Supplementary Information for

Catalytic hydrotreatment of fast pyrolysis liquids in batch and continuous set-ups using a bimetallic Ni-Cu catalyst with a high metal content

Wang Yin[1], Arjan Kloekhorst[1], Robertus H. Venderbosch[2], Maria V. Bykova[3], Sofia A. Khromova[3], Vadim. A. Yakovlev[3], Hero J. Heeres*[1]

[1] Department of Chemical Engineering, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands

[2] Biomass Technology Group BV, Josink Esweg 34, 7545 PN Enschede, The Netherlands

[3] Boreskov Institute of Catalysis, 5, pr. Akad. Lavrentieva, 630090 Novosibirsk, Russia

(*) corresponding author: h.j.heeres@rug.nl Tel.: +31 50 3634174

Content:

Tables: 2

Figures: 5

Table S1 Summary of studies about catalytic hydrotreatment of pyrolysis liquids over nickel based catalysts

Entry	Catalyst	Feed	Reaction Temperature	H_2 Pressure	Reaction time, LHSV	Reactor type	Product properties	Reference
1	Ru/C for stabilization Sulfided Ni-Mo/C for HDO	Pyrolysis oil from sawdust	170-250 °C for stabilization 400 °C for HDO	13.8 MPa	0.19 h^{-1}	Two-stage fixed bed	Product yield 0.35-0.45g/g dry feed, oxygen content 0.2-0.3 wt.%	[1]
2	Sulfided Ni-Mo/γ-Al_2O_3	Pyrolysis oil from oak	150 °C for stabilization 340-400 °C for HDO	6.9-16.9 MPa	1 h for stabilization and 1 h for HDO	Semibatch reactor	63-68 % carbon yield in organic phase, around 5 wt.% oxygen content	[2]
3	Sulfided Ni-Mo/γ-Al_2O_3	10 wt.% pyrolysis oil in 1-methylnaphthalene	280-350 °C	0.34-0.97 MPa	0.4-2 h^{-1}	Fixed bed reactor	TAN in products from 2.2 to 8.6 mg KOH/g, acid conversion from 63 to 91%, O/C from 4.06 to 1.04, H/C from 1.17 to 1.26	[3]
4	Sulfided Ni-Mo/γ-Al_2O_3	Pyrolysis oil from sawdust	270 °C	2.07 MPa	0.0011-0.0065 m/s	Packed bed microreactor	HDO up to 40%	[4]
5	Sulfided Ni-Mo/γ-Al_2O_3	Rapeseed pyrolysis oil	260-350 °C	3 MPa	2.0 h^{-1}	Packed bed reactor	Oxygen content from 8.12 to 2.82 wt.%	[5, 6]
6	Reduced Ni-Mo/γ-Al_2O_3	Pyrolysis oil from pine sawdust	200 °C	3 MPa	2 h	Batch autoclave	pH increased from 2.16 to 2.84, hydrogen content increased from 6.61 to 6.93 wt.%	[7]
7	Reduced Ni-Mo/CNT	Pyrolysis oil from pine sawdust	100-250 °C	5-6 MPa	2-10 h	Batch autoclave	pH from 2.92 to 3.68, hydrogen content from8.40 to 11.26 wt.%	[8]

8	Raney Ni	Pyrolysis oil from liquid phase pyrolysis	250 °C for stabilization 400 °C for HDO	8.5 MPa for stabilization and 15.0-17.0 MPa for HDO	2-4 h for stabilization and 2 h for HDO	Batch autoclave	Oxygen content 1.9 wt.%	[9]
9	Raney Ni	Pyrolysis oil in methanol and formic acid	200 °C	Formic acid as hydrogen donor and the pressure around 8 MPa	5-8 h	Batch autoclave	Water content 17.7 wt.%, viscosity 4.16 mm^2/s, pH=4.35, heating value 22.06 MJ/kg, organic yield 86.7 wt.%	[10]
10	Ni/HZSM-5	Pyrolysis oil from sawdust	240 °C	4.0 MPa	3 h	Batch autoclave	Oxygen content 38.66 wt.%	[11]
11	Ni/HZSM-5(Ni content 20 wt.%), Ni/SiO_2-ZrO_2(Ni content from 10 to 25 wt.%)	Pyrolysis oil in ethanol	280 °C	1.5 MPa	5 h	Batch autoclave	acid, phenolics, esters, alcohols, ketones, aldehydes detected	[12]
12	Ni/TiO_2-ZrO_2	Pyrolysis oil in decalin	300 °C	4.0 MPa	8 h	Batch autoclave	Upgraded oil: 19.3 wt.% oxygen content, pH=4.21, water content 1.5 wt.%, heating value 25.8 MJ/kg	[13]
13	Ni/ZrO_2	Bio-oil from hydrothermal liquefaction of cornstalks in cyclohexane	300 °C	5 MPa	4 h	Batch autoclave	Oxygen content of product decreased from 26.79 to 0.75 wt.%	[14]
14	Ni-Co-Pd/γ-Al_2O_3	Pyrolysis oil from Chlorella	300 °C	2 MPa	3 h^{-1}	Fixed bed reactor	Oxygen content of product was 2.1 wt.%, deoxygenation degree 80.5%	[15]

15	Ni-Fe/γ-Al_2O_3	Pyrolysis oil from straw	400 °C	Atmospheric pressure	0.03 ml/min	Tubular quartz reactor	pH=7.5, heating value 43.9 MJ/kg, H/C ratio 2.15	[16]
16	Ru/C for stabilization Ni-Fe/γ-Al_2O_3 for HDO	Pyrolysis oil in organic solvents (tetraline, decalin, diesel or diesel/isopropanol)	300 °C for stabilization and 400 °C for HDO	10 MPa for stabilization and 13 MPa for HDO	3 h for stabilization and 20 ml/h for HDO	Batch reactor for stabilization and fixed bed reactor for HDO	Deoxygenation degree from 92-94%	[17]
17	Ni-Cu/ZrO_2 (Cu/Ni ratio from 0.14-1.00 w/w) with a fixed metal loading 22 wt.%	Pyrolysis oil from alge (Chlorella and Nanochloropsis sp.)	350 °C	2 MPa	3.5 h^{-1}	Tricked bed reactor	Oxygen content decreased from 7.19 to 1.30 wt.% and from 5.81 to 1.63 wt.%, highest HDO efficiency of 82%	[18]
18	Ni-Cu on CeO_2-ZrO_2, ZrO_2, TiO_2, Carbon from rice husk, Sibunite, δ-Al_2O_3	Pyrolysis oil from pine wood	150 °C for stabilization and 350 °C for HDO	11.0 MPa	1 h for stabilization and 3 h for HDO	Batch autoclave	Oxygen content of product Ranging from 5.4 to 17.7 wt.%	[19]
19	Ni-Cu/δ-Al_2O_3(Ni content 20.8-5.92 wt.% and Cu content 0-18.2 wt.%)	Pyrolysis oil from pine wood	150 °C for stabilization and 350 °C for HDO	10.0 MPa	1 h for stabilization and 3 h for HDO	Batch autoclave	Oxygen content of products ranging from 12.2 to 17.1 wt.%	[20]

Table S2 ^{1}H-NMR of pyrolysis liquids and upgraded oils after catalytic hydrotreatment using Ni-Cu catalyst in the batch set-up

Chemical shift region (ppm)	Proton assignments	PL (%-H)	80 °C (%-H)	180 °C (%-H)	250 °C (%-H)	300 °C (%-H)	350 °C (%-H)
10.0-8.0	-CHO, -COOH, downfield ArH	1	1	0	0	0	0
8.0-6.8	ArH, HC=C (conjugated)	4	4	2	1	2	3
6.8-6.4	HC=C(nonconjugated)	3	4	4	4	5	4
6.4-4.2	$-CH_n-O-$, ArOH, HC=C (nonconjugated)	18	24	13	4	2	2
4.2-3.0	CH_3O-, $-CH_2O-$, -CHO-	28	23	27	29	16	7
3.0-2.2	$CH_3(=O)-$, CH_3-Ar, $-CH_2Ar$	12	14	12	11	16	17
2.2-1.6	$-CH_2-$, aliphatic OH	22	20	17	17	21	20
1.6-0.0	$-CH_3$, $-CH_2-$	12	10	25	34	38	47

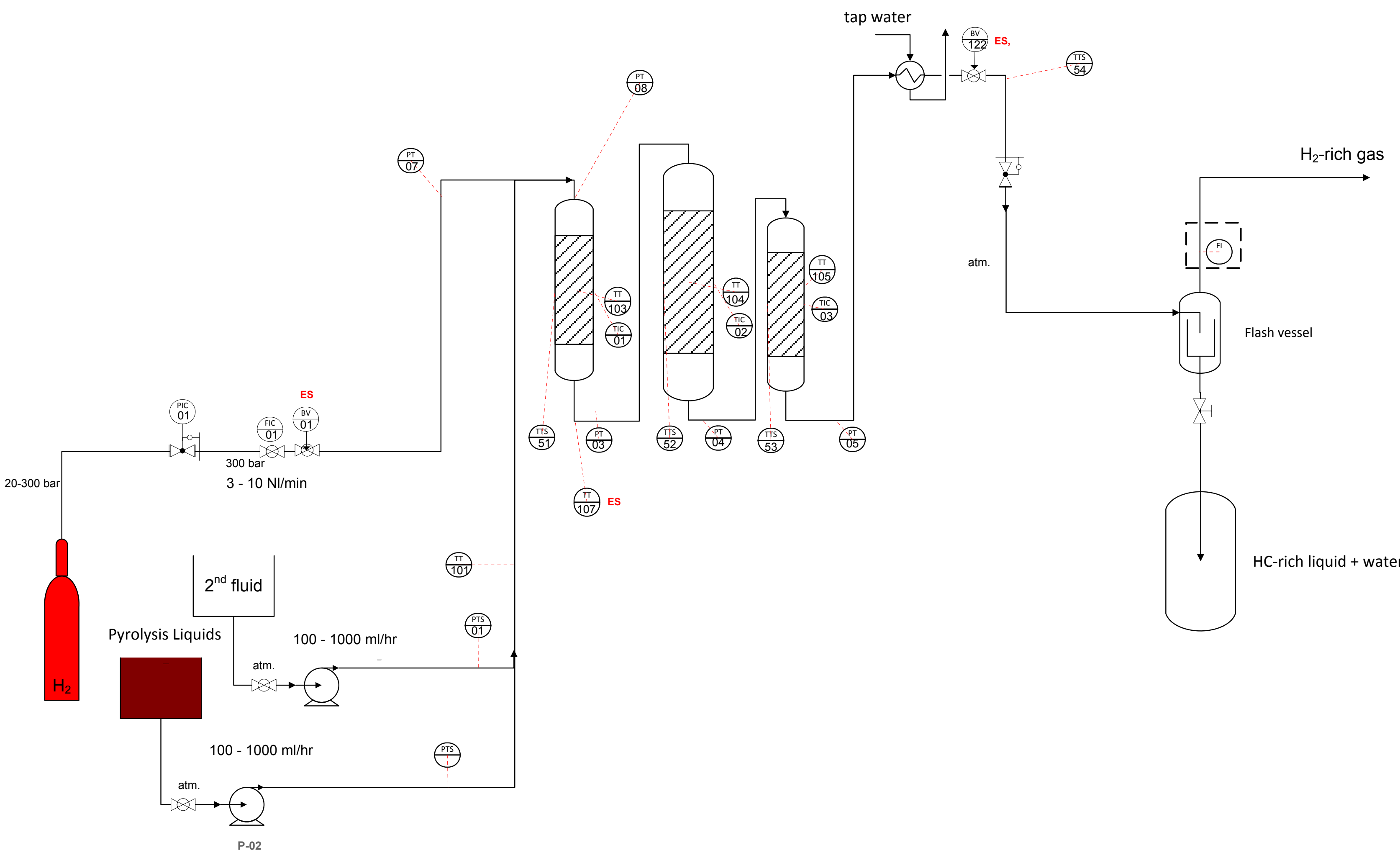

Figure S1. Schematic overview of the continuous hydrotreatment set-up

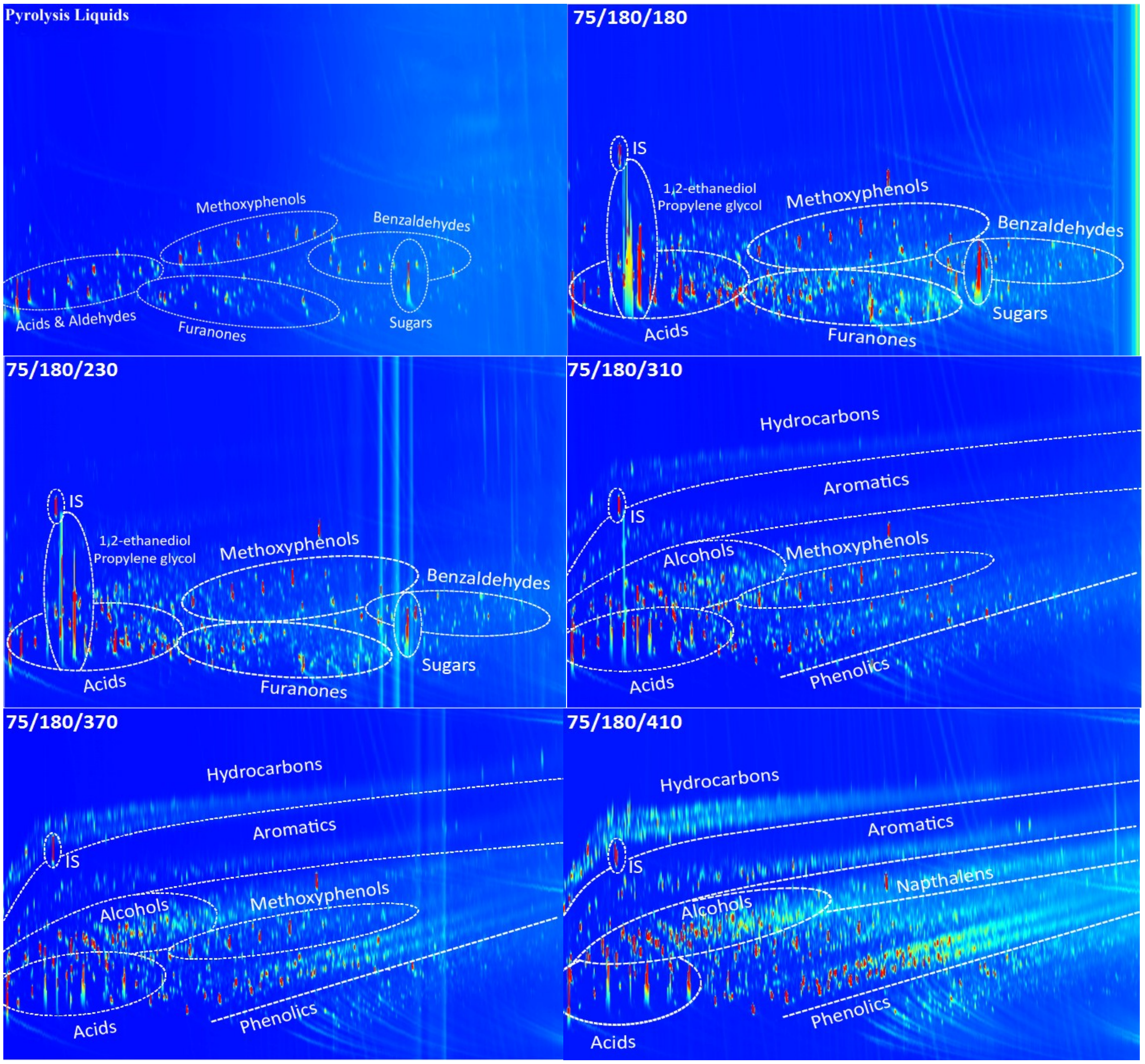

Figure S2 GC x GC spectrum of pyrolysis liquids and upgraded oils obtained in the continuous set-up using Ni-Cu catalyst (IS: internal standard, di-n-butyl ether)

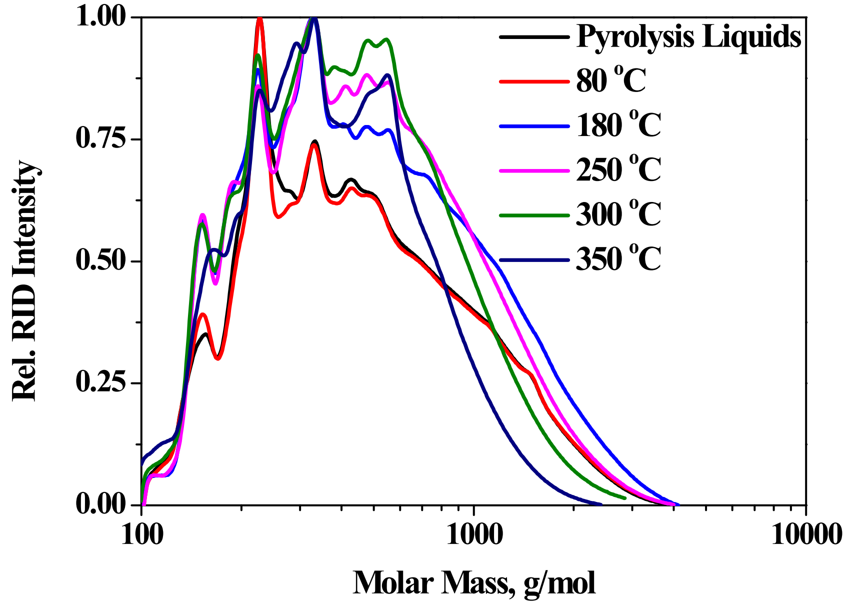

Figure S3 Molecular weight distribution by GPC analysis for pyrolysis liquids and upgraded oils in the batch set-up

Flash points of the organic phases

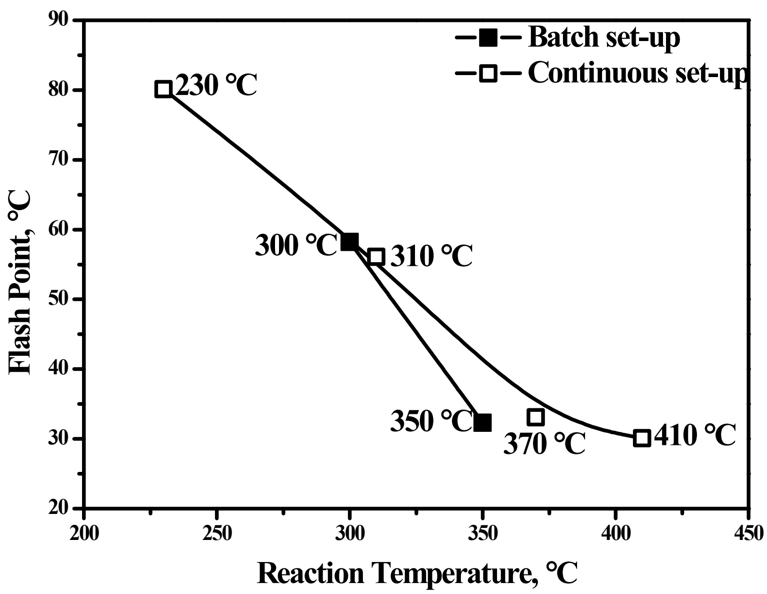

Figure S4 Flash point of the product oils obtained using Ni-Cu catalyst in the batch reactor and continuous set-up

The flash points for the product oils from the batch and continuous set-up were determined and the results are given in Figure S4. Clear flash points were not detected for the pyrolysis liquids feed and the product oils obtained at 180 ^{o}C from continuous set-up and for the product oils at 80-250 ^{o}C from batch reactor, presumably due to the large amount of water in these samples (22.6-15.9 wt.% for continuous reactor and 32.1-9.7 wt.% for the batch reactor). For the other products, a clear trend is visible; the flash point reduces dramatically when increasing the hydrotreatment temperature, especially for the product oils from continuous reactor. This indicates the presence of larger amounts of volatile compounds with a lower molecular weight by deoxygenation and hydrocracking reactions when increasing the hydrotreatment temperature. Compared to the products from continuous set-up, the product oils from batch set-up have a slightly lower flash point, presumably due to the higher H/C ratio of the product oils as shown in Figure 2.

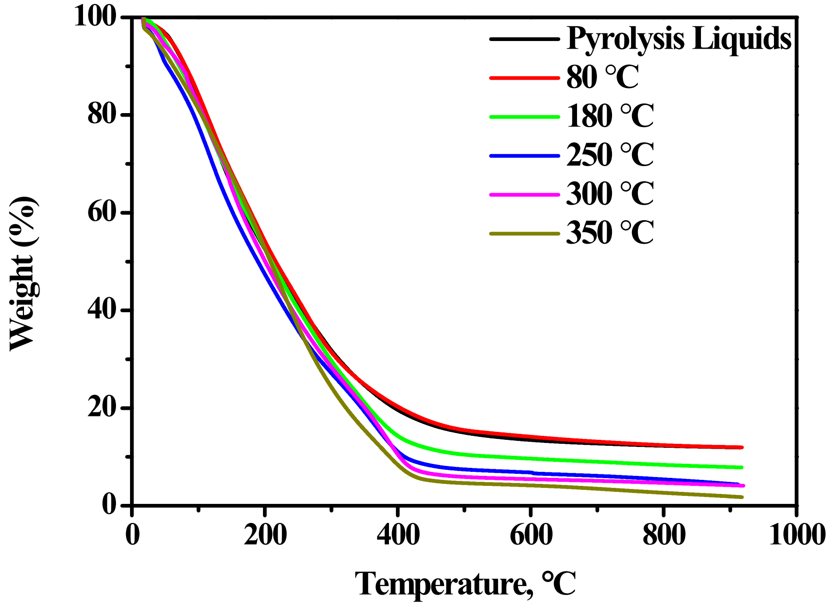

Figure S5 TG residue of pyrolysis liquids and product oils using Ni-Cu catalyst in the batch set-up

References for supplementary material

1 D. C. Elliott, T. R. Hart, G. G. Neuenschwander, L. J. Rotness, M. V. Olarte, A. H. Zacher and Y. Solantausta, *Energy Fuels,* 2012, **26**, 3891-3896.

2 R. J. French, J. Stunkel, S. Black, M. Myers, M. M. Yung and K. Iisa, *Energy Fuels,* 2014, **28**, 3086-3095.

3 Y. Wang, H. Lin and Y. Zheng, *Catalysis Science & Technology,* 2014, **4**, 109-119.

4 N. Joshi and A. Lawal, *Chemical Engineering Science,* 2012, **74**, 1-8.

5 K. Pstrowska, J. Walendziewski, R. Łużny and M. Stolarski, *Catalysis Today,* 2014, **223**, 54-65.

6 K. Pstrowska, J. Walendziewski and M. Stolarski, *Fuel Process Technol,* 2014, **128**, 191-198.

7 Y. Xu, T. Wang, L. Ma, Q. Zhang and L. Wang, *Biomass Bioenergy,* 2009, **33**, 1030-1036.

8 M. Zhou, L. Tian, L. Niu, C. Li, G. Xiao and R. Xiao, *Fuel Process Technol,* 2014, **126**, 12-18.

9 H. Pucher, N. Schwaiger, R. Feiner, L. Ellmaier, P. Pucher, B. S. Chernev and M. Siebenhofer, *Green Chem.,* 2015, **17**, 1291-1298.

10 W. Xiong, Y. Fu, F. Zeng and Q. Guo, *Fuel Process Technol,* 2011, **92**, 1599-1605.

11 X. Zhang, T. Wang, L. Ma, Q. Zhang and T. Jiang, *Bioresour. Technol.,* 2013, **127**, 306-311.

12 X. Zhang, L. Chen, W. Kong, T. Wang, Q. Zhang, J. Long, Y. Xu and L. Ma, *Energy,* 2015, **84**, 83-90.

13 X. Zhang, J. Long, W. Kong, Q. Zhang, L. Chen, T. Wang, L. Ma and Y. Li, *Energy Fuels,* 2014, **28**, 2562-2570.

14 W. Shi, Y. Gao, S. Song and Y. Zhao, *Ind Eng Chem Res,* 2014, **53**, 11557-11565.

15 W. ZHONG, Q. GUO, X. WANG and L. ZHANG, *Journal of Fuel Chemistry and Technology,* 2013, **41**, 571-578.

16 S. Leng, X. Wang, X. He, L. Liu, Y. Liu, X. Zhong, G. Zhuang and J. Wang, *Catalysis Communications,* 2013, **41**, 34-37.

17 X. Xu, C. Zhang, Y. Liu, Y. Zhai and R. Zhang, *Chemosphere,* 2013, **93**, 652-660.

18 Q. Guo, M. Wu, K. Wang, L. Zhang and X. Xu, *Ind Eng Chem Res,* 2015, **54**, 890-899.

19 A. R. Ardiyanti, S. Khromova, R.H. Venderbosch, V. Yakovlev, I. Melián-Cabrera and H.J. Heeres, *Applied Catalysis A: General,* 2012, **449**, 121-130.

20 A. R. Ardiyanti, S. Khromova, R. H. Venderbosch, V. Yakovlev and H. J. Heeres, *Applied Catalysis B: Environmental,* 2012, **117**, 105-117.