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ARTICLE

## Production of liquid hydrocarbon fuels with acetoin and platform molecules derived from lignocellulose

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Acetoin, a novel C<sub>4</sub> platform molecule derived from new ABE (acetoin-butanol-ethanol) type fermentation via metabolic engineering, was used for the first time as a bio-based building block for the production of liquid hydrocarbon fuels. A series of diesel or jet fuel range C<sub>9</sub>-C<sub>14</sub> straight, branched, or cyclic alkanes were produced in excellent yields by means of C-C coupling followed by hydrodeoxygenation reactions. The hydroxyalkylation/alkylation of acetoin with 2-methylfuran was investigated over a series of solid acid catalysts. Among the investigated candidates, zirconia supported trifluoromethanesulfonic acid showed the highest activity and stability. In the aldol condensation step, basic ionic liquid [H<sub>3</sub>N<sup>+</sup>-CH<sub>2</sub>-CH<sub>2</sub>-OH][CH<sub>3</sub>COO<sup>-</sup>] was identified as an efficient and recyclable catalyst for the reactions of acetoin with furan based aldehydes. The scope of the process has also been studied by reacting acetoin with other aldehydes, and it was found that abnormal condensation products were formed from the reactions of acetoin with aromatic aldehydes through aldol condensation - pinacol rearrangement route when amorphous aluminium phosphate was used as a catalyst. And the final hydrodeoxygenation step could be achieved by using simple and handy Pd/C + H-beta zeolite system, no or a negligible amount of oxygenates were observed after the reaction. Excellent selectivity was also observed under the present system, the clean formation of hydrocarbons with a narrow distribution of alkanes was occurred for 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 to supplement or gradually replace the petroleum-based industry is highly desirable.<sup>1-7</sup> In this sense, lignocellulosic biomass is a promising candidate due to it is an abundant and carbon-neutral energy resource.<sup>8-12</sup> Generally, there are several major strategies to convert lignocellulose into liquid hydrocarbon fuels: fast pyrolysis,<sup>13-16</sup> liquefaction,<sup>17-19</sup> and gasification followed by Fischer-Tropsch synthesis.<sup>20-22</sup> These routes usually deal with whole lignocellulose leading to upgradeable platforms such as bio-oil or syngas. Another important route involves depolymerization of lignocellulose to yield platform molecules such as furfural, hydroxymethylfurfural (HMF), or levulinic acid, *etc.* Catalytic transformation of platform molecules for the production of liquid hydrocarbon fuels can be obtained by oxygen removal process (*e.g.* dehydration, hydrogenation, hydrogenolysis, decarbonylation) or in some cases along with increase the length of carbon chain *via* C-C

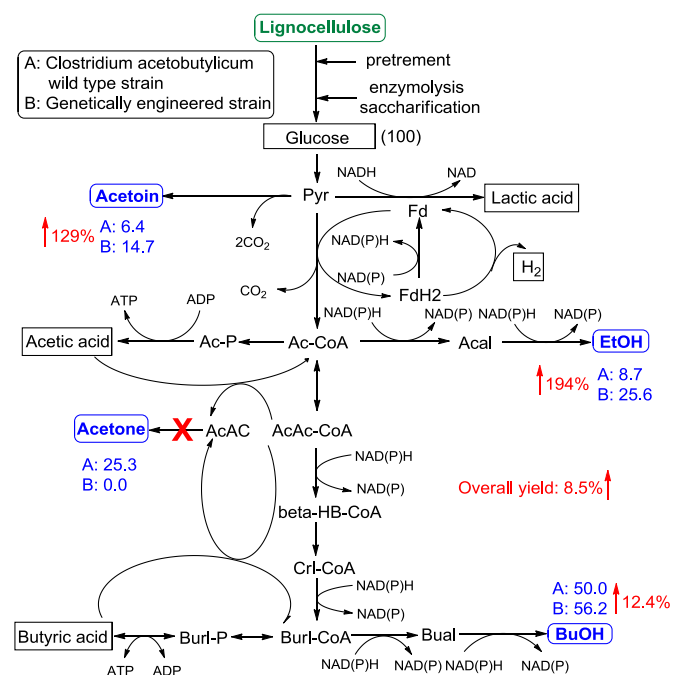
coupling reactions (*e.g.* aldol condensation, hydroxyalkylation, ketonization, oligomerization) with reactive intermediates.<sup>23,24</sup> The latter method is a very promising way to go, because it offers pathways for the desired chain extensions to meet the number of carbon atoms for the aimed fuel range, such as diesel and jet fuels, which are two types of fuel in greatest demand and currently sourced mainly from petroleum. Various reactive intermediates such as acetone,<sup>25-28</sup> 2-hexanone,<sup>29</sup> hydroxyacetone or dihydroxyacetone,<sup>30,31</sup> mesityl oxide,<sup>32</sup> methyl isobutyl ketone (MIBK),<sup>33</sup> propanal,<sup>34</sup> butanal,<sup>35-37</sup> and levulinic acid<sup>38</sup> have been employed as synthons for the synthesis of liquid hydrocarbon fuels. This route is especially important and meaningful when the synthon is derived from biomass.

On the other hand, recent advances in metabolic engineering have enabled the biological production of transportation fuels via non-fermentative pathway,<sup>39,40</sup> however, these processes usually suffer from low yields and titers. Alternatively, sugar molecules derived from cellulose or hemicellulose can be fermented into hydrocarbons by microorganisms or genetically altered microorganisms.<sup>41-43</sup> For example, acetone-butanol-ethanol (ABE) fermentation is one of the oldest known industrial processes with a history of more than 100 years. The typical mass ratio of acetone: butanol: ethanol in the fermentation broth is 3:6:1 (2.3: 3.7: 1 in molar ratio). However, the economics of this process was hampered by a number of bottlenecks such as co-production of low value product acetone and high cost of separation. Moreover, high acetone levels in the fermentation broth result in serious mass loss

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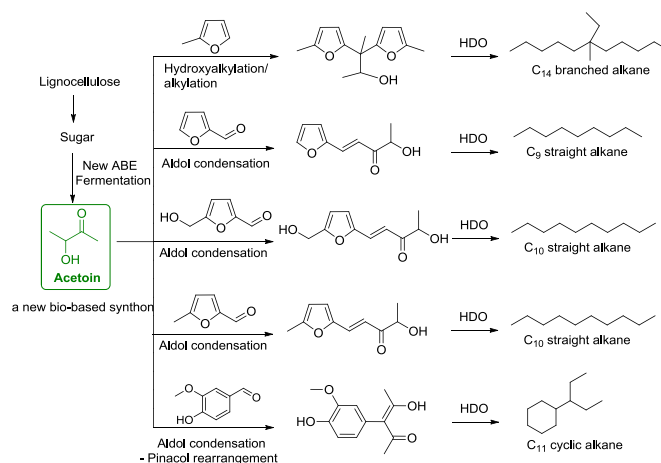
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**Fig. 1** Metabolic flux distributions in the *Clostridium acetobutylicum* wild-type strain and the genetically engineered strains. Flux for glucose uptake was set to 100 mol and the other fluxes were determined as relative molar flux normalized to the flux for glucose uptake.

of acetone due to its high volatility, thus leading to a lower solvent yield.<sup>44</sup> Recently, we used metabolic engineering strategies to replace the volatile  $C_3$  compound acetone with non-volatile value-added  $C_4$  compound acetoin (3-hydroxy-2-butanone) during ABE fermentation.<sup>45</sup> By overexpressing the  $\alpha$ -acetolactate decarboxylase gene *alsD* in *Clostridium acetobutylicum*, the acetoin yield was markedly increased while acetone formation was reduced. Subsequent disruption of *adc* gene effectively abolished acetone formation and further increased acetoin yield (Fig. 1). Furthermore, the removal and separation of ABE products from the fermentation broth was achieved based on adsorption methodology using hyper-cross-linked resin.<sup>46,47</sup> Finally, the *alsD*-overexpressing *adc* mutant generated butanol (13.8 g/L), ethanol (3.9 g/L), and acetoin (4.3 g/L), but no acetone. When one glucose molecule is converted to the  $C_4$  compound acetoin (molecular weight, 88) instead of the  $C_3$  compound acetone (molecular weight, 58), both mass yield and atom economy were improved. Butanol and ethanol produced in the present system can be directly used as renewable transportation fuels for blending with gasoline.

Acetoin, a novel product formed from the present new type of ABE fermentation (Acetoin-Butanol-Ethanol) system, is amenable to C-C bond formation with other platform molecules due to it possesses  $\alpha$ -hydrogen atoms. We were interested in the exploration of using acetoin as a potential bio-based  $C_4$  building block for the synthesis of renewable liquid hydrocarbon fuels. To the best of our knowledge, there is no report on the production of diesel or jet range alkanes that use acetoin as a platform molecule. Herein, we report the highly efficient synthesis of  $C_9$ - $C_{14}$  straight, branched, or cyclic alkanes from the reaction of acetoin with lignocellulose derived platform molecules (Scheme 1).

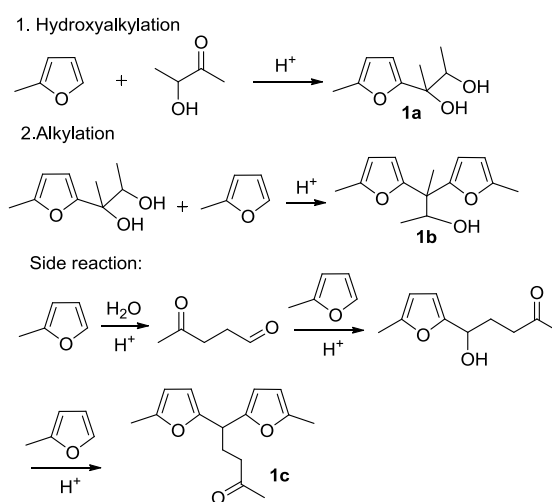


**Scheme 1** The protocol for the synthesis of diesel or jet range alkanes using acetoin as a bio-based synthon.

## 2. Results and discussion

### 2.1 Hydroxyalkylation and alkylation of acetoin with 2-methylfuran

Inspired by the pioneering work of Corma *et al.*,<sup>35,36</sup> initial experiments were carried out using 2-methylfuran (2-MF) as a model substrate, which can be obtained by the selective hydrogenation of furfural.<sup>48</sup> The HAA of acetoin and 2-MF was first carried out using *para*-toluenesulfonic acid as a catalyst under solvent-free condition, **1b** was obtained as the main product in 82% yield (Scheme 2 and Figure S1), **1a** was not detected in the reaction mixture, which can be explained by the much higher rate of the alkylation reaction than the hydroxyalkylation reaction, this result was consistent with that found using acetone as the substrate.<sup>49</sup> Under the same conditions, only 47% yield of **1b** was obtained by using  $H_2SO_4$  as a catalyst, besides, 18% yield of **1c** was obtained due to the trimerization of 2-MF, and which is also a suitable diesel precursor.<sup>36</sup>



**Scheme 2** Pathway for the reaction between acetoin with 2-MF.

However, taking into account the operation safety, equipment corrosion, the cost of separation and waste disposal, solid acid is preferable for use in the reaction. Therefore, a series of solid acid catalysts were tested for the reaction, which include zeolites, heteropolyacids, acid resins, and functionalized solid acids. Using zeolite catalysts for the reaction were unsuccessful, the yields of **1b** were either much lower or null (Table 1, entries 1-4), increased the Si/Al ratio to enhance the acid strength of the acid sites in the H-Y zeolite did not show any improvement (Table 1, entries 2 and 3).<sup>50</sup> The use of heteropolyacids such as H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>, H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> or Cs<sub>2</sub>H<sub>2</sub>PMo<sub>11</sub>VO<sub>40</sub> as catalysts was also unsatisfactory due to the poor reaction selectivity caused by over-alkylation (Table 1, entries 5-7).

In the previous work of Zhang's group,<sup>31,32,37,49</sup> Nafion-212 film was found to be an efficient solid acid catalyst for the HAA reaction. However, the high cost and inconvenient operation of Nafion-212 film as well as recent significant advances in designing new solid acids for biomass conversion prompted us to develop alternative catalyst for this reaction.<sup>51</sup> According to the previous research results,<sup>52</sup> the HAA reaction is sensitive to the acid strength of the catalyst, strong acid is more active than weak acid for this reaction. Trifluoromethanesulfonic acid (CF<sub>3</sub>SO<sub>3</sub>H) is known to be a strong acid ( $H_0 = -13$ ),<sup>53</sup> and has been used as a homogeneous acid catalyst for a variety of chemical transformations due to its extremely high thermal and chemical stability.<sup>54,55</sup> However, the direct use of CF<sub>3</sub>SO<sub>3</sub>H as a catalyst in the present HAA process led to a violent reaction, the formation of black tar was observed during the reaction (Figure S2). We envisaged that immobilization of CF<sub>3</sub>SO<sub>3</sub>H would properly address this problem by providing a readily recyclable catalyst with reasonably catalytic activity. Recently, zirconium compounds have drawn considerable attention for various organic transformations, and the search for zirconium oxide as supports for different catalysts has also received keen interest in the past decade.<sup>56,57</sup> Thus, zirconia supported trifluoromethanesulfonic acid (TFA-ZrO<sub>2</sub>) was prepared and tested

for the reaction, we were very pleased to find that noticeable conversion and excellent selectivity was achieved in the case of using TFA-ZrO<sub>2</sub> as a catalyst (Figure S3), the desired product **1b** was isolated in 93% yield (Table 1, entry 9). In the control experiments, there was no product formation when using ZrO<sub>2</sub> as a catalyst (Table 1, entry 10).

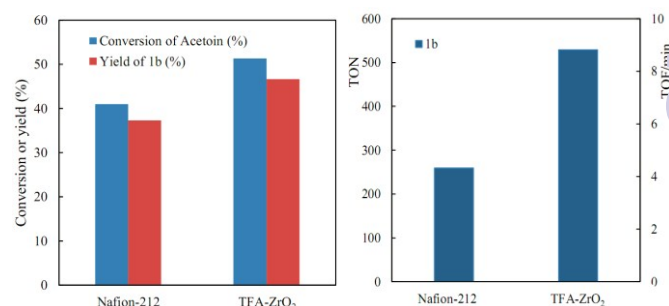
Encouraged by these results and in order to search for the optimum reaction conditions, we then screened a variety of parameters of this reaction, such as different loading of TFA over zirconia support (5 to 30 wt%, designated as TFA<sub>5~30</sub>-ZrO<sub>2</sub>), dosage of catalyst, reaction temperature and reaction time (Table S1). Under optimum conditions, 100% conversion of acetoin and 96% yield of **1b** were obtained over 0.1 g TFA<sub>20</sub>-ZrO<sub>2</sub> after reacting at 323 K for 1 h under solvent free condition. It is noteworthy that the reaction can also proceed smoothly even at room temperature, albeit a longer reaction time was required (Table 1, entry 11). Under the same reaction conditions, the yield of **1b** was much lower when using Nafion-212 resin as a catalyst (Table 1, entry 12), which clearly demonstrates the superior catalytic activity of TFA-ZrO<sub>2</sub>. According to the yield of **1b** over TFA-ZrO<sub>2</sub> and Nafion-212 at low catalyst dosage (Fig. 2a) and the acid amount measured by NH<sub>3</sub> chemisorption (0.56 mmol g<sup>-1</sup> for TFA-ZrO<sub>2</sub>) or provided by supplier (1.1 mmol g<sup>-1</sup> for Nafion-212), we also calculated the TONs and TOFs for the conversion of 2-MF to **1b** over these two catalysts (Fig. 2b). As shown in the Figure 2b, TFA-ZrO<sub>2</sub> showed much higher catalytic efficiency for the alkylation of 2-MF with acetoin compared to the Nafion-212 catalyst.

The reusability of the catalyst TFA-ZrO<sub>2</sub> was also investigated by the HAA of acetoin with 2-MF. As can be seen in Figure S9, the catalyst could be recycled for 5 times with no apparent loss of activity, however, the acetoin conversion decreased by 14% and the yield of **1b** decreased by 22% for the recycle runs 6, the decrease of the activity of TFA-ZrO<sub>2</sub> may be due to the adsorption of reactants and HAA products on the strong acid sites of the catalyst. After washed by MeOH and calcinated at 473 K for 6 h, the acetoin conversion and the yield of **1b** returned to the original levels (Figure S9, run 7). The recovery of the activity means that the irreversible poisoning did not take place in the catalyst. Elemental analysis showed that the sulfur content of the catalyst fell only a little from 4.88 to 4.79 after seven reaction cycles. According to the high activity and stability of TFA-ZrO<sub>2</sub>, it can be considered as a promising catalyst for further study.

**Table 1** Results of the HAA of acetoin with 2-MF<sup>a</sup>

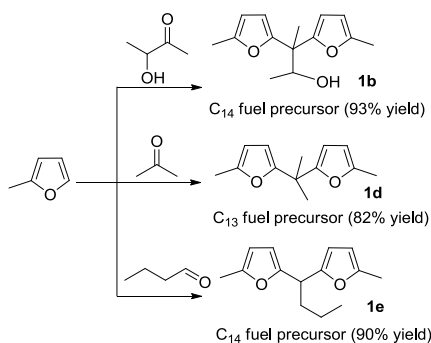
Entry	Catalyst	Conv. (%) <sup>b</sup>	Product selectivity <sup>c</sup> (%)		
			<b>1b</b>	<b>1c</b>	other
1	H-β (Si/Al = 40)	4	--	--	100
2	H-Y (Si/Al = 5)	30	33	45	22
3	H-Y (Si/Al = 20)	34	28	35	37
4	H-ZSM-5 (Si/Al = 38)	13	57	--	43
5	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	87	19	8	73
6	H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub>	82	23	11	66
7	Cs <sub>2</sub> H <sub>2</sub> PMo <sub>11</sub> VO <sub>40</sub>	90	20	16	64
8	Amberlyst-15	92	78	10	12
9	TFA-ZrO <sub>2</sub>	100	95	--	5
10	ZrO <sub>2</sub>	--	--	--	--
11 <sup>d</sup>	TFA-ZrO <sub>2</sub>	100	91	--	9
12	Nafion-212	74	80	6	14

<sup>a</sup> Reactions were performed by using 2-MF (22 mmol), acetoin (10 mmol), catalyst (0.1 g) under solvent-free condition at 333K for 2 h unless otherwise noted. <sup>b</sup> Conversion with respect to the limiting reactant acetoin. <sup>c</sup> Determined by GC. <sup>d</sup> The reaction was performed at room temperature for 6 h.



**Fig. 2** a) Conversion of acetoin and yield of **1b** under the catalysis of Nafion-212 or TFA-ZrO<sub>2</sub> at low catalyst dosage. Reaction conditions: 2-MF (22 mmol), acetoin (10 mmol), catalyst (0.015 g) under solvent-free condition at 323K for 1 h; b) TONs and TOFs for the conversion of acetoin to **1b** calculated based on the yield of **1b** and the acid amounts of catalysts.

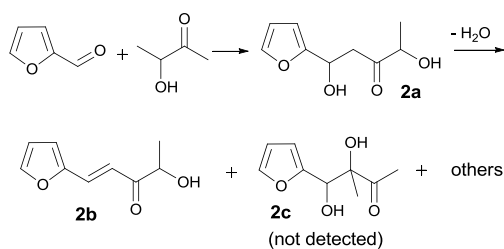
Furthermore, the reactivity of acetoin, acetone, and butanal with 2-MF in the HAA reaction was compared under same conditions. As can be seen from Scheme 3, the highest yield of the HAA product **1b** was observed when acetoin was used as the feedstock. This is quite different from previous reports,<sup>36,49</sup> where an aldehyde usually shows higher reactivity compared to a ketone in the HAA reaction. The higher reactivity of acetoin could be explained by the enhanced electrophilicity of the carbonyl group by the electron-withdrawing effect of the hydroxyl group attached to one of the  $\alpha$ -carbon atoms. Furthermore, butanol needs to be partially oxidized or dehydrogenated to butanal before its use in the reaction, which will increase the cost of the process. Acetoin is one of the major products from the present new type of ABE fermentation and can be directly used as carbonyl compound for the HAA reaction. This can be considered as an advantage of acetoin route. Under the same reaction conditions, an evidently higher yield of the HAA product (93 % of **1b** vs. 82 % of **1d**) can be achieved when acetoin was used to replace acetone as the carbonyl compound (Scheme 3).



**Scheme 3** The comparison of the reactivity of acetoin, acetone, and butanal with 2-MF in the HAA. Reaction conditions: 2-MF (22 mmol), carbonyl compounds (10 mmol), TFA- $ZrO_2$  (0.1 g), 333K, 2h.

## 2.2 Aldol condensation of acetoin with lignocellulose derived aldehydes

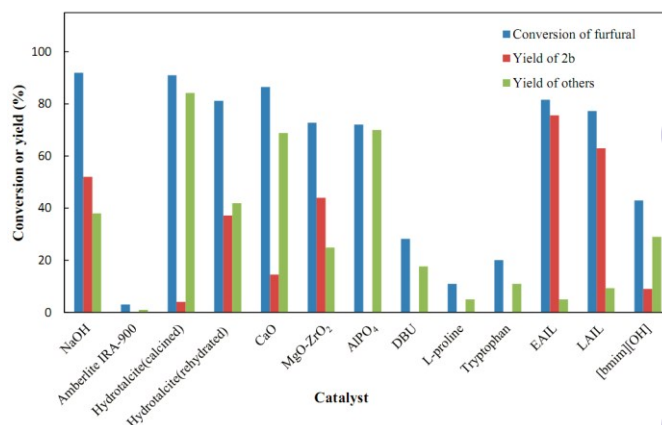
Encouraged by the results obtained from HAA of acetoin with 2-MF, we then wondered if furfural could be direct used for the reaction with acetoin via Claisen-Schmidt reaction, due to it has been produced for decades on an industrial scale by the hydrolysis-dehydration of the hemicellulose part of lignocellulosic biomass.<sup>58,59</sup> The aldol condensation of furfural and acetoin was first carried out using NaOH as a catalyst, the results showed that the reaction of furfural with acetoin at its methyl group which is connected to carbonyl group to give **2b** as the main product in 52% yield via dehydration of **2a** (Scheme 4 and Figure S10).  $^1H$  NMR spectrum of **2b** showed two olefinic protons of the enone system at 6.93 and 7.49 ppm as two doublets with 16 Hz coupling constant, indicating



**Scheme 4** Pathway for the reaction between acetoin with furfural.

the *trans*-geometry. Surprisingly, 1,2-diol compound **2c** was not detected in the reaction mixture, this result is quite different from previously report about similar aldol condensation reaction between  $\alpha$ -hydroxylated ketone with aldehyde, where 1,2-diol compound was usually obtained as the major product.<sup>30,60,61</sup> This abnormal regioselectivity is probably due to this reaction is kinetic control versus thermodynamic control. Meanwhile, no  $C_{13}$  oxygenate was detected in the reaction mixture, which is generated through the aldol condensation of one furfural molecule with two acetoin molecules. Compared to the reaction of furfural with acetoin, the condensation reaction between two acetoin molecules is much slower, the steric hindrance and electron donating properties of the attached hydroxyl groups prevent the formation of reactive enolate intermediate, therefore, the self-condensation product of acetoin, 2,3,5,6-tetramethyl-1,4-dioxane-2,5-diol, was also not observed during this reaction due to this route is not thermodynamics favored. However, 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 be happened during the reaction,<sup>62,63</sup> resulting in generation of some unfavourable polymers. Thin layer chromatography monitoring (Silica, 15% MeOH in  $CH_2Cl_2$ ) of the reaction showed the formation of 4-5 products in the reaction mixture withdrawn after 0.5 h, and polymerization afterwards. HPLC-MS also showed that a serious of high molecular weight products ( $m/z > 400$ ) was formed during the reaction.

Although the present NaOH catalytic system is practical due to it is a cost effective base, it still have disadvantages such as low yield, poor selectivity, and downstream processing issues. Thus, numerous catalysts were tested for the reaction in order to solve the selectivity and environmental issue from using of such mineral base, which including heterogeneous catalysts, organocatalysts, and task-specific ionic liquids. The conversions of the furfural, the yields of **2b** and others over different catalysts are shown in Figure 3. A range of solid base catalysts were first tested for the reaction, however, all of them were unsatisfactory except for hydrotalcite (rehydrated) and  $MgO-ZrO_2$  exhibited moderate catalytic activity. Amine-based organocatalysts such as L-proline, tryptophan, and 1,8-diazabicycloundec-7-ene (DBU), which were previously efficient organocatalysts for the aldol reaction,<sup>30,60,61,64</sup> failing to catalyze this reaction probably due to the steric reasons.

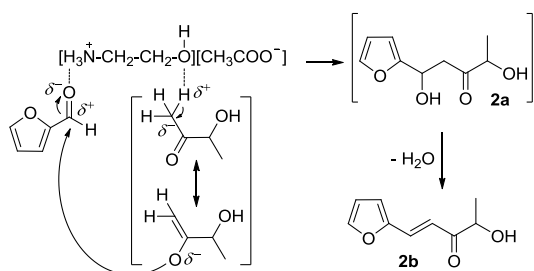


**Fig. 3** Results of the reaction between acetoin with furfural over different catalysts (For detailed experimental protocols, see the Supporting Information).

On the other hand, room-temperature ionic liquids (RTILs), as eco-friendly reaction media, have attracted increasing attention due to their particular properties, such as the extremely low vapor pressure, high thermal stability, and excellent solubility. In addition, RTILs have also been referred to as “designer catalysts” as their chemical and physical properties could be adjusted by careful choice of the cation or anion. Recent advances in ionic liquids provided efficient routes to the preparation of task-specific ionic liquids (TSILs).<sup>65</sup> Thus, two low-cost basic ionic liquid  $[\text{H}_3\text{N}^+\text{-CH}_2\text{-CH}_2\text{-OH}][\text{CH}_3\text{COO}^-]$  (EAIL) and  $[\text{H}_3\text{N}^+\text{-CH}_2\text{-CH}_2\text{-OH}][\text{CH}_3\text{CH}(\text{OH})\text{COO}^-]$  (LAIL) were designed and prepared using our previous method,<sup>66</sup> and tested as catalysts for this reaction. To our delight, the reaction was performed with reasonable conversion and excellent selectivity, 83% conversion of furfural and 78% yield of **2b** were obtained when EAIL was used as a catalyst (Fig. 3). LAIL shows comparable catalytic activity to EAIL and serves as another good catalyst to enhance the reaction remarkably. For product separation and recycling of these TSIL catalysts, the protocol was indeed quite easy and simple. For example, the EAIL is completely soluble in water, but insoluble in EtOAc (Figure S11), this could be beneficial since it can provide an easy route to separate the product and catalyst. After the reaction, extraction of the mixture with EtOAc led to the separation between the catalyst EAIL and products. Fresh substrates were then recharged to the residual water layer which contains the catalyst EAIL and the mixture was heated to react once again. It was found that the catalyst EAIL could be recycled for five times with no apparent loss of catalytic activity (Figure S12), and only 2.7% loss of weight in EAIL was observed after five times recycling.

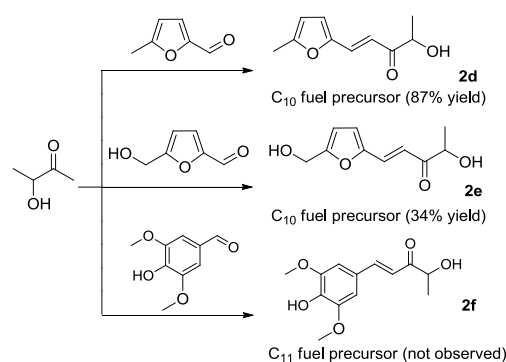
Although, so far, we cannot be certain of the actual role of EAIL in this reaction, on the basis of the result obtained from the comparative experiment using another basic ionic liquid 1-butyl-3-methylimidazolium hydroxide  $[\text{bmim}][\text{OH}]$  as a catalyst (Fig. 3), we believe that the reaction pathway was more than base-catalyzed condensation, a synergistic catalysis effect might be occurred in this reaction. A tentative mechanism is depicted in Scheme 5. The  $-\text{NH}_3$  and  $-\text{OH}$  group in the EAIL could form hydrogen-bonding network with furfural and acetoin, respectively. Such hydrogen-bonding network not only activates the furfural by increasing the positive charge on the corresponding carbon atom, but also facilitates the departure of  $\alpha$ -H of acetoin to form the enolate intermediate.

With the aim to develop and define the scope and limitation of the present novel catalytic system, this procedure was then extended for the reaction of acetoin with other aldehydes, which including 5-hydroxymethylfurfural or 5-methylfurfural derived from cellulose,<sup>67,68</sup> and syringaldehyde derived from lignin.<sup>69</sup> As shown in

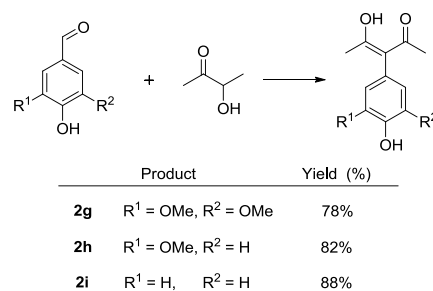


**Scheme 5** Tentative mechanism for the reaction of furfural and acetoin catalyzed by EAIL.

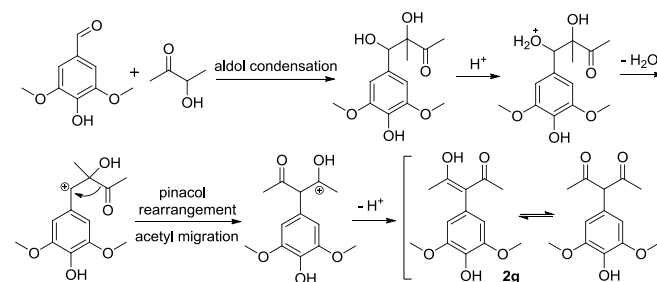
Scheme 6, 5-MF was an ideal substrate, the  $\text{C}_{10}$  fuel precursor **2d** can be obtained with a high yield up to 87% (Figure S14). However, the reaction of acetoin with HMF was not satisfactory (Figure S15), some unidentified polymers were formed during the reaction probably due to polymerization of HMF, which may be ascribed to the low stability of HMF under the present alkaline aqueous conditions.<sup>38,70</sup> When the substrate changed to aromatic aldehyde, such as syringaldehyde, the results showed that no aldol condensation reaction was occurred under the present system, and the corresponding condensation product **2f** that could be expected in analogy with furan aldehyde and acetoin was not detected after the reaction. After further screening of catalysts and optimizing the procedure, we found that replacing the catalyst EAIL with acid-base bifunctional catalyst amorphous aluminium phosphate (ALPO)<sup>71</sup> and increasing the reaction temperature significantly promoted the reaction (Scheme 7 and Figure S16), and the abnormal  $\text{C}_{11}$  fuel precursor product **2g** was identified as the exclusive product through aldol condensation - pinacol rearrangement (Scheme 8 and Figure S17).



**Scheme 6** The reaction of acetoin with other aldehydes derived from lignocellulose catalyzed by EAIL.



**Scheme 7** The reaction of lignin model compounds (*p*-hydroxy benzaldehyde, vanillin or syringaldehyde) with acetoin catalyzed by ALPO.

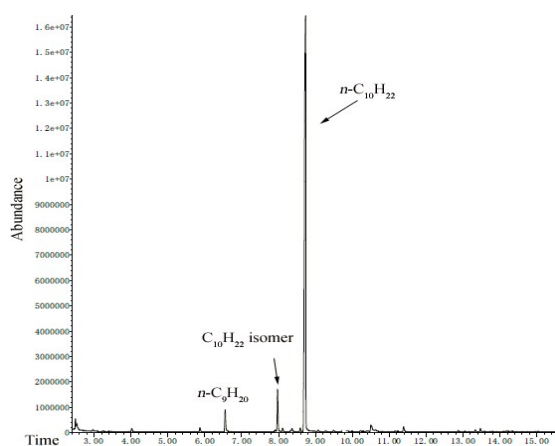


**Scheme 8** Tentative mechanism for the reaction of acetoin with syringaldehyde catalyzed by ALPO.

To check the substituent effects on the lignin model compound conversion, vanillin and *p*-hydroxy benzaldehyde were also tested under the present system (Scheme 7 and Figure S17-S19), the results showed that the presence of the methoxy group slightly decreased the reactivity of the substrate, probably due to the electron-donating property of the methoxy group. In view of the fact that the aldol reaction of electron-rich aromatic aldehydes is much more difficult than the reaction of electron-poor aromatic aldehydes,<sup>64</sup> the results obtained with the present procedure are very satisfactory.

### 2.3 Hydrodeoxygenation of fuel precursors into alkanes

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 of acetoin and 5-MF **2d** was first chosen as a model fuel precursor for this study. According to the previous research results on the HDO reaction mechanism of biomass derived oxygenates,<sup>72,73</sup> the dehydration over acid sites followed by the hydrogenation over metal sites is the major pathway for the C-O cleavage reaction. Noble metal nanoparticles supported on acidic solid carriers have proven to be effective and recyclable catalysts in the HDO process.<sup>49,70,74,75</sup> To investigate the role of each component in the catalysts, commercially available hydrogenation catalysts such as Pd/C and Pt/C combined with different solid acids were tested for the reaction. After initial catalyst screening, three solid acids NbOPO<sub>4</sub>, TaOPO<sub>4</sub>, and H-Beta zeolite (Si/Al = 40) were chosen and used for the HDO process. In most cases, Pd/C shows comparable catalytic activity to Pt/C in removing the oxygen atoms in the substrate, however, Pt/C shows a more strong cracking capacity of C-C bond compared to Pd/C. Thus, Pd/C was chosen as hydrogenation catalyst for further studies. Most excitingly, changing the solid acid such as NbOPO<sub>4</sub> or TaOPO<sub>4</sub>, which were traditional effective catalysts in the HDO process,<sup>70,74</sup> to commercial available H-beta zeolite, led to the highest alkane selectivity of 96%, and the clean formation of C<sub>9</sub>H<sub>20</sub> and C<sub>10</sub>H<sub>22</sub> alkanes through this highly effective HDO process is remarkable (Figure 4 and Figure S20). Encouraged by these results and in order to search for the optimum reaction conditions, we screened a variety of parameters of this reaction, such as reaction temperature,



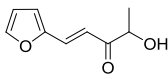
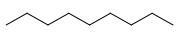
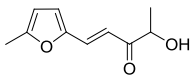
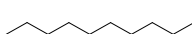
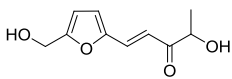
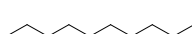
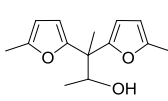
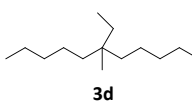
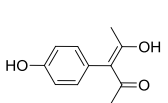
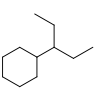
**Fig. 4** GC-MS chromatogram of the organic-phase products produced by HDO of **2d** with Pd/C + H-beta zeolite.

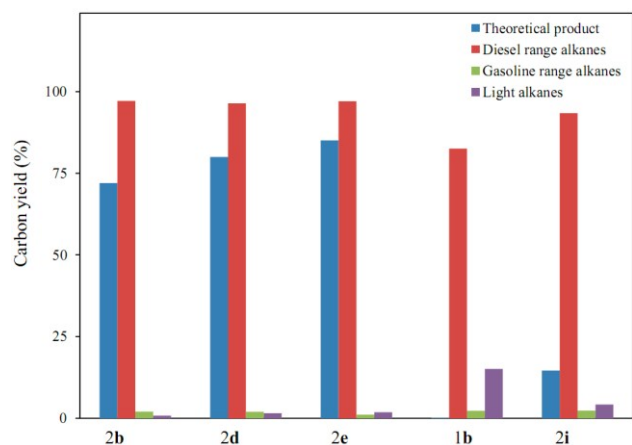
H<sub>2</sub> pressure, solvent and reaction time. The Pd/C + H-beta zeolite system under moderate conditions (473 K and 3 MPa H<sub>2</sub> pressure) was finally selected for the HDO process.

By maintaining all of the key parameters of the present catalytic system, we then applied the procedure for other fuel precursors (Table 2). As shown in Fig. 5, 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 observed based on the results from the GC-MS. The carbon balance was almost quantitative for most of the HDO reactions, about 95% of the carbon was in the liquid organic products according to the TOC analysis while the rest of the carbon containing products were CO, CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>4</sub>H<sub>10</sub>. It is noteworthy that for most HDO system, the products are very complicated by furan-ring opening, carbon chain fragmentation, rearrangement and cyclization reactions, rendering a wide distribution of hydrocarbons. However, excellent selectivity was observed under the present system, the clean formation of hydrocarbons with a narrow distribution of alkanes was occurred for most cases (Figure S20-S24). Cyclic alkanes can also be obtained in high yield though this effective catalytic system (Figure S24), which is the second most abundant component required in the commercial and military jet fuels with the mass percent of 20-50 wt%.<sup>76,77</sup> Compared to straight alkanes, cyclic alkanes have higher densities and volumetric heating values due to the strong ring strain.<sup>78,79</sup>

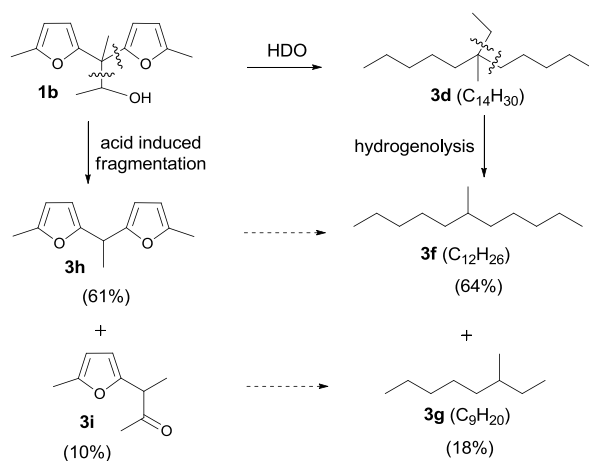
However, if we take a closer look into the product distribution (Fig. 6), it was found that the carbon yield of diesel range alkanes is lowest when **1b** was used as a feedstock, and its corresponding theoretical alkane product or other C<sub>14</sub> isomer alkanes were not

**Table 2** The structures of the fuel precursors and their theoretical HDO products

Fuel precursors	Theoretical alkane product
 <b>2b</b>	 <b>3a</b> C <sub>9</sub> H <sub>20</sub> straight alkane
 <b>2d</b>	 <b>3b</b> C <sub>10</sub> H <sub>22</sub> straight alkane
 <b>2e</b>	 <b>3c</b> C <sub>10</sub> H <sub>22</sub> straight alkane
 <b>1b</b>	 <b>3d</b> C <sub>14</sub> H <sub>30</sub> branched alkane
 <b>2i</b>	 <b>3e</b> C <sub>11</sub> H <sub>22</sub> cyclic alkane

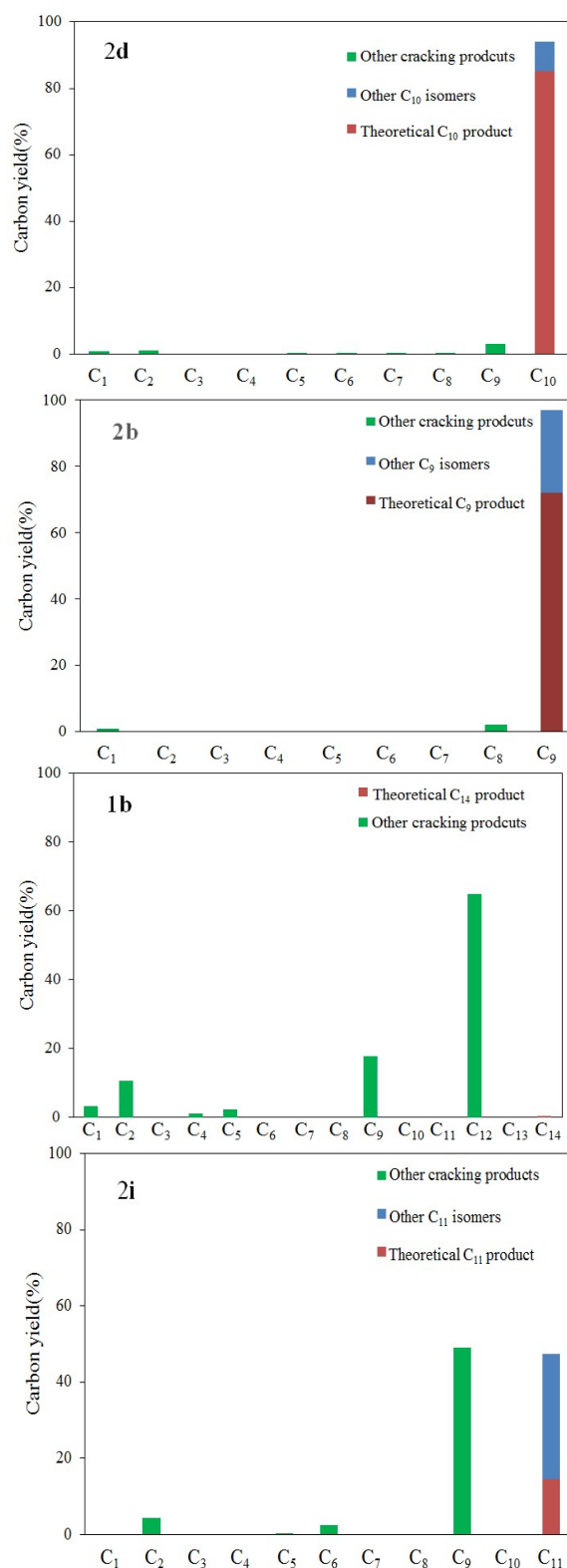


**Fig. 5** Carbon yields of different alkanes from the HDO of different precursors over the Pd/C+H- $\beta$  system. The diesel range alkanes, gasoline range alkanes and light alkanes account for C<sub>9</sub>-C<sub>15</sub>, C<sub>5</sub>-C<sub>8</sub> and C<sub>1</sub>-C<sub>4</sub> alkanes, respectively.



**Scheme 9** Products identified in the HDO of **1b** and control experiment catalyzed by H-beta zeolite.

identified after the reaction. As shown in Scheme 9 and Figure S22, two main compounds **3f** (C<sub>12</sub>H<sub>26</sub>) and **3g** (C<sub>9</sub>H<sub>20</sub>) were observed after the reaction with **3f** as the dominant product. These two products were generated from C-C bond cleavage adjacent to the quaternary carbon atom in the middle of the undecane chain, and removal of a C<sub>2</sub> (ethyl) or C<sub>5</sub> (pentyl) group from the main chain, respectively. This phenomenon can be explained by the stability of carbocation, which is an important intermediate during the HDO process.<sup>80</sup> It is well known that the stability of carbocation increases in the order of primary > secondary > tertiary. The C-C cleavage of **1b** at the carbon atom adjacent to furan ring will generate tertiary carbocation, the formation of the most stable tertiary carbocation led to the C-C cleavage products. Similarly, the lower yield of theoretical alkane when **2i** was used as a feedstock is due to the formation of secondary carbocation. However, for products **3f** or **3g**, either was derived from C-C cleavage of **3d** through the formation of tertiary carbocation, in principle, the selectivity of these two products should be about equal. Thus, we speculated that the fragmentation does not occur at the final stage of the HDO, but earlier in the reaction coordinate. To check this point, control experiment was carried out using only H-Beta zeolite as a catalyst under similar



**Fig. 6** Products distribution of alkanes from the HDO of the fuel precursors.

reaction conditions, **3h** and **3i** were detected in 61% and 10% yields, respectively (Scheme 9 and Figure S25 and 26). These results confirmed that acid induced cracking reaction plays a dominant role in the HDO process. A similar phenomenon has also been recently observed for the acidic amorphous silica-alumina catalyzed cracking reaction of biomass derived oxygenate.<sup>36</sup>



### 3. Conclusions

In conclusion, a novel C<sub>4</sub> building block “acetoin”, which is derived from lignocellulose by new ABE type fermentation, has been used as a bio-based synthon for the production of liquid hydrocarbon fuels. It was found that TFA-ZrO<sub>2</sub>, ionic liquid EAIL, and aluminium phosphate were efficient and recyclable catalysts for the HAA reaction and aldol condensation, respectively. And the HDO step could be achieved by using simple and handy Pd/C + H-beta zeolite system, which was found to have high activity in the conversion of various furan- or aromatic- based oxygenates, a series of well-defined diesel or jet fuel range C<sub>9</sub>-C<sub>14</sub> straight, branched, or cyclic alkanes could be produced in excellent yields under the present catalytic system. This work not only provides a new bio-based platform chemical for the direct synthesis of liquid alkanes, but also offers new opportunities to upgrade biomass to clean fuels and chemicals by bridging the biological and chemical catalysis gap.<sup>81,82</sup>

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