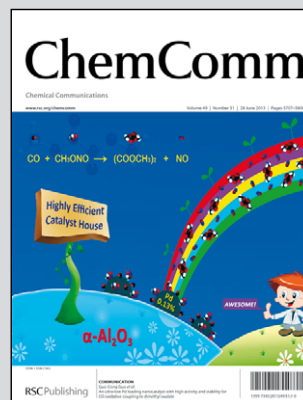


Showcasing research from Tao Zhang's
Laboratory/State Key Laboratory of Catalysis,
Dalian Institute of Chemical Physics, Chinese Academy
of Sciences, Dalian, China

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

Diesel or jet fuel range branched alkanes were synthesized for the first time by the combination of hydroxyalkylation-alkylation (HAA) of 2-methylfuran with hydroxyacetone and hydrodeoxygenation. Compared with the previous acetone route, hydroxyacetone route exhibited higher HAA reactivity and diesel yield.

As featured in:



See Tao Zhang,
Chem. Commun., 2013, **49**, 5727.

RSC Publishing

www.rsc.org/chemcomm

Registered Charity Number 207890

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

Cite this: *Chem. Commun.*, 2013, **49**, 5727Received 29th March 2013,
Accepted 7th May 2013

DOI: 10.1039/c3cc42296h

www.rsc.org/chemcomm

Guangyi Li,^{ab} Ning Li,^a Shanshan Li,^{ab} Aiqin Wang,^a Yu Cong,^a Xiaodong Wang^a and Tao Zhang^{*a}

Diesel or jet fuel range branched alkanes were synthesized for the first time by the combination of hydroxyalkylation–alkylation (HAA) of 2-methylfuran with hydroxyacetone and subsequent hydrodeoxygenation. Due to the electron-withdrawing effect of the hydroxyl group, the hydroxyacetone route exhibited evident advantages (higher HAA reactivity and diesel yield) over the previous acetone route.

The efficient utilization of biomass for the production of fuels and chemicals is a solution to the excessive dependence of our society on fossil energy and the environmental problems caused by the utilization of fossil fuels. In recent years, alkyl-fatty ester or biodiesel has been used as an important alternative fuel due to its renewability, low toxicity, low sulphur content, high biodegradability and cetane value.^{1–4} Glycerol is the by-product of biodiesel production. The production of every 10 tons of biodiesel will lead to the generation of approximately one ton of glycerol. With the rapid growth of annual biodiesel production from <1 million tons in 2000 to about 10 million tons in 2010, a large quantity of glycerol was generated.⁵ The over-supply of glycerol led to the sharp decrease in glycerol price from 1.2–2 USD kg^{−1} to 0.4 USD kg^{−1}.⁶ From the point of view of atom economy, the utilization of excess glycerol as the feedstock for fuels and high value-added chemicals is of great significance.^{6,7}

Diesel and jet fuel are two kinds of most in demand fuels. These fuels are mainly obtained from petroleum currently. Lignocellulose is the main component of agricultural waste and forest residues. Following the pioneering work of Dumesic's group^{8–10} and Huber *et al.*,^{11,12} the synthesis of diesel and jet fuel range alkanes from lignocellulose derived platform chemicals has attracted tremendous attention.^{13–16} Hydroxyacetone is the dehydration product of glycerol.^{17,18} This compound has a similar structure to acetone and can be used as a potential platform compound in the synthesis of renewable diesel or jet fuel by the combination of C–C coupling reaction and hydrodeoxygenation (HDO).² In the previous work of

Dumesic's group⁸ and Huber *et al.*,¹⁹ it was found that the aldol-condensation of hydroxyacetone with furfural or 5-hydroxymethyl-furfural could take place under the catalysis of a solid base or organic base. However, due to the serious C–C cleavage, which occurred during the HDO of aldol condensation products, low yields of liquid alkanes (<30%) were obtained. To fulfill the need for real application, some new routes with higher selectivity to diesel or jet fuel range alkanes should be developed. In the recent work of Corma *et al.*^{13,20,21} and our group,^{22,23} it was found that diesel or jet fuel range branched alkanes could be synthesized by the hydroxyalkylation–alkylation (HAA) of 2-methylfuran (2-MF) with lignocellulose derived carbonyl compounds followed by the HDO. 2-MF can be prepared by the selective hydrogenation of furfural which has been produced for decades on an industrial scale by the hydrolysis–dehydration of the hemicellulose part of agricultural waste and forest residues.²⁴ The lignocellulose derived carbonyl compounds can be aldehydes (such as furfural, 5-hydroxymethylfurfural, methylfurfural, butanal and ethanal), ketones (*e.g.* acetone and 2-pentanone) and levulinic acid or esters. However, to the best of our knowledge, there is no report on the HAA of furan compounds with hydroxyacetone, let alone the use 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 hydroxyacetone over a series of solid acid catalysts is reported for the first time. The as prepared HAA product was hydrodeoxygenated over the Pd/C catalyst.

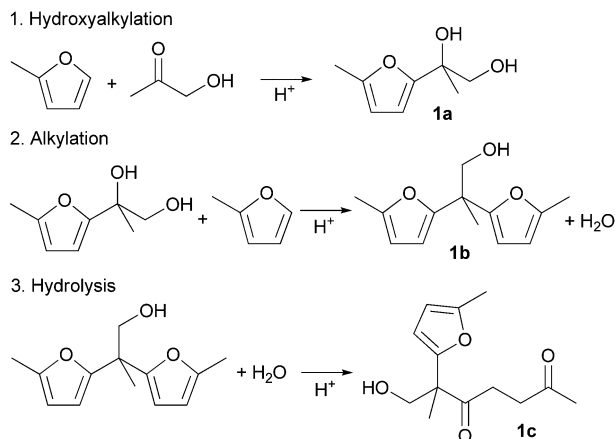
The HAA of 2-MF and hydroxyacetone was carried out over a series of solid acid catalysts. From HPLC, NMR and HR-GC-MS (see Fig. S1–S4, ESI†) analyses, 2,2-bis(5-methylfuran-2-yl)propan-1-ol (*i.e.* **1b** in Scheme 1) was identified as the main product. Small amount of 7-hydroxy-6-methyl-6-(5-methylfuran-2-yl)heptane-2,5-dione (*i.e.* **1c** in Scheme 1) was detected as the by-product. This compound was produced by the hydrolysis of **1b**. Based on the above information, the reaction pathway for the HAA of 2-MF with hydroxyacetone is proposed in Scheme 1. The absence of 2-(5-methylfuran-2-yl)propane-1,2-diol (*i.e.* **1a** in Scheme 1) in liquid products can be explained by the much higher rate of the alkylation step than that of hydroxyalkylation.²²

Fig. 1 shows the conversion of 2-MF and yields of **1b** and **1c** over a series of solid acid catalysts. Among them, Nafion-212

^a State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China. E-mail: taozhang@dicp.ac.cn; Fax: +86 411 84691570

^b Graduate University of Chinese Academy of Sciences, Beijing 10049, China

† Electronic supplementary information (ESI) available: Experimental section, NMR and mass spectra. See DOI: 10.1039/c3cc42296h



Scheme 1 Reaction pathway for the HAA of 2-methylfuran (2-MF) with hydroxyacetone.

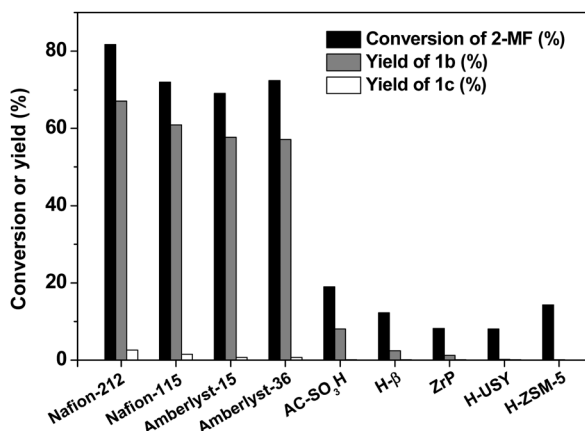


Fig. 1 Conversion of 2-MF and the yields of **1b** and **1c** over different solid acid catalysts. Reaction conditions: 338 K, 2 h; 3.28 g (40 mmol) 2-MF, 1.48 g (20 mmol) hydroxyacetone (2-MF : hydroxyacetone molar ratio was 2 : 1), and 0.15 g catalyst.

exhibited the highest activity for the HAA of 2-MF with hydroxyacetone. The advantage of Nafion-212 resin is more significant at low catalyst loading (see Fig. S5, ESI†). According to the results shown in Fig. 1 and Fig. S5 (ESI†), the activity sequence of the different catalysts is Nafion-212 > Nafion-115 > Amberlyst-15 > Amberlyst-36 > AC-SO₃H > H-β > ZrP > H-USY > H-ZSM-5. As far as the TON and TOF of 2-MF to **1b** (deduced from the **1b** yield in Fig. S5 (ESI†) and the acid amount measured by the chemisorption of NH₃) are concerned, the Nafion resins also demonstrated an evidently higher catalytic efficiency than other solid acid catalysts (see Fig. 2).

To find out the intrinsic reason for the difference in activity of various catalysts, we also compared the activities of H₂SO₄, H₃PO₄, and CH₃COOH (these acids were chosen to represent strong acid, medium acid and weak acid respectively). To facilitate the comparison, the H⁺ molar concentration and the total acid amounts of three acid solutions were kept the same (5 mol L⁻¹ and 0.75 mmol). According to the results shown in Fig. S6 (ESI†), the sequence for the yield of **1b** under the catalysis of different acids is H₂SO₄ (33.0%) > H₃PO₄ (0.5%) > CH₃COOH (0.0%). Such a sequence is consistent with that of acid strength. According to this result, the HAA of 2-MF is sensitive to the acid strength of the

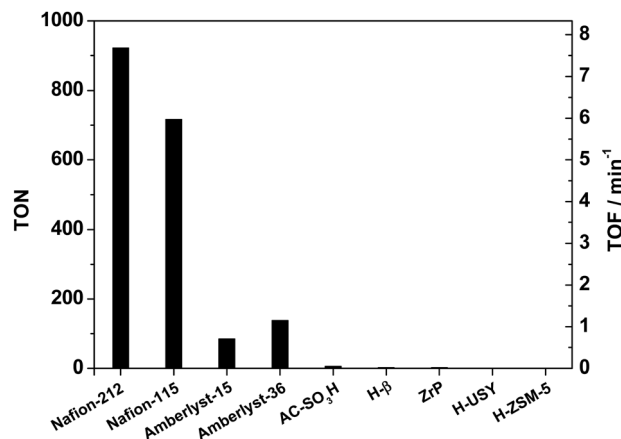


Fig. 2 TON and TOF of 2-MF to **1b** over different solid acid catalysts. Reaction conditions: 338 K, 2 h; 3.28 g (40 mmol) 2-MF, 1.48 g (20 mmol) hydroxyacetone (2-MF : hydroxyacetone molar ratio was 2 : 1), and 0.015 g catalyst.

catalyst. Strong acid is more active than medium acid and weak acid for this reaction. Analogously, the activity sequence of Nafion resins, Amberlyst resins and sulfated active carbon can also be rationalized by their acid strength. According to the literature,^{25–27} Nafion is a perfluorinated sulfonic acid resin that is often denoted as a superacid. Amberlyst is a sulfonic-acid-functionalized cross-linked polystyrene resin. However, sulfated active carbon is amorphous carbon bearing SO₃H, COOH and phenolic OH groups which function as acid sites. In Nafion resins, the acid strength of the SO₃H group is enhanced by the presence of fluorine, which makes its acid strength higher than that of Amberlyst resins and sulfated active carbons. Consequently, Nafion resins have the highest activity and efficiency for the HAA of 2-MF with hydroxyacetone.

The stability of Nafion-212 in the HAA of 2-MF with hydroxyacetone was also studied. To exclude the influence of reaction residues (including hydroxyalkylation and HAA products, unreacted hydroxyacetone and 2-MF), the catalyst was washed thoroughly with methanol after each usage and dried at 353 K for 1 h. From the result shown in Fig. S7 (ESI†), no evident change in activity of Nafion-212 resin was observed even after being repeatedly used six times. This result shows that the Nafion-212 resin is very stable under the investigated conditions. According to the high activity and stability of Nafion-212 resin, it can be considered as a promising catalyst for real application.

Fig. S8–S10 (ESI†) illustrate the influence of catalyst loading, reaction temperature and reaction time on the yields of **1b** and **1c** over Nafion-212 resin. Under optimum conditions, 70.8% yield of **1b** and 8.3% yield of **1c** were obtained over 0.15 g Nafion-212 resin after reacting at 338 K for 6 h. Both **1b** and **1c** can be used as precursors for synthesis of renewable diesel or jet fuel.

In the previous work of Corma *et al.*¹⁶ and our group,^{22,23} 5,5'-(propane-2,2-diyl)bis(2-methylfuran) was prepared by the HAA of 2-MF with acetone. In this work, the reactivity of hydroxyacetone and acetone in the HAA of 2-MF was compared at 323 K. Under the same reaction conditions, an evidently higher yield of the HAA product (41.6% vs. 24.7%) can be achieved over Nafion-212 resin when hydroxyacetone was used to replace acetone as the carbonyl compound to react with 2-MF (see Fig. S11, ESI†). This can be considered as an advantage of

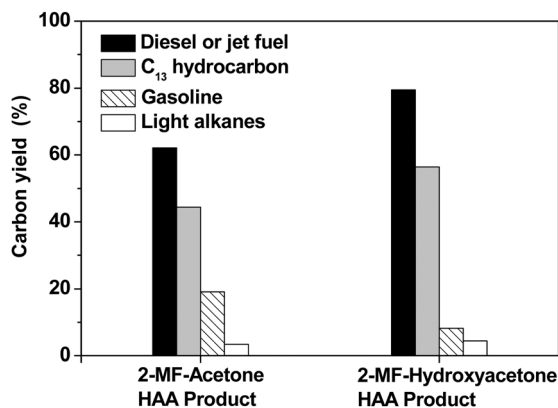


Fig. 3 Carbon yields of different alkanes from the hydrodeoxygenation (HDO) of HAA products between 2-MF and acetone or hydroxyacetone over the Pd/C catalyst. Reaction conditions: 1.8 g catalyst; 643 K; liquid feedstock flow rate: 0.04 mL min⁻¹; hydrogen flow rate: 120 mL min⁻¹. The diesel, gasoline and light alkanes account for C₉–C₁₃, C₅–C₈ and C₁–C₄ alkanes respectively. The method used for the calculation of carbon yield is described in the ESI.†

the hydroxyacetone route. The higher reactivity of hydroxyacetone can be explained by the enhanced electrophilicity of the carbonyl group by the electron-withdrawing effect of the hydroxyl group attached to one of the α -carbon atoms.

As the final aim of this work, the HDO of HAA products of 2-MF and hydroxyacetone (with **1b** as the main component) was also explored over the Pd loaded active carbon catalyst. The results are shown in Fig. 3. From GC-MS analysis, the HAA products of 2-MF and hydroxyacetone were totally converted at 643 K, with CO₂ and hydrocarbons as the final products. This result shows that 643 K is enough for the complete HDO of **1b** and **1c**. Compared with the HDO of the HAA product of 2-MF with acetone under the same reaction conditions, an evidently higher carbon yield for diesel or jet fuel range alkanes (79.5% vs. 62.1%) and C₁₃ alkanes (56.5% vs. 44.4%) can be obtained by the HDO of HAA products of 2-MF with hydroxyacetone. The predominant component of the C₁₃ alkanes from the HDO of HAA products of 2-MF with hydroxyacetone is 2,2-dimethyl-undecane. The higher carbon yield of diesel or jet fuel range alkanes in the HDO of HAA products of 2-MF with hydroxyacetone can be also explained by the presence of the hydroxyl group. In the previous work of Corma *et al.*²¹ and our group,²³ it was found that C–C cleavage in the HDO of HAA products is preferable at branched carbon atoms. Carbocations will be generated by C–C cleavage which can decrease the diesel or jet fuel yield. The extent of C–C cleavage depends on the stability of carbocations formed during the HDO process. In the HDO of HAA products of 2-MF with acetone and hydroxyacetone, tertiary carbocations will be generated with the C–C cleavage at branched carbon atoms. Due to the electron-withdrawing effect of the hydroxyl group, the electron donating effect of one methyl group to the branched carbon atom in HAA products of 2-MF with hydroxyacetone is weakened. As a result, the carbocation intermediate produced after the C–C cleavage becomes less stable and the C–C cleavage reaction is restrained.

In this work, a brand new route for the synthesis of diesel or jet fuel range branched alkanes was developed by the HAA of 2-MF with hydroxyacetone followed by the HDO. Among the investigated solid acids, Nafion-212 resin exhibited the highest

activity and stability. Under solvent-free conditions, 79.1% yield of HAA products was obtained over Nafion-212 resin. After the HDO of the HAA products over the Pd/C catalyst, 79.5% carbon yield for diesel or jet fuel range alkanes could be achieved. Compared with the 2-MF-acetone route described in our previous work, the hydroxyacetone route has many advantages such as the higher HAA reactivity and higher carbon yield of diesel or jet fuel range alkanes in the HDO process, which can be explained by the electron-withdrawing effect of the hydroxyl group.

This work was supported by the Natural Science Foundation of China (no. 21106143), 100 talent project of the Dalian Institute of Chemical Physics (DICP), and the Independent Innovation Foundation of State Key Laboratory of Catalysis (no. R201113) of DICP.

Notes and references

- G. W. Huber, S. Iborra and A. Corma, *Chem. Rev.*, 2006, **106**, 4044–4098.
- D. M. Alonso, J. Q. Bond and J. A. Dumesic, *Green Chem.*, 2010, **12**, 1493–1513.
- L. C. Meher, D. V. Sagar and S. N. Naik, *Renewable Sustainable Energy Rev.*, 2006, **10**, 248–268.
- F. R. Ma and M. A. Hanna, *Bioresour. Technol.*, 1999, **70**, 1–15.
- C.-H. Zhou, J. N. Beltramini, Y.-X. Fan and G. Q. Lu, *Chem. Soc. Rev.*, 2008, **37**, 527–549.
- Y. Nakagawa and K. Tomishige, *Catal. Sci. Technol.*, 2011, **1**, 179–190.
- C. H. C. Zhou, J. N. Beltramini, Y. X. Fan and G. Q. M. Lu, *Chem. Soc. Rev.*, 2008, **37**, 527–549.
- G. W. Huber, J. N. Chheda, C. J. Barrett and J. A. Dumesic, *Science*, 2005, **308**, 1446–1450.
- E. L. Kunkes, D. A. Simonetti, R. M. West, J. C. Serrano-Ruiz, C. A. Gartner and J. A. Dumesic, *Science*, 2008, **322**, 417–421.
- J. Q. Bond, D. M. Alonso, D. Wang, R. M. West and J. A. Dumesic, *Science*, 2010, **327**, 1110–1114.
- R. Xing, A. V. Subrahmanyam, H. Olcay, W. Qi, G. P. van Walsum, H. Pendse and G. W. Huber, *Green Chem.*, 2010, **12**, 1933–1946.
- H. Olcay, A. V. Subrahmanyam, R. Xing, J. Lajoie, J. A. Dumesic and G. W. Huber, *Energy Environ. Sci.*, 2013, **6**, 205–216.
- A. Corma, O. de la Torre, M. Renz and N. Vollandier, *Angew. Chem., Int. Ed.*, 2011, **50**, 2375–2378.
- S. Crossley, J. Faria, M. Shen and D. E. Resasco, *Science*, 2010, **327**, 68–72.
- P. Anbarasan, Z. C. Baer, S. Sreekumar, E. Gross, J. B. Binder, H. W. Blanch, D. S. Clark and F. D. Toste, *Nature*, 2012, **491**, 235–239.
- B. G. Harvey and R. L. Quintana, *Energy Environ. Sci.*, 2010, **3**, 352–357.
- S. S. Niu, Y. L. Zhu, H. Y. Zheng, W. Zhang and Y. W. Li, *Chin. J. Catal.*, 2011, **32**, 345–351.
- S. Sato, D. Sakai, F. Sato and Y. Yamada, *Chem. Lett.*, 2012, **41**, 965–966.
- A. V. Subrahmanyam, S. Thayumanavan and G. W. Huber, *ChemSusChem*, 2010, **3**, 1158–1161.
- A. Corma, O. de la Torre and M. Renz, *ChemSusChem*, 2011, **4**, 1574–1577.
- A. Corma, O. de la Torre and M. Renz, *Energy Environ. Sci.*, 2012, **5**, 6328–6344.
- G. Li, N. Li, Z. Wang, C. Li, A. Wang, X. Wang, Y. Cong and T. Zhang, *ChemSusChem*, 2012, **5**, 1958–1966.
- G. Li, N. Li, J. Yang, A. Wang, X. Wang, Y. Cong and T. Zhang, *Bioresour. Technol.*, 2013, **134**, 66–72.
- J.-P. Lange, E. van der Heide, J. van Buijtenen and R. Price, *ChemSusChem*, 2012, **5**, 150–166.
- R. Weingarten, G. A. Tompsett, W. C. Conner and G. W. Huber, *J. Catal.*, 2011, **279**, 174–182.
- K. A. Mauritz and R. B. Moore, *Chem. Rev.*, 2004, **104**, 4535–4586.
- B. G. Harvey, M. E. Wright and R. L. Quintana, *Energy Fuels*, 2010, **24**, 267–273.