ARTICLE

Production of BTX through Catalytic Depolymerization of Lignin

Ming-hui Fan[a], Shu-mei Deng[a], Tie-jun Wang[b], Quan-xin Li[a*]

a. Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China
b. Key Laboratory of Renewable Energy and Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, China

Lignin is the only nature renewable resource which can provide large quantities of aromatic compounds. In the work, transformation of lignin into benzene, toluene, and xylenes (BTX) was investigated over the HZSM-5, HY, and MCM-22 catalysts, and the HZSM-5 catalyst showed the highest carbon yield of BTX. The reaction condition, including temperature, the gas flow rate, and the catalyst/lignin ratio, was also investigated. The carbon yield of BTX reached about 25.3 C-mol% over HZSM-5 catalyst under T=550 °C, $f(\text{N}_2)$=300 cm^3/min, and catalyst/lignin ratio of 2.

Key words: Lignin, Benzene, Toluene, Xylenes, Depolymerization

I. INTRODUCTION

Biomass is an important feedstock for the renewable production of fuels, chemicals, and energy. Lignin, together with cellulose and hemicelluloses, is the major component of lignocellulosic biomass. Lignin is by far the most abundant substance composed of aromatic moieties in nature [1]. The global paper industry produced over 50 million tons/year and the second generation ethanol fuel using the crop waste produced a large amount of lignin as by-product [1−3]. In the plant cell walls, lignin serves to maintain the integrity of the cellulose/hemicellulose/pectin matrix. Composition, molecular weight, and amount of lignin differ from plant to plant. In softwood lignin represents about 30% of the total mass, while in hardwood the share falls to 20%−25% [2]. Cellulose consists of long linear fibrils of β-(1,4)-glucopyranoside chains and hemicelluloses is branched polysaccharides composed of 1,4-linked β-D-hexosyl residues. Lignin exhibits distinctly different macromolecular structure which is polymerized through three primary phenylpropane monomers-coniferyl alcohol, sinapyl alcohol, and coumaryl alcohol. The composition of softwood and hardwood lignin also varies in the relative abundance of the p-coumaryl, coniferyl, and sinapyl alcohols. The linkages in lignin structure include β-O-4, 5-5, β-5, 4-O-5, β-1, dibenzodioxocin, and β-β linkages, of which the β-O-4 linkage is dominant, consisting of more than half of the linkage structures of lignin [1−6].

Benzene, toluene, and xylenes (BTX) are important aromatic platform compounds which can be hydrogenated to alkanes or used in the synthesis of other fine chemicals such as fiber, rubber, dyestuff, coatings and pesticide [1]. The annual output of BTX is one of the important symbols to measure a country's development in the petrochemical industry. By now, the production process of BTX is deeply dependent on petrochemical industry but in order to cope with the increasing energy consumption of fossil fuel and environmental problems, alternative renewable sources are now investigated by many institutions across the world. Much effort has been devoted to finding appropriate method to produce BTX from bio-resource [7−9]. As the lignin macromolecule consisted of methoxylated phenylpropane structures, the removal of the extensive functionality of the lignin subunits can provide a route to produce BTX [3].

Products derived from the lignin generally contain a wide range of compounds such as phenols, aromatic hydrocarbons, alkanes, and low oligomers [4, 10−14]. Disruption of the complicated lignin polymer into smaller subunits is an important step for lignin cracking. Catalysis is considered as a key enabling technology for biomass conversion in general and for fulfilling the promise of lignin valorization in particular [1]. Zeolites represent the most important inorganic materials for catalysis and more than 180 different structural types of zeolites have been already recognized and the individual types of zeolites differ in the size of the channels [15]. The conversion of lignin into BTX can go through the reactions occurring inside the zeolite such as dehydration, decarboxylation, decarbonylation, hydrogen transfer, alkylation, isomerization and aromatization [3, 16]. Several catalysts such as HZSM-5, Y-zeolite, Al-MCM-22, β-zeolite, H-USY, SPA and Al-MSU catalysts can serve to crack lignin into low molec-

___

*Author to whom correspondence should be addressed. E-mail: liqx@ustc.edu.cn

ular weight compounds [15−26]. The performances of the catalysts mentioned above are strongly dependent on structural characteristics of the catalyst, including the presence and strength of acid sites and framework [3, 15]. Jackson and co-workers investigated several zeolite catalysts for the pyrolysis of lignin and HZSM-5 produced the highest yield of deoxygenated liquid fraction with high yield of aromatic compounds and naphthenic compounds relative to other zeolites [27]. So the challenge is to find a way to improve the yield of target products [28].

In this work, we used the renewable lignin to produce the important aromatic platform compounds-BTX, and studied the transformation of lignin into BTX through the catalytic depolymerization of lignin into aromatic monomers and the highest carbon yield reached about 25.3 C-mol% over HZSM-5 catalyst under the optimum reaction condition. This transformation may potentially provide an approach for the production of BTX and the development of aromatic platform compounds using the renewable lignin.

II. EXPERIMENTS

A. Feedstocks

The brown and sulfur-free lignin powder was manufactured from wheat straw, and purchased from Lanxu Biotechnology Co. Ltd. (Hefei, China). Dried lignin mainly consists of 62.55%carbon, 29.91%oxygen, 5.89%hydrogen, and 1.65%nitrogen, measured by an elemental analyzer (Vario EL-III, Elementar, Germany). Analytical reagents such as ethanol, acetone benzene, toluene, xylenes, and phenol were purchased from Sinopharm Chemical Reagent Company Limited in China (Shanghai, China).

B. Catalysts and characterization

Different kinds of zeolites such as HZSM-5, MCM-22, and HY-zeolite were supplied by Nankai University catalyst Co., Ltd., and catalysts were calcined in nitrogen atmosphere at 550 °C for 4 h prior to use. The elemental contents of these catalysts were measured by inductively coupled plasma and atomic emission spectroscopy (ICP/AES, Atomscan Advantage, Thermo Jarrell Ash Corporation, USA). The catalysts were investigated by BET (Brunauer-Emmett-Teller surface area) and NH_3-TPD (temperature programmed desorption of ammonia) analyses. The N_2 adsorption/desorption isotherms of the catalysts were measured at −196 °C using the COULTER SA 3100 analyzer. For the NH_3-TPD tests, the catalysts were dried in a vacuum oven for 12 h prior to test. Then the catalyst samples were heated to 500 °C under helium flow (ultrahigh purity, 100 mL/min) for 2 h. The adsorption of ammonia was carried out at 120 °C for 1 h. After the catalysts were flushed with He at 120 °C for 1 h to expel the unab-
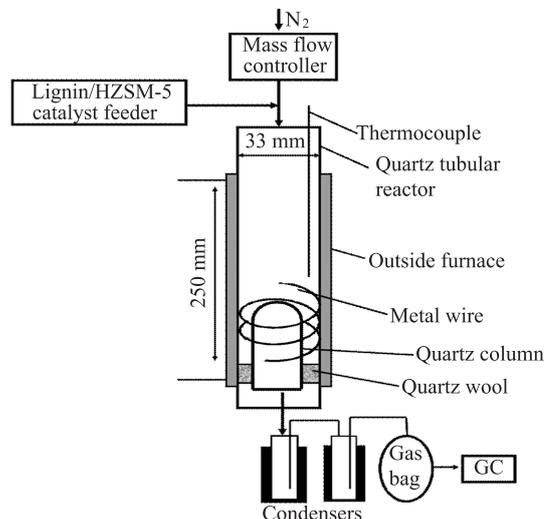

FIG. 1 The experimental setup for catalytic depolymerization of lignin.

sorbed ammonia, the programmed-desorption of NH_3 was run from 120 °C to 700 °C with a heating rate of 10 °C/min. Gas chromatograph (GC-SP6890, Shandong Lunan Ruihong Chemical Instrument Co., Ltd., Tengzhou China) were used to measure the desorbed ammonia with a thermal conductivity detector (TCD).

C. Experimental setups and procedures

Figure 1 shows the reaction device used for catalytic depolymerization of lignin. The basic building blocks of the system are a tube reactor (inner diameter: 33 mm; length: 500 mm), a solid reactants feeder, two condensers, and a gas analyzer. Exclusion of oxygen was carried before each experiment by flushing the tube with nitrogen at a flow rate of 300 cm^3/min for 2 h, then heated to target temperature by the carborundum heater (10 °C/min). The reactant sample was made by mixing the dried lignin powder and catalyst (40−60 mesh) at different weight ratio, and the solid mixture was then fed into the reactor by the feeder in 30 min. The stability of the catalyst was also studied. For run 1, 10 g lignin powder and 20 g fresh HZSM-5 were continuously fed into the reactor with a feeding rate of 30 g lignin/h. After the reaction, the HZSM-5 was separated from the solid residue and was used for the next run.

Gas products were analyzed using a gas chromatograph (GC-SP6890, Shandong Lunan Ruihong Chemical Instrument Co., Ltd., Tengzhou, China) with two detectors. H_2, CO, CH_4 and CO_2 were separated on TDX-01 column, and were analyzed by TCD (thermal conductivity detector). The gas hydrocarbons products were analyzed by FID (flame ionization detector). The liquid products (oil and water) in each test were collected by two liquid nitrogen/ethanol bath condensers

TABLE I Main characteristics of the catalysts used in this work*.

Catalyst	Si/Al	$S_{\text{BET}}/(\text{m}^3/\text{g})$	$V_{\text{p}}/(\text{cm}^3/\text{g})$	Total acid/(μmol/$g_{\text{cat.}}$)	Pore size/(nm$\times$nm)
HZSM-5(25)	25	282.4	0.20	580.6	0.53$\times$0.56, 0.51$\times$0.55
HY	6	620.0	0.40	2206.3	0.74$\times$0.74
MCM-22	25	429.0	0.41	610.5	0.71$\times$0.71

* Si/Al: the ratio of silicon to aluminum in the zeolites, S_{BET}: Brunauer-Emmett-Teller surface area, and V_{p}: pore volume. The values are average of three trials and standard deviations were less than 8.3%.
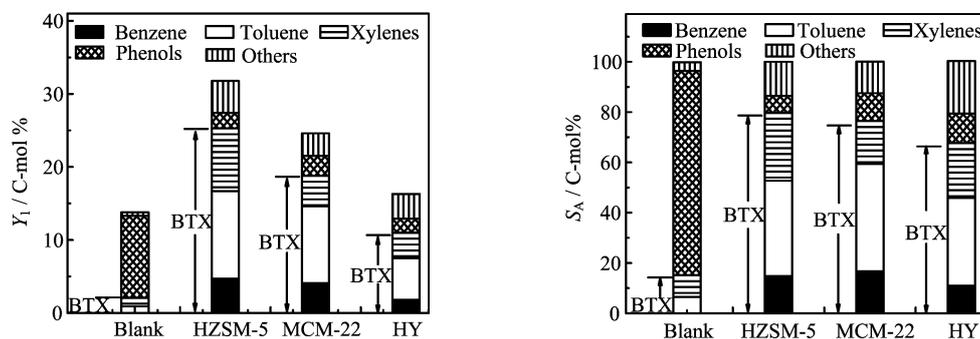

FIG. 2 Catalytic depolymerization of lignin using different catalysts at T=550 °C, $f(\text{N}_2)$=300 cm^3/min, and catalyst/lignin ratio of 2.

and then weighed to obtain the mass of liquid products. The main components of the organic liquid products were analyzed by GC-MS (Thermo Trace GC/ISQ MS, USA) and the total carbon contents in the liquid products were measured by a Vario EL III elemental analyzer. Water content was analyzed by a moisture analyzer (Model ZSD-1, Shanghai, China). For GC-MS analysis, the liquid components such as benzene, toluene, xylenes were determined by the calibrated GC-MS peak area with the standard samples. We also measured the solid residues by the TGA analysis (Q5000IR thermogravimetric analyzer, USA) after cooling to room temperature in a N$_2$ flow when the experiment was over.

Carbon yield (Y_1 (C-mol%)) of a specific product, and aromatic selectivity (S_{A} (C-mol%)) were calculated based on Eqs. (1) and (2) [29].

$$Y_1 = \frac{x_1}{x_{\text{fed}}} \times 100\% \tag{1}$$

$$S_{\text{A}} = \frac{x_{\text{a}}}{x_{\text{A}}} \times 100\% \tag{2}$$

where x_1, x_{a}, and x_{A} are carbon moles in a product, an aromatic product, and aromatics respectively, and x_{fed} is carbon moles fed in. Each datum was the mean values based on three tries.

III. RESULTS AND DISCUSSION

A. Catalyst screening for lignin depolymerization

The comparative tests of the transformation of lignin into BTX were performed using three different zeo-

lite catalysts (Table I). As shown in Fig.2, in absence of catalyst, only small amount of BTX was formed by thermal cracking and the main components in the liquid product were phenols' mixtures. However, the carbon yields of BTX were notably enhanced as the zeolite catalysts were used. The catalytic depolymerization of lignin with different zeolites decreased in the following order: HZSM-5>MCM-22>HY-zeolite. Using HZSM-5 gives the highest carbon yield of BTX (25.3 C-mol%). The BTX selectivity using HZSM-5 (pore size: 0.53 nm×0.56 nm), MCM-22 (pore size: 0.71 nm×0.71 nm) and HY (pore size: 0.74 nm×0.74 nm) were 79.8 C-mol%, 76.5 C-mol% and 67.7 C-mol%, respectively at T=550 °C, $f(\text{N}_2)$=300 cm^3/min, and catalyst/lignin ratio of 2. Among the tested catalysts, HZSM-5 gives both the highest BTX carbon yield and BTX selectivity. The strong acidity of HY (2206 μmol/$g_{\text{cat.}}$) and MCM-22 (610 μmol/$g_{\text{cat.}}$) are beneficial to produce more coke than that over HZSM-5, leading to a decrease of carbon yield of BTX.

B. Effect of temperature on transformation of lignin

Temperature has an important effect on the catalytic transformation of the lignin to BTX with the selected HZSM-5 catalyst. As shown in Fig.3, the aromatic selectivity of BTX increases from 30.8 C-mol% to 90.9 C-mol% in our experiments which has a positive dependence on the reaction temperature. For the formation of the aromatic monomers, the ether/carbon-carbon bonds of lignin were disrupted and then fur-
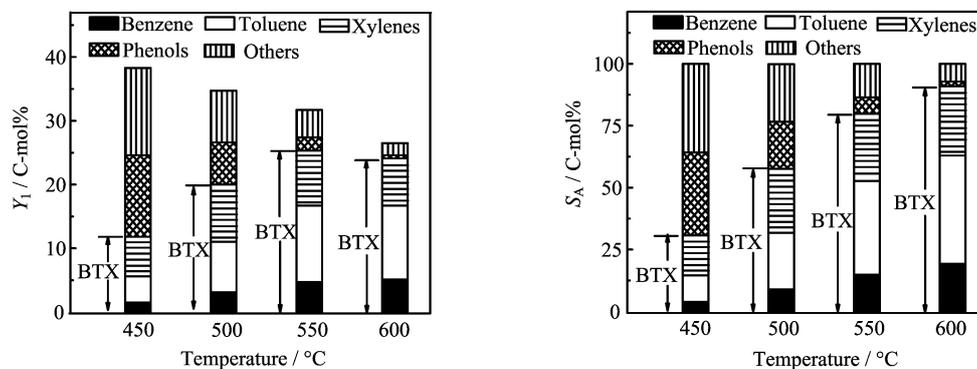
FIG. 3 Effect of temperature on depolymerization of lignin to BTX over the HZSM-5 catalyst at $f(N_2)=300$ cm^3/min and catalyst/lignin ratio of 2.
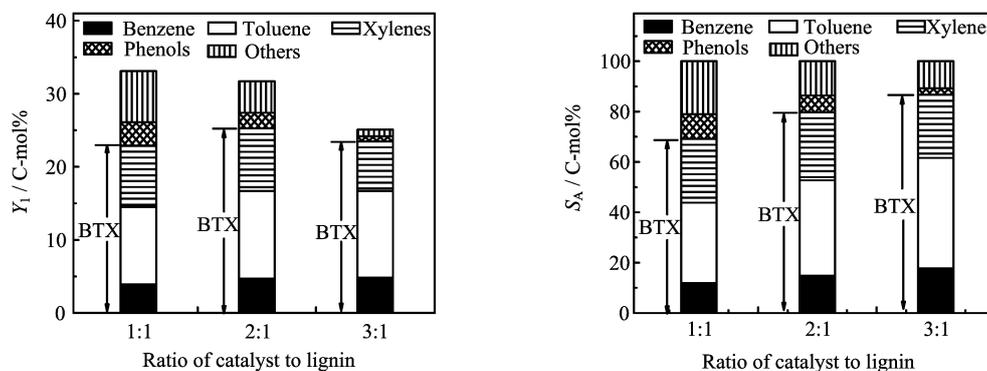

FIG. 4 Effect of the catalyst/lignin ratio on the production of BTX from lignin over HZSM-5 at $f(N_2)=300$ cm^3/min.

ther deoxygenation over the catalyst. But extremely high temperatures over 550 °C will lead to the second cracking of organics liquid, giving a slight decrease of BTX carbon yield from 25.3 C-mol% at 550 °C to 24.1 C-mol% at 600 °C. The formation of phenols and heavier aromatics was significantly decreased when rising the reaction temperature, indicating that the phenols and the heavier aromatics were further converted into smaller aromatic monomers through the removal of the groups in the aromatic rings (such as methyl, hydroxyl and methoxy groups) at higher temperature. Naphthalene and methylnaphthalene were also observed, due to the oligomerization reactions of lighter aromatics.

Temperature also strongly impacted the distribution of the products. The end products were divided into three categories: liquid organics (mainly BTX), gaseous products and coke. With increasing the reaction temperature, the carbon yield of organic liquid decreased from 38.3 C-mol% to 26.5 C-mol% due to the second cracking of organics liquid to form gas products, mainly consisting of CO, CO_2, CH_4, C2−C4 alkanes and C2$^=$−C4$^=$ olefins. The oxygen element in the lignin was mainly removed by decarbonylation and dehydroxylation reactions to form CO, CO_2, and H_2O. The carbon yield of gaseous products increased from

15.2 C-mol% at 450 °C to 28.1 C-mol% at 600 °C, indicating that the deoxygenation and cracking processes were enhanced as the temperature increases. Moreover, the formation of coke decreased with increasing temperature.

C. Effect of the catalyst/lignin ratio on the production of BTX from lignin

Catalyst plays an important role in the process of depolymerization and the ultimate organic liquid has a very low yield of BTX without the addition of catalyst (see Fig.2). The influence of the weight ratio of catalyst to lignin on the production of BTX is presented in Fig.4. Both the carbon yield and the carbon selectivity of BTX were improved when the catalyst/lignin ratio increased from 1:1 to 2:1. It was found that the BTX selectivity showed a positive dependence on the catalyst/lignin ratio. Further increasing the catalyst/lignin by 3:1, however, the BTX yield showed a slight decrease, which accounted for an increase in yield of gas products and a decrease in liquid yield. The optimal ratio of catalyst to lignin is about 2:1 for production of BTX.
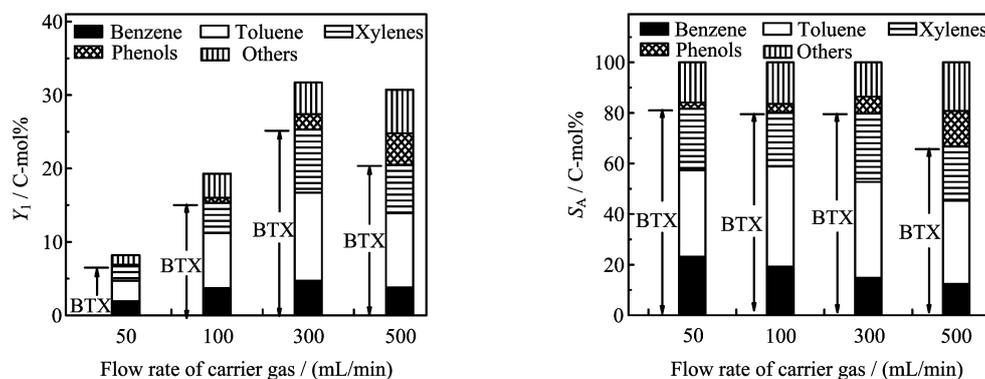
FIG. 5 The influence of carrier gas flow rate on the production of BTX from lignin over HZSM-5 at T=550 °C and catalyst/lignin ratio of 2.
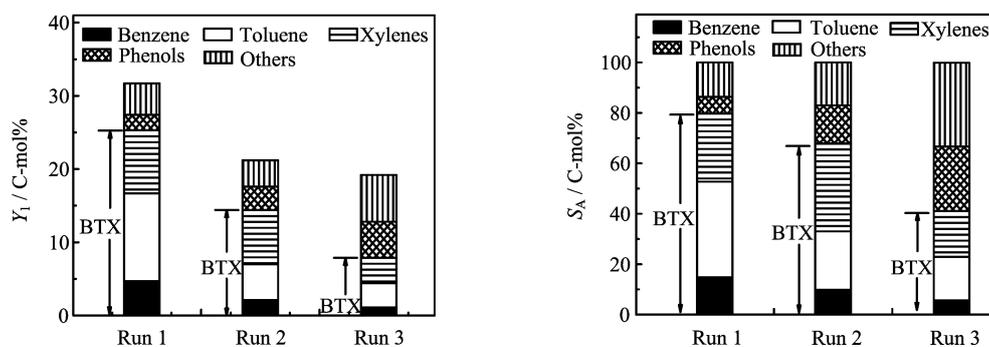

FIG. 6 Catalyst stability in lignin depolymerization over the HZSM-5 at T=550 °C, $f(N_2)$=300 cm^3/min and catalyst/lignin ratio of 2.

D. Influence of flow rate of carrier gas on the production of BTX

The flow rate of carrier gas also has important impact on production of BTX from lignin. As shown in Fig.5, the BTX selectivity was about 81.7 C-mol% at the lower flow rate of 50 mL/min, and gradually decreased with an increase in flow rate to 500 mL/min. This means that increasing reaction time via varying flow rate will enhance the BTX selectivity through the catalytic depolymerization of lignin.

On the other hand, the weight yield of the organic liquid dramatically increased from 5.9% to 23.3% as the flow rate rising from 50 mL/min to 300 mL/min, accompanied by the decrease in the BTX yield from 6.7 C-mol% to 79.8 C-mol%. It was noticed that the weight yield of gas products increased from 20.4% to 39.8% when the flow rate changed from 500 mL/min to 50 mL/min. A low carrier gas flow rate had a long residence time in the catalytic reaction zone and enhanced the gasification of the organic liquid via the serious secondary cracking of aromatic products, mainly forming CO, CO_2, gas alkanes and olefins. Thus, the carrier gas flow rate should be kept at a higher level for production of BTX from lignin.

E. Catalyst stability

As shown in Fig.6, the catalyst stability of HZSM-5 in the lignin depolymerization was test under the optimum reaction condition (T=500 °C, $f(N_2)$=300 mL/min and catalyst/lignin ratio of 2). The carbon yield of BTX significantly decreased from 25.3 C-mol% to 7.9 C-mol% after HZSM-5 was used for three runs (run 1, run 2 and run 3). The yield of BTX selectivity over the used HZSM-5 obviously reduced to about 41.1 C-mol% for run 3. The loss of the catalyst activity mainly attribute to the decrease in the acidity and the surface area of the HZSM-5. Although we separated the most of coke from used HZSM-5 after each run, the residual coke on the catalyst surface may also occupy part of the active center and this negative impact on the performance of catalytic depolymerization will be depressed by the catalyst regeneration in our future work.

IV. CONCLUSION

Production of benzene, toluene, and xylenes (BTX) from lignin was investigated via the catalytic depolymerizaton of lignin using different zeolitie catalysts under various reaction condition. HZSM-5 shows the best results as the moderate acidity, and the small pore

size are beneficial for lignin cracking and the deoxygenation process. Temperature influences distribution of products seriously, and the selectivity of BTX increases as the temperature rising. But high temperature will lead to the second cracking to form alkanes and olefins. The BTX selectivity showed a positive dependence on the catalyst/lignin ratio, and the optimal ratio of catalyst to lignin was about 2:1. Further increasing the catalyst/lignin ratio will decrease the BTX yield, which accounts for an increase in yield of gas products. And we need to carefully control the reaction time in order to obtain more BTX. The highest carbon yield and selectivity of BTX reached 25.3 C-mol% and 90.9 C-mol% over HZSM-5 catalyst at T=550 °C, f(N_2)=300 cm^3/min, and catalyst/lignin ratio of 2. Formation of BTX proceeded through lignin depolymerizaton followed by the deoxygenation process. Production of BTX from lignin can be potentially served as high-valued chemicals for the petrochemical industry.

V. ACKNOWLEDGMENTS

[1] J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius, and B. M. Weckhuysen, Chem. Rev. **110**, 3552 (2010).

[2] F. G. Calvo-Flores and J. A. Dobado, ChemSusChem. **3**, 1227 (2010).

[3] P. Sannigrahi, Y. Pu, and A. Ragauskas, Curr. Opin. Environ. Sustainability **2**, 383 (2010).

[4] D. K. Shen, S. Gu, K. H. Luo, S. R. Wang, and M. X. Fang, Bioresour. Technol. **101**, 6136 (2010).

[5] F. Chakar and A. Ragauskas, Ind. Crop. Prod. **20**, 131 (2004).

[6] R. N. Olcese, J. Francois, M. M. Bettahar, D. Petitjean, and A. Dufour, Energy Fuels **27**, 975 (2013).

[7] B. Valle, A. G. Gayubo, A. T. Aguayo, M. Olazar, and J. Bilbao, Energy Fuels **24**, 2060 (2010).

[8] H. J. Park, K. H. Park. J. K. Jeon, J. Kim, R. Ryoo. K. E. Jeong, S. H. Park, and Y. K. Park, Fuel **97**, 379 (2012).

[9] G. W. Huber and A. Corma, Angew Chem. Int. Ed. **46**, 7184 (2007).

[10] M. Kleinert, J. R. Gasson, and T. Barth, J. Anal. Appl. Pyrolysis **85**, 108 (2009).

[11] F. A. Agblevor, S. Beis, O. Mante, and N. Abdoulmoumine. Ind. Eng. Chem. Res. **49**, 3533 (2010).

[12] W. Y. Xu, S. J. Miller, P. K. Agrawal, and C. W. Jones, ChemSusChem **5**, 667 (2012).

[13] J. Zakzeski, A. L. Jongerius, and B. M. Weckhuysen, Green Chem. **12**, 1225 (2010).

[14] N. Yan, C. Zhao, P. J. Dyson, C. Wang, L. T. Liu, and Y. Kou, ChemSusChem **1**, 626 (2008).

[15] N. Žilková, M. Bejblová, B. Gil, S. I. Zones, A. Burton, C. Y. Chen, Z. Musilová-Pavlačková, G. Košová, and J, Čejka. J. Catal. **266**, 79 (2009).

[16] G. Sena-Martins, E. Almeida-Vara, and J. C. Duarte. Ind. Crop. Prod. **27**, 189 (2008).

[17] K. Giannakopoulou, M. Lukas, A. Vasiliev, C. Brunner, and H. Schnitzer, Bioresour Technol. **101**, 3209 (2010).

[18] M. Olazar, R. Aguado, J. Bilbao, and A. Barona, AIChE J. **46**, 1025 (2000).

[19] P. Wang, S. Zhan, H. Yu, X. Xue, and N. Hong, Bioresour Technol. **101**, 3236 (2010).

[20] (a) R. Rinaldi and F. Schüth, Energy Environ Sci. **2**, 610 (2009).
(b) E. Putun, B. B. Uzun, and A. E. Putun, Energy Fuels **23**, 2248 (2009).

[21] H. Zhang, R. Xiao, D. Wang, Z. Zhong, M. Song, Q. Pan, and G. He, Energy Fuels **23**, 6199 (2009).

[22] F. A. Agblevor, S. Beis, O. Mante, and N. Abdoulmoumine, Ind. Eng. Chem. Res. **49**, 3533 (2010).

[23] T. R. Carlson, T. R. Vispute, and G. W. Huber, ChemSusChem **1**, 397 (2008).

[24] T. Q. Hoang, X. Zhu, T. Danuthai, and L. L. Lobban, Energy Fuels **24**, 3804 (2010).

[25] J. Jae, G. A. Tompsett, A. J. Foster, K. D. Hammond, S. M. Auerbach, R. F. Lobo, and G. W. Huber, J. Catal. **279**, 257 (2011).

[26] D. M. Alonso, J. Q. Bond, and J. A. Dumesic, Green Chem. **12**, 1493 (2010).

[27] M. A. Jackson, D. L. Compton, and A. A. Boateng, J. Anal. Appl. Pyrolysis **85**, 226 (2009).

[28] Z. Ma, E. Troussard, J. A. Bokhoven, Appl. Catal. A **423**, 130 (2012).

[29] W. W. Huang, F. Y. Gong, M. H. Fan, Q. Zhai, C. G. Hong, and Q. X. Li, Bioresour. Technol. **121**, 248 (2012).