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Synthesis of high-density liquid fuel *via* Diels-Alder reaction of dicyclopentadiene and lignocellulose-derived 2-methylfuran

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ARTICLE INFO	A B S T R A C T				
Keywords: High-density fuel Diels-Alder reaction 2-Methylfuran Dicyclopentadiene Biomass	A process <i>via</i> Diels-Alder reaction of lignocellulose-derived 2-methylfuran and petroleum-derived dicyclo- pentadiene following by hydrodeoxygenation was proposed to synthesize a new kind high-density liquid fuel. The results show that the catalysts, temperature and reactant ratio can affect the product distribution of Diels- Alder reaction greatly. Among the investigated catalysts, HY zeolite exhibited the best catalytic activity and showed good recycling ability. Over HY zeolite, high conversion of reactants along with acceptable selectivity of the target products was obtained, under the reaction temperature of $150 ^{\circ}$ C and 2-MF/DCPD ratio of 2:1. After hydrodeoxygenation, the as-obtained fuel has a density of 0.984 g/mL, much higher than that of widely used JP- 10 fuel (0.94 g/mL), a low freezing point of $-58 ^{\circ}$ C and a volumetric neat heat of combustion of 41.96 MJ/L. Furthermore, a blended fuel with 25% JP-10 exhibits high density and excellent cryogenic properties, which is				

very promising to serve as high-density fuel for advanced propulsion application.

1. Introduction

High-density liquid fuels can greatly improve the flight distance and aircrafts payload without increasing the volume of fuel tank, owing to their relatively higher energy density than traditional refined fuels [1,2]. Besides, the good cryogenic properties including the freezing point and viscosity are also very important to ensure the proper function of fuel in a high altitude or cold area [3]. Traditional high-density fuels are mainly derived from petroleum, including JP-10 (with exotetrahydrodicyclopentadiene, exo-THDCPD, as the major composition, 0.94 g/mL), RJ-4-I (with exo-tetrahydrodimethylcyclopentadiene as the major composition, 0.91-0.92 g/mL) and RJ-7 or HDF-T1 (with exotetrahydrotricyclopentadiene, exo-THTCPD, as the major composition, 1.02 g/mL) [1,4-9]. To synthesize the above high-density fuels, the commonly used reagent is dicyclopentadiene (DCPD), which is an abundant and cheap by-product of naphtha pyrolysis and coal tar process [10,11]. And the high density of the resulted fuels arises from the polycyclic structure of DCPD molecules. However, a further catalytic isomerization is needed to convert the fuels from endo-structure to exo-structure to greatly improve their cryogenic properties [12].

In recent years, the renewable biomass feedstocks have been explored to synthesize fuels and valuable chemicals [13–17]. Specifically, many biofuels have been obtained from biomass-derived platform

chemicals *via* C–C coupling reactions including alkylation, aldol condensation, Michael addition and oligomerization [18–22], and they usually possess low freezing point and viscosity owing to the presence of abundant alkyl groups [23,24]. However, except for several bicycloalkanes and polycycloalkanes [18,25–27], most of the reported biofuels are linear hydrocarbons or branched monocycloalkanes with a density < 0.85 g/mL, which is much lower than that of petroleumbased fuels [28–35]. To combine the properties of high density and good cryogenic properties, the fossil-based polycyclic chemicals and biomass derivatives with alkyl substituents can be simultaneously utilized as the reactants to produce high-performance fuels.

Herein, a process *via* Diels-Alder reaction of DCPD and lignocellulose-derived 2-methylfuran (2-MF) following by hydrodeoxygenation was carried out to synthesize a new kind high-density liquid fuel. 2-MF can be obtained by the selective hydrogenation of furfural which has been produced on an industrial scale *via* the hydrolysis-dehydration of the hemicellulose part of forest residues and agriculture wastes [36,37]. Notably, both the density (0.984 g/mL) and volumetric neat heat of combustion (NHOC, 41.96 MJ/L) of the obtained fuel are better than that of JP-10 (0.94 g/mL and 39.6 MJ/L), and the freezing point of the fuel is as low as -58 °C. This would be a very potential high-density fuel for practical application.

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2. Experimental section

2.1. Reagents

2-MF (99%) was obtained from J&K Scientific Ltd. DCPD (98%) was supplied by Shanghai Titan Scientific Co., Ltd. Pd/C (5 wt%) was purchased from Shaanxi Rock New Materials Co., Ltd. All chemicals were used without further purification. HZSM-5 (SiO₂/Al₂O₃ = 25), H β (SiO₂/Al₂O₃ = 25), HY (SiO₂/Al₂O₃ = 5.4) and LaY were received from Nankai Catalysts Company and calcined in air at 580 °C for 3 h.

2.2. Diels-Alder reaction of 2-MF and DCPD

The Diels-Alder reaction was carried out in a 100 mL autoclave (Easy Chem E100) with a mechanical agitation. A certain molar ratio of DCPD and 2-MF, and 1.2 g acidic zeolite catalyst were sealed in the reactor and heated under specific temperature and N₂ pressure of 0.5 MPa for 5 h. The reaction solution was sampled periodically and then centrifuged for analysis by a gas chromatography (Agilent-7820A) equipped with an FID detector and a capillary column HP-1 capillary column (30 m × 0.53 mm). Products were determined qualitatively using an Agilent 6890/5975 gas chromatography-mass spectrometry (GC–MS) equipped with HP-5 capillary column (30 m × 0.5 mm).

The conversion and selectivity were calculated as follows:

Conversion (wt%) =
$$\frac{m(\text{reactant converted})}{m(\text{original reactant})} \times 100\%$$

Selectivity (wt%) = $\frac{m(\text{target product produced})}{\sum m(\text{reactant converted})} \times 100\%$

2.3. Hydrodeoxygenation (HDO) reaction

After Diels-Alder reaction, the fuel precursors were purified by filtration and vacuum distillation. Then, the HDO reaction was performed in the autoclave with 2 g fuel precursors, 50 mL water, 0.2 g Pd/C and 2 g HY zeolite loaded. The reactor was first flushed with N₂ gas for 3 times. After that, the HDO reaction was conducted under H₂ pressure of 6 MPa and temperature of 150 °C for 5 h. Finally, the target fuels were purified by vacuum distillation.

2.4. Measurements of fuel properties

The fuel density was measured by a Mettler Toledo DE40 density meter according to ASTM D4052. Freezing point was measured in accordance with ASTM D2386. Kinematic viscosity was determined using capillary viscometer (ASTM D445). The NHOC was measured by the IKA-C6000 isoperibol Package 2/10 Calorimeter according to ASTM D240-02 [4].

3. Results and discussion

3.1. Diels-Alder reaction of 2-MF and DCPD

3.1.1. Reaction pathway for Diels-Alder reaction

Firstly, the blank reaction with pure raw material (2-MF or DCPD) was carried out, and there are no products generated using pure 2-MF as reactant, while DCPD exhibits a relatively high reactivity to produce tricyclopentadiene (**TCPD**) and higher oligomers with the selectivity of 90.9% and 9.1%, respectively (Fig. S1 and Scheme S1 in Supporting information, SI) [38]. Then, 2-MF and DCPD are used together to participate in the Diels-Alder reaction. According to the time-dependent product distribution in Fig. 1, the substrates are converted continuously with the extension of the reaction time. The consumption rate of DCPD is much faster than that of 2-MF, because DCPD participates in three reaction pathways to produce 4-methyl-4,4a,4b,5,8,8a,9,9a-octahydro-



Fig. 1. Product distribution in Diels-Alder reaction of DCPD and 2-MF. Reaction conditions: 0.1 mol 2-MF, 0.05 mol DCPD, 1.2 g HY zeolite, 150 °C.

1H-1,4-epoxy-5,8-methanofluorene and 8-methyl-3a,4,4a,5,8,8a,9,9aoctahydro-1H-5,8-epoxy-4,9-methanocyclopenta[b]naphthalene (labelled as DCMF), 4-methyl-3a,4,7,7a-tetrahydro-1H-4,7-epoxyindene (labelled as CPMF) and TCPD while two reaction pathways involves 2-MF (Scheme 1 and the mass spectra in Fig. S2 and S3, SI). However, after 2 h reaction, the side products, 6-methyl-4,4a,4b,5,5a,6,9,9a,10,10a,11,11a-dodecahydro-1H-6,9-epoxy-1,4:5,10dimethanobenzo[b] fluorene, 1-methyl-4,4a,4b,5,5a,6,9,9a,10,10a,11, 11a-dodecahydro-1H-1,4-epoxy-5,10:6,9-dimethanobenzo[b] fluorene and 9-methyl-3a,4,4a,5,5a,6,9,9a,10,10a,11,11a-dodecahydro-1H-6,9epoxy-4,11:5,10-dimethanocyclopenta[b]anthracene (labelled as TCMF) produced from further Diels-Alder reaction of TCPD and 2-MF, begins to emerge and increase with TCPD amount gradually decreased (Mass spectra, Fig. S4 in SI). After 5 h reaction, the DCPD concentration is as low as 5%, resulting into a concentration balance for the products. Therefore, the main products of Diels-Alder reaction of 2-MF and DCPD are DCMF, CPMF and TCPD, which should be the promising precursor for high-performance high-energy-density fuels because DCMF and TCPD will contribute to the high density and volumetric NHOC owing to the polycyclic structures while CPMF and DCMF will lead to good cryogenic properties attributed to the branched substitution.

Based on the results of Fig. 1, the pathways for Diels-Alder reaction of DCPD and 2-MF are proposed in Scheme 1. DCPD can decompose to CPD (Mass spectra, Fig. S5 in SI) at high temperature [39]. Meanwhile, 2-MF, DCPD and CPD will react with each other to form DCMF, CPMF and TCPD. Then, a side reaction from TCPD and 2-MF will happen to produce TCMF. To achieve the high yield of target products and good fuel properties, the reaction parameters (catalyst, temperature, and 2-MF/DCPD molar ratio) were then modulated to optimize the products distribution.

3.1.2. Optimization of reaction conditions for Diels-Alder reaction

Many kinds of molecular sieves, including HY, HZSM, H β and alkali metal or transition metal modified zeolites, *etc.* have been applied for Diels-Alder reaction of furan because Diels-Alder reaction can be promoted by microporous materials and Lewis acidic sites [40–44]. Considering the relatively large molecular size of the side-product TCMF (average diameter 13.3 Å), several commonly used microporous acidic zeolites were used as the catalyst to suppress the production of TCMF. As shown in Fig. 2, the DCPD conversion is much higher than that of 2-MF under all applied catalysts. Over HY catalyst, the high conversion of DCPD (88.5%) and 2-MF (56.4%) are achieved with relatively high selectivity of DCMF (30.2%, average diameter 10.9 Å), CPMF (30.9%, average diameter 9.3 Å) and TCPD (23.0%, average diameter 10.8 Å). The high selectivity of DCMF and CPMF is attributed to the large micropore volume and appropriate average pore diameter of HY zeolite.



Scheme 1. Reaction pathway for Diels-Alder reaction of DCPD and 2-MF.



Fig. 2. Effect of catalyst types on Diels-Alder reaction of DCPD and 2-MF. Reaction conditions: 0.1 mol DCPD, 0.2 mol 2-MF, 1.2 g catalyst, 150 °C, 5 h.

Compared with HY, $H\beta$ zeolite shows a relatively lower DCPD conversion (82.2%) and lower selectivity of DCMF (22.3%) and CPMF (22.4%) with higher selectivity of TCPD (35.9%) and TCMF (18.3%). For HZSM-5 zeolite, both the conversion of DCPD and 2-MF are the lowest (31.0% of DCPD and 14.4% of 2-MF) while the selectivity of DCMF is only 10.8%, and a large amount of TCPD (50.5%) is obtained by Diels-Alder reaction of CPD and DCPD, which further leads to the production of TCMF (18.2%). The reason should be that the smaller pore diameter of HZSM-5 (5.0 Å) makes DCPD (9.0 Å) polymerize outside the pore. Diffusion limitation and the smaller surface area of HZSM-5 zeolite limits the conversion of the reactants (Table S1, SI). The surface area, average pore diameter and micropore volume of these catalysts decrease in the order HY > H β > HZSM-5 (Table S1, SI), and the conversion of DCPD and the selectivity of DCMF and CPMF also decrease in the order of $HY > H\beta > HZSM-5$, implying that the bigger surface area and suitable average pore diameter can strengthen the conversion of reactant and the larger micropore volume and appropriate average pore size can lead to a higher selectivity of DCMF and CPMF. Compared with HY, LaY zeolite has more Lewis acid sites [45]. Over LaY, although the large

surface area guarantees the high conversion of DCPD (83.6%) and Lewis acidic sites improve the selectivity of Diels-Alder adducts (total selectivity of DCMF, CPMF and TCPD is 88.6%), the selectivity of CPMF is far more than that of DCMF (35.1% vs 11.8%). That is because the small pore size of LaY catalyst (Table S1, SI) will suppress the formation of DCMF. Thus, we will discuss Diels-Alder reaction of DCPD and 2-MF over HY zeolite in the following experiments.

Using HY as catalyst, the reaction temperature was further optimized because Diels-Alder reaction is very sensitive to temperature [46,47]. The increase of reaction temperature will enhance the effective collision between reactant molecules, significantly improving the conversion of the reactants (as shown in Fig. 3). However, the difference between the conversion of DCPD and 2-MF enlarges obviously with the rising temperature, owing to the intensified self-aggregation of DCPD at high temperature [48]. At the temperature of 130 °C, the selectivity of DCMF (33.6%) and TCPD (35.3%) are very high and the selectivity of TCMF is as low as 5.6%, but the conversion of the substrates is too low. At high temperature of 170 °C, the conversions of 2-MF and DCPD are 60.9% and 94.4%, respectively, however, TCMF is the major product



Fig. 3. Effect of reaction temperature on Diels-Alder reaction of DCPD and 2-MF. Reaction conditions: 0.1 mol DCPD, 0.2 mol 2-MF, 1.2 g HY zeolite, 5 h.



Fig. 4. Effect of 2-MF/DCPD molar ratio on the Diels-Alder reaction of DCPD and 2-MF. Reaction conditions: 0.1 mol 2-MF, 1.2 g HY zeolite, 150 °C, 5 h.



Fig. 5. Recycling performance of HY zeolite in Diels-Alder reaction of DCPD and 2-MF.



Scheme 2. HDO of Diels-Alder adducts to high-density-fuel molecules.

with a high selectivity of 37.5% and the resulted reaction solution becomes black and viscous. Further higher temperature leads to more oligomer TCMF, which will not only accelerate the consumption of raw materials DCPD, but also make it difficult for the subsequent by-product separation. Under moderate temperature of 150 °C, the conversion of DCPD and 2-MF reaches 88.5% and 56.4%, respectively, and the

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selectivity of DCMF is as high as 30.2% with a low TCMF selectivity of 13.5%. Therefore, 150 °C is the most suitable temperature for Diels-Alder reaction of 2-MF and DCPD.

Since the side product TCMF is resulted from Diels-Alder reaction of TCPD and 2-MF, the molar ratio of 2-MF/DCPD was then optimized. Fig. 4 shows the selectivity of DCMF and CPMF increase significantly with the rising molar ratio while that of TCPD and TCMF decrease. At the ratio of 1:1, although the conversion of 2-MF (67.5%) and DCPD (88.4%) are relatively high, the selectivity of DCMF is 22.3% and the proportion of TCPD and TCMF are the highest. At the ratio of 4:1, although the selectivity of DCMF is the highest (34.0%) and that of TCPD reaches 15.0%, the excessive 2-MF will increase the production costs. Accordingly, the molar ratio of 2:1 is optimal, and the selectivity of DCMF are 30.2% and 13.5%, respectively, with acceptable conversion of the reactants.

The recycling stability of HY zeolite was further evaluated in Diels-Alder reaction. After the reaction, the catalyst was centrifuged, washed with ethanol for 3 times, calcined at 580 °C for 3 h to remove the coke deposition, and used for next run. As shown in Fig. 5, after 4 runs, the selectivity of DCMF is almost unchanged, but the conversion of 2-MF and DCPD are slightly decreased by 13% and 16%, respectively. It is caused by the collapse of partial mesoporous channels and reduction of surface area during the thermal calcination (Table S1, SI). In addition, considering that HY zeolite is commercially available and relatively thermal stable, it is a suitable catalyst for the Diels-Alder reaction of DCPD and 2-MF.

3.2. Hydrodeoxygenation (HDO) reaction

In order to improve the energy density and thermal stability of the final fuels, HDO was further carried out to transfer Diels-Alder adducts to hydrocarbon fuels by physical mixture of acidic zeolite HY and Pd/C, because acidic support can catalyze the dehydration of biomass derived oxygenates followed by catalyzing hydrogenation with the metals [49–51]. As illustrated in Scheme 2, the Diels-Alder adducts, *i.e.* CPMF, DCMF and TCPD, can be converted to the saturated C₁₀ and C₁₅ naphthene completely (Mass spectra, Fig. S6, S7 and S8 in SI) under the reaction temperature of 150 °C and H₂ pressure of 6 MPa. After filtration and vacuum distillation, the obtained fuel contains 13.04% C₁₀ (4-*methyloctahydro-1H-indene*, obtained from CPMF), 61.71% DCMF-derived C₁₅ (8-*methyldodecahydro-1H-1,4-methanofluorene* and 5-methyl-dodecahydro-1H-4,9-methanocyclopenta[b]naphthalene) and 24.73% TCPD-derived C₁₅ (dodecahydro-1H-1,4:5,8-dimethanofluorene and dodecahydro-1H-4,9:5,8-dimethanocyclopenta[b]naphthalene).

3.3. The properties of produced high-density fuel

The properties of the obtained fuel were tested and summarized in Table 1. This fuel possesses a high density of 0.984 g/mL, which is higher than the reported biofuels and the widely used JP-10 (0.94 g/mL), and comparable to THTCPD (1.02 g/mL) [10]. Importantly, the freezing point of the fuel is -58 °C, which is much lower than that of THTCPD (a solid at room temperature) [5,6,12]. The fuel has a high volumetric NHOC of 41.96 MJ/L, which is 2.36 MJ/L higher than that of JP-10. Besides, the viscosity of the obtained biofuel is 15.5 mm²/s and 166.5 mm²/s at 20 °C and -20 °C, respectively.

Since high viscosity at low temperature will affect the transportation of fuel in the tank, we studied the potential of this fuel as additive

 Table 1

 Properties of fuel synthesized by Diels-Alder reaction of DCPD and 2-MF

Properties	Density (g/mL)	Viscosity (mm ² /s)			Freezing point (°C)	NHOC (MJ/kg)	volumetric NHOC (MJ/L)
Fuel	20 °C 0.984	20 °C 15.5	0 °C 40.0	– 20 °C 166.5	- 58	42.64	41.96



Fig. 6. (a) Viscosity (20 °C, 0 °C, -20 °C) and (b) density (20 °C) of the fuel blending with JP-10.

of conventional fuel by blending with JP-10. As exhibited in Fig. 6, the viscosity of the blended fuel has been greatly improved (especially under low temperature of -20 °C) without obvious decrease in density and the density of the blended fuel has a good linear correlation with the content of JP-10. Notably, when the composition of JP-10 is 25%, the blended fuel has a density of 0.972 g/mL, volumetric NHOC of 41.31 MJ/L, a viscosity of 57.8 mm²/s at -20 °C and a freezing point lower than -75 °C, which is very promising to serve as high-density fuel for practical applications.

4. Conclusion

In summary, a new process for the production of high-density jet fuel was developed by co-conversion of lignocellulose-derived 2-MF and petroleum-derived DCPD *via* Diels-Alder reaction. Among the studied acidic zeolites, HY zeolite exhibits the best performance for the Diels-Alder reaction of DCPD and 2-MF and presents good recycling stability. Under optimal conditions, the conversion of DCPD and 2-MF reaches 88.5% and 56.4%, with the selectivity of CPMF, DCMF and TCPD as 30.9%, 30.2% and 23.0%, respectively. After HDO, the obtained fuel has a density of 0.984 g/cm³, a freezing point of -58 °C and a volumetric NHOC of 41.96 MJ/L, which shows much better performance than the reported biofuels. Furthermore, by blending this fuel with JP-10, a superior aviation fuel with high density and excellent cryogenic properties is obtained. Hence, this process provides a promising way to co-convert biomass derivatives and petroleum derivatives into high-density aviation fuels.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cattod.2018.04.053.

References

- H.S. Chung, C.S.H. Chen, R.A. Kremer, J.R. Boulton, Energy Fuels 13 (1999) 641–649.
- [2] L. Pan, Q. Deng, X.-T.-F. E, G. Nie, X. Zhang, J.-J. Zou, Prog. Chem. 27 (2015) 1531–1541.
- [3] B.G. Harvey, W.W. Merriman, T.A. Koontz, Energy Fuels 29 (2015) 2431–2436.
- [4] Q. Deng, J. Xu, P. Han, L. Pan, L. Wang, X. Zhang, J.-J. Zou, Fuel Process. Technol. 148 (2016) 361–366.
- [5] J.-J. Zou, Z. Xiong, X. Zhang, G. Liu, L. Wang, Z. Mi, Ind. Eng. Chem. Res. 46 (2007)

4415-4420.

- [6] J.-J. Zou, Z. Xiong, L. Wang, X. Zhang, Z. Mi, J. Mol. Catal. A-Chem. 271 (2007) 209–215.
- [7] Y. Li, J.-J. Zou, X. Zhang, L. Wang, Z. Mi, Fuel 89 (2010) 2522-2527.
- [8] G. Nie, X. Zhang, P. Han, J. Xie, L. Pan, L. Wang, J.-J. Zou, Chem. Eng. Sci. 158 (2017) 64–69.
- [9] X. Zhang, L. Pan, L. Wang, J.-J. Zou, Chem. Eng. Sci. 180 (2018) 95–125.
- [10] Q. Deng, X. Zhang, L. Wang, J.-J. Zou, Chem. Eng. Sci. 135 (2015) 540-546.
- [11] J.D. Rule, J.S. Moore, Macromolecules 35 (2002) 7878-7882.
- [12] L. Wang, X. Zhang, J.-J. Zou, H. Han, Y. Li, L. Wang, Energy Fuels 23 (2009) 2383–2388.
- [13] G.W. Huber, J.N. Chheda, C.J. Barrett, J.A. Dumesic, Science 308 (2005) 1446–1450.
- [14] R. Xing, A.V. Subrahmanyam, H. Olcay, W. Qi, G.P.V. Walsum, H. Pendseb, G.W. Huber, Green. Chem. 12 (2010) 1933–1946.
- [15] J. Yang, N. Li, G. Li, W. Wang, A. Wang, X. Wang, Y. Cong, T. Zhang, ChemSusChem 6 (2013) 1149–1152.
- [16] H.A. Meylemans, R.L. Quintana, B.G. Harvey, Fuel 97 (2012) 560–568.
- [17] Q. Xia, Z. Chen, Y. Shao, X. Gong, H. Wang, X. Liu, S.F. Parker, X. Han, S. Yang, Y. Wang, Nat. Commun. 7 (2016) 11162.
- [18] W. Wang, N. Li, G. Li, S. Li, W. Wang, A. Wang, Y. Cong, X. Wang, T. Zhang, ACS Sustain. Chem. Eng. 5 (2017) 1812–1817.
- [19] J.C. Serrano-Ruiz, J.A. Dumesic, Energy Environ. Sci. 4 (2011) 83-99.
- [20] H. Olcay, A.V. Subrahmanyam, R. Xing, J. Lajoie, J.A. Dumesic, G.W. Huber, Energy Environ. Sci. 6 (2013) 205–216.
- [21] A. Corma, O. de la Torre, M. Renz, N. Villandier, Angew. Chem. 123 (2011) 2423–2426.
- [22] E.R. Sacia, M. Balakrishnan, M.H. Deaner, K.A. Goulas, F.D. Toste, A.T. Bell, ChemSusChem 8 (2015) 1726–1736.
- [23] K. Harrison, B.G. Harvey, Sustain. Energy Fuels 1 (2017) 467-473.
- [24] B.G. Harvey, K.W. Harrison, M.C. Davis, A.P. Chafin, J. Baca, W.W. Merriman, Energy Fuels 30 (2016) 10171–10178.
- [25] J. Yang, N. Li, G. Li, W. Wang, A. Wang, X. Wang, Y. Cong, T. Zhang, Chem. Commun. 50 (2014) 2572–2574.
- [26] X. Sheng, G. Li, W. Wang, Y. Cong, X. Wang, G.W. Huber, N. Li, A. Wang, T. Zhang, AIChE J. 62 (2016) 2754–2761.
- [27] J. Xie, X. Zhang, L. Pan, G. Nie, X.-T.-F. E, Q. Liu, P. Wang, Y. Li, J.-J. Zou, Chem. Commun. 53 (2017) 10303–10305.
- [28] G.W. Huber, S. Iborra, A. Corma, Chem. Rev. 106 (2006) 4044-4098.
- [29] Q.N. Xia, Q. Cuan, X.H. Liu, X.Q. Gong, G.Z. Lu, Y.Q. Wang, Angew. Chem. Int. Ed. 53 (2014) 9755–9760.
- [30] J. Yang, S. Li, N. Li, W. Wang, A. Wang, T. Zhang, Y. Cong, X. Wang, G.W. Huber, Ind. Eng. Chem. Res. 54 (2015) 11825–11837.
- [31] G. Li, N. Li, X. Wang, X. Sheng, S. Li, A. Wang, Y. Cong, X. Wang, T. Zhang, Energy Fuels 28 (2014) 5112–5118.
- [32] Q. Deng, P. Han, J. Xu, J.-J. Zou, L. Wang, X. Zhang, Chem. Eng. Sci. 138 (2015) 239–243.
- [33] Q.-N. Xia, Q. Cuan, X.-H. Liu, X.-Q. Gong, G.-Z. Lu, Y.-Q. Wang, Angew. Chem. Int. Ed. 53 (2014) 9755–9760.
- [34] X. Zhang, Q. Deng, P. Han, J. Xu, L. Pan, L. Wang, J.-J. Zou, AIChE J. 63 (2017) 680–688.
- [35] P. Han, G. Nie, J. Xie, X.-T.-F. E, L. Pan, X. Zhang, J.-J. Zou, Fuel Process. Technol. 163 (2017) 45–50.
- [36] J.P. Lange, D.H.E. Van, B.J. Van, R. Price, ChemSusChem 5 (2012) 150–166.
- [37] Y. Nakagawa, M. Tamura, K. Tomishige, ACS Catal. 3 (2013) 2655–2668.
- [38] Z. Xiong, Z. Mi, X. Zhang, React. Kinet. Catal. Lett. 85 (2005) 89–97.
- [39] M.E. Jamróz, S. Gałka, J.C. Dobrowolski, J. Mol. Struct.-THEOCHEM 634 (2003) 225–233.
- [40] Y.T. Cheng, G.W. Huber, Green Chem. 14 (2012) 3114–3125.
- [41] Y.T. Cheng, Z. Wang, C.J. Gilbert, W. Fan, G.W. Huber, Angew. Chem. Int. Ed. 51

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(2012) 11097–11100.

- [42] C.L. Williams, C.C. Chang, P. Do, N. Nikbin, S. Caratzoulas, D.G. Vlachos, R.F. Lobo,
- W. Fan, P.J. Dauenhauer, ACS Catal. 2 (2012) 935–939.
 [43] R.E. Patet, N. Nikbin, C.L. Williams, S.K. Green, C.C. Chang, W. Fan, S. Caratzoulas, Deputy of Control Science 10, 001101 (2012) 2027.
- P.J. Dauenhauer, D.G. Vlachos, ACS Catal. 5 (2015) 2367–2375.
- [44] E. Mahmoud, J. Yu, R.J. Gorte, R.F. Lobo, ACS Catal. 5 (2015) 6946–6955.
 [45] A. Corma, B.W. Wojciechowski, Can. J. Chem. Eng. 58 (1980) 620–625.
- [46] C.O. Kappe, S.S. Murphree, A. Padwa, Tetrahedron 53 (1997) 14179–14233.
- [47] Y. Hayashi, M. Nakamura, S. Nakao, T. Inoue, M. Shoji, Angew. Chem. Int. Ed. 41 (2002) 4079–4082.
- [48] H. Han, J.-J. Zou, X. Zhang, L. Wang, L. Wang, Appl. Catal. A-Gen. 367 (2009) 84–88.
- [49] F. Cheng, C.E. Brewer, Renew. Sustain. Energy Rev. 72 (2017) 673-722.
- [50] C. Zhao, W. Song, J.A. Lercher, ACS Catal. 2 (2012) 2714–2723.
- [51] C. Zhao, D.M. Camaioni, J.A. Lercher, J. Catal. 288 (2012) 92-103.