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Synthesis of renewable diesel with 2-methylfuran and angelica lactone derived from carbohydrates†

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Diesel and jet fuel range branched alkanes were first synthesized by the combination of hydroxyalkylation/alkylation (HAA) of 2-methylfuran with angelica lactone and subsequent hydrodeoxygenation. Compared with the previous ethyl levulinate route, the angelica lactone route exhibited evident advantages at higher HAA reactivity.

As a solution to the energy and environment problems we are facing today, the catalytic conversion of abundant, inedible and renewable lignocellulosic biomass to fuels[1] and chemicals[2] has drawn a lot of attention. Diesel and jet fuels are two kinds of often used transportation fuels. Following the pioneering work of Dumesic,[3] Huber[4] and Corma groups,[5,6] tremendous efforts have been devoted to the synthesis of jet fuel range alkanes with lignocellulose derived platform compounds.[7]

2-Methylfuran (2-MF) is the selective hydrogenation product of furfural which has been manufactured on the industrial scale by the hydrolysis–dehydration of the hemicellulose part of agricultural waste and forest residues.[8] In the past few years, several routes have been developed by the hydroxyalkylation/alkylation (HAA) of 2-MF and lignocellulose derived carbonyl compounds (such as furfural, 5-hydroxymethylfurfural, butanal, acetone, hydroxyacetone, cyclopentanone, *etc.*), followed by hydrodeoxygenation (HDO).[5,9,10] Angelica lactone is the dehydration product of lignocellulose derived levulinic acid. Recently, it was found that gasoline and diesel range alkanes can be prepared by the base catalysed dimerization and trimerization of angelica lactone, followed by HDO.[11] To the best of our knowledge, there is no report about the HAA of 2-MF and angelica lactone, let alone the utilization of the HAA product as the precursor for the synthesis of diesel or jet fuel range branched alkanes. In this work, the HAA of 2-MF and angelica lactone was carried out, for the first time, over a series of acid catalysts. The HAA product was further hydrogenated and hydrodeoxygenated to diesel and jet fuel range alkanes over active carbon loaded noble metal catalysts.

The HAA of 2-MF and angelica lactone was carried out over a series of acid catalysts under mild conditions (323 K) (see Fig. 1–3). From the analysis of GC-MS and NMR (see Fig. S1–S3 in the ESI†), 4,4-bis(5-methylfuran-2-yl) pentanoic acid (*i.e.* **1a** in Scheme 1) was identified as the main product from the condensation of 2-MF and angelica lactone. According to its chemical structure, compound **1a** as obtained can be used as a potential precursor for diesel and jet fuel range branched alkanes.

The catalytic performances of several Brønsted acids for the HAA of 2-MF and angelica lactone were studied. As shown in

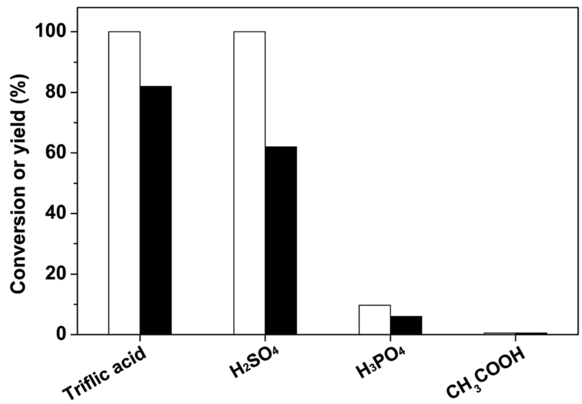

Fig. 1 Conversions of angelica lactone (white bars) and the carbon yields of **1a** (black bars) under the catalysis of different Brønsted acids. Reaction conditions: 323 K, 1 h; 0.98 g (10 mmol) angelica lactone, 1.68 g (20 mmol) 2-methylfuran (2-MF) and 0.05 g catalyst.

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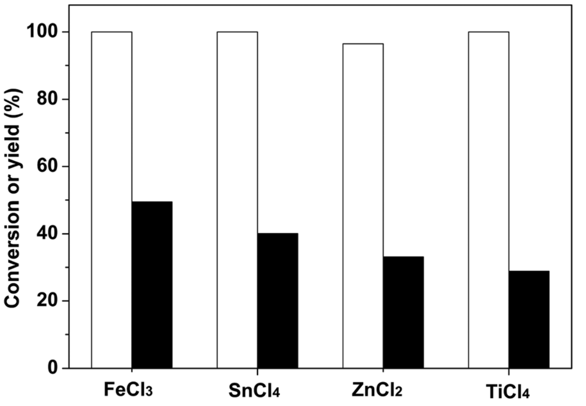


Fig. 2 Conversions of angelica lactone (white bars) and the carbon yields of **1a** (black bars) under the catalysis of different Lewis acids. Reaction conditions: 323 K, 1 h; 0.98 g angelica lactone, 1.68 g 2-MF, and 0.1 g catalyst.

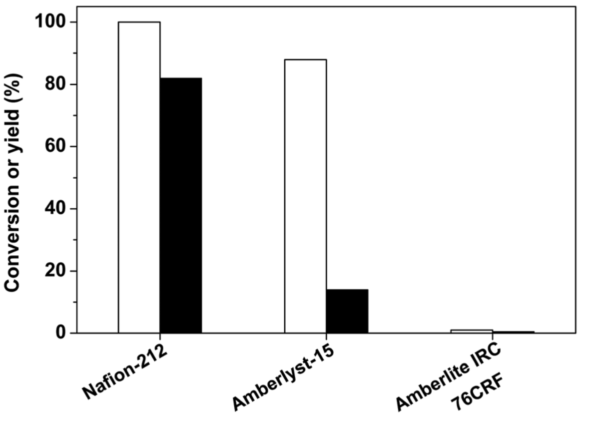
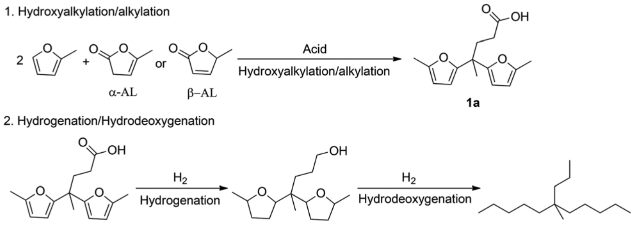


Fig. 3 Conversions of angelica lactone (white bars) and the yields of **1a** (black bars) over different acidic resins. Reaction conditions: 323 K; 1 h; 0.98 g angelica lactone, 1.68 g 2-MF and 0.1 g catalyst.



Scheme 1 Reaction pathway for the synthesis of diesel and jet fuel range alkanes with 2-methylfuran (2-MF) and angelica lactone (AL).

Table 1 Dissociation constant (pK_a) values of the different Brønsted acids[12] used in HAA of 2-MF and angelica lactone

Catalyst	pK_a
Triflic acid	0.52
H_2SO_4	1.99
H_3PO_4	2.16
CH_3COOH	4.76

Fig. 1, the angelica lactone conversion and the carbon yield of **1a** decrease in the order of triflic acid > sulphuric acid > phosphoric acid > acetic acid. This sequence is consistent with the acid strength of these acids which is indicated by their dissociation constants (pK_a) listed in Table 1. From this result, we can see that the HAA of 2-MF and angelica lactone is sensitive to the acid strength of the catalyst. A strong acid is more active than a weak acid for this reaction. Furthermore, we also studied the influence of the acid type on the HAA of 2-MF and angelica lactone. From Fig. 2, we can see that the HAA of 2-MF and angelica lactone can also be catalysed by some well-known Lewis acid catalysts (such as $FeCl_3$, $SnCl_4$, $ZnCl_2$ and $TiCl_4$). Based on the above results, we believe that both Brønsted acids and Lewis acids have a promotion effect on the HAA of 2-MF and angelica lactone.

To avoid the corrosion and environmental problems which may be caused by the utilization of liquid acids or metal chlorides, we also explored the possibility to use a solid acid as the catalyst for the HAA of 2-MF and angelica lactone. To do this, we chose Nafion-212, Amberlyst-15 and Amberlite IRC 76CRF as the representatives for solid acid catalysts with strong acidity, medium strong acidity and weak acidity. According to Fig. 3, the activities of the acidic resins decrease in the order of Nafion-212 > Amberlyst-15 > Amberlite IRC 76CRF. This can be explained by the chemical structure of these acidic resins. As we know, Nafion is a perfluorinated sulfonic acid resin, which is often denoted as a superacid.[13] Amberlyst is a sulfonic-acid-functionalized cross-linked polystyrene resin.[14] However, Amberlite IRC 76CRF is a high capacity weakly acidic cation exchange resin containing the carboxylic functionality within a porous crosslinked acrylic matrix.[15] In Nafion resins, the acid strength of the SO_3H group is enhanced by the presence of fluorine, which makes its acid strength higher than the Amberlyst resin. Meanwhile, the SO_3H group has a higher acid strength than that of the COOH group. Due to these reasons, the Nafion resin exhibits the highest activity for the HAA of 2-MF and angelica lactone among the investigated solid acid catalysts.

In the previous work of our group,[9] it was found that the Nafion-212 resin is also active for the HAA of 2-MF with levulinic acid or ethyl levulinate. Compared to these compounds, angelica lactone is more reactive in the HAA reaction with 2-MF. Under the same reaction conditions, evidently a higher carbon yield of the HAA product (81.3% *vs.* 12.0% and 4.8%) can be achieved when angelica lactone was used as the feedstock (see Fig. 4). This can be considered as the advantage of our new route. The higher reactivity of angelica lactone can be rationalized by the competitive adsorption of water which will be generated in the HAA of 2-MF and levulinic acid or ethyl levulinate (see Scheme 2). As we know, water is a Lewis base. Therefore, it can compete with 2-MF, levulinic acid or ethyl levulinate for adsorption to the acid sites on the Nafion-212

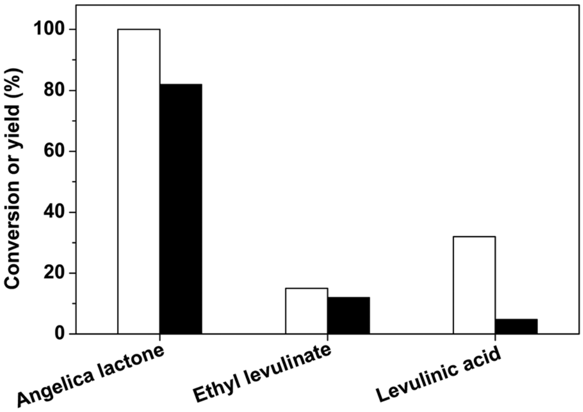
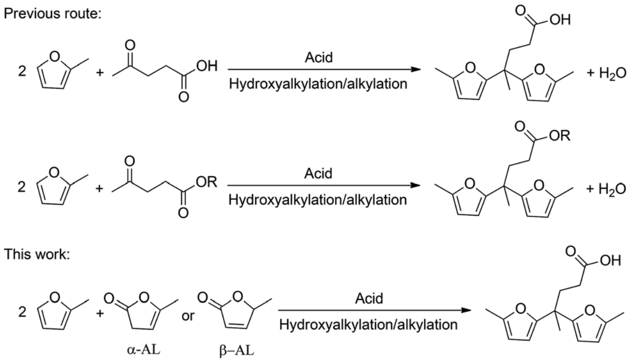


Fig. 4 Conversions of angelica lactone, ethyl levulinate or levulinic acid (white bars) and the carbon yields of the corresponding HAA products (see Scheme 2) (black bars). Reaction conditions: 323 K, 1 h; 1.68 g (20 mmol) 2-MF, 10 mmol angelica lactone, ethyl levulinate or levulinic acid and 0.1 g Nafion-212 resin.



Scheme 2 Reaction pathways for the synthesis of diesel and jet fuel precursors by the HAA reactions between 2-MF and levulinic acid, ethyl levulinate or angelica lactone.

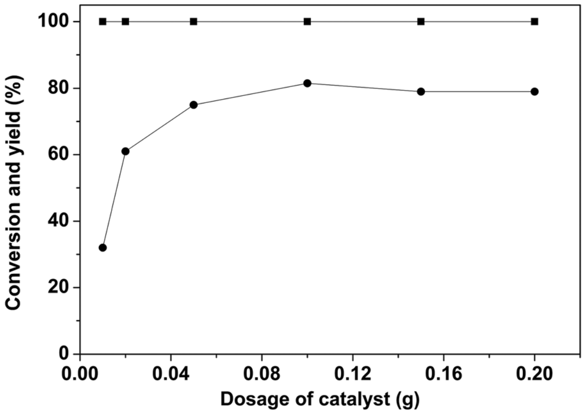


Fig. 5 Conversion of angelica lactone (■) and the carbon yield of **1a** (●) as a function of catalyst dosage. Reaction conditions: 323 K, 1 h; 0.98 g angelica lactone and 1.68 g 2-MF.

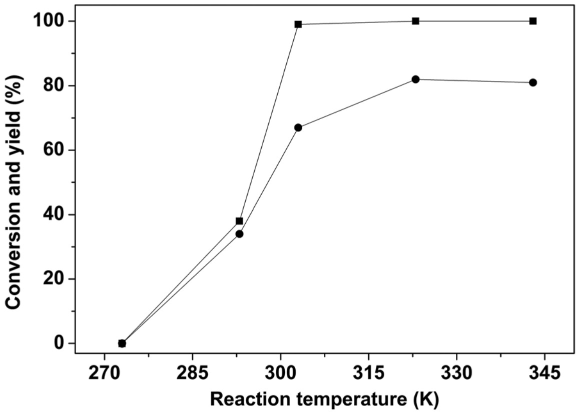


Fig. 6 Conversion of angelica lactone (■) and the carbon yield of **1a** (●) as a function of reaction temperature. Reaction conditions: 1 h; 0.98 g angelica lactone, 1.68 g 2-MF and 0.1 g Nafion-212 resin.

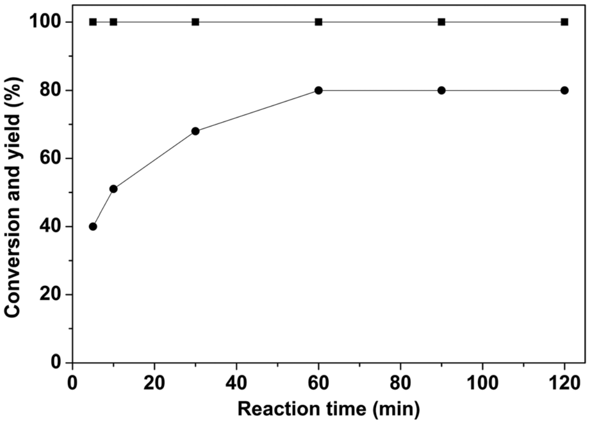


Fig. 7 Conversion of angelica lactone (■) and the carbon yield of **1a** (●) as a function of reaction time. Reaction conditions: 323 K; 0.98 g angelica lactone, 1.68 g 2-MF and 0.1 g Nafion-212 resin.

resin. To verify this hypothesis, we studied the effect of water on the catalytic performance of the Nafion-212 resin for the HAA of 2-MF and angelica lactone. As we expected, the presence of stoichiometric water (the molar ratio of angelica lactone to water is 1 : 1) significantly restrains the HAA of 2-MF and angelica lactone (see Fig. S4 in the ESI†).

The effects of reaction conditions (such as catalyst dosage, reaction temperature and reaction time) on the carbon yield of **1a** over the Nafion-212 resin were investigated. According to the results shown in Fig. 5–7, there is an optimum value for the catalyst dosage, reaction temperature and reaction time, respectively. The highest carbon yield of **1a** (81.3%) was achieved over 0.1 g Nafion-212 resin after reacting at 323 K for 1 h.

The reusability of the Nafion-212 resin was also studied. To do this, the Nafion-212 resin was repeatedly used under the optimum conditions (0.1 g catalyst, 323 K, 1 h). To exclude the disturbance of the residues (including the HAA product, unreacted angelica lactone and 2-MF) on the used catalysts, the catalyst was washed thoroughly with 10 wt% hydrogen peroxide at 353 K for 2 h after each usage and dried at 353 K for 2 h. From the results illustrated in Fig. 8, the Nafion-212 resin is very stable under the investigated conditions. The carbon yield of **1a** over the Nafion-212 resin varied a little even after being used for 6 times (the slight decrease after the third run may be rationalized by the loss of the catalyst during the filtration and drying process). Taking into account the high activity and good stability of the Nafion-212 resin in the HAA of 2-MF and angelica lactone, we believe that it may be a promising catalyst in future application.

As the final aim of this work, we also investigated the hydrodeoxygenation (HDO) of **1a** from the HAA of 2-MF and angelica lactone. Because **1a** as obtained is a liquid with high viscosity, it is difficult to be delivered by an HPLC pump. As a solution to this problem, **1a** was hydrogenated before being used in the HDO process. The hydrogenation was carried out over the 5 wt% Pd/C catalyst with the 30 wt% methanol solution of purified **1a**. From the GC-MS analysis of the hydrogenation product (see Fig. S5–S8 in the ESI†), **1a** was completely converted after being hydrogenated at 433 K and 6 MPa H_2. 4,4-Bis(5-methyl-tetrahydrofuran-2-yl)pentan-1-ol (*i.e.* **1b** in Scheme 3) was identified as the main product from the hydrogenation of **1a**. Besides **1b**, 5,5′-(ethane-1,1-diyl)bis(2-methyltetrahydrofuran) and bis(5-methyltetrahydrofuran-2-yl) methane (*i.e.* **1c** and **1d** in Scheme 3) were also detected in the hydrogenation product. These compounds may be generated by the hydrogenolysis of **1a**.

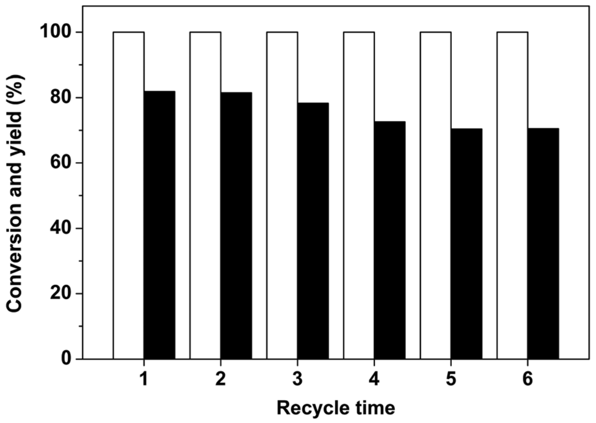
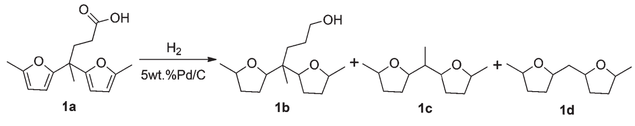


Fig. 8 Conversion of angelica lactone (white bars) and the carbon yield of **1a** (black bars) as a function of recycle time. Reaction conditions: 323 K, 1 h; 0.98 g angelica lactone, 1.68 g 2-MF and 0.1 g Nafion-212 resin.



Scheme 3 Reaction pathway for the generation of different products from the hydrogenation of **1a** over the 5 wt% Pd/C catalyst. Reaction conditions: 433 K, 6 MPa H_2, 1.8 g catalyst; liquid feedstock flow rate of 0.16 mL min^{-1}; H_2 flow rate of 120 mL min^{-1}.

After removal of methanol by vacuum distillation, the mixture of **1b**, **1c** and **1d** was used in the solvent-free HDO process. According to the analysis of GC and GC-MS, **1b**, **1c** and **1d** were completely converted to alkanes over the activated carbon loaded noble metal (Pt, Pd and Ru) catalysts at 623 K and 6 MPa H_2. As we can see from Fig. 9, higher carbon yields of diesel and jet fuel range alkanes (81.0% and 81.6%) can be achieved over the 5 wt% Pt/C and 5 wt% Pd/C catalysts than that over the 5 wt% Ru/C catalyst (60.4%). Moreover, it is also noticed that the carbon yield of C_1–C_4 light alkanes over the 5 wt% Ru/C (25.1%) is evidently higher than those over the Pt/C (1.3%) and Pd/C (1.6%) catalysts. Based on this result, we can attribute the lower selectivity of diesel and jet fuel range alkanes over the Ru/C catalyst to the higher activity of Ru for hydrogenolysis or methanation (leading to the generation of C_1–C_4 light alkanes).[16] Taking into account the relatively lower price of Pd than that of Pt, we think Pd/C is a promising HDO catalyst in future application.

The stability of the Pd/C catalyst in the HDO process was also investigated. From the result shown in Fig. 10, we can see that the Pd/C catalyst is stable under the investigated conditions. No evident decrease of activity was observed during a 24 h continuous test. The density and freezing point of the alkane products from the HDO process over the Pd/C catalyst were measured as 0.786 g mL^{-1} and 173 K, respectively.

According to the literature, levulinic acid can be obtained from the hydrolysis–dehydration of cellulose at a high molar yield of ~61%, while furfural can be produced by the hydrolysis–dehydration of hemicellulose at a carbon yield of ~56%.[17] The angelica lactone can be synthesized by the dehydration of levulinic acid at a carbon yield of 90–97%.[11] 2-MF can be prepared by the selective hydrogenation of furfural over

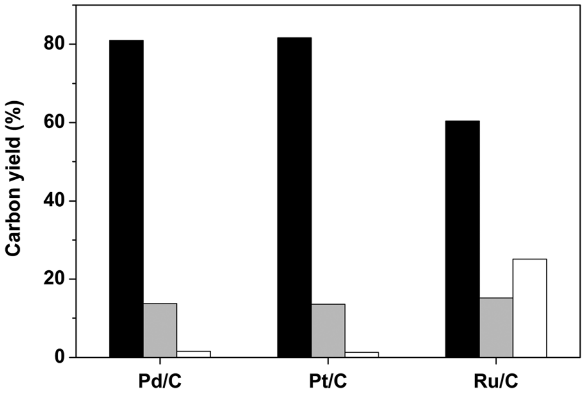


Fig. 9 Carbon yields of C_9–C_{15} diesel range alkanes (black bars), C_5–C_8 gasoline range alkanes (grey bars), and C_1–C_4 light alkanes (white bars) over active carbon loaded noble metal catalysts. Reaction conditions: 623 K, 6 MPa, 1.8 g catalyst; liquid feedstock flow rate 0.04 mL min^{-1}, hydrogen flow rate: 120 mL min^{-1}.

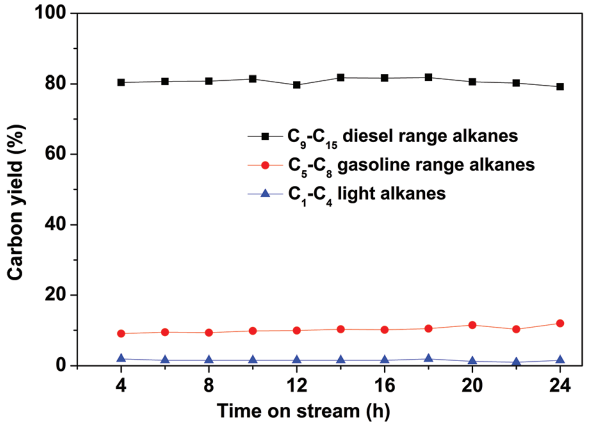


Fig. 10 Carbon yields of $C_9–C_{15}$ diesel range alkanes (■), $C_5–C_8$ gasoline range alkanes (●), and $C_1–C_4$ light alkanes (▲) over the Pd/C catalyst as a function of time on stream. Reaction conditions: 623 K, 6 MPa, 1.8 g catalyst; liquid feedstock flow rate 0.04 mL min^{-1}, hydrogen flow rate: 120 mL min^{-1}.

a Cu-based catalyst at a carbon yield of ~90%.[18] Based on the above information and the results obtained in this work, the overall carbon yield of diesel and jet fuel range alkanes from cellulose and hemicellulose was estimated as ~35%. From the viewpoint of environment and economics, the 2-MF-angelica lactone route developed in this work has two advantages: (1) the simultaneous utilization of the platform compounds from cellulose and hemicellulose which are the two major components of agriculture and forest wastes; (2) the utilization of the solid acid and Pd/C as catalysts which are reusable and environmentally friendly. However, the 2-MF-angelica lactone route proposed in this work also has a disadvantage because it contains many synthesis steps. In the future research, the process integration is expected to decrease the cost and energy consumption of this route.

Conclusions

In this work, a brand new route for the synthesis of diesel or jet fuel range branched alkanes was developed by the hydroxyalkylation/alkylation (HAA) of lignocellulose derived 2-methylfuran (2-MF) and angelica lactone, followed by hydrodeoxygenation (HDO). Among the investigated solid acid catalysts, Nafion-212 resin exhibited the highest activity and stability for the HAA of 2-MF and angelica lactone, which can be rationalized by the higher acid strength of this material. Under the solvent-free conditions, 81.3% yield of HAA products was obtained over the Nafion-212 resin. After the HDO of the hydrogenated HAA products over 5 wt% Pd/C catalyst, 81.0% carbon yield of diesel or jet fuel range alkanes could be achieved. Compared with the 2-MF–levulinic acid (or ester) route proposed in our previous work, the 2-MF–angelica lactone route investigated in this work has evident advantages at higher HAA reactivity, which can be explained by the absence of water in the HAA product. This work provides a new strategy for the synthesis of diesel and jet fuel range branched alkanes with the platform chemicals from the hydrolysis–dehydration products of both hemicellulose and cellulose.

Acknowledgements

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