Catalytic Production of Renewable Lubricant Base-Oils from Bio-Based 2-Alkylfurans and Enals

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Catalytic Production of Renewable Lubricant Base-Oils from Bio-Based 2-Alkylfurans and Enals

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Abstract

Lubricants are an essential part of modern society with an over \$146 billion market but have significant environmental footprint. Bio-based lubricant base-oils can offer performance advantages over existing oils and mitigate environmental challenges. We describe, for the first time, the synthesis of new bio-based base-oils with tunable molecular branches and properties at high yields (>80%) from biomass derived 2-alkylfurans with enals via conjugate addition-hydroxylalkylation/alkylation (CA-HAA) and hydrodeoxygenation reactions. Among several liquid and solid sulfonic acid catalysts tested for the CA-HAA condensation, Aquivion PW79S, a perfluorinated sulfonic acid resin, exhibits the best performance. Subsequent hydrodeoxygenation of the condensation products with an Ir-ReO$_x$/SiO$_2$ catalyst achieves up to 88% yield of lubricant ranged branched alkanes with high selectivity and superior properties than commercial mineral group III and synthetic poly-α-olefins (PAOs) base-oils. Importantly, the molecular size and number of branches of the products can be tuned by varying the molecular sizes of substrates in the CA-HAA step. The as-synthesized base-oils possess tunable properties and are promising for a wide range of applications.

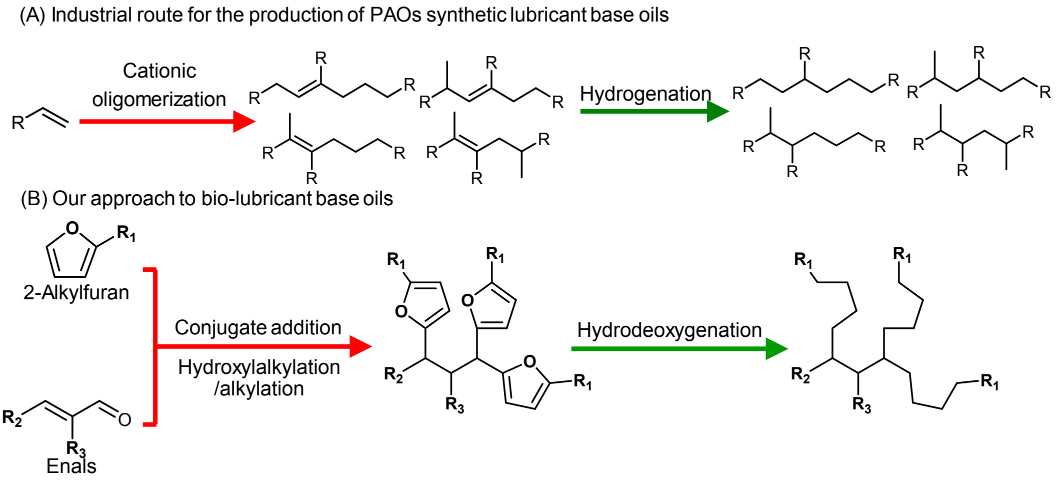
1. **Introduction**

Lubricants are used in numerous applications, including industrial machinery, automobiles, aviation engines and equipment, agriculture and food processing equipment, refrigeration compressors, and turbines among others. They comprise a global market worth of more than \$146 billion/year.[1] Their main components are base oils derived from petroleum mineral oils or synthetic oils, e.g., poly-α-olefins (PAOs). The synthesis of the latter (Scheme 1) uses corrosive, homogeneous, and hard to separate catalysts, e.g., BF_3, HF, or $AlCl_3$; furthermore, the linear-α-olefin oligomerization is unselective preventing good control over molecular weight distribution and branching[2, 3]. In order to tailor lubricant properties, a significant fraction of additives is employed, increasing cost and environmental footprint. There is increasing need for development of improved energy-efficiency, high performance, durable, and environmentally-acceptable base oils that operate under extreme environmental conditions[2]. Their production from non-food biomass is an attractive alternative to reduce reliance on petroleum and mitigate the environmental footprint[4-8].

Bio-ester base oils, produced by chemical modification of fatty acids, have recently been commercialized for this purpose. They have, unlike hydrocarbon-base oils, limited applicability because they lack desired molecular structures and properties and have compatibility issues[2, 9-13]. For example, unlike partly interchangeable hydrocarbon base oils, bio-esters, used in engine oil formulation as an additive, are not interchangeable with other synthetic esters without performing new engine tests[2]. In addition, ester base-oils are hydrolyzed more easily producing corrosive acids. Furthermore, some current commercial additives used in lubricant formulation are not miscible with bio-esters[2].

A few efforts have been devoted to the synthesis of bio-based hydrocarbons for lubricant base-oils. Bell and co-workers reported self-condensation of biomass derived alkyl or furyl ketones and hydrogenation/hydrodeoxygenation (HDO) of the condensation products to produce cycloalkane base oils.[14-16] The synthesized base-oils have some property-compatibility issues, e.g., in viscosity and viscosity index (VI), when compared with commercial synthetic PAOs.[15] Wang et al.[17] described synthesis of bio-based base-oils employing four steps - aldol condensation of furfural with acetone, hydrogenation of condensation products, secondary aldol condensation of hydrogenated ketone compounds with furfural and finally HDO. The yield of the synthesized C_{23} branched alkane was only 50% and the properties were not evaluated. The separation of homogeneous catalysts used in aldol condensation is another challenge. We have recently reported the synthesis of bio-based branched hydrocarbons via an atom- and energy-efficient hydroxylalkylation/alkylation (HAA) scheme followed by HDO using biomass-derived 2-alkylfurans and aldehydes.[18] The ASTM specification data for our bio-based C_{30} branched alkane suggest better viscosity index (VI) and volatility than those of commercially, petroleum-derived synthetic C_{30} PAOs base-oils. However, the pour point (PP) of our base-oil was higher due to the presence of only one branch on the carbon chain compared to more carbon-branched PAOs.[18]

As more branches on the carbon chain is key for a lower PP,[2] we disclose an efficient catalytic route to synthesize renewable, branched lubricant base-oils in excellent yields. The reaction consists of tandem conjugate addition (CA) and HAA of biomass-derived 2-alkylfurans with enals to form trifuran compounds over acid catalysts, followed by HDO catalyzed by metal/metal oxide catalysts (Scheme 1). This novel concept enables the synthesis of a range of structurally diverse base-oils using different molecular size alkylfurans and enals. Methylfuran can be derived from direct HDO of furfural,[19-22] a dehydration product of hemicellulosic xylose. Long chain 2-alkylfurans can be produced via acylation of furan with carboxylic acids or their anhydrides and subsequent HDO of the acylated intermediate[23-25] (Scheme S1). The enals can be obtained by aldol condensation of biomass derived aldehydes[26-29] or dehydration of glycerol derived from natural oils or waste cooking oil[30-32] (Scheme S2). The properties of synthesized base-oils, such as viscosities at 40 and 100 °C (KV40, KV100), VI, PP, oxidation stability and volatility, were determined and compared with commercial petroleum-derived base-oils.



Scheme 1. Approaches to the synthesis of synthetic lubricant base-oils.

2. Methods

2.1 Chemicals and Materials

Aquivion® PW79S (coarse powder, Brunauer-Emmett-Teller (BET) surface area <1 m^2/g, and 1.26 mmol H^+/g), Aquivion® PW98 (coarse powder, BET surface area <1 m^2/g, and 1.0 mmol H^+/g), Amberlyst®-15 (dry hydrogen form, BET surface area 42 m^2/g, and 4.8 mmol H^+/g), methanesulfonic acid (≥99.0%), *p*-toluenesulfonic acid monohydrate (≥98.5%), and triflic acid (≥99.0%) were purchased from Sigma-Aldrich. Amberlyst® 36 dry resin (BET surface area 33 m^2/g, and 5.4 mmol H^+/g) was manufactured by Rohm and Haas. 5 M H_2SO_4 was purchased from Fluka. Crotonaldehyde (≥99.5%), 2-methyl-2-pentenal (97%), 2-pentylfuran (≥98.0%), eicosane (99%), H_2IrCl_6 (99.98%, trace metal basis) were purchased from Sigma-Aldrich. 2-propylfuran (>98%) and 2-butylfuran (>98%) were purchased from Tokyo Chemical Industry Co., Ltd. Cyclohexane (99.9%) was purchased from Fisher Chemical. Ammonium perrhenate (VII), (99.999%, metals basis) was purchased from Alfa-Aesar. Silica gel G6 (BET surface area 535 m^2/g) was kindly provided by Fuji Silysia Chemical Ltd.

2.2 Catalyst Preparation

Ir-ReO_x/SiO_2 (Ir 4 wt% loading, Re/Ir =2 on molar basis) was prepared by a sequential impregnation method according to our previous method[33, 34]. First, Ir/SiO_2 was prepared by impregnating an aqueous solution of H_2IrCl_6 on SiO_2 (Fuji Silysia G-6). After evaporating the solvent at 75 °C on a hotplate and drying at 110 °C for 12 h in an oven, the resulting Ir/SiO_2 was impregnated with an aqueous solution of NH_4ReO_4. The resulting material was calcined in a crucible in air at 500 °C for 3 h at a heating rate of 10 °C /min. The reported metal loadings in all catalysts used in this study are based on the theoretical amount of metals used for impregnation.

2.3 Activity Tests

2.3.1 Conjugate addition-hydroxyalkylation/alkylation (CA-HAA) reaction

The CA-HAA reaction was carried out under neat condition in a glass vial equipped with a magnetic stirrer. In a typical reaction, 6 mmol 2-alkylfuran and 2 mmol enal or double these amounts were added in a vial. The vial was clamped in a preheated oil bath placed on a stirring hotplate and the solution was stirred at 500 rpm using a magnetic bar. The total time to heat the solution to the set temperature was about 15 min. The reaction began after the catalyst was added to the solution and the reaction time for each reaction is indicated in the figures and tables. After reaction, the solution was filtered to separate solid catalysts (when heterogeneous catalysts were used) and diluted in 10 ml cylcohexane for GC/GC-MS analysis. A small amount of eicosane was added into the diluted solution as an internal standard.

2.3.2 Hydrodeoxygenation (HDO) reaction

HDO of condensation products, referred hereto as lubricant precursors, over Ir-ReO_x/SiO_2 was performed in a 50 mL Parr reactor with an inserted Teflon liner and a magnetic stirrer. First, catalyst (0.15 g) and solvent (cyclohexane, 10 mL) were added along with 5 MPa H_2 for catalyst pre-reduction at 200 °C and 1 h at 240 rpm. Upon pre-reduction, the reactor was cooled to room temperature and H_2 was released. Then, the lubricant precursors (0.3 g) were added. Subsequently, the reactor head was closed immediately and the reactor was purged with H_2 (1 MPa) for three times, pressurized to 5 MPa H_2, and heated to the desired temperature with continuous stirring at 500 rpm. The heating time to reach the set temperature was about 25 min. After reaction, the reactor was immediately transferred to a water bath to be quenched and the pressure was released. The solution was diluted in 10 ml cyclohexane containing a small amount of eicosane as an internal standard and the catalyst was separated from the solution by filtration. The catalyst was regenerated by calcination in air at 500 °C for 3 h at a heating rate of 10 °C /min before reusing in the next cycle.

2.3.3 Analysis of products

The products were analysed and quantified by a gas chromatograph (GC, Agilent 7890A) equipped with an HP-1 column and a flame ionization detector (FID) using eicosane (C_{20}) as an internal standard. A GC (Agilent 7890B) mass spectrometer (Agilent 5977A with a triple-axis detector) equipped with a DB-5 column, a high-resolution MS with liquid injection field desorption ionization (LIFDI). ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AV400 NMR (400 MHz) equipped with a cryogenic QNP probe. Chloroform-d was used as a solvent. For the ^1H NMR analysis, the chemical shifts for proton signals are reported in parts per million (ppm) with reference to the solvent peak. ^{13}C NMR was fully decoupled by broad band proton decoupling and the chemical shifts are reported in ppm with reference to the center line of a triplet at 77.16 ppm of chloroform-d.

The conversion and the yield of all products were calculated on a carbon basis using the following equations:

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

$$\text{Yield of detected products [\% - C]} = \frac{\text{mol}^{\text{product}} \times \text{C atoms in product(s)}}{\text{mol of total C atoms in initial reactants}} \times 100$$

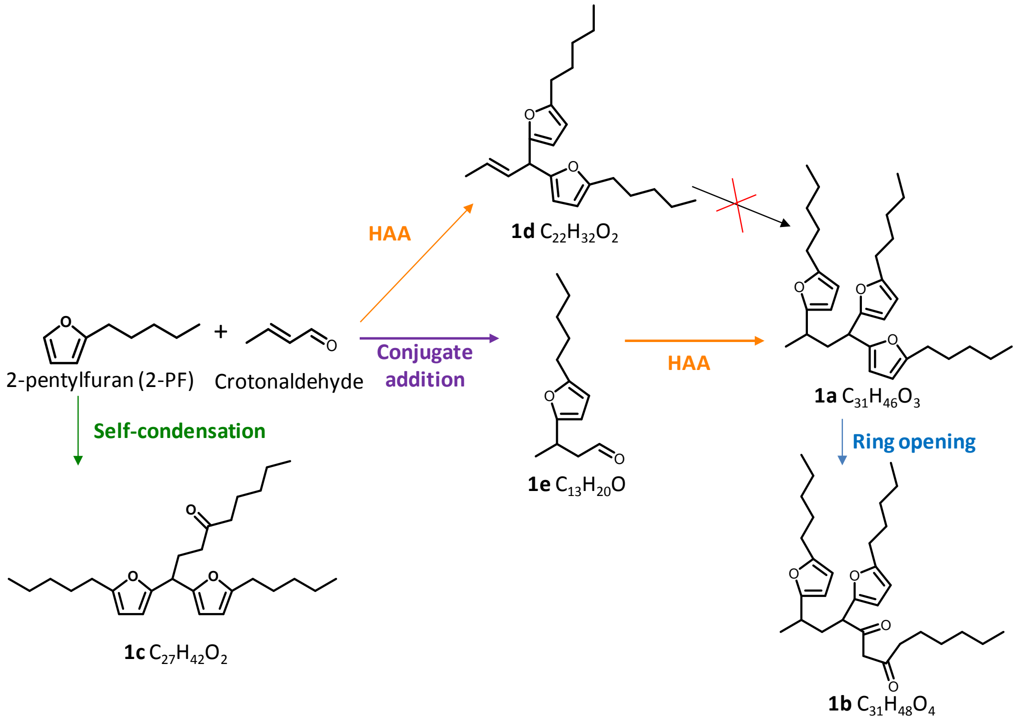
2.4 Lubricant Properties-Measurements

Important properties of lubricant base-oils were measured using ASTM methods. The kinematic viscosities at 100 °C and 40 °C (KV100 and KV40) were determined using the ASTM D445 method. The viscosity index (VI) was calculated from KV100 and KV40 using the ASTM D2270 method. The pour point tests were carried out according to the ASTM D97. These measurements were performed in the fuel and lubricant analysis facility at Southwest Research Institute, San Antonio, Texas, USA. The DSC oxidation onset temperature and Noack volatility were measured according to the ASTM E2009 (method B, 500 pis O2) and ASTM D6375, respectively, at the Petro-lubricant Testing Laboratories, Inc, in Lafayette, N. J., USA.

3. Results and Discussion

3.1 Catalyst Screening for the CA-HAA Reaction

We target the C_{31} condensed furan from crotonaldehyde and 2-pentylfuran because (1) commercial petroleum-based PAO lubricant base-oils typically contain molecules of 20-40 carbon atoms, (2) of its similar branching to commercial PAOs, and (3) the precursors, bio-based crotonaldehyde and 2-pentylfuran, have been synthesized via self-condensation of acetaldehyde from bio-ethanol[28] and via acylation of furan with valeric acid or valeric anhydride followed by HDO[23], respectively. First, homogeneous acid catalysts, e.g., sulfuric acid (H_2SO_4), methanesulfonic acid (CH_3SO_3H), *p*-toluenesulfonic acid (*p*-TSA) and triflic acid (CF_3SO_3H) were screened to eliminate transport limitations (Fig. 1). At 3 to 1 molar ratio of 2-pentylfuran and crotonaldehyde, the C_{31} CA-HAA product ($C_{31}H_{46}O_3$, **1a**) dominates. Small fractions of other products form via ring opening of the CA-HAA product ($C_{31}H_{48}O_4$, **1b**), HAA reaction ($C_{22}H_{32}O_2$, **1d**), CA reaction ($C_{13}H_{20}O$, **1e**) and self-condensation of 2-pentylfuran ($C_{27}H_{42}O_2$, **1c**) (Scheme 2). All products, except **1e,** have $>C_{20}$ carbon atoms and a branched backbone. H_2SO_4 is less effective than organic sulfonic acids whose performance, regarding the conversion of 2-pentylfuran and the formation rates of CA-HAA products (**1a** and **1b**), follows the ranking CF_3SO_3H> *p*-TSA >CH_3SO_3H (Fig. 1 and 2), consistent with their acid strength[35]. The yield of the CA-HAA product and total lubricant precursors (**1a-1d**) over trifilic acid at longer reaction time and higher conversion is lower (62%) compared to that with *p*-TSA (72%) and methanesulfonic acid (70%), probably due to the high degree of polymerization of 2-pentylfuran and/or condensation caused by the high acid strength of trifilic acid[36]. While the liquid sulfonic acids are effective, they are corrosive and their separation and disposal are challenging.



Scheme 2. Proposed reaction pathway for condensation of 2-pentylfuran and crotonaldehyde.

To overcome the above challenges, we used commercial solid sulfonic acid resin catalysts, e.g., Aquivion PW79S, Aquivion PW98, Amberlyst-15 and Amberlyst-36. The yields of **1a** and total lubricant precursors are significantly higher over Aquivion PW79S and Aquivion PW98 than those over Amberlyst-15 and Amberlyst-36, which promote the CA product **1e.** Both Aquivion PW79S and Aquivion PW98 are perfluorinated sulfonic acid resins while Amberlyst 15 and 36 are sulfonic-acid-functionalized cross-linked polystyrene resins. The latter have higher surface areas than the former but are weaker acids. Thus, the acid strength is likely responsible for the superior activities of the Aquivion resins. The higher rate over Aquivion PW79S, compared to Aquivion PW98, is attributed to the higher acid density of Aquivion PW79S, enabling better accessibility of H^+ for the tandem C-C coupling reaction[37, 38]. Jérôme et al. have also reported that Aquivion PW79S performed better for biphasic glycosylation of glucose with fatty alcohols[39].

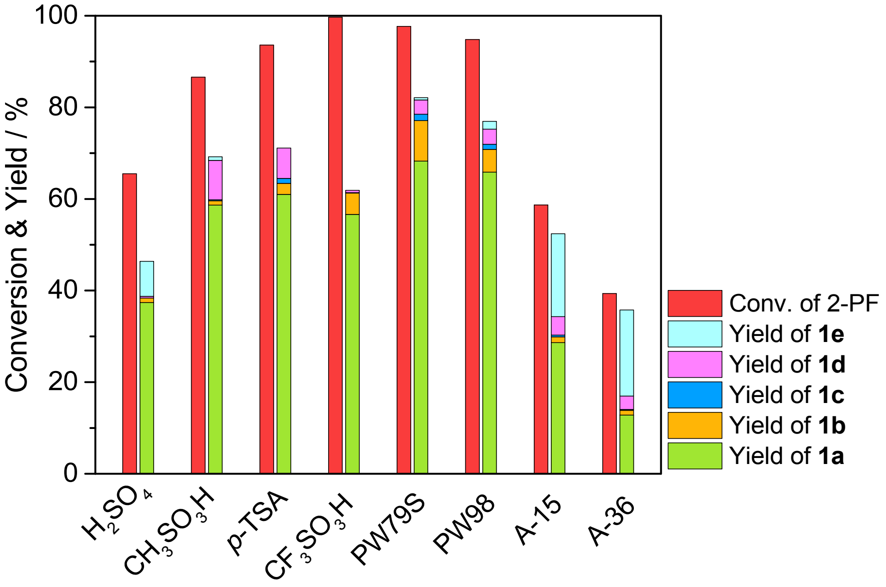


Fig. 1 Condensation of 2-pentylfuran and crotanaldehyde over various acid catalysts. Reaction conditions: 6 mmol 2-pentylfuran, 2 mmol crotonaldehyde, 0.063 mmol H^+ ($[H^+]$ was kept fixed by adjusting the amount of catalysts, e.g. 0.05g Aquivion PW79S), 65 °C, 2 h. A-15 and A-36 refer to Amberlyst-15 and Amberlyst-36, respectively.

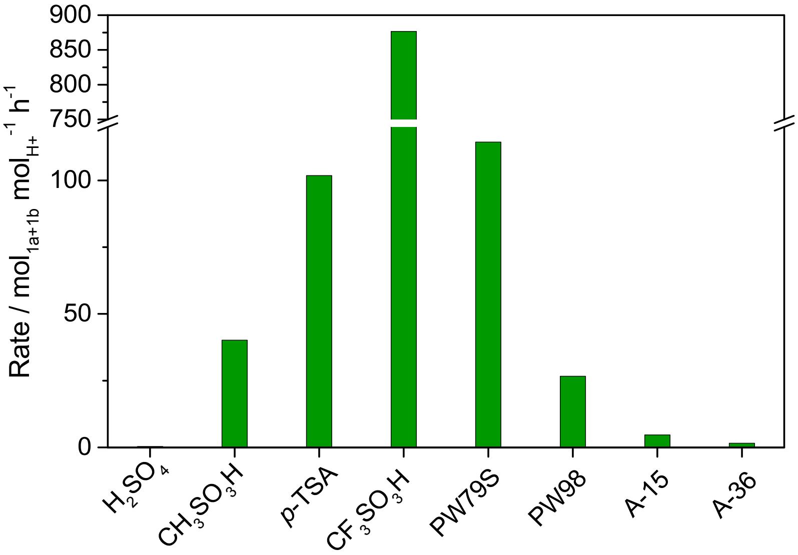


Fig. 2 Formation rates of CA-HAA products (**1a** and **1b**) over various acid catalysts. Reaction conditions: 12 mmol 2-pentylfuran, 4 mmol crotonaldehyde, 0.0126 mmol H^+ ($[H^+]$ kept fixed by using different amounts of catalysts, e.g. 0.01g Aquivion PW79S), 50 °C, conversion of 2-pentylfuran <35%. A-15 and A-36 refer to Amberlyst-15 and Amberlyst-36, respectively.

3.2 Reaction Pathways

Time dependent experiments were conducted to elucidate the reaction pathway. Since this reaction is very fast at 65 °C with 0.05 g Aquivion PW79S (Fig. S1), the reactions were conducted at 50 °C using less catalyst (0.01 g) and by doubling the amounts of reactants. Figure

3 shows almost quantitative conversion of crotonaldehyde within 30 min, yielding **1a** and **1e** as the major products. The yield of **1a** increases as the concentration of **1e** decreases, suggesting **1a** forms via HAA between **1e** and 2-pentylfuran. **1d** forms concurrently via HAA of 2-pentylfuran with crotonaldehyde but its concentration is much lower than that of **1e** at the onset of the reaction, indicating the CA reaction rate is faster than that of the HAA reaction. **1d** forms in parallel to **1a** and **1e** at the onset of the reaction and its concentration virtually remains constant throughout the reaction. This indicates that **1a** does not form from condensation of **1d**. This is further corroborated by the fact that there was no C-C coupling reaction between 2-pentylfuran with 2-octene under comparable reaction conditions. A small fraction of **1b** forms via furan ring-opening of **1a** at longer times. The ring-opening, via cleavage of C-O bond, is probably due to acid catalyzed hydrolysis, as water is a by-product of the condensation reaction[40]. Water also causes self-condensation of 2-pentylfuran to produce a trace amount of **1c**. An overall reaction network is proposed in Scheme 2.

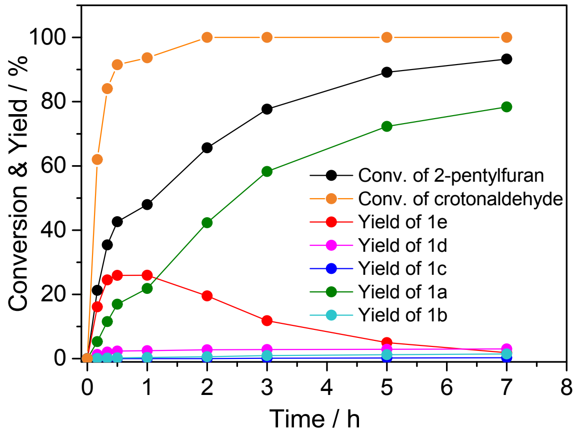


Fig. 3 Time course of condensation of 2-pentylfuran and crotonaldehyde over Aquivion PW79S. Reaction conditions: 12 mmol 2-pentylfuran, 4 mmol crotonaldehyde, 0.01g Aquivion PW79S, 50 °C.

3.3 Temperature Effect

The effect of reaction temperature at low and high conversions of 2-pentylfuran is shown in Fig. 4. To compare the selectivities at different reaction temperatures, comparable conversions were achieved by tuning the reaction time. At ~35% conversion of 2-pentylfuran, the selectivity to **1a** increases at the expense of **1e** with increasing reaction temperature. This suggests the HAA reaction of **1e** with 2-pentylfuran is favored at higher reaction temperature. At high conversion of 2-pentylfuran (>90%), the selectivity of **1a** decreases while the selectivity of **1b** increases with increasing reaction temperature, indicating that the furan ring-opening of **1a** is favored at higher temperature. The overall selectivity to CA-HAA products (**1a**+**1b**) and total lubricant precursors are slightly lower at higher temperatures likely because of polymerization of 2-pentylfuran and/or the products. Thus, low reaction temperature promotes the CA-HAA product selectively.

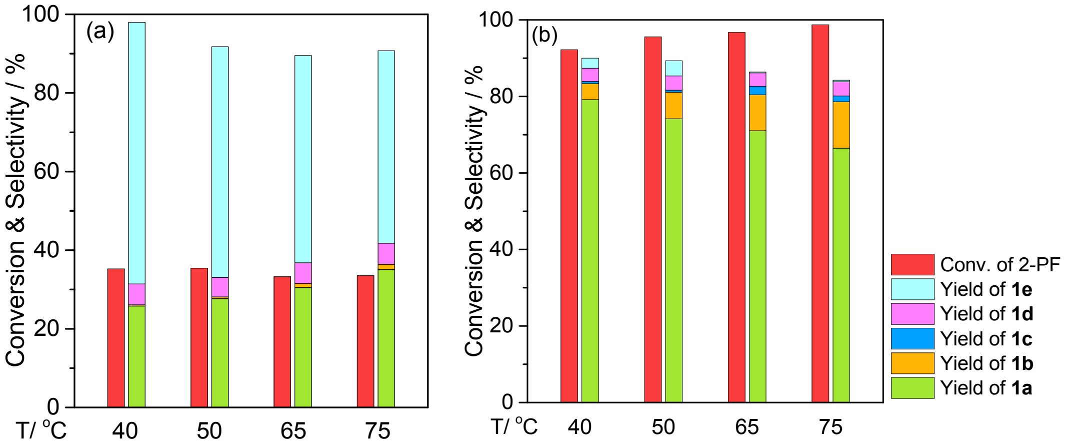


Fig. 4 Effect of temperature on the condensation of 2-pentylfuran and crotonaldehyde over Aquivion PW79S at low (a) and high (b) conversions of 2-pentylfuran. Reaction conditions: (a) 12 mmol 2-pentylfuran, 4 mmol crotonaldehyde, 0.01 g Aquivion PW79S, 30 min at 40 °C, 20 min at 50 °C, 10 min at 65 °C and 6 min at 75 °C. (b) 6 mmol 2-pentylfuran, 2 mmol crotonaldehyde, 0.05 g Aquivion PW79S, 5 h at 40 °C, 3 h at 50 °C, 2 h at 65 °C and 1 h at 75 °C. 2-PF = 2-pentylfuran.

3.4 Reusability of Aquivion PW79S Catalyst

The recyclability of Aquivion PW79S was studied. After each cycle, the catalyst was allowed to settle down and the liquid product was pipetted out. The recovered catalyst was washed thoroughly with cyclohexane to remove any surface adsorbed unreacted reactants and products, dried in a vacuum oven at 60 °C for 1 h, and reused in the next cycle. Under comparable conditions, the catalyst achieves similar conversion of 2-pentylfuran and yield of all products (Fig. 5) for five consecutive cycles, indicating Aquivion PW79S is stable. Its high stability is promising regarding the commercialization potential of this process.

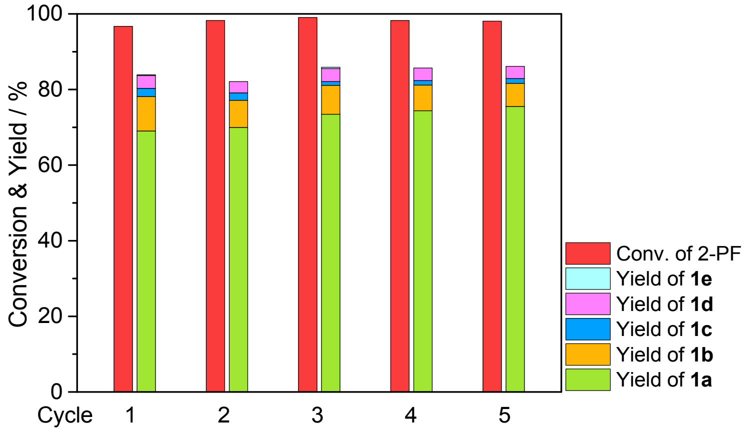


Fig. 5 Reusability of Aquivion PW79S in the condensation of 2-pentylfuran and crotonaldehyde. Reaction conditions: 6 mmol 2-pentylfuran, 2 mmol crotonaldehyde, 0.05 g Aquivion PW79S, 65 °C, 1.5 h.

3.5 Production of Branched Alkanes via HDO of Condensation Products

Lubricant condensation precursors underwent HDO over an Ir-ReO_x/SiO_2 catalyst. This catalyst was selected due to its excellent HDO performance on C_{12}-C_{34} condensation products containing multiple furan rings in our earlier work[18, 34]. The excellent performance arises from a synergy between Ir and ReO_x sites, whereby the Ir sites hydrogenate the furan rings and the acidic sites of partially reduced ReO_x activate the C-O bonds of furan rings. The condensation products are quantitatively converted to lubricant ranged branched C_{22}-C_{31} alkanes with a yield 81% with C_{31} alkane the dominant product within 12 h at 170 °C and 5 MPa H_2 (Fig. 6). Small fractions of C-C cracking alkanes (C_9 and C_{22}) also form, consistent with our prior report[18, 34]. C-C cracking likely occurs at the tertiary carbon linked to the two rings[34]. The alkane mixture contains 8% of a C_{31} oxygenate of one saturated furan ring, which can provide polarity and enhance the solubility of the base-oils with several lubricant additives, such as antioxidants, friction modifiers, detergent additives, etc.[2] At slightly higher temperature (180 °C) and a longer reaction time (18 h), a moderately higher yield to C_{22}-C_{31} branched alkanes (88%) is achieved in which the C_{31} branched alkane is the major product (68%).

Catalyst recycling experiments reveal comparable catalyst performance up to five cycles tested (Fig. 6b). The amount of unconverted oxygenates was slightly higher in the solution after the 5th run. The catalyst after five cycles was characterized by XRD and TEM. The XRD peaks of the recovered catalyst assigned to the metallic Ir phase become slightly sharper (Fig. S2). TEM images (Fig. S3) of the recovered catalyst show an average particle size of ~4.0 nm, which is slightly larger than that of the fresh catalyst (~3.6 nm). These characterization data suggest slight sintering of the catalyst during reaction and/or regeneration, leading to a slightly higher fraction of unconverted oxygenates at the 5th run.

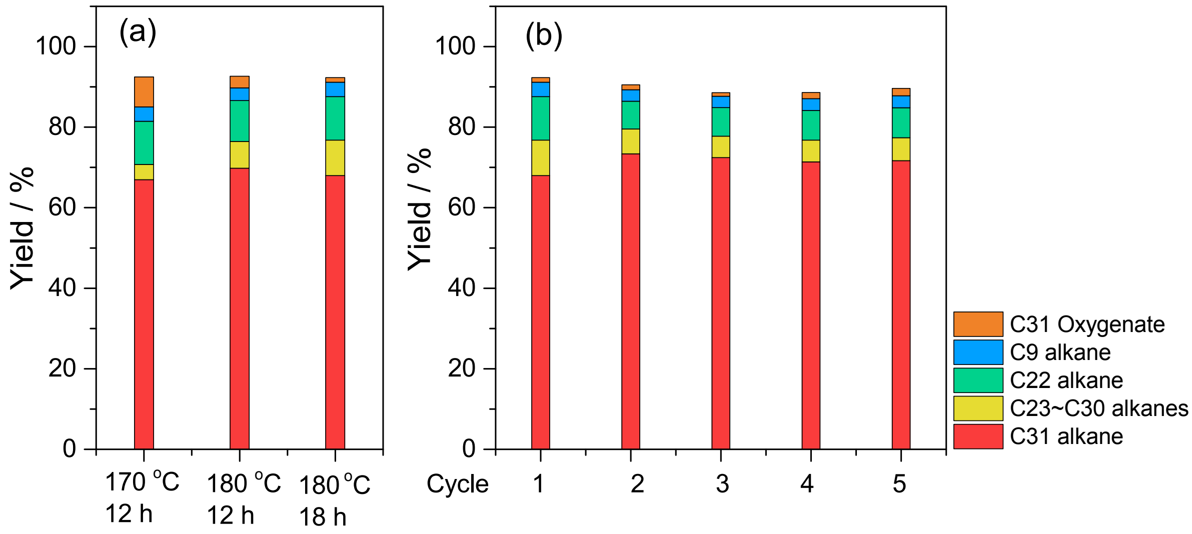


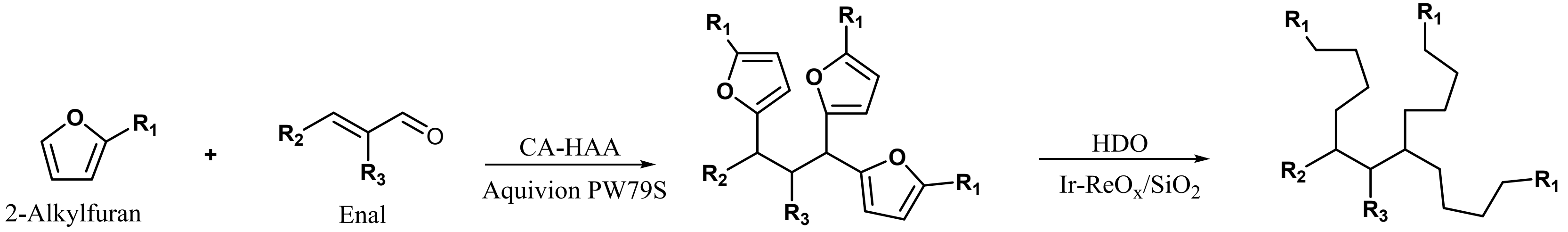
Fig. 6 HDO of condensation products, obtained from 2-pentylfuran and crotonaldhyde, at (a) varying reactions conditions and (b) evaluating catalyst recyclability. Reaction conditions: 0.3 g condensation products, 0.15 g Ir-ReO_x/SiO_2, 5 MPa.

3.6 Effect of Substrates

Because commercial mineral base-oils contain a mixture of C_{20}-C_{50} linear hydrocarbons and synthetic PAO base-oils are composed of C_{20}, C_{30} and C_{40} branched alkanes, we synthesize C_{25}-C_{33} branched alkanes using 2-alkylfuran and enals of different molecular sizes. CA-HAA reactions of 2-alkylfurans of different chain length, e.g., 2-propylfuran, 2-butylfuran, and 2-pentylfuran, with crotonaldehyde produce C_{25}, C_{28} and C_{31} condensates containing three furan rings as the major products. Similar yields of CA-HAA products and total lubricant base-oils precursors were obtained over Aquivion PW79S. Subsequent HDO of the condensates over Ir-ReO_x/SiO_2 led to lubricant ranged C_{20}-C_{33} branched alkanes with high yields (Table 1). ^1H and ^{13}C NMR (supporting information) spectra evidenced that the HDO products are alkanes. The yield of alkanes with the highest carbon number as their precursors, e.g., C_{25}, C_{28} and C_{31} alkanes, is similar (~68%). However, the yield to total lubricant ranged alkanes, C_{20}-C_{33}, decreases with decreasing chain length of 2-alkylfuran. This is due to different degree of C-C cracking of condensates during HDO, arising from different carbon chain length in the molecular structures of condensates. The main C-C cracking products from $C_{25}H_{34}O_3$, $C_{28}H_{40}O_3$ and $C_{31}H_{46}O_3$ are branched C_{18}, C_{20} and C_{22} alkanes, respectively. Total branched alkanes yield from the HDO of $C_{25}H_{34}O_3$ is lower than that of others because the amount of C_{18} alkane, formed via C-C cracking, was not considered in the calculation of total yield of lubricant ranged alkanes.

Next, we investigate the CA-HAA reaction of enals of different carbon numbers, e.g. acrolein, crotonaldehyde and 2-methyl-2-pentenal, with 2-pentylfuran to obtain C_{30}-C_{33} condensates with varying branches (one, two, and three). The yields of CA-HAA product and total lubricant precursors using acrolein are similar to those obtained using crotonaldehyde, however, these yields are lower when 2-methyl-2-pentenal is used. This could be attributed to the steric hindrance during condensation of 2-methyl-2-pentenal, imparted by its higher molecular size and the presence of a high degree of branching. The HDO of the latter set of condensates shows a decrease in the yield of desired alkanes with the highest carbon numbers as their condensates, e.g. C_{30}, C_{31} and C_{33} alkanes, which could be ascribed to the presence of branch chains adjacent to furan rings, facilitating C-C cracking and forming the linear C_{21} alkane. Because the linear C_{21} alkane was not considered in the calculation of total lubricant ranged base oils, the total yield from the HDO of condensates obtained from acrolein condensation is lower than that obtained from the HDO of crotonaldehyde condensation precursors.

Table 1. HAA reaction of 2-alkylfuran with aldehyde and HDO to corresponding alkane.



Entry	2-Alkylfuran R₁	Enal R₂	R₃	CA-HAA Product	Yield / %	Total yield C_{20}~C_{33} precursors / %	HDO Product	Yield /%	Total yield C_{20}~C_{33} alkanes /%
1	*n*-Propyl	Methyl	H	$C_{25}H_{34}O_3$	72	82	$C_{25}H_{52}$	68	72
2	*n*-Butyl	Methyl	H	$C_{28}H_{40}O_3$	73	84	$C_{28}H_{58}$	68	81
3	*n*-Pentyl	Methyl	H	$C_{31}H_{46}O_3$	71	82	$C_{31}H_{64}$	68	88
4[a]	*n*-Pentyl	H	H	$C_{30}H_{44}O_3$	72	77	$C_{30}H_{62}$	73	77
5[b]	*n*-Pentyl	Ethyl	Methyl	$C_{33}H_{50}O_3$	59	73	$C_{33}H_{68}$	31	70

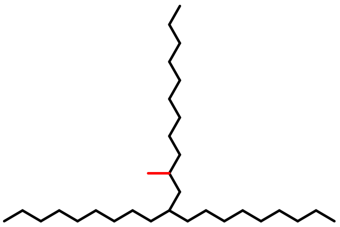
Reaction conditions: CA-HAA reaction: 6 mmol 2-alkylfuran, 2 mmol aldehyde, 0.05 g Aquivion PW79S, 50 °C, 3 h, a: 40 °C, 5 h, b: 50 °C 7 h; HDO reaction: 0.3 g condensation products, 0.15 g Ir-ReO$_x$/SiO$_2$, 5 MPa, 180 °C, 18 h. b: 180 °C, 48 h.

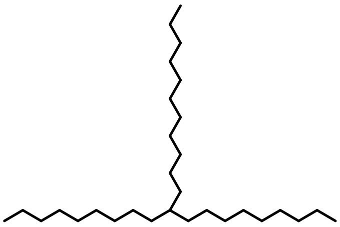
3.7 Properties of Synthesized Lubricant Base-oils

Key properties of branched alkanes, produced by sequential CA-HAA and HDO steps of 2-pentylfuran and acrolein or crotonaldehyde, were determined following various ASTM methods. The synthesized C_{30} and C_{31} branched alkanes are hereafter referred to as Bio-Poly-α-Olefin Lubricant, C_{30}-BPAOL1 and C_{31}-BPAOL. C_{31}-BPAOL has two branches while C_{30}-BPAOL1, which has the same structure as in our prior report[18], has only one branch. Table 2 compares their properties against those of a commercial mineral group III base oil and a commercial group IV PAO3.6 base oil. C_{30}-BPAOL1 and C_{31}-BPAOL base-oils have lower kinematic viscosities (KV40 and KV100) than the commercial products. The VI is noticeably higher than that of the commercial base-oils. Low viscosities promise higher energy efficiency in the automotive application, while high VI ensures low variation of viscosity of oils with temperature[41]. The KVs of C_{31}-BAPOL are higher than those of C_{30}-BPAOL1, due to its larger size[2]. The PP of C_{31}-BPAOL with two branches (-48 °C) is significantly lower than that of C_{30}-BPAOL1 with one branch (-21 °C)[18]. Importantly, the PP of both base-oils (C_{30}-BPAOL1 and C_{31}-BPAOL) is superior to mineral group III base oil. The volatility of our synthesized molecules is better than or comparable to that of commercial PAO3.6. The oxidation stability values are similar.

These specific examples suggest that our chemistry can enable the synthesis of base-oils with different branches and properties for low temperature applications where mineral base oils solidify[34]. Tunable properties of base-oils can enable production of formulated lubricants for various targeted applications, which unlike conventional petroleum lubricants, do not require excessive additives. Importantly, our bio-based base oils have the potential to minimize environmental carbon footprint.

Table 2. Comparison of properties of our synthesized base oils and commercial synthetic and Group III base-oils.


C_{31}-BPAOL


C_{30}-BPAOL1

Lubricant	KV$_{100}$[a] (cSt)	KV$_{40}$[a] (cSt)	VI[b]	PP[c] (°C)	Noack Volatility[d]/ wt%	DSC oxidation onset T[e] / °C
C_{31}-BPAOL	3.47	13.58	138	-48	17.2	181
C_{30}-BPAOL1	3.19	11.84	140	-21	13.8	201
ExxonMobil PAO-3.6[f]	3.6	15.4	120	-65	17.0	184

Phillips 66 Ultra-S 4[g]	4.25	19.64	123	-20	-	-

[a]KV100 and KV40 are kinematic viscosities at 100 °C and 40 °C, respectively (ASTM D445). [b]VI: Viscosity index calculated from KV100 and KV40 (ASTM D2270). [c]PP: Pour point (ASTM D97). [d]Volatility (ASTM D6375). [e]Oxidation stability (ASTM E2009, method B, 500 psi O_2). [f]Commercial PAO-3.6 synthetic base-oil manufactured by ExxonMobil. [g]Commercial group III mineral base oil. Properties of commercial products were obtained from products' specifications datasheet disclosed by the manufacturers.

4. Conclusions

We introduced a synthetic process, conjugate addition/hydroxylalkylation/alkylation (CA-HAA) of biomass derived 2-alkylfurans with enals followed by hydrodeoxygenation (HDO), to produce lubricant ranged branched alkanes of controlled branching and molecular size with excellent yields. Homogeneous and solid sulfonic acid catalysts have been screened for the CA-HAA step. Their catalytic performance correlated with their acidic strength. Aquivion PW79S achieves the best yield and selectivity of condensation products and catalyst stability. A maximum 80% yield is obtained. The reaction pathway of the complex CA-HAA step has been elucidated. The CA and HAA steps occur in a tandem manner. Subsequent HDO of the condensation products over an $Ir-ReO_x/SiO_2$ catalyst in a separate step yielded up to 88% lubricant ranged branched alkanes. The carbon number and branching of alkanes can be tailored by condensing different molecular sizes of 2-alkylfurans and enals. The synthesized alkanes have similar or superior properties to the commercial mineral group III and synthetic PAOs base oils. This work not only opens up an unprecedented route from biomass to alkanes lubricant base oils with controlled architecture, but may also encourage efforts towards the development of new tandem C-C coupling reactions beyond the well-studied C-C coupling reaction (e.g., HAA, aldol condensation) for production of high-performance lubricant base oils and fuels.

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TOC Graph

Lubricant ranged alkanes of controlled branching and molecular size with excellent yields were synthesized by catalytic conjugate addition-hydroxylalkylation/alkylation (CA-HAA) of biomass derived 2-alkylfurans with enals followed by hydrodeoxygenation.