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- Effect of metal formates on hydrothermolysis of organosolv lignin for the
   production of bio-oil
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#### 22 Abstract

23 This research work investigated the use of various metal formates with emphasis on sodium 24 formate for catalyzing depolymerization of organosolv lignin to bio-oils rich in monoaromatic 25 phenolic compounds. The addition of sodium or calcium formate to the reaction mixture greatly 26 influenced the bio-oil composition, whereas magnesium formate showed minor influence compared to non-catalytic reactions. The optimum yield of bio-oil was 13.9 % of feed lignin 27 28 achieved at 310 °C after 60 min of reaction time using sodium formate and contained 92 mg 29 monoaromatics per gram of feed lignin. All the bio-oils samples demonstrated narrow molar mass distribution having an average molar mass of 207 - 277 g mol<sup>-1</sup> containing syringol, 30 31 guaiacol, catechol and methoxy catechol as major compounds.

32 Keywords

33 Bio-oil, Metal formates, Hydrothermolysis, Lignin, Depolymerization

## 34 1. Introduction

35 The fulfilment of the growing need for fuels and chemicals in a sustainable manner is a 36 profound concern of the modern-day society. One reason is the difficult access to cheap and 37 easy-to-process petroleum oil due to its depletion [1]. Another reason is to replace the fossil 38 carbon with renewable carbon in order to mitigate the greenhouse gases especially in urban 39 areas [2]. These reasons support the use of lignocellulosic biomass as a potential alternative 40 and resource for producing renewable fuels and chemicals [3,4]. Hemi-rich cellulosic pulp has 41 established industrial applications such as paper and board manufacture, whereas lignin 42 utilization for value added chemicals is currently under the development phase.

43 Lignin is the most abundant natural resource for aromatic compounds. Industrially, 50 - 5544 million tons of dissolved lignin is produced on a yearly basis in the waste streams of chemical 45 pulp production [5]. This amount will be further supplemented by lignin produced as a side 46 stream in emerging cellulosic ethanol biorefineries [6]. Despite its high availability, only a 47 small fraction of lignin is separated and utilized for low value applications such as dispersants 48 and flocculating agents. Lignosulfonates is the only industrial scale product obtained mostly 49 from sulfite lignin today [7]. Most of the lignin is incinerated as a low value fuel in the recovery 50 boilers of the pulp industry for steam and power generation. However, lignin utilization is 51 currently a hot topic and many current research activities focus on finding new strategies for the valorisation of lignin to diverse and high-value products such as carbon fibres, polymersand oxygenated aromatic compounds [8–10].

The key challenge in achieving well-defined chemicals from lignin is its complex, severely oxygenated and amorphous structure. The versatile network structure originates from the polymerization of three basic building units, namely coniferyl alcohol, sinapyl alcohol and pcoumaryl alcohol. These building units are interconnected with a variety of C - O and C - Cbonds [11]. The C - O bonds in lignin structure are higher in frequency compared to C - Cbonds but weaker in strength [12]. However, the abundance of aromatic moieties in the lignin structure makes it a promising resource to produce oxygenated aromatic chemicals.

61 One of the strategies to valorise lignin is to produce mono-aromatic phenolic compounds such 62 as, phenol, catechol and methoxycatechol through depolymerization. Among the 63 depolymerization techniques, base catalyzed hydrothermal depolymerization of lignin [5,13– 64 24] has gained considerable attention due to certain advantages over contemporary techniques 65 such as pyrolysis, solvothermolysis and gasification. These advantages are higher yield of mono-aromatic phenols, less energy intensive process compared to pyrolysis, no aromatic ring 66 67 alkylation which is usually observed in acid catalyzed reactions in alcohols, and lower molar 68 mass distribution of product compared to solvothermolysis reactions [20,25–27]. Last but not 69 least is the ease of integrating base-catalyzed lignin depolymerization in the current chemical 70 pulp industry due to the highly alkaline nature of the lignin-containing waste stream i.e. black 71 liquor.

72 In previous studies, addition of bases in the reaction medium have demonstrated the catalytic 73 effect on lignin depolymerization to monoaromatic compounds. Base-catalyzed reactions of 74 lignin were significantly influenced by the severity of the reaction conditions in terms of lignin 75 conversion to mono-aromatic phenols as studied by Thring [28]. The change in the strength 76 and nature (weak or strong) of the applied base has a vital impact on the yield and composition 77 of the bio-oil [20]. Increasing the concentration of alkali in the reaction mixture consistently 78 increased the yield of mono-aromatic compounds in the bio-oil [23]. For further enhancement 79 of monoaromatic compounds' yield, phenol was tested as a capping agent in the base-catalyzed 80 reactions and the results showed high quantities of monomeric phenolic compounds [29]. Some 81 researchers have separately demonstrated the use of hydrogen forming agents such as formic 82 acid and tetralin for stabilizing lignin degradation products. However, the idea of treating lignin 83 in the presence of a chemical that can produce in-situ base and hydrogen such as metal formates

was seldom investigated [13]. It was reported by Onwudili and Williams [30] that sodium
formate can produce sodium carbonate upon hydrothermolysis according to the following
reaction:

$$2 \operatorname{HCOONa} + \operatorname{H_2O} \rightarrow 2\operatorname{H_2} + \operatorname{Na_2CO_3} + \operatorname{CO_2}$$
(1)

Furthermore, in-situ formation of homogeneous base from metal formates can catalyze the formation of monoaromatic phenols from lignin intermediates and the in-situ hydrogen generation can stabilize the reaction intermediates and hinder the repolymerization reactions.

91 In our earlier work [31], we demonstrated the production of bio-oil through non-catalytic 92 hydrothermolysis of the same lignin used in the current study. It was shown that a maximum 93 of 100 mg of monoaromatic compounds can be produced from one gram of feed lignin under 94 optimized reaction conditions (350 °C and 60 min). In contrast, the focus of our current research 95 work is to closely study the effects of various metal formates on the yield and composition of 96 monoaromatic phenols in the resulting bio-oil from sulphur-free organosolv lignin. Moreover, 97 water-soluble compounds, such as methanol, ethanol, acetic acid and formic acid, are 98 quantified to shed some light on the composition of these compounds in aqueous phase. In 99 addition to these, a deeper characterization of undesired char material is also presented in this 100 study. Last but not the least, the composition of the gaseous phase is also determined which 101 was missing from earlier reports on base-catalyzed reactions of lignin [14,19,20,23].

102 2. Materials and methods

#### 103 2.1. Materials

104 Organosolv lignin extracted by ethanol / water from beech wood was supplied by Fraunhofer105 Institute, Germany. The characterization of lignin is presented in Table 1.

Lignin model compounds, including phenol (99.5%) guaiacol (98%), catechol (99.0%), 4-106 107 (95.0%), syringaldehyde (98.0%), 4-methylsyringol (97.0%), methylcatechol 3-108 methoxycatechol (99.0%), 4-methylguaiacol (98.0%), and syringol (99.0%) were purchased 109 from Sigma Aldrich and were used as standard compounds in GC-MS. Anisole (purity 99.0%) 110 purchased from Sigma Aldrich was used as internal standard in GC-MS. Sodium formate (99.0%), calcium formate (99.0%) and magnesium formate (98.0%) were purchased from 111 Sigma Aldrich. Tetrahydrofuran (THF; 99.9%), and ethylacetate (99.7%) were also from 112

Sigma Aldrich and used either for extraction or solubilizing bio-oil for analysis. Millipore water was used as the reaction medium. Sodium hydroxide (99.2%, VWR chemicals BDH Prolabo) was used for separating residual lignin from char. Sulphuric acid (95.0 – 97.0%, Sigma Aldrich) was used for acidification. All chemicals were used as received except sodium hydroxide and sulphuric acid which were diluted to required concentrations in distilled water.

118 Table 1. Properties of feed organosolv lignin [31,32].

Ash	Sugars	$M_{ m w}{}^{ m a}$	$M_{ m n}{}^{ m a}$	$D^{\mathrm{b}}$	С	Н	N	0	S	S / G Ratio <sup>c</sup>	Amount of β-O-4 linkages
wt. %	wt. %	g mol <sup>-1</sup>	g mol <sup>-1</sup>			% of	Dry l	ignin			Moieties per aromatic ring
0.05	2.4	3428	606	5.66	62.5	5.9	0.3	30.9	0.00	1.29	0.27

119 a. Number-average  $(M_n)$  and Weight-average  $(M_w)$  molar masses b. Dispersity (D) c. Syringyl to guaicyl units.

120 2.2. Metal formates catalyzed depolymerization reactions

121 All the depolymerization reactions were carried out in a 500 mL Parr reactor model 4575 made 122 of stainless steel 316T. The reactor vessel was charged with 5 g of air-dried lignin and 200 mL 123 water. The amount of metal formate i.e. sodium formate (NaFo), calcium formate (CaFo), and 124 magnesium formate (MgFo) was varied between 0.5 to 5 g. Metal formates were used as an in-125 situ base producer due to their alibility of producing basic solutions upon heating. A reference 126 experiment was also conducted in the absence of metal formates for comparing the reactions 127 with and without metal formates. After sealing, the reactor was purged with 20 bar nitrogen 128 and finally heated to the required temperature, which was maintained for 60 min under 129 continuous stirring at 500 rpm. At the end of the reaction time, the reactor was cooled to room 130 temperature by circulating cold water in the cooling tube inside of the reactor vessel. After 131 collecting a gas sample, the gases produced during the reaction were vented through the relief 132 valve.

133 2.3. Products separation

All the products were separated according to the scheme presented in Figure 1. The aqueous phase containing phenolic compounds from lignin depolymerization was separated from solids through filtration. A 20 ml sample from the filtered aqueous phase was collected for total organic carbon (TOC) analysis. 100 mL of ethyl acetate was mixed with the remaining aqueous phase at 500 rpm for 20 min to extract the bio-oil in ethyl acetate phase. Bio-oil was obtained after removing ethyl acetate through rotary evaporation.

- 140 The reactor was washed by adding 200 mL of 1 M NaOH to remove solids (residual lignin and 141 char) from the reactor's inner surfaces and stirrer, through constant stirring at 700 rpm for 30 142 min at room temperature. NaOH solution from reactor washing was mixed with filtered solids 143 obtained from aqueous phase filtration. In the next step, NaOH solution was filtered again to 144 separate char, which was left for air drying afterwards, and the filtered solution was acidified 145 to a pH < 2 by the addition of 5 M H<sub>2</sub>SO<sub>4</sub>. The precipitated residual lignin was filtered, washed
- 146 with water, and left for drying at room temperature.



- 148 Fig 1. Procedure for products separation and recovery.
- 149 2.4. Analytical methods

The amount of organic carbon originating from water solubles after hydrothermal treatment was determined by analyzing the aqueous phase obtained after solids separation from the reaction mixture. The aqueous phase was analysed with total organic carbon (TOC) analyser (TOC-V<sub>CPH</sub>) by Shimadzu. The amount of TOC was then converted to the stoichiometric amount of lignin by using the C-9 formulae for organosolv lignin. The details for the determination of the C-9 formula are given elsewhere [32].

- 156 Gaseous products were analysed with Agilent 6890 GC system consisting of 25  $\mu$ l gas sampling
- loop and two analysis lines for permanent gases and hydrocarbons. HP-PLOT-Q (30 m x 0.53
- 158 mm x 40 mm) and Molesieve 0.5 nm (30m x 0.53mm x 25 µm) columns with TCD were used

- for permanent gases analysis and  $Al_2O_3/KCl$  (50m x 0,32mm x 8 µm) column with flame ionization detector (FID) was used for analysis of hydrocarbons.
- 161 The aqueous phase from selected samples was analysed for the quantification of methanol,
- 162 ethanol and acetic acid with WATERS 2690 Alliance model HPLC equipped with a WATERS
- 163 2414 refractive index detector. The column used was a Phenomenex Rezex ROA-organic acid
- 164 300 x 7.8 mm H<sup>+</sup> column. The temperature of the column was 65  $^{\circ}$ C and the eluent used was
- 165 0.005 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. The flow was 0.6 mL min<sup>-1</sup> and injection volume 10  $\mu$ L.
- 166 The molar mass of lignin and the bio-oil was determined with Agilent HPLC-system by means 167 of Phenogel (5  $\mu$ m – 5 nm and 100 nm) columns and UV detector at 280 nm. THF was used as 168 an eluent at a rate of 1.0 mL min<sup>-1</sup> and the analysis was carried out at room temperature. 169 Calibration was performed using polystyrene standards ranging from 76,600 g mol<sup>-1</sup> to 208 g 170 mol<sup>-1</sup>. In addition, syringol and biphenyl (154 g mol<sup>-1</sup>) were utilised as low molecular weight 171 standards.
- 172 Volatile compounds present in the bio-oil samples were analysed using a Shimadzu GC-MS 173 with an HP-MS column (30 m x 0.25 mm x 0.25 µm). The bio-oil sample was dissolved in 174 ethyl acetate to a pre-determined concentration along with 10 ppm of anisole as internal 175 standard and 1 µL of the solution was injected at an inlet temperature of 280 °C with a split 176 ratio of 10. Temperature of the column was kept at 40 °C for 2 min, then increased at a rate of 6 °C min<sup>-1</sup> to 300 °C and kept for 10 min. Electron impact ionization was used at 70 eV. NIST 177 database and model compounds were used for the interpretation of the peaks. Guaiacol was 178 179 used as calibration standard for calculating the response factor (RF) in order to quantify the 180 amount of monoaromatic compound in the injected sample.
- 181 Elemental analyses were carried out by Perkin Elmer model 2400 series II CHNS elemental
  182 analyser (230 V). The amount of oxygen in the samples was calculated by subtracting the sum
  183 of other elements from 100%.
- 184 IR spectra for the char samples were recorded using unicam Mattson 3000 with PIKE 185 technologies Gladi ATR. Absorbance mode was used with 16 scans per spectrum and 186 resolution of 16. The range of the spectrum was selected from 0 - 4000 cm<sup>-1</sup>. Air spectrum was 187 used as background.

188 Pyrolysis GC-MS was used to analyse the chemical composition of feed lignin and char 189 material using a Shimadzu GC-MS with an HP-MS column (30 m x 0.25 mm x 0.25 µm). Small 190 amount of material was pyrolysed at 500 °C for 2 min, starting from 50 °C with a heating rate 191 of 10 °C/sec, then cooled to 50 °C and held for 19 min. The temperature programme for products analysis was: temperature of the column kept at 50 °C for 1 min, then increased at a 192 193 rate of 10 °C min<sup>-1</sup> to 200 °C, and then raised to 320 °C at a rate of 30 °C min<sup>-1</sup> and kept for 2 194 min. Electron impact ionization was used at 70 eV. NIST database was used for the 195 identification of the compounds.

196 2.5 Calculation for products yield

197 The yield of products are mentioned as weight percentage (%) of dried feed lignin mass and198 were calculated according to the equations 2 to 6.

199 Yield of Residual lignin (%) = 
$$\frac{Mass of residual lignin (g)}{Mass of dried lignin (g)} * 100$$
 (2)

200 Yield of Water solubles (%) = 
$$\frac{Mass \ of \ water \ solubles \ (g)}{Mass \ of \ dried \ lignin(g)} * 100$$
 (3)

201 Yield of Char (%) = 
$$\frac{\text{Mass of char}(g)}{\text{Mass of dried lignin}(g)} * 100$$
 (4)

202 
$$Yield \ of \ Bio - oil \ (\%) = \frac{Mass \ of \ bio - oil \ (g)}{Mass \ of \ dried \ lignin \ (g)} * 100$$
(5)

203 
$$Yield of Gas(\%) = \frac{Mass of gas(g)}{Mass of dried lignin(g)} * 100$$
(6)

# 204 3. Results and discussion

#### 205 3.1. Mass balance

The depolymerization reactions resulted in five products, namely residual lignin, char, gases, water solubles and bio-oil. Bio-oil is the most valuable product due to the presence of monoaromatic compounds, whereas char is the undesired product containing highly condensed chemical structures with high molar mass.

- 210 Figure 2 presents the comparison of products yield obtained after hydrothermolysis reactions
- of lignin with and without metal formates at 310 °C and 60 min. In the reference experiment,
- the yield of reaction products were 12.1% of bio-oil, 20.2% water solubles, 4.9% gas and rest

213 to solid residues consisting of 16.8% char and 41.9% residual lignin. The yield of residual 214 lignin recovered after the metal formate catalyzed reactions was significantly lower in contrast 215 to the reference, i.e. non-catalyzed, reaction. The yield of bio-oil achieved from NaFo catalyzed 216 reaction was higher than that of the reference, while the reactions in the presence of CaFo and 217 MgFo resulted in the same bio-oil yield of 12.1% as achieved in the reference trial. It was 218 reported that the bio-oil yield depended on the type of base used in the reactions [20]. Sodium 219 carbonate was produced upon hydrothermal degradation of NaFo; similarly it can be assumed 220 that calcium carbonate and magnesium carbonate were formed as the degradation products 221 from hydrothermolysis of CaFo and MgFo, respectively. Based on this assumption, it was 222 inferred that calcium carbonate and magnesium carbonates were weak bases due to their 223 limited solubility in water which in turn decreased their dissociation to form OH<sup>-</sup> ions 224 compared to sodium carbonate. Sodium carbonate promoted the hydrolysis reactions and 225 resulted in a higher bio-oil yield compared to other metal formates. This assumption could be 226 well supported by the fact that the pH of the resulting aqueous phase with NaFo was 7.1 227 compared to 6.2, 5.7 and 3.5 from CaFo, MgFo, and the reference, respectively, manifesting 228 the stronger alkaline nature of the reaction medium resulting from sodium formate.



229

Fig 2. The yields of degradation products as wt % of feed lignin obtained at 310 °C and 60 min. The yield of char increased significantly to 28.9% for MgFo, 28.2% for CaFo, and 21.0% for NaFo in contrast to 16.8% obtained in the reference reaction. Magnesium carbonate and calcium carbonate were insoluble in water whereas sodium carbonate was water soluble (217 g L<sup>-1</sup>, 20 °C). Water-insoluble particles in the case of magnesium and calcium carbonate

provided enough surface for the agglomeration of lignin fragments and caused more charformation than what was observed in the trial with water soluble sodium formate.

The yield of water solubles was 31.1% for NaFo and 26.5% for CaFo which was higher compared to 20.2% observed in the reference reaction. These results clearly indicated that the reaction was more efficient in the presence of metal formates compared to the non-catalyzed reaction. However, the water solubles yield for MgFo catalyzed reaction (18.9%) was slightly smaller than in the reference reaction, which is in line with the high yield of residual lignin indicating lower lignin degradation.

243 Methanol formation is a good indicator for analysing the effectiveness of each metal formate 244 to depolymerize lignin. Methanol is produced due to degradation of methoxy groups present in 245 the lignin macro structure as well as in the degraded fragments. This was the main cause of 246 higher water solubles yield in the presence of metal formates. It can be observed in Table 2 that 247 the highest amount of 90.8 mg of methanol per gram of lignin was formed in the case of NaFo assisted reaction and the lowest amount of 39.8 mg methanol per gram of lignin was formed in 248 249 the case of MgFo catalyzed reaction, clearly demonstrating the superior hydrolysing effect of NaFo compared to other metal formates. Other major compounds analysed in the aqueous 250 251 phase are ethanol, acetic acid and formic acid as shown in Table 2.

Metal Formate	Amount of metal formate	Temperature	Formic Acid	Acetic Acid	Ethanol	Methanol	Total
	g	°C	1	ng g <sup>-1</sup> o	of feed lig	nin	
Reference	NO	310	3.4	16.6	24.8	32.9	77.7
MgFo	0.5	310	4.1	17.8	25.0	39.8	86.7
CaFo	0.5	310	4.9	19.6	27.0	60.2	111.7
NaFo	0.5	310	13.0	22.9	31.0	90.8	157.7

Table 2. Composition of various water soluble compounds obtained from the depolymerization of lignin at 310 °C and 60 min using 0.5 g of metal formates.

The composition of gas samples is given in Table 3. It can be observed from Table 3 that the gas formation was generally higher in the case of metal formates compared to non-catalyzed hydrothermolysis reaction. The yield of gas was 4.9% in the reference reaction consisting mainly carbon dioxide and carbon monoxide. In metal formate catalyzed reactions, 12.5% gas was formed in the presence of CaFo followed by 12.0% in the case of NaFo and a minimum of 10.3% was achieved in the presence of MgFo. The gas samples obtained from metal formate catalyzed reactions contain also methane in addition to carbon dioxide and carbon monoxide. The formation of carbon dioxide and carbon monoxide is mainly due to the decarboxylation and decarbonylation reactions. The formation of methane could result from demethylation reactions in the presence of in-situ hydrogen generated from the decomposition of metal formates.

Table 3. Composition of gas samples obtained from the depolymerization of lignin at 310 °C and 60 min. 0.5 g of metal formate was used in metal formate catalyzed reactions.

	Wt % of Feed Lignin						
	Reference	NaFo	CaFo	MgFo			
Carbon monoxide	0.6	1.1	3.3	2.9			
Carbon dioxide	4.3	9.2	8.3	7.4			
Methane	0	1.7	0.9	0			
Sum	4.9	12.0	12.5	10.3			

The overall mass balances were higher than 100% in metal formate catalyzed reactions. This 267 268 could be attributed to the formation of carbon dioxide from the dissociation of metal formates 269 and resulting metal carbonates i.e. sodium-, calcium- and magnesium together with the possible 270 presence of unreacted metal formate in the aqueous phase. The material balance calculations 271 for hydrothermal degradation of metal formates were however extremely challenging with the 272 analytical methods applied. The reasons were simultaneous degradation of metal formates into 273 inorganic compounds i.e. sodium carbonate, unreacted metal formates as organic part and 274 carbon dioxide gas, as evident from equation 1. Unreacted metal formates cannot be removed 275 before the TOC analysis of aqueous phase hence interfere with water solubles in aqueous phase 276 originating from lignin. Similarly, carbon dioxide originated from sodium formate dissociation 277 was analysed together with the carbon dioxide produced from lignin hydrothermolysis.

278 To analyse the effect of temperature on products formation, a series of experiments were performed at 270, 290, 310, 330 and 350 °C in the presence of sodium formate. The reason for 279 280 prioritizing sodium formate was the higher bio-oil yield and lower char yield in contrast to the 281 reactions carried out with CaFo and MgFo. Figure 3 presents the results obtained at different 282 reaction temperatures. A steady decline in the yield of residual lignin from 42.8% at 270 °C to 283 10.9% at 350 °C, was a clear sign of significant influence of the temperature. Results 284 demonstrated that the yield of bio-oil increased gradually from 8.4% at 270 °C to 12.6% at 290 285 °C and reached a maximum of 13.9% at 310 °C. A further increase in the temperature to 350 286 °C showed a decline in bio-oil yield to 12.9%. These results indicated that bio-oil yield could 287 not be further promoted even if the temperature was increased significantly. As mentioned earlier that several bonds, connecting the phenolic and non-phenolic groups, exist in the lignin structure having different bond strengths. But  $\beta$ -O-4 ether bond is the most important to be broken down for producing bio-oil consisting monoaromatic phenolic compounds [33]. Therefore, the lack of further increment in bio-oil yield in the current study could be related to the number of available  $\beta$ -O-4 linkages (0.27 moieties per aromatic ring) in the feed lignin and the limiting factor for bio-oil-yield. Another reason could be further degradation to smaller molecules contributing in water soluble fraction and gases.

The yield of both char and water solubles increased significantly from 20.8 and 19.9% at 270 °C to 30.5 and 33.0% at 350 °C, respectively. The increase in char yield has possibly occurred through repolymerization reactions of reactive intermediates whereas enhanced hydrolysis of lignin due to increased ion product of water could be the reason for the rise in water soluble compounds. A sharp increase in gas formation from 13.1% at 330 °C to 18.9% at 350 °C was also observed.





Fig 3. The yields of degradation products obtained at various reaction temperatures after 60 min of reaction time in the presence of 0.5 g sodium formate. Reference reaction was performed

304 at 310 °C.

To analyse the effect of metal formate concentration, reactions with different NaFo concentration were performed and the results are presented in Figure 4. It was demonstrated in earlier studies that increasing the amount of homogeneous catalyst could enhance the 308 production of bio-oil. Similarly, an increase in the bio-oil yield from 13.9 to 16.2 % was 309 observed in this study with the increase in NaFo amount from 0.5 to 5.0 g respectively. The 310 reason was more hydrolysis reactions which caused the increase in formation of small 311 molecular products and increased formation of water soluble compounds. However, the 312 significant increase in the yield of water solubles from 31.1% to 44.2%, when 5 g of NaFo was 313 used instead of 0.5 g, is plausibly due to the contribution from the unreacted sodium formate. 314 The yield of char increased from 21 to 23% when NaFo amount was increased from 0.5 to 0.75 315 g but decreased to 18.3% upon further increase in NaFo to 5 g.

Hence, it can be concluded that both reaction temperature and amount of metal formate affectthe products distribution and the best bio-oil yield was 16.4% achieved with 5 g of sodium



318 formate at 310 °C.



- 321 various amounts of metal formate.
- 322 3.2. Bio-oil characterization
- 323 3.2.1. Monoaromatic compounds quantification

The compositional changes in the bio-oils obtained under different reaction conditions are presented in Figures 5 a, b, and c. The presented results are the averages of two trials having small deviations; results from each trial are provided in Tables A1- A3 (Appendix A). The composition of bio-oils obtained in the presence of NaFo and CaFo were different than in the 328 reference experiment, whereas MgFo did not affect the composition of the bio-oil in 329 comparison to the reference reaction.

330 Phenolic compounds were formed due to transformation of phenoxy and alkyl aromatic 331 radicals, generated upon hydrolytic cleavage of the low energy ether linkages in lignin. The 332 formation of in-situ base, i.e. sodium carbonate, further catalyzed the hydrolysis process 333 causing an increase in the formation of smaller phenolic compounds such as catechol and 334 methoxycatechols. In reference reaction, the yield of monoaromatic compounds was 5.5% (55 335 mg per g of feed lignin) of the initial amount of lignin achieved. Syringol, 3-methoxycatechol, 336 guaiacol, 4-methylsyringol and syringaldehyde were the dominating compounds in the bio-oil 337 sample. With metal formates, the highest yield of monoaromatic compounds achieved was 338 9.2% (92 mg per g of feed lignin) in the presence of sodium formate. Bio-oil obtained with 339 sodium formate catalyst contained catechol and 4-methylcatechol in addition to syringol, 3-340 methoxycatechol and guaiacol as major compounds. A moderate yield of 7.6% monoaromatic 341 compounds (76 mg per g of feed lignin) was achieved in bio-oil obtained in the calcium formate 342 catalyzed reactions. Both sodium formate and calcium formate yielded bio-oil having similar 343 monoaromtic compounds. There was no significant difference in the yield and composition of 344 bio-oil obtained with magnesium formate catalyzed reaction in contrast to the reference.

345 The impact of increasing temperature from 270 to 310 °C had a positive impact on the yield of 346 monoaromatic compounds as shown in Figure 5b. The yield of monoaromatics increased from 347 5% at 270 °C to 9.2% at 310 °C. However, a further increase in the temperature decreased the 348 yield of the monoaromatic compounds present in bio-oil. The yield of monoaromatics 349 decreased to 7.2% at 330 °C and 6.9% at 350 °C. The composition of bio-oil significantly 350 changed with the increase in the reaction temperature due to enhanced hydrolysis and 351 dealkylation reactions. The yield of guaiacol, syringol, and 3-methoxycatechol increased from 352 0.8, 2.7 and 0%, respectively, at 270 °C to 2.4, 3.6 and 0.9%, respectively, at 310 °C. In our 353 previous non-catalyzed hydrothermolysis experiments of similar lignin [31], we observed 2.3% 354 of syringol and 3.2% of 3-methoxycatechol in the bio-oil obtained after 60 min of reaction time 355 at 350 °C. In this study, the yield of both syringol and 3-methoxycatechol in the bio-oil samples 356 declined gradually to zero from 310 to 350 °C obtained from NaFo catalyzed reaction. The 357 yield of guaiacol also declined to 0.9 % at 350 °C. Catechol, methylcatechol and ethylcatechol, 358 which were not present in bio-oil samples obtained at 270 °C, started to form after 310 °C and 359 gradually increased with temperature and reached to 3.2, 1.1 and 0.4% at 350 °C. Catechol has

360 been reported to form by cleavage of a methyl group from the methoxy group of the guaiacol 361 under severe hydrothermal conditions [34,35]. A gradual increase in the yield of pyrocatechol 362 with increasing temperature above 310°C with a simultaneous decrease in the yield of syringol, 363 3-methoxycatechol and guaiacol is pointing towards increased hydrolysis of these compounds under basic conditions. Forchheim et al [36] mentioned an existence of a parallel reaction path 364 which is still unknown that could transform the bulk reactive intermediates to catechol. The 365 366 observed 4-methylcatechol and ethylcatechol could possibly result from the hydrolysis of 367 methoxy group present in 4-methylguaiacol and 4-ethylguaiacol. A decrease in the yield of 368 abundant monoaromatics such as syringol and 3-methoxycatechol with increasing temperature 369 could also indicate their repolymerization to dimers, trimers, and oligomers leading eventually 370 to formation of char.

371 Increasing the amount of sodium formate from 0.5 to 5 g caused significant transformations in 372 composition and yield of monoaromatic compounds. Maximum production of catechol and 4-373 methyl catechol was achieved when 5 g of NaFo was used, whereas a low amount of guaiacol 374 was present in the sample and syringol completely vanished when 5 g of NaFo was used. This 375 also indicated that higher amount of metal formate was required to fully convert compounds 376 of lower reactivity, such as syringol (both ortho-positions of benzene ring are methoxylated), 377 to higher reactivity compounds with one or no methoxy group i.e. catechol, 4-methylcatechol, 378 and ethylcatechol.





Fig 5. Quantification of identified monoaromatic phenolic compounds present in bio-oil samples obtained (a) with different metal formates at 310 °C, 60 min of reaction time and 0.5 g metal formate (b) at different reaction temperatures after 60 min of reaction time and 0.5 g of sodium formate (c) with different amount of sodium formate at 310 °C and 60 min of reaction time.

388 3.2.2. Molar mass distribution

382

389 Figures 6 a - c illustrate the molar mass distributions of bio-oil samples obtained at various 390 reaction conditions. The chromatogram of bio-oil obtained from the experiment performed in 391 the absence of metal formate is presented as a reference. It can be clearly seen that metal 392 formates significantly affected the molar mass distribution of bio-oils and that the peaks shifted 393 from higher molar mass region to lower molar mass region. In all chromatograms, except those 394 obtained at 270 and 290 °C, there were two prominent peaks in the region of log 2.10 to 2.40 395 molecular mass. Most of the monomeric compounds were considered to be present in the first 396 peak, whereas, second peak plausibly consisted of dimers with a possibility of containing some 397 monomeric compounds.

Figure 6a illustrates the chromatogram of bio-oil obtained from various metal formates. Thesodium formate trial showed narrow molar mass distributions compared to the reference and

400 other metal formates. Moreover, no shoulder was present between log 2.20 to log 2.25 in NaFo
401 bio-oil, observed in other bio-oil samples. This phenomenon indicated the improved
402 homogeneity of the bio-oil obtained in the presence of sodium formate.

403 As the temperature and amount of sodium formate was increased, an increase in the intensity 404 of peak in the molar mass range of log 2.25 to log 2.40, together with a decrease in the intensity 405 of the peak in the molar mass range log 2.10 to log 2.25 were observed as illustrated in figures 406 6 b and c. UV detection was applied for analysing the molar mass distributions of bio-oil 407 samples. In UV detection, the detector response depends on the molar absorptivity of the UV 408 chromophores present in the sample. Therefore, based on UV absorption two phenomena could 409 plausibly occur along with the increase in temperature or the concentration of sodium formate. 410 Firstly, the formation of condensed structures having higher molar mass and being capable of 411 absorbing more UV radiations such as stilbenes [37], is possible. Secondly, the degradation of 412 monoaromatic structures consisting of unsaturated side chains substituted on benzene ring, 413 such as syringaldehyde, would lead to the same result.

414 Results of molar mass distributions of bio-oils at different reaction conditions are shown in Table 4. A decrease in molar mass of bio-oil samples from metal formate reactions can be 415 416 observed in contrast to the reference reaction. Bio-oil produced in the presence of sodium 417 formate showed the lowest molar mass of all tested metal formates which indicated its higher 418 potential for depolymerizing lignin. The polydispersity of bio-oils from metal formates 419 reactions is 1.1 which was lower than that of the reference (1.3), indicating narrower molar 420 mass distribution. Similar pattern of decreasing molar mass was observed when the reaction 421 temperature was increased from 270 to 310 °C in the presence of sodium formate. However, a 422 further increase in the temperature to 350 °C slightly increased the average molar mass of the 423 bio-oil possibly due to radical-induced polymerization. There is no change in the average molar 424 mass distribution with increase in the amount of sodium formate used in the reaction.





427

Fig 6. Molar mass distribution of bio-oil samples obtained (a) with different metal formates at 310 °C, 60 min of reaction time and 0.5 g metal formate, (b) at different reaction temperatures

430 after 60 min of reaction time and 0.5 g sodium formate, (c) with different amount of sodium

431 formate at 310  $^{\circ}$ C and 60 min of reaction time.

432	Table 4. Weight-average $(M_w)$ and number average $(Mn)$ molar masses and dispersity $(D)$ of
433	bio-oil samples at various reaction conditions.

Metal Formate	Metal Formate Metal Formate Amount		iperature Time		Mw	Ð			
	Effect	of various metal	formate	5					
	( <b>g</b> )	(° C)	(min)	g mol <sup>-1</sup>	g mol <sup>-1</sup>				
Reference	No	310	60	209	267	1.3			
NaFo	0.5	310	60	187	207	1.1			
CaFo	0.5	310	60	200	231	1.2			
MgFo	0.5	310	60	193	212	1.1			
Effect of increasing temperature									
	(g) (° C) (min) g mol <sup>-1</sup> g mol <sup>-1</sup>								
NaFo	0.5	270	60	209	277	1.3			
NaFo	0.5	290	60	188	221	1.2			
NaFo	0.5	310	60	187	207	1.1			
NaFo	0.5	330	60	202	222	1.1			
NaFo	0.5	350	60	203	219	1.1			
	Effect of increasing metal formate amount								
	( <b>g</b> )	(° C)	(min)	g mol <sup>-1</sup>	g mol <sup>-1</sup>				
NaFo	0.5	310	60	187	207	1.1			
NaFo	0.75	310	60	189	209	1.1			
NaFo	5.0	310	60	202	222	1.1			

#### 434 3.2.3 Elemental analysis

Results of the elemental composition of selected bio-oil samples obtained after the reactions 435 436 are presented in Table 5. The carbon content of the bio-oil obtained from the reference reaction 437 was similar to the feed lignin. However, the hydrogen content decreased after the reaction. The 438 carbon and hydrogen contents of bio-oils from all metal formate catalyzed reactions increased 439 compared to reference. The largest increase in the carbon content was achieved in the bio-oil 440 obtained from the sodium formate catalyzed reaction compared to reference. A similar trend of 441 increase in the carbon content of bio-oil samples was observed when the reaction temperature 442 was increased from 270 to 350 °C. Hydrolysis of lignin macromolecule was regarded as the 443 prime reaction responsible for the increase of carbon content of bio-oils. Moreover, the 444 decarbonylation and decarboxylation reactions of intermediates also played their role in increasing the carbon content of bio-oils. However, increased hydrolysis also led to a slight 445 446 decrease in the carbon content due to conversion of primary monoaromatic compounds such 447 as syringol and guaiacol to catechol as observed in the analysis of bio-oil obtained when 5g of 448 NaFo was used.

Table 5. Elemental compositions of bio-oil samples obtained from hydrothermolysis of lignin
with various metal formates at 310 °C, with sodium formate at different temperatures and with
different amounts of sodium formate at 310 °C. Reaction time in all experiments was 60 min.
Heating value was calculated by Dulong formula.

Metal Formate	Amount of metal formate	Temperature	С	Н	Ν	0	Heating Value
	g	°C		W	t %		MJ/kg
Feed Lignin			62.5	5.9	0.3	30.9	24.1
Reference	NO	310	62.9	5.5	0.1	31.5	23.5
MgFo	0.5	310	63.9	6.8	0.1	29.2	26.1
CaFo	0.5	310	63.3	6.8	0.1	29.8	25.8
NaFo	0.5	310	65.1	6.8	0.2	27.9	26.7
NaFo	0.5	270	62.0	6.7	0.1	31.2	25.0
NaFo	0.5	310	65.1	6.8	0.2	27.9	26.7
NaFo	0.5	350	67.3	6.6	0.1	26.0	27.5
NaFo	5	310	64.3	6.9	0.1	28.7	26.5

## 453 3.3 Char characterization

454 To understand the structure and chemical composition of the char obtained after the 455 depolymerization reactions, char samples from the reference reaction and from the metal 456 formate catalyzed reactions were analysed with elemental analysis, pyrolysis GC-MS and457 FTIR.

458 3.3.1 Elemental analysis

459 It can be observed from the elemental analysis of char samples presented in Table 6 that the 460 carbon content of char from the reference and the sodium formate catalyzed reactions is higher 461 than the carbon content in the feed lignin. In contrast, the carbon content of the char sample 462 obtained from the calcium formate catalyzed reaction is lower than the respective content in 463 the feed lignin. Hydrogen content of char is lower than the hydrogen content in the feed lignin 464 in all cases. These changes indicated the difference in the structure of the char compared to the 465 feed lignin. The prominent decline in hydrogen content of char could occur due to formation 466 of methane as a result of demethylation reactions as observed in gas phase. In addition, removal 467 of aliphatic hydrocarbon chains from lignin structure at 310 °C under subcritical water 468 conditions, causing fusion of aromatic rings, could also decrease the hydrogen content of the 469 resulting char samples [38,39].

Table 6. Elemental analysis of char samples obtained from various metal formate catalyzed
reactions, reference reaction obtained after 60 min and feed lignin. Heating value was
calculated by Dulong formula.

Metal Formate	Amount	Temperature	С	Н	Ν	S	0	Heating Value
	g	°C		V	Vt %			MJ / kg
Feed Lignin			62.5	5.9	0.3	0	30.9	24.1
Reference	NO	310	63.4	3.3	0.4	0	32.9	20.3
MgFo	0.5	310	62.2	4.7	0.4	0	32.7	21.9
CaFo	0.5	310	60.0	4.3	0.4	0	35.3	20.1
NaFo	0.5	310	63.8	4.3	0.5	0	31.4	22.1

473 3.3.2 Pyrolysis GC-MS

For deepening the knowledge about composition of char samples, pyrolysis GC-MS analyses were carried out. Pyrolysis GC-MS enables the analysis of compounds present in the volatile gas originated from fast pyrolysis of solid materials such as lignin and char. The composition of volatile gas could indicate the structural differences between char and feed lignin. Pyrograms from feed organosolv lignin and selected char samples are presented in Figure A.1 of Appendix A, and the data obtained from the pyrograms is presented in Table 7.

480 The pyrolysis products of feed lignin include the basic thermal degradation compounds such481 as aldehydes (vanillin and syringaldehyde), ketones (acetosyringone, acetovanillone and

482 syringylacetone), sinapic aldehyde, 4 – propenylsyringol, syringol, guaiacol, creosol, 4 –
483 ethylguaiacol and 4 – methyl syringol. Phenols were absent in the pyrolysis products of feed
484 lignin.

485 Clear differences in the composition of pyrolysis products obtained from feed lignin compared 486 to char samples can be observed in Table 7. Phenol, methyl phenol, various di-methyl phenols, and substituted catechols were detected in pyrolysis products from char samples. On contrary, 487 488 aldehydes (vanillin and syringaldehyde), ketones (acetosyringone, acetovanillone and syringylacetone) and compounds containing 3 carbons side chain such as sinapic aldehyde and 489 490 4 – propenylsyringol were absent from pyrolysis products of char samples. The % peak area of 491 syringol units was higher than guaiacol units in feed lignin, whereas guaiacol is dominant in 492 the char samples in comparison to syringol, indicating higher conversion of syringol than 493 guaiacol to char structure. These differences indicated several transformations in lignin 494 structure before the formation of char. The presence of phenol, various alkylated phenols and 495 substituted catechols in pyrolysis products of char with absence of mentioned aldehydes, 496 ketones and longer side chain compounds were indicative of condensation of lignin degradation 497 fragments. The absence of aldehydes could be explained by the absence or loss of hydroxyl 498 group at alpha position of the propyl side chain during the course of the reaction. Another 499 possibility is that the aldehyde and ketone groups are removed through decarbonylation 500 reactions under sub-critical water and the remaining lignin fragment is condensed to char. The 501 type of phenolic compounds found in all char samples were basically the same, which 502 indicateed similar char forming mechanisms under all reaction conditions.

Metal Formate	<b>Retention Time</b>	Feed Lignin	Reference	MgFo	CaFo	NaFo
Compound	(min)		% Area of	chromatog	ram	
Phenol	6.05	-	2.9	2.1	2.1	3.8
p-Cresol	7.44	-	4.8	4.6	6.5	-
Guaiacol	7.72	3.9	10.2	17.2	14.9	14.2
2,5-Dimethyl phenol	8.52	-	-	-	5.8	9.7
3,4-Dimethyl phenol	8.83	-	-	1.6	3.2	2.4
2,3-Dimethyl phenol	8.98	-	-	-	-	2.6
Creosol	9.26	7.4	6.3	4.1	7.2	3.6
3-Methyl catechol	10.17	1.1	2.6	3.8	4.3	2.4
3-Methoxy catechol	10.26	4.0	-	3.9	-	2.6
4-Ethyl guaiacol	10.49	2.1	1.9	3.1	2.7	1.2
4-Methyl catechol	10.59	-	1.7	2.4	-	-

Table 7. % Area of identified compounds in pyrolysis GC-MS chromatograms of char samples obtained from various metal formate catalyzed reactions, reference reaction and feed lignin.

2,3-	10.90	-	-	2.1	2.6	5.5
Dimetnyinydroquinone	10.00	2.0				
2-Methoxy-4-vinylphenol	10.99	3.0	-	2.1	-	-
Syringol	11.48	9.4	6.5	14.1	10.5	7.2
3,4-dimethoxy- Phenol	11.64	2.2	-	1.4	-	-
1,2,3-Trimethoxybenzene	11.71	-	-	1.5	1.5	1.1
Vanillin	12.17	3.4	-	-	-	-
4-Methylsyringol	12.79	12.6	1.3	-	1.8	-
Acetovanillone	13.29	1.1	-	-	-	-
1,2,3-Trimethoxy-5- methyl benzene	13.74	2.47	-	1.2	1.0	-
Vinylsyringol	14.23	3.3	-	-	-	-
Syringaldehyde	15.41	7.0	-	-	-	-
Trans-4-Propenylsyringol	15.84	8.3	-	-	-	-
Acetosyringon	16.23	3.9	-	-	-	-
Syringylacetone	16.54	2.2	-	-	-	-
Sinapic Aldehyde	17.99	1.3	-	-	-	-

## 505 3.3.3 FTIR analysis

506 For elucidating the structure of lignin and residual solids, FTIR technique has been frequently 507 used [38,40,41]. The FTIR spectra's fingerprint region of the feed lignin and the analysed char 508 samples obtained after reference and metal formates catalyzed reactions are shown in Figure 509 7. The characteristic peaks in the FTIR spectra were based on the literature and presented in 510 Table 8 [41,42].

511 Table 8. List of characteristic peaks observed in FTIR spectra.

Observed Band	literature	Origin
Lignin		
cm <sup>-1</sup>	cm <sup>-1</sup>	
1727	1726 - 1732	C=O streching in non-conjugated ketone and carbooxyl group
1670	1660 - 1675	C=O streching non conjugated to the aromatic ring
1600	1600 - 1605	Aromatic ring vibrations
1511	1505 - 1515	Aromatic ring vibrations
1463	1462 - 1470	C-H deformations (asymmetric)
1425	1425 -1430	Aromatic ring vibrations with C-H in plane deformation
1365	1365 - 1370	C-H deformations (symmetric)
1329	1325 - 1330	Syringyl ring breathing with C-O stretching
1271	1270 - 1275	Guaiacyl ring breathing with C-O stretching
1226	1221 - 1230	C-C, C-O and C=O stretch; G condensed > G etherified
1124	1120	Aromatic C-H in plane deformation, Syringyl Type
1035	1030	Aromatic C-H in plane deformation, Guaiacyl Type

512 It is obvious from Figure 7 that the absorbances in the char samples were lower compared to 513 the absorbances of the feed lignin. For this reason, absorbance in feed lignin and char samples 514 were plotted on separate axis for easy comparison. A shift in most of the bands in char samples 515 was observed compared to feed lignin. The sharpness of all the bands except the one observed at 1600 cm<sup>-1</sup> in all char sample had significantly decreased compared to the feed lignin. In 516 addition, prominent band broadenings were observed in the char samples obtained from 517 518 magnesium and calcium formate catalyzed reactions. The band observed at 1727 cm<sup>-1</sup> was 519 assigned to non-conjugated ketone and carboxyl group whereas the band observed at 1670 cm<sup>-</sup> <sup>1</sup> was assigned to C=O stretching conjugated to aromatic ring. Both of these bands diminished 520 in all char samples and cannot be observed as separate bands but appeared as a weak shoulder 521 522 centring around 1700 cm<sup>-1</sup> indicating the depletion of this functionality in char samples. The absorbance bands representative of aromatic ring vibrations were observed at 1600, 1511 and 523 1425 cm<sup>-1</sup> in lignin. Bands at 1511 and at 1425 cm<sup>-1</sup> merged together with bands 1463 and 1365 524 cm<sup>-1</sup> assigned to C-H deformations in char samples obtained from MgFo and CaFo catalyzed 525 526 reactions. This is indicating the higher fusion of aromatic rings which is the characteristic 527 phenomenon during char formation [43]. This also explains that MgFo and CaFo were 528 promoting the char formation as observed in the higher yield of char obtained from the reactions catalyzed by MgFo and CaFo. The peaks at 1329 cm<sup>-1</sup> and 1271 cm<sup>-1</sup>, representative 529 of syringyl and guaiacyl ring vibrations, diminished in all char samples and formed a shoulder 530 at 1271 cm<sup>-1</sup>. A significant decrease in the intensity of peak at 1226 cm<sup>-1</sup> in all char samples 531 owing to the condensed G rings indicated repolymerization of reactive lignin fragments 532 533 produced during depolymerization reactions.



Fig 7. FTIR spectra of feed lignin and char samples from reference and metal formate catalyzed
(0.5 g) reactions at 310 °C and 60 min.

538 4. Reaction Pathways

The formation of a large number of products due the occurrence of multiple reactions during lignin depolymerization makes it extremely challenging to propose a precise reaction mechanism for lignin depolymerization. For a detailed study on the reaction mechanisms more sophisticated techniques, such as trapping of intermediate products, are required. Therefore, a simplified reaction pathway is proposed based on the literature and the reaction conditions applied together with the results obtained in this study.

545 It is generally agreed that under hydrothermal conditions ether bonds, such as  $\alpha$ -O-4 and  $\beta$ -O-546 4, are readily cleaved due to lower bond strengths compared to C-C bonds [11]. The presence 547 of a base or basic salt such as metal carbonates can enhance the cleavage of ether bonds and 548 the formation of secondary products. Under the conditions applied in this study, the alpha-OH 549 group would be deprotonated, followed by the cleavage of  $\beta$ -O-4 bond through an SN2 reaction 550 mechanism via epoxide formation [44]. Metal formate decomposes to carbonate and together 551 with the high temperature the system reacts strongly alkaline. The role of cations is still unclear 552 since the type of products formed after sodium- and calcium formate catalyzed reactions were

535

of similar nature. However, some studies have suggested that cations would also support the cleavage of  $\beta$ -O-4 bonds through the polarization of the bond [13, 23].

555 The results indicate that the yield of residual lignin from sodium formate catalyzed reactions 556 is significantly lower than that of uncatalyzed reactions, suggesting more reactions in the 557 presence of sodium formate. Sodium formate catalyzed reactions showed higher quantities of 558 guaiacol, syringol and catechols compared to uncatalyzed reactions. Moreover, formation of 559 catechols was favored with the increase in the amount of sodium formate and temperature, 560 whereas syringol and 3-methoxycatechol diminished in the bio-oil. These findings suggest that 561 an increased alkali concentration due to the decomposition of sodium formate to carbonate 562 increases both the extent of lignin depolymerization and other alkali-induced degradation 563 reactions such as the cleavage of the methoxy group(s) and thus the formation of catecholic 564 structures and methanol, as already discussed in section 3.2.1. The noteworthy increment in 565 char formation under catalyzed conditions indicates a repolymerization path of the reactive intermediates. 566

#### 567 5. Conclusion

568 This study demonstrated the catalytic effect of sodium formate on the production of 569 monoaromatic phenolic compounds in bio-oil. Hence, the amount of monoaromatics (92 mg g<sup>-</sup> <sup>1</sup> of lignin) in bio-oil produced in sodium formate catalyzed reaction at 310 °C and 60 min is 570 comparable to the amount of monoaromatics (100 mg  $g^{-1}$  of lignin) obtained in bio-oil from 571 572 non-catalyzed reaction at 350 °C and 60 min in our earlier study [31]. The composition of bio-573 oil fraction was significantly influenced by sodium formate and contained higher reactive 574 moieties (catechol and methyl catechol) compared to the bio-oil obtained from non-catalyzed 575 hydrothermolysis of the same lignin under similar reaction conditions. Moreover, bio-oils from 576 sodium formate catalyzed reactions exhibited significantly narrower molar mass distribution  $(Mw = 207 - 277 \text{ g mol}^{-1} \text{ with PD of } 1.1 - 1.3)$  as compared to the feed lignin (Mw = 3428 g)577 578 mol<sup>-1</sup> with PD of 5.66). The results suggested that the formation of reactive moieties could be 579 controlled by controlling the gravimetric ratio of lignin and sodium formate. The formation of 580 char was a challenge. The analysis of char through pyrolysis GC-MS and FTIR confirmed that repolymerization of lignin degradation fragments occured under hydrothermolysis reactions. 581 582 The low molar masses and presence of reactive monoaromatic phenolic compounds in the bio-583 oil calls for its use in phenol-based resins. The role of in-situ hydrogen formed due to the

hydrothermolysis of metal formates in lignin depolymerization reactions requires furtherinvestigation.

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