of the first lubricants were the bioesters sourced from plants, today poly(α-olefin)s (PAOs) containing 30 or more carbon atoms are obtained by oligomerization (trimerization) of oct-1-ene or dec-1-ene derived from petroleum. However, the PAO process is environmentally unfriendly since it utilizes corrosive catalysts such as BF$_3$, HF, and AlCl$_3$, with only limited success achievable with environmentally benign catalysts.[32]
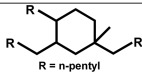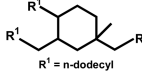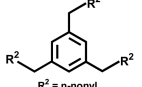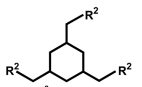
The key properties of lubricants are their kinematic viscosity at 40 °C (KV$_{40}$) and 100 °C (KV$_{100}$), viscosity index (VI), pour point (PP), and oxidation stability (DSC Oxidation) and volatility (TGA Noack). VI is an empirical measure of how the viscosity of a lubricant sample changes with temperature, and PP relates to the temperature at which the sample becomes

semisolid and loses its flow character, while TGA Noack is a measure of evaporation loss at high temperatures.[30,32]

We have found that self-condensation (trimerization) of biomass-derived C_8–C_{15} alkyl methyl ketones in the presence of either Lewis acidic or basic heterogeneous catalysts can produce C_{24}–C_{45} cyclic compounds that have very good lubricant properties. Long-chain alkyl methyl ketones can be produced via alkylation of acetone with the electrophilic alcohols produced by hydrogenation of C_8–C_{16} fatty acids. Base-catalyzed condensation of these alkyl methyl ketones by Mg(Al)O (calcined hydrotalcite) and subsequent hydrodeoxygenation of the products over Pt/NbOPO$_4$ produce C_{24}–C_{45} cyclic alkanes. Meanwhile, condensation of C_8–C_{15} alkyl methyl ketones over a Lewis acidic catalyst such as silica-supported Ta$_2$O$_5$ produces aromatic lubricants, which upon further hydrogenation produce cyclic alkanes.[33] More importantly, these structurally unique lubricants exhibit excellent PPs and VIs that are comparable to those of PAO synthetic lubricants (Table 1). Our work revealed that the VI increases with increasing alkyl side chain length; however, a very long side chain negatively affects the PP of the lubricant. As part of our studies, we examined the impact of our process strategy on the GHG emissions and compared them to the GHG emissions for producing the same products from petroleum. This effort revealed that coproducing bioderived lubricants in a Brazilian biorefinery with ethanol could reduce GHG emissions by as much as 83% compared with production of the same product mixture from petroleum.
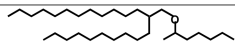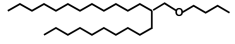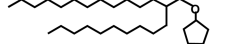
While most of the lubricant properties of the newly developed cyclic alkanes are comparable to those of synthetic C_{30} PAO, their viscosity and volatility are inversely related. A higher viscosity of the cyclic alkanes relative to PAO base oil is undesirable given the fuel economy targets set by various automobile manufacturers. The synthetic challenge is thus to design lubricants that have low viscosity, low volatility, and high VI. Symmetrical and unsymmetrical ethers produced in yields

Table 1. Property Evaluation of Biolubricants Produced by Condensation−Hydrodeoxygenation of C_8–C_{15} Methyl Ketones[33]

Lubricant	KV_{100} (cSt)	KV_{40} (cSt)	VI	PP (°C)	TGA Noack (wt%)
R = n-pentyl	3.35	17.01	40	-69	58.32
R^1 = n-dodecyl	9.64	59.48	146	-9	1.15
R^2 = n-nonyl	4.36	18.54	150	-24	3.6
R^2 = n-nonyl	4.29	18.49	-	3	-
C_{30} PAO mixture	3.63	15.23	124	-72	9.64

close to 90% via reductive etherification of carbonyl compounds with C_{24} Guerbet alcohols using a Pd/C and silica-supported sulfonic acid (Si-SO$_3$H) catalyst can meet these objectives. Our studies have shown that Si-SO$_3$H is more active than conventional Amberlyst-15 and that a wide variety of aldehydes and ketones can be condensed with Guerbet alcohols to produce a range of bioethers that are suitable as synthetic lubricants. As shown in Table 2, the viscosity, volatility, and VI of these newly made ether-based lubricants are superior to those of synthetic and mineral oils used today.[34]

Table 2. Property Evaluation of Bioethers as Lubricants Produced by Reductive Etherification of C_{24} Guerbet Alcohols and Carbonyl Compounds[34]

Lubricant	KV_{100} (cSt)	KV_{40} (cSt)	VI	PP (°C)	TGA Noack (wt%)
	3.06	10	150	-60	6.0
	2.8	9.6	149	-21	12.8
	3.63	14.17	147	-30	7.5
C_{30} PAO mixture	3.63	15.23	124	-72	9.64

III. BIOMASS TO BIOCHEMICALS

More than 25 billion gallons/year of ethanol is produced, making it the most important chemical produced from biomass today. While a majority of this product is blended into gasoline, it can also be viewed as a potential feedstock for producing a range of olefins, aromatics, and oxygenates. For example, ethanol can be dehydrated to ethene, the most widely used organic chemical, with an annual production of 140 million tons per year.[11] Alternatively, new and more sustainable routes employing ethanol and other C_3–C_5 alcohols as feedstocks could be used to produce a range of aldehydes, valuable intermediates for a number of commodity chemicals used as plasticizers and detergents. Though the alkene hydroformylation reaction can produce aldehydes, nonoxidative dehydrogenation of alcohols to aldehydes is particularly interesting since it produces hydrogen as a byproduct. We have shown that gold nanoparticles supported on acid−base supports such as hydrotalcite (Au/HT) and hydroxyapatite (Au/HAP) catalyze this reaction very effectively. Starting from ethanol or C_3–C_5 alcohols, the respective carbonyl compounds (aldehydes or ketones) can be produced at 473 K with over 90% selectivity.[35] Strongly acidic supports, such as silica–alumina (Si–Al), catalyze the dehydration of C_2–C_5 alcohols to form alkenes and ethers, while purely basic supports, such as MgO, produce significant yields of Guerbet products (Figure 6).

Another compound of interest is 1,3-butadiene (1,3-BD), a high-value chemical intermediate used mainly as a monomer for the production of synthetic rubbers. Approximately 95% of 1,3-BD is currently produced as a coproduct of ethylene production from naphtha steam crackers. However, the C_4 fraction contains a mixture of butadiene, butane, and butenes, compounds that are difficult to separate because of their close boiling points. Energy-intensive extractive distillation with a solvent that enhances the relative volatilities of different C_4 hydrocarbons is used to separate 1,3-BD. An alternative to this approach is the condensation of ethanol to give 1,3-BD. As shown in Figure 7, the conversion of ethanol to 1,3-BD involves five critical steps: (a) acetaldehyde formation from ethanol by dehydrogenation; (b) aldol addition of two acetaldehyde molecules to form an acetaldol; (c) dehydration of the acetaldol to crotonaldehyde; (d) Meerwein−Ponndorf−Verley reduction of crotonaldehyde with ethanol to form crotyl alcohol and acetaldehyde; and (e) dehydration of crotyl alcohol to form 1,3-BD.
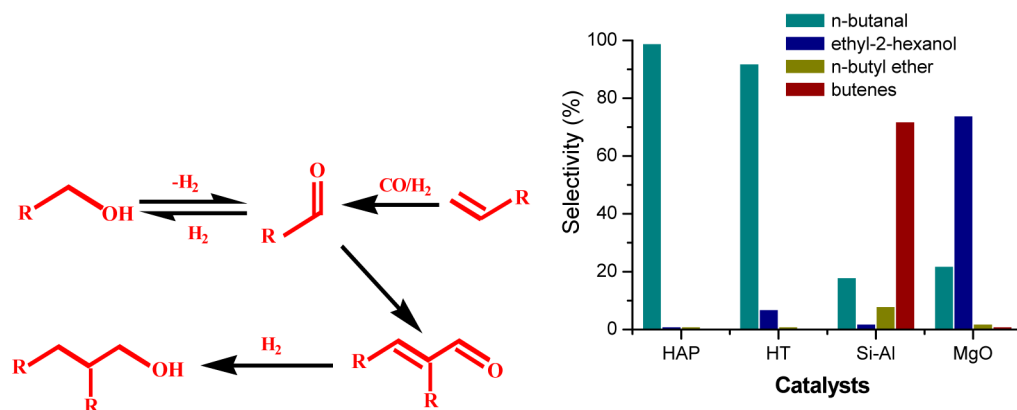
Figure 6. Selectivity patterns of Au-doped acidic, basic, and acid−base supports in the nonoxidative dehydrogenation reaction of *n*-butanol.[35] Reaction conditions: T = 423 K, $P_{alcohol}$ ≈ 2 kPa, $M_{Cat.}$ = 100 mg, Q_{tot} = 150 cm^3 min^{-1}.
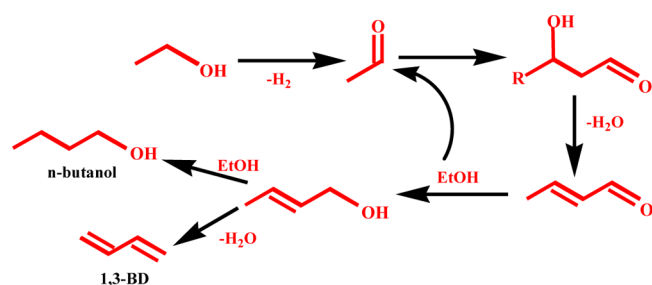
Figure 7. Reaction pathways for the formation of 1,3-butadiene and *n*-butanol from ethanol.

The catalyst needed for the ethanol to butadiene reaction requires proper tuning of redox, basic, and acidic sites in order to optimize the selectivity for 1,3-BD. If the catalyst is too acidic, ethanol will preferentially undergo dehydration to form ethene and diethyl ether. Meanwhile, if the catalyst is too basic or the metal is too active, excessive hydrogenation will lead to butene/butane formation, which increases the difficulty of product separation. We have designed a Au-doped MgO−SiO₂ catalyst that exhibits high activity for ethanol conversion with more than 60% selectivity for 1,3-BD. By contrast MgO−SiO₂ without Au exhibits a high selectivity for ethene (Figure 8).[36]
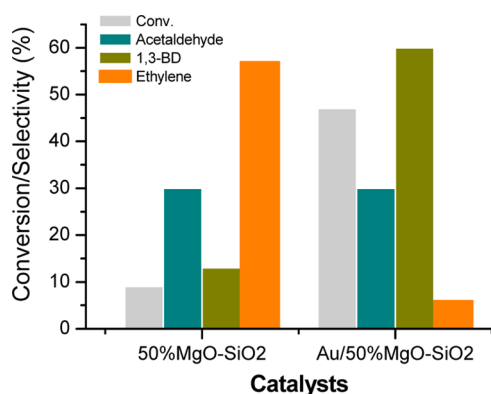

Figure 8. Catalytic activity of MgO−SiO₂ and Au-doped MgO−SiO₂ catalyst in the one-step conversion of ethanol to 1,3-BD.[36] Reaction conditions: T = 573 K, weight hourly space velocity = 1.1 h^{-1}, $P_{ethanol}$ ≈ 20 kPa, $M_{Cat.}$ = 300 mg, Q_{tot} = 20 cm^3 min^{-1}.

While a 1,3-BD selectivity of 60% seems modest, it is noteworthy that the major byproduct formed is acetaldehyde, which can be readily separated and recycled back to the reactor to improve the overall yield. Life cycle and techno-economic analyses of the overall 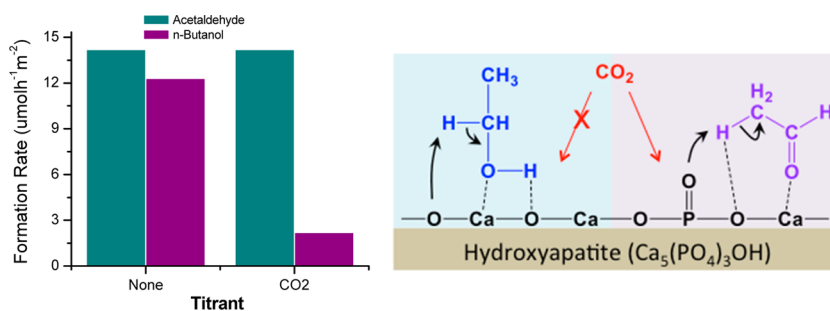process were performed for three different ethanol feedstock sources—U.S. corn grain, U.S. corn stover, and Brazilian sugar cane—in order to assess their impact on GHG emissions. These analyses revealed that production of 1,3-BD from Brazilian sugar cane or corn stover has the potential to lower GHG emissions by over 140% compared with producing 1,3-BD from petroleum, whereas the production of ethanol from corn kernels increases GHG emissions by 12%.[36]

n-Butanol is another compound that can be synthesized from ethanol via the Guerbet reaction. Butanol is considered as a second-generation biofuel because of its low miscibility with water and high energy density (29.2 MJ/L compared with 19.6 MJ/L for ethanol) and as a valuable chemical intermediate in the production of paints, solvents, flavorings, and polymers. Butanol is traditionally produced by hydroformylation of propene and subsequent hydrogenation of *n*-butanal. However, this process requires an expensive rhodium-based organometallic catalyst and high pressures of H₂; an alternative is the environmentally friendly Guerbet coupling of ethanol. Similar to the synthesis of 1,3-BD, this reaction begins with ethanol dehydrogenation to form acetaldehyde, followed by self-condensation of acetaldehyde to crotonaldehyde and hydrogenation of crotonaldehyde to butanol. In this case, the acidity and basicity of the catalyst must be carefully balanced to minimize side reactions (Figure 7). By screening a variety of heterogeneous catalysts, we found that hydroxyapatite (Ca-HAP; Ca₅(PO₄)₃OH) can produce butanol with 81% selectivity at an ethanol conversion of 20% at 523 K. FT-IR and in situ titration experiments using pyridine and CO₂ as titrants revealed that dehydrogenation is catalyzed by Ca−O sites while aldol condensation requires bifunctional calcium oxide/phosphate pairs (Figure 9). The rate of *n*-butanol formation can be enhanced by increasing the basicity of HAP, either through substitution of Ca with Sr or by increasing the Ca/P ratio.[37] The length of the alcohol chain does not significantly affect the coupling rate over Ca-HAP, and Guerbet alcohols such as ethyl-2-hexanol could be obtained from *n*-butanol with >80% selectivity at 573 K.

■ CONCLUDING REMARKS

In this Account, we have described how the carbohydrate portion of biomass can be converted to a small number of synthons such as alcohols, aldehydes, ketones, and carboxylic acids. These building blocks were used for the production of various compounds that are suitable as octane enhancers for gasoline, high-cetane diesel, and jet fuel. The chemical reactions by which these products are made include dehydration of sugars, ring opening of furanics to ketones, etherification, aldol

Figure 9. Poisoning experiments conducted using CO₂ as a titrant in the coupling reaction of ethanol to form *n*-butanol over a Ca-HAP catalyst.[37] Reaction conditions: T = 603 K, $P_{ethanol}$ ≈ 6 kPa, $M_{Cat.}$ = 50 mg, Q_{tot} = 30 cm^3 min^{-1}.

condensation, and ketonization to form ethers, enones, and aromatic compounds. By strategic use of these reactions we have produced blends of linear, branched, and cyclic alkanes and linear and branched ethers that meet the energy content, cetane number, lubricity, and volatility requirements of diesel and jet fuel. We have made lubricants having properties that are similar or even superior to those of synthetic PAO base oil derived from petroleum by extending the reaction schemes for synthesizing hydrocarbons and ethers containing 30−33 carbon atoms. Products used by the energy industry are often mixtures of compounds, and since the success of a commercial process often hinges on advantaged feedstocks, we have focused on the effective use of mixtures of synthons that could be sourced from biomass using relatively inexpensive reagents and processing steps. Furthermore, by integration of various catalytic sequences and the use of multifunctional, recyclable catalysts, biomass-based process technologies can be made cost-effective. Our work has also addressed the selective synthesis of butanol and butadiene from ethanol. In addition to demonstrating our approach for producing targeted products, we have carried out life cycle analyses of selected processes in order to assess whether such pathways have the potential for reducing GHG emissions. Such analyses are particularly important for setting guidelines for policy incentives for reducing GHG emissions.

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Alexis T. Bell received his S.B. and Sc.D. degrees in chemical engineering from the Massachusetts Institute of Technology and then joined the faculty of the Department of Chemical and Biomolecular Engineering at the University of California, Berkeley, in 1967, where he currently holds the position of the Dow Professor of Sustainable Chemistry. Since 1975 he has also been a senior faculty scientist at Lawrence Berkeley National Laboratory. His research is devoted to fundamental studies of the structure−function relationships for heterogeneous catalysts and the application of such catalysts in a variety of contexts, including synthesis of fuels and chemicals from CO and H_2, conversion of biomass to fuels and chemicals, electrochemical splitting of water, and reduction of CO_2. These efforts have involved both experimental and theoretical studies. His work has received extensive recognition, and he is a member of the National Academy of Engineering, the National Academy of Sciences, and the American Academy of Arts and Sciences.

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