Supporting Information

Synthesis of renewable diesel with hydroxyacetone and 2-methyl-furan

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1. Experiment

1.1 Catalysts

Nafion-115 and Nafion-212 resins with average pore size about 4 nm were supplied by DuPont Company. Amberlyst-15 and Amberlyst-36 resins were purchased from Sigma-Aldrich. According to the information offered by supplier, the average pore diameters of Amberlyst-15 and Amberlyst-36 resin are about 29 nm and 24 nm respectively. H-β (SiO$_2$/Al$_2$O$_3$ = 25), H-USY (SiO$_2$/Al$_2$O$_3$ = 12) and H-ZSM-5 (SiO$_2$/Al$_2$O$_3$ = 140) were provided by Nankai University. Sulfated active carbon, (denoted as AC-SO$_3$H) was homemade according to the method described in our previous work. As the precursor, 2.0 g active carbon (supplied by NORIT Company) was added to 30 mL concentrated sulfuric acid (H$_2$SO$_4$, 98%) in a glass tube at room temperature. Then, the tube was heated at 523 K for 24 h under the protection of nitrogen flow (10 mL min$^{-1}$). After cooling down to room temperature and filtration, the solid was washed thoroughly with plenty of hot water (353 K) until no SO$_4^{2-}$ was detected in the filtrate. Zirconium phosphate (ZrP) was obtained according to literature by the precipitation of 1.0 mol L$^{-1}$ ZrCl$_2$O$\cdot$8H$_2$O and 1.0 mol L$^{-1}$ NH$_4$H$_2$PO$_4$ aqueous solution at a molar ratio of P/Zr = 2.0. The precipitate was filtrated, washed with water, dried at 373 K overnight and calcined in air at 673 K for 4 h.

The AC-SO$_3$H, ZrP, H-ZSM-5, H-USY, H-β catalysts used in this work were powders with particle size less than 0.4 mm. The Amberlyst-15 and Amberlyst-36 resins used in this work were beads with diameters around 0.7 mm and 0.4 mm respectively. The Nafion resins used in this work were films (thickness: 51 μm for
Nafion-212 and 127 μm for Nafion-115) which were cut into about 2×5 mm pieces by scissors before used for the reaction.

Pd/C catalyst used in HDO step was prepared by incipient wetness impregnation of the HNO₃ treated active carbon with the aqueous solutions of PdCl₂. The products were kept at room temperature for 12 h, dried at 393 K for 6 h, and then reduced by hydrogen flow (60 mL min⁻¹ g⁻¹) at 623 K for 2 h. After cooled down in hydrogen to room temperature, the catalysts were passivated with 1% O₂ in N₂ (V/V). The metal content in Pd/C catalyst was 5% by weight (denoted as 5 wt%).

1.2 Hydroxyalkylation/alkylation (HAA)

HAA reaction was carried out in a round-bottom flask equipped with a reflux condenser and a magnetic stirrer. The reaction temperature was controlled by water bath. Typically, 0.15 g catalyst, 3.28 g (40 mmol) 2-methylfuran (2-MF), 1.48 g (20 mmol) hydroxyacetone were used for each reaction. The mixture was stirred at set temperature, filtrated, and analyzed by an Agilent 1100 HPLC equipped with a ZORBAX SB-C18 (4.6 × 150 mm, 5 μm) column and refractive index detector (RID). A mixture of methanol and water (the volume ratio of methanol and water is 4:1) was used as mobile phase.

As we have reported previously,⁴,⁵ the conversion of 2-MF is higher than the yield of HAA products. The missing carbon in HAA reaction can be attributed to the large polymeric molecules (or coke) generated by over-alkylation. These compounds have high molecular weight (can’t be analyzed by GC) and low solubility in the mobile phase of HPLC. Therefore, it is very hard to give quantitative information about them.
1.3 Hydrodeoxygenation (HDO)

The HDO reaction of HAA product was carried out in a 316L stainless steel tubular flow reactor described in our previous work.\textsuperscript{4, 5} For each reaction, 1.8 g catalyst was used. The HAA product was feed into the reactor by a HPLC pump at 0.04 mL min\textsuperscript{-1} from the bottom along with hydrogen at a flow rate of 120 mL min\textsuperscript{-1}. The products from the reactor passed through a gas-liquid separator and became two phases. The gaseous products flowed through a back pressure regulator to maintain the pressure in reaction system and were analyzed online by an Agilent 6890N GC. Liquid products were drained periodically from the gas-liquid separator and analyzed by another Agilent 6890N GC.

Method for the calculation of carbon yield in HDO step:

Carbon yield of diesel (%) = \( \frac{\text{Sum of carbon in the C}_{9}-\text{C}_{16} \text{ alkanes detected from the liquid phase product}}{\text{Carbon fed into the reactor}} \times 100\% \)

Carbon yield of gasoline (%) = \( \frac{\text{Sum of carbon in the C}_{5}-\text{C}_{8} \text{ alkanes detected from the gas phase product in unit time}}{\text{Carbon fed into the reactor in unit time}} \times 100\% + \frac{\text{Sum of carbon in the C}_{5}-\text{C}_{8} \text{ alkanes detected from liquid phase products}}{\text{Carbon fed into the reactor}} \times 100\% \)

Carbon yield of light alkanes (%) = \( \frac{\text{Sum of carbon in the C}_{1}-\text{C}_{4} \text{ alkanes detected from the gas phase product in unit time}}{\text{Carbon fed into the reactor in unit time}} \times 100\% \)

According to our analysis, the carbon balance for the HDO of 2-MF-Acetone HAA product and 2-MF-Hydroxyacetone HAA product were 84.6\% and 92.1\% respectively. The missing carbon may be explained by two possible reasons. One reason is the volatilization of gasoline range alkanes during the draining of liquid
products from the gas-liquid separator and sample analyzing. Another reason is the coke formation on the surface of Pd/C catalyst. This is difficult to be proved because active carbon was used as the support.
Figure S1. HPLC chromatogram of liquid products for the HAA of 2-methylfuran (2-MF) with hydroxyacetone. Reaction conditions: 338 K, 2 h, 3.28 g 2-MF (40 mmol), 1.48 g hydroxyacetone (20 mmol) (2-MF: hydroxyacetone molar ratio was 2:1), 0.15 g Nafion-212.
Figure S2. $^{13}$C and $^1$H NMR spectra of the 1b produced by the HAA of 2-MF and hydroxyacetone.
Figure S3. $^{13}$C and $^1$H NMR spectra of the $1c$ produced by the HAA of 2-MF and hydroxyacetone.
**Figure S4.** HR-GC-MS spectra of the 1b produced by the HAA of 2-MF and hydroxyacetone.
Figure S5. Conversion of 2-MF (black bars) and yields of HAA products (gray bars) over different solid acid catalyst. Reaction conditions: 338 K, 2 h, 3.28 g 2-MF (40 mmol), 1.48 g hydroxyacetone (20 mmol) (2-MF: hydroxyacetone molar ratio was 2:1), 0.015 g catalyst.
Figure S6. Conversion of 2-MF, yields of 1b and 1c under the catalysis of different acids. Reaction conditions: 338 K; 2 h; 3.28 g 2-MF (40 mmol), 1.48 g hydroxyacetone (20 mmol) (2-MF: hydroxyacetone molar ratio was 2:1) and 0.15 mL catalyst. The concentrations of the three acids were 5 N.
Figure S7. Conversion of 2-MF, the yields of 1b and 1c over Nafion-212 resin.

Reaction conditions: 338 K, 2 h; 3.28 g (40 mmol) 2-MF, 1.48 g (20 mmol) hydroxyacetone (2-MF: hydroxyacetone molar ratio was 2:1), and 0.15 g catalyst.
**Figure S8.** Conversion of 2-MF (■), yields of 1b (▲) and 1c (▼) over Nafion-212 resin. Reaction conditions: 2 h; 3.28 g 2-MF (40 mmol), 1.48 g hydroxyacetone (20 mmol) (2-MF: hydroxyacetone molar ratio was 2:1) and 0.15 g catalyst. The reaction at 353 K was carried out in the autoclave.
Figure S9. Conversion of 2-MF (■), yields of 1b (▲) and 1c (▼) over Nafion-212 resin. Reaction conditions: 338 K; 3.28 g 2-MF (40 mmol), 1.48 g hydroxyacetone (20 mmol) (2-MF: hydroxyacetone molar ratio was 2:1) and 0.15 g catalyst.
**Figure S10.** Conversion of 2-MF (■), yields of 1b (▲) and 1c (▼) over Nafion-212 resin. Reaction conditions: 338 K, 2 h; 3.28 g 2-MF, 1.48 g hydroxyacetone (2-MF: hydroxyacetone molar ratio was 2:1).
**Figure S11.** Conversion of 2-MF (black bars) and yield of HAA products (gray bars) over Nafion-212 resin. Reaction conditions: 323 K, 2 h, 3.28 g 2-MF (40 mmol), 1.16 g acetone or 1.48 g hydroxyacetone (20 mmol) (2-MF: acetone or hydroxyacetone molar ratio was 2:1) and 0.15 g Nafion-212.
References


