Supporting Information

Production of value-added chemicals from bio-oil via acid catalysis coupled with liquid-liquid extraction

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Experimental

Materials

The chemicals used in this study were analytical grade and were purchased from Sigma Aldrich, Merck Australia, LC Scientific Inc. (Canada), and Carbosynth Limited (U. K.), respectively. The commercially available solid acid catalyst Amberlyst 70 (Rohm & Haas) was used directly without any further pre-treatments. The bio-oils used were obtained by the fast pyrolysis of mallee eucalypts wood (E. loxophleba ssp. gratiae) in a fluidised-bed reactor at 500°C. The detailed experimental procedures can be found in the literature [J. Shen, X. S. Wang, M. Garcia-Perez, D. Mourant, M. J. Rhodes and C.-Z. Li, Fuel, 2009, 88, 1810.].

Experimental procedure

The original wood bio-oil was naturally one phase. By adding water (41 wt.% to the bio-oil) the bio-oil was separated into an upper water-like phase and a lower paste-like phase. The two phases were further separated with centrifuge. The further extraction of the aromatics in the water-like phase of bio-oil were performed by adding the chloroform ($V_{chloroform}/V_{water-like phase of bio-oil} = 1$) into the water-like phase of bio-oil and then followed the similar procedures.

Acid-treatments of bio-oil were performed in a 130 mL Hastalloy batch autoclave reactor with the variation of the reaction temperatures and methanol/bio-oil mass ratios. The autoclave was purged with nitrogen initially and then heated to desired reaction

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temperature with a stirring rate of 600 rpm under an autonomous pressure. A sample was taken immediately after reaching reaction temperature and further samples were taken at 30 min interval for 180 min.

As for the extraction experiment, a water solution containing twenty-one chemicals (methyl levulinate, ethyl levulinate, levulinic acid, guaiacol, phenol, 1,2,4-trimethoxybenzene, eugenol, vanillin, 1,1,3-trimethoxy ethene, furfural, formic acid, acetic acid, hydroxyl acetone, cyclopentanone, 2-methyl-cyclopentanone, glycol, methyl formate, methyl acetate, methanol, levoglucosan, and methyl α -D-glucopyranoside) with the concentration of 1 wt.% each were prepared. Twelve solvents (ethyl butyrate,

2-octanol, 1-butanol, ethyl acetate, dichloromethane, chloroform, petroleum spirit, petroleum ether, hexadecane, ethyl ether, methyl acetate, and toluene) were selected to extract the chemicals. Typically, 4 ml of the water solution containing the chemicals was added into a vial containing the same volume of solvent. After that, the vial was shaking vigorously for 30 min and then processed with ultrasonic for another 30 min and then put at room temperature for 12 h for analysis.

Analytical methods

The products were analysed with an Agilent GC-MS (6890 series GC with a 5973 MS detector) equipped a capillary column (HP-INNOWax) (length: 30 m; internal diameter: 0.25 mm; film thickness: 0.25 µm of crosslinked polyethylene glycol.). The sample was injected into the injection port set at 250°C with a split ratio of 50:1. The column was operated in a constant flow mode using 2.0 mL min⁻¹ of helium as the carrier gas. The column temperature was initially maintained at 35°C for 1.8 min before increasing to 260°C at a heating rate of 10°C min⁻¹. The identification of each compound was based on matching its mass spectrum with that in the spectral library and was further confirmed by injecting standards. Standard solutions covering concentration range of the samples were used to obtain calibration curves for calculating concentrations of compounds of interest.

Table S1 Distribution of the selected compounds in the water-like phase and the paste-like phase of bio-oil^a

	Abundance)	Area percentage in		
The selected compounds in the bio-oil after	distribution (%)		spectrum (%)		
extraction with water	Water-like	Paste-like	Water-like	Paste-like	
	phase	phase	phase	phase	
Water	79.7	20.3	32.1	9.9	
Sugars					
levoglucosan	83.4	16.6	19.3	7.9	
1,4:3,6-Dianhydroalphad-glucopyranose	63.4	36.6	0.4	0.3	
2,3-Anhydro-d-mannosan	100.0	0.0	0.1	0.0	
1,6-Anhydrobetad-talopyranose	100.0	0.0	1.7	0.0	
Anhydro-d-mannosan	100.0	0.0	0.3	0.0	
3,4-Anhydro-d-galactosan	67.7	32.3	0.2	0.0	
Aromatics					
Phenol	27.2	72.8	0.6	1.9	
Phenol, 4-ethyl-2-methoxy-	12.9	87.1	0.3	2.7	
Phenol, 2,5-dimethyl-	26.7	73.3	0.5	1.8	
Phenol, 3-methyl-	58.4	41.6	0.8	0.7	
Phenol, 2-methoxy-4-propyl-	41.1	58.9	1.0	1.7	
Eugenol	17.4	82.6	0.8	4.8	
2-Methoxy-4-vinylphenol	6.3	93.7	0.1	1.8	
Phenol, 2-methoxy-4-(1-propenyl)-	9.1	90.9	0.3	3.7	
Vanillin	28.6	71.4	1.6	4.9	
Phenol, 2-methoxy-4-propyl-	22.0	78.0	0.6	2.4	
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	31.3	68.7	1.3	3.5	
2-Propanone,					
1-(4-hydroxy-3-methoxyphenyl)-	29.6	70.4	0.6	1.7	
4-Ethoxy-3-anisaldehyde	26.7	73.3	0.3	0.8	
Benzeneacetic acid, 4-hydroxy-3-methoxy-	32.6	67.4	0.9	2.3	
Hydroquinone	52.3	47.7	0.4	0.4	
4-Hydroxy-2-methoxycinnamaldehyde	17.3	82.7	0.8	4.5	
Benzoic Acid	33.1	66.9	0.1	0.3	
Phenol, 2-methoxy-4-methyl-	19.1	80.9	1.8	9.0	
Phenol, 2-methoxy-	27.0	73.0	1.8	5.7	
Phenol, 4-methoxy-3-methyl-	35.0	65.0	0.2	0.4	
2-Hydroxy-5-methylbenzaldehyde	21.5	78.5	0.0	0.1	
Furans					
Furfural	31.1	68.9	0.8	2.1	
5-(Hydroxymethyl)furfural	50.4	49.6	1.6	1.9	
2-Furancarboxaldehyde, 5-methyl-	20.1	79.9	0.1	0.5	
2(5H)-Furanone, 5-methyl-	33.9	66.1	0.2	0.5	

2-Furanmethanol	54.4	45.6	0.2	0.2
2(5H)-Furanone, 3-methyl-	37.9	62.1	0.3	0.7
2(5H)-Furanone	51.4	48.6	1.0	1.1
2(3H)-Furanone, dihydro-4-hydroxy-	39.5	60.5	0.2	0.3
4-Methyl-5H-furan-2-one	48.1	51.9	0.5	0.6
Carboxylic acids				
Acetic acid	73.6	26.4	6.7	2.9
Formic acid	78.9	21.1	1.6	0.5
Propanoic acid	79.7	20.3	0.5	0.2
2-Propenoic acid	53.7	46.4	0.1	0.1
Pentanoic acid	68.0	32.0	0.9	0.5
3-Butenoic acid	36.3	63.7	0.1	0.1
Pentanoic acid, 4-oxo-	59.5	40.5	0.3	0.3
Crotonic acid	53.2	46.8	0.2	0.2
Aldehydes and ketones				
2-Propanone, 1-hydroxy-	70.0	30.0	5.4	2.8
Acetaldehyde, hydroxy-	73.7	26.3	4.3	1.8
2,3-Butanedione	50.1	49.9	0.3	0.4
1-Hydroxy-2-butanone	61.0	39.0	0.5	0.4
Cyclopentanones				
Cyclopentanone	26.7	73.3	0.1	0.2
2-Cyclopenten-1-one	38.2	61.8	0.4	0.8
2-Cyclopenten-1-one, 2-methyl-	25.4	74.6	0.2	0.6
2-Cyclopenten-1-one, 3-methyl-	25.0	75.0	0.1	0.4
2-Cyclopenten-1-one, 2-hydroxy-	49.7	50.3	0.7	0.8
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	42.2	57.9	1.0	1.7
1,3-Cyclopentanedione, 2-methyl-	43.3	56.8	0.2	0.4
Alcohols				
1,2-Ethanediol	81.6	18.4	1.3	0.4
Glycerin	75.7	24.3	0.5	0.2
2-Propen-1-ol	54.1	45.9	0.1	0.1
Esters				
1,2-Ethanediol, monoacetate	48.3	51.7	0.2	0.2
1,2-Ethanediol, diacetate	41.6	58.5	0.1	0.2
Butanoic acid, 3-hydroxy-, methyl ester	64.3	35.7	0.3	0.2
Others				
1,3,5-Trioxane	56.3	43.7	0.1	0.1
[1,4,7]Trioxonane	55.7	44.3	0.2	0.2
Maltol	38.4	61.6	0.2	0.3
4H-Pyran-4-one, 3,5-dihydroxy-2-methyl-	12.0	88.0	0.2	2.0

^aBy adding water to increase the water content in bio-oil to ca. 41 wt.%, the bio-oil separated into a water-like phase and a paste-like phase automatically.

	Ethyl	2 Octornal	1-Butanol	Ethyl		CHCl ₃
	butyrate	2-Octanol		Acetate		
Methyl levulinate	70.8 ^b	72.9	72.5	79.7	95.0	96.4
Ethyl levulinate	86.1	53.3	85.2	90.2	98.1	98.9
Levulinic acid	21.4	29.4	56.7	43.0	19.0	14.9
Guaiacol	96.7	93.3	93.1	96.7	97.3	97.2
Phenol	97.2	95.8	94.8	97.3	86.6	82.9
1,2,4-Trimethoxybenzene	98.4	95.7	95.0	97.8	99.7	99.8
Eugenol	99.7	99.0	98.8	99.5	99.7	99.7
Vanillin	93.0	90.1	91.8	94.5	94.0	94.7
1,1,3-trimethoxy ethene	59.1	53.7	63.5	66.3	90.5	95.0
Furfural	86.2	32.7	78.8	88.8	94.6	94.8
Formic acid	18.0	100.0	44.0	34.5	0.0	0.0
Acetic acid	24.7	9.0	56.5	37.4	10.5	10.4
Hydroxyl acetone	8.7	100.0	29.7	18.0	17.4	17.4
Cyclopentanone	76.9	75.2	77.3	80.0	94.8	96.6
Cyclopentanone, 2-methyl-	92.3	91.0	89.5	92.3	98.4	98.9
Glycol	1.0	75.7	21.6	3.1	0.5	0.3
Methyl formate	74.8	57.4	63.7	87.3	88.3	89.0
Methyl acetate	76.2	66.9	71.4		90.7	92.2
Methanol	10.0	21.0	36.3	79.3	7.2	6.8
Levoglucosan	0.0	0.0	18.8	0.0	0.0	0.0
MGP	0.0	0.0	0.0	0.0	0.0	0.0

Table S2 Extraction of the typic	cal compounds with the selected solvents ^a
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^aTo extract the compounds, a water solution containing the chemicals with the concentration of 1 wt.% each were prepared and were extracted with the solvents (v/v =1). ^bThe numbers in the table means percentages of the compounds distributed in the solvents.

	Petroleum	Petroleum	Hexadecane	Ethyl	Methyl	Toluene
	spirit	ether		ether	acetate	
Methyl levulinate	16.1 ^b	17.6	31.8	60.7	68.8	70.1
Ethyl levulinate	37.3	39.4	0.0	80.4	78.7	87.1
Levulinic acid	0.0	0.7	0.8	26.4	44.9	3.1
Guaiacol	57.9	59.7	50.5	94.4	86.7	92.3
Phenol	37.4	40.1	27.4	96.0	88.6	81.0
1,2,4-Trimethoxybenzene	76.2	77.6	70.8	95.6	88.2	98.6
Eugenol	92.5	92.6	89.6	99.2	95.0	99.2
Vanillin	10.6	12.0	8.4	87.5	81.5	79.6
1,1,3-trimethoxy ethene	31.3	31.4	19.0	57.4	57.2	61.9
Furfural	28.3	31.6	22.0	77.8	76.8	80.4
Formic acid	4.5	0.1	0.3	27.5	41.8	2.1
Acetic acid	1.0	1.0	0.7	34.0	42.8	4.5
Hydroxyl acetone	5.5	0.6	0.7	7.9	25.5	4.2
Cyclopentanone	42.0	42.8	32.0	72.3	69.0	81.1
Cyclopentanone, 2-methyl-	76.0	76.7	67.1	90.2	81.3	94.3
Glycol	0.2	0.0	0.0	1.1	7.5	0.2
Methyl formate	51.5	35.8	32.1	78.3	73.5	71.3
Methyl acetate	46.2	42.2	32.0	72.0	60.6	74.5
Methanol	1.8	1.0	0.7	12.8	26.5	2.7
Levoglucosan	0.0	0.0	0.0	0.0	0.0	0.0
MGP	0.0	0.0	0.0	0.0	0.0	0.0

Table S3 Extraction of the typical compounds with the selected solvents^a

^aTo extract the products, a water solution containing the chemicals with the concentration of 1 wt.% each were prepared and were extracted with the solvents (v/v =1).

^bThe numbers in the table means percentages of the compounds distributed in the solvents.



Figure S1 The conversion of levoglucosan and the typical products from sugars versus reaction temperatures. Catalyst loading: 13.3 wt.%; Bio-oil/methanol mass ratio = 1: 4; Stirring rate = 600 rpm. "RT" in x-axis means the reaction mixture at room temperature. "0 min" means that the temperature just reached the required ones. Definition of the abbreviations: MGP: methyl α -D-glucopyranoside; HMF: (hydroxymethyl)furfural; MMF: 5-(methoxymethyl)-2-furancarboxadhyde.



Figure S2 Water content and acetic acid conversion versus reaction temperatures and reaction time. Catalyst loading: 13.3 wt.%; Water-like phase of bio-oil/methanol mass ratio = 1: 4; Stirring rate = 600 rpm. "RT" in x-axis means the reaction mixture at room temperature. "0 min" means that the temperature just reached the required reaction temperatures.



Figure S3 Conversion of hydroxyl aldehyde versus reaction temperatures. Catalyst loading: 13.3 wt.%; Water-like phase of bio-oil/methanol mass ratio = 1: 4; Stirring rate = rpm. "RT" in x-axis means the reaction mixture at room temperature. "0 min" means that the temperature just reached the required reaction temperatures.



Figure S4 Conversion of hydroxyl acetone versus reaction temperatures. Catalyst loading: 13.3 wt.%; Water-like phase of bio-oil/methanol mass ratio = 1: 4; Stirring rate = 600 rpm. "RT" in x-axis means the reaction mixture at room temperature. "0 min" means that the temperature just reached the required reaction temperatures.



Figure S5 Conversion of levoglucosan and the typical products from sugars versus bio-oil/methanol mass ratios. Catalyst loading: 13.3 wt.%; Reaction temperature = 165° C; Stirring rate = 600 rpm. "RT" in x-axis means the reaction mixture at room temperature. "0 min" means that the temperature just reached the required reaction temperatures. Definition of the abbreviations: MGP: methyl α -D-glucopyranoside; HMF: (hydroxymethyl)furfural; MMF: 5-(methoxymethyl)-2-furancarboxadhyde.



Figure S6 Conversion of hydroxyl aldehyde versus bio-oil/methanol mass ratio. Catalyst loading: 13.3 wt.%; $T = 165^{\circ}C$; Stirring rate = 600 rpm. "RT" in x-axis means the reaction mixture at room temperature. "0 min" means that the temperature just reached the required reaction temperatures.



Figure S7 Conversion of hydroxyl acetone versus the bio-oil/methanol mass ratio. Catalyst loading: 13.3 wt.%; T = 165°C; Stirring rate = 600 rpm. "RT" in x-axis means the reaction mixture at room temperature. "0 min" means that the temperature just reached the required reaction temperatures.