Supporting information

Green Materials: Adhesive properties of bio-oils derived from various biorenewable waste streams: from wood to paper to paper deinking residue

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Number of figures: 12
Number of tables: 4

Section 1. Experimental set-up for the microwave-assisted pyrolysis

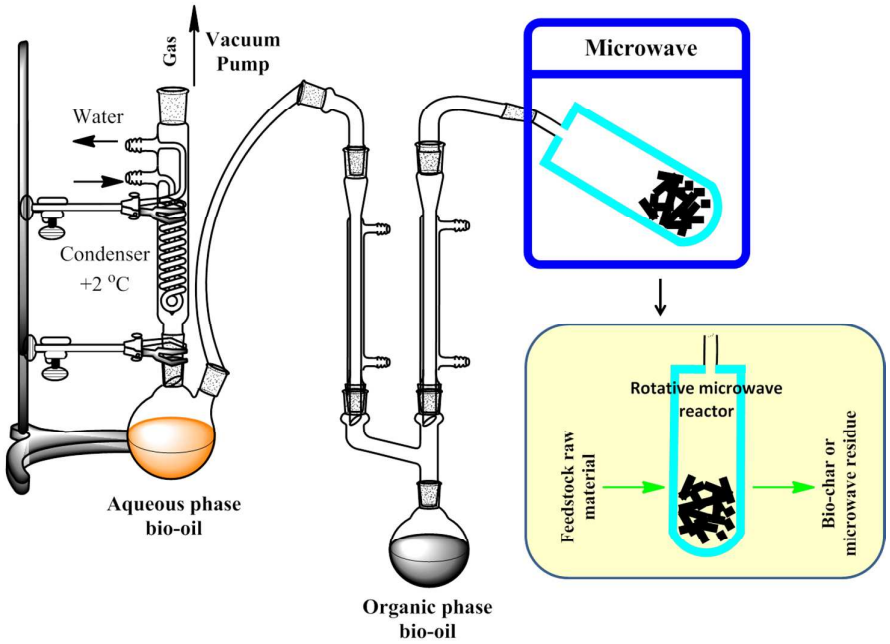

Figure S1. Experimental set-up for the microwave-assisted low-temperature (<200 °C) pyrolysis of spruce wood chips, waste paper and DIR

Process temperatures gradually increased from room temperature (around 25 °C) with reaction time, the microwave-assisted pyrolysis processes generally finished (no volatiles came out from the microwave vessel) and maximum temperatures (between 190 °C and 200 °C) were reached after about 12 – 13 minutes of irradiation. Using the fitted vacuum system, condensable volatile compounds were collected as two phases of bio-oils (*i.e.*, organic phase bio-oil and aqueous phase bio-oil) and incondensable gaseous products were removed from the reaction system by the vacuum pump (Figure S1). More specifically, during microwave-irradiation of waste biomass within the rotating microwave vessel in the microwave chamber, an aqueous phase was firstly generated and collected at the round-bottom flask connected to the water cooled condenser. After 3 to 4 minutes, a dark-brown liquid was produced and collected separately in another round-bottom flask (*i.e.*, organic phase bio-oil).

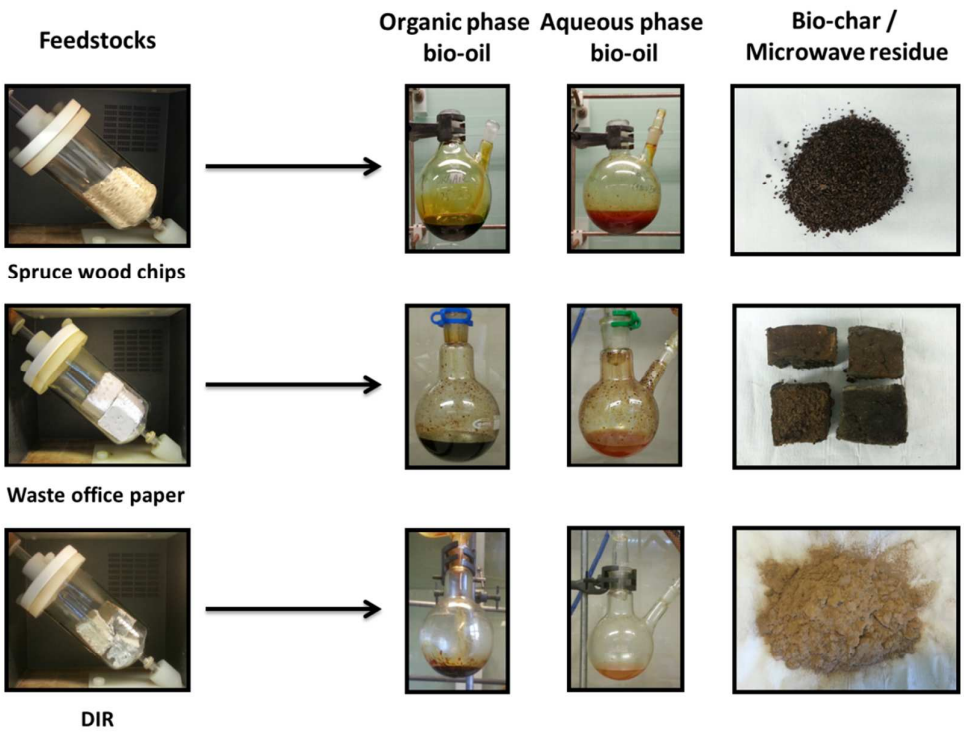

Figure S2. Appearances of raw materials and products generated from microwave-assisted low-temperature processing of spruce wood chips, waste paper and DIR

Section 2. Proximate and ultimate characterization of spruce wood chips and their pyrolysis products

Table S1. Proximate and ultimate characterization of spruce wood chips and their microwave-assisted pyrolysis products

	Spruce wood chips	Organic phase bio-oil	Aqueous phase bio-oil	Bio-char
Proximate analysis (wt.%)				
Moisture	6.2	---	---	2.0
Volatile matter	73.1	---	---	39.9
Fixed carbon	19.8	---	---	55.8
Ash	0.9	<1.0	1.1	2.3
Ultimate analysis				
C (%)	46.10 ± 0.21	52.03 ± 0.31	26.41 ± 0.18	71.33 ± 0.31
H (%)	5.60 ± 0.08	6.40 ± 0.03	7.71 ± 0.02	4.20 ± 0.05
N (%)	N.D.[a]	N.D.	N.D.	N.D.
S (%)	0.020 ± 0.003	0.005 ± 0.001	0.009 ± 0.002	0.041 ± 0.002
O (%)[b]	48.3 ± 0.29	41.60 ± 0.34	65.89 ± 0.20	24.5 ± 0.36
Water content (%)	1.1	2.1 ± 0.2	---	<1.0
CV (MJ kg^{-1})[d]	18.57 ± 1.32	22.75 ± 1.16	---	27.76 ± 1.05

[a] N.D.: not detected; [b] Calculated by difference; [c] TOC: total organic carbon; [d] CV: calorific value

Table S2. Mineral contents of spruce wood chips and their relative low-temperature microwave-assisted pyrolysis products as determined by ICP-MS

Element (ppm[a])	Spruce wood chips	Organic phase bio-oil (21 wt.%)	Aqueous phase bio-oil (32 wt.%)	Bio-char (34 wt.%)
Na	11.81	8.42	3.51	9.53
Mg	3.52	4.01	4.23	10.04
Al	108.82	84.31	N.D.[b]	178.21
Si	5877.41	26187.22	19130.82	2636.31
K	9.22	1.21	1.62	21.61
Ca	16.81	4.43	4.43	89.24
Cr	190.91	1.82	2.11	153.41
Mn	65.73	0.62	1.01	305.62
Fe	352.12	15.63	17.31	521.33
Cu	6.71	2.32	3.42	7.71
Zn	39.12	14.01	16.43	67.02
As	1.62	0.51	0.06	1.86
Nb	0.23	0.17	0.13	0.37
Pd	0.27	0.11	0.08	0.53
Sn	3.27	0.18	0.56	3.66
Ir	0.12	0.02	N.D.	0.17
Pt	0.03	0.03	0.02	0.05
Au	0.86	0.05	0.01	1.13
Pb	0.41	0.09	0.72	0.93

[a] ppm refers to parts per million in mass; [b] N.D. = not detected

Section 3. ATR-IR analysis of spruce wood chips and derived pyrolysis products

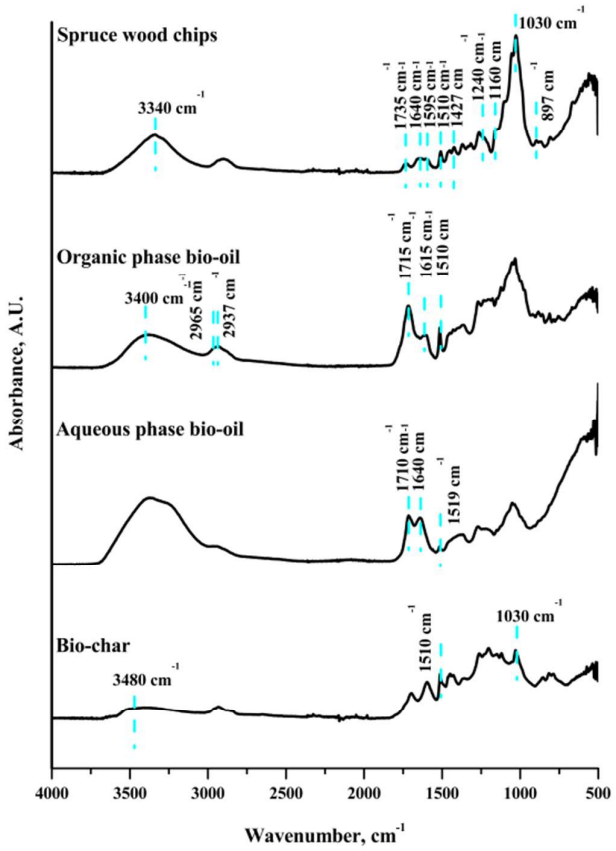

Figure S3. ATR-IR spectra of spruce wood chips and the generated organic phase bio-oil, aqueous phase bio-oil and bio-char.

From the infrared spectrum of spruce wood chips, strong hydrogen bonded (O-H) stretching vibration and prominent C-H stretching vibration absorption bands are observed in the 3700 cm^{-1} – 3000 cm^{-1} region and 3000 cm^{-1} – 2800 cm^{-1} region, respectively. The intense, broad O-H stretching vibration band between 3700 cm^{-1} and 3000 cm^{-1} is mainly attributed to the intra- and intermolecular hydrogen bonded hydroxyl groups associated with residual moisture, cellulosic matter and lignin in spruce wood chips. Characteristic lignin absorption bands due to a variety of aromatic skeletal vibrations are observed at 1607 cm^{-1}, 1595 cm^{-1}, 1510 cm^{-1}, 1427 cm^{-1} and

1265 cm^{-1}.[1] The absorption bands at 1735 cm^{-1}, 1372 cm^{-1}, 1240 cm^{-1}, 1160 cm^{-1}, 1035 cm^{-1} are typical C=O, C-H, C-O-C, C-O deformation and/or stretching vibrations associated with carbohydrates (mainly cellulose and hemicellulose).[1] The absorption band at 1735 cm^{-1} is attributed to the C=O stretching vibrations in unconjugated carbonyl compounds, primarily originating from uronic acids of xylans. Hence this band is also a characteristic absorption band of hemicellulose. The C-H deformation vibration in cellulose is observed at 897 cm^{-1}.

The broad O-H stretching vibration band between 3700 cm^{-1} and 3020 cm^{-1} in the ATR-IR spectrum of the organic phase bio-oil indicates the possible presence of phenols, alcohols, carboxylic acids, and residual water. Compared with the O-H stretching band of spruce wood raw materials, the O-H stretching band of the organic phase bio-oil drifts to a higher wavenumber (from about 3340 cm^{-1} to 3400 cm^{-1}), suggesting a reduction in hydrogen bonding. The symmetrical and asymmetrical C-H stretching vibrations are observed at 2937 cm^{-1} and 2965 cm^{-1}, respectively. This indicates the presence of alkyl structures, which is further evidenced by the small C-H deformation vibration band at around 1456 cm^{-1}. The most significant change compared with the spruce wood chips raw material is the appearance of a medium intensity carbonyl (C=O) absorption band centred at 1715 cm^{-1}. This carbonyl stretching vibration band corresponds to ketone, aldehyde and carboxylic acid compounds present within the organic phase bio-oil. In addition, the absorption band centred at 1615 cm^{-1} is assigned to the C=C stretching of alkene, furans and aromatic compounds, indicating the presence of aromatic compounds. However, this absorption band may also correspond to residual water in the organic phase bio-oil. The region between 1630 cm^{-1} and 1450 cm^{-1} is a typical region where aromatic skeletal vibrations are observed. The absorption bands in this region indicate the presence of aromatic compounds in the organic phase bio-oil. Despite the bands are significantly overlapped due to the complex chemical composition of bio-oil, the characteristic absorption band for aromatic skeletal vibrations at around 1510 cm^{-1} is clearly visible in the ATR-IR spectrum of organic phase bio-oil.[1] The weak absorbances observed

below 1000 cm^{-1} are mainly attributed to C-H out of plane bending vibrations of (substituted) aromatic compounds. The ATR-IR spectrum of organic phase bio-oil also shows many differences in this region compared with that of the spruce wood chips.

The ATR-IR spectrum of the aqueous phase bio-oil reveals a significantly different chemical composition in comparison with the organic phase bio-oil. The presence of possible carboxylic acids is indicated by the broad O-H stretching vibration (3700 cm^{-1} to 3000 cm^{-1}) and the high-intensity carbonyl stretching vibration band centred at 1715 cm^{-1}. The absorption band at around 1640 cm^{-1} further suggests the aqueous phase bio-oil contains high amounts of water. The aqueous phase bio-oil also contains organic matter as evidenced by the vast number of absorption bands in the range between 1750 cm^{-1} and 750 cm^{-1}. It is noteworthy that aromatic compounds were also trapped into this phase of bio-oil as evidenced by the small absorption band centred at 1519 cm^{-1}, which is attributed to skeletal vibrations in aromatic compounds.[1] Probably due to the presence of large amounts of inorganic matter (*e.g.*, water, carboxylic acids), this absorption band of aqueous phase bio-oil (1519 cm^{-1}) drifts slightly to a higher wavenumber compared with that of the organic phase bio-oil (at 1510 cm^{-1}).

The ATR-IR spectrum of the bio-char (residues in the rotating microwave vessel after pyrolysis) indicates many significant structural changes occurred during the pyrolysis process. The intensity of the O-H stretching vibration band significantly decreased. Also, this band of bio-char drifts significantly to a higher wavenumber (3480 cm^{-1}) compared to that of the spruce wood chips (3340 cm^{-1}), indicating a dramatic reduction in hydrogen bonding. In addition, the intensity of the C-O vibration band centred at 1030 cm^{-1} decreased dramatically as a result of the decomposition of the spruce wood chips during pyrolysis. The absorption bands between 1600 cm^{-1} and 1000 cm^{-1} are possibly due to the residual lignin and carbohydrates.[1] Compared with the ATR-IR spectrum of spruce wood chips, many changes could be observed in this region, suggesting the formation of new chemical bonds during pyrolysis. This is

largely due to increased aromatisation and rearrangement of chemical bonds in the bio-char. The aromatisation of bio-char is further evidenced by the changes of absorption bands in the typical aromatic C-H out of plane bending region (950 cm^{-1} to 600 cm^{-1}).

Section 4. Liquid-state ^{1}H and ^{13}C NMR characterization of spruce wood chips derived organic and aqueous phase bio-oils

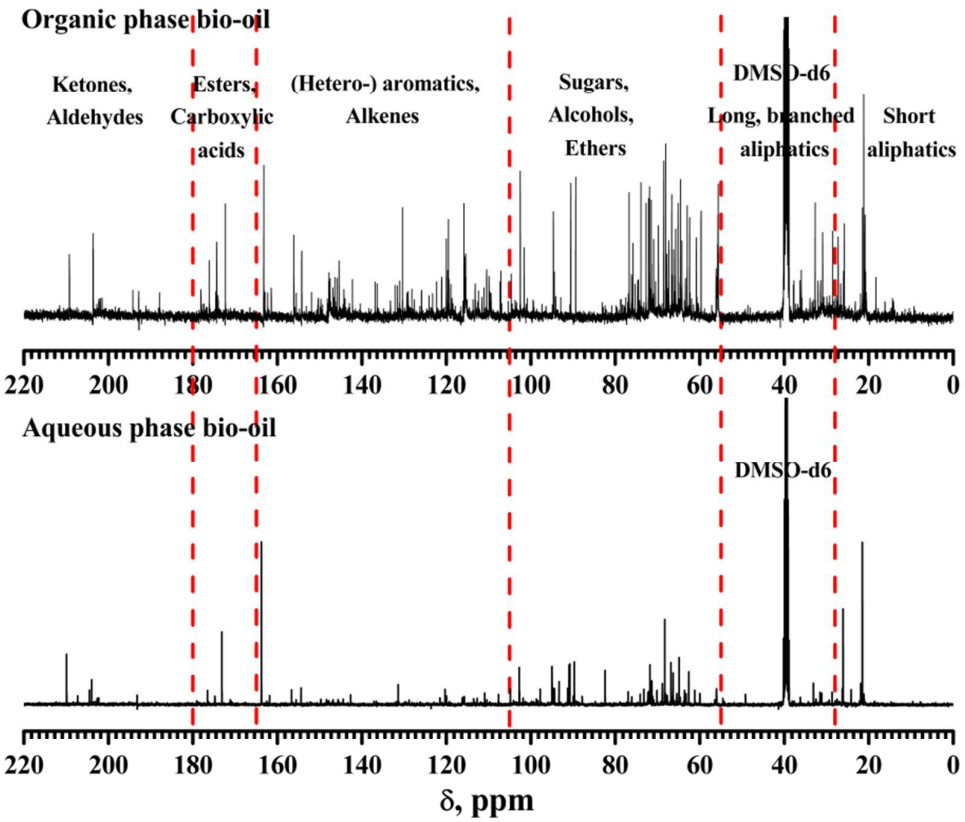

Figure S4. ^{13}C NMR spectra of organic and aqueous phase bio-oil generated from microwave-assisted processing of spruce wood chips. All spectra used the central resonance of DMSO-d_6 (δC, 39.52 ppm) as internal reference.

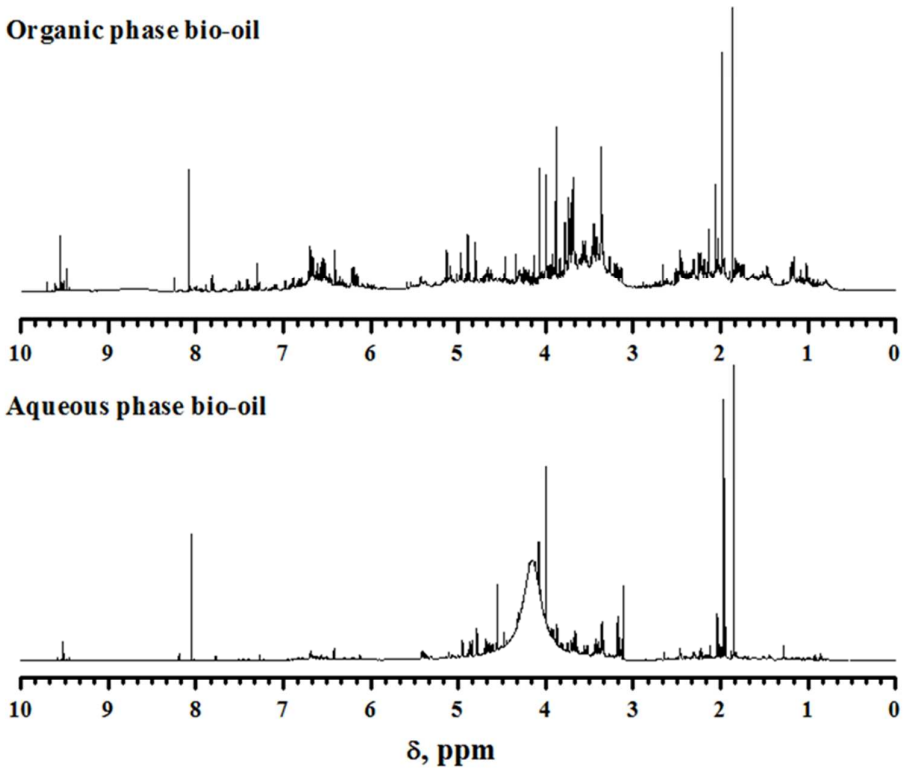

Figure S5. ^{1}H NMR spectra of organic and aqueous phase bio-oil generated from microwave-assisted processing of spruce wood chips

For the ^{13}C NMR spectra of bio-oils (Figure S4), the central resonance of DMSO-d_6 (δC, 39.52 ppm) was used as the internal reference. Most carbohydrate sugars and their derivatives (*e.g.*, levoglucosan, levoglucosenone) generated from thermal degradation of cellulose and hemicellulose are present in the organic phase bio-oil, as indicated by the many complex signals in the typical sugar region (55 – 105 ppm). Compared with the ^{13}C NMR spectrum of the organic phase bio-oil, that of the aqueous phase bio-oil contains fewer and much simpler signals in this region. Also, the intensities of these resonance signals in the ^{13}C NMR spectrum of aqueous phase bio-oil are much lower, suggesting only small amounts of carbohydrate sugars and their derivatives were trapped in the aqueous phase bio-oil. The vast numbers of resonance signals in this region also indicate the possible presence of alcohols and ethers which contain carbon atoms adjacent to an oxygen atom. The high-intensity and sharp resonance signal observed at around 55 ppm in the ^{13}C NMR spectrum of

organic phase bio-oil is attributed to the carbon atoms in methoxy groups on phenolics such as guaiacol and syringol derivatives, which are common pyrolysis products of lignin.

The region between 105 ppm and 165 ppm in the ^{13}C NMR spectra represents carbon atoms in (hetero-) aromatic structures. By assessing the ^{13}C NMR spectra of these two phases of bio-oils, it is obvious that the organic phase bio-oil contains much many and higher amounts of (hetero-) aromatic components than the aqueous phase bio-oil. Also, most furan compounds are present in the organic phase bio-oil, as indicated by the resonance signals between 145 ppm and 165 ppm in the organic phase bio-oil. Similar trends can be observed in other regions of the ^{13}C NMR spectra, indicating that the chemical composition of the organic phase bio-oil is much more complicated than that of the aqueous phase bio-oil.

The ^{1}H NMR spectra of spruce wood chips derived organic and aqueous phase bio-oil (Figure S5) also indicates that the organic phase bio-oil has a much more complex chemical composition profile than the aqueous phase bio-oil. The presence of aromatic compounds in the organic phase bio-oil is evidenced by the complex signals between 6.0 ppm and 8.5 ppm. The signals in this region not only represent hydrogen atoms in benzenoids, but also those in hetero aromatic compounds which contain oxygen atoms. Compared with the ^{1}H NMR spectrum of organic phase bio-oil, few signals were detected in the aromatic region (6.0 ppm – 8.5 ppm) of the ^{1}H NMR spectrum of aqueous phase bio-oil. This observation further confirms that most (hetero-) aromatic compounds were condensed in the organic phase bio-oil).

The resonance signals of the aromatic ether protons presenting in guaiacol and syringol derivatives (lignin degradation products) are observed between 4.4 ppm and 6.0 ppm. This is in good agreement with the ^{13}C NMR analysis of the organic phase bio-oil discussed above. Resonance signals in this region also represent many of the hydrogen atoms in carbohydrate sugars and their derivatives. Due to the high amounts

of carbohydrates produced from thermal degradation of cellulose and hemicellulose during pyrolysis, this region (4.4 ppm – 6.0 ppm) is the most populated and complex region in the ^{1}H NMR spectrum of the bio-oils.

High amounts of water were generated and collected in the aqueous phase bio-oil during the microwave-assisted pyrolysis process, resulting in a broad resonance signal centred around 4.20 ppm in the ^{1}H NMR spectrum of the spruce wood chips derived aqueous phase bio-oil. In contrast, water content of the organic phase bio-oil is very low (only around 2 wt.%). Hence the ^{1}H NMR spectrum of the organic phase bio-oil does not contain an obvious water resonance signal. Resonance signals in the region between 3.0 and 4.4 ppm suggest the possible presence of alcohols and ethers. In addition, this region also represents protons in methylene groups that join two aromatic rings. These moieties may exist in partially degraded lignin oligomers. The resonance signals in the most downfield region (9.5 ppm – 10 ppm) of the ^{1}H NMR spectra indicate the presence of aldehydes and also possible trace amounts of carboxylic acids. The intensities of these signals in the spectrum of the aqueous phase bio-oil are lower than those of the signals in the spectrum of the organic phase bio-oil.

Section 5. GC-MS characterization of spruce wood chips derived organic and aqueous phase bio-oils

Figure S6 demonstrates the GC traces of spruce wood chips derived organic (Figure S6 A) and aqueous phase bio-oil (Figure S6 B). The major identified compounds according to the NIST 2008 mass spectral library in the organic and aqueous phase bio-oils are summarized in Table S3 and Table S4, respectively.

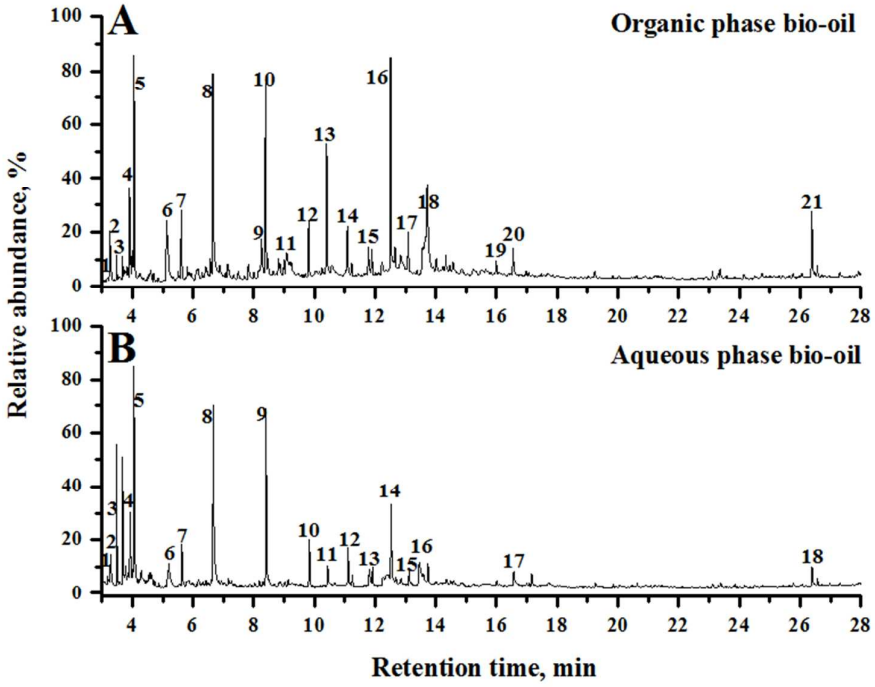

Figure S6. GC-MS spectra of (A) organic and (B) aqueous phase bio-oils produced from microwave-assisted pyrolysis of spruce wood chips.

Table S3: Major identified compounds in spruce wood chips derived organic phase bio-oil[a]

Peak number	Retention time (min)	Identified compound
1	3.18	Acetic acid
2	3.28	Furfural
3	3.48	Tetrahydro-2,5-dimethoxyfuran
4	3.91	2(5*H*)-Furanone
5	4.05	2-Hydroxycyclopent-2-en-1-one
6	5.17	1-Hydroxy-2-pentanone
7	5.61	3-Methyl-1,2-cyclopentanedione
8	6.65	2-Methoxyphenol (Guaiacol)
9	8.18	Levoglucosenone
10	8.39	2-Methoxy-4-methylphenol
11	9.07	1,2-Benzenediol (Catechol)
12	9.81	4-Ethyl-2-methoxyphenol
13	10.40	2-Methoxy-4-vinylphenol
14	11.09	3-Allyl-6-methoxyphenol
15	11.78	5-(Hydroxymethyl)-2-furaldehyde (HMF)
16	12.51	2-Methoxy-4-(1-propenyl)phenol
17	13.09	1-(4-Hydroxy-3-methoxyphenyl)ethanone
18	13.72	Levoglucosan
19	15.99	4-Hydroxy-3-methoxy-phenylacetyl formic acid
20	16.54	4-Hydroxy-2-methoxycinnamaldehyde
21	26.39	10,11-Dihydro-10-hydroxy-2,3-dimethoxydibenz(b,f)oxepin

[a]According to the NIST 2008 database.

Table S4: Major identified compounds in spruce wood chips derived aqueous phase bio-oil[a]

Peak number	Retention time (min)	Identified compound
1	3.18	Acetic acid
2	3.28	Furfural
3	3.48	Tetrahydro-2,5-dimethoxyfuran
4	3.92	2(5*H*)-Furanone
5	4.06	2-Hydroxycyclopent-2-en-1-one
6	5.20	1-Hydroxy-2-pentanone
7	5.62	3-Methyl-1,2-cyclopentanedione
8	6.66	2-Methoxyphenol (Guaiacol)
9	8.40	2-Methoxy-4-methylphenol
10	9.83	4-Ethyl-2-methoxyphenol
11	10.43	2-Methoxy-4-vinylphenol
12	11.11	3-Allyl-6-methoxyphenol
13	11.81	5-(Hydroxymethyl)-2-furaldehyde (HMF)
14	12.53	2-Methoxy-4-(1-propenyl)phenol
15	13.10	1-(4-Hydroxy-3-methoxyphenyl)ethanone
16	13.75	Levoglucosan
17	16.56	4-Hydroxy-2-methoxycinnamaldehyde
18	26.38	10,11-Dihydro-10-hydroxy-2,3-dimethoxydibenz(b,f)oxepin

[a]According to the NIST 2008 database.

Carboxylic acids such as acetic acid were detected in both phases of bio-oils (Peak marked '1' in Figure S6 A and B), the compounds identified between three and seven minutes mainly include furans and their derivatives such as furfural (peak marked '2' Figure S6 A and B) and tetrahydro-2, 5-dimethoxyfuran (peak marked '3' in Figure S6 A and B), together with several small polar molecules.

5-(Hydroxymethyl)-2-furaldehyde (HMF) was also observed at around 11.78 min in both phases of bio-oils (peak marked '15' in Figure S6 A and peak marked '13' in Figure S6 B). The high-intensity chromatographic peaks observed between 6 and 13 minutes in both GC traces of the two phases of bio-oils are mainly assigned to phenolic compounds. Compounds identified in this region (about 6 – 13 min) essentially comprise 2-methoxyphenol (guaiacol, peak marked '8' in Figure S6 A and B), 2-methoxy-4-methylphenol (creosol, peak marked '10' in Figure S6 A and peak marked '9' in Figure S6 B), 4-ethyl-2-methoxyphenol (4-ethylguaiacol, peak marked '12' in Figure S6 A and peak marked '10' in Figure S6 B), 2-methoxy-4-vinylphenol (peak marked '13' in Figure S6 A and peak marked '11' in Figure 2.17 B), 2-methoxy-4-(1-propenyl)phenol (peak marked '16' in Figure S6 A and peak marked '14' in Figure S6 B). Also, 1, 2-benzenediol (catechol) is present in the organic phase bio-oil (peak marked '11' in Figure S6 A). The many (substituted) phenolic compounds detected in both bio-oil phases indicate significant breakdown/decomposition of the lignin content of spruce wood chips during the microwave-assisted low-temperature (<200 ^{o}C) pyrolysis process. In addition, it is obvious that many more chromatographic peaks (also of greater intensities) appear in the GC trace of organic phase bio-oil (Figure S6 A) compared to that of the aqueous phase bio-oil (Figure S6 B) in the region between 6 – 13 minutes. This suggests that the chemical composition of the volatile fraction of the organic phase bio-oil is much more complex than that of the aqueous phase bio-oil, and the concentrations of these organic compounds are probably higher in the organic phase bio-oil.

In addition, sugars such as levoglucosan and levoglucosenone are observed in the GC trace of organic phase bio-oil (peak marked '18' for levoglucosan and peak marked '9' for levoglucosenone in Figure S6 A). These carbohydrate derivatives were generated from thermal decomposition of cellulosic matter of spruce wood chips. Interestingly, trace amounts of levoglucosan was also trapped into the aqueous phase bio-oil (peak marked '16' in Figure S6 B). The chromatographic peak for levoglucosan in the GC trace of aqueous phase bio-oil (Figure S6 B) is significantly smaller than that in the

GC trace of organic phase bio-oil (Figure S6 A), indicating most of carbohydrate sugar derivatives were condensed into the organic phase bio-oil. Levoglucosenone was not detected in the aqueous phase bio-oil.

The chromatographic peak shown at around 26.3 min in the GC traces of both organic (peak marked '21' in Figure S6 A) and aqueous phase bio-oil (peak marked '18' in Figure S6 B) at around 26.4 min is assigned to a poly-aromatic compound named 10, 11-dihydro-10-hydroxy-2,3-dimethoxydibenz(b,f)oxepin, which is probably an oligomer derived from lignin. The same compound was observed before by Liu and Zhang in their study about liquefaction of biomass for the production of fuels and chemical feedstocks.[2] The size of this chromatographic peak in the GC trace of organic phase bio-oil (Figure S6 A) is significantly larger than that in the GC trace of aqueous phase bio-oil (Figure S6 B). Similarly, this also confirms that most organic pyrolysis products were collected in the organic phase bio-oil despite few amounts of organic matter was also trapped into the aqueous phase bio-oil during the pyrolysis process.

Section 6. Adhesive properties of bio-oils

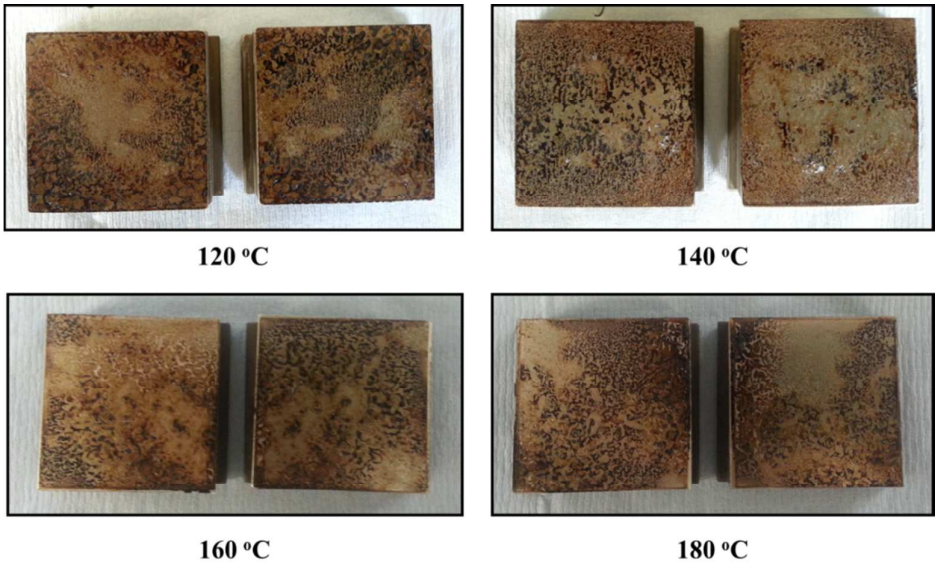

Figure S7. Appearances of the Al – bio-oil –Al interfaces of Al plates oven cured by the spruce wood chips derived organic phase bio-oil at various temperatures for 8 h

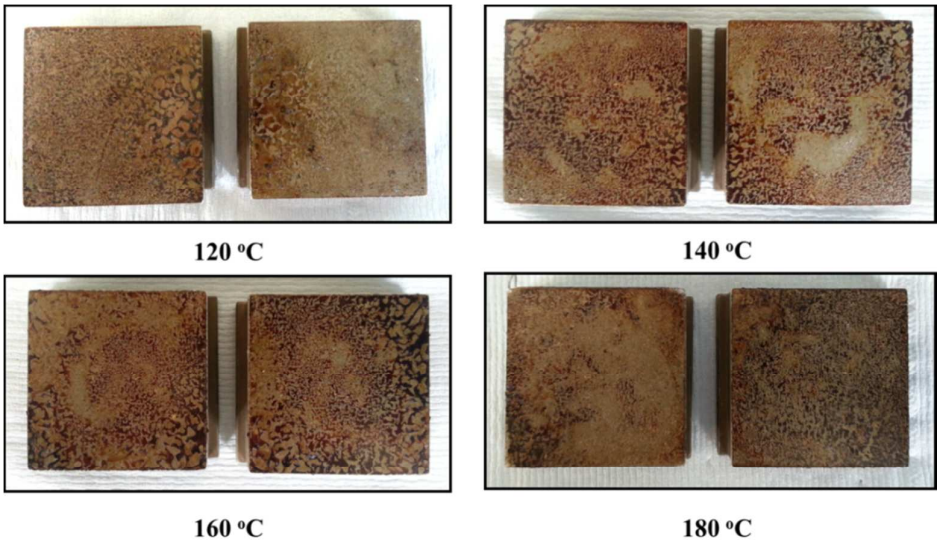

Figure S8. Appearances of the Al – bio-oil –Al interfaces of Al plates oven cured by the waste paper derived organic phase bio-oil at various temperatures for 8 h

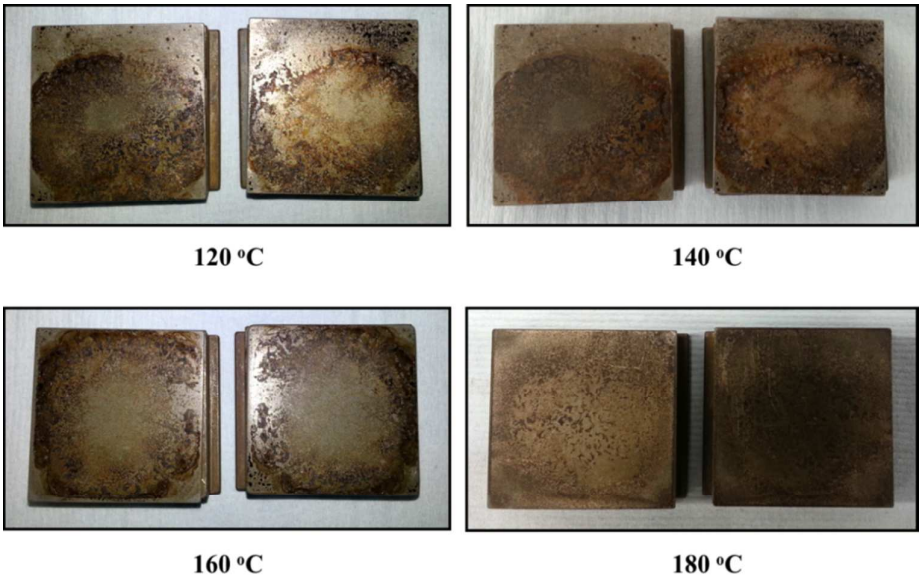

Figure S9. Appearances of the Al – bio-oil –Al interfaces of Al plates oven cured by the DIR derived organic phase bio-oil at various temperatures for 8 h

Section 7. Model compound study

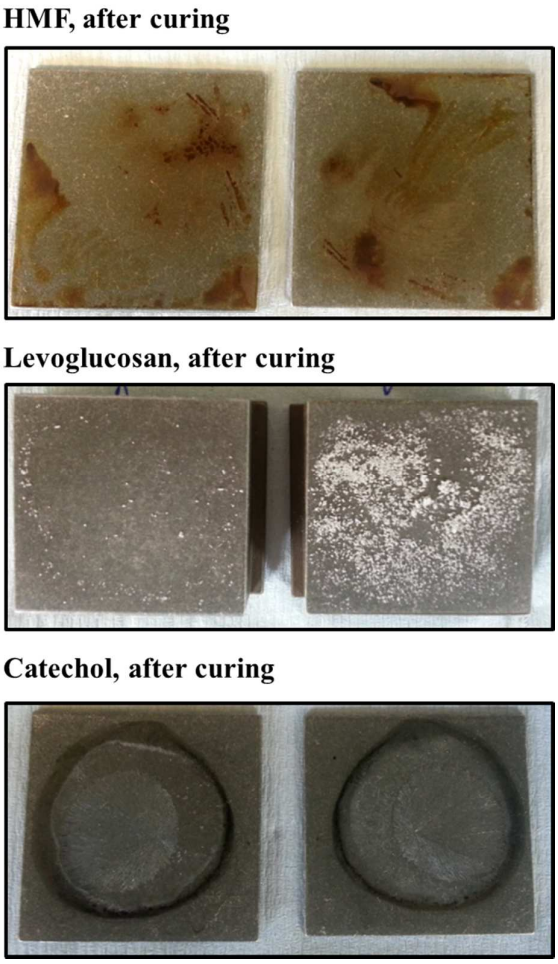

Figure S10. Appearances of the Al – single compound –Al interfaces of Al plates oven cured by single model compound (70 mg) at 140 ^{o}C for 4 h

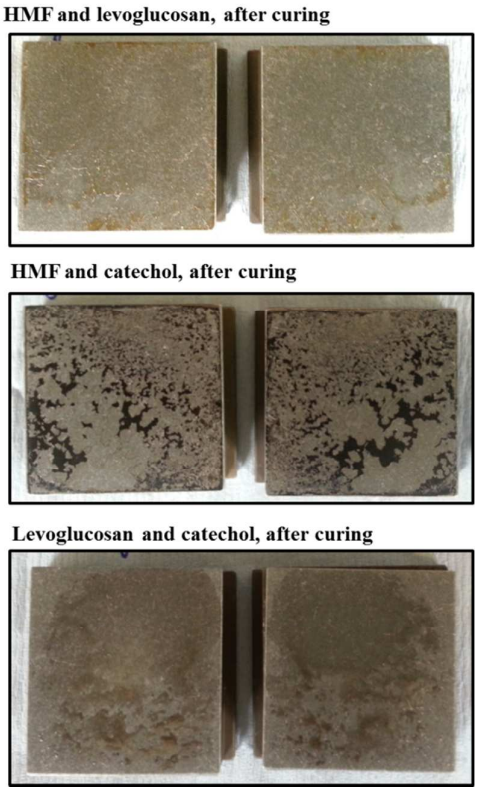

Figure S11. Appearances of the Al–mixture–Al interfaces of Al plates oven cured by mixtures of two model compounds (70 mg) at 140 ^{o}C for 4 h (molar ratio of HMF and levoglucosan: 5 : 5; molar ratio of catechol and HMF: 1 : 9; molar ratio of catechol and levoglucosan: 1 : 9)

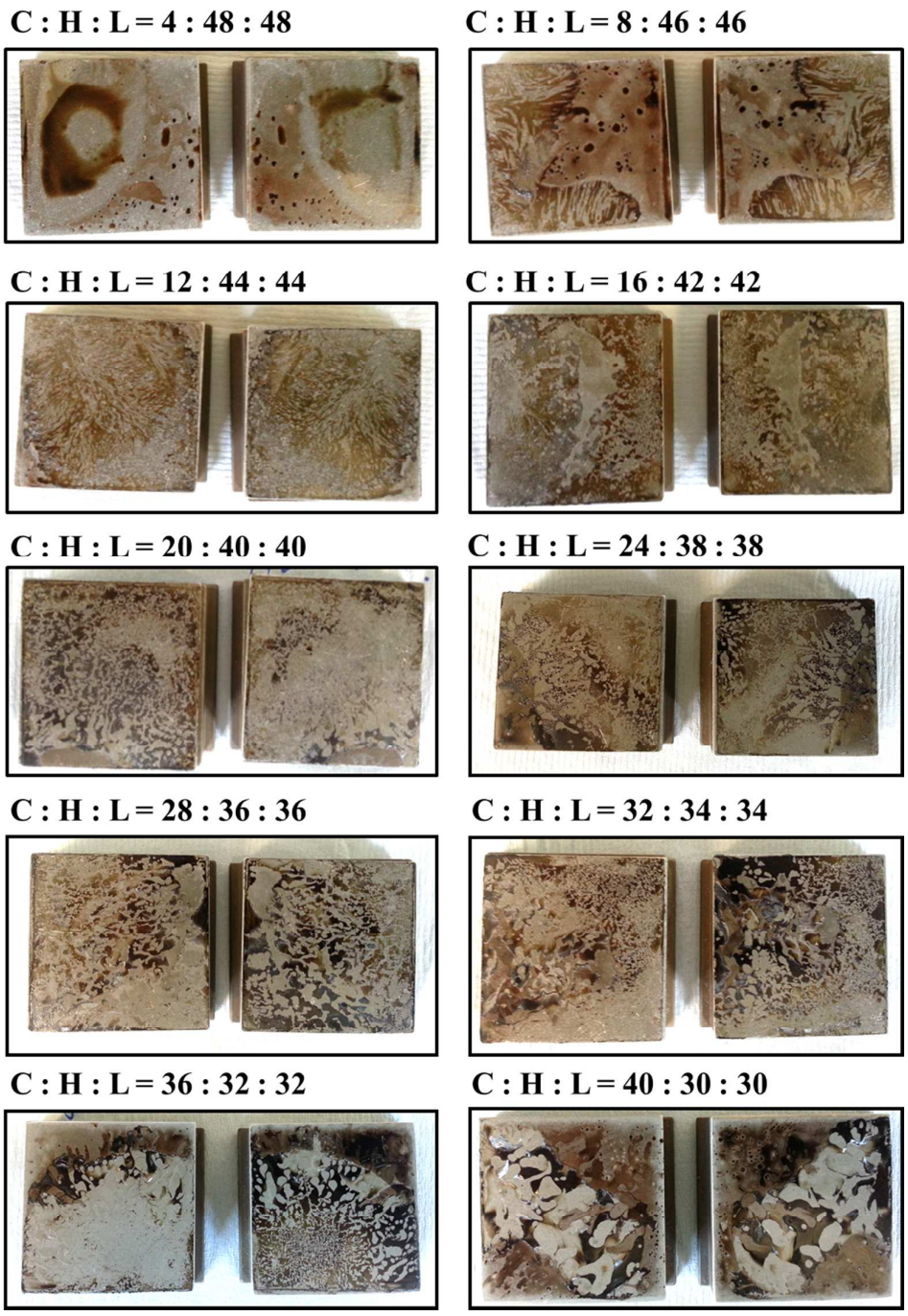

Figure S12. Appearances of the Al – mixture –Al interfaces of Al plates oven cured by mixtures of three model compounds (70 mg) with various molar ratios at 140 ^{o}C for 4 h. C: catechol; H: HMF; L: levoglucosan

References:

(1) Schwanninger, M.; Rodrigues, J. C.; Pereira, H.; Hinterstoisser, B., Effects of short-time vibratory ball milling on the shape of FT-IR spectra of wood and cellulose. *Vib. Spectrosc* **2004,** *36* (1), 23-40.

(2) Liu, Z.; Zhang, F.-S., Effects of various solvents on the liquefaction of biomass to produce fuels and chemical feedstocks. *Energy Convers. Manage.* **2008,** *49* (12), 3498-3504.