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Synthesis of renewable lubricant alkanes from biomass-derived platform chemicals

Mengyuan Gu,[a] Qineng Xia,*[a] Xiaohui Liu,[a] Yong Guo[b] and Yanqin Wang[a]

Abstract: Catalytic synthesis of liquid alkanes from renewable biomass has received tremendous attention in recent years. However, highly branched lubricant alkanes are not yet synthetically exploited from biomass and are currently produced by hydrocracking and hydroisomerization of long-chain n-paraffins. Here we describe a selective catalytic synthetic route for the production of highly branched C_{23} alkanes for lubricant base oil component from biomass-derived furfural and acetone, through a tandem four-step process, namely aldol condensation of furfural with acetone to produce a C_{13} double adduct, then selective hydrogenation to a C_{13} ketone, followed by a second condensation of the C_{13} ketone with furfural to generate a C_{23} aldol adduct and finally to highly branched C_{23} alkanes by hydrodeoxygenation. The overall yield of C_{23} alkanes reaches 50.6% (97.9% × 72.8% × 83.8% × 84.8%) from furfural. This work opens a general strategy for the synthesis of high-quality lubricant alkanes from renewable biomass.

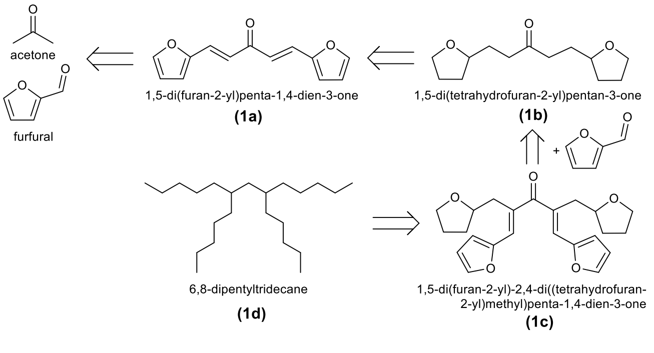
Introduction

In the last two decades, tremendous endeavors have been made to the catalytic upgrading of the biomass-derived compounds to value-added fuels and fine chemicals.[1] Liquid alkanes are well-known transportation fuels that can be produced from biomass *via* either Fischer-Tropsch synthesis of syngas,[2] upgrading of thermochemical-based bio-oils[3] or catalytic hydrodeoxygenation of biomass-derived oxygenates.[4]

Recently, there are many excellent works in the literature dealing with the selective synthesis of liquid alkanes with targeted molecular weight from biomass platform chemicals.[5] For example, through aldol condensation of acetone with biomass-derived furans (e.g., 5-hydroxymethylfurfural, furfural) followed by total hydrodeoxygenation, C_8-C_{15} alkanes can be selectively produced for using as gasoline or jet fuels.[5a-c, 6] However, the synthesized alkanes are mainly linear with relatively low octane number. As an alternative, self-condensation of acetone or methyl isobutyl ketone combined with subsequent hydrodeoxygenation over a dual-bed catalyst system was attempted for producing branched alkanes.[7] For synthesis of diesel-range branched alkanes, approaches involving alkylation/hydroxyalkylation of 2-methylfuran with lignocellulose-derived carbonyl compounds and subsequent total hydrodeoxygenation were developed.[5d, 8] In addition to the above two strategies for C-C bond coupling, benzoin condensation of two molecules of HMF and/or furfural catalyzed by N-heterocyclic or supported carbene catalysts was also reported.[5e, 9] Other than *via* C-C coupling reaction, targeted liquid alkanes can also be produced *via* C-C dissociation (hydrogenolysis) reactions of alga-derived squalene or botryococcene.[10]

Apart from being served as high-grade fuels, branched alkanes, especially with high carbon length, are used as unconventional base oil components in the production of high-quality lubricants.[11] Environmental and technological factors have raised higher performance requirements for automotive and industrial lubricants, such as low volatility, high thermal and oxidation stability, and improved cold flow properties, which cannot be satisfied using traditional solvent refined mineral oil.[11b] The ideal base oil components are branched alkanes and long-alkyl monocyclic naphthenes, which have improved oxidation stability compared to aromatic products. Lubricant alkanes are predominantly produced by hydrocracking and hydroisomerization of long-chain n-paraffins and are not yet synthetically exploited from biomass platform chemicals.[11b, 12]

Herein, for the first time, we describe the selective catalytic synthesis of highly branched C_{23} alkanes (6,8-dipentyl tridecane, **1d**) from the biomass-derived furfural and acetone, through four successive steps including aldol condensation, selective hydrogenation, second aldol condensation and finally total hydrodeoxygenation. This opens a general strategy for the synthesis of high-quality base oil components for lubricant production from renewable biomass.



Scheme 1. Retrosynthetic analysis for a pathway to C_{23} highly branched alkane from biomass-derived furfural and acetone.

Scheme 1 shows how branched C_{23} alkanes (**1d**) can be traced back to furfural and acetone as feedstocks using retrosynthetic analysis used in modern organic synthesis. In this process, furfural and acetone are readily converted to 1,5-di(furan-2-yl)penta-1,4-dien-3-one (**1a**) by double aldol condensation, followed by subsequent selective hydrogenation

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to a long-chain C_{13} ketone (1,5-di(tetrahydrofuran-2-yl)pentan-3-one, **1b**). The obtained **1b** has two α-H in C(2) and C(4) positions that are accessible for second aldol condensation with an aldehyde such as furfural. Thus, a selective formation of C_{23} alkane precursor (**1c**) can be envisaged with proper reaction condition control. Combined with total hydrodeoxygenation, a highly branched C_{23} alkanes (**1d**) can be selectively synthesized with two long side chains in the middle of the main chain. It is worth noting that the branching positions and length have a remarkable influence on the decrease of melting point, and branchings in the middle of the chain and longer side chains lead to a greater decrease of melting point.[11b]

Results and Discussion

Aldol condensation of furfural with acetone

For the first step (aldol condensation) of the process, homogeneous catalytic system was employed with molar ratio of furfural to acetone being exactly 2:1. It is possible to almost quantitatively convert furfural and acetone into **1a** (>97% isolated yield) when catalyzed by 0.5 M NaOH aqueous solution at 40 ^oC for 5 h (Table 1). The condensation parameters such as reaction temperature, reaction time, feed ratio and NaOH concentration have a significant influence on the yield of **1a** (Table S1). Because of the suitable solubility of **1a** in 0.5 M NaOH aqueous solution and high monotonicity of the product after reaction, the **1a** can readily crystallize and precipitate in the form of yellow acicular crystal (Figure S1a,b). This brings at least three advantages: 1) the produced **1a** can be easily separated with high purity by filtration, which is an energy-saving process; 2) the alkaline filtrate can be reused for the next run by simply replenishing furfural and acetone; 3) the dissolved **1a** in the first crystallization process can be transfer to the next run with almost no waste emissions, which is atom economic and environmentally friendly.

Table 1. Recyclability test of aldol condensation of furfural with acetone over NaOH aqueous solution.

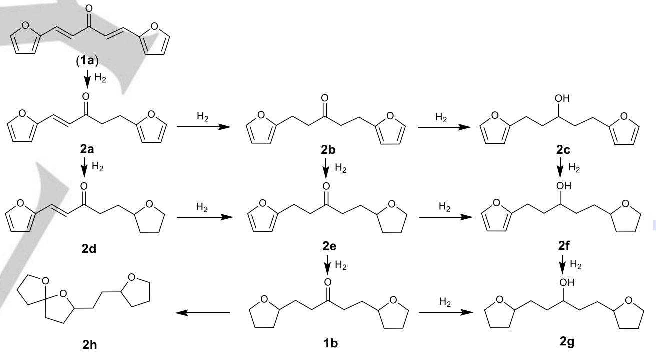
Run	Conversion (%)		GC selectivity (%)		Isolated yield of 1a by crystallization (%)
	furfural	acetone	FA[c](C_8)	**1a**(C_{13})	
1[a]	>99.9	>99.9	0.8	98.2	88.0
2[b]	>99.9	>99.9	0.4	99.0	97.9
3[b]	>99.9	>99.9	0.6	98.7	97.4
4[b]	>99.9	>99.9	1.1	97.4	97.1
5[b]	>99.9	>99.9	1.0	98.1	97.0

[a]Reaction condition: Furfural (38.4 g), acetone (11.6 g), NaOH (3.0 g), H_2O (150 mL), 40 ^oC, 5 h. [b]Additional furfural (38.4 g) and acetone (11.6 g) were added to the filtrate of the prior run, 40 ^oC, 5 h. [c]"FA" is the abbreviation for single aldol adduct furfural-acetone.

As we can see from Table 1 that the yield of **1a** reaches 98.2% as analyzed by GC-FID, but the isolated yield of **1a** of the first run is relatively lower (88.0%), this is because a part of **1a** is dissolved to form a saturated **1a** aqueous solution. It should be mentioned that although **1a** is only slightly soluble in water, its solubility remarkably improves with the increase of the NaOH concentration. After separating the **1a** by in-situ crystallization and filtration, the filtrate was direct used for the next run by replenishing furfural and acetone, and >97% isolated yield of **1a** was achieved. Although homogeneous catalytic system is employed here, this system is of high recyclability with high efficiency and selectivity, as there is no decrease of the isolated yield of **1a** after five successive runs (Table 1). As a result, it is an extremely promising catalytic system for the scale-up industrial production of **1a** from furfural and acetone.

C_{13} ketone synthesis by selective hydrogenation

For the second step (selective hydrogenation), Scheme 2 shows the possible reaction products that can be generated from the hydrogenation of **1a**. It seems that the products **2b**, **2e**, **1b** all have two α-H in C(2) and C(4) positions that are accessible for condensation. However, our subsequent tests show that **1b** is the best candidate for double condensation with furfural, partially because the tetrahydrofuran ring is more flexible than the furan ring. Therefore, massive efforts were made to improve the yield of the **1b** by catalyst screening and reaction optimization.



Scheme 2. The possible reaction products that can be generated from the selective hydrogenation of **1a**.

With as-prepared **1a** (>98% purity, See Figure S2 for NMR spectra) as feedstock, the selective hydrogenation reactions were firstly carried out over a series of catalysts under solvent-free condition (Table 2). Considering that the melting point of **1a** is 60.5 ^oC, so we implemented the reactions at a slightly higher temperature (70 ^oC) firstly. After hydrogenation at 70 ^oC, 5 MPa initial H_2 for 5 h, the conversion of **1a** is >99.9% in all cases. No **2a**, **2c** or **2d** was detected in all of the tested reactions, indicating that the hydrogenation reactivity of functional groups in **1a** decreases as follows: exocyclic C=C double bond > furan ring > C=O double bond, which is in accordance with the results reported by Tomishige.[13] It can be seen that the Pd/γ-Al_2O_3 gives the highest yield of **1b**, while Pt/γ-Al_2O_3 and Ru/γ-Al_2O_3 give **2b** as the major product. The main by-products over Pd/γ-Al_2O_3 are over-hydrogenation product **2g** and isomeric cyclization product **2h**, which are both typical products in the hydrogenation of **1a**.[5b, 14] We then tried various supported Pd catalysts and their catalytic performance decease as follows: Pd/γ-Al_2O_3 > Pd/C > Pd/NbOPO$_4$ > Pd/ZrO$_2$ > Pd/SiO$_2$. Non-noble Ni/SiO$_2$ was also attempted because of its relative high activity for furan-ring hydrogenation,[15] however, only 12.1% yield of **1b** was obtained. In view of the fact that the Ni/SiO$_2$ catalyst was surely reduced at 450 °C (Figure S3), the low performance of Ni/SiO$_2$ is probably due to the low catalyst dosage (substrate/catalyst = 35:1) and low reaction temperature.

It is noticed that the other catalysts (except for Pd/γ-Al_2O_3) show the insufficient catalytic performance with more up-stream intermediates at 5 h (e.g., 2b, 2e). Therefore, In order to compare these catalysts from the viewpoint of reaching the highest yield of **1b**, we further prolonged the reaction time from 5 to 20 h (Table S3). It can be seen that although the reaction time was extended to 20 h, their yields of **1b** were still lower than that over Pd/γ-Al_2O_3 at 5 h (66.4%). This results confirm that the Pd/γ-Al_2O_3 presents the best catalytic performance for the selective hydrogenation of **1a** to **1b**.

Table 2. Reaction results of the selective hydrogenation of **1a** over various catalysts.[a]

Entry	Catalysts	Yield (%)					
		2b	**2e**	**2f**	**1b**	**2g**	**2h**
1	Pt/γ-Al_2O_3	80.9	8.7	0	0	0	0
2	Ru/γ-Al_2O_3	57.8	24.7	3.0	3.8	0.6	4.3
3	Pd/γ-Al_2O_3	0	0.4	0	66.4	11.9	20.0
4[b]	Ni/SiO$_2$	36.9	36.9	3.1	12.1	1.1	0
5	Pd/C	1.4	14.9	6.1	38.9	13.2	14.5
6	Pd/SiO$_2$	30.0	39.6	5.3	15.2	0.9	6.4
7	Pd/ZrO$_2$	5.9	24.3	13.0	28.4	10.2	17.8
8	Pd/NbOPO$_4$	0	3.5	1.7	33.9	6.7	25.0

[a] Reaction condition: **1a** (1.4 g), catalyst (0.04g), 70 °C, 5 MPa H_2, 5 h. The metal loading was 5 wt% for Pt, Ru and Pd catalysts. [b] The Ni/SiO$_2$ catalyst was pre-reduced at 450 °C for 3 h before use and the Ni loading was 33 wt%.

Given the best catalytic performance of Pd/γ-Al_2O_3, we then systematically optimized the reaction conditions for the selective formation of **1b** from **1a**. The variation of the reaction temperature shows that the yield of **1b** slightly increases from 66.4% to 72.8% with the elevation of reaction temperature from 70 to 130 °C. The by-product **2g** remains almost constant in the range of 11.3-14.7%, while **2h** presents a slight decrease from 20.0% to 12.2% with the increase of temperature from 70 to 130 °C (Figure 1a). The change of initial H_2 pressure at 130 °C has no distinct influence on the product distributions, but we do notice the decrease of intermediate **2e** and the slightly increase of over-hydrogenation product **2g** with the increase of initial H_2 pressure (Figure 1b). As a result, the yield of **1b** reaches a peak value (72.8%) at 5 MPa initial H_2 pressure. The reaction time course shows that the hydrogenation of furan rings completed at 5 h and overly long reaction time will lead to the increase of **2g**, although not so remarkably (Figure 1c). For cost reduction of catalyst, a high ratio of substrate to catalyst (35:1) was employed here, however, further raising the ratio to 50:1 and 70:1 resulted an incomplete hydrogenation that significantly drops the yield of **1b** (Figure 1d). For industrial application purpose, the stability test of Pd/γ-Al_2O_3 was also carried out, and the results show that Pd/γ-Al_2O_3 presents high reusability for the selective hydrogenation of **1a** (Figure S4).

Aldol condensation of 1a with furfural

After the selective hydrogenation, the mixture containing C_{13} ketone **1b** was separated from the catalyst by semipermeable membrane filtration to form a clear brown liquid (Figure S1c), which was used as a starting material for the second aldol condensation without further purification (contains 72.8% **1b**, 13.5% **2g**, 12.2% **2h** and 1.5% of other C_{13} oxygenates). In this step, two possible aldol adducts can be produced accordingly, namely single adduct C_{18} oxygenate **3a** and double adduct C_{23} oxygenate **1c**, as shown in Scheme 3.

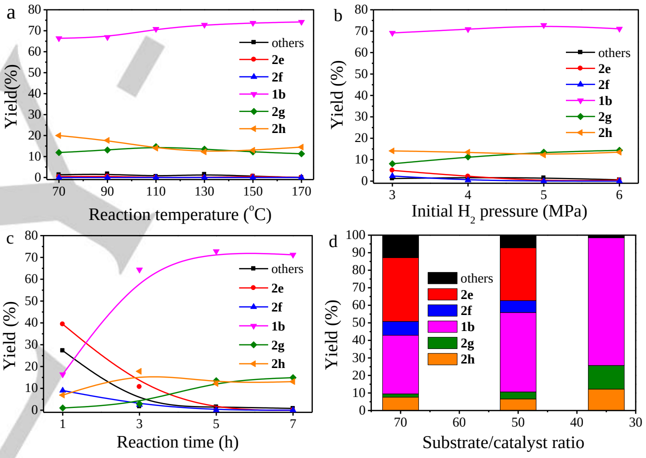
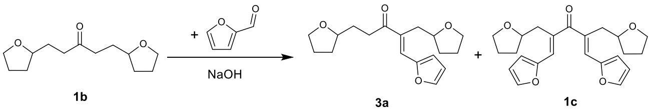


Figure 1. Reaction condition optimization for selective formation of **1b** from **1a** a) reaction temperature, b) H_2 pressure, c) reaction time, d) catalyst dosage. Reaction conditions: a) **1a** (1.4 g), catalyst (0.04g), 70~170 °C, 5 MPa H_2, 5 h; b) **1a** (1.4 g), catalyst (0.04 g), 130 °C, 3~6 MPa H_2, 5 h; c) **1a** (1.4 g), catalyst (0.04g), 130 °C, 5 MPa H_2, 1~7 h; d) **1a** (1.4 g), catalyst (0.02~0.04 g), 130 °C, 5 MPa H_2, 5 h.



Scheme 3. Possible products in the aldol condensation of furfural with **1b**.

For an initial attempt, methanol/water (w/w = 1:1) was employed as a co-solvent for the aldol condensation of **1b** with furfural, in full consideration of the solubility of organic compounds (furfural, **1b**, **1c, 3a)** and the catalyst NaOH. An excessive amount of furfural (Fur:**1b** = 8:1) was used to reach a high conversion of **1b**, since the remaining furfural can be easily recycled by rotary-evaporation. The reactions at different temperatures show that 50 ^{o}C is a proper temperature for the condensation (Table 3, entries 1-3). Lower temperatures result in slow condensation rates, but higher temperatures shift the reaction equilibrium to the left. Condensations at 50 ^{o}C for different reaction time show that increase of the reaction time from 10 to 20 h boosts the yield of C_{23} precursor from 33.1% to 52.4%, but extending the reaction time from 20 to 30 h has no obvious difference, probably because the reaction has reached its equilibrium at 20 h (Table 3, entries 2,4,5). The above results clearly indicate that the reaction equilibrium dominates the yield of single (**3a**) and double adducts (**1c**).

To shift the reaction equilibrium to the right, we reduce the ratio of water in the co-solvent to CH_3OH:H_2O = 9:1. As a result, the yield of double adduct **1c** significantly increased from 52.8% to 73.5% with the decrease of water content (Table 3, entry 6). We further tried methanol as a sole solvent, and the yield of C_{23} precursor **1c** further increased to 83.8% (Table 3, entry 7). The variation of furfural/**1b** ratio from 2:1 to 8:1 significantly enhances the yield of C_{23} precursor 1c from 22.1% to 83.8%, but further increase of the furfural/**1b** ratio from 8:1 to 16:1 makes no difference (Table 3, entries 7-10). The concentration of NaOH also has a remarkable influence on the condensation performance, as it can be seen that decrease of the NaOH concentration from 1.0 to 0.5 M leads to the decline of **1b** conversion and selectivity to double adduct (Table 3, entry 11). It is worth noting that although the C_{13} ketones **2b**, **2e**, **1b** all have two α-H in C(2) and C(4) positions that are accessible for condensation, **1b** is the best candidate for double condensation with furfural, as we can see from entry 12 that a much worse reaction performance is given when using **2b** and **2e** as condensation feedstock, partially because the tetrahydrofuran ring is more flexible than the furan ring.

Table 3. Results of the second aldol condensation under various reaction conditions.[a]

Entry	Solvent	Fur/**1b**	Conc. of NaOH (mol/L)	Temp. (^{o}C)	Time (h)	Conv. of **1b** (%)	Selectivity	
							3a	**1c**
1	CH_3OH:H_2O = 1:1	8:1	1.0	30	10	92.1	90.6	9.4
2		8:1	1.0	50	10	95.2	66.9	33.1
3		8:1	1.0	70	10	95.0	71.5	30.1
4		8:1	1.0	50	20	97.2	47.6	52.4
5		8:1	1.0	50	30	97.5	47.2	52.8
6	CH_3OH:H_2O = 9:1	8:1	1.0	50	20	>99.9	26.5	73.5
7	CH_3OH	8:1	1.0	50	20	>99.9	16.2	83.8
8		2:1	1.0	50	20	91.7	77.9	22.1
9		4:1	1.0	50	20	94.0	47.8	52.2
10		16:1	1.0	50	20	>99.9	17.6	82.4
11		8:1	0.5	50	20	93.6	54.9	45.1
12[b]		8:1	1.0	50	20	36.0	37.3	62.7

[a]Reaction condition: 0.1g of selective hydrogenation products of **1a,** 3.33 g of solvent. The feedstock contains 72.8% **1b**, 13.5% **2g**, 12.2% **2h** and 1.5% of other C13 oxygenates. [b]The feedstock contains 80.9% **2b**, 8.7% **2e** and 10.4 % of other C_{13} oxygenates.

After the aldol condensation, the methanol and furfural were rotary-evaporated before the products were washed and extracted by dichloromethane. Subsequently, the extractant and excessive furfural were removed by rotary-evaporation to gave a dark, viscous oil (Figure S1d), which mainly contains the mixture of aldol adducts (3a and 1c) and remaining C_{13} oxygenates (1b, 2g and 2h).

Total hydrodeoxygenation of second aldol condensation products

For the finally total hydrodeoxygenation, Pd/$NbOPO_4$ was employed as the catalyst because of it's excellent catalytic performance for hydrodeoxygenation reactions, owing to the significant promotion effect of NbO_x species on C-O bond cleavage.[4c, 5c, 16] Figure 2 shows the hydrodeoxygenation results of aldol adducts obtained from the second aldol condensation (13.4 wt% C_{13} oxygenates, 11.4 wt% C_{18} oxygenate, 75.2 wt% C_{23} oxygenate) at 175 ^{o}C, 5 MPa for 24 h. All the oxygen atoms in the condensation products were completely removed as no oxygenates was detected after hydrodeoxygenation (Figure S5). As a result, the yield of C_{23} alkanes reaches 84.8% from C_{23} oxygenate **1c** as analyzed by the internal standard method. It can be seen that the carbon distribution in the final alkanes (13.6% C_{13} alkanes, 10.9% C_{18} alkanes, 75.5% C_{23} alkanes) is similar to that in the condensation products input for hydrodeoxygenation, and only trace amount of n-1 alkanes (namely C_{12}, C_{17} and C_{22} alkanes) were found, indicating no obvious C-C cleavage was occur. This results clearly show that the hydrodeoxygenation reactivities of C_{18} and C_{23} oxygenates are very similar to that of C_{13} oxygenates and readily to be hydrodeoxygenated over Pd/$NbOPO_4$ under mild conditions, owing to the high efficiency of Pd/$NbOPO_4$ for total hydrodeoxygenation. More importantly, the catalyst shows a high reusability for the total hydrodeoxygenation of C_{23} precursor (Figure S6), presenting a promising industrial application.

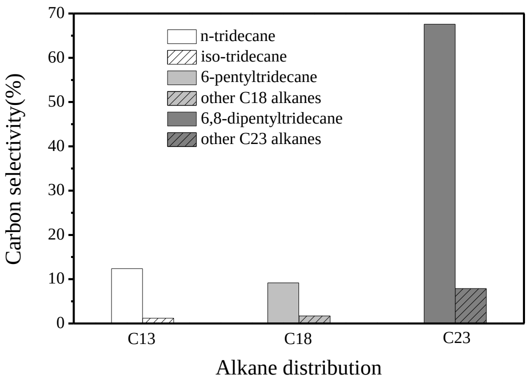


Figure 2. Hydrodeoxygenation results of aldol adducts obtained from the second aldol condensation over 4% Pd/$NbOPO_4$. Reaction condition: 0.166 g of aldol products, 0.1 g of catalyst, 6.5 g of cyclohexane, 175 ^{o}C, 5 MPa, 24 h.

Conclusions

In summary, we have demonstrated a selective catalytic synthetic route for the production of highly branched C_{23} alkanes for lubricant base oil component from biomass-derived furfural and acetone, through a tandem four-step (aldol condensation, selective hydrogenation, second aldol condensation and hydrodeoxygenation) process in 50.6% overall yield (97.9% × 72.8% × 83.8% × 84.8%). For aldol condensation of furfural with acetone, although homogeneous catalytic system was employed, almost quantitative conversion of furfural and acetone into C_{13} aldol adduct **1a** (>97% isolated yield) was achieved with high recyclability. For the selective hydrogenation of C_{13} aldol adduct to C_{13} ketone **1b**, Pd/γ-Al_2O_3 exhibits the best catalytic performance with 72.8% yield of C_{13} ketone **1b** when reaction at 130 ^oC and 5 MPa for 5 h. For second aldol condensation, 83.8% yield of C_{23} oxygenate **1c** was achieved from the condensation of C_{13} ketone **1b** with furfural in methanol at 50 ^oC for 20 h, with furfural/**1b** molar ratio being 8:1. Finally, 84.8% yield of high branched C_{23} alkanes was achieved from C_{23} oxygenate **1c** by the total hydrodeoxygenation over Pd/$NbOPO_4$ at 175 ^oC, 5 MPa H_2 for 24 h. This work opens a general strategy for the synthesis of high-quality base oil components for lubricant production from renewable biomass.

Experimental Section

Chemicals

$Pd(NO_3)_2$ and $Pt(NO_3)_2$ aqueous solution was purchased from Heraeus Materials Technology Shanghai Co., Ltd. $RuCl_3{\cdot}3H_2O$ was purchased from Aladdin Reagent Co.,Ltd. γ-Al_2O_3 was purchased from BASF Chemical Company. Active carbon was provided by SCM Industrial Chemical Co., Ltd. All other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. All purchased chemicals were of analytical grade and used without further purification.

Catalyst preparation

M/N(M=Pt, Pd, Ru, N=γ-Al_2O_3, C, SiO_2, ZrO_2) was prepared through incipient-wetness impregnation with a calculated amount of aqueous solutions of $Pt(NO_3)_2$, $Pd(NO_3)_2$, $RuCl_3$, respectively. After impregnation, the catalyst was dried at 100 ^oC for 12 h, followed by calcination at 450 ^oC for 3h with a heating rate of 2 $^oC{\cdot}min^{-1}$. $NbOPO_4$ was synthesized at pH 2 according to our previous literature.[17] SiO_2 and ZrO_2 were prepared through coprecipitation method.

Catalytic reaction and product analysis

The aldol condensation of furfural with acetone was carried out in a 400-mL beaker, covered with a black box to protect from light. Typically, Furfural (38.4 g), acetone (11.6 g), NaOH (3.0 g) and H_2O (150 mL) were put into the beaker with magnetic stirring. The reaction was then heated to 40 ^oC and kept for 5 h. After the reaction, the reactor was quenched in an ice/water bath for crystallization, after which the solid (**1a**) was filtered, washed with 0.5 M HCl aqueous solution and distilled water respectively, then dried at 50 ^oC for 12 h to give a highly pure yellow crystal (Figure S1a,b). The solid was then weighed to calculate the isolated yield, and analyzed the purity by H-NMR and GC-FID (Agilent 7890B) equipped with a HP-5 column. For the analysis of the filtrate, 5 mL filtrate was sampled and neutralize by 0.5 M HCl aqueous solution, which was then extracted by dichloromethane (5.0 mL × 2) and the organic phase was analyzed by GC-FID equipped with a HP-5 column. The alkaline filtrate can be reused for the next run by adding additional furfural and acetone. Typically, Furfural (38.4 g), acetone (11.6 g) and the alkaline filtrate of the prior run were put into the beaker and reaction for 5 h at 40 ^oC with magnetic stirring.

The selective hydrogenation of C_{13} adduct **1a** was conducted in a 50-mL Teflon-lined stainless-steel autoclave. In a typical run, **1a** (1.4g) and the catalyst (0.04g) were put into the autoclave (solvent free), the reactor was then sealed and flushed three times with H_2 before it was charged with the desired pressure (5 MPa). The reactor was then heated to a set temperature (70 ^oC) for a certain of time (5 h), it was quenched in an ice/water bath to stop the reaction immediately. The liquid mixture containing C_{13} ketones was separated from the catalyst by semipermeable membrane filtration to form a clear brown liquid (Figure S1c). For analysis, the products (0.10 g) were dissolved in ethanol (2.0 mL) and analyzed with GC-FID equipped with an HP-5 column with benzyl alcohol as the internal standard. The yields of products were calculated by using the equation: yield [%] = (moles of carbon in product)/ (moles of carbon in 1a) ×100%.

The aldol condensation of C_{13} ketone **1b** with furfural was carried out in a 25-mL round bottom flask. Typically, 0.1 g of the mixture of selective hydrogenation products (contains 72.8% **1b** (0.32 mmol), 13.5% **2g**, 12.2% **2h** and 1.5% of other C_{13} oxygenates), 0.25 g (2.56 mmol) of furfural, 3.33 g of methanol and 0.133 g of NaOH were added into the flask, which was then placed in an oil bath at 50 ^oC for 20 h. After reaction, the reaction was cooled down to room temperature. The methanol and furfural were rotary-evaporated before the products were washed with deionized water and extracted by dichloromethane (5.0 mL×2). After product analysis by GC-MS (Agilent 7890A-5975C), dichloromethane was removed by rotary-evaporated to give the second aldol adducts (Figure S1d) for hydrodeoxygenation.

The total hydrodeoxygenation of the second aldol adducts was carried out in a 50-mL Teflon-lined stainless-steel autoclave. Typically, 0.166 g of the mixture from second aldol condensation (18.0 wt% C_{13} oxygenates 10.8 wt% C_{18} oxygenate, 71.2 wt% C_{23} oxygenate) and 0.1 g of 4% Pd/$NbOPO_4$ were mixed with cyclohexane (6.5 g) in the autoclave. The reactor was then sealed, purged with H_2 for three times and charged to 5 MPa H_2 pressure. Then it was heated to 175 ^oC under magnetic stirring for 24 h. After the completion of the reaction, the reactor was quenched in a water bath to room temperature. The liquid solution was separated from the solid catalyst by centrifugation and analyzed qualitatively by GC-MS (Agilent 7890A-5975C) and quantitatively by GC-FID (Agilent 7890) with pentadecane as a internal standard. The yields of products were calculated by using the equation: yield [%] = (moles of carbon in C_{13}/C_{18}/C_{23} alkanes) / (moles of carbon in C_{13}/C_{18}/C_{23} oxygenates)×100%

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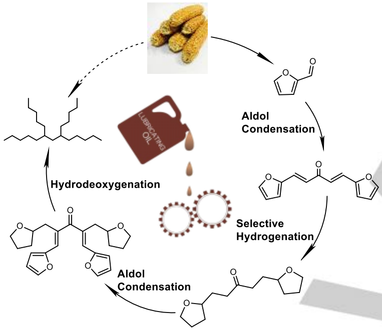
Entry for the Table of Contents

Layout 1:

FULL PAPER

Highly branched lubricant alkanes are not yet synthetically exploited from biomass. Here we describe a selective catalytic synthetic route for the production of highly branched C23 alkanes for lubricant base oil component from biomass-derived furfural and acetone, through a tandem four-step process, in an overall carbon yield of ca. 50%.



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Synthesis of renewable lubricant alkanes from biomass-derived platform chemicals