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Production of Biomass-Based Automotive Lubricants by Reductive Etherification

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Growing concern with the effects of CO_2 emissions due to the combustion of petroleum-based transportation fuels has motivated the search for means to increase engine efficiency. The discovery of ethers with low viscosity presents an important opportunity to improve engine efficiency and fuel economy. We show here a strategy for the catalytic synthesis of such ethers by reductive etherification/O-alkylation of alcohols using building blocks that can be sourced from biomass. We find that long-chain branched ethers have several properties that make them superior lubricants to the mineral oil and synthetic base oils used today. These ethers provide a class of potentially renewable alternatives to conventional lubricants produced from petroleum and may contribute to the reduction of greenhouse gases associated with vehicle emissions.

Introduction

Over the past decade, increased public awareness, acceptance of climate change, and a growing political will to curb greenhouse gas (GHG) emissions associated with the combustion of petroleum-based fuels has led to strict regulations and efficiency standards for the automotive sector. These factors have also served to stimulate an advance in engine technology and altered the consumption of lubricants. As a result, lower viscosity lubricants are increasingly being required in the market, which leads to fuel economy improvements.[1] Indeed, Pearson and co-workers have noted that a 3.7 % fuel economy benefit can be achieved by using an SAE 8 grade lubricant instead of a standard 5w-30 oil over the New European Drive Cycle (NEDC), the legislated emissions cycle in the European Union.[2] A 3.7 % fuel economy saving over 2014[3] US emissions could

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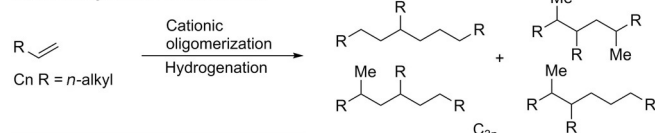University of California
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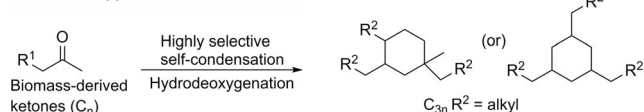Technology Centre, Whitchurch Hill
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result in a decrease of more than 66 million metric tonnes of CO_2 emissions across the whole transport sector. In addition, there is an increased interest in raw materials that have a lower carbon footprint. Notably, the United States Department of Agriculture (USDA) has recently added crankcase oils to the bio-preferred program, which requires federal agencies and their contractors to give preferential treatment to lubricants containing more than 25 % renewable content.[4] Further motivation for the development of biomass-based lubricants comes from the recognition that biomass-derived compounds can be used to produce ether-based lubricants that exhibit low viscosity, low volatility, and high viscosity index (VI), properties that are favorable for formulating fuel economy lubricants.[1, 5] We report here a strategy for the catalyzed synthesis of ethers by reductive etherification of ketones and aldehydes by alcohols, in which all the building blocks can be sourced from biomass. Long-chain ethers produced in this way are shown to have properties that make them superior lubricants to the synthetic and mineral-based oils used today.

Biomass-based lubricants are not new and indeed some of the first lubricants used were esters sourced from plants.[6] However, with the advent of the petroleum age, lubricant formulations came to depend on the superior properties of mineral base oils obtained from petroleum refining.[1] Today, the desired lubricant properties are achieved with poly-α-olefin (PAOs) base stocks produced by the cationic oligomerization/hydrogenation of ethylene-derived linear α-olefins (Scheme 1).[7] The PAO process utilizes catalysts such as BF_3, HF, or $AlCl_3$ that are highly corrosive. Although attempts have been made to find less corrosive catalysts, only limited success has been achieved.[8, 9]

We have recently reported the synthesis of biomass-derived cyclic hydrocarbons (Scheme 1) and shown that these compounds have VIs and volatilities comparable to conventional synthetic C_{30} PAO lubricants, but somewhat higher viscosi-
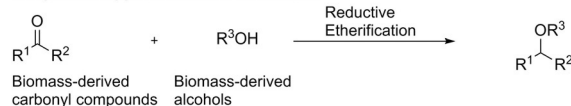
Industrial synthesis of lubricants:

Our earlier approach to biolubricants:

Our present approach to biolubricants:

Scheme 1. Alternative approaches for the synthesis of synthetic lubricant.

ties.[10, 11] Though these compounds can be produced with low GHG emissions starting from Brazilian sugar cane, their higher viscosity relative to PAO makes them unattractive given the fuel economy targets set by regulatory authorities and by automobile manufacturers.[4] Lower viscosity could be achieved by substituting C_{30}-range alkanes used in synthetic base oils with lower molecular weight hydrocarbons, however, the higher volatility of such compounds would lead to greatly increased oil consumption, resulting in frequent oil top-ups, a failure of which may result in engine seizure, a phenomenon that is not acceptable to either the consumer or the automotive industry. The challenge, therefore, is to design lubricants that have a low viscosity and a low volatility, thereby minimizing oil consumption and avoiding the need for frequent oil top-ups, while simultaneously maximizing fuel economy gains.[2] Recent work indicates that high-molecular-weight ethers synthesized by Williamson synthesis can provide the desired lubricant properties.[12] However, Williamson synthesis requires strong base and generates stoichiometric amounts of salt as a byproduct, which can be difficult to remove, requires extensive purification, and is uneconomic for large-scale

production. Here, we show that high-molecular-weight ethers can be produced in high yield by reductive etherification, using synthons readily sourced from both cellulosic biomass and fatty acids. We also show that the lubricant properties of such compounds are equivalent or superior to those of PAO base stocks.

Reductive etherification involves the reaction of alcohol with either an alkanal or a ketone, as shown in Scheme 1. By proper choice of catalyst and reaction conditions this process can be operated so that reductive etherification is preferred over direct etherification of the alcohol. Figure 1 illustrates how the synthons may be preferentially sourced from renewable and bio-derived sources. The initial feedstocks are C_5 and C_6 sugars and fatty acids. Fermentation of the sugars produces ethanol, which can then be converted to acetaldehyde, butyraldehyde, 1-butanol, or hydrogen.[13] Fermentation of the sugars in the presence of strains of clostridia produces a mixture of acetone, butanol, and ethanol (ABE), which can be used to synthesize methyl ketones such as 2-heptanone.[14] Butyraldehyde can be prepared by biobutanol dehydrogenation.[15] Synthesis of 2-ethylhexanal can be achieved by aldol condensation of butyraldehyde and subsequent hydrogenation.[16] Cyclopentanone can be produced from furfural via three key intermediates: furfuryl alcohol, 4-hydroxy-2-cyclopentenone, and 2-cyclopentenone by hydrogenation–rearrangement–hydrogenation reaction sequence.[17] 8-pentadecanone can be obtained by ketonization of octanoic acid.[18] Glucose fermentation in the presence of *Escherichia coli* can result in the formation of isobutyraldehyde.[19] 1-octanol can be obtained by aldol condensation of furfural and acetone, followed by hydrogenation, deoxygenation, and ring opening,[20a] and subsequent dehydrogenation of 1-octanol can lead to octanal.[20b] Higher-molecular-weight alcohol, such as 1-dodecanol, can be obtained by hydrogenation of vegetable oils derived from fatty acids.[21] The Guerbet reaction can be used to synthesize 2-decyl-1-tetradecanol and 2-hexyl-1-decanol from 1-dodecanol and 1-octanol, respectively.[22] Finally, the hydrogen required for reductive etherification can be produced by ethanol steam
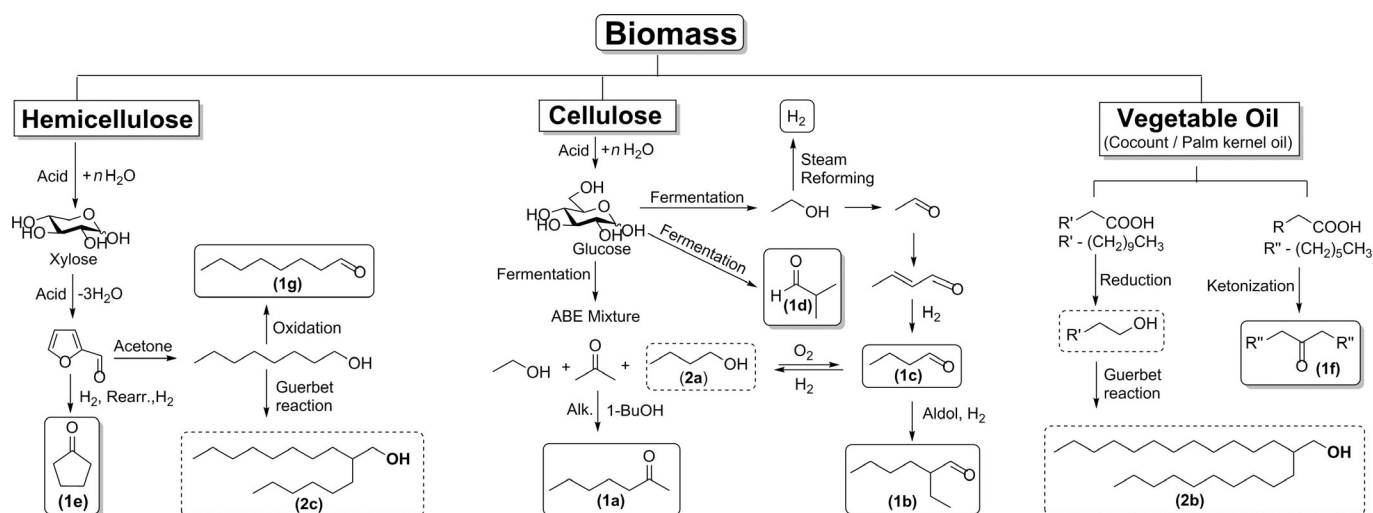
Figure 1. A general approach to biomass derived carbonyl compounds and alcohols.

reforming (ESR).[13] These illustrations show how the aldehyde, ketone, alcohol, and hydrogen required for reductive etherification may be sourced from biomass.
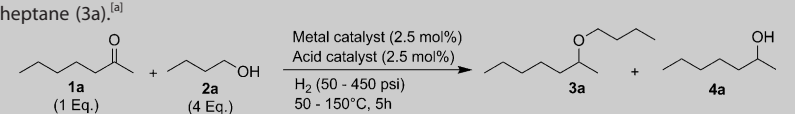
Result and Discussion

We began our studies by investigating the reductive etherification of **1a** with **2a** (Figure 1) to produce of 2-butoxyheptane (**3a**) with the aim of identifying catalysts and reaction conditions that would be most suitable for obtaining high yields of the desired ether. The results of these experiments are presented in Table 1. Entries 1–4 show that at 150 psi H_2 (1 psi = 6894.76 Pa) and 50 °C reaction of **1a** with **2a** over 5% Pt/C and 5% Ru/C either in absence or presence of an acid catalyst produced mainly 2-heptanol; whereas, as previously observed,[23] reaction over 5% Pd/C together with an acid catalyst increased the conversion of **1a** to **3a** (entries 5–7). Investigation of the effects of temperature and H_2 pressure revealed that high yields of **3a** could be obtained at 120 °C and 150 psi H_2, using Pd/C and silica-supported 4-ethylbenzenesulfonic acid (EBSA/SiO$_2$) or A-15. Entries 11 and 12 show 88 to 84% yields of **3a**, along with small yields of 2-heptanol (12–16%) and traces of dibutyl ether. However, no noticeable change in the yield of **3a** was found upon further increasing the temperature and pressure. It is important to observe that in the absence of an acid catalyst and using only Pd/C very little **3a** was formed (entry 19). Previous work suggested that when the carbon support is basic, as is the case for the present Pd/C (see the Experimental Section), reductive etherification may be

catalyzed by low activity of Pd for this reaction.[23c,d] However, **3a** was not formed in absence of either Pd/C or H_2 (entries 20–21). Additional experiments, involving the effects of alcohol to ketone stoichiometry and catalyst loading, are summarized in the Supporting Information (Table S1). The results of catalyst reusability are also reported. No loss in catalyst activity was observed upon reuse of the catalyst and no evidence was found for leaching of Pd.

The reductive etherification of 2-heptanone (**1a**) and 1-butanol (**2a**) was compared with the O-alkylation of 1-butanol (**2a**) with 2-ethylhexanal (**1b**). In both cases, 1-butanol was used in four-fold excess. As seen in Table 2 (entries 1 and 2), reductive etherification produced **3a** with 88% yield and O-alkylation of butanol produced **3b** with 85% yield. Therefore, there is no significant difference between the two processes.

Having established the feasibility to perform reductive etherification of biomass-derived ketones and aldehydes with high ether yields, we investigated next the use of reductive etherification to form ethers with 28 to 32 carbons atoms. We found that to achieve high conversions of Guerbet alcohols it was necessary to use four equivalents of the ketone or aldehyde and one equivalent of the alcohol, together with 5–10 mol% of the acid catalyst. In all cases, reactions were performed for 5 h to obtain high conversions of the limiting reagent. Utilization of EBSA/SiO$_2$ rather than A-15 provided better access of the reactants to acid sites, as can be seen in Table 2 (entries 3a, 3b). Table 2 also shows that with the exception of entries 8 and 9, it was possible to achieve alcohol conversions in excess of 93% and a yield of the desired ether in excess of 85%. For
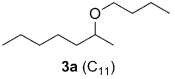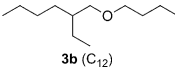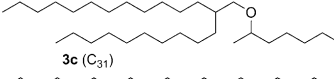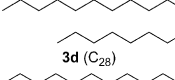
Table 1. Synthesis of 2-butoxyheptane (3a).[a]
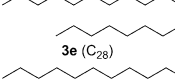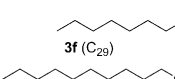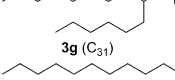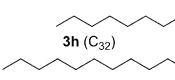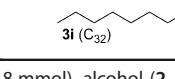
Entry	Metal catalyst[b]	Acid catalyst[b]	T [°C]	H_2 [psi]	Conversion[c] 1a [%]	Yield[c] 3a [%]	4a [%]
1	Pt/C	–	50	150	99	2	97
2	Ru/C	–	50	150	100	–	97
3	Pt/C	EBSA[d]/SiO$_2$	50	150	100	3	97
4	Ru/C	EBSA/SiO$_2$	50	150	100	< 1	95
5	Pd/C	–	50	150	4	–	2
6	Pd/C	A-15[e]	50	150	28	21	7
7	Pd/C	EBSA/SiO$_2$	50	150	53	45	08
8	Pd/C	EBSA/SiO$_2$	60	150	80	59	21
9	Pd/C	EBSA/SiO$_2$	80	150	98	76	22
10	Pd/C	EBSA/SiO$_2$	100	150	> 99	85	13
11	Pd/C	EBSA/SiO$_2$	120	150	100	88	12
12	Pd/C	A-15	120	150	100	84	16
13	Pd/C	EBSA/SiO$_2$	150	150	100	85	11
14	Pd/C	EBSA/SiO$_2$	120	50	71	66	5
15	Pd/C	EBSA/SiO$_2$	120	75	93	84	7
16	Pd/C	EBSA/SiO$_2$	120	100	95	85	9
17	Pd/C	EBSA/SiO$_2$	120	300	100	85	14
18	Pd/C	EBSA/SiO$_2$	120	450	100	87	13
19	Pd/C	–	120	150	41	11	28
20	–	EBSA/SiO$_2$	120	150	10	–	–
21	Pd/C	EBSA/SiO$_2$	120	–	2	–	–

[a] Reagents and conditions: 2-heptanone (1a, 2 mmol),1-butanol (2a, 8 mmol), 5% Pt/C or 5% Ru/C or 5% Pd/C (2.5 mol%), A-15 or EBSA/SiO$_2$ (2.5 mol%), 50–150 °C, 5 h. [b] 2.5 mol%. [c] Determined by GC. [d] EBSA: 4-ethylbenzenesulfonic acid. [e] A: Amberlyst.

Table 2. Conversion of biomass-derived carbonyl compounds and alcohols to ethers.

$$\underset{\mathbf{1}}{R^1\underset{O}{\overset{\parallel}{C}}R^2} + \underset{\mathbf{2}}{R^3OH} \xrightarrow[\substack{120\,°C,\,5\,h}]{\substack{Pd/C\,(2.5\,mol\%)\\ Si\text{-}SO_3H\,(2.5\,-\,10\,mol\%),\\ H_2\,(150\,psi),}} \underset{\mathbf{3}}{R^1\underset{OR^3}{\overset{|}{C}}R^2}$$

| Entry	Carbonyl compound	Alcohol	Ether	EBSA/SiO$_2$ [mol%]	Conversion of limiting substrate [%]	Yield[b] **3** [%]
1	2-heptanone (**1a**, 1 equiv.)	1-butanol (**2a**, 4 equiv.)	**3a** (C$_{11}$)	2.5	100	88
2	2-ethylhexanal (**1b**, 1 equiv.)	1-butanol (**2a**, 4 equiv.)	**3b** (C$_{12}$)	2.5	100	85
3a/3b[c]	2-heptanone (**1a**, 4 equiv.)	2-decyl-1-tetradecanol (**2b**, 1 equiv.)	**3c** (C$_{31}$)	10/10	100/72	91/48
4	butanal (**1c**, 4 equiv.)	2-decyl-1-tetradecanol (**2b**, 1 equiv.)	**3d** (C$_{28}$)	5	97	88[d]
5	isobutanal (**1d**, 4 equiv.)	2-decyl-1-tetradecanol (**2b**, 1 equiv.)	**3e** (C$_{28}$)	5	100	86
6	cyclopentanone (**1e**, 4 equiv.)	2-decyl-1-tetradecanol (**2b**, 1 equiv.)	**3f** (C$_{29}$)	10	100	87
7	8-pentadecanone (**1f**, 4 equiv.)	2-hexyl-1-decanol (**2c**, 1 equiv.)	**3g** (C$_{31}$)	10	93	88
8	octanal (**1g**, 4 equiv.)	2-decyl-1-tetradecanol (**2b**, 1 equiv.)	**3h** (C$_{32}$)	5	94	59
9	2-ethylhexanal (**1b**, 4 equiv.)	2-decyl-1-tetradecanol (**2b**, 1 equiv.)	**3i** (C$_{32}$)	5	79	51

[a] Reagents and conditions: carbonyl compound (**1**, 2 or 8 mmol), alcohol (**2**, 2 or 8 mmol), 5% Pd/C (2.5 mol%), EBSA/SiO$_2$ (2.5–10 mol%), 120 °C, 150 psi H$_2$, 5 h. [b] Isolated yield after purification. [c] Using A-15. [d] **3l** (<2%) also formed.

entries 8 and 9, the ether yields dropped to 59 and 51%, respectively, whereas the alcohol conversion dropped to 79% for entry 9. The low yields for the two C$_{32}$ ethers (**3h** and **3i**) are quite likely a consequence of the bulkiness of the reaction partners. The use of excess ketone or aldehyde and the acid catalyst (5–10 mol%) loading required to achieve high yields for products **3c**–**3i**, means that at high yields of the desired ether, a part of the stoichiometric excess may be diverted to other additional reduced and dimeric side products. This issue was investigated in some detail for entry 3a in Table 2. O-alkylation of 2-decyl-1-tetradecanol (**2b**, 1 equiv.) with excess of 2-heptanone (**1a**, 4 equiv.), produced the desired **3c** ether (C$_{31}$) with a 91% yield; however, during the reaction about 23% (nearly one equivalent) of 2-heptanone was used for **3c**, the remaining 77% of 2-heptanone was converted to 2-heptanol (35%), heptane (7%), a C$_{14}$ mixture (18%) containing bis(2-heptyl)ether and traces of 8-methyltridecan-6-one confirmed by GC–MS analysis, and other unidentified products (<12%). These byproducts can be separated by fractional distillation. Heptane can be used as a solvent and the recovered 2-heptanone (<5%) and 2-heptanol can be used as synthons useful for lubricant and other applications.

Reductive etherification has been envisaged to occur by either hydrogenolysis of hemiacetal/acetal intermediates (path A) or hydrogenation of an enol ether (path B), as illustrated in Scheme 2.[23c] It is known that the initial activation of the carbonyl group compound is acid-catalyzed and is followed by the addition of alcohol to form hemiacetal (**I**) or acetal (**II**) intermediates. The **I/II** intermediates can undergo hydrogenolysis to form an ether (**3**) (path A) or they can undergo a loss of H$_2$O or R^{3}OH to form an enol ether intermediate (**III**) followed by hydrogenation to produce **3** (path B). GC–MS analysis of the reaction mixture leading to product **3b** showed the presence of 3-(dibutoxymethyl)heptane [acetal (**II**)] and a mixture of 3-(butoxymethylene)heptane [enol ether (**III**)] intermediates produced by the loss of butanol, suggesting that path B is the preferred pathway for **3b** formation. This mechanism is also supported by the observation that during the formation of **3i** a mixture of 11-{[(2-ethylhex-1-en-1-yl)oxy]methyl}tricosane [enol ether (**III**)] intermediates is observed by GC–MS.

The lubricant properties of the ethers **3c**-**3i** were evaluated using standard ASTM (American Society for Testing and Material) methods and compared with those of C$_{30}$ PAOs—the group IV American Petroleum Institute (API) base stock. The properties of particular interest are the kinematic viscosity at 40 °C (KV$_{40}$) and 100 °C (KV$_{100}$), the VI, the pour point (PP), the oxidation stability (DSC oxidation), and the volatility (TGA Noack). The optimum parameters for low-viscosity lubricants are
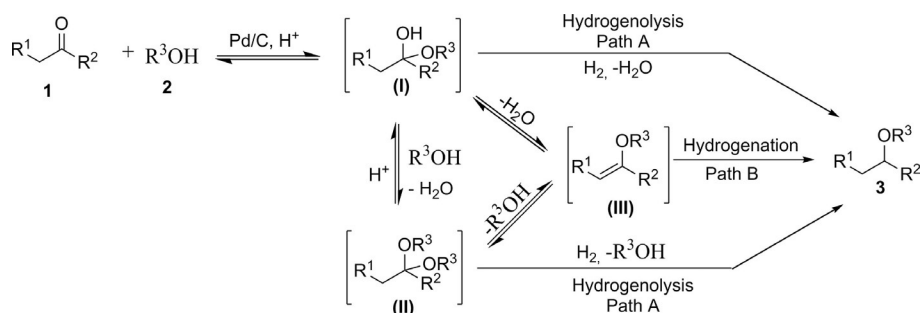
Scheme 2. Plausible pathways for the reductive etherification reaction (Ref. 23c).

values of KV100 and KV40 that are as low as possible paired with a volatility below 15%, according to test method ASTM D5800B. Low-viscosity lubricants are less resistant to flow, hence their fuel economy benefits, in conjunction with maximizing the VI ensures that the oil viscosity varies as little as possible with temperature. This means that the lubricant should have a low viscosity upon cold-start, so that the oil reaches engine parts rapidly, and should not drop in viscosity at higher temperatures, thereby maintaining wear protection once the engine has warmed up. As seen in Table 3, ethers **3c**–**3i** have lower kinematic viscosities (KV$_{40}$ and KV$_{100}$) and higher VIs than PAO, indicating that they may be able to offer fuel economy benefits over current PAO lubricants. The PP of the ethers was measured as an indication of cold-flow properties. Whilst the PP of the ethers is higher than that of PAO, their PPs are greatly superior to group III base oils ($-15\,^{\circ}$C). Furthermore, the cold-cranking simulator viscosity (CCS) of **3i** is almost half that of PAO, again offering the possibility of further fuel economy benefits. The volatility of ethers is comparable to (**3d**, **3e**, and **3g**) or superior than (**3c**, **3f**, **3h**, and **3i**) that of PAO. However, as these compounds all have lower viscosities than PAO, their viscosity/volatility characteristics are more favorable to the lubricant formulator. The DSC oxidation stability of the ethers is acceptable.

A lubricant formulated with compound **3i** was tested in a TU-5 automotive engine to assess the resistance of the lubricant to oxidative thickening and deposit formation compared to a lubricant formulated with a comparable group III mineral oil. Table 4 describes the two oil formulations, one based on

Table 4. Components contained in a baseline lubricant and one containing compound **3i**.

Components	Baseline	**3i** formulation
additive combination	20.65	20.65
4 cSt base-oil	67.45	30.474
6 cSt base-oil	11.9	11.9
ether **3i**	0	36.976

commercial group III base-stocks of 4 and 6 cSt KV100 viscosity oil (1 cSt = 10^{-6} m^2 s^{-1}), and the other in which 36.9% of the 4 cSt group III base-stock has been replaced with compound **3i**. The engine oil additive system has been kept the same to ensure all changes in performance are owed to the change in base-stock.

The two lubricant formulations described in Table 4 were evaluated according to a European engine oil performance test designed to test oil stability under oxidative stress (Table 5). This test performed according to procedures described in CEC L-088-02, and it involves heating the oil in the valve-train gallery to $150\,^{\circ}$C for the duration of 72 h. The degree to which the oil thickens during the test is measured, with less thickening indicative of a more oxidation-stable and higher-performance lubricant. The test also rates the level of deposit formed on the piston from a scale of 0 to 10 merits, with a higher score meaning the piston has fewer deposits. Piston deposits may impair engine performance, thus, minimizing piston deposits is advantageous to prolonging engine life-

Table 3. Evaluation of lubricant properties of ethers.

Entry	Ether	KV100 [cSt][a]	KV40 [cSt][a]	VI[b]	Pour point [°C][c]	DSC oxidation onset T [°C][d]	TGA Noack [wt.%][e]	CCS [cP][f]
1	**3c**	3.1	10.0	150	−60	186	6.0	not measured
2	**3d**	3.1	11.1	143	−21	210	11.9	not measured
3	**3e**	3.3	12.2	142	−12	210	11.5	not measured
4	**3f**	3.6	14.2	147	−30	189	10.8	not measured
5	**3g**	2.7	9.6	123	−18	195	12.9	not measured
6	**3h**	3.3	11.9	146	−27	213	3.9	not measured
7	**3i**	3.5	12.0	145	−36	206	5.1	769
8	commercial PAO	4.0	17.8	126	−75	221	18.8	1276

[a] KV$_{100}$ and KV$_{40}$ are kinematic viscosities at 100 °C and 40 °C respectively (ASTM standard D7279-14). [b] Viscosity Index calculated from KV$_{100}$ and KV$_{40}$ (ASTM standard D2270). [c] Pour point (ASTM standard D7346-07). [d] Oxidation stability (ASTM standard E2009). [e] Volatility (ASTM standard D6375). [f] Cold crank simulator viscosity (ASTM D5293), −35 °C.

Table 5. Performance parameters for baseline lubricant and one containing compound **3 i**.

Parameter	Baseline	3 i Formulation	Limit[a]
absolute viscosity increase at 40 °C [mm^2 s^{-1}]	47.3	27	≤ 57.3
viscosity at 40 °C, 0 h [mm^2 s^{-1}]	53.8	45.1	none
viscosity at 40 °C, 72 h [mm^2 s^{-1}]	101.1	72.1	none
overall piston merit ($\times$/10) (5 elements, CRC rating)	8.2	9.2	≥ 7.6
ring sticking merit 1st ring (worst)	10	10	≥ 9

[a] Limits are as defined by the ACEA European Oil Sequences 2012 document.

time. Sticking of the first piston ring—the nearest to the combustion chamber—is also rated, with a score of 10 indicating no ring sticking.

Conclusions

We demonstrated that reductive etherification/reductive O-alkylation of alcohols can be used to produce a range of ethers that can serve as renewable lubricants. The synthons, electrophilic carbonyl compounds (aldehyde and ketones), and nucleophilic alcohols, can be readily obtained from biomass by various chemical or biochemical processes. The lubricant-range ethers produced in this study have viscosity and volatility characteristics superior to those of poly-α-olefin (PAO), making this new class of materials favorable for future fuel economy applications. Finally, we consider that the integrated approach described here provides a novel strategy for producing lubricants from biomass in a manner that has a potentially lower greenhouse gas (GHG) footprint than that for the production of lubricants from some petroleum sources.

Experimental Section

Materials

All chemicals were used as received without further purification. All chemicals (2-heptanone, 2-ethylhexanal, butanal, isobutanal, cyclopentanone, 8-pentadecanone, octanal; alcohols such as 1-butanol, 2-decyl-1-tetradecanol, 2-hexyl-1-decanol; 5 % Pd/C (matrix-activated carbon support); Amberlyst-15 (A-15), hydrogen form dry; and celite) were purchased from Sigma–Aldrich. 5 % Pt/C and 5 % Ru/C were purchased from Acros Organics. Silica support (surface area: 300 m^2 g^{-1}, average pore diameter: ≈ 6 nm) was purchased from Silicycle, 4-[2-(trimethoxysilyl)ethyl]benzene sulfonyl chloride was purchased from Sigma–Aldrich. ACS grade solvents such as acetone, ethyl acetate, and hexanes were purchased from Fisher Scientific.

Catalyst synthesis and characterization

Silica-supported 4-ethylbenzenesulfonic acid [SiO$_2$—(CH$_2$)$_2$—(C$_6$H$_4$)—SO$_3$H, EBSA/SiO$_2$] was synthesized according to our previously reported procedure.[24] Silica (Silicycle, surface area: 300 m^2 g^{-1}, average pore diameter: ≈ 6 nm) was calcined in flowing air (50 mL min^{-1}.) at 773 K for 5 h and then stored in vacuum prior to use. Sulfonic acid was grafted onto the silica support as follows: calcined silica (1 g) was stirred in ethanol (100 mL) at 343 K in a 250 mL round bottom flask. To the stirred reaction mixture, the silylating agent, 4-[2-(trimethoxysilyl)ethyl]benzene sulfonyl chloride (≈ 1 mmol), in ethanol (5 mL) was added dropwise using a syringe. The reaction mixture was stirred for 12 h under inert conditions at 343 K. The hot solution was then cooled to room temperature, filtered, washed with copious amounts of water, and then dried in a vacuum oven at 373 K overnight to produce the final EBSA/SiO$_2$ catalyst. The catalyst had a surface area of 217 m^2 g^{-1} and a total acidity of 0.95 mmol g^{-1} of H$^+$ (determined by acid-base titration).

The surface area of 5 % Pd/C, determined by the Brunauer–Emmett–Teller (BET) method, was 250 m^2 g^{-1}. To determine the acid/base characteristics of the supporting carbon, 5 % Pd/C (1 g) was stirred in deionized water (10 mL) at room temperature for 1 h, the pH of the resulting suspension was 10.04, indicating that the support was basic. The particle size of Pd determined by high-angle annular dark field scanning tunneling electron microscopy (HAADF-STEM) was ≈ 5 nm (see the Supporting Information for HAADF image of Pd/C).

General procedure for reductive etherification

Reductive etherification reactions were performed in an HEL Chem-Scan II high pressure parallel synthesizer equipped with 8$\times$ 16 mL capacity, independently controlled, Hastelloy reactors. In a typical experiment, carbonyl compound **1** (2 or 8 mmol), alcohol **2** (2 or 8 mmol), 5 % Pd/C (2.5 mol %), and acid catalyst (2.5–10 mol %) were added to the HEL reactor. A polytetrafluoroethylene (PTFE)-coated stir bar was attached and the reactor was sealed. The reactor was flushed with 200 psi N$_2$ (two times) and 150 psi H$_2$ (three times) prior to heating to the reaction temperature. The reaction mixture was stirred at 500 rpm under a constant H$_2$ pressure of 150 psi and maintained at 120 °C temperature for 5 h. After the reaction, the reactor was cooled to room temperature, depressurized, and opened. The reaction mixture was filtered through a small pad of celite and washed with (3$\times$10 mL) acetone to remove the solid catalyst particles. Acetone was rotary-evaporated and excess carbonyl compound or alcohol and volatile side products were removed by vacuum distillation. The obtained product was further purified by flash column chromatography.

Conflict of interest

The authors declare no conflict of interest.

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