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

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1 Experimental Section

1.1 Catalysts

Nafion-212 resin was supplied by Dupont. Amberlyst-15 and Amberlyst-36 resin were purchased from Sigma Aldrich. FeCl₃, SnCl₄, ZnCl₂ and TiCl₄ were bought from Sigma-Aldrich.

The Pd/C catalyst used for low-temperature hydrogenation and hydrodeoxygenation was prepared by the incipient wetness impregnation of the HNO₃ treated active carbon with an aqueous solution of PdCl₂. The Pt/C catalyst used for hydrodeoxygenation was prepared by the incipient wetness impregnation of the HNO₃ treated active carbon with an aqueous solution of H₂PtCl₆·6H₂O. The Ru/C catalyst used for hydrodeoxygenation was prepared by the incipient wetness impregnation of the HNO₃ treated active carbon with an aqueous solution of RuCl₃·3H₂O. The catalyst precursors as-obtained were dried at 353 K for 24 h and then reduced by H₂ (160 mL min⁻¹ g cat⁻¹) at 773 K for 2 h. After cooling in H₂ to room temperature, the catalysts were passivated with 1 vol.% O₂ in N₂. To facilitate comparison, the metal content in each catalyst was fixed at 5% by weight (denoted as 5wt.%).

1.2 Preparation of angelica lactone

Angelica lactone (a mixture of α-angelica lactone and β-angelica lactone) was prepared by the dehydration of levulinic acid according to the method described in the literature.¹ Typically, 25.0 g levulinic acid and 1.0 g H-ZSM-5 (SiO₂/Al₂O₃ molar ratio = 25, supplied by Nankai University) were loaded in a distillation flask and stirred at 453 K in an oil bath. The outlet of the flask was connected to a fractionation
column (20 cm) and a vacuum pump which was set at 60 mmHg. The dehydration products \(i.e.,\) angelica lactones and water) vaporized from the distillation flask, passed through a water-cooled condenser and became two phases in another flask. The \(^1\)H and \(^{13}\)C NMR spectra of the angelica lactones as obtained were illustrated in Figure S8. According to our analysis, up to 90% isolated carbon yield of angelica lactone was achieved by the dehydration of levulinic acid over the H-ZSM-5 catalyst under the investigated conditions. Before being used for the hydroalkylation/alkylation (HAA) test, the angelica lactone was dried by anhydrous sodium sulfate for 2 h.

### 1.3 Hydroxyalkylation/alkylation (HAA)

The HAA of 2-methylfuran (2-MF) and angelica lactone was carried out in a round-bottomed flask equipped with a reflux condenser and a magnetic stirrer. The reaction temperature was controlled with a water bath. Typically, a mixture of catalyst, 2-MF, and angelica lactone was stirred at the set temperature for 1 h. The product was extracted with dichloromethane and analyzed by an Agilent GC 7890A equipped with HP-5 column (30 m, 0.25 mm ID, 0.5 mm film) and a flame ionization detector (FID).

### 1.4 Low-temperature hydrogenation

The low-temperature hydrogenation of the HAA product was carried out in a 316 L stainless steel tubular flow reactor described in our previous work. For this process, 1.8 g 5wt.% Pd/C catalyst was used. A 30wt.% methanol solution of HAA product (purified by the vacuum distillation) was fed into the reactor using a HPLC pump (at the rate of 0.16 mL min\(^{-1}\)) from the bottom along with \(\text{H}_2\) at a flow rate of 120 mL min\(^{-1}\). The system pressure was controlled at 6 MPa by a back pressure regulator. The
reaction temperature was controlled at 433 K. After hydrogenation, the methanol was removed by vacuum distillation. The product as obtained was directly used as the feedstock for the following solvent-free hydrodeoxygenation. From the results of GC-MS, the HAA product of 2-MF and angelica lactone was completely converted to 4,4-bis(5-methyl-tetrahydrofuran-2-yl)pentan-1-ol, 5,5′-(ethane-1,1-diyl)-bis-(2-methyltetrahydrofuran) and bis(5-methyltetrahydrofuran-2-yl)methane under the investigated conditions. According to the elemental analysis, the weight percentages of C, H, O in the hydrogenated HAA product were measured as 67.1%, 8.9% and 24.0%, respectively.

1.5 Hydrodeoxygenation (HDO)

The solvent-free HDO of the hydrogenated HAA product was carried out by the same reactor as we used for low-temperature hydrogenation. For each test, 1.8 g of active carbon loaded noble metal catalyst was used. The hydrogenated HAA product of (i.e. a mixture of 4,4-bis(5-methyl-tetrahydrofuran-2-yl)pentan-1-ol, 1,1-bis(5-methyltetrahydrofuran-2-yl)ethane and bis(5-methyl -tetrahydrofuran-2-yl)methane) was fed into the reactor (at the rate of 0.04 mL min⁻¹) by a HPLC pump from the bottom along with H₂ at a flow rate of 120 mL min⁻¹. The HDO process was carried out at 623 K. The products from the outlet of the reactor tube passed through a gas-liquid separator and became two phases. The gaseous products flowed through a back pressure regulator to maintain the pressure in the reaction system at 6 MPa and were analyzed online by an Agilent 6890N GC. The CO₂ in the gaseous product was measured by a thermal conductivity detector (TCD) equipped with an Alltech
HAYESEP DB 100/120 column (30 feet, 1/8 inch outer diameter, 2.0 mm inner diameter). The alkanes in the gaseous product were analyzed by a flame ionization detector (FID) equipped with an Rt-Q-BOND capillary column (30 m, 0.32 mm ID, 10 μm film). Liquid products were drained periodically from the gas-liquid separator and analyzed by an Agilent 7890A GC equipped with a HP-INNOWAX capillary column (30 m, 0.25 mm ID, 0.5 mm film) and FID detector.

The carbon yields of different alkanes in the HDO process were calculated according to the following formulas:

Carbon yield of C₉-C₁₅ diesel and jet fuel range alkanes (%) = \frac{\text{Total carbon of C₉-C₁₅ alkanes in the liquid products}}{\text{Total carbon of feedstock pumped into the reactor}} \times 100\%

Carbon yield of C₅-C₈ gasoline range alkanes (%) = \frac{\text{Total carbon of C₅-C₈ alkanes in the gas products per unit time}}{\text{Total carbon of feedstock pumped into the reactor per unit time}} \times 100\% + \frac{\text{Total carbon of the C₅-C₈ alkanes in liquid phase products}}{\text{Total carbon of feedstock pumped into the reactor}} \times 100\%

Carbon yield of C₁-C₄ light alkanes (%) = \frac{\text{Total carbon of the C₁-C₄ alkanes in the gas products per unit time}}{\text{Total carbon of feedstock pumped into the reactor per unit time}} \times 100\%
**Figure S1.** GC chromatogram of the liquid products from the HAA of 2-methylfuran (2-MF) and angelica lactone. Reaction conditions: 323 K, 1 h; 0.98 g (10 mmol) angelica lactone, 1.68 g (20 mmol) 2-methylfuran (2-MF), 0.1 g Nafion-212 resin.
Figure S2. Mass spectrogram of the 1a produced by the HAA of 2-MF and angelica lactone. Reaction conditions: 323 K, 1 h; 0.98 g (10 mmol) angelica lactone, 1.68 g (20 mmol) 2-MF, 0.1 g Nafion-212 resin.
Figure S3. $^1$H and $^{13}$C NMR spectra of the 1a from the HAA of 2-MF and angelica lactone.
Figure S4. Effect of stoichiometric water on the conversion of angelica lactone (white bars) and the carbon yield of 1a (black bars) over the Nafion-212 resin. Reaction conditions: 323 K, 1 h; 0.98 g angelica lactone, 1.68 g 2-MF, 0 (or 0.18) g H₂O, and 0.1 g Nafion-212 resin.
Figure. S5. GC chromatogram of the liquid products from the hydrogenation of 1a over the 5wt.% Pd/C catalyst. Reaction conditions: 433 K, 6 MPa H₂, 1.8 g catalyst; liquid feedstock (30wt.% 1a in methanol) flow rate of 0.16 mL min⁻¹; H₂ flow rate of 120 mL min⁻¹.
Figure S6. Mass spectrogram of the 1b from the hydrogenation of 1a over the 5wt.% Pd/C catalyst. Reaction conditions: 433 K, 6 MPa H₂, 1.8 g catalyst; liquid feedstock (30wt.% 1a in methanol) flow rate of 0.16 mL min⁻¹; H₂ flow rate of 120 mL min⁻¹.
Figure S7. Mass spectrogram of the 1c generated during the hydrogenation of 1a over the 5wt.% Pd/C catalyst. Reaction conditions: 433 K, 6 MPa H2, 1.8 g catalyst; liquid feedstock (30wt.% 1a in methanol) flow rate of 0.16 mL min⁻¹; H2 flow rate of 120 mL min⁻¹.
Figure S8. Mass spectrogram of the 1d generated during the hydrogenation of 1a over the 5wt.% Pd/C catalyst. Reaction conditions: 433 K, 6 MPa H₂, 1.8 g catalyst; liquid feedstock (30wt.% 1a in methanol) flow rate of 0.16 mL min⁻¹; H₂ flow rate of 120 mL min⁻¹.
Figure S9. $^1$H and $^{13}$C NMR spectra of angelica lactone from the dehydration of levulinic acid.
**Figure S10.** 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-MF and 0.1 g catalyst.

In this work, we also found that the too high dosage of Brønsted acid catalyst has negative effect on the HAA of 2-MF and angelica lactone. For example, when we used 0.1 g Brønsted acid catalysts, some solid product was generated, which led to the lower carbon yield of HAA product (*i.e.* 1a) and some confusing results. According to literature, this phenomenon can be explained because the utilization of excessive Brønsted acid catalysts will lead to the polymerization of angelica lactone and the decrease of 1a selectivity.
 References

