Renewable lubricants with tailored molecular architecture

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We present a strategy to synthesize three types of renewable lubricant base oils with up to 90% yield using 2-alkylfurans, derived from nonfood biomass, and aldehydes, produced from natural oils or biomass through three chemistries: hydroxyalkylation/alkylation (HAA), HAA followed by hydrogenation, and HAA followed by hydrodeoxygenation. These molecules consist of (i) furan rings, (ii) saturated furan rings, and (iii) deoxygenated branched alkanes. The structures of these molecules can be tailored in terms of carbon number, branching length, distance between branches, and functional groups. The site-specific, energy-efficient C–C coupling chemistry in oxygenated biomass compounds, unmatched in current refineries, provides tailored structure and tunable properties. Molecular simulation demonstrates the ability to predict properties in agreement with experiments, proving the potential for molecular design.

INTRODUCTION

Lubricants are widely used in industrial machinery, automobiles, aviation machinery, refrigeration compressors, agricultural equipment, marine vessels, and many other applications and represent an over $60 billion global chemical enterprise (1, 2). Base oils are key components [75 to 90 weight % (wt %)] of commercially formulated lubricants and account for up to 75% of lubricant cost (3). The majority of the current base oils are mineral oils (petroleum based), comprising a mixture of C20–C50 hydrocarbons and formulated with different additives [antioxidant, viscosity index (VI) improver, pour point (PP) depressant, corrosion inhibitors, antiwear reagents, and others] to achieve certain property specifications (1). These lubricants thicken quickly because they contain high-volatility, low–molecular weight hydrocarbons. As a result, frequent replacement is needed, which generates waste.

Better specifications can be achieved with synthetic base oils, such as poly-α-olefins (PAOs; Fig. 1A), alkylbenzenes, polyalkylenes, and synthetic esters (1). However, selectively tuning their molecular size and architecture is challenging (3). For example, cationic oligomerization of linear α-olefins (C4–C12 olefins), using homogeneous acid catalysts (BF3, H2F, or AlCl3), results in uncontrolled oligomerization and formation of several products, which necessitate expensive separations following hydrogenation (3). In addition, homogeneous acid catalysts are corrosive. Reducing reliance on petroleum and mitigating the environmental footprint demand the production of high-performance lubricants from sustainable feedstocks (4–6). Biolubricants are produced using various chemical modifications of natural oils, i.e., animal fats and vegetable oils (7–10). High catalyst consumption, poor economics, and lack of effective heterogeneous catalysts (e.g., for hydroformylation) are common drawbacks in these transformations. Their structures result in high-temperature fluidity, low oxidative stability, and hydrolysis that limit their applicability. Similarly, recent strategies for the production of biolubricants, such as aldel condensation of alkyl methyl ketones or furanic molecules combined with hydrogenation or hydrodeoxygenation (HDO) (11–13) and ether- and ester-based lubricants, using biomass-derived alcohol or levulinic acid (14–16), are challenged by the use of high amounts of catalyst, harsh reaction conditions, lack of control of architecture, and the need for separation of the homogeneous catalysts from the product for some reactions. Innovative approaches to synthesize biolubricant base oils with better and tunable properties can be transformative.

Here, we report a strategy to produce three broad classes of biolubricant base oils containing (i) furan rings with aromatic properties, (ii) fully saturated furan rings, and (iii) branched alkanes. These three products, hereafter referred to as furan-containing lubricant (FL), saturated FL (SFL), and bio-poly-α-olefin lubricant (BPAOL) base oils (Fig. 1B), are obtained via the hydroxyalkylation/alkylation (HAA) of 2-alkylfurans with aldehydes, HAA followed by hydrogenation, and HAA followed by HDO reactions, respectively. The C–C coupling of furans is a recently exploited reaction strategy to increase the carbon chain and produce diesel and jet fuels (17–21), but its adaptation to produce biolubricant base oils is still in its infancy. The synthesis of 2-alkylfurans of different carbon numbers via direct HDO of C5 sugars of biomass (22), i.e., 2-methylfuran (2MF), or furan acylation with carboxylic acids (or their anhydrides) followed by HDO of the acylated products (scheme S1) (23) has been reported. Similarly, aldehydes of different carbon lengths can be synthesized via dehydrogenation of biomass-derived alcohols (24) or selective hydrogenation of fatty acids from natural oils or waste cooking oils (WCO) (25). The use of aldehydes and aldehydes of varying carbon lengths and branching enables the synthesis of lubricant base oils of different molecular sizes, structures, branching sizes, and distances between branches. This enables unprecedented flexibility in tuning lubricant specifications for a wide range of applications that are currently achieved by complex formulation of mineral and synthetic base oils with chemical additives. Their well-defined structure also enables the application of molecular simulation to predict the base oil properties, such as viscosity and VI, and to direct the design and synthesis of new lubricant base oils with desirable properties.

RESULTS

First, we synthesized C30–FL1, a furan-containing base oil whose rings have aromatic properties. Furan–based oils have no analogs in the crude oil–based economy. C30–FL1 contains the same number of carbon
base oils. Last, HDO of FL1 produces C30-BPAOL1 that is compositionally identical to C30 alkane in commercial PAOs. For the HAA reaction, the screening of homogeneous catalysts (sulfuric acid, methanesulfonic acid, and acetic acid) was conducted using 2-pentylfuran and lauraldehyde as substrates (Fig. 1B). The former substrate can be produced from acylation of furan with valeric acid or valeric anhydride followed by HDO (Fig. 1B). The latter can be synthesized from lauric acid of coconut oil by selective hydrogenation of FL1 under neat conditions at a 2:1 molar ratio of 2-pentylfuran and lauric acid (Fig. 1B). The reaction follows a tandem pathway (scheme S2) and alkyla-
tion is faster than hydroxyalkylation, as reported in the literature (18, 19). The apparent activation energy ($E_a$) of the overall reaction is 16 kJ mol$^{-1}$ (fig. S4). Controlled experiments show no leaching of acid sites in the solution and almost constant catalytic performance of Aquivion PW98 over four consecutive cycles (fig. S6). About 30% activity loss occurs in the fifth cycle with concurrent mass gain and brown coloration of the recovered Aquivion PW98, indicating blocking of the acid sites of the catalyst by the viscous condensation product. Aquivion PW98 is not thermally stable at >160°C, which makes regeneration by traditional calcination impossible.

Next, microporous acid zeolites (HZSM-5 and HY) were evaluated. HY gives a moderate yield (58%) of C30-FL1, whereas HZSM-5 is ineffective (<1% C30-FL1) (Fig. 1C). Since diffusion limitations are expected for large molecules in microporous zeolites, we chose a mesoporous aluminosilicate with a pore diameter of ~5.4 nm. The

A 90% yield with >98% selectivity to C30-FL1 is achieved in 6 hours, at 65°C and neat condition, using 0.05 g of Aquivion PW98 due to its strong acid strength and high surface area (table S1) (18, 19). Reaction conditions, such as reaction time, catalyst amount, and reaction temperature, have been optimized (figs. S2 to S4). The dominant product is C30-FL1 along with a small amount of C21H38O2, an intermediate formed in the first step (hydroxyalkylation), suggesting that the reaction follows a tandem pathway (scheme S2) and alkylation is faster than hydroxyalkylation, as reported in the literature (21). A slightly higher yield (92%) is achieved after 8 hours (fig. S2). The apparent activation energy ($E_a$) of the overall reaction is 16 kJ mol$^{-1}$ (fig. S4). Controlled experiments show no leaching of acid sites in the solution and almost constant catalytic performance of Aquivion PW98 up to four consecutive cycles (fig. S6). About 30% activity loss occurs in the fifth cycle with concurrent mass gain and brown coloration of the recovered Aquivion PW98, indicating blocking of the acid sites of the catalyst by the viscous condensation product. Aquivion PW98 is not thermally stable at >160°C, which makes regeneration by traditional calcination impossible.

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aluminosilicate catalyst exhibits comparable performance as HY, likely due to the larger pore diameter being counterbalanced by a lower acid strength in a noncrystalline environment. In recent work, P-containing zeolites with unique acid properties were reported. A P-containing mesoporous siliceous (P-SiO2) catalyst, prepared by simple impregnation, exhibits superior performance to mesoporous aluminosilicate and yields C30-FL1 comparable to Aquivion PW98 in a much shorter reaction time (1.5 hours versus 6 hours) (figs. S1 and S7). Homogeneous phosphoric acid shows no activity, even with double the amount of P concentration.

No reaction occurs using the filtrate of the catalyst, indicating that P-SiO2 functions as a heterogeneous catalyst (fig. S7). Product condensation (fig. S9) with concurrent dark brown coloration caused a loss of catalytic activity in the second cycle (fig. S8). The regenerated P-SiO2, upon calcination at 500°C in air for 3 hours, regains comparable performance to the fresh catalyst (fig. S8).

Next, we refine the C30-FL1 either by hydrogenation or by HDO to produce C30-SFL1 and C30-BPAOL1 base oils, respectively (Fig. 1, D and E). A commercial Pd/C catalyst was used for the former under mild reaction conditions, as Pd is active for furan ring hydrogenation. Reaction time and hydrogen pressure experiments (fig. S10) suggest that a high hydrogen pressure facilitates ring saturation with an optimum yield of C30-SFL1 of ~90%.

C30-FL1 HDO over an Ir-ReOx/SiO2 catalyst, which demonstrated excellent catalytic performance for furan ring opening and deoxygenation via synergy of Ir hydrogenation sites and acidic sites of partially reduced ReOx, yields 86% C30-BPAOL1 (Fig. 1E). Small fractions of C21- and C30-alkanes form via C-C cracking. The regeneration of the catalyst by calcination before each cycle demonstrates comparable performance in five consecutive runs (figs. S12 and S13). Notably, C30-FL1, SFL1, and BPAOL1 base oils form with high selectivity, minimizing expensive and complex separations associated with commercial mineral and synthetic base oils.

The proposed synthetic platform is general. We demonstrate this using 2-alkylfurans and aldehydes of different carbon lengths and substituents, using Aquivion PW98 and P-SiO2 as the HAA catalysts, followed by HDO of the products over the Ir-ReOx/SiO2 catalyst (Table 1 and Table S2). Both the Aquivion PW98 and P-SiO2 catalysts exhibit similar performance with yields of FLs of 80 to 94% depending on the molecular sizes. Similarly, HDO of FLs yields 81 to 91% BPAOLs depending on the molecular sizes of FLs and the lengths of alkyl groups of 2-alkylfurans and aldehydes. The formation rates of C26–C30 FLs at low conversion (<25%) linearly decrease with increasing alkyl chain length of 2-alkylfurans or aldehydes, but the effect of size on the rate is not dramatic (figs. S14 and S15). Our C20- and C30-BPAOLs have structural similarity with current commercial PAO2 and PAO4 lubricant base oils to enable direct comparison of properties.

Base oils with multiple branches have lower PPs for low-temperature applications, e.g., refrigeration and aircrafts. HAA reaction of 2-alkylfurans with branched aldehydes, e.g., 2-ethylhexanal, which can be obtained by dehydrogenation of Guerbet alcohols, forms C26–C30 FLs (Table 1, entries 12 to 14). High yields of C26–C30 FLs were achieved over both Aquivion PW98 and P-SiO2 catalysts (Table 1, entries 12 to 14, and Table S2, entries 12 to 14). The formation rate of C26-FL3 with two branches is three times lower than that of C26-FL2 with one branch (fig. S16), likely due to a steric hindrance during the condensation arising from the additional branching of 2-ethylhexanal. HDO over Ir-ReOx/SiO2 produces C26–C30 BPAOLs in high yield (Table 1, entries 12 to 14).

Table 1. Synthesis of FL and BPAOL base oils using 2-alkylfurans and aldehydes of varying molecular sizes. Reaction conditions: HAA reactions of 2-alkylfurans with aldehyde to FL were conducted using 0.05 g of Aquivion PW98, 10 mmol 2-alkylfuran, and 5 mmol aldehyde at 65°C for 6 hours. HDO of FL to the corresponding BPAOL over the Ir-ReOx/SiO2 catalyst was performed using 0.3 g of FL in 10 ml of cyclohexane solvent and 0.15 g of catalyst at 5 MPa H2 and 170°C for 12 hours.

| Entry | R1     | R2     | Products Yield (%) | Products Yield (%) |
|-------|--------|--------|--------------------|--------------------|
| 1     | Methyl | n-Undecyl | C26-FL1 80 | C26-BPAOL1 91 |
| 2     | Ethyl  | n-Undecyl | C24-FL1 82 | C24-BPAOL1 85 |
| 3     | n-Propyl | n-Undecyl | C22-FL1 94 | C22-BPAOL1 87 |
| 4     | n-Butyl | n-Undecyl | C20-FL1 89 | C20-BPAOL1 84 |
| 5     | n-Pentyl | n-Undecyl | C18-FL1 90 | C18-BPAOL1 87 |
| 6     | n-Hexyl | n-Undecyl | C16-FL1 88 | C16-BPAOL1 82 |
| 7*    | n-Heptyl | n-Undecyl | C14-FL1 85 | C14-BPAOL1 83 |
| 8     | n-Pentyl | Methyl   | C12-FL1 89 | C12-BPAOL1 87 |
| 9     | n-Pentyl | n-Pentyl | C10-FL2 93 | C10-BPAOL2 89 |
| 10    | n-Pentyl | n-Heptyl | C12-FL2 91 | C12-BPAOL2 91 |
| 11    | n-Pentyl | n-Nonyl  | C10-FL2 87 | C10-BPAOL2 87 |
| 12*   | n-Pentyl | 2-Ethylpentyl | C8-FL3 85 | C8-BPAOL3 87 |
| 13*   | n-Hexyl | 2-Ethylpentyl | C6-FL3 86 | C6-BPAOL3 82 |
| 14*   | n-Heptyl | 2-Ethylpentyl | C4-FL2 88 | C4-BPAOL2 81 |

*Eight hours. †Twelve hours.

Important properties {VI, PP, volatility [thermogravimetric analysis (TGA) Noack] and oxidation stability} of C30-FL1, C30-SFL1, and C30-BPAOL1 base oils are compared with those of commercial mineral group II and synthetic PAO4 group IV base oils, categorized by the American Petroleum Institute in Table 2. Our C30 base oils have better volatility than commercial base oils, while the VIs of C30-FL1 and C30-SFL1 are comparable or slightly lower than those of the commercial products because of the presence of furan and tetrahydrofuran rings in the structures. C30-SFL1 has higher KVs and VI than C30-FL1, indicating that molecular structure and oxygen content strongly affect these properties. The oxidation stability of C30-SFL1 and C30-FL1 is lower than that of commercial PAO4, but their PPs are comparable to those of commercial PAO4, making them suitable for low-temperature applications. The hydrophilic ring improves the polarity of base oils, which is beneficial for their solubility with polar additives, which is currently a challenge (1). The PP of C30-BPAOL1 is better than that of mineral group II base oil, with C30-BPAOL1 having superior VI than commercial group II and synthetic PAO4 base oils (high VI ensures low viscosity changes with temperature). The PP of BPAOL3 is expected to be even lower because of the two branches in its molecular structure. The biodegradability of our lubricants is yet to be determined, but our synthesized biolubricants could lead to low fossil carbon use and reduced CO2 emissions.
The proposed synthetic platform provides unprecedented control over the molecular size of nearly monodispersed C$_{22}$-C$_{34}$ lubricant base oils with site-specific branching (Table 1). This control arises from the selective acylation at the alpha carbon of the furan in producing alkyl-furans and the site-specific C$\rightarrow$C coupling of the HAA chemistry on the opposite alpha carbon of the 2-alkylfuran. This site specificity is lacking from olefins, whose oligomerization and C$\rightarrow$C bond migration lead to a broad distribution of products. As a result, the oxygen of biomass opens up opportunities for site-specific C$\rightarrow$C coupling strategies, unmatched in hydrocarbon chemistry in refineries. As a result, product specifications can be unique and allow targeting various applications easily. Our strategy enables the synthesis of molecules with very narrow size distribution as compared with commercial products (fig. S17). This narrow molecular weight distribution provides another opportunity for molecular design of these products. Molecular simulation is an ideal tool to estimate properties of tailored molecules with very narrow size distribution as compared with commercial products (40). The calculated viscosity relative to BPAOL1 without significantly affecting the predicted VI compared with the single-branched isomers with heptyl or longer side chains. The additional branching is also likely to reduce the PP, although there is no method yet for predicting PP using molecular simulation. Expanding these simulations to a library of potential molecules could direct synthesis efforts.

Technoeconomic analysis predicts the selling price of C$_{30}$-BPAOL1 to be $5191/metric ton using commercial furfural as a feedstock and $4535/metric ton using furfural obtained from a biorefinery in which cellulose from deconstructed lignocellulosic biomass is converted to xylene and lignin (constituting ~20 wt % of dry weight of biomass). Lignin is considered as a waste stream with no value (detailed analysis, process block flow diagram, and assumptions are given in the Supplementary Materials). The price of our product, which is expected to be even lower upon consideration of a reasonable price for lignin value, is very competitive with the price of current commercial synthetic PAO4 (~$4475/metric ton) provided by a business insider from the J.A.M. Distributing Company. A higher price premium of our products is expected for synthesizing designer molecules, guided by MD simulation, with desired specifications for targeted applications that will likely minimize the use of expensive chemical additives required for formulation, and branding the products as environmentally acceptable lubricants (EALs) upon biodegradability testing. Some premium EALs, e.g., gear, stern tube, and hydraulic oils manufactured by GulfSea,
are currently sold at $15 to $17/liter, i.e., at a price significantly higher than that of our products.

**DISCUSSION**

We demonstrated a strategy to synthesize new and existing lubricant base oils with structural diversity and excellent control over molecular weight, size distribution, and branching using energy-efficient C–C coupling without complex separations needed for current petroleum-based base oils. Nonfood biomass and natural or WCO can be harnessed to obtain synthons (alkylfurans and aldehydes) of varying carbon lengths and branching for various targeted applications. Efficient and easily separable heterogeneous catalysts enable high product selectivity and yield (up to 95%). In addition, low-temperature processing compared with the current refinery processing (cracking, isomerization, and distillation for synthetic and mineral base oils) and use of sustainable, abundant feedstock provide a sustainable route to biolubricants. Structural control enables tuning of product properties, and use of one-step chemistry (HAA) or two-step chemistry (HAA followed by HDO) leads to diverse classes of products with aromatic rings (F L), oxygen-containing cyclic (HAA) or two-step chemistry (HAA followed by HDO) leads to diverse classes of products with aromatic rings (F L), oxygen-containing cyclic (HAA) or two-step chemistry (HAA followed by HDO) leads to diverse classes of products with aromatic rings. Efficient and easily separable heterogeneous catalysts enable high product selectivity and yield (up to 95%). In addition, low-temperature processing compared with the current refinery processing (cracking, isomerization, and distillation for synthetic and mineral base oils) and use of sustainable, abundant feedstock provide a sustainable route to biolubricants. Structural control enables tuning of product properties, and use of one-step chemistry (HAA) or two-step chemistry (HAA followed by HDO) leads to diverse classes of products with aromatic rings (HAA) or two-step chemistry (HAA followed by HDO) leads to diverse classes of products with aromatic rings.

**Catalyst preparation**

The P-SiO2 catalyst (H3PO4, 10 wt % loading) was prepared by impregnation. First, SiO2 (Sigma-Aldrich) was impregnated with aqueous H3PO4 solution. After evaporating the solvent at 75°C on a hotplate and subsequently drying at 110°C for 12 hours in an oven, the catalyst was calcined in a crucible in air at 500°C for 3 hours with a 2°C/min temperature ramp. The Ir-ReOx/SiO2 (Ir, 4 wt % loading; Re/Ir = 2 M) catalyst was prepared using sequential impregnation. First, Ir/SiO2 was prepared by impregnating Ir on SiO2 (Fuji Silysia G-4) using an aqueous solution of H2IrCl6. After evaporating the solvent at 75°C on a hotplate and drying at 110°C for 12 hours in an oven, the resulting Ir/SiO2 was impregnated with ReO3 using an aqueous solution of NH4ReO4. The catalysts were calcined in a crucible in air at 500°C for 3 hours with a 10°C/min temperature ramp. The reported metal loadings in the catalysts were based on the theoretical amount of metals used in impregnation.

**Reaction procedures**

**HAA reaction**

In a typical reaction, 10 mmol 2-alkylfuran and 5 mmol aldehyde without any solvent were mixed in a 20-ml glass vial. The vial was placed in a preheated oil bath and stirred at 500 rpm using a magnetic bar on a stirring cum hotplate. Last, the catalyst was added into the vial, and the reaction continued at the desired temperature (65°C unless otherwise mentioned) for 6 hours. After the reaction, the solution was diluted using 10 ml of cycohexane solvent. A small amount of eicosane was added as an internal standard.

**HAA rate measurements**

Because different 2-alkylfurans and aldehydes have different densities and their mixing without a solvent changes the volume for different reactions, we used cycohexane as the solvent for the measurement of reaction rates. Typically, 10 mmol 2-alkylfuran and 5 mmol aldehyde were dissolved in cycohexane, and their concentrations were kept at 1 and 0.5 mol/liter, respectively. The reactions were performed in the same way as HAA reactions described above. After the reaction, the solution was diluted with 10 ml of cycohexane containing a small amount of eicosane as an internal standard.

**Hydrogenation reaction**

Hydrogenation of HAA condensation products, hereto referred to as unsaturated FLs, was carried out in a 50-ml Parr reactor with an inserted Teflon liner and a magnetic stirrer. First, Pd/C catalyst was pretreated at 200°C with a temperature ramp of 10°C/min for 1 hour with H2 (50 ml/min). Then, Pd/C catalyst (0.03 g), FL (0.5 g), and 10 ml of cycohexane were added to the reactor, and the mixture was heated at 60°C. Upon completing the reaction, the reactor was immediately transferred to an ice-water bath. Upon cooling down the solution to room temperature, the reactor was opened, the solution was diluted using 10 ml of cycohexane containing a small amount of eicosane as an internal standard, and the catalyst was separated from the solution by filtration.

**HDO reaction**

HDO of FLs over Ir-ReOx/SiO2 was performed in a 50-ml Parr reactor with an inserted Teflon liner and a magnetic stirrer. First, the catalyst (0.15 g) and solvent (10 ml of cycohexane) were added to the reactor for catalyst prereduction, and the reactor was sealed with the reactor head.
equipped with a thermocouple, a rupture disk, a pressure gauge, and a gas release valve. The mixture was heated at 200°C and 5 MPa H₂ for 1 hour at 240 rpm. Upon prerelaxation, the reactor was cooled to room temperature and H₂ was released. Then, we added FLs (0.3 g), closed the reactor head immediately, purged the reactor with 1 MPa H₂ for three times, pressurized to 5 MPa H₂, and heated the reactor mixture to the desired temperature with continuous stirring at 500 rpm. The heating time to reach the set temperature was about 25 min. Upon reaction, the reactor was immediately transferred to a water bath. The reaction solution was diluted using 15 ml of cyclohexane with a small amount of eicosane as an internal standard, and the catalyst was separated from the solution by centrifugation or filtration.

### Analysis of products

The products were analyzed using a gas chromatograph (GC, Agilent 7890A) equipped with an HP-1 column and a flame ionization detector using eicosane (C₂₀) as an internal standard. The products were identified by a GC (Agilent 7890B) mass spectrometer (MS) (Agilent 5977A with a triple-axis detector) equipped with a DB-5 column, high-resolution MS with liquid injection field desorption ionization, ¹H nuclear magnetic resonance (NMR), and ¹³C NMR (Bruker AV400, CDCl₃ solvent).

The conversion and the yield of all products from the HAA, hydrogenation, and HDO reactions were calculated on a carbon basis using the following equations.

\[
\text{Conversion[\%]} = \frac{\text{mol of initial reactant} - \text{mol of unreacted reactant}}{\text{mol of initial reactant}} \times 100
\]

\[
\text{Yield of detected products[\%·C]} = \frac{\text{mol of product} \times \text{C atoms in product}}{\text{mol of total C atoms of initial reactants}} \times 100
\]

### Lubricant properties

The lubricant properties of select Cₙ₀ compounds (C₃₀-FL₁, C₃₀-SFL₁, and C₃₀-BPAOL₁) were evaluated according to American Society for Testing and Materials (ASTM) methods. The kinematic viscosities at 100° and 40°C (KV100 and KV40) were determined using the ASTM D445 method. The VI was calculated using the KV100 and KV40 following the ASTM D2270 method. The PP tests were carried out according to ASTM D97. The kinematic viscosities and PP measurements were performed at Southwest Research Institute in San Antonio, Texas, USA. The differential scanning calorimetry (DSC) oxidation onset temperature and Noack volatility were measured according to ASTM E2009 (method B, 500 pis O₂) and ASTM D6375, respectively, at Petro-lubricant Testing Laboratories Inc. in Lafayette, NJ, USA.

### Technoeconomic analysis

Using the available data, a simulation of the production processes was performed using Aspen Plus version 8.8.2. The technoeconomic analysis was performed using a Monte Carlo (MC) simulation in the NpT ensemble for 2 × 10⁵ MC cycles (one MC cycle consisting of N randomly selected MC steps). MC simulations were run using the MC for Complex Chemical Systems—Minnesota software program (46) with the k-d tree data structure (47). Center-of-mass translation, center-of-mass rotation, conformational (44), and volume moves were used to equilibrate the system at desired T and p = 1 atm. Four independent MC simulations were performed starting from different initial structures. A time step of 2 fs was used, and the pressure tensor was output every two time steps. A Nose-Hoover thermostat (48, 49), with a coupling time constant of 5 ps, was used to control temperature. Each simulation lasted for at least 1500 ns. The initial part (first 100 ns) of each trajectory was discarded, and the remainder was used for analysis. The method developed by Zhang et al. (50) was used to obtain the viscosity for each independent run using the Green-Kubo integral (51) with a block size of 10 ns. Uncertainties were calculated as SEM from eight independent simulations and were reported as 95% confidence intervals. Viscosities obtained at 313 and 373 K were used to calculate the VI using ASTM D2270. Simulation snapshots were visualized using visual molecular dynamics (52) and Tachyon (53).

### Supplementary materials

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/5/2/eaav5487/DC1

**Scheme S1. Strategies for the synthesis of 2-alkylfurans.

**Scheme S2. Reaction pathway for HAA of 2-alkylfuran with an aldehyde over acid catalyst.

**Table S1. Properties of commercial solid acid catalysts.

**Table S2. HAA reaction of different 2-alkylfurans with aldehydes over P-SiO₂.

**Table S3. Simulated kinematic viscosities and viscosity index at 40° and 100°C of C₃₀-BPAOL lubricant base oils.

**Table S4. Reaction specifications.

**Table S5. Summary of capital and operating cost for combined production of p-xylene and lubricants.

**Table S6. Summary of capital and operating cost.

**Fig. S1. Catalysts screening for the synthesis of C₃₀-FL₁.

**Fig. S2. Effect of catalyst (Aquivion PW98) amount on the yield of C₃₀-FL₁ at low and high conversions of reactants.

**Fig. S3. Effect of reaction temperature on the production of C₃₀-FL₁.

**Fig. S4. Arrhenius plot for HAA of 2-pentylfuran with laurialdehyde over Aquivion PW98.

**Fig. S5. Time course of the HAA reaction over Aquivion PW98 catalyst.

**Fig. S6. Recyclability of Aquivion PW98.

**Fig. S7. Time course of the HAA reaction for C₃₀-FL₁ synthesis over the P-SiO₂ catalyst.

**Fig. S8. Recyclability of P-SiO₂ for the synthesis of C₃₀-FL₁.

**Fig. S9. Effect of reaction temperature on the production of C₃₀-FL₁.

**Fig. S10. Effect of catalyst (Aquivion PW98) amount on the yield of C₃₀-FL₁ at low and high conversions of reactants.

**Fig. S11. Effect of reaction temperature on the production of C₃₀-FL₁.

**Fig. S12. Arrhenius plot for HAA of 2-pentylfuran with laurialdehyde over Aquivion PW98.

**Fig. S13. Time course of the HAA reaction over Aquivion PW98 catalyst.

**Fig. S14. Recyclability of Aquivion PW98.

**Fig. S15. Time course of the HAA reaction for C₃₀-FL₁ synthesis over the P-SiO₂ catalyst.

**Fig. S16. Recyclability of P-SiO₂ for the synthesis of C₃₀-FL₁.
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**Acknowledgments:** We acknowledge the Advanced Materials Characterization Laboratory at the University of Delaware for providing the TGA facility and W. Zheng for the help with the HR-TEM.

**Funding:** This work was supported as part of the Catalysis Center for Energy Innovation, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under award number DE-SC0001004. **Author contributions:** S.L., B.S., and D.G.V. conceived the project and designed the experiments. S.L. executed all the experiments. A.N. reproduced some experiments. T.R.J., Q.P.C., and J.I.S. designed and performed the molecular simulations. A.A. and M.I. performed the techno-economic analysis. S.L., T.R.J., A.A., B.S., and D.G.V. wrote the article. All the authors proofread the manuscript. **Competing interests:** S.L., B.S., and D.G.V. have submitted a Patent Cooperation Treaty patent application as inventors. All the other authors declare that they have no competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 26 September 2018
Accepted 17 December 2018
Published 1 February 2019
10.1126/sciadv.aav5487

**Citation:** S. Liu, T. R. Josephson, A. Athaley, Q. P. Chen, A. Norton, M. Ierapetritou, J. I. Siepmann, B. Saha, D. G. Vlachos, Renewable lubricants with tailored molecular architecture. Sci. Adv. **5**, eaav5487 (2019).