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Production of liquid hydrocarbon fuels with 3-pentanone and platform molecules derived from lignocellulose†

Tao Shen,[ab] Chenjie Zhu,*[abc] Chenglun Tang,[ab] Zhi Cao,[ab] Linfeng Wang,[d] Kai Guo[a] and Hanjie Ying*[abc]

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Diesel or jet fuel range C_{10}–C_{17} branched and cyclic alkanes were produced by reaction of 3-pentanone derived from lactic acid with bio-based aldehydes through aldol condensation followed by hydrodeoxygenation. DBU (1,8-diazabicycloundec-7-ene) was identified as an efficient catalyst for the aldol reaction of 3-pentanone with furan based aldehydes, and the selectivity of single or double aldol condensation product could be easily controlled by adjusting the reaction temperature. For the reaction with aromatic aldehydes, aluminium phosphate demonstrated a higher catalytic activity than DBU and mechanisms were proposed for the difference in the catalytic activity. The final hydrodeoxygenation step could be achieved by using a simple Pd/C + H-beta zeolite system, excellent selectivity was observed under the present system, the clean formation of hydrocarbons with a narrow distribution of alkanes occurred in most cases.

1 Introduction

Due to the depleting fossil fuel reserves and increasing greenhouse gas emission, the exploration of feasible pathways for the conversion of abundant and renewable biomass into clean fuels has drawn considerable attention.[1–3] In this sense, lignocellulosic biomass is a promising candidate due to it being an abundant and carbon-neutral energy resource.[4,5] Catalytic transformation of platform molecules through an oxygen removal process (*e.g.* dehydration, hydrogenation, hydrogenolysis, decarbonylation) or in some cases along with an increase in the length of the carbon chain *via* C–C coupling reactions (*e.g.* aldol condensation, hydroxyalkylation, ketonization, oligomerization) is an important route to convert lignocellulose into liquid hydrocarbon fuels.[6,7] To meet the number of carbon atoms for the target fuel range, such as diesel and jet fuels, various reactive intermediates such as acetone,[8–11] hydroxyacetone or dihydroxyacetone,[12,13] mesityl oxide,[14] methyl isobutyl ketone,[15] and butanal[16–18] have been employed as synthons for the carbon chain elongation. This route is especially important and meaningful when the synthon is derived from biomass. Recently, we reported the use of acetoin as a novel C_4 building block for the production of C_9–C_{14} liquid hydrocarbon fuels.[19] However, this method suffers from that only straight alkanes can be obtained after the reaction with lignocellulose derived aldehydes. Compared to branched alkanes, these straight alkanes have lower octane numbers and higher freezing points, and cannot be directly used as jet fuel without hydroisomerization. Furthermore, the production capacity of acetoin is relatively small compared to the other bulk chemicals.

On the other hand, lactic acid is the most widely occurring carboxylic acid in nature. Annual production reaches 120 000 tons per year, and 90% of which is produced by bacterial fermentation of biomass sugars.[20] It possesses a rich chemistry due to its two functional groups (adjacent hydroxyl and carboxylic groups), numerous transformations of lactic acid into valuable chemicals such as acetaldehyde *via* decarbonylation, acrylic acid *via* dehydration, 2,3-pentanedione *via* condensation, polylactic acid *via* self-esterification-polymerization, propanoic acid *via* reduction, and 3-pentanone *via* reduction-ketonization has been reported.[21] Among them, 3-pentanone is a potential bio-based C_5 building block for the synthesis of renewable liquid hydrocarbon fuels due to it possesses ideal carbon number and α-hydrogen atoms. In the recent work of Zhang's group,[22] it was suggested that single condensation product C_{10} fuel precursor 1-(furan-2-yl)-2-methylpent-1-en-3-one **1a** (generated by the condensation of one furfural molecule and one 3-pentanone molecule) could be obtained through the aldol condensation of furfural and 3-pentanone using CaO as a solid base catalyst (Scheme 1). However, this method still

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[a] *College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing, China. E-mail: zhucj@njtech.edu.cn; yinghanjie@njtech.edu.cn; Tel: +86 25 58139389*

[b] *National Engineering Technique Research Center for Biotechnology, Nanjing, China*

[c] *Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), China*

[d] *State Key Laboratory of Motor Vehicle Biofuel Technology, Nanyang, China*

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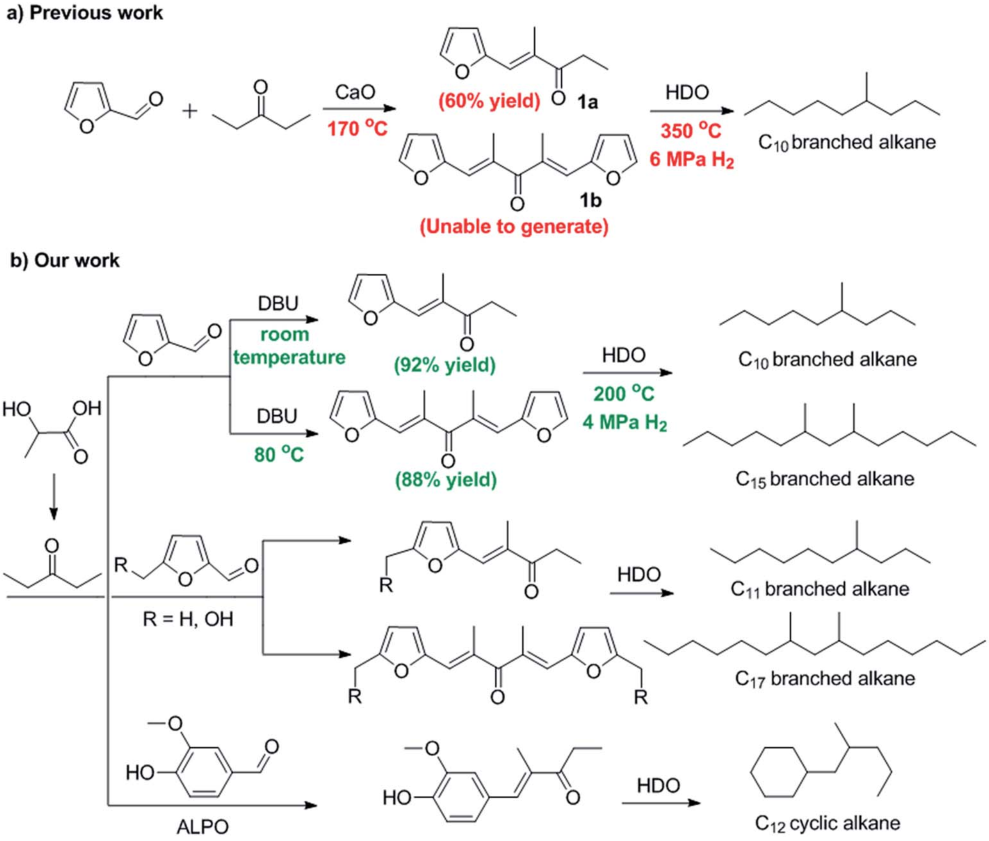


Scheme 1 (a) Previous work *versus* (b) our new protocol for the synthesis of liquid alkanes using 3-pentanone as a bio-based synthon.

has some shortcomings: (i) double condensation product C_{15} precursor 1,5-di(furan-2-yl)-2,4-dimethylpenta-1,4-dien-3-one **2a** (generated by the condensation of two furfural molecules and one 3-pentanone molecule) cannot be synthesized through this method; (ii) low yield of C_{10} precursor (60%) was achieved due to the adsorption of furfural on the surface of CaO and other side reactions; (iii) harsh reaction condition, the reaction need to carried out at high temperature (443 K). The poor catalytic efficiency of CaO as well as recent advances in C–C coupling reactions[23] prompted us to reconsider the solid base catalyst and provided an opportunity of finding a more reactive catalyst. Herein, we report the highly efficient synthesis of C_{10}–C_{17} branched and cyclic alkanes from the reaction of 3-pentanone with lignocellulose derived platform molecules (Scheme 1).

2 Experimental

Aldol condensation of 3-pentanone with furan aldehyde

For single condensation product: to a solution of 3-pentanone (10 mmol) and furan aldehyde (10 mmol) was added DBU (1 mmol), the mixture was stirred at room temperature under solvent-free condition; for double condensation product: to a solution of 3-pentanone (10 mmol) and furan aldehyde (25 mmol) was added DBU (3 mmol), the mixture was stirred at 80 °C under solvent-free condition. After completion, the mixture was diluted with EtOAc, the obtained organic layer was evaporated and purified by column chromatography to provide the analytically pure product for further HDO.

Aldol condensation of 3-pentanone with vanillin

To a solution of 3-pentanone (20 mmol) and vanillin (20 mmol) was added amorphous aluminium phosphate (0.4 g). The mixture was stirred at 120 °C under solvent-free condition for 12 h. After completion, the mixture was diluted with EtOAc and ALPO was removed by filtration. The obtained organic layer was evaporated and purified by column chromatography to provide the analytically pure product for further HDO.

Hydrodeoxygenation (HDO)

Typically, **2a** (1,5-di(furan-2-yl)-2,4-dimethylpenta-1,4-dien-3-one, 2.5 mmol) was dissolved in 25 mL distilled water and transferred to a 100 mL Parr pressure reactor. To this reactor was added Pd/C (5 wt%, 0.25 g) and H-beta zeolite (0.25 g). The reactor was purged thrice with nitrogen and charged to 4 MPa H_2. After that, the reactor was heated to 200 °C under vigorous stirring for 8 h. After the system reached to room temperature, the gas was collected in a gas cylinder of known volume and the pressure of the gas cylinder was adjusted to 1 atm using high purity nitrogen as a makeup gas. The gaseous products were analyzed by GC using methanizer (for CO and CO_2) and TCD analyzer (for other gaseous hydrocarbons), and the gas overall yield was determined. Then, the catalysts were removed by centrifugation, and the liquid solution was extracted with EtOAc and analyzed by GC-MS. Alkane selectivity was reported based on the percentage of peak areas measured by GC. Total organic carbon (TOC) analysis was performed on final concentrated liquid organic products to quantify the total carbon present and calibrate the GC for reaction products.

3 Results and discussion

Aldol condensation of 3-pentanone with furfural

Inspired by the pioneering work of Dumesic and Huber group,[8–10] initial experiments for the aldol condensation of furfural and 3-pentanone was first carried out using NaOH as a catalyst, and the molar ratio of furfural to 3-pentanone was kept constant at 2. According to the NMR and GC-MS spectrum (Fig. S1 and S8†), the single condensation product **1a** was identified as the main product, only a small quantity of double condensation product C_{15} oxygenate **2a** (<5%) was detected in the reaction mixture. Unfortunately, further optimization about the amount of NaOH, reaction temperature, time, or using biphasic system did not shown any improvement for the yield of **2a**. This result is quite different from previously report about aldol condensation reaction between furfural with acetone,[8–11] which probably due to the lower reactivity of α-carbon atoms in 3-pentanone molecule (caused by the steric hindrance and electron donating properties of the methyl groups attached to α-carbon atoms of 3-pentanone). Under such strong basic condition, other side reactions such as Cannizzaro reaction, radical polymerization, resinification of furfural, and Michael addition to the formed enone may also happened during the reaction,[24,25] resulting in generation of some unfavorable polymers. The use of other inorganic base such as Na_2CO_3 also did not show any improvement for the present reaction.[26]

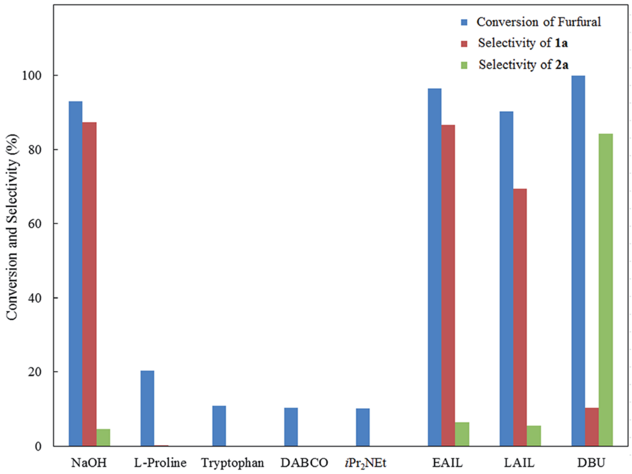


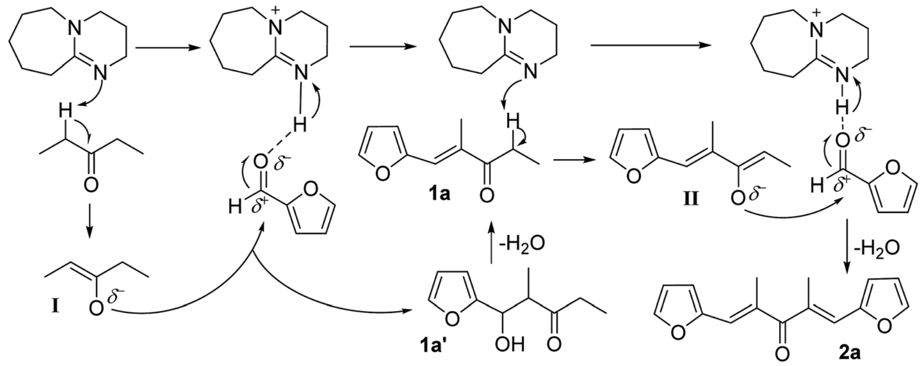
Fig. 1 Results of the aldol condensation between of 3-pentanone with furfural over different catalysts (for detailed experimental protocols, see the ESI†).

In order to solve the selectivity issue and improve the yield of the double condensation product **2a**, catalysts including organocatalysts, and task-specific ionic liquids were tested for the reaction (Fig. 1). Amine-based organocatalysts such as *i*Pr_2NEt, L-proline, tryptophan, and 1,4-diazabicyclo[2.2.2]octane (DABCO), failed to catalyze this reaction. The task-specific ionic liquid catalysts $[H_3N^+–CH_2–CH_2–OH][CH_3COO^-]$ (EAIL) and $[H_3N^+–CH_2–CH_2–OH][CH_3CH(OH)COO^-]$ (LAIL), which were previously efficient catalysts for the aldol reaction,[19] were also only able to get the single condensation product **1a**. To our delight, DBU (1,8-diazabicycloundec-7-ene) exhibited excellent selectivity towards to double condensation product **2a** (Fig. S9†). Encouraged by this result, further optimization of reaction using DBU as a catalyst were performed (Table 1). The results show that the yield of **2a** increases from 76% to 91% as the furfural/3-pentanone molar ratio increases from 2 to 3 (Table 1, entries 1–3), which may be caused by the partial of furfural was consumed from negative side reactions during the process. With regard to the catalyst dosage, it was possible to decrease the amount of DBU to as low as 10 mol%, albeit a longer reaction time was required (Table 1, entry 5). It is noteworthy that a strong effect of temperature was observed on the product distribution. The yield of **2a** increases up to 90% when the reaction was performed at room temperature even at the molar ratio of furfural/3-pentanone is 2.5 (Table 1, entry 6), which means the selectivity of this reaction is thermodynamic control *versus* kinetic control. This finding is very meaningful due to it offers a useful method to tune the ultimate desired composition of single or double condensation product. To check this point, confirmatory experiment was carried out at the molar ratio of furfural/3-pentanone is 1 at room temperature, as

Table 1 Optimization of aldol condensation of furfural with 3-pentanone catalyzed by DBU

Entry	Furfural/3-pentanone (molar ratio)	DBU loading[a] (mol%)	*T* (°C)	Time (h)	Yield[a] (%) **1a**	Yield[a] (%) **2a**
1	2.0	30	80	12	16	76
2	2.5	30	80	10	8	88
3	3.0	30	80	10	7	91
4	2.5	20	80	14	10	86
5	2.5	10	80	22	9	84
6	2.5	10	r.t.	16	90	7
7	1	10	r.t.	48	92	3

[a] With respect to the limiting reactant 3-pentanone.



Scheme 2 Proposed pathway for the formation of **2a** catalyzed by DBU.

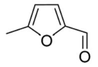
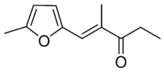
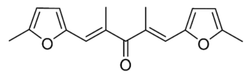
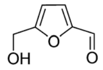
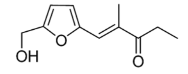
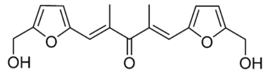
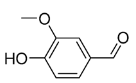
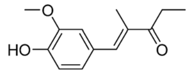
expected, an excellent selectivity was achieved using this method even in the condition of prolonging the reaction time up to 48 h, and the desired single condensation product **1a** can be obtained in 92% yield (Fig. S2 and S9†).

A plausible mechanism for the formation of **2a** is depicted in Scheme 2. The reaction begins with generation of enolate **I** by DBU induced the deprotonation of 3-pentanone, which behaves as a carbonyl donor to attack furfural, whereby providing the single condensation product **1a** *via* dehydration of **1a**′. The protonated DBU-H derived from the formation of enolate **I** can activate the furfural by increasing the positive charge on the corresponding carbon atom through hydrogen-bonding network to promote the above process. The regenerated DBU then react with **1a** to produce enolate **II**, which undergoes similar reaction process to afford the double condensation product **2a.** As can be seen, DUB plays an important role in the reaction, which not only facilitates the departure of α-H of 3-pentanone to form the enolate intermediate, but also activates the furfural through forming hydrogen-bonding network.

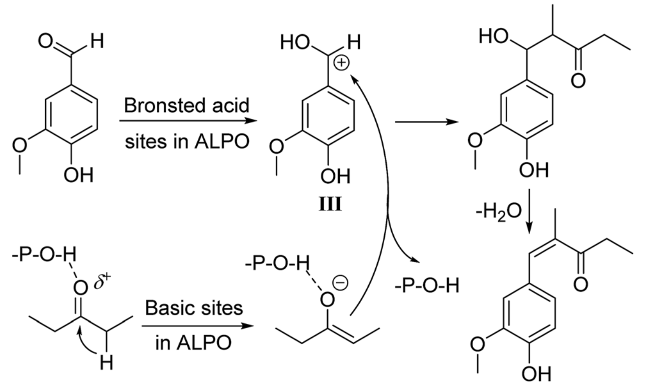
Aldol condensation of 3-pentanone with other aldehydes derived from lignocellulose

With the aim to develop and define the scope and limitation of the present catalytic system, this procedure was then extended for the reaction of 3-pentanone with other aldehydes, which including 5-methylfurfural (5-MF), 5-hydroxymethylfurfural (HMF) derived from cellulose,[27,28] and vanillin derived from

Table 2 The reaction of 3-pentanone with bio-based aldehydes

Entry	Substrate	Product	T (°C)	Time (h)	Yield (%)
1[a]		 **3a**	r.t.	24	90
2[b]		 **4a**	80	8	85
3[a]		 **5a**	r.t.	24	87
4[b]		 **6a**	80	10	73
5[c]		 **7a**	120	12	64

[a] Molar ratio of aldehyde/3-pentanone is 1. [b] Molar ratio of aldehyde/3-pentanone is 2.5. [c] Reaction were catalyzed by ALPO under solvent-free condition.



Scheme 3 Tentative mechanism for the reaction of 3-pentanone with vanillin catalyzed by ALPO.

lignin.[29] As shown in Table 2, DBU works well for the reaction with furan aldehydes, 5-MF and HMF underwent smooth transformation to afford their corresponding C_{11} single condensation product or C_{17} double condensation products in moderate to excellent yields (Table 2, entries 1–4). However, when the substrate changed to aromatic aldehyde, such as vanillin, and the corresponding condensation product **7a** that could be expected in analogy with furan aldehyde and 3-pentanone was not detected after the reaction, the low activity of vanillin was considered to be originated from the electron rich property of aromatic ring, and the activation of the carbonyl group in vanillin only through hydrogen-bonding network induced by $DBUH^+$ is not sufficient to trigger the reaction. After further screening of catalysts and optimizing the procedure, we found that replacing DBU with amorphous aluminium phosphate (ALPO) and increasing the reaction temperature significantly promoted the reaction, C_{13} single condensation product could be obtained over 10 wt% of ALPO after reacting at 120 °C for 12 h under solvent free condition (Table 2, entry 5). Unfortunately, further optimization in order to obtain the C_{21} double condensation product was unsuccessful. Although, so far, we cannot be certain of the actual role of ALPO in this reaction, on the basis of the previous study,[30] we believe that the superior behavior of ALPO over DBU catalyst is due to a combined acid–base synergistic catalysis effect, especially for the Bronsted acid sites on the surface of ALPO (–POH group), which could interact with the carbonyl group of vanillin to produce the corresponding carbocation **III** (Scheme 3). Furthermore, the Bronsted acid sites could also enhance the acidity of α-H by interacting with the carbonyl group of 3-pentanone, which makes it more easier to react with the Lewis basic sites of ALPO to generate a carbanion species. This should favor the attack of **III** derived from the activated vanillin. To check this point, verification experiment were performed using Na-exchanged ALPO, in which the acidity was neutralized by treating ALPO with sodium acetate, and the result showed that no aldol reaction was occurred using Na-exchanged ALPO, which provided a strong support towards this mechanism.

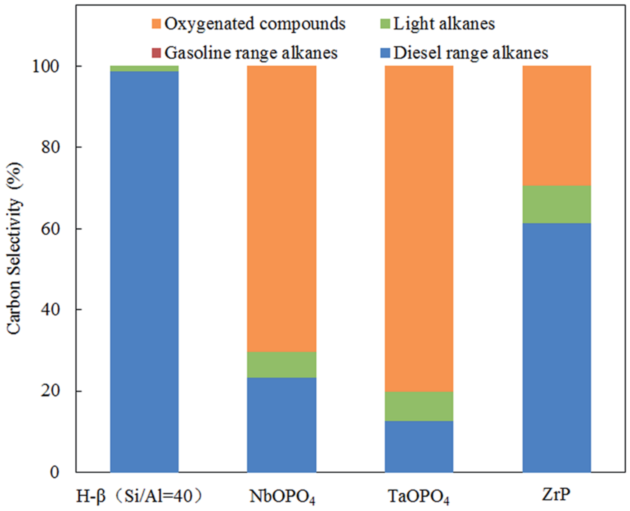
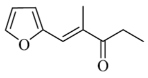
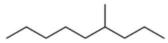
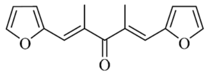
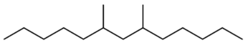
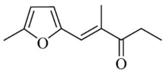
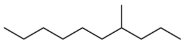
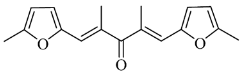
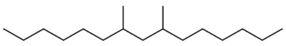
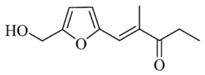
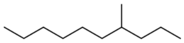
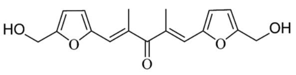
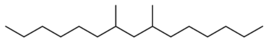
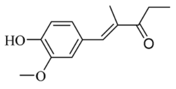
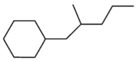


Fig. 2 Carbon selectivity of different products from the HDO of **3a** over Pd/C and different solid acid catalysts. Reaction conditions: Pd/C (5 wt%, 0.25 g) and solid acid (0.25 g), 200 °C, 4 MPa H_2, 8 h. The diesel range alkanes, gasoline range alkanes and light alkanes account for C_9–C_{18}, C_5–C_8 and C_1–C_4 alkanes, respectively.

Table 3 The structures of the fuel precursors and their theoretical HDO products

Fuel precursors	Theoretical alkane product
 **1a**	 $C_{10}H_{22}$ branched alkane **1b**
 **2a**	 **2b** $C_{15}H_{32}$ branched alkane
 **3a**	 $C_{11}H_{24}$ branched alkane **3b**
 **4a**	 $C_{17}H_{36}$ branched alkane **4b**
 **5a**	 $C_{11}H_{24}$ branched alkane **5b**
 **6a**	 $C_{17}H_{36}$ branched alkane **6b**
 **7a**	 $C_{12}H_{24}$ cyclic alkane **7b**

Hydrodeoxygenation

As the final aim of this work, the direct hydrodeoxygenation of these fuel precursors into alkanes were performed in batch reactor. The aldol condensation product from 5-MF and 3-pentanone **3a** was first chosen as a model fuel precursor for this study. In previous works, it was found that supported Pd catalysts were efficient for the HDO of oxygenate,[19,31] thus, this catalyst was also tested for the present study. According to the previous research, the dehydration over acid sites followed by the hydrogenation over metal sites is the major pathway for the C–O cleavage reaction,[32,33] thus, several solid acid such as $NbOPO_4$, $TaOPO_4$, and ZrP were selected for the purpose of comparison.[34–38] As shown in Fig. 2, $NbOPO_4$, $TaOPO_4$ and ZrP system tend to have a more selectivity to produce oxygenated compounds (Fig. S10†). Among them, H-β + Pd/C system exhibited excellent catalytic performance and highest selectivity to alkane. The almost clean formation of theoretical alkane product $C_{11}H_{24}$ under mild conditions (200 °C and 4 MP H_2 pressure) is remarkable (Fig. S11†). Hence, this procedure was further extended for the HDO of other fuel precursors to check its applicability (Table 3). As shown in Fig. 3, most substrates underwent smooth transformation to afford their corresponding theoretical alkane products in moderate to excellent yields, and the present catalytic system showed high selectivity for the production of diesel range alkanes. In all cases, these fuel precursors were completely converted to alkanes and no or a negligible amount of oxygenates were detected based on GC-MS analysis. The carbon balance was almost quantitative for most of the HDO reactions, >90% of the carbon was in the liquid organic products according to the TOC analysis. It is noteworthy that excellent selectivity was observed under the present system, the clean formation of hydrocarbons with a narrow distribution of alkanes was occurred for most cases (Fig. S11–S14†). Cyclic alkanes can also be obtained in high yield though this effective catalytic system (Fig. S15†), which is the second most abundant component required in the commercial and military jet fuels with the mass percent of 20–50 wt%.[39,40] Compared to straight alkanes, cyclic alkanes have higher densities and volumetric heating values due to the strong ring strain.[41,42]

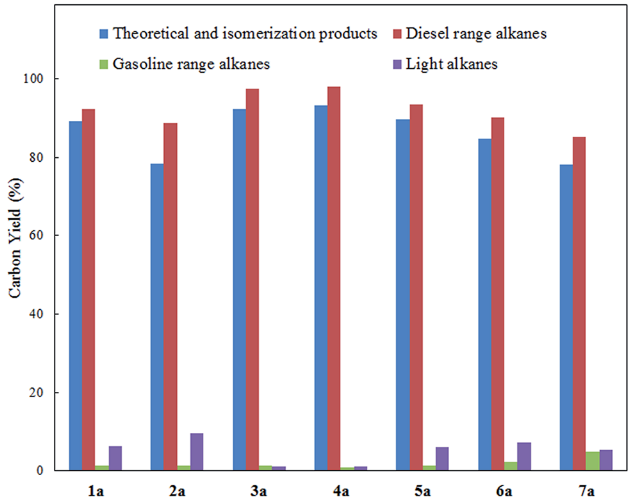


Fig. 3 Carbon yield of different alkanes from the HDO of different precursors over the Pd/C + H-β system. The diesel range alkanes, gasoline range alkanes and light alkanes account for C_9–C_{18}, C_5–C_8 and C_1–C_4 alkanes, respectively.

4 Conclusions

In conclusion, a novel C_5 building block 3-pentanone derived from lactic acid has been used as a bio-based synthon for the production of liquid hydrocarbon fuels. It was found that 1,8-diazabicycloundec-7-ene and aluminium phosphate were efficient catalysts for the aldol condensation of 3-pentanone with furan based aldehyde and aromatic aldehyde, respectively. A series of well-defined diesel or jet fuel range C_{10}–C_{17} branched or cyclic alkanes could be produced in excellent yields under Pd/C + H-beta zeolite catalytic system through hydrodeoxygenation.

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