Green Chemistry

PAPER

View Article Online
View Journal | View Issue

Cite this: *Green Chem.*, 2014, **16**, 4740

Catalytic depolymerization of alkali lignin in subcritical water: influence of formic acid and Pd/C catalyst on the yields of liquid monomeric aromatic products†

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Alkali lignin was subjected to depolymerization in subcritical water at 265 °C, 6.5 MPa for reaction times between 1–6 h in a batch reactor and in the presence of formic acid (FA) and Pd/C catalyst. The oil products were extracted into diethyl ether and contained >90% of single-ring phenolic compounds. The reaction of lignin in subcritical water alone yielded 22.3 wt% oil containing 56% guaiacol as the main product. A maximum oil yield of 33.1 wt% was obtained when the lignin was reacted in the presence of formic acid alone. In the presence of FA, catechol became the predominant compound, with more than 80% of the ether extract after 6 h. The conversion of guaiacol to catechol in the presence of formic acid suggested the hydrolysis of O–CH_3 ether bonds. In addition, the yields of alkyl guaiacols increased in the presence of FA. The use of 5 wt% Pd/C catalyst with FA slightly decreased the yields of oil products but led to compounds indicative of hydrogenolysis of aryl–O ether bonds as well as hydrogenation of C=C bonds.

Received 9th May 2014,
Accepted 13th August 2014

DOI: 10.1039/c4gc00854e

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1. Introduction

Lignin makes up to 30 wt% of lignocellulosic biomass and nearly 40% of its energy content, hence its conversion and utilization will contribute to the efficiency, sustainability and viability of the lignocellulosic biorefinery industry. Besides, based on the structure of lignin, it is potentially a likely renewable source of aromatic chemicals. This is probably driving the increasing research on the valorization of lignin for chemical and liquid fuel production around the world in recent years.[1–8] In this regard, different thermochemical methods of depolymerizing lignin into high-value aromatic chemicals are being investigated, including fast pyrolysis, wet oxidation and hydrothermal processing. One of the challenges of thermochemical processing of lignin is the rampant re-polymerization of products of depolymerization, which are themselves highly reactive under reaction conditions. This often results in extensive char formation, leading to poor yields of aromatic chemicals. A number of processes have been investigated to minimize char formation including the use of ionic liquids[9] and capping agents such as boric acid[10] and phenol[8,11,12] as well as the use of organic solvents as depolymerization media.[5,13] The application of ionic liquids and organic solvents as the reaction medium for lignin depolymerization has been reported to give high conversion rates, with good yields of aromatic chemicals. However, there are issues regarding the recovery of these solvents and the use of fossil-based solvents which may impact on the sustainability of the process.

Hydrothermal conversion involving water and added acid, base and metal catalysts has been proposed for lignin depolymerization since most lignin streams come with very high moisture contents, thus avoiding a drying step; and depending on the reaction conditions, char formation may be suppressed.[14–18] Hydrothermal media presents a benign environment for green chemistry and lignin depolymerization research has been progressing in this direction. In hydrothermal conditions, water can act as a reaction medium, catalyst and reactant. In particular, lignin depolymerization in the subcritical region of water is seen as a greener process and has become increasingly more attractive to researchers than supercritical water due to the lower temperatures and pressures used which may reduce costs and offer thermodynamic limitations to char formation. Results from hydrothermal depolymerization in literature show that base-catalyzed depolymerization (BCD) using alkalis can effectively convert lignin into a variety of aromatic chemicals but with the yields of monomeric aromatic products are still at around 20%.[14] As a result, hydrothermal lignin conversion is now being investi-

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4gc00854e

gated with or without metal-based catalysts, with water alone or with organic co-solvents, particularly ethanol. For instance, Wahyudiono *et al.*,[15] obtained up to 35 wt% of monomeric phenols with catechol as the major product during the decomposition of lignin in near- and supercritical water from 350–400 °C in a batch reactor. Although, they were unable to measure the gas products, they found that changes in water density affected the yields and composition of the phenolic compounds with increasing reaction times. Pińkowska *et al.*[6] reported a maximum combined yield of 11.23 wt% for guaiacol, catechol, phenol and cresol isomers at 280 °C (zero holding time) in the absence of any catalysts. Zakzeski *et al.*[16] obtained 17 wt% yield of monomeric aromatic oxygenates such as guaiacols during liquid-phase reforming of Organosolv lignin in a water–ethanol mixture at 225 °C, 58 bar with Pt/Al_2O_3 catalyst. They further hydrotreated the liquid products with external oxygen supply to obtain 6% aromatic and cyclic hydrocarbons.

The use of biomass-derived simple carboxylic acids for hydrothermal lignin conversion has also been receiving attention. Formic and acetic acids can be produced from biomass and lignin under certain hydrothermal conditions[16–18] and using them for lignin processing into valuable products will improve sustainability. Besides, formic acid can easily be reformed into hydrogen[19] required for the hydrogenolysis and/or hydrodeoxygenation of lignin into valuable chemicals.[20] Xu *et al.*[20] used formic acid (FA) for the depolymerization and hydrodeoxygenation of Organosolv lignin obtained from switch grass in the presence of 20 wt% Pt/C catalysts at 280 °C. They obtained 21 wt% yields of seven monomeric phenols after 4 h of reaction and concluded that reaction time was critical to lignin conversion under the investigated conditions.

In this present study, alkali lignin has been subjected to subcritical water depolymerization reactions with the application of formic acid (FA) as capping agent and hydrogen source and 5 wt% palladium supported on carbon (Pd/C) as hydrodeoxygenation (HDO) catalyst at 265 °C, 6.5 MPa. Pd/C has been used in literature for hydrodeoxygenation of bio-oils and oxygenates in alcohols[21] and a recent publications showed that Pd/C can be effective for deoxygenation of triglycerides in subcritical water with external hydrogen supply.[22] At first, the hydrothermal reaction of FA was investigated at the given reaction conditions to determine the influence of reaction time and the presence of Pd/C catalyst on its ultimate conversion according to eqn (1):[19]

$$\mathrm{HCOOH} \rightarrow \mathrm{CO_2} + \mathrm{H_2} \qquad (1)$$

Thereafter, the separate and combined influence of the FA and Pd/C on the yields and variety of liquid depolymerization products from the lignin sample was investigated. This work was aimed at preliminary understanding of the interactions between the lignin and the additives which influenced the yields of liquid products under the hydrothermal conditions studied. Hence, detailed analyses of the liquid products from each test have been carried out in this regard. The liquid products here refer to contents of the liquid residual extracted into diethyl ether solvent.

2. Results and discussion

2.1. Hydrothermal reactions of formic acid

It was important to understand the hydrothermal reactions of formic acid with or without the Pd/C in order to understand its activities in lignin conversion. The results of the hydrothermal reactions of 1.0 g of FA at 265 °C, with reaction time from zero to 6 h, both in the presence and absence of Pd/C are presented in Table 1. The results show that both reaction time and Pd/C catalyst influenced the hydrothermal conversion of formic acid into hydrogen and carbon dioxide according to eqn (1).[19]

Eqn (1) shows that the standard enthalpy change $(\Delta H^{\circ}_{298\ \mathrm{K}})$ for the hydrothermal reaction of formic acid is +32.1 kJ mol^{-1}. This indicates that the position of equilibrium would shift to favour the yield of products with increase in temperature.

The yields of CO_2 and hydrogen have been used to estimate the conversion of FA during these reactions, since literature and this work show that complete reaction of FA would yield about 50 vol% each of CO_2 and H_2. Therefore, barring experimental errors, and some dissolution of gases (especially CO_2) in the aqueous residuals, the experimental yields of both gases can be directly used to determine FA conversion. As shown in Table 1, the decomposition of FA increased with time, with only 24.9% conversion when the reaction was stopped immediately the reaction temperature was reached (zero min hold time). However, after 1 h hold time at the reaction temperature, the conversion reached 89%, followed by complete conversion after 3 h of reacting FA alone.

Conversely, the presence of Pd/C led to complete conversion of FA even at zero minute reaction time. The results in Table 1 also show that yields of gases in the presence of Pd/C at 0 min, 1 h and 3 h reaction times, respectively were similar, indicating that the Pd/C catalyst catalyzed FA conversion in subcritical water but did not consume any hydrogen produced from it. The solid catalyst was separated by filtration, dried and

Table 1 Yields of hydrogen and CO_2 in relation to time during hydrothermal reactions of formic acid at 265 °C, 6.5 MPa

	Hold time (min)	CO_2 (vol%)	H_2 (vol%)	CO_2 (wt%)	H_2 (wt%)	Conversion (wt%)
FA	0	66.1	31.0	21.3	0.45	24.9
FA + Pd/C	0	51.5	48.5	94.3	3.97	98.3
FA	60	47.4	52.6	84.7	4.28	89.0
FA + Pd/C	60	50.3	49.4	94.8	4.10	98.9
FA + Pd/C[a]	60	50.2	49.8	94.5	4.11	98.6
FA	180	50.8	49.2	94.5	4.16	98.7
FA + Pd/C	180	51.1	48.9	94.4	4.12	98.5
FA	360	50.3	49.7	95.4	4.27	99.7
FA + Pd/C	360	50.2	49.8	96.9	4.31	101

[a] Catalyst re-used once.

weighed. Up to 99.3 wt% of the catalyst was recovered indicating little losses during these reactions. Furthermore, results of the reaction of FA alone and FA in the presence of Pd/C for 6 h also gave very similar yields of CO_2 and hydrogen. This is further evidence of the stability of the Pd/C catalyst; in particular, it can be concluded that the Pd/C did not contribute to gas yields. The recovered catalyst for the 1 h run was re-used with results showing similar gas yields. More future work will be carried out on the structural stability of the Pd/C catalyst under hydrothermal conditions.

Considering that it took 12 min to heat the reactor to 265 °C, the results from the reactions at zero min holding time can be used to estimate the specific rate of conversion of the formic acid without and with the Pd/C;

$$\text{Specific rate of FA conversion (mol h}^{-1}) = \frac{\text{Mole of FA converted}}{\text{Reactor Heat-up Time (h)}}$$

Clearly, without the Pd/C the specific rate of FA conversion was 0.024 mol h^{-1}, while in the presence of the catalyst, the specific rate increased 4.5 times to 0.108 mol h^{-1}. Hence, the Pd/C has very high catalytic effect on FA conversion and this may affect the depolymerization of lignin with these additives.

2.2. Product yields from lignin depolymerization

A total of 12 experiments were carried out with lignin as feed. In these tests, the lignin sample was reacted alone and with the addition of formic acid and Pd/C catalyst for reaction hold times of 1, 3 and 6 h, respectively. The yields of products designated as liquid, solid residue and gas from these tests are presented in Table 2. The percentage yields of products were calculated based on the amount of lignin and FA used, where applicable, since the preceding section 2.1 showed that FA reacted to produce H_2 and CO_2 under the test conditions. The product mass balances gave very good closures of >94 wt% in all cases. Mass balances >100 wt% were only obtained during the reaction of lignin in the presence of both FA and Pd/C at extended hold times, which may indicate the participation of water during the reactions, especially the water–gas shift reaction.[23] A test with only Pd/C (without lignin and FA) was carried out for 6 h and neither gas nor liquid products were obtained, instead 98.5 wt% of the catalyst was recovered.

Table 2 Product yields from lignin depolymerization with additives at 265 °C, 6.5 MPa from 1–6 h hold time

Sample	Hold time (h)	Liquid (wt%)	Solid residue (wt%)	Gas (wt%)	% Balance
Lignin	1.0	58.2	30.6	5.56	94.4
Lignin	3.0	51.6	35.9	9.12	96.6
Lignin	6.0	33.3	46.0	17.0	96.3
Lignin/FA	1.0	61.6	0.64	36.5	98.7
Lignin/FA	3.0	52.3	0.19	46.1	98.6
Lignin/FA	6.0	41.1	1.12	58.3	101
Lignin/Pd/C	1.0	41.3	54.4	0.84	96.5
Lignin/Pd/C	3.0	36.1	57.3	1.25	94.7
Lignin/Pd/C	6.0	35.6	59.1	2.25	97.0
Lignin/FA-Pd/C	1.0	45.8	16.3	38.7	101
Lignin/FA-Pd/C	3.0	38.5	18.3	49.8	107
Lignin/FA-Pd/C	6.0	31.6	22.9	53.4	108
Pd/C	6.0	—	98.5	—	98.5

In Table 2, liquid products refers the combined yields of oil (ether-extractable liquid products) and water-soluble products. The water-soluble products were in the form of semi-solids, which only appeared when the aqueous residuals had been shaken with diethyl ether during liquid–liquid extraction. They extracted into the ether but remained as dissolved solids and could easily re-dissolve in water. These were separated from the ether phase by filtration, air-dried and weighed. The extracted aqueous phases were clear and nearly colourless after 6 h but at lower reaction times, particularly after 1 h, the extracted aqueous phases had light brown colours.

The reactions of lignin alone at 265 °C, 6.5 MPa for 1–6 h reaction hold times were first studied for reference. In this tests, the yields of liquid products decreased while the yields of solid residues and gas increased with increasing reaction time. The formation of solid residue was evidence of the rapid polymerization of lignin and possibly, its degradation products to form char. Wahyudiono *et al.*[15] obtained up to 25 wt% solid residue yields from alkali lignin after 4 h, which is lower than the yields of solid residues (31 wt% after 1 h to 46 wt% after 6 h) in this present study. The differences in solid residue yields may be attributed to the types and sizes of reactors used. Wahyudiono *et al.*[15] used a 5 ml Hastelloy C-276 reactor with water densities of 0.16–0.67 g ml^{-1}, while in this work, a 500 ml stainless steel reactor was used, with a fixed low water density of 0.12 g ml^{-1}. The highest gas yield of 17 wt% was obtained after reacting for 6 h and the gas comprised mainly carbon dioxide (83.4 vol%), methane (10.2 vol%) and hydrogen (5.84 vol%). The high yield of methane suggested the cracking of C–C linkage in lignin. While the yield of liquid products decreased, the proportion of ether-extractable oils in the liquid products increased with reaction time, indicating the possible refining of the liquid products by heat. On the basis of the lignin feed, extracted oil was 5.23 wt% after 1 h, increased to 13.9 wt% after 3 h and finally to 22.3 wt% after 6 h. The yields of the main components in the oil products are presented and discussed in section 2.3.

2.2.1. Effect of FA. From the preceding section, 89% of FA was converted after 1 h of reaction hold time at 265 °C, 6.5 MPa, therefore experiments were carried out with lignin and formic acid from 1–6 h reaction hold times under the same conditions. The amounts of char/solid residue recovered from these increased slightly with reaction times from 0.64 wt% after 1 h to 1.12 wt% after 6 h. As the hydrothermal reaction of FA in section 2.1 did not produce any solid residue, any solid residue obtained during the reaction of lignin and FA was therefore attributed to lignin. Compared to the reaction of lignin alone, the presence of FA decreased the yield of solid residue by up to 98%, showing that FA helped in solubilizing lignin, so that the water-soluble products could contain both depolymerized and unreacted lignin. This indicated the ability of formic acid to act as a capping agent to prevent or delay re-polymerization of products. Hence, nearly 98 wt% conversion of the original lignin mainly into liquid and gas products, was obtained in these tests, which agreed with some reported results in literature.[24]

The yield of oil products increased with time and was highest after 6 h. Again based on the dry weight of lignin, oil yields more than doubled from 15.3 wt% to 33.1 wt% between 1 h and 6 h, which compares well to the work of Xu *et al.*[20] who used formic acid and Pt/C for lignin depolymerization, although at a slightly higher temperature of 280 °C. In the opposite direction, the yield of water-soluble products decreased with time, showing that some of the water soluble products were being converted into char and extractable oil products.

The gas products from these tests mainly composed of CO_2, CO and hydrogen. The trends in the yields of gases are presented in Fig. 1, with CO_2 as the predominant gas product. A large proportion of the yields of CO_2 and H_2 must have arisen from the hydrothermal reaction of formic acid.[19] However, compared to the gas yields from FA and lignin when reacted separately, the total gas yields obtained when FA and lignin reacted together were consistently lower at the different residence times. This observation indicated the occurrence of liquid–liquid reactions between FA and lignin, thereby reducing the overall gas-forming potential. With increasing reaction times, the yields of hydrogen and CO increase slightly but consistently, while the yields of CO_2 gave the most dramatic increase, indicating possible reforming reactions. CO yields increased from about 3 wt% after 1 h to 5.23 wt% after 6 h. Considering that no CO was produced during the reactions of FA alone under similar conditions, it can be concluded that the interaction between FA and lignin led to CO production. The yield of hydrogen was consistently$\approx$1 wt% of the gas product. After 1 h and 3 h, hydrogen yields were 0.023 and 0.028 g, respectively, which were much lower than its theoretical yield (0.0435 g) from FA based on eqn (1), suggesting hydrogen utilization during lignin depolymerization. Hydrogen consumption was possibly *via* the participation of FA in lignin hydrolysis as well as in other possible reactions requiring hydrogen, such as hydrogenation and hydrogenolysis. However, after reacting for 6 h, the yield of hydrogen increased to 0.032 g, which was still 26.4% less than its theoretical yield from FA but about 28% more than its yield during the experiment for 1 h. This may indicate hydrogen production from the reforming of small organic molecules such as methanol that could form from the hydrolysis of O–CH_3 ether bonds.

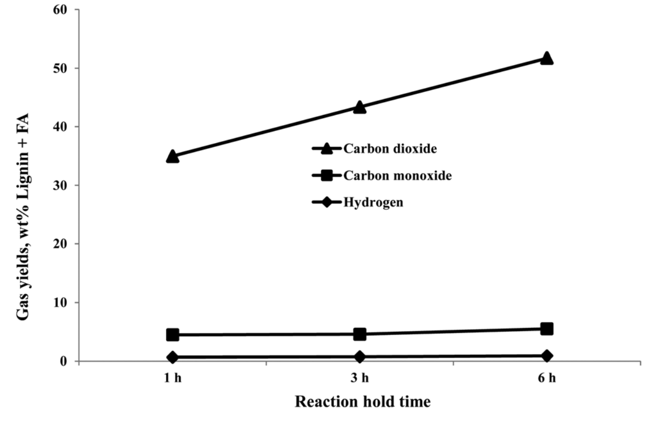

Fig. 1 Gas yields from the depolymerization of lignin with FA only.

2.2.2. Effect of Pd/C.

The use of Pd/C alone during lignin depolymerization produced the lowest yields of gas and the highest yields of solid residues. CO_2 was the only gas detected even after 3 h, and after 6 h the gas composition changed slightly to 97 vol% CO_2, 0.37 vol% H_2 and 2.23 vol% methane. Yet the total gas yield was only 2.25 wt% of lignin feed after 6 h. Apparently, Pd/C catalyzed the polymerization of lignin to form char, so that the oil products obtained was only 0.21 wt% after 1 h and increased to just 5.10 wt% after reacting for 6 h.

2.2.3. Effect of combining formic acid and Pd/C catalyst.

When Pd/C and formic acid were combined for lignin depolymerization, oil yield was much higher than with Pd/C alone but was lower than when formic acid alone was used, still indicating that Pd/C influenced the formation of char. Oil yield increased from 7.60 wt% at 1 h to 25.7 wt% after 6 h reaction time.

Total gas yields were similar to that obtained during the reaction of lignin in the presence of FA alone. However, there were slight differences in the overall gas compositions, which suggested evidence of the participation of Pd/C in the yields and compositions of the gas products. Fig. 2 shows that there was a consistent decrease in CO yields which may indicate its conversion to hydrogen *via* water–gas shift (WGS) reaction. Indeed, CO yields decreased from 2.84 wt% after 1 h to 0.98 wt% after 6 h, while hydrogen yield increased from 0.71 wt% to 1.2 wt% after 6 h. Compared to the reaction of lignin with FA alone, which produced increasing yields of CO, which reached 5.23 wt% at 6 h, these results thus show that the presence of Pd/C influenced WGS reaction.

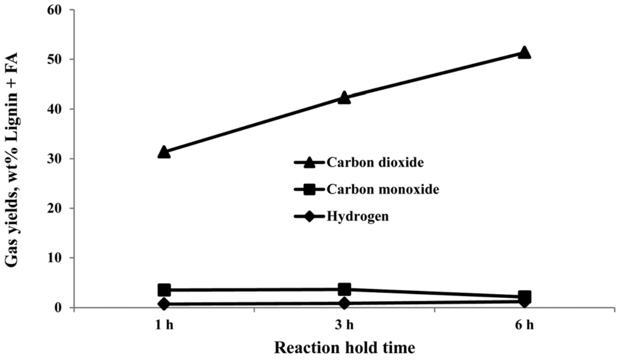

Fig. 2 Gas yields from lignin depolymerization with FA in the presence of Pd/C.

The yields of CO_2 was again much higher, reaching 48.5 wt% after 6 h, also suggesting the possible conversion of lignin and its decomposition products with increasing hold time. Hydrogen yield was 0.028 g and 0.035 g at 1 h and 3 h, respectively but increased to 0.048 g after reacting for 6 h. Hence, hydrogen yield increased by 9.4% of the theoretical yield after 6 h in the presence of Pd/C indicating that the catalyst may have promoted both the reforming of small molecules and the water–gas shift reaction. In addition, hydrogen yields during lignin depolymerization with the combination of FA and Pd/C were consistently higher than hydrogen yields when only FA was reacted with lignin. In section 2.1 Pd/C has been shown to catalyze FA decomposition but the lower yields of hydrogen obtained here after 1 h and 3 h may indicate that the presence of lignin altered the catalytic effect of Pd/C on FA due to competition for active sites by both FA and lignin. However, it is clear from these results that the metal catalyst promoted gas-phase hydrogen production and therefore, could have reduced the extent of liquid–liquid interactions between FA and lignin. This would influence the hydrolytic ability of FA and therefore may affect the yields of oil products.

2.3. Detailed analysis of the oil products

A clearer picture of the predominant reaction pathway for the effect of FA could be seen from compositional analysis of the oil products. In this section, the yields of oils and their components have been calculated on the basis of the dry weight of lignin feed (1.0 g). The major compounds in the ether extracts were guaiacol, 1,2-benzenediol (catechol), methylguaiacol, ethylguaiacol and propylguaiacol. In addition, minor compounds identified from the GC/MS/MS analysis included phenol, dimethoxybenzene, dimethoxytoluene, eugenol, 2,3,6-trimethylguaiacol, vanillin and 2′,4′-dihydroxy-3′-methylpropiophenone. Indeed, some of the oil products gave a pleasant smell as a result of the presence of some of these compounds which are commonly used in flavourings. Fig. 3 and 4 show the annotated GC/MS/MS chromatogram for the ether extractable oil from the uncatalyzed and catalyzed (FA and Pd/C) lignin depolymerization tests.

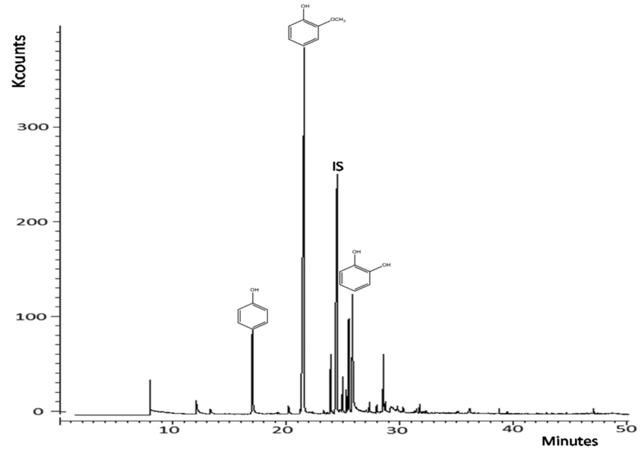

Fig. 3 GC/MS/MS chromatogram of oil product from lignin depolymerization without any additives.

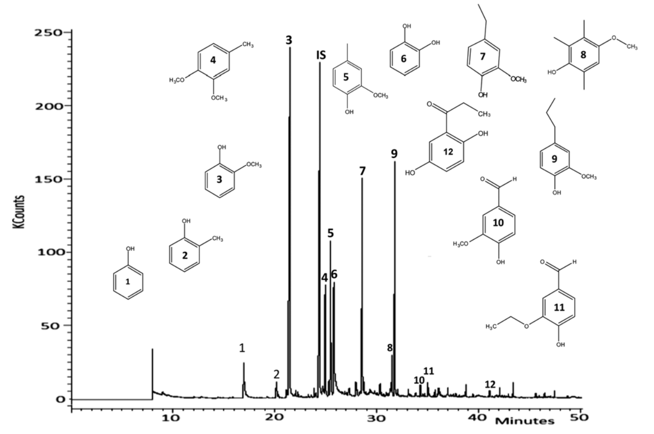

Fig. 4 GC/MS/MS chromatogram of oil product from lignin depolymerization with formic acid and Pd/C.

The yields of the major components of the oil products obtained from the depolymerization of lignin after from 1 h to 6 h reaction time are shown in Fig. 5. In all cases, these compounds made up more than 90% of the oil products. In the absence of any additives, lignin depolymerization in subcritical water produced only 5.23 wt% of ether-extractable oil after 1 h hold time. This increased to 13.9 wt% after 3 h and finally to 22.3 wt% oil after 6 h. Guaiacol was consistently the dominant product and after 6 h, the oil comprised of 56% guaiacol, 25% catechol and 8% phenol and 5% alkyl guaiacols. This corresponded to a guaiacol/catechol yield ratio of 2.2.

While, it was earlier observed that Pd/C catalyzed the decomposition of FA, these results showed that the catalysis of Pd/C on FA may have been inhibited by the presence of lignin. In this sense, the presence of lignin could block some active sites in Pd/C, preventing the immediate catalytic decomposition of FA. However, the oil yields from lignin in the presence of FA and Pd/C were consistently lower compared with those obtained with lignin and FA alone. The oil yields on lignin feed-basis increased from 7.60 wt% after 1 h to 20.7 wt% after 3 h and then to 25.7 wt% after 6 h. Hence, the rate of depolymerization increased dramatically between 1 h and 3 h but increased at slower rate from 3 h up to 6 h. With the combination of FA and Pd/C, the pattern of product yields similar to when only FA was used, was obtained. Therefore, results in Fig. 5[B] and 5[C] suggest that the rate of guaiacol conversion to catechol only increased between 3–6 h. This may indicate that the hydrogen produced from FA became more active in the presence of Pd/C. The yield ratio of guaiacol/catechol after 3 h was 1 : 1.28. After 6 h reaction time, the yield ratio of catechol and guaiacol was in favour of catechol at 1 : 4.6.

From the results, it is apparent that the presence of formic acid altered the reaction pathway in favour of catechol over guaiacol after long reaction hold times. This agrees with the recent work of Forchheim *et al.*[25] who studied the kinetic modelling of hydrothermal lignin depolymerization. They found

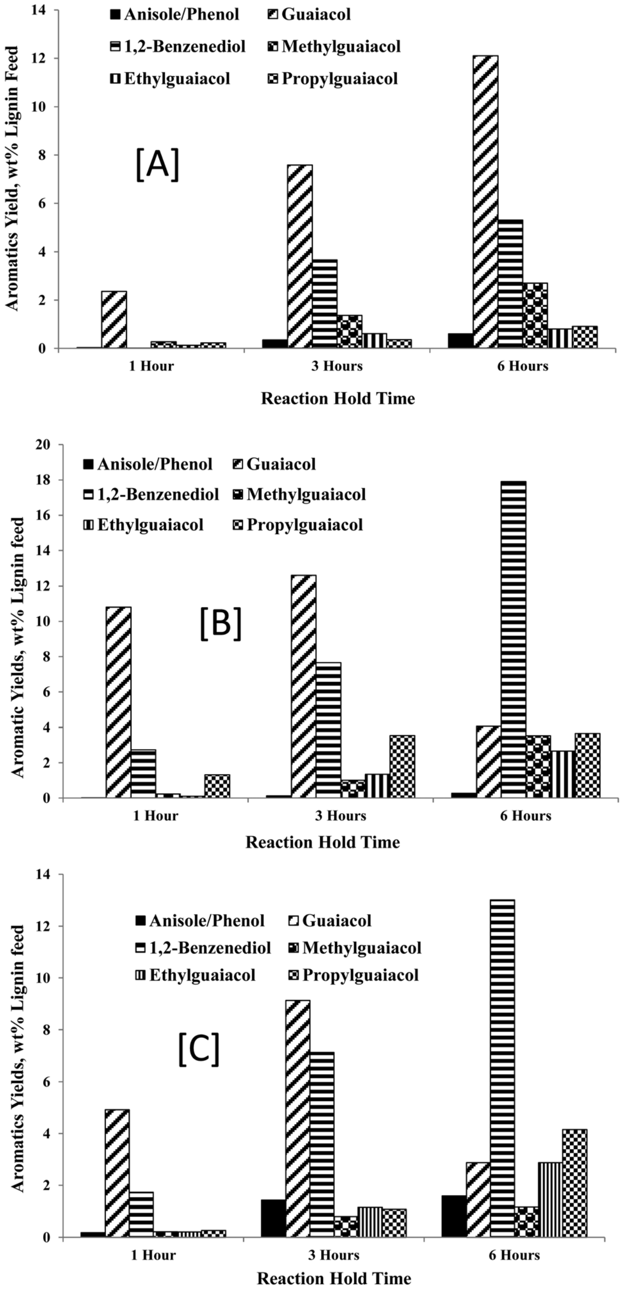

Fig. 5 Yields of aromatic compounds during lignin depolymerization in relation to reaction hold time [A] lignin alone; [B] lignin with FA [C] lignin with FA and Pd/C.

that, the yields of catechols increased with increasing temperature and residence time. It would appear that the active reaction pathway involving formic acid was *via* hydrolytic cleavage of the O–CH_3 ether linkage to produce catechol. The alternative mechanism of hydrogenolysis using *in situ* produced hydrogen from formic acid would invariably lead to methane formation if the O–CH_3 bond was cleaved or to substantial phenol formation on cleaving the aryl–OCH_3 bond. Little or no methane was observed during the reactions of the alkali lignin in the presence of formic acid.

However, the increase in the yield of alkylguaiacols suggested that the mechanism of lignin depolymerization alone and with FA may also involve hydrogenolysis or cracking of C–C bonds along the propane units in lignin. The higher yields of these compounds in the presence of FA at longer reaction times suggested possible significant contributions from hydrogenolysis. This is underscored by the improved yield in oil, indicating that formic acid also influenced the overall depolymerization process. The decrease in the total yield of oil in the presence of Pd/C and FA may be explained by the influence of the catalyst on the conversion of FA as shown in Table 1 and the promotion of re-polymerization reactions by Pd/C. The faster rate of conversion of FA may prevent its hydrolytic ability in depolymerizing the lignin. It may also decrease its capping ability to prevent re-polymerization of products.

In essence, the hydrolytic depolymerization of the lignin by FA would occur as long as FA remained and could provide H^+ ions. Hence, its hydrolytic ability would be impaired as soon as it is converted to hydrogen and CO_2. It would therefore mean that lignin conversion to water-soluble products resulted from hydrolysis, and this was followed by the conversion of the water-soluble products to oil products. The conversion of the water-soluble products was time-dependent as shown by results of increased oil yield with reaction time. The formation of alkyl guaiacols suggested that during the reaction, the hydrogen gas produced was able to participate in the conversion of the water-soluble products to oil products even without a hydrogenation catalyst. These results indicate that substantial hydrothermal depolymerization of lignin can be achieved *via* hydrolysis but the use of hydrothermally reactive additives that can also generate *in situ* hydrogen for HDO of liquid products would require careful reactor design. This will be necessary to allow them sufficient time to act as depolymerization agents before acting as hydrogen donors for HDO.

2.4. Hydrothermal reactions of guaiacol

To further understand the reaction schemes of the two additives with guaiacol five sets of experiments were carried out for 6 h reaction time. From the reactions of lignin, 6 h reaction time gave the highest yields of oil and highest yields of catechol in the presence of FA. Hence, a reference experiment was carried out with 1.0 g of guaiacol for 6 h, in the absence of any additives. In this test, 97% of the original guaiacol was recovered. Only small amounts of phenol and dimethoxybenzene (*ca.* 0.2 wt% each) were identified but no catechol was found. Then the same amount of guaiacol was reacted with formic acid for 6 h and this yielded 82.5 wt% of catechol and 15.3 wt% guaiacol. Further, the combination of formic acid and Pd/C was used to investigate the reaction of guaiacol from 1–6 h as presented in Fig. 6. Results show that guaiacol was highly resistance to degradation after 1 h of reaction even in the presence of these additives, so that 95 wt% guaiacol was recovered. It was only after 3 h of reacting that the formation of catechol was observed. However, the yield of catechol again increased dramatically beyond 3 h reaction time, so that the composition

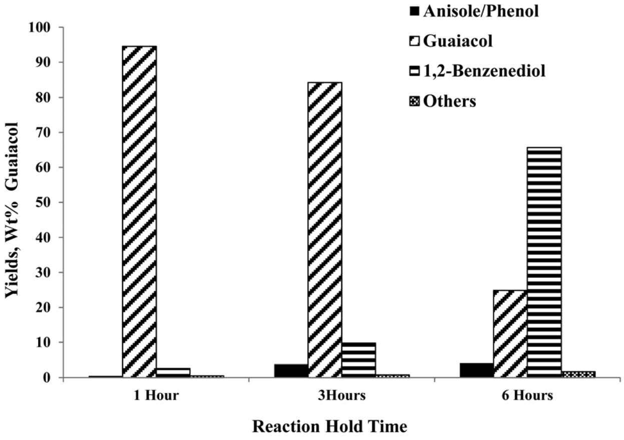

Fig. 6 Yield of aromatic compounds in relation to time from the hydrothermal reaction of guaiacol in the presence of FA and Pd/C.

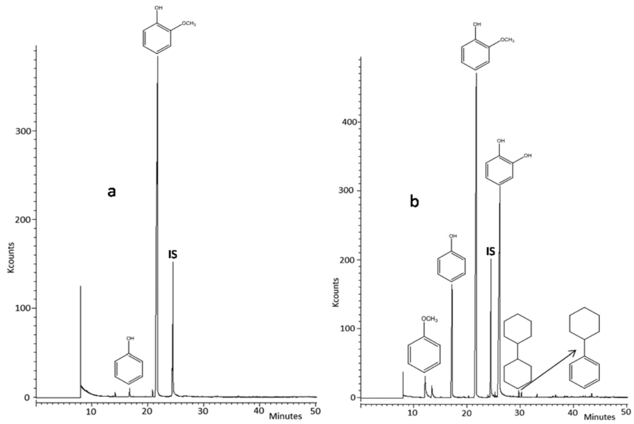

Fig. 7 GC/MS/MS chromatograms of oil products from the hydrothermal reactions of (a) guaiacol alone; (b) guaiacol with formic acid and Pd/C (6 h hold time).

of oil was 65.7 wt% yield of catechol, 24.9 wt% of the original guaiacol and 3.01 wt% yield of phenol after 6 h.

The production of phenol indicated the cleavage of aryl–O bond *via* hydrogenolysis possibly catalysed by Pd/C using the *in situ* generated hydrogen. Moreover, the high yield of catechol also suggested the cleavage of O–CH_3 bond *via* acid catalysed hydrolysis.

These results therefore suggest that while formic acid favoured hydrolysis of the O–CH_3 ether linkage, the Pd/C catalyst appeared to favour hydrogenolysis to form phenol and possibly methanol, which would be a substantial component of the aqueous residuals or could be reformed to hydrogen and CO_2 at extended reaction hold times.

Fig. 7 shows the two chromatograms of oils from these reactions. It can be seen from Fig. 7b that the presence of Pd/C also influenced the formation of hydrodeoxygenation products. Examples of these included 1,1′-bicyclohexyl, 2-propenyl cyclohexane and cyclohexyl benzene. However, their yield was only 0.13 wt% after 1 h and increased to 1.72 wt% after 6 h. Though the yields of these hydrogenation products were low, their presence indicated the possibility of catalytic hydrogenation or hydrodeoxygenation of oxygenates such as guaiacol.

3. Conclusion

The results presented here show the possibility of alkali lignin depolymerization under acidic conditions using a carboxylic acid that can be derived from biomass. The yields of monomeric phenolic compounds are considerable compared with what is presently possible in literature. The presence of formic acid influenced both the extent of depolymerization and the composition of the oil products. Without any additive/catalyst, lignin depolymerized in subcritical water to produce mainly guaiacol. However, in the presence of formic acid, catechol became the predominant phenolic compound possibly due to hydrolysis of the O–CH_3 ether bond in guaiacol. In addition, Pd/C appeared to catalyse the hydrogenolysis of the aryl–O ether bond resulting in significant yield of phenol from guaiacol also promoted char formation. The continued presence of significant amount of water-soluble products after 6 h indicated that the reaction time could further be manipulated and the use of appropriate catalysts can improve yields. Moreover, there are many variables still to be considered in future research including the use of different lignin samples based on sources and methods of isolation, use of different operating conditions of temperature, pressure and reaction time as well as the application of different catalysts/additives for hydrothermal lignin conversion.

4. Experimental

Samples of alkali lignin (low sulfonate grade), formic acid (99% purity), diethyl ether (solvent) and Pd/C (5 wt%) were obtained from Sigma-Aldrich UK and used as received. The proximate composition of the alkali lignin was; 3.23% moisture, 3.57% ash, 60.6% volatiles and 32.6% fixed carbon; while the elemental analysis results gave 61.7% carbon, 5.11% hydrogen, 31.3% oxygen, 1.22% nitrogen and 0.67% sulfur. The reactor used was a stainless steel batch reactor with 500 ml volume capacity and can reach a maximum temperature and pressure of 500 °C and 30 MPa, respectively.[26]

In each experiment, 1.0 g of alkali lignin was added into the reactor along with 60 ml of deionized water. This amount of the lignin sample completely dissolved in the water. The volume of water was chosen to give a pressure of 6.5 MPa at the chosen reaction temperature of 265 °C. When required, 1.0 g of formic acid and 0.5 g of Pd/C were added either separately or in pre-determined combinations. The reactor vessel was closed and purged for 10 minutes with nitrogen gas at a flow rate of 1 ml min^{-1}. The reactor was then heated to 265 °C in 12 min and held at this temperature for 1–6 h. At the end of the heating, the reactor was quickly withdrawn from the heated and cooled to room temperature with a large fan within one hour. The liquid products were extracted with diethyl ether and analyzed using a was a Varian CP-3800 gas chromatograph coupled with a Varian Saturn 2200 mass spectrometer (GC/MS/MS) (please see ESI† for details). The weight of solid residue was determined after drying in an oven at 105 °C and for the experiments involving Pd/C, temperature programmed oxidation (TPO) method was used to determine the amount of solid residue produced.

4.1. Analysis of products

4.1.1. Gas analysis. On cooling, the gas samples (especially when formic acid had been used) were sampled for offline analysis. The analytical protocol used for gas products analysis has been widely published.[27,28] Briefly, the gas samples were analysed using three packed column gas chromatographs. The permanent gases, hydrogen, oxygen, nitrogen and carbon monoxide, were separated on a molecular sieve column and analysed using a Varian CP-3380 gas chromatograph with a Thermal Conductivity Detector (GC/TCD). Hydrocarbon gases, C_1 to C_4, were separated on a Haysesp column and analysed using a second Varian CP-3380 gas chromatograph with a Flame Ionisation Detector (GC/FID). Carbon dioxide was analysed using a third gas chromatograph fitted with a TCD. The results obtained from the GCs were given as a volume percent and were converted into masses of each gas using the ideal gas equation.

After gas analysis, the reactor was opened to sample the contents (liquid and solids) into a beaker and weighed. The reactor contents were transferred into a clean glass bottle, followed by rinsing with 30 ml of diethyl ether as solvent and re-weighed. The mixtures were filtered under vacuum to separate the solids from the liquids. The solids retained on the filter paper were dried in an oven at 105 °C for 2 h and weighed. The weight of solid residue was subtracted from the weight of the reactor contents to obtain the weight of the liquid products (less weight of solvent used).

In all cases, the liquid products were partitioned by liquid–liquid extraction technique in a separating funnel with the organic layer separated into diethyl ether. The addition of two drops of hydrochloric acid (1.0 M) helped to ensure complete separation of the distinctive phases. The aqueous phases were subsequently extracted twice more with 15 ml of diethyl ether. For extended reaction times, the aqueous phases were largely clear while the ether phases were unclear and required centrifugation to separate the clear liquid from a dark brown semi-solid product, most of which dissolved when shaken with water. Fig. 8 shows the typical phases of the liquid products; (a) the extracted aqueous phase, (b) the clear ether extract, and (c) water-soluble semi-solid fraction from ether phase. The clear ether (oil) portion had a colour range between light yellow to brown. The weight of the oil fractions were determined after vacuum evaporation. The ether extracts were combined and dried over anhydrous sodium sulfate prior to analysis by GC/MS/MS.

The equipment used was a Varian CP-3800 gas chromatograph coupled with a Varian Saturn 2200 mass spectrometer (GC/MS/MS) fitted with a 30 m DB-5 equivalent column. For the GC/MS/MS analysis, 2 μl of the diethyl ether extract were injected into the GC injector port at a temperature of 290 °C; the oven programme temperature was 35 °C for 8 min, then ramped to 120 °C at 5 °C min^{-1} heating rate, held for 1 min and ramped at 4 °C min^{-1} to 210 °C and finally ramped at 20 °C min^{-1} to 280 °C (total analysis time of 55.5 min). The transfer temperature line was at 280 °C, manifold at 120 °C and the ion trap temperature was held at 200 °C. The ion trap was initially switched off for 8 min to allow the elution of the solvent prior to data acquisition to safeguard the life of the trap. The compounds present in the extracts were quantified by internal standard method with 2-hydroxyacetophenone as internal standard (IS). List of compounds and the properties used for their quantitative analysis are shown in the ESI.†

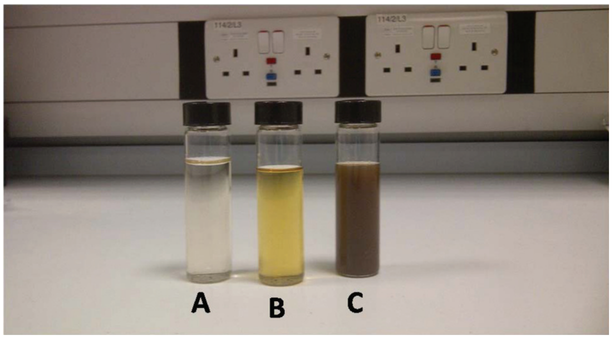

Fig. 8 Picture showing the different fractions of the liquid products; (a) extracted aqueous phase, (b) clear ether extract and, (c) water-soluble semi-solid fraction from ether phase.

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