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PAPER

Bio-oil upgrading at ambient pressure and temperature using zero valent metals†

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As a liquid product from the fast pyrolysis of renewable biomass, bio-oil has a great potential use as a fuel or high-value chemicals resource, but it is accompanied by inherent drawbacks, such as strong corrosiveness and chemical instability. A facile method for bio-oil upgrading by zero valent metals (Al, Fe, Mg, and Zn) at ambient temperature and pressure was reported for the first time in this work. The chemical features of the raw and upgraded bio-oils were analyzed by Nuclear Magnetic Resonance (NMR) and GC-MS. The results show that the zero valent Zn favorably demonstrated improvement of the quality of bio-oil. In the upgraded bio-oil, the C=O compounds are reduced from 9.8 to 3.1 mol%, and the pH value was elevated from 3.53 to 4.85, which significantly increased the chemical stability and decreased the corrosiveness of bio-oil. The possible formation mechanism of 13 newly formed compounds in the upgraded bio-oil was explored, and most of them were found to be derived from hydrogenation of C=O compounds. This work provides an economical and environmentally friendly approach for bio-oil upgrading.

Introduction

The declining of fossil fuel resources, increasing demands of energy and resources, and growing concerns over global climate change make it imperative to develop new economical and environmentally friendly processes for the conversion of renewable biomass to liquid fuels and chemicals.[1] As a liquid product from the fast pyrolysis of renewable biomass, bio-oil has a great potential to be used as fuel or high-value chemicals resource.[1b,c,2]

Bio-oil is a multi-component mixture of different types of compounds (*e.g.*, water, hydrocarbons, oxygenated compounds, and pyrolytic lignin) derived primarily from thermal decomposition reactions of three key biomass building blocks, *i.e.*, lignin, cellulose, and hemicellulose.[3] Some of the compounds are closely related to the undesirable properties of bio-oil (*e.g.*, strong corrosiveness, low heating value, and chemical instability), which are the inherent drawbacks limiting its widely use.[2] For example, the strong corrosiveness is due to the presence of carboxylic acids (*e.g.*, acetic acid) in bio-oil;[4] the low heating value is attributed to the large amounts of oxygenated compounds present in the bio-oil;[2,5] and the chemical instability is mainly because of the presence of aldehydes and other compounds with unsaturated bonds (*e.g.*, C=C and C=O bonds) in bio-oil, which are active for polymerization and condensation reactions.[6] To improve the quality of bio-oil and make it more suitable to use as a fuel and chemical resource, an upgrading process is needed.

The techniques for bio-oil upgrading include hydrogenation,[6b,7] catalytic cracking,[8] and steam reforming.[9] Among these, hydrogenation is the most widely used method for bio-oil upgrading, which mainly involves hydro-deoxygenation and hydro-esterification processes.[7b,c,10] The hydro-deoxygenation process can convert the aldehydes and other compounds with unsaturated bonds into stable compounds (*e.g.*, hydrocarbons and alcohols), as well as reduce the oxygen content, thus increasing the heating value and chemical stability of bio-oil. The hydro-esterification process can significantly reduce the organic acid contents by esterification reactions, thus decreasing the corrosiveness of the bio-oil.

These processes, however, often require complicated equipment, noble metal catalysts (*e.g.*, Pd, Pt and Ru), and high pressure and temperature.[10,11] Furthermore, the hydrogenation process is often halted by catalyst deactivation and reactor clogging at a high temperature.[4a,11a] In order to avoid these problems, more effective methods should be established to upgrade bio-oil at ambient temperature and pressure.

Some zero valent metals (ZVMs), *e.g.*, Fe, Zn, Al, and Mg, are strong reductants widely used in organic reactions. For example, zero valent Fe and Zn are the commonly used reductants in reducing nitro compounds into amines,[12] while in the Clemmensen reduction, the zero valent Zn is a key reductant in the conversion of carbonyl groups (*e.g.*, ketones and aldehydes)

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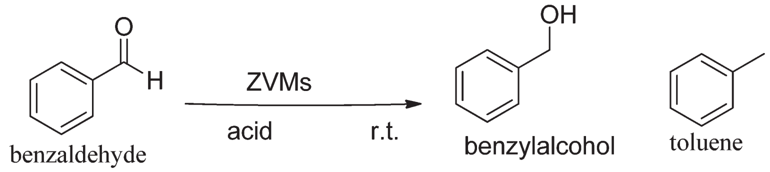
† Electronic supplementary information (ESI) available: Additional experimental descriptions, Tables S1 and S2, and Fig. S1 and S2 are provided. See DOI: 10.1039/c2gc35426h

Table 1 Hydrogenation of model compound of bio-oil by ZVMs under different conditions



Entry	Solvent[a]	ZVMs	Acid	Time (min)	Benzaldehyde conversion (%)	Benzalcohol selectivity (%)	Toluene selectivity (%)
1	THF	Al	CH_3COOH	180[b]	Trace	Trace	Trace
2	THF	Fe	CH_3COOH	180[b]	Trace[d]	Trace	Trace
3	THF	Mg	CH_3COOH	30[c]	11	87	13
4	THF	Zn	CH_3COOH	60	95	>99	<1
5	CH_3OH	Zn	CH_3COOH	60	96	>99	<1
6	CH_2Cl_2	Zn	CH_3COOH	60	95	>99	<1

[a] The solvent is mixture of the listed organic solvent and water with a ratio of 3 : 1 (m/m). [b] Because the reaction between zero valent Fe, Al and CH_3COOH is very slow. [c] The reaction between zero valent Mg and CH_3COOH is very fast, and the reaction is complete within 30 min. [d] Means not detectable.

into methylene groups.[13] These reactions are usually conducted in acidic conditions at ambient temperature and pressure, with a high product yield and selectivity.

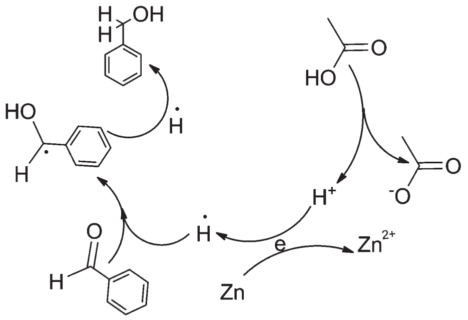
In bio-oil, there are many ketones and aldehydes, which are mainly responsible for the instability of bio-oil, and organic acids, which are mainly responsible for the corrosiveness of bio-oil. When the ZVM is added into bio-oil, it can react with the organic acids to generate active atomic hydrogen.[14] The formed hydrogen can actively react with the ketones and aldehydes *in situ* to form the hydrogenation products (*e.g.*, alcohols and alkanes), which can significantly improve the stability and increase the heating value of the bio-oil. Meanwhile, the consumption of organic acids in this process can reduce the corrosiveness of bio-oil. Therefore, the use of ZVM for bio-oil upgrading can effectively improve the quality of bio-oil. More importantly, compared to the conventional hydrogenation process, this process can be conducted at ambient temperature and pressure, and no catalyst and additional hydrogen gas are needed. However, to the best of our knowledge, there is no report about the use of ZVMs for bio-oil upgrading till now.

In this work, ZVMs were used for bio-oil upgrading. The main objective of this work is to investigate the feasibility and mechanism involved in such a process. Zero-valent Zn was selected as a representative metal. The changes of chemical composition of bio-oil before and after upgrading were compared and analyzed in detail using NMR and GC-MS to elucidate the effect of the ZVMs on the upgrading process. Our results show that the quality of bio-oil could be significantly improved by adding zero valent Zn into it. This study provides a multipurpose method for bio-oil upgrading, which can simultaneously reduce the corrosiveness, increase the chemical stability and heating value of the bio-oil.

Results and discussion

Hydrogenation of model compound of bio-oil

Benzaldehyde, a typical carbonyl compound with high reactivity and chemical instability,[15] was selected as a model compound of bio-oil to investigate the hydrogenation using ZVMs at ambient temperature and pressure without addition of hydrogen gas and catalyst. Acetic acid, a common carboxyl acid abundant in the bio-oil, was chosen to create the acidic conditions of bio-oil. Four ZVMs (*i.e.*, Al, Fe, Mg, and Zn) were tested in this work, and the results are presented in Table 1. It can be seen that the zero-valent Zn worked well in the hydrogenation of benzaldehyde. The conversion of benzaldehyde was higher than 95% under different reaction conditions (entries 4–6), and the benzaldehyde is almost stoichiometrically converted to benzalcohol (with a selectivity higher than 99%). The results, both in benzaldehyde conversion and benzalcohol selectivity, are comparable, even better than other results reported using hydrogen gas for hydrogenation with catalysts at high temperature or pressure.[16]



Scheme 1 A proposed mechanism for the Zn-mediated hydrogenation of benzaldehyde.

The mechanism of Zn-involving hydrogenation is proposed as follows: Zn first adsorbs the hydrated proton ionized by the acid, then the electron of Zn is transferred to the proton, and the proton changes into atomic hydrogen, which is a strong reducing radical with a half-life of 0.3 s. The active atomic hydrogen quickly transfers its electron to another acceptor (the carbonyl group of benzaldehyde) and itself bind to the acceptor to form the hydrogenation product[17] (Scheme 1). The benzaldehyde cannot be hydrogenated to benzylalcohol and/or toluene in the presence of zero-valent Al and Fe even after 180 min (entries 1

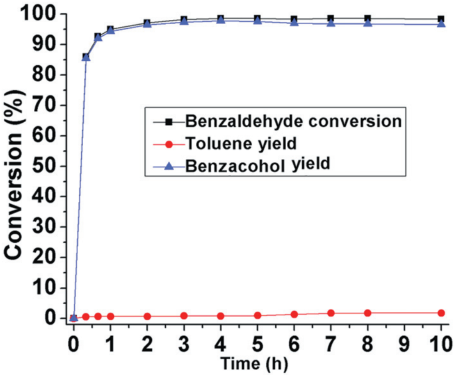


Fig. 1 The conversion of benzaldehyde, and yields of benzalcohol and toluene at different reaction times.

and 2). One possible explanation is that the active hydrogen generated from the reactions of zero-valent Al and Fe with acetic acid is in very small amounts, which is not enough to hydrogenate the benzaldehyde. For the zero-valent Mg (entry 3), due to its high activity, it can quickly react with the acetic acid to generate hydrogen gas (H_2) instead of active atomic hydrogen. While compared with the *in situ* formed active hydrogen, H_2 is very inactive and cannot hydrogenate benzaldehyde at ambient temperature and pressure without a catalyst.[15]

The conversion of benzaldehyde and the yields of benzalcohol and toluene at different reaction times is shown in Fig. 1. The hydrogenation of benzaldehyde by zero valent Zn was a very rapid process, and more than 85% of the benzaldehyde could be converted within 20 min, accompanied by almost stoichiometric formation of benzalcohol. While for toluene, the deoxygenation product of benzaldehyde, its yield was still lower than 1% after 10 h reaction, indicating that the deoxygenation cannot occur in the zero-valent Zn and acetic acid system. From the above analysis, it is concluded that among four ZVMs, zero-valent Zn shows the most favorable performance in the hydrogenation of a bio-oil model compound, and the process is very fast and highly selective. Therefore, in the subsequent upgrading of real bio-oil, zero-valent Zn was chosen as the model ZVM.

Total analysis of the bio-oils before and after upgrading

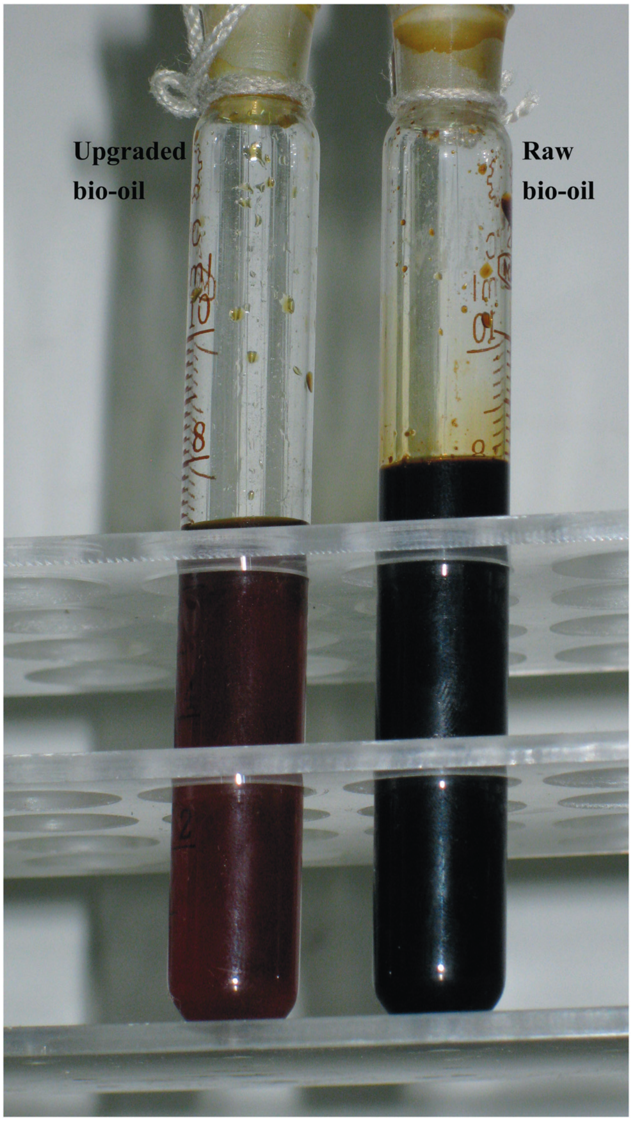


Fig. 2 Images of the raw and upgraded bio-oil samples.

Fig. 2 shows the images of the bio-oil samples before and after upgrading. The raw bio-oil was a black opaque liquid, while after upgrading, the bio-oil became a transparent reddish brown liquid. The main properties and elemental compositions of the bio-oils are given in Table 2. The oxygen content of the upgraded bio-oil was lower than that of the raw bio-oil, while its carbon and hydrogen contents were higher than those of the raw bio-oil. The heating value of the upgraded bio-oil was 13.4 MJ kg^{-1}, slightly higher than that of the raw bio-oil (12.5 MJ kg^{-1}). The pyrolytic lignin, one of the main factors influencing the thermal stability and homogeneity of bio-oil,[18] was decreased from 5.83 to 4.62 wt% after upgrading by zero-valent Zn. The pH value, a main parameter reflecting the acidity of a solution, was 4.85 in the upgraded bio-oil, much higher than that in the raw bio-oil (3.53), indicating that the acid content of bio-oil was decreased with the upgrading of zero-valent Zn, thus significantly reducing the corrosiveness of bio-oil. The above results confirm that the quality of bio-oil, *e.g.*, heating value, stability, and corrosiveness, was significantly improved by the upgrading by zero-valent Zn.

The Zn concentration in the upgraded bio-oil was 69.0 mg kg^{-1} after reaction. A calculation was carried out on the basis of the Zn mass balance in the entire reaction (eqn (1))

$$Zn_{add} = Zn_{bio-oil} + Zn_{solid\ residue} \qquad (1)$$

where Zn_{add} is the amount of Zn dosed into the reaction (0.5 g Zn to 10.0 g raw bio-oil); $Zn_{bio-oil}$ (69.0 mg kg^{-1}) is the Zn concentration in the bio-oil after upgrading; $Zn_{solid\ residue}$ is the Zn content in the solid residue after reaction.

The results show that more than 99.8% of the added Zn remained in the solid phase, which can be easily recycled and reused. However, compared with the Zn concentration in the raw bio-oil, the Zn concentration in the upgraded bio-oil is still high. Considering that the Zn^{2+} cation in the bio-oil is usually hydrophilic and that the bio-oil is easily phase-separated, a phase separation process in the upgraded bio-oil was carried out, and the Zn concentration in the organic phase, the main part of the bio-oil to be used as a fuel or chemicals source, was 2.6 mg kg^{-1} only, indicating that the pollution of Zn in the final bio-oil could be avoided well.

Comparison between the NMR spectra of the raw and upgraded bio-oils

The chemical features of the raw and upgraded bio-oils were further investigated by ^{13}C-NMR and the results are provided in Table 3, while the typical ^{13}C-NMR spectra of the bio-oils are shown in Fig. S2.† The assignment of peaks to carbon atoms in different chemical environments is based on previous reports for bio-oils.[19] The most significant trend is the decrease in C=O group (170–215 ppm of chemical shift), which is accompanied mostly by an increase in aliphatic C–O groups (50–90 ppm of chemical shift) for the upgraded bio-oil. For example, the content of C atoms in the C=O group of raw bio-oil is 9.8 mol %, much higher than that of the upgraded bio-oil (3.1 mol%), indicating the decrease in aldehyde, ketones, and carboxylic acids, which are mainly responsible for the chemical instability and corrosiveness of bio-oil. The content of C atoms in the C–O group of the upgraded bio-oil was 44.3 mol%, significantly higher than that of the raw bio-oil (36.8 mol%), suggesting the increase in alcohols, which are the reduction products of C=O compounds. Compared to the C=O compounds (*e.g.*, aldehyde and ketones), which are usually chemically instable and easily polymerized and oxidized, the C–O compounds (*e.g.*, alcohols) are more stable.

Table 2 Comparison among the elemental compositions and other properties of the raw and upgraded bio-oils

	Raw bio-oil	Upgraded bio-oil
C (wt%)	34.1	36.4
H (wt%)	9.0	9.5
N (wt%)	0.2	0.2
O (wt%)	50.6	48.4
Zn (mg kg^{-1})	n.d.[a]	69.0 (2.6)[b]
Heating value (MJ kg^{-1})[c]	12.5	13.4
Pyrolytic lignin (wt%)	5.83	4.62
Water content (wt%)	46.3	42.5
pH	3.53	4.85

[a] Not detected. [b] 69.0 mg kg^{-1} is the Zn concentration in the total upgraded bio-oil, while 2.6 mg kg^{-1} is the Zn concentration in the organic phase of the upgraded bio-oil after a phase separation process. [c] Heating-value (MJ kg^{-1}) = $(3.55C^2 - 232C - 2230H + 51.2C \times H + 131N + 20\,600)/1000$.[5a]

Changes of organic components in the upgrading process

The organic components of raw and upgraded bio-oils were analyzed by GC-MS, and their GC-MS chromatograms are shown in Fig. 3. A significant change in upgraded bio-oil is that 13 peaks (*i.e.*, **S1–S13** in chromatogram of upgraded bio-oil) were newly formed in the upgrading process. The peaks in the chromatograms were identified, and compound assignments are presented in Table 4. Acetic acid (peak 1), which was the most abundant compound in the raw bio-oil, was significantly decreased in the upgraded bio-oil. Other carboxylic acids, such as 2-hydroxypropanoic acid (peak 4), and 2,3-dihydroxypropanoic acid (peak 7) were also greatly decreased. The decrease in carboxylic acids can result in the increase in pH value of bio-oil,

Table 3 ^{13}C-NMR chemical shift assignment ranges and carbon contents of the raw and upgraded bio-oils

Chemical shift range (ppm)	Type of carbon atom	Content[a] Raw bio-oil	Content[a] Upgraded bio-oil
0–50	C–C (aliphatic)	13.9	16.9
50–90	C–O (alcohols and ethers)	36.8	44.3
90–120	C–C (aromatics) and C=C (olefinces)	26.8	23.5
120–150	C–O (phenols and aromatic ethers)	12.7	12.2
170–215	C=O (ketones, aldehydes, and carboxyls)	9.8	3.1

[a] mol% of total carbon.

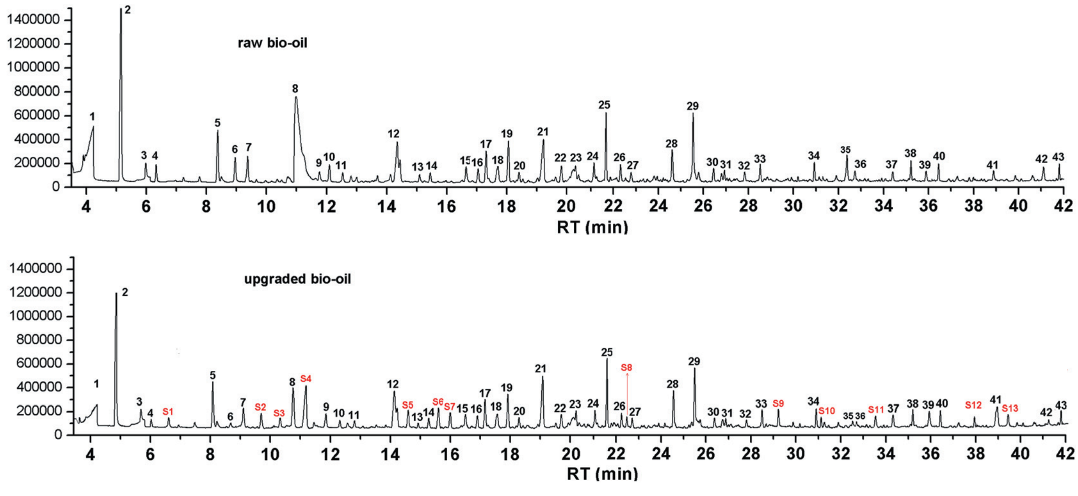


Fig. 3 GC-MS chromatograms of the raw and upgraded bio-oils.

Table 4 Main components of the raw and upgraded bio-oils

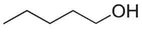
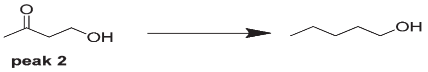
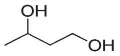
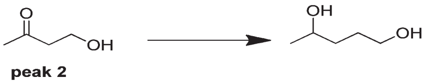
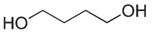
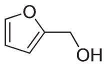
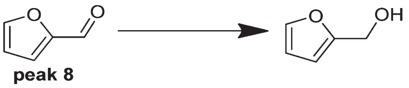
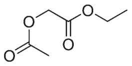
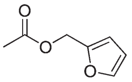
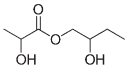
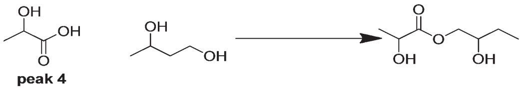
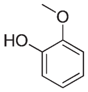
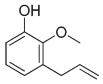
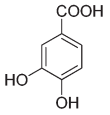
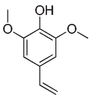
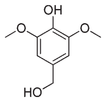
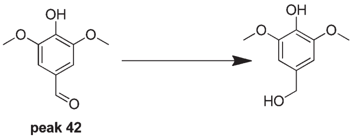
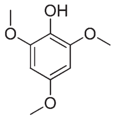
				Content (area%)	
Peak no.	R.T. (min)	Molecular formula	Compounds assignment[a]	Raw bio-oil	Upgraded bio-oil
1	3.989	$C_2H_4O_2$	Acetic acid	12.2	3.7
2	4.852	$C_3H_6O_2$	4-Hydroxybutan-2-one	13.7	10.2
3	5.681	$C_4H_8O_3$	Ethyl-2-hydroxyacetate	3.4	2.6
4	6.025	$C_3H_6O_3$	2-Hydroxypropanoic acid	1.7	0.5
5	8.082	$C_4H_8O_2$	1-Hydroxybutan-2-one	3.1	2.9
6	8.674	$C_4H_6O_2$	Succinaldehyde	2.2	0.3
7	9.102	$C_3H_6O_4$	2,3-Dihydroxypropanoic acid	1.7	0.7
8	10.763	C_5H_4O	Furfural	11.3	2.8
9	12.322	$C_6H_{10}O_3$	3-Oxobutyl acetate	0.6	1.0
10	13.510	$C_6H_8O_3$	2,5-Dimethoxyfuran	1.1	0.3
11	13.952	$C_5H_6O_2$	3-Methylfuran-2(5*H*)-one	0.3	0.3
12	14.140	$C_4H_4O_2$	Furan-2(3*H*)-one	3.9	4.1
13	14.935	$C_6H_{10}O_2$	3-Methylpentane-2,4-dione	0.3	n.d.[b]
14	15.288	$C_5H_6O_2$	2-Methoxyfuran	0.6	0.7
15	16.515	C_6H_8O	2,5-Dimethylfuran	1.1	1.4
16	16.914	$C_5H_6O_2$	4-Methylfuran-2(5*H*)-one	1.0	1.1
17	17.169	C_6H_6O	Phenol	2.1	2.3
18	17.532	—	Cannot be identified	1.4	1.3
19	17.993	—	Cannot be identified	2.7	2.6
20	18.302	$C_6H_8O_2$	1,3-Dimethoxycyclopentane	0.4	0.5
21	19.093	$C_7H_{14}O_2$	3-Methylcyclopentane-1,2-dione	3.9	5.1
22	19.947	$C_7H_{12}O_2$	5-Isopropyldihydrofuran-3(2*H*)-one	0.6	0.5
23	20.225	C_7H_8O	*o*-Cresol	1.4	1.6
24	21.064	C_7H_8O	*p*-Cresol	1.6	1.6
25	21.595	$C_7H_8O_2$	2-Methoxyphenol	4.7	4.9
26	22.356	$C_6H_{10}O_3$	4-Hydroxy-4-methyltetrahydro-2*H*-pyran-2-one	0.6	0.4
27	22.853	$C_8H_{10}O_2$	2-Methylbenzene-1,3-diol	0.3	0.3
28	24.560	$C_8H_{10}O$	4-Ethylphenol	3.1	3.3
29	25.502	$C_8H_{10}O_2$	2-Methoxy-4-methylphenol	4.7	4.5
30	25.742	$C_4H_6O_3$	4-Methyl-1,3-dioxolan-2-one	0.6	0.4
31	26.987	—	Cannot be identified	0.3	n.d.
32	27.873	—	Cannot be identified	0.3	n.d
33	28.499	$C_9H_{12}O_2$	4-Ethyl-2-methoxyphenol	0.8	0.7
34	30.192	$C_8H_{10}O_2$	2,6-Dimethoxyphenol	0.8	0.6
35	32.534	$C_8H_8O_3$	4-Hydroxy-3-methoxybenzaldehyde	1.7	n.d
36	32.694	$C_8H_{12}O_3$	2-Hydroxy-6-methylcyclohex-3-enecarboxylic acid	0.6	n.d
37	34.313	—	Cannot be identified	0.5	0.7
38	35.209	$C_{10}H_{12}O_3$	1-(4-Hydroxy-3-methoxyphenyl)propan-2-one	1.0	0.8
39	35.991	—	Cannot be identified	0.5	0.8
40	36.434	$C_8H_8O_4$	1-(2,3,4-Trihydroxyphenyl)ethanone	1.2	1.0
41	39.851	$C_{10}H_{14}O_3$	2-Ethoxy-6-(methoxymethyl)phenol	0.4	1.6
42	40.116	$C_9H_{10}O_3$	4-Hydroxy-3,5-dimethoxybenzaldehyde	0.5	n.d.
43	41.923	$C_{10}H_{10}O_3$	3-(4-Hydroxy-2-methoxyphenyl)acrylaldehyde	0.5	0.3

[a] The newly formed compounds in the upgraded bio-oil are not shown. [b] n.d. means less than 0.3 area%.

thus reducing the corrosiveness of bio-oil. Another notable change is the decrease in aldehydes in the upgraded bio-oil. Furfural (peak 8), the third most abundant compound in the raw bio-oil (11.3%), was decreased to 2.8% in the upgraded bio-oil. Other aldehydes, like succinaldehyde (peak 6), 4-hydroxy-3-methoxybenzaldehyde (peak 35), and 4-hydroxy-3,5-dimethoxybenzaldehyde (peak 42), were also significantly decreased in the upgraded bio-oil.

The identification of the 13 newly formed compounds and their possible formation routes are presented in Table 5. Compounds **S1–S4** and **S12** are alcohols derived from the hydrogenation of aldehydes and ketones. The compounds **S5–S7** are esters, possibly deriving from the esterification of carboxylic acid and alcohols. Other newly formed compounds (**S8–S11** and **S13**), which are all phenolic compounds, are considered as the fragments from the pyrolytic lignin.[20] PL is the oligomer generated from the thermal cracking of lignin, which is an amorphous polymer consisting of methoxylated phenylpropane structures.[21] In the presence of active hydrogen generated from the reaction of Zn and carboxylic acids, the methoxylated phenylpropane structures of the PL were broken, and some aryl ether bonds were hydrogenated to form aryl hydroxyl bonds, which are the main functional groups in the newly formed compounds (**S8–S13**). Furthermore, the Zn(II)-carboxyl acid complexes formed *in situ* might act as a catalyst in the hydrogenation of aryl ether bonds to aryl hydroxyl compounds.[22] The formation of compounds **S8–S13**, which are the reduced fragments from PL, is also confirmed by the results in Table 1 that the content of PL in the upgraded bio-oil is lower than that in the raw bio-oil.

Table 5 The newly formed compounds in the upgrading process and their possible formation pathways

Peak no.	Compounds assignment	Area (%)	Possible formation pathway
S1	 pentan-1-ol	0.5	
S2	 butane-1,3-diol	0.7	
S3	 butane-1,4-diol	0.4	
S4	 furan-2-ylmethanol	3.1	
S5	 ethyl 2-acetoxyacetate	1.0	
S6	 furan-2-ylmethyl acetate	1.4	
S7	 2-hydroxybutyl 2-hydroxypropanoate	0.8	
S8	 2-methoxyphenol	0.4	Fragment from the pyrolytic lignin
S9	 2-methoxy-3-(2-propenyl)phenol	0.8	Fragment from the pyrolytic lignin
S10	 3,4-dihydroxybenzoic acid	0.3	Fragment from the pyrolytic lignin
S11	 2,6-dimethoxy-4-vinylphenol	0.6	Fragment from the pyrolytic lignin
S12	 4-(hydroxymethyl)-2,6-dimethoxyphenol	0.3	
S13	 2,4,6-trimethoxyphenol	0.9	Fragment from the pyrolytic lignin

Conclusions

A facile method for bio-oil upgrading by zero valent metals (Al, Fe, Mg, and Zn) at ambient temperature and pressure without catalyst and additional hydrogen gas was proposed and tested. Four ZVMs (*i.e.*, Al, Fe, Mg, and Zn) were tested using benzaldehyde as a model compound of bio-oil, and the results shows that the zero-valent Zn could almost stoichiometrically convert benzaldehyde into benzalcohol with a selectivity higher than 99%. In a real bio-oil system, zero-valent Zn also demonstrated improvement of the bio-oil quality. The formation mechanism of the new compounds in the upgraded bio-oil was proposed. The compounds **S1–S4** and **S12** were derived from the hydrogenation of aldehydes and ketones; the compounds **S5–S7** were possibly derived from the esterification of carboxyl acid and alcohols; and **S8–S11** and **S13** were considered to be fragments from the PL. The results from this work provide a new approach to produce liquid fuels and chemicals from renewable biomass.

Experimental section

Materials

Benzaldehyde was used as a model compound for the unstable components of the bio-oil. Four types of ZVMs, *i.e.*, Fe, Zn, Al, and Mg, used in this study were in powder form with particle size smaller than 0.12 mm. All reagents used in this work (except specifically mentioned) were purchased from Sinopharm Chemical Reagent Co., Shanghai, China, and were used without further purification. The bio-oil was obtained from fast pyrolysis of rice husk in a fluidized-bed reactor under nitrogen flux. Bio-oil collected from the condensation section was selected as real matrix for upgrading experiments without any pretreatment (hereafter named as raw bio-oil).

Typical procedure for the hydrogenation of model compound of bio-oil

ZVMs powder (5.0 mM) was placed in a 25 mL reaction tube, followed by the addition of benzaldehyde (2.0 mM, 0.212 g), acetic acid (10.0 mM, 0.580 g), organic solvent (3.0 g), and water (1.0 g). Then the mixture was vigorously stirred (600 rpm with a magnetic stirrer) at ambient pressure and temperature. After reaction, the mixture was filtered with a membrane filter (0.45 μm). The conversion and product selectivity were periodically determined by gas chromatography (Model 1690, Kexiao Co., Hangzhou, China) equipped with a capillary column (1.0 μm, 50 m, and 0.25 mm) and a flame ionization detector using naphthalene ($C_{10}H_8$) as an internal standard. The injection and detector temperatures were both 523 K, and a heating program of column temperature from 333 to 503 K with a rate of 8 K per minute was applied. The reactant and products (*i.e.*, benzaldehyde, benzalcohol, and toluene) were identified by comparing the retention time with that of the pure components. The conversion of reactant and selectivity of products were calculated as eqn (2) and (3), respectively.

$$\text{Conversion}\ (\%) = \frac{C_{r0} - C_{rt}}{C_{r0}} \times 100\% \qquad (2)$$

$$\text{Selectivity}\ (\%) = \frac{C_{pt}}{C_{r0} - C_{rt}} \times 100\% \qquad (3)$$

where C_{r0} is the initial concentration (mmol) of the reactant, C_{rt} is the concentration (mmol) of reactant at time t (min), and C_{pt} is the concentration (mmol) of the product at time t (min).

Bio-oil upgrading

Typical procedure for the bio-oil upgrading. Zero-valent zinc powder (0.50 g), raw bio-oil (10.0 g), and tetrahydrofuran (THF, 2.0 g) were put into a 100 mL round bottomed flask, then the mixture was vigorously stirred (600 rpm) with a magnetic stirrer at ambient pressure and temperature. After reaction for 300 min, the mixture was filtered with a membrane filter (0.45 μm) and stored in a refrigerator for further analysis.

Product analysis. The hydrogen (H), carbon (C), nitrogen (N) and oxygen (O) contents of the raw and upgraded bio-oils were determined using an elemental analyzer (VARIO EL III, Elementar Inc., Germany). The Zn contents in the raw and upgraded bio-oils were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Optima 7300 DV, Perkin Elmer Co., USA). The pH values of the raw and upgraded bio-oils were measured with a pH meter (PHS-25, China). The pyrolytic lignin (PL) of the bio-oils are determined as described by Scholze and Meier.[23] Generally, 100 g of bio-oil was added dropwise to 1000 mL of ice-cooled NaCl aqueous solution (0.1 mol L^{-1}) with stirring in a magnetic stirrer. Thereafter, the formed PL was separated by pumping filtration, resuspended in ice-cooled water, and stirred for about 240 min to wash out water soluble components. Finally, the mixture was filtered and the wet PL was vacuum dried at 303 K. The dried PL was weighed to determine its yield.

The ^{13}C NMR spectra of the bio-oil were recorded using a 400 MHz nuclear magnetic resonance (NMR) spectrometer (AV 400, Bruker Inc., Switzerland) at room temperature. The NMR experiments were quantitative, and the samples were prepared by dissolving accurately weighed ~50 mg of bio-oil in dimethyl sulfoxide-d_6 (Sigma-Aldrich Co., Shanghai, China). In spectral analysis, the integration values of given peaks were compared to the total area of all peaks, resulting in mol% units.

As for the GC-MS analysis, the bio-oils were separated into two fractions by dichloromethane (CH_2Cl_2) extraction. The compounds in the CH_2Cl_2 soluble fraction were analyzed by gas chromatography–mass spectrometry (GC-MS, 7890A GC/5975C MS with a HP-5MS capillary column, 30 m × 0.25 mm × 0.25 μm, Agilent Inc., USA). High purity He gas was employed as carrier gas at a constant flow rate of 1.0 mL min^{-1}, and a split of the carrier gas (1 : 20) was used. The temperature of the GC injector was 523 K. The GC oven temperature was programmed from 313 to 453 K at 4 K min^{-1} and then to 523 K at 10 K min^{-1}, and the final temperature was kept for 5 min.

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