



Cutting-edge research for a greener sustainable future

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: T. Cai, Q. Deng, H. Peng, J. Zhong, R. Gao, J. Wang, Z. Zeng, J. Zou and S. Deng, Green Chem., 2020, DOI: 10.1039/D0GC00195C.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/greenchem

Green Chemistry

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/



Taimei Cai^a, Qiang Deng^{a,b*}, Hailong Peng^a, Jin Zhong^a, Rui Gao^a, Jun Wang^a, Zheling Zeng^a, Ji-Jun Zou^{c*}, Shuguang Deng^{a,b*}

The major challenge in the synthesis of high-density biofuel is to identify biobased source of C-C cyclic compounds and C-C coupling reactions with a suitable selectivity. Herein, we selectively synthesize 1,2,4-benzenetriol (BTO) with a yield of 51.4% from cellulose-derived 5-hydromethylfurfural via a ring-rearrangement reaction. The cellulose-derived route is a more meaningful route for C-C cyclic compounds compared to the traditional hemicellulose- and lignin-derived routes. Subsequently, BTO is very easily dimerized via a C-C oxidative coupling reaction, presenting a yield of 94.4% and selectivity of nearly 100% at environmentally friendly reaction conditions. After hydrodeoxygenation, bicyclohexane is obtained with a yield of 87.4%. This work not only provides a promising route to produce C-C cyclic fine compounds based on a cellulose-derived route but also shows a highly efficient synthesis route for high-density biofuel via the C-C oxidative coupling reaction.

Introduction

Published on 20 February 2020. Downloaded by LA TROBE UNIVERSITY on 2/22/2020 1:09:18 PM

High-density jet fuel consisting of cycloalkanes has a higher density and volumetric heat value than conventional jet fuels. It is an indispensable propellant for volume-limited aircraft (e.g., missiles and rockets) because of extended flight distance and loading capacity.¹ Conventionally, the synthesis of high-density jet fuel is mainly based on petroleum-based cyclopentadiene.¹ Due to the excessive depletion of petroleum and the massive amount of greenhouse gas emissions, substantial efforts have been devoted to the production of high-density fuels from renewable biomass.² Lignocellulosic biomass represents an attractive renewable feedstock that can be mainly converted into three main families of compounds: (1) small oxygenates (e.g., acetone, butanol and ethanol); (2) hemicelluloses- and celluloses-derived compounds (e.g., furfural, 5hydroxymethylfurfural, 2-methyl furan, furfural alcohol); and (3) lignin-derived compounds (e.g., guaiacol, anisole, phenol, benzyl ether, benzyl alcohols).³ To synthesize jet fuel with carbon chains consisting of 10-17 carbons, these smallmolecule compounds are required to undergo a C-C coupling



DOI: 1

Currently, the biomass-derived route of aforementioned C-C six-membered ring aromatic oxygenates (phenol, anisole, guaiacol) are mainly synthesized via the fast pyrolysis of lignin with a natural aromatic structure.¹⁵ Even, cyclohexanone requires further conversion by the selective hydrodeoxygenation of lignin-derived phenols.¹⁶ Unfortunately, because of the complicated structure of lignin, the product composition of the fast pyrolysis is complex, and the yield of target aromatic molecules is very low. On the other hand, some

a Key Laboratory of Poyang Lake Environment and Resource Utilization (Nanchang University) of Ministry of Education, School of Resource, Environmental and Chemical Engineering, Nanchang University, No. 999 Xuefu Avenue, Nanchang 330031, PR China

b School for Engineering of Matter, Transport and Energy, Arizona State University, 551 E. Tyler Mall, Tempe, AZ 85287, USA

c Key Laboratory for Green Chemical Technology of the Ministry of education, School of Chemical Engineering and Technology, Tianjin University; Collaborative Innovative Center of Chemical Science and Engineering (Tianjin), No.92 Weijin Road, Tianjin 300072, PR China

E-mail: Shuguang.Deng@asu.edu (Shuguang Deng); jj_zou@tju.edu.cn (Ji-Jun Zou); dengqiang@ncu.edu.cn (Qiang Deng).

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

ARTICLE

C-C five-membered ring compounds (e.g., cyclopentanone and cyclopentanol) can be selectively synthesized by the hydrogenative ring-rearrangement of hemicelluloses-derived furfural (Scheme 1).¹⁷ In the hydrogenative ring-rearrangement reaction process, furfural can convert to 2,5-dicarbonyl compound via subsequent C=O hydrogenation, hydrolysis and dehydration steps. Then, 2,5-dicarbonyl compound can build a C-C five-membered ring structure by a intramolecular aldol step, and cyclopentanone and cyclopentanol are synthesized after the followed hydrogenation and dehydration steps. These synthesis routes for C-C five-membered ring compounds are limited because the amount of hemicellulose precursor is low.³ Similar to the formation of furfural, cellulose can be transformed to 5-hydroxymethylfurfural (HMF) via hydrolysis and subsequent hydration reactions. Compared with furfural, 5hydroxymethylfurfural is a more promising platform compound because the amount of cellulose precursor is much higher than hemicelluloses precursor. Hence, the conversion of HMF is more meaningful. Recently, 5-hydroxymethylfurfural used as a feedstock for the synthesis of various high-valued compounds, including 2,5-furandicarboxylic acid, 2,5dihydroxymethyltetrahydrofuran, 2,5-furandimethanol, 2,5dimethylfuran, linear alcohols, and so on.18 Similar to the hydrogenative ring-rearrangement of furfural to cyclopentanone, HMF has been used for the synthesis of C-C five-membered ring compounds (e.g., 3-hydromethyl cyclopentanone and 3-hydromethyl cyclopentanol).19 In contrast, the use of HMF to synthesize C-C six-membered ring compounds is rarely reported. It should be mentioned that, besides the synthesis of high-density fuel, the C-C ring compounds are important fine chemicals, which are widely used for the synthesis of medicines, spices, pesticides, dyes, and rubber.^{7a} The synthesis of C-C six-membered compounds from HMF means a selective route from cellulose rather than the traditional low efficient route from lignin.



Scheme 1. Synthetic routes for the production of C-C ring compounds and bicycloalkanes.

About thirty years ago, van Bekkum's group optimized the reaction conditions for the ring-rearrangement reaction of HMF to 1,2,4-benzenetriol (BTO) and achieved a yield of up to 25% at reaction temperatures ranging from 330-350 °C.²⁰ Different from the hydrogenative ring-rearrangement reaction, HMF is

directly hydrolyzed to a 1,5-dicarbonyl compound, and then converted to BTO with a C-C six-membere thing tracture by the intramolecular aldol, and subsequent dehydration steps. Subsequently, some other groups mentioned BTO as a byproduct in the transformation of HMF or fructose.²¹ Until recently, Deuss's group synthesized BTO as the main product with a yield of 54% from HMF via Lewis acid catalysis under a reaction temperature of 400 °C.²² Interestingly, BTO is unstable and easily generates a dimer via a C-C oxidative coupling. Although the dimerization is considered as a side reaction in their work, which inspired us to synthesize a C-C six-membered ring compound from 5-hydroxymethylfurfural and develop an advanced synthesis route for bicycloalkanes.

To the best of our knowledge, although the C-C coupling reaction of biomass derivatives has been widely reported for the synthesis of biofuel, a green and efficient C-C oxidative coupling reaction has not been reported yet. Herein, we report for the first time a novel route to synthesize high-density fuel directly using HMF as feedstock (Scheme 1). The reaction process consists of three steps, including the ringrearrangement of HMF to BTO, C-C oxidative coupling reaction of BTO to the dimer, and the hydrodeoxygenation of the dimer to high-density bicycloalkanes.

Experimental

Materials and Characterizations

Acetic acid, cyclohexane, Al_2O_3 and Nb_2O_5 were obtained from Xi Long scientific Co., China. 5-Hydroxymethylfurfural and 5-methylfurfural were purchased from Beijing Fang Cheng Biotechnology Co., China. 1,2,4-benzenetriol and 1,4benzenediol were supplied by Sigma-Aldrich. Pd/C (5 wt%), terephthalic acid and formic acid were obtained from Aladdin Industrial Co.. ZrO_2 , TiO₂, benzoic acid, 1,2,4-benzenetriol and monochloroacetic acid were purchased from Shanghai Mackin Co., China. All chemicals were reagent grade and used without further purification. HZSM-5 (SiO₂/Al₂O₃ = 27) supplied by Nankai Catalysts Co., China, was calcined in air for 12 h at 550 °C.

The specific surface area and pore size were obtained by performing N_2 adsorption-desorption at -196 °C on an ASAP 2046 surface analyzer. The acid amount was characterized by determining the temperature-programmed desorption of ammonia (NH₃-TPD) on a Micromeritics AutoChem II 2920 instrument.

Ring-rearrangement of HMF

The ring-rearrangement of HMF was conducted in a 2 mL stainless-steel reactor. Typically, a mixture of HMF (0.04 mmol), water (1.0 mL) and the catalyst (8.75 mmol acid amount of liquid acids or 0.42 mmol acid amount of solid acids) was added into the reactor, then heated to target temperature, and sampled periodically. If not mentioned, the reaction temperature is 300 °C, and the duration of the reaction was 15 min. The liquid products were qualified by liquid chromatography-mass spectrometry (LC-MS, Triple TOF 5600/Agilent QTOF 6545 mass spectrometer detector), and

Journal Name

Published on 20 February 2020. Downloaded by LA TROBE UNIVERSITY on 2/22/2020 1:09:18 PM

Journal Name

quantified by high performance liquid chromatography (UltiMate 3000) equipped with an ultraviolet visible spectrophotometer detector (detection wavelength: 293 nm) and C₁₈ column (Zorbax Eclipse Plus, 4.6 mm × 250 mm, 5 μ m). The mobile phase was consisted of methanol and water (volume ratio = 1:9) with a flow rate of 0.8 ml·min⁻¹. The column was operated at 25 °C. Meanwhile, the gaseous products were analyzed by gas chromatography (GC, Agilent 7890B) equipped with a FID detector and Hayesep Q 80/100 mesh packed column (1.8 m × 2 mm). Only hydrogen can be measured in the gaseous products. The concentrations of liquid products were determined using calibration curves obtained by an internal standard. The rest was defined as carbon loss. The reported data were the mean values of three trials with small error bars. **Dimerization of BTO**

The dimerization of BTO was performed in a three-necked round-bottomed flask. A mixture of BTO (1 mmol) and water (60 mL) was heated to 100 °C under an air atmosphere. After a certain reaction time, the product was qualified by LC-MS, and quantified by high-performance liquid chromatography. The structure of the product was also determined by ¹³C NMR spectra collected on a Varian Inova 500 MHz NMR.

Hydrodeoxygenation of dimer

The hydrodeoxygenation of dimer was carried out in a 100 ml batch autoclave (Anhui Kemi Machinery Technology Co., LTD) equipped with mechanical stirring. A mixture of dimer (1.2 mmol), HZSM-5 (1.00 g), Pd/C (0.08 g), water (15 mL) and cyclohexane (15 mL) were added to the autoclave and heated to 240 °C under 8.0 MPa H₂ pressure. After a certain reaction time, the reaction mixture was quenched in a cold-water bath. The products in cyclohexane solution were qualified by gas chromatography-mass spectrometry (GC-MS, Agilent 6890 N GC/5973 MS detector) and quantified by gas chromatography (Thermo TRACE-1300) equipped with a FID detector and TG-WAXMS capillary column (30 m × 0.32 mm, 0.25 μ m). The products in aqueous solution were extracted with ethyl acetate, then qualified by LC-MS and quantified by high-performance liquid chromatography.

Results and Discussion

Ring-rearrangement of HMF

As shown in Figure 1A, the ring-rearrangement of HMF to BTO involves a hydrolysis ring-opening reaction to a 6-hydroxyhexane-1,2,5-trione intermediate with a 1,5-dicarbonyl structure, intramolecular aldol condensation reactions to 2,3dihydroxy-cyclohexane-1,4-dione, and a dehydration reaction to BTO. Figure 1B shows the catalytic kinetics under acetic acid catalysis. A trace amount of 6-hydroxy-hexane-1,2,5-trione is detected in LC-MS (Figure S1), confirming the reaction mechanism. Additionally, the result also indicates that the intramolecular aldol and dehydration reactions occurred quickly, and that the ring-opening reaction is a rate-limiting step. HMF was gradually transformed with the extension of reaction time. However, the yield of BTO first increased and then decreased, and a large quantity of humins was generated. The active furan ring, carbonyl and hydroxyl groups in HMF. intermediates and BTO can easily Olition 1021 geor Costone intermolecular C-C coupling reactions, and the generation of large molecular compounds results in carbon loss. Interestingly, some 5-methylfurfural and 1,4-benzenediol were also synthesized. Combined with previous work, H₂ can be in situ generated by the decomposition of formic acid that is the hydration product of HMF. ^23 The in situ generated ${\rm H}_2$ is detected by GC (Figure S2). The production of 5-methylfurfural may be ascribed to the reduction of HMF by H₂.²⁴ Similar to HMF, 5-methylfurfural can be converted to 1,4-benzenediol via the ring-rearrangement reaction. To verify the reaction mechanism, 5-methylfurfural was directly used as a reactant, and 1,4-benzenediol was obtained with an approximately 10% yield of BTO after 15 min (Figure S3). Likewise, a large quantity of humins was generated by the intermolecular C-C coupling reaction. Finally, 99.3% conversion of HMF was achieved, and a 38.7% yield of BTO and a 0.6% yield of 1,4-benzenediol were generated after 15 min.



Figure 1. (A) Proposed reaction pathway for BTO preparation, (B) time-dependent product distribution using acetic acid as a catalyst, (C) catalytic performance of several acid catalysts, (D) effect of reaction temperature, (E) effect of amount of acetic acid. Reaction conditions: (B) HMF (0.04 mmol), acetic acid (8.75 mmol), water (1 mL), 300 °C; (C) HMF (0.04 mmol), liquid acids (8.75 mmol acid amount) or solid acids (0.42 mmol acid amount), 300 °C, reaction time 15 min; (D) HMF (0.04 mmol), acetic acid (43.75 mmol), water (1 mL), 300 °C, reaction time 15 min.

Then, we compared some common homogeneous acids (such as terephthalic acid, benzoic acid, formic acid, monochloroacetic acid and acetic acid) with the same acid amount (Figure 1C). All of these homogeneous acids showed a Published on 20 February 2020. Downloaded by LA TROBE UNIVERSITY on 2/22/2020 1:09:18 PM

near 100% catalytic activity, indicating that HMF is easily transformed. Meanwhile, a small amount of 5-methylfurfural and 1,4-benzenediol was generated. The yield of BTO is dependent on the acid strength: acetic acid (38.7%, PKa = 4.74) > benzoic acid (31.2%, PKa = 4.21) > terephthalic acid (23.9%, PKa = 3.54) > monochloroacetic acid (7.6%, PKa = 2.86). Weak acidity is beneficial to the synthesis of BTO because the carbon loss is more easily occurred by strong acidity. Exceptionally, formic acid (PKa = 3.77) has a weaker acidity than terephthalic acid (PKa = 3.54), but the yield of BTO was lower (20.9% vs 23.9%). A considerable amount of 1,4-benzenediol was synthesized with a yield of 4.4% due to the reduction of HMF to 5-methylfurfural via the in situ generated H₂.²⁵ Meanwhile, various solid acids (such as ZrO₂, TiO₂, Nb₂O₅, Al₂O₃ and HZSM-5) were further used in this reaction. The textural properties of solid acids were assessed from $N_{2}% \left(A_{1}^{2}\right) =0$ adsorption-desorption (Figure S4, Table S1). ZrO₂, TiO₂ and Nb₂O₅ only show specific surface areas of approximately 4 $m^2 \cdot g^{-1}$, whereas Al₂O₃ and HZSM-5 possess specific surface areas of 150.9, and 305.6 m²·g⁻¹, respectively. The NH₃-TPD shows the acid concentration of TiO₂ (0.0038 mmol·g⁻¹), ZrO₂ (0.0021 mmol·g⁻¹), Nb₂O₅ (0.0034 mmol·g⁻¹), Al₂O₃ (0.0902 mmol·g⁻¹), and HZSM-5 (0.4211 mmol·g⁻¹) (Figure S5, Table S1). Meanwhile, the acidity of the catalyst was illuminated by the desorbed temperature of NH₃. Obviously, the order of acidity of these metal oxides is HZSM-5 (213, 439 °C) > Al₂O₃ (140 °C) > Nb₂O₅ (137 °C) > TiO₂ (135 °C) > ZrO₂ (130 °C). To better study the effect of acidity and specific surface area, the same acid amount with different catalyst mass was used in the reaction. ZrO₂, TiO₂, Nb₂O₅ and Al₂O₃ show high catalytic activity. HZSM-5 possesses a low catalytic activity with 48.2% of conversion because of their microporous structure (0.55 nm). The yield of BTO is also decreased with the acidity: ZrO_2 (24.2%) > TiO_2 (22.0%) > Nb₂O₅ (18.9%) > Al₂O₃ (15.9%) > HZSM-5 (8.6%). The result further proves that the acidity of the catalyst has a significant effect on the reaction.

Subsequently, the reaction conditions (catalyst amount, reaction temperature) are optimized. As shown in Figure 1D, as the acid amount of acetic acid increases from 8.75 mmol to 43.75 mmol, the yield of BTO and 1,4-benzenediol is increased from 38.7% and 0.6% to 51.4% and 3.6%, respectively. When the reaction temperature decreases to 260 °C, 94.2% of HMF is converted. However, when the reaction temperature increases to 320 °C, the BTO yield is decreased to 36.2% and 1,4-benzenediol yield is increased to 18.3%, because hydrogen is largely generated via the decomposition of in situ generated formic acid.²³ (Figure 1E) Under the optimal conditions, 100% of HMF is converted with a 51.4% BTO yield via acetic acid catalysis at 300 °C for 15 min.

Dimerization of BTO

The dimerization of BTO was conducted via a C-C oxidative coupling in an environmentally friendly aqueous solvent under an air atmosphere. During the reaction, a dimer is generated and precipitated, which is very easily separated by filtering (Figure 2A) The dimer formation was verified by the NMR and LC-MS (Figures S6, S7). The reaction kinetics are presented in Figure 2B. After 72 h, the conversion of BTO was 94.4%, the

Page 4 of 7

selectivity of the dimer was 100% and no other byproducts were created. DOI: 10.1039/D0GC00195C

During the oxidative coupling reaction, O₂ is a reactant for the oxidation of BTO to obtain a radical intermediate (Figure 2A). Due to the stabilization of two phenolic groups in the ortho/para or ortho/ortho positions, the generation of 5-radical and 3-radical intermediates is preferential. These radicals can be transformed between one another. Subsequently, due to the $C_{\rm 5}$ position having a lower steric hindrance, a dimer was formed via the combination of the C5 position.²⁶ When the reaction was conducted under a N_2 atmosphere, the reaction became inactive. The control experiment shows the importance of O₂. Usually, traditional C-C coupling reactions (such as, alkylation, aldol condensation) need acid/base catalysts, which increases the cost. Meanwhile, the yield of bicycloalkane precursors is always unsatisfactory because of the generation of tricycloalkane precursors via excessive coupling reactions. It should be mentioned that tricycloalkane is not suitable for liquid fuel because of the high freezing point. On the contrary, the oxidative coupling reaction provides a non-catalytic reaction system with high yield and easy separation for bicycloalkane precursors.



Figure 2. (A) Proposed reaction pathway for dimer preparation, (B) catalytic kinetics curve in the oxidative coupling reaction under different gas atmosphere. Reaction conditions: BTO (1 mmol), water (60 mL), 100 °C.

Hydrodeoxygenation of dimer

The hydrodeoxygenation of the dimer was conducted over Pd/C and HZSM-5 catalysts in a mixture solvent of water and cyclohexane. The Pd/C and HZSM-5 provide the noble metal and acid sites for hydrogenation and dehydration reactions, respectively. The reactant dimer and product bicyclohexane dissolve preferentially in water and cyclohexane, respectively. The mixed solvent of water and cyclohexane was used as the reaction medium to facilitate the approach of the reactant and hinder the coverage of product to the catalyst surface.²⁷ As shown by the reaction kinetics (Figure 3A, B), the dimer is converted to 2-cyclohexylcyclohexenylene via a series of hydrogenation and dehydration reactions at the beginning, and then 2-cyclohexylcyclohexanol is formed by C=C hydrogenation. Finally, bicyclohexane is obtained by C=C hydrogenation of the dehydrated 1-cyclohexyl-cyclohexene. These intermediates and products were confirmed by GC-MS (Figure S8). At last, a dimer

Nanus

MIStr

Journal Name

conversion of 96.7%, bicyclohexane selectivity of 90.4%, and a bicyclohexane yield of 87.4% were obtained after 10 h. The bicyclohexane, with a high density of 0.886 g·mL⁻¹, is desirable and has potential applications for direct use or by mixing with other fuels.^{10b}

Figure 3. (A) Proposed reaction pathway for bicyclohexane preparation, (B) catalytic kinetics curve in the hydrodeoxygenation reaction. Reaction conditions: dimer (1.2 mmol), HZSM-5 (1.00 g), Pd/C (0.080 g), water (15 mL), cyclohexane (15 mL), 240 °C, 8.0 MPa of H₂ pressure.

Conclusions

In summary, this work provides a synthesis route for a C-C six-membered ring BTO from cellulose-derived HMF. The cellulose-derived synthesis route for C-C ring compounds is more efficient than the lignin- and hemicelluloses-derived routes. Moreover, a green and efficient route for high-density fuel is reported for the first time via a C-C oxidative coupling reaction combined with subsequent hydrodeoxygenation reaction. As a result, final bicyclohexane is obtained with an overall yield of 42.4 %. Thus, this work offers a promising route for producing C-C ring fine compounds and high-density fuel using HMF as a reactant.

Conflicts of interest

The authors declare no conflict of interests.

Acknowledgements

The authors appreciate the supports from the National Natural Science Foundation of China (21878138, 21666021, 21706112), Postdoctoral Science Foundation of China (2017KY21, 2018T110660) and the new faculty start-up funds from both Nanchang University and Arizona State University.

Notes and references

- (a) L. Wang, J.-J. Zou, X. Zhang and L. Wang, Fuel, 2012_91 164-169; (b) Q. Deng, X. Zhang, L. Wang, and dod reaction inter-Eng. Sci., 2015, 135, 540-546; (c) H. A. Meylemans, R. L. Quintana, B. R. Goldsmith and B. G. Harvey, ChemSusChem, 2011, 4, 465-469; (d) H. A. Meylemans, L. C. Baldwin and B. G. Harvey, Energy Fuels, 2013, 27, 883-888.
- 2 (a) B. Zhang, J. Li, L. Guo, Z. Chen and C. Li, *Appl. Catal. B Environ.*, 2018, 237, 660-664; (b) Y. Zhang, V. Degirmenci, C. Li and E. J. M. Hensen, *ChemSusChem*, 2011, 4, 59-64; (c) C. Sener, A. H. Motagamwala, D. M. Alonso and J. A. Dumesic, *ChemSusChem*, 2018, 11, 2321-2331; (d) R. Galaverna, M. C. Breitkreitz and J. C. Pastre, *ACS Sustain. Chem. Eng.*, 2018, 6, 4220-4230.
- 3 (a) T. Prasomsri, T. Nimmanwudipong and Y. Román-Leshkov, *Energy Environ. Sci.*, 2013, **6**, 1732-1738; (b) 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; (c) B. G. Harvey and R. L. Quintana, *Energy Environ. Sci.*, 2010, **3**, 352-357; (d) J. Q. Bond, D. M. Alonso, D. Wang, R. M. West and J. A. Dumesic, *Science*, 2010, **327**, 1110-1114; (e) P. Sudarsanam, R. Zhong, S. Van den Bosch, S. M. Coman, V. I. Parvulescu and B. F. Sels, *Chem. Soc. Rev.*, 2018, **47**, 8349-8402.
- 4 (a) G. W. Huber, J. N. Chheda, C. J. Barrett and J. A. Dumesic, *Science*, 2005, **308**, 1446-1450; (b) S. Rojas-Buzo, P. García-García and A. Corma, *Green Chem.*, 2018, **20**, 3081-3091.
- 5 (a) A. Corma, O. Torre, M. Renz and N. Villandier, 2011, 50, 2375-2378; (b) L. J. Konwar, A. Samikannu, P. Mäki-Arvela and J.-P. Mikkola, *Catal. Sci. Technol.*, 2018, 8, 2449-2459; (c) G. Li, N. Li, S. Li, A. Wang, Y. Cong, X. Wang and T. Zhang, *Chem. Commun.*, 2013, 49, 5727-5729.
- 6 (a) O. Kikhtyanin, D. Kadlec, R. Velvarská and D. Kubička, *ChemCatChem*, 2018, **10**, 1464-1475; (b) Q. Deng, J. Xu, P. Han, L. Pan, L. Wang, X. Zhang and J.-J. Zou, *Fuel Process. Technol.*, 2016, **148**, 361-366.
- 7 J. Xie, L. Zhang, X. Zhang, P. Han, J. Xie, L. Pan, D.-R. Zou, S.-H. Liu and J.-J. Zou, *Sustainable Energy Fuels*, 2018, 2, 1863-1869.
- 8 (a) G. Li, N. Li, X. Wang, X. Sheng, S. Li, A. Wang, Y. Cong, X. Wang and T. Zhang, *Energy Fuels*, 2014, **28**, 5112-5118; (b) Q. Deng, P. Han, J. Xu, J.-J. Zou, L. Wang and X. Zhang, *Chem. Eng. Sci.*, 2015, **138**, 239-243; (c) X. Zhang, Q. Deng, P. Han, J. Xu, L. Pan, L. Wang and J.-J. Zou, *AIChE J.*, 2017, **63**, 680-688; (d) Y. Zhong, Q. Deng, P. Zhang, J. Wang, R. Wang, Z. Zeng and S. Deng, *Fuel*, 2019, **240**, 270-277; H. Li, Q. Deng, H. Chen, X. Cao, J. Zheng, Y. Zhong, P. Zhang, J. Wang, Z. Zeng, S. Deng, *Appl. Catal. A: Gen.*, 2019, **580**, 178-185.
- 9 P. Han, G. Nie, J. Xie, X.-T.-F. E, L. Pan, X. Zhang and J.-J. Zou, Fuel Process. Technol., 2017, 163, 45-50.
- (a) J. Yang, N. Li, G. Li, W. Wang, A. Wang, X. Wang, Y. Cong and T. Zhang, *Chem. Commun.*, 2014, **50**, 2572-2574; (b) Q. Deng, G. Nie, L. Pan, J.-J. Zou, X. Zhang and L. Wang, *Green Chem.*, 2015, **17**, 4473-4481; (c) W. Wang, N. Li, G. Li, S. Li, W. Wang, A. Wang, Y. Cong, X. Wang and T. Zhang, *ACS Sustainable Chem. Eng.*, 2017, **5**, 1812-1817.
- (a) G. Nie, X. Zhang, P. Han, J. Xie, L. Pan, L. Wang and J.-J. Zou, *Chem. Eng. Sci.*, 2017, **158**, 64-69; (b) G. Nie, X. Zhang, L. Pan, P. Han, J. Xie, Z. Li, J. Xie and J.-J. Zou, *Chem. Eng. Sci.*, 2017, **173**, 91-97; (c) Y. Zhong, P. Zhang, X. Zhu, H. Li, Q. Deng, J. Wang, Z. Zeng, J.-J. Zou and S. Deng, *ACS Sustainable Chem. Eng.*, 2019, **7**, 14973-14981.
- 12 F. Chen, N. Li, X. Yang, L. Li, G. Li, S. Li, W. Wang, Y. Hu, A. Wang, Y. Cong, X. Wang and T. Zhang, ACS Sustainable Chem. Eng., 2016, 411, 6160-6166
- 13 J. Xie, X. Zhang, L. Pan, G. Nie, X.-T.-F. E, Q. Liu, P. Wang, Y. Li and J.-J. Zou, *Chem. Commun.*, 2017, **53**, 10303-10305.
- 14 J. Xie, L. Pan, G. Nie, J. Xie, Y. Liu, C. Ma, X. Zhang and J.-J. Zou, Green Chem., 2019, 21, 5886-5895.

Published on 20 February 2020. Downloaded by LA TROBE UNIVERSITY on 2/22/2020 1:09:18 PM

View Article Online DOI: 10.1039/D0GC00195C

- 15 (a) R. Chaudhary and P. L. Dhepe, *Green Chem.*, 2017, **19**, 778-788; (b) G.-H. Wang, Z. Cao, D. Gu, N. Pfänder, A.-C. Swertz, B. Spliethoff, H.-J. Bongard, C. Weidenthaler, W. Schmidt, R. Rinaldi, and F. Schüth, *Angew. Chem. Int. Ed.*, 2016, **55**, 8850-8855; (c) A. K. Deepa and P. L. Dhepe, *ACS Catal.*, 2015, **5**, 365-379.
- 16 (a) Q. Meng, M. Hou, H. Liu, J. Song and B. Han, *Nature Commun.*, 2017, **8**, 14190; (b) H. Liu, T. Jiang, B. Han, S. Liang and Y. Zhou, *Science*, 2009, **326**, 1250-1252.
- (a) G.-S. Zhang, M.-M. Zhu, Q. Zhang, Y.-M. Liu, H.-Y. He and Y. Cao, *Green Chem.*, 2016, **18**, 2155-2164; (b) R. Fang, H. Liu, R. Luque and Y. Li, *Green Chem.*, 2015, **17**, 4183-4188; (c) N. Pino, G. Hincapié and D. López, *Energy Fuels*, 2018, **32**, 561-573; (c) X. Li, Q. Deng, S. Zhou, J. Zou, J.Wang, R. Wang, Z. Zeng and S. Deng, *J. Catal.*, 2019, **378**, 201-208.
- (a) E. Hayashi, Y. Yamaguchi, K. Kamata, N. Tsunoda, Y. Kumagai, F. Oba and M. Hara, *J. Am. Chem. Soc.*, 2019, 141, 890-900; (b) J. Tan, J. Cui, Y. Zhu, X. Cui, Y. Shi, W. Yan and Y. Zhao, *ACS Sustainable Chem. Eng.*, 2019, 7, 10670-10678; (c) A. J. Kumalaputri, G. Bottari, P. M. Erne, H. J. Heeres and K. Barta, *ChemSusChem*, 2014, 7, 2266; (d) J. Artz, S. Mallmann, and R. Palkovits, *ChemsusChem*, 2015, 8, 672-679; (e) B. Xiao, M. Zheng, X. Li, J. Pang, R. Sun, H. Wang, X. Pang, A. Wang, X. Wang and T. Zhang, *Green Chem.*, 2016, 18, 2175-2184.
- (a) S. Zhang, H. Ma, Y. Sun, Y. Luo, X. Liu, M. Zhang, J. Gao and J. Xu, *Green Chem.*, 2019, **21**, 1702-1709; (b) R. Ramos, A. Grigoropoulos, N. Perret, M. Zanella, A. P. Katsoulidis, T. D. Manning, J. B. Claridge and M. J. Rosseinsky, *Green Chem.*, 2017, **19**, 1701-1713; (c) J. Ohyama, R. Kanao, A. Esakia and A. Satsuma, *Chem. Commun.*, 2014, **50**, 5633-5636; (d) J. Ohyama, R. Kanao, Y. Ohira and A. Satsuma, *Green Chem.*, 2016, **18**, 676-680.
- 20 (a) G. C. A. Luijkx, F. van Rantwijk and H. van Bekkum, *Recl. Trav. Pay-Bas*, 1991, **110**, 343-344; (b) G. C. A. Luijkx, F. van Rantwijk and H. van Bekkum, *Carbohydr. Res.*, 1993, **242**, 131-139.
- 21 (a) G. C. A. Luijkx, W. der Horst, S. O. A. Koskinen, F. Rantwijk and H. van Bekkum, *J. Anal. Appl. Pyrol.*, 1994, 28, 245-254;
 (b) Z. Srokol, A. G. Bouche, A. van Estrik, R. C. J. Strik, T. Maschmeyer, J. A. Peters, *Carbohydr. Res.*, 2004, 339, 1717-1726;
 (c) T. M. Aida, Y. Sato, M. Watanabe, K. Tajima, T Nonaka, H. H. Hattori and K. Arai, J. Supercrit. Fluids, 2007, 40, 381-388;
 (d) A. Chuntanapum, T. L. K. Yong, S. Miyake and Y. Matsumura, *Ind. Eng. Chem. Res.*, 2008, 47, 2956-2962.
- 22 A. J. Kumalaputri, C. Randolph, E. Otten, H. J. Heeres and P. J. Deuss, *ACS Sustainable Chem. Eng.*, 2018, **6**, 3419-3425.
- 23 A. Chuntanapum and Y. Matsumura, *Ind. Eng. Chem. Res.*, 2009, **48**, 9837-9846.
- 24 G. Chen, J. Tao, C. Liu, B. Yan, W. Li and X. Li, *Renew. Sustainable Energy Rev.*, 2017, **79**, 1091-1098.
- 25 A. B. Ross, P. Biller, M. L. Kubacki, H. Li, A. Lea-Langton and J. M. Jones, *Fuel*, 2010, **89**, 2234-2243.
- 26 C. Randolph, C. W. Lahive, S. Sami, R. W. A. Havenith, H. J. Heeres and P. J. Deuss, *Org. Process Res. Dev.*, 2018, **22**, 1663-1671.
- 27 M. I. Alam, T. S. Khan, M. A. Haider, ACS Sustainable Chem. Eng., 2019, 7, 2894-2898.

Breen Chemistry Accepted Manuscript

Table of Contents Entry

Green Chemistry Accepted Manuscript