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Supporting Information for

**Efficient and controllable ultrasound-assisted depolymerization of organosolv
lignin catalyzed to liquid fuels by MCM-41 supported phosphotungstic acid**

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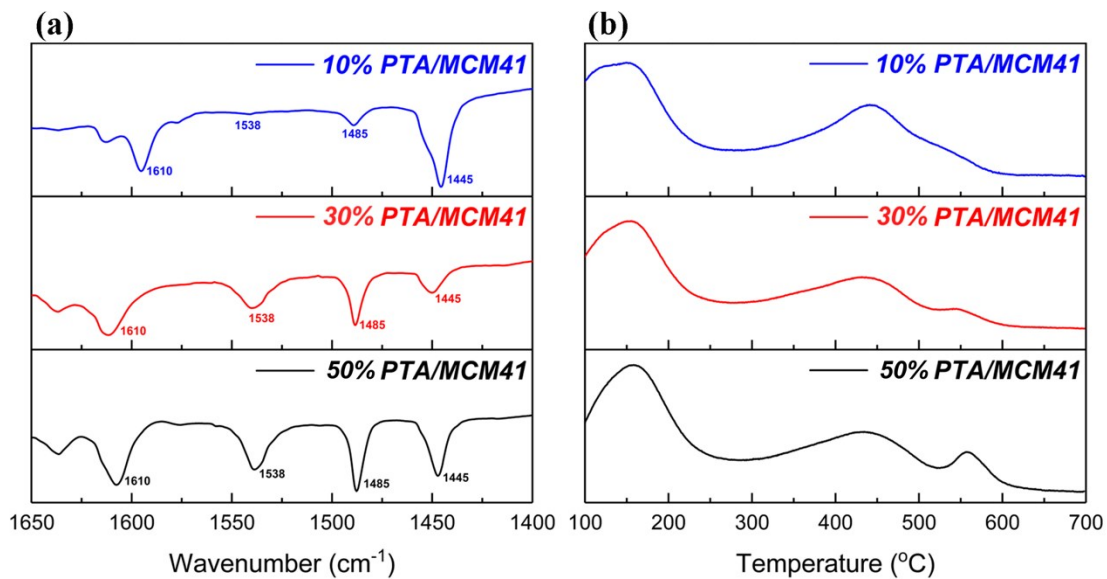
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24 **1. Ultrasound-assisted depolymerization of organosolv lignin**

25 The combined mixture collected from reactor was subsequently subjected to
26 filtration. The filter cake was washed with isopropanol several times and then washed
27 with THF several times in order to retrieve the unreacted lignin solid residue (SR). The
28 SR was dried and weighed which including bio-char (BC) and catalyst. The dried SR
29 was calcined in air at 550°C for 2 h, and the obtained solid was retrieved, dried, weighed
30 and named as regenerated catalyst. The filtrate included two parts. One was phenolic
31 monomer (PM) product which would go through qualitative and quantitative analysis
32 by gas chromatography–mass spectrometry (GC–MS) and gas chromatography-flame
33 ionization detector (GC-FID). The filtrate was subjected to liquid–liquid extraction
34 with dichloromethane (DCM). Approximately 49 mL of extraction phase was mixed
35 with a known quantity of N-tetradecane internal standard. The main aromatic
36 monomers yields were calculated concentration using the effective carbon number
37 (ECN) method ^{1, 2}. The other was bio-oil (BO) which was obtained by removing
38 isopropanol and THF in the filtrate using a rotary evaporator. After that, solid fraction
39 was dried at 60°C until a constant weight. In particular, the yield of liquid fuels (LF)
40 was obtained by summing the yields of PM and BO, and the yield of lignin conversion
41 (LC) was obtained by summing the yields of PM, BO and BC.

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43 **2. Analysis of catalysts**

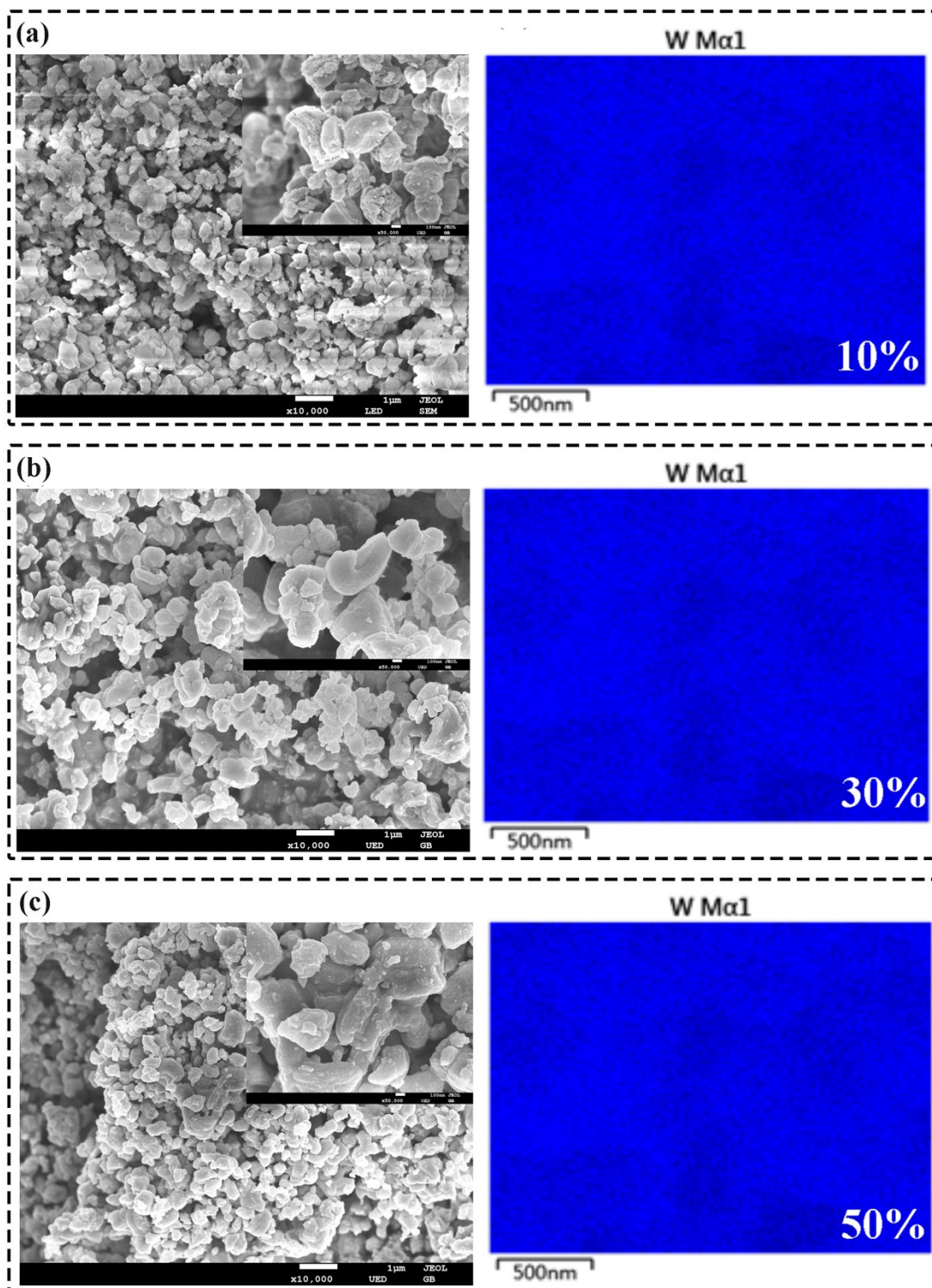


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45 **Fig. S1.** The acidity of different catalysts: (a) FT-IR pyridine spectra, (b) NH₃-TPD
 46 spectra.

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48 The SEM and EDS analyses of the different PTA/MCM-41 catalysts are illustrated
 49 in Fig. S2. From the SEM images, it can be clearly inferred that the fresh different
 50 PTA/MCM-41 catalysts show irregular morphology and has a heterogeneous particle
 51 size distribution, which demonstrates a typical crystal structure. According to EDS
 52 image, it indicates the uniform dispersion of PTA on the MCM-41 support.



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 54 **Fig. S2.** The SEM and EDS images of different PTA/MCM-41 catalysts: (a) 10%
 55 PTA/MCM-41 catalyst, (b) 30% PTA/MCM-41 catalyst and (c) 50% PTA/MCM-
 56 41 catalyst.

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58 **3. Analysis of organosolv lignin**

59 **Table S1** Assignment of main lignin signals in the 2D-HSQC NMR spectra of
60 organosolv lignin ^{3,4}.

Lignin structure	δ_c/δ_h (ppm)	Assignment
C _{β}	53.1/3.46	C _{β} -H _{β} in phenylcoumaran (C)
OCH ₃	56.4/3.70	C-H in methoxyls
A _{γ}	59.9/3.35-3.80	C _{γ} - H _{γ} in B-O-4 substructures (A)
C _{γ}	62.2/3.76	C _{γ} - H _{γ} in phenylcoumaran (C)
I _{γ}	61.2/4.09	C _{β} - H _{β} in cinnamyl alcohol end-groups (I)
B _{γ}	71.2/3.82-4.18	C _{β} - H _{β} in β - β resinol (B)
A _{α}	71.8/4.86	C _{α} - H _{α} in B-O-4 unit (A, Erythro)
A β (G)	83.4/4.38	C _{β} - H _{β} in B-O-4 linked to G (A)
A β (S)	85.8/4.12	C _{β} - H _{β} in B-O-4 linked to S (A, Erythro)
C _{α}	86.8/5.45	C _{α} - H _{α} in phenylcoumaran (C)
S _{2,6}	103.9/6.70	C _{2,6} - H _{2,6} in syringyl units (S)
S' _{2,6}	106.3/7.32	C _{2,6} - H _{2,6} in oxidized S units (S')
G ₂	110.8/6.97	C ₂ - H ₂ in guaiacyl units (G)
G ₅	114.5/6.70	C ₅ - H ₅ in guaiacyl units (G)
G ₆	119.0/6.78	C ₆ - H ₆ in guaiacyl units (G)
H _{2,6}	127.7/7.17	C _{2,6} - H _{2,6} in H units (S)
PCA _{2,6}	130.2/7.48	C _{2,6} - H _{2,6} in p-coumarate (p-CE)
PCA ₈	113.7/6.24	C ₈ - H ₈ in p-coumarate (p-CE)
FA ₂	110.7/7.35	C ₂ - H ₂ in ferulate (p-FA)
FA ₈	123.1/7.20	C ₆ - H ₆ in ferulate (p-FA)

61

62 **Table S2** Element composition and heating value of organosolv lignin.

Entry	Sample	Elemental composition (wt.%)						HHV ^a
		C	H	O	N	O/C	H/C	
1	OL	53.52	5.36	44.95	0.17	0.82	0.08	19.08

63 ^a HHV (MJ/kg) = (34C+124.3H+6.3N+19.3S-9.8O)/100, where C, H, N, S, and O are
64 the weight percentages of carbon, hydrogen, nitrogen, sulfur, and oxygen ^{5,6}.

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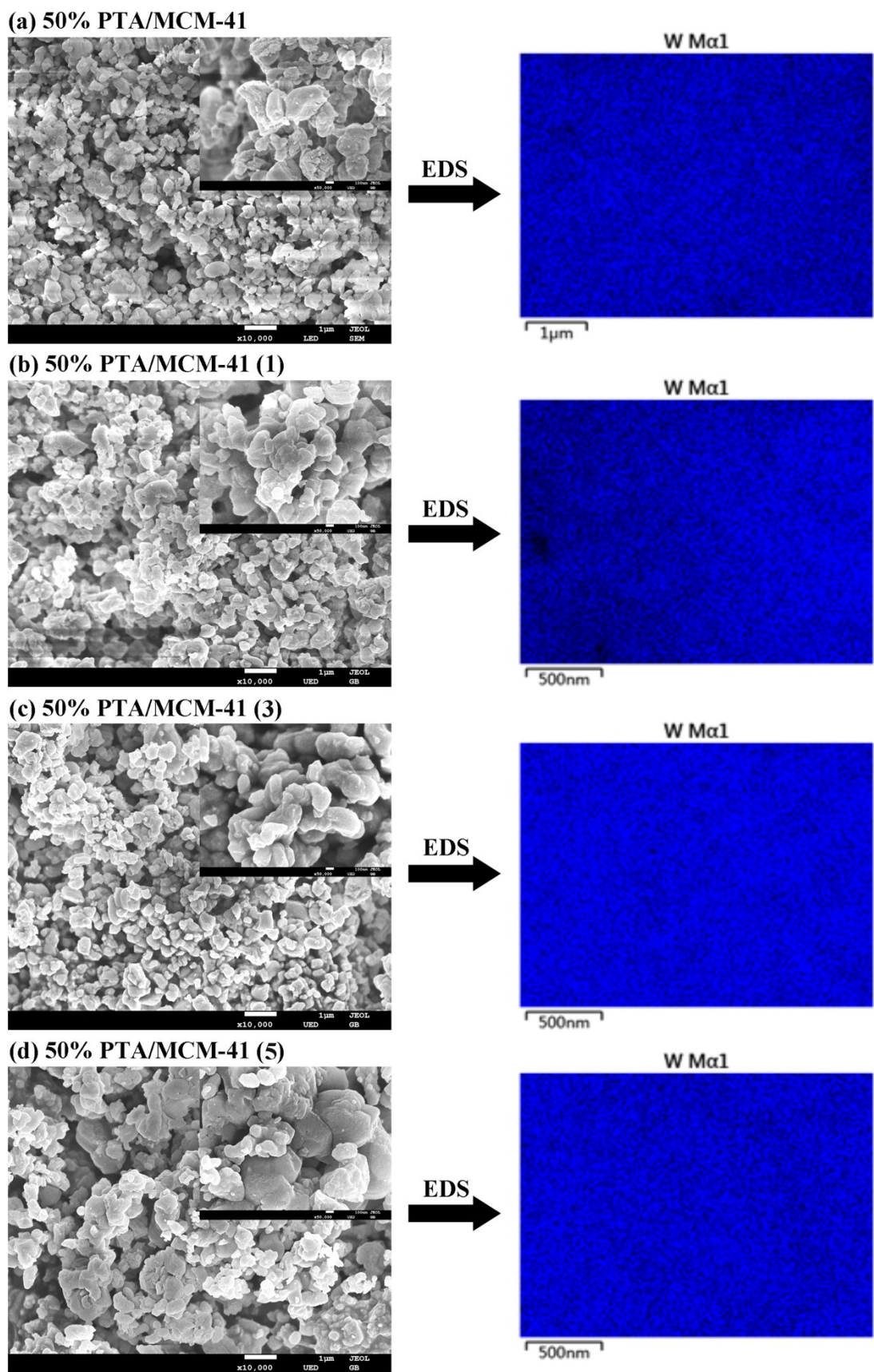
66 **Table S3** Average molecular weight of organosolv lignin.

Entry	Catalysts	Mw ^a (g/mol)	Mn ^a (g/mol)	PDI ^a (g/mol)
1	OL	4750	1540	3.08

67 ^a Mw: weight average molecular weight, Mn: number average molecular weight, PDI:
68 polydispersity index and PDI=Mw/Mn.

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70 **4. Catalytic depolymerization of organosolv lignin in isopropanol**



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Fig. S3. The SEM and EDS images of original catalyst and different regenerated catalysts.

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75 **5. Analysis of bio-oil depolymerization products**

76 **Table S4** Average molecular weight of depolymerization product bio-oil obtained from
77 different reaction conditions.

Entry	Reaction conditions	Mw ^a	Mn ^a	PDI ^a
1	270°C ^b	1280	510	2.53
2	290°C ^b	940	520	1.83
3	310°C ^b	810	510	1.58
4	330°C ^b	980	560	1.76
5	350°C ^b	1160	640	1.81
6	0.5 h ^c	1720	670	2.56
7	2 h ^c	1560	710	2.21
8	4 h ^c	930	530	1.75
9	8 h ^c	1040	620	1.69
10	Ethanol ^d	1050	530	1.99
11	Methanol ^d	940	540	1.73
12	10 % ultrasonic frequency ^e	790	500	1.57
13	20 % ultrasonic frequency ^e	730	490	1.48
14	30 % ultrasonic frequency ^e	650	520	1.24
15	40 % ultrasonic frequency ^e	720	530	1.36
16	50 % ultrasonic frequency ^e	990	660	1.51

78 ^a Mw: weight average molecular weight, Mn: number average molecular weight and
79 PDI: polydispersity index.

80 ^b Reaction condition: 0.5 g OL, 0.25 g 50% PTA/MCM-41 catalysts, 30 mL
81 isopropanol, 30 ml deionized-water and 6 h.

82 ^c Reaction condition: 0.5 g OL, 0.25 g 50% PTA/MCM-41 catalysts, 30 mL
83 isopropanol, 30 ml deionized-water and 310°C.

84 ^d Reaction condition: 0.5 g OL, 0.25 g 50% PTA/MCM-41 catalysts, 30 ml deionized-

85 water, 310°C and 6 h.

86 ^e Reaction condition: 0.5 g OL, 0.25 g 50% PTA/MCM-41 catalysts, 30 mL

87 isopropanol, 30 ml deionized-water, 310°C and 6 h.

88

89 **Table S5** The effect of different reaction conditions on elemental compositions and

90 heating value of depolymerization product bio-oil.

Entry	Reaction conditions	Elemental composition (wt.%)						HHV ^a
		C	H	O	N	O/C	H/C	
1	270°C ^b	60.69	6.57	32.62	0.12	0.54	0.11	25.61
2	290°C ^b	64.13	8.38	27.38	0.11	0.43	0.13	29.54
3	310°C ^b	67.39	10.94	21.58	0.09	0.32	0.16	34.41
4	330°C ^b	65.12	10.42	24.35	0.11	0.37	0.16	34.01
5	350°C ^b	62.17	10.12	27.56	0.15	0.44	0.16	31.02
6	0.5 h ^c	57.27	7.49	35.13	0.11	0.61	0.13	25.34
7	2 h ^c	60.35	7.65	31.86	0.14	0.53	0.13	26.92
8	4 h ^c	65.22	8.89	25.73	0.16	0.39	0.14	30.71
9	8 h ^c	66.05	9.98	23.84	0.13	0.36	0.15	32.53
10	Ethanol ^d	63.79	8.21	27.85	0.15	0.44	0.13	29.17
11	Methanol ^d	64.88	10.46	24.53	0.13	0.38	0.16	32.67
12	10 % ultrasonic frequency ^e	69.46	10.46	19.95	0.13	0.29	0.15	34.67
13	20 % ultrasonic frequency ^e	68.35	11.37	20.17	0.11	0.29	0.17	35.40
14	30 % ultrasonic frequency ^e	73.79	10.84	15.31	0.06	0.26	0.15	37.07
15	40 % ultrasonic frequency ^e	73.03	10.36	16.48	0.13	0.23	0.14	36.10
16	50 % ultrasonic frequency ^e	72.79	8.78	18.34	0.09	0.25	0.12	33.88

91 ^a HHV (MJ/kg) = (34C+124.3H+6.3N+19.3S-9.8O)/100, where C, H, N, S, and O are
92 the weight percentages of carbon, hydrogen, nitrogen, sulfur, and oxygen ^{6,7}.

93 ^b Reaction condition: 0.5 g OL, 0.25 g 50% PTA/MCM-41 catalysts, 30 mL

94 isopropanol, 30 ml deionized-water and 6 h.

95 ^c Reaction condition: 0.5 g OL, 0.25 g 50% PTA/MCM-41 catalysts, 30 mL
96 isopropanol, 30 ml deionized-water and 310°C.

97 ^d Reaction condition: 0.5 g OL, 0.25 g 50% PTA/MCM-41 catalysts, 30 ml deionized-
98 water, 310°C and 6 h.

99 ^e Reaction condition: 0.5 g OL, 0.25 g 50% PTA/MCM-41 catalysts, 30 mL
100 isopropanol, 30 ml deionized-water, 310°C and 6 h.

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102 **6. Reference**

103 1. L.-P. Xiao, S. Wang, H. Li, Z. Li, Z.-J. Shi, L. Xiao, R.-C. Sun, Y. Fang and G.
104 Song, ACS Catalysis, 2017, 7, 7535-7542.

105 2. X. Wang, B. Du, L. Pu, Y. Guo, H. Li and J. Zhou, Journal of Analytical and
106 Applied Pyrolysis, 2018, 129, 13-20.

107 3. J.-L. Wen, B.-L. Xue, S.-L. Sun and R.-C. Sun, Journal of Chemical
108 Technology & Biotechnology, 2013, 88, 1663-1671.

109 4. J.-L. Wen, T.-Q. Yuan, S.-L. Sun, F. Xu and R.-C. Sun, Green Chem., 2014, 16,
110 181-190.

111 5. M. Zhou, B. K. Sharma, J. Li, J. Zhao, J. Xu and J. Jiang, Fuel, 2019, 239, 239-
112 244.

113 6. L. Kong, C. Liu, J. Gao, Y. Wang and L. Dai, Bioresource Technology, 2019,
114 276, 310-317.

115 7. X. Liu, Z. Jiang, S. Feng, H. Zhang, J. Li and C. Hu, Fuel, 2019, 244, 247-257.
116