energy&fuels

Biofuels and Biomass

Catalytic fast pyrolysis of demineralized biomass in a fluidized bed reactor: effects of acid-leaching and torrefaction pretreatment

Xing Xin, Kirk M. Torr, Shusheng Pang, Daniel Jason van de Pas, Martin Cooke-Willis, and Ferran de Miguel Mercader

Just Accepted

1   # Catalytic fast pyrolysis of demineralized biomass in

2   # a fluidized bed reactor: effects of acid-leaching and

3   # torrefaction pretreatment

4   *Xing Xin,* *,†,§ *Kirk M. Torr,* ‡ *Shusheng Pang,* § *Daniel van de Pas,* ‡ *Martin Cooke-Willis,*

5   ‡ *and Ferran de Miguel Mercader* ‡

6   †Department of Chemical and Materials Engineering, The University of Auckland,

7   Private Bag 92019, Auckland 1142, New Zealand

8   ‡Scion, Private Bag 3020, Rotorua 3046, New Zealand

9   §Department of Chemical and Process Engineering, University of Canterbury, Private

10   Bag 4800, Christchurch 8140, New Zealand

11

14   **ABSTRACT:** *In situ* catalytic fast pyrolysis of pretreated wood was investigated using a

15   fluidized bed reactor. The pretreatments included acid-leaching, torrefaction, and a

16 combined pretreatment of acid-leaching followed by torrefaction. Acid-leaching reduced

17 amounts of biomass minerals introduced into the process. However, acid-leaching

18 caused agglomeration during pyrolysis leading to reactor defluidization. Acid-leaching

19 also resulted in an upgraded bio-oil that was less deoxygenated compared to the

20 corresponding bio-oil obtained from raw wood. Conversely, torrefaction had a beneficial

21 effect leading to an increased yield of upgraded bio-oil without affecting its chemical

22 composition. Torrefaction of the acid-leached wood prevented agglomeration, reversed

23 the negative effect acid-leaching had on bio-oil quality, and gave an improvement in

24 upgraded bio-oil yield. These effects, combined with the removal of biomass minerals that

25 are detrimental to the catalyst, suggests acid-leaching coupled with torrefaction is a

26 promising pretreatment to improve *in situ* catalytic fast pyrolysis of lignocellulosic biomass

27 from a technical viewpoint.

1. INTRODUCTION

29   Lignocellulosic biomass is an abundant and renewable resource that can be used to

30 produce liquid fuels and valuable chemicals by thermochemical processes. The bio-oil

31 obtained from biomass pyrolysis can be upgraded to transport fuels by processes

32   including hydrotreating, catalytic cracking, etc. Hydrotreating process requires a high

33   pressure up to 20 MPa and a hydrogen supply. In comparison, catalytic cracking is

34   realized at an atmospheric pressure and does not need hydrogen supply. Catalytic fast

35   pyrolysis (CFP) is a promising process that combines fast pyrolysis with catalytic

36   upgrading to produce upgraded bio-oils[1]. *In situ* CFP processes use fluidized bed reactors

37   where solid particles are used as both active catalyst and bed material[2]. Among the solid

38   catalysts studied, the zeolite HZSM-5 has been shown to be effective to produce high-

39   quality bio-oils[3]. HZSM-5 is a shape-selective zeolite that contains micropores with pore

40   diameters of approximately 0.5 nm[4]. During CFP, oxygenated molecules can diffuse into

41   the pores of the zeolite and be transformed into aromatic hydrocarbons by reacting with

42   acidic active sites within the pores[5, 6].

43   The formation of coke during CFP leads to rapid deactivation of zeolite catalysts[7, 8]. It

44   is necessary to periodically regenerate the used catalyst by burning off the coke[9, 10].

45   Several studies have shown that the activity of zeolite catalysts decreases as the number

46   of regeneration cycles increases[11-13]. The main reason for this is that biomass minerals,

47   mainly alkali and alkali earth metals (AAEMs), accumulate on the catalyst after repetitive

48   cycles of catalytic pyrolysis and regeneration. These metals can block the pores or poison

49   the active sites of the zeolite, eventually leading to irreversible catalyst deactivation[14, 15].

50   The catalytic activity gradually decreases over time and new catalyst is required. Techno-

51   economic analysis has shown that the price of the CFP upgraded bio-oil product is very

52   sensitive to the catalyst cost[10]. Prolonging the catalyst lifespan is crucial in making the

53   CFP process more cost effective. Meanwhile, AAEMs reduce hydrocarbon yields in

54   catalytic pyrolysis of biomass leading to less aromatics and olefins[16].

55   Biomass pretreatment as one of the key steps in the thermochemical process can

56   uniform and improve biomass characteristics for the following conversion[17]. The

57   pretreating methods include thermal methods[18, 19], chemical methods[20-22], biological

58   methods[23, 24], etc. Acid-leaching pretreatment as a chemical method is effective in

59   removing AAEMs from lignocellulosic biomass and can significantly increase the organic

60   oil yield in thermal pyrolysis[22, 25, 26]. This pretreatment reduces the amount of biomass

61   minerals introduced into the CFP process, potentially prolongs the catalyst lifespan[27].

62   Recently, a few studies have been reported on applying acid-leaching pretreatment in

63   catalytic pyrolysis of biomass. Hernando et al. studied catalytic pyrolysis of acid-leached

64   wheat straw, but did not report on the effect of the acid-leaching pretreatment relative to

65   un-leached straw[28]. Wang et al. reported that acid-leaching of red oak wood increased

66   the yield of aromatic hydrocarbons in catalytic pyrolysis[16]. In previous work, we studied

67   the effects of acid-leaching and torrefaction pretreatments on catalytic pyrolysis of pine

68   wood using Py-GC/MS[29]. It was concluded that the acid-leaching pretreatment had only

69   a minor effect on the relative composition of the GC-volatile products compared to

70   reaction conditions, i.e. temperature and catalyst loading. Persson et al. studied catalytic

71   pyrolysis of demineralized softwood using HZSM-5 in Py-GC/MS and fix-bed reactor[30]. It

72   was found that acid-leaching pretreatment resulted in an increased yield of aromatics in

73   ex-bed catalytic pyrolysis of acid-leached biomass at 600° compared to the

74   corresponding raw material. While the performance of in-bed catalytic pyrolysis of acid-

75   leached wood was limited.

76   There have been no studies reported on CFP of acid-leached biomass using a fluidized

77   bed reactor. Previous studies have shown that fast pyrolysis of acid-leached wood in a

78   fluidized bed reactor caused an operational issue that is referred to as bed material

79   agglomeration or char agglomeration[26, 31]. This issue is caused by the formation of a sticky

80 melt material that coats the bed particles and binds them together to form agglomerates,

81 which can eventually lead to reactor defluidization[13, 26]. Bed material agglomeration has

82 been a barrier to research into CFP of acid-leached biomass. In recent work, we have

83 reported that bed material agglomeration can be mitigated by pyrolyzing at low

84 temperature, through continually refreshing the bed material, or by applying a mild

85 torrefaction pretreatment to the acid-leached wood[26].

86 Torrefaction is a relatively mild thermal treatment that can be used to increase the

87 energy density of lignocellulosic biomass and decrease its hydrophilicity[17]. The liquid

88 obtained from biomass torrefaction is considered a valuable product as it is rich in acids

89 and ketones[32]. This acidic liquid can also be used as a leachate to remove biomass

90 minerals for an acid-leaching pretreatment[33]. Several analytical pyrolysis studies have

91 shown that a mild to moderate torrefaction pretreatment can improve the selectivity for

92 aromatic hydrocarbon products in catalytic pyrolysis of biomass[34-36]. Studies on analytical

93 catalytic pyrolysis of torrefied cellulose[36] and torrefied lignin[37] also indicate that

94 torrefaction pretreatment can enhance the selectivity of aromatic hydrocarbon products.

95   Combining acid-leaching with torrefaction is an attractive pretreatment to improve

96   organic oil yield and the quality in pyrolysis processes[38-40]. Zhang et al. used Py-GC/MS

97   to study catalytic pyrolysis of rice husk biomass that had been pretreated by both acid-

98   leaching and torrefaction[41]. They found that this combined pretreatment improved the

99   relative content of aromatic hydrocarbons in the GC/MS-analyzable products compared

100   to untreated rice husks. This combined pretreatment is promising to improve CFP

101   process, however no study has been done using a fluidized bed reactor.

102   It is important to study CFP of pretreated biomass in large scale reactors. Compared to

103   Py-GC/MS work, these lab-scale fluidized bed reactors are a step towards better

104   mimicking CFP process. In this study, a bubbling fluidized bed reactor was employed for

105   CFP experiments on pine wood that had been pretreated by acid-leaching, torrefaction,

106   and acid-leaching followed by torrefaction. The effects of these three pretreatments on

107   catalytic fast pyrolysis were discussed respectively.

108   **2. EXPERIMENTAL SECTION**

109   **2.1. Materials.** Fresh wood chips (Radiata pine) were obtained from a local sawmill in

110   Rotorua, New Zealand. These chips were dried and then ground and sieved to wood

111   particle sizes in the range of 0.25-2.00 mm. This raw (non-pretreated) wood was labelled

112   Rwood.

113   Acid-leaching of raw wood was performed by soaking and stirring the wood particles in

114   1 wt.% acetic acid solution for 4 hours at 30 °C. Dilute acetic acid was selected as the

115   demineralization agent as it is possible to recover acetic acid from both pyrolysis oil and

116   wood torrefaction condensate[22, 42]. Following acid-leaching, the wood particles were

117   washed with deionized water and oven-dried at 60 °C overnight, and then at 105 °C

118   overnight. This acid-leached wood was labelled ALwood.

119   Torrefaction pretreatment was carried out with Rwood and ALwood using a 316

120   stainless steel vessel. Details of this procedure are described elsewhere[22]. During

121   torrefaction, the vessel that contained the biomass was heated in an oven set to 270 °C

122   for 260 minutes. Nitrogen was used as a sweep gas to remove generated volatiles. The

123   average heating rate was ca. 0.9 °C /min, with the vessel reaching a maximum

124   temperature of 258 ± 3 °C. Afterwards, the vessel was cooled at a rate of ca. 2.0 °C /min.

125   The torrefied Rwood was labelled as Twood, and the torrefied ALwood as ALTwood.

126   The moisture content of the wood samples was measured before each CFP experiment.

127   The chemical characteristics of the Rwood, ALwood, Twood and ALTwood samples have

128   been reported in our previous study[26]. The results are presented in Supporting

129   Information (Table S1).

130   A spray-dried HZSM-5 zeolite catalyst, obtained from Saint Chemical Material Company

131   (Shanghai, China) was used in this study. This catalyst had a Si/Al ratio of 30:1, a particle

132   size of 0.3-0.4 mm, a specific surface area of ≥ 350 m^2/g and a binder (alumina gel)

133   content of 50 wt.%. Before each CFP experiment, the catalyst was heated at 525 ^{o}C in a

134   muffle furnace for 4 hours to remove any moisture that was absorbed during storage.

135   **2.2. Fluidized bed reactor system and operating procedure.** A bubbling fluidized bed

136   reactor was employed for the CFP experiments. The reactor system is shown in Figure

137   1. Details of this reactor were reported previously.[26] A brief description is presented below.

138   Screw augers transported the biomass and catalyst into the fluidized bed reactor at

139   controlled feeding rates. The reactor bed was fluidized by preheated nitrogen that passed

140   through a sintered metal plate at the bottom of the reactor. An overflow tube inside the

141   reactor collected excess bed material to keep the bed level constant. The inner diameter

142   of the reactor was 100 mm, and the bed height was 420 mm. Five thermocouples were

143   located inside the reactor at different heights, four inside the fluidized bed, and one in the

144   freeboard above the overflow tube. The difference in temperature between these

145   thermocouples never exceeded 5 °C when the bed was fully fluidized. The average

146   temperature of the four thermocouple readings within the bed was defined as the reaction

147   temperature.

148   The hot vapors generated from the reactor were cleaned in a gas cleaning system that

149   was composed of a knock-out vessel, a cyclone and a hot filter, in series. The hot filter

150   consisted of a cylindrical cartridge filter of 316 stainless steel wire-mesh (pore size = 2

151   μm) contained within a filter housing. The hot filter was primarily used to remove fine

152   entrained catalyst dust. After cleaning, the vapor and non-condensable gas passed into

153   a quenching system that was composed of an electrostatic precipitator (ESP) column and

154   an intensive cooling (IC) column, both jacketed with coolant (water and ethylene glycol

155   mixture). The liquid product was collected at the base of these columns. A wound

156   polypropylene filter located after the IC column collected any aerosols remaining in the

157   non-condensable gas.

158 Before each experiment, 0.7 kg catalyst was preloaded in the reactor and the load

159 height was approximately 280 mm. This amount was the maximum quantity of catalyst

160 that could be loaded into the reactor without catalyst being blown out of the reactor when

161 fluidization was started. The pyrolysis reactor was then heated to the target temperature,

162 and the gas cleaning system was heated to 440 ^{o}C for all experiments. The temperatures

163 of the ESP and IC columns were -5 °C and -15 °C, respectively. The minimum fluidization

164 velocity was approximately 0.05 m/s. The gas velocity in fluidized bed was maintained at

165 approximately 0.1 m/s by adjusting the nitrogen flowrate in the range of 14.0-17.4 L/min

166 at normal conditions. The residence time of the hot vapor in the reaction zone was

167 approximately 2-3 seconds as estimated.

168 At the beginning of the CFP experiment (t = 0 h), the biomass and catalyst were

169 simultaneously fed into the bed. The feed rate of biomass was always 0.35 kg/h to keep

170 the weight hourly space velocity at 0.5 (1/h). The duration of the pyrolysis run was 1.5

171 hours for all experiments. The feed rate of catalyst required to give a specific catalyst to

172 biomass (C/B) ratio, by the end of the experiment, was determined from the following

173 equation:

174 $$C/B = \frac{f_c t + W_c}{f_b t} \qquad\qquad (1)$$

175 where C/B = ratio of catalyst to biomass (wt./wt.), f_c = feed rate of catalyst (kg/h), f_b =

176 feed rate of oven-dry biomass (kg/h), t = experiment duration (h) and W_c = weight of

177 preloaded catalyst (kg).

178 **2.3. Analysis of liquid products.** The liquid products collected in the CFP experiments

179 consisted of a lighter aqueous phase and a heavier organic phase (upgraded bio-oil). The

180 two phases were formed in approximately 10 minutes using a separating funnel, then they

181 were separated and stored at -20 °C prior to analysis.

182 The water content was measured in triplicate by Karl-Fischer titration (Metrohm 870 KF

183 Titrino plus). Elemental analysis was performed in triplicate using a FLASH 2000 CHN

184 analyzer (Thermo Scientific, USA). The carbon, hydrogen and nitrogen contents were

185 determined, and the oxygen content was calculated by difference.

186 Gas chromatography/mass spectrometry (GC/MS) of the upgraded bio-oils was

187 performed on an Agilent 7890 GC equipped with an Ultra 2 capillary column (50 m × 0.2

188 mm × 0.33 μm) and coupled to a 5977B MSD. Duplicate bio-oil samples were dissolved

189   in dichloromethane, filtered and diluted to a concentration of 0.4 mg/mL for analysis. The

190   injector temperature was held at 260 °C and injection volume was 1 μL. High purity helium

191   was used as carrier gas at a constant flow rate of 1.0 mL/min. A split of the carrier gas

192   (1:10) was used. The temperature schedule of the oven was set as follows: 50 °C for 2

193   min, 5 °C/min to 130 °C, 10 °C/min to 300 °C, held at 300 °C for 5 min. MS data was

194   collected in scan mode over a range of 50–350 amu. Agilent MassHunter Quantitative

195   Analysis software equipped with NIST 2011 database was used to analyze the

196   chromatograms and identify the eluted compounds from their mass spectra.

197   Chromatographic peaks with areas larger than 5 % of the largest peak area in the

198   chromatograph were included for identification. Only those peaks with a high degree of

199   certainty in terms of an identity match to a library database compound (over 80%) were

200   included and relative abundances were determined based on the peak area percentages.

201   98 compounds in total were identified, and the total area of the identified peaks accounted

202   for 87-91 % of the peak area of all the detected peaks. Details are shown in Supporting

203   Information (Figure S1 and Table S2).

204   Gel permeation chromatography (GPC) analysis of the upgraded bio-oils was

205   performed on a Knauer/Polymer Standards Service GPC equipped with a PSS SDV Lux

206   1000 Å column heated at 30 °C. Duplicate samples were analyzed at a concentration of

207   5 mg/mL in tetrahydrofuran using a refractive index detector. The system was calibrated

208   using low molecular weight polystyrene standards. Cumulative detector responses were

209   calculated from the GPC chromatograms and used to estimate that 93-96 % of organics

210   in the upgraded bio-oils were below 350 Da in molecular weight and therefore assumed

211   to be largely detectable by GC/MS.

212   Analysis of the aqueous phase products by ^{1}H-NMR spectroscopy was performed to

213   determine the chemical functionality of the organics. A Bruker Avance III 400 MHz

214   spectrometer equipped with a 5 mm BBO probe was used. The spectra were obtained at

215   300 K in acetone-d6. At least 64 transients were collected. A presaturation pulse was

216   applied during acquisition to suppress the signal of water. The spectra were reprocessed,

217   and the hydrogens in the organics were divided into six groups based on their chemical

218   shifts. The resonance signals assigned to different hydrogen types were described

219   elsewhere [43]. Results are shown in Supporting Information (Table S3).

220   **2.4. Analysis of gas and char.** A gas flow meter (bellows meters type) measured the

221   total flow of the non-condensed gas in each experiment. The gas was sampled every 10

222   minutes during the experiment. The gas composition was measured by gas

223   chromatography (GC) analysis using a portable Agilent 490 Micro GC instrument

224   equipped with a molecular sieve 5A column and a PoraPLOT Q column. The column

225   temperature was 80 °C, and it was calibrated using a standard gas mixture based on the

226   reported composition of the non-condensable gas, including N_2, O_2, H_2, CH_4, CO, CO_2,

227   C_2H_4, C_2H_6, C_3H_6 and C_3H_8. After analysis, the gas composition was normalized to N_2-

228   free and O_2-free contents (vol.%). The volume-based contents of gas species were then

229   converted to mass-based contents, and the yields (wt.%) of the individual gases were

230   calculated.

231   The char and used catalyst were collected as a mixture. The used catalyst containing

232   the coke byproduct could not be completely separated from the char. Therefore, the

233   combined yield of coke and char was reported. Samples of char and spent catalyst

234   materials for analysis by scanning electron microscopy (SEM) were mounted on carbon

235   tabs, coated with chromium and examined on a JEOL 6700F field emission scanning

236   electron microscope at an accelerating voltage of 15 kV using a backscattered electron

237   detector.

238   **2.5. Catalytic fast pyrolysis experiments.** A summary of the CFP experiments is shown

239   in Table 1. Firstly, control experiments were conducted in triplicate using Rwood and

240   pyrolysing at 500 °C. The final C/B ratio was 2.5 by setting the catalyst feed rate at 0.43

241   kg/h (see Eq. (1)). These experiments were used to provide benchmark data on liquid,

242   gas and char/coke yields and compositions, and to demonstrate experimental

243   repeatability. These experiments were given a code R500L. In the experiment code, the

244   first capital letter(s) referred to the wood sample, i.e. R = Rwood, AL = ALwood, this is

245   followed by the pyrolysis temperature in °C and finally the level of C/B ratio (L = low; M =

246   medium and H = high).

247   Bed material agglomeration was anticipated as an issue in conducting CFP experiments

248   with ALwood. An experiment was conducted at 500 °C with a C/B ratio of 2.5 with ALwood

249   to confirm the occurrence of bed material agglomeration. To overcome bed material

250   agglomeration, CFP experiments were conducted at 500 °C with C/B ratios of 4 and 6 by

251   increasing the catalyst feed rate to 1.0 kg/h and 1.5 kg/h, respectively. Additionally, CFP

252   experiments with the C/B ratio of 2.5 were conducted at 450 $^{\circ}$C and 360 $^{\circ}$C. The

253   corresponding CFP experiments with Rwood were also conducted to enable valid

254   comparisons to be made. To complete the series of experiments, CFP was conducted

255   with ALTwood and Twood at the optimal pyrolysis temperature (500 $^{\circ}$C) and at low to high

256   C/B ratios by varying the catalyst feed rate from 0.43 to 1.5 kg/h (Table 1). This gave a

257   total of sixteen CFP experiments (Table 1) that enabled CFP product yields and bio-oil

258   compositions to be compared for the same experimental conditions across the four wood

259   samples.

3. RESULTS AND DISCUSSION

261   **3.1. Characterization of pretreated wood.** Chemical characterization data of the Rwood,

262   ALwood, Twood and ALTwood has previously been reported[26] (Table S1 in Supporting

263   Information). Briefly, the ALwood was chemically very similar to the Rwood, with the only

264   significant difference being a substantial reduction in the ash content from 0.26 wt.% in

265   Rwood to 0.03 wt.% in ALwood. Levels of AAEMs, K^+, Ca^{2+}, Mg^+ were all significantly

266   reduced in ALwood. The Twood and ALTwood samples were chemically different from

267   the Rwood as a result of the mild torrefaction pretreatment. The main differences were a

268   substantial reduction in the hemicellulose content and an increase in the apparent lignin

269   content[26]. This was due to thermal degradation of the hemicelluloses, resulting in loss of

270   volatile components and degraded hemicelluloses that analyzed as lignin. In addition,

271   thermal degradation products in torrefaction may also been measured as acid-insoluble

272   lignin and included in the lignin content. Torrefaction pretreatment resulted in mass losses

273   of 17% and 14% for Twood and ALTwood, respectively. The ALTwood had reduced levels

274   of AAEMs compared to the Twood.

275   **3.2. Catalytic fast pyrolysis of raw wood.** Catalytic fast pyrolysis of Rwood at 500 °C

276   with a C/B ratio of 2.5 gave yields of the upgraded bio-oil of 8.3, 8.7 and 8.4 wt.%

277   (standard deviation (sd) = 0.2 wt.%) in the triplicate pyrolysis experiments. The

278   corresponding yields of the aqueous phase liquid, which was essentially produced water,

279   were 23.8, 22.1 and 22.6 wt.%, respectively (sd = 0.9 wt.%). The non-condensable gas

280   yields were 38.5, 38.4 and 38.5 wt.% (sd = 0.06 wt. %) and the yields of combined

281   char/coke were 23.8, 24.0 and 24.2 wt.% (sd = 0.2 wt.%). These results demonstrated

282   good reproducibility of the CFP experiments with product mass balances in the order of

283   93-94 wt.%. The loss of liquid product mainly consisted of the mass loss as some liquid

284   remained in the condensation columns and the separating funnel. The variability in the

285   product yields found in these triplicate experiments was used in assessing whether

286   product yields, in subsequent experiments, were the same or significantly different. For

287   instance, a difference of 1 wt.% in upgraded bio-oil yield was deemed significant

288   considering the 0.2 wt.% standard deviation found for bio-oil yield. The substantially lower

289   bio-oil yield, and higher yields of coke/char and non-condensable gas, compared to non-

290   catalytic fast pyrolysis[26], were indicative of the high activity of the HZSM-5 catalyst, which

291   was consistent with the literature[2, 16].

292   **3.3**. **Catalytic fast pyrolysis of acid-leached wood.** *3.3.1. Overcoming bed material*

293   *agglomeration.* The attempted CFP of ALwood under the same conditions used for

294   Rwood (500 °C, C/B ratio of 2.5, AL500L) resulted in rapid defluidization of the reactor

295   due to bed material agglomeration. On dissembling the reactor, agglomerates of catalyst

296   and char material were found located near the biomass input auger. To overcome this

297   issue, two different types of experiments were investigated based on our previous work

298   with non-catalytic fast pyrolysis of ALwood[26]. Firstly, CFP experiments were undertaken

299   using increased catalyst feed rates of 1.0 kg/h (AL500M, C/B ratio = 4) and 1.5 kg/h

300   (AL500H, C/B ratio = 6). The aim was to continually refresh the bed material in the reactor

301   so that the problematic agglomerates were removed, via the overflow pipe, before they

302   could cause defluidization problems. This approach proved successful for the AL500H

303   experiment. In this case, the full 1.5 hour run was achieved and the CFP products could

304   be compared with corresponding products from the Rwood experiment (see Section

305   3.3.2). In the AL500M experiment, defluidization of the reactor occurred within 35 minutes

306   of starting the run.

307   The second approach was to lower the pyrolysis temperature to 450 or 360 °C while

308   keeping the catalyst feeding rate at 0.43 kg/h (i.e. C/B ratio = 2.5). These experiments

309   (AL450L and AL360L, respectively) were both successful at mitigating bed material

310   agglomeration over the 1.5 hour run. Figure 2 shows SEM images of char and catalyst

311   bed material collected from the CFP experiments of AL360L, AL450L and AL500L. The

312   char from the AL360L experiment (Figure 2A) showed a fibrous structure with no evidence

313   of biomass melting. Conversely, evidence of melting of the biomass during char formation

314   was observed in experiments AL450L and AL500L. The severity of the melting behavior

315   increased with temperature, leading to the bed material agglomeration observed in

316   experiment AL500L. This behavior of biomass melting during CFP, leading to bed

317   material agglomeration, was the same behavior as that previously observed in non-

318   catalytic fast pyrolysis of acid-leached pine wood[26, 31].

319   A third approach to successfully mitigating bed material agglomeration in CFP, involving

320   a torrefaction pretreatment of the acid-leached wood, is discussed in section 3.5.

321   *3.3.2. Catalytic fast pyrolysis products.* The results for successful CFP experiments

322   using acid-leached wood are shown in Table 2, along with the corresponding results for

323   raw wood. Product yields are presented on a raw wood basis with the mass loss on acid-

324   leaching pretreatment of 1 wt.% taken into account. The liquid products were classified

325   into three groups: upgraded bio-oil, aqueous-phase organics and produced water. Most

326   of the organics are found in the upgraded bio-oil with very few organics remaining in the

327   aqueous phase, except in the case of CFP experiments at 360 °C.

328   Measured properties of the upgraded bio-oils included elemental content and chemical

329   composition of the organics as analyzed by GC/MS (Table 2). The GC/MS results are

330   based on relative peak area percentages of identified compounds, which have been

331   classified into seven chemical groups based on their main functionalities. GPC analysis

332   indicated 93-96% of the organics in the upgraded bio-oils were of sufficiently low

333   molecular weight to potentially be amenable to analysis by GC/MS. Key non-condensable

334   gaseous products included CO, CO_2, CH_4, C_2H_4 and C_3H_6, while the yields of H_2, C_2H_6

335   and C_3H_8 were negligible. ^{1}H NMR analysis results of aqueous phase products are

336   available in the Supporting Information (Table S3).

337   Firstly, the results of CFP of ALwood at 500 °C are compared with Rwood under the

338   same conditions, i.e. experiments AL500H and R500H. At this higher temperature the

339   catalyst was more active. However, a high catalyst feed rate was required to prevent bed

340   material agglomeration (see Section 3.3.1). The yields of upgraded bio-oil (9 wt.%) and

341   combined char/coke (29 wt.%) were the same for ALwood and Rwood. Produced water

342   and total non-condensable gas yields were also similar. Because of an excess catalyst

343   loading, no improvement in upgraded bio-oil yield was observed under these CFP

344   conditions. This contrasts to results for thermal pyrolysis in our previous study where

345   organic oil yield was significantly enhanced by acid-leaching pretreatment[26]. It is

346   speculated that levoglucosan is difficult to be upgraded over HZSM-5 zeolite, as it is

347　known that acid-leaching pretreatment primarily improves the production of levoglucosan

348　in non-catalytic fast pyrolysis.[42] Further discussion is presented in Section 3.3.3.

349　　A comparison of the non-condensable gases from the AL500H and R500H experiments

350　revealed that acid-leaching resulted in decreased CO_2 production and increased CO

351　production (Table 2). Correspondingly, the upgraded bio-oil from the AL500H experiment

352　contained a lower carbon content and a higher oxygen content (Table 2). The GC/MS

353　analysis of the upgraded bio-oil indicated the presence of less aromatics, and more

354　phenols and oxygenated aromatics, than the R500H upgraded bio-oil. These results

355　indicated that acid-leaching pretreatment mildly hindered the degree of deoxygenation of

356　the upgraded bio-oil. These results are consistent with our Py-GC/MS study which

357　indicated that acid-leaching pretreatment prior to CFP resulted in a slightly lower relative

358　proportion of aromatic hydrocarbons in the GC/MS-detectable products[29].

359　　Lowering the pyrolysis temperature and catalyst loading resulted in a decrease of the

360　catalyst activity[29]. However, the effects of acid-leaching pretreatment were still clear in

361　CFP experiments at 450 °C (Table 2). CFP of ALwood at 450 °C resulted in a higher yield

362　of upgraded bio-oil compared to Rwood (i.e. 12 wt.% cf. 10 wt.%). The AL450L bio-oil

363   had a lower carbon and higher oxygen content than the R450L bio-oil, with relatively lower

364   proportions of aromatic hydrocarbons. These experiments at 450 °C supported the finding

365   that acid-leaching prior to CFP leads to a bio-oil product that is less deoxygenated.

366   At 360 °C, the pyrolysis and catalysis conditions were far from optimal. Pyrolysis of the

367   biomass is incomplete[26] and the HZSM-5 catalyst is considerably less active[29]. CFP of

368   ALwood at 360 °C was investigated despite these disadvantages because: i) bed material

369   agglomeration was completely mitigated[26] and ii) acid leaching substantially increased

370   organic oil yield at this temperature in non-catalytic fast pyrolysis[31]. CFP of ALwood at

371   360 °C gave a 11 wt.% yield of upgraded bio-oil compared to 8 wt.% for Rwood. The

372   AL350L bio-oil had an oxygen to carbon ratio of 0.27 compared to 0.22 for the R360L bio-

373   oil, indicating it was less deoxygenated (Table 2). GC/MS analysis of the AL360L bio-oil

374   showed higher relative proportions of guaiacols, phenols, ketones and furans compared

375   to the R360L bio-oil. Correspondingly, the relative proportion of aromatic hydrocarbons

376   was lower. In addition, there was a further 8 wt.% of organics in the aqueous phase that

377   had not been sufficiently upgraded to pass into the oil-phase.

378   *3.3.3. Discussion of effect of acid-leaching pretreatment on CFP.* Acid-leaching

379   pretreatment prior to CFP improved the yield of upgraded bio-oil compared to raw wood,

380   but only at carefully controlled conditions to simultaneously prevent bed agglomeration

381   and avoid excess catalyst loading. In non-catalytic fast pyrolysis, acid leaching

382   pretreatment is known to increase the production of levoglucosan[25]. However,

383   levoglucosan is firstly converted to furans which can then be further converted to

384   aromatics during zeolite upgrading. Alternately, the furans can polymerize and

385   decompose to form coke[44]. Possibly, coke formation is favored over the production of

386   aromatic hydrocarbons at high catalyst loadings (i.e. experiment AL500H). With ALwood

387   known to produce less char than raw wood in non-catalytic fast pyrolysis[26, 33], the

388   observation that ALwood and Rwood gave the same yield of combined char/coke (Table

389   2) is consistent with the production of more coke from the ALwood.

390   The experimental results in Table 2 also indicated acid-leaching pretreatment mildly

391   suppressed the deoxygenation degree in catalytic fast pyrolysis. Zeolite upgrading

392   removes oxygen from the pyrolysis vapors by dehydration, decarbonylation and

393   decarboxylation to form water, carbon monoxide and carbon dioxide, respectively[28].

394 Decarboxylation is the most favored pathway as it consumes the least carbon and no

395 hydrogen. The decreased CO_2 and increased CO production as a result of the acid-

396 leaching pretreatment (Table 2), is therefore undesirable and is likely to be a contributing

397 factor in the less deoxygenated bio-oil obtained from CFP of acid-leached wood.

398 **3.4. Catalytic fast pyrolysis of torrefied wood.** *3.4.1. Catalytic fast pyrolysis products.*

399 Catalytic fast pyrolysis experiments with torrefied wood were conducted at 500 °C using

400 C/B ratios of 2.5, 4 and 6 (Table 3). CFP of torrefied wood at 500 °C did not result in bed

401 material agglomeration as was encountered with acid-leached wood. The results were

402 compared with results from Rwood obtained under the same experimental conditions.

403 Product yields for the Twood in Table 3 are reported on dry torrefied wood basis and dry

404 raw wood basis (in parentheses) corrected for the 17 wt.% mass loss that occurred on

405 torrefaction. In these experiments, the aqueous-phase liquids were all >99% water and

406 so contained very little, if any, aqueous-phase organics. ^{1}H NMR analysis results of

407 aqueous phase products are available in the Supporting Information (Table S3).

408 Firstly, the results of CFP of Twood and Rwood at 500 °C and a C/B ratio of 2.5 were

409 compared (i.e. experiments T500L and R500L). This comparison showed that the

410 torrefaction pretreatment resulted in an improved yield of upgraded bio-oil (13 wt.% cf.

411 8.5 wt.% when calculated on a torrefied wood basis). Taking into account the mass loss

412 that occurred on torrefaction pretreatment, the upgraded bio-oil yield was still 2% higher

413 than that achieved with Rwood (Table 3). The torrefied wood also gave a substantially

414 lower yield of produced water, an increased yield of combined char/coke, and similar

415 yields of CO and CO_2 compared to Rwood (Table 3). It has been previously reported that

416 torrefaction pretreatment promotes catechols in non-catalytic fast pyrolysis.[29] These

417 molecules may contribute to the increased yield of upgraded bio-oil as they can be easily

418 converted to aromatic hydrocarbons in zeolite upgrading.

419 The torrefaction pretreatment altered the composition of the wood, resulting in less

420 hemicelluloses and a lower overall oxygen content in the Twood compared to Rwood (i.e.

421 39 *vs.* 43 wt.%). Thermal degradation of the hemicellulose during torrefaction was the

422 main cause of the observed 17 wt.% mass loss and the resultant lower oxygen content.

423 This is consistent with reported evolution of water, CO and CO_2 during torrefaction[18, 22].

424 These chemical changes had contributed to the lower levels of water produced on CFP

425 of Twood.

426   The upgraded bio-oil produced in the T500L and R500L experiments had similar carbon

427   and oxygen contents (Table 3). GC/MS analysis confirmed that the T500L and R500L

428   upgraded bio-oils had very similar chemical compositions (Table 3). This confirmed that

429   the torrefaction pretreatment, under these conditions, only improved the yield of the

430   upgraded CFP bio-oil and did not impact on its quality.

431   Catalytic fast pyrolysis of Twood at the higher C/B ratios of 4 and 6 resulted in the yield

432   of upgraded bio-oil decreasing from 13 wt.% to 8 wt.% (Table 3). These bio-oil yields were

433   slightly lower than those achieved with Rwood under the same conditions, when corrected

434   for the mass loss on torrefaction (Table 3). Conversely, more combined char/coke was

435   produced using higher C/B ratios (Table 3). The yields of water and non-condensable

436   gases were largely unchanged. Higher C/B ratios have been reported to lead to more

437   coke formation in CFP[15]. Hence, it is likely the higher C/B ratio led to a higher coke yield

438   at the expense of upgraded bio-oil. The upgraded bio-oil produced with a C/B ratio of 6

439   appeared to contain a slightly higher proportion of aromatic hydrocarbons and a slightly

440   lower proportion of oxygenated species than the corresponding bio-oil produced with a

441   C/B ratio of 2.5.

442   *3.4.2. Discussion of effects of torrefaction pretreatment on CFP.* Catalytic fast pyrolysis

443   of torrefied wood, using the lower C/B ratio, gave a higher yield of a similarly-upgraded

444   bio-oil compared to raw wood. In our previous study, non-catalytic fast pyrolysis of the

445   same torrefied wood gave a lower yield of a bio-oil that contained a higher carbon content

446   compared to raw wood[26]. These two results suggest that the pyrolysis vapors produced

447   from torrefied wood were more amenable to zeolite upgrading to oil-phase organics (i.e.

448   mainly aromatic hydrocarbons). Under the right conditions, this resulted in a higher yield

449   of upgraded bio-oil.

450   Several studies provide evidence in support of this conclusion. Analytical pyrolysis

451   studies have indicated that torrefaction pretreatment produces pyrolysis vapors which are

452   enriched in lignin-derived molecules[18, 45]. This is believed to be partly because the

453   torrefied wood contains more lignin and partly because torrefaction can cleave aryl ether

454   linkages in the lignin to promote volatilization[18, 45]. In the presence of HZSM-5 catalyst,

455   these lignin-derived compounds are upgraded to aromatic hydrocarbons[18, 29].

456   Torrefaction pretreatment of organosolv lignin promotes the production of aromatic

457   hydrocarbons in CFP[35]. Several other studies using pyroprobe or fixed bed reactors have

458   reported mild torrefaction pretreatments to have positive effects on the aromatic yield,

459   total carbon yield or the selectivity for aromatic hydrocarbons in CFP[18, 34, 46].

460   **3.5. Catalytic fast pyrolysis of acid-leached and torrefied wood.** *3.5.1 Catalytic fast*

461   *pyrolysis products.* Acid-leached and torrefied wood was pyrolysed at 500 °C using a C/B

462   ratio of 2.5 (experiment ALT500L). Unlike acid-leached wood, this CFP experiment was

463   successfully carried out in the reactor without encountering bed material agglomeration.

464   We have previously reported a similar result for non-catalytic fast pyrolysis and proposed

465   that the torrefaction pretreatment induced chemical changes in the lignin which ultimately

466   prevented bed material agglomeration from occurring[26]. CFP of ALTwood was also

467   successfully carried out at 500 °C using C/B ratios of 4 and 6 (experiments ALT500M and

468   ALT500H), with the results provided in Table 4.

469   Product yields are reported on the basis of dry torrefied-acid-leached wood in Table 4.

470   Yields on dry raw wood basis, corrected for the mass loss (14 wt.%) that occurred on

471   torrefaction, are also provided in parentheses. The mass loss on torrefaction of acid-

472   leached wood was less than that on torrefaction of raw wood (i.e. 17 wt.%). This was due

473   to less thermal degradation of the hemicelluloses[26], possibly due to removal of AAEMs

474   that catalysed this process. The aqueous-phase liquids from these experiments were

475   all >99% water. ^{1}H NMR analysis results of aqueous phase products are available in the

476   Supporting Information (Table S3).

477   Comparing the results of CFP of ALTwood and Rwood at 500 °C and a C/B ratio of 2.5

478   (i.e. experiments ALT500L and R500L) shows the combined pretreatment resulted in an

479   improved yield of upgraded bio-oil (10 wt.% cf. 8 wt.% calculated on an ALTwood basis).

480   The yield of upgraded bio-oil was 1% higher than that achieved with Rwood when

481   corrected for the mass loss on torrefaction (Table 4). CFP of the ALTwood gave a

482   substantially lower yield of produced water and increased yield of combined char/coke

483   compared to Rwood (Table 4), consistent with the Twood results. The yield of CO_2 from

484   CFP of ALTwood was lower than that from Rwood, which was consistent with the ALwood

485   results (Tables 2 and 4).

486   Elemental and GC/MS analysis of the upgraded bio-oil from ALTwood showed that the

487   bio-oil had the same carbon and oxygen contents, and a very similar composition of GC-

488   volatile chemicals, as the Rwood upgraded bio-oil (Table 4). Hence, the combined

489   pretreatment did not lead to less deoxygenation of the upgraded bio-oil as was found with

490   the acid-leaching pretreatment (Table 2).

491   Catalytic fast pyrolysis of ALTwood at the higher C/B ratios of 4 and 6 resulted in the

492   yield of upgraded bio-oil decreasing from 10 wt.% to 7 wt.%, and the yield of combined

493   char/coke increasing from 29 wt.% to 37 wt.% (Table 4). These trends were consistent

494   with the results for CFP of Twood (Table 3). The compositions of the upgraded bio-oil

495   produced from ALTwood using the three different C/B ratios were all very similar (Table

496   4). Hence, using excess catalyst in CFP of ALTwood did not improve bio-oil quality and

497   likely led to more coke formation.

498   *3.5.2. Discussion of effects of the combined pretreatment on CFP.* Applying a

499   torrefaction pretreatment to acid-leached wood resulted in an improvement in the yield of

500   upgraded bio-oil in CFP compared to raw wood, and also mitigated the problem of bed

501   material agglomeration. The degree of deoxygenation of the upgraded bio-oils was the

502   same for ALTwood and Rwood. This indicated the torrefaction pretreatment negated the

503   adverse effect that acid-leaching had on deoxygenation levels. Non-catalytic fast

504   pyrolysis of the same ALTwood produced a lower yield of bio-oil compared to raw wood[26].

505 Hence, the pyrolysis vapors from ALTwood were more selectively upgraded by the zeolite

506 to aromatic hydrocarbons and this resulted in an increase in upgraded bio-oil yield. These

507 findings are consistent with a previous Py-GCMS study on CFP of acid-leached and

508 torrefied lignocellulosic rice husks[41]. They reported that the combined pretreatment

509 improved the relative contents of benzene, toluene, xylene in the GC-volatile products

510 compared to raw rice husks.

511   Overall, this combined pretreatment can improve upgraded bio-oil yield in catalytic fast

512 pyrolysis with the benefits of biomass demineralization. Recently promising results have

513 been reported to use metal oxides as the catalysts for bio-oil upgrading [2, 47]. Biomass

514 minerals can poison these catalysts by fouling on catalyst surface. Combined acid-

515 leaching and torrefaction overcomes many of the problems associated with acid-leaching

516 alone, while still removing biomass minerals that can shorten catalyst lifespans. This

517 combined pretreatment offers a promising approach to improving *in situ* catalytic fast

518 pyrolysis process.

519   **4. CONCLUSION**

520   The effects of acid-leaching and torrefaction pretreatments on the products of *in situ*

521   catalytic fast pyrolysis of pine wood were investigated in this study. Acid-leaching

522   pretreatment caused bed agglomeration in a fluidized bed reactor. It also resulted in a

523   reduced level of deoxygenation in the upgraded bio-oil product. Torrefaction pretreatment

524   resulted in small improvements in the yield of upgraded bio-oil at a low catalyst loading,

525   and it hardly changed the chemical composition of upgraded oil. Torrefaction of acid-

526   leached wood was effective in mitigating the adverse effects from acid-leaching

527   pretreatment alone. Bed material agglomeration was overcome and the degree of

528   deoxygenation of upgraded bio-oil was improved when combining acid-leaching and

529   torrefaction. This combined pretreatment is promising to improve *in situ* catalytic fast

530   pyrolysis process from a technical viewpoint. It is necessary to validate the economic

531   feasibility considering the extra biomass pretreating step that increases cost to the whole

532   process.

533   **ASSOCIATED CONTENT**

534   **Supporting Information**

535   **Figure S1.** Representative GC/MS chromatograms of upgraded bio-oils.

536   **Table S1.** Elemental composition, trace elements and biomass chemical composition of

537   pretreated biomass feedstocks.

538   **Table S2.** GC/MS analysis results of upgraded bio-oils (peak area percentage of total

539   identified peak area).

540   **Table S3.** ^{1}H NMR analysis results of aqueous phase products (% of all hydrogens).

541   **AUTHOR INFORMATION**

542   **Corresponding Author**

543   *Telephone: + 64 9 923 1424. Fax: 0800 61 62 64. E-mail: x.xin@auckland.ac.nz

544   **Notes**

545   The authors declare no competing financial interest.

551 **NOMENCLATURE**

552 AAEMs = alkali and alkali earth metals

553 ALwood = acid-leached wood

554 AL500L = CFP experiment of ALwood at 500 °C with C/B ratio of 2.5

555 AL500M = CFP experiment of ALwood at 500 °C with C/B ratio of 4

556 AL500H = CFP experiment of ALwood at 500 °C with C/B ratio of 6

557 AL450L = CFP experiment of ALwood at 450 °C with C/B ratio of 2.5

558 AL360L = CFP experiment of ALwood at 360 °C with C/B ratio of 2.5

559 ALTwood = acid-leached and torrefied wood

560 ALT500L = CFP experiment of ALTwood at 500 °C with C/B ratio of 2.5

561 ALT500M = CFP experiment of ALTwood at 500 °C with C/B ratio of 4

562 ALT500H = CFP experiment of ALTwood at 500 °C with C/B ratio of 6

563 C/B ratio = catalyst to biomass ratio

564 CFP = catalytic fast pyrolysis

565 ESP = electrostatic precipitator

566 GC = gas chromatography

567   GC/MS = gas chromatography/mass spectrometry

568   GPC = gel permeation chromatography

569   IC = intensive cooling

570   Rwood = raw wood without pretreatment

571   R500L = CFP experiment of raw wood at 500 °C with C/B ratio of 2.5

572   R500M = CFP experiment of raw wood at 500 °C with C/B ratio of 4

573   R500H = CFP experiment of raw wood at 500 °C with C/B ratio of 6

574   R450L = CFP experiment of raw wood at 450 °C with C/B ratio of 2.5

575   R360L = CFP experiment of raw wood at 360 °C with C/B ratio of 2.5

576   SEM = scanning electron microscopy

577   Stdev = standard deviation

578   Twood = torrefied wood

579   T500L = CFP experiment of Twood at 500 °C with C/B ratio of 2.5

580   T500M = CFP experiment of Twood at 500 °C with C/B ratio of 4

581   T500H = CFP experiment of Twood at 500 °C with C/B ratio of 6

582   **REFERENCES**

583 (1) Huber, G. W.; Iborra, S.; Corma, A., Synthesis of Transportation Fuels from

584 Biomass: Chemistry, Catalysts, and Engineering. *Chem. Rev.* **2006,** 106, (9), 4044-

585 4098.

586 (2) Liu, C.; Wang, H.; Karim, A. M.; Sun, J.; Wang, Y., Catalytic fast pyrolysis of

587 lignocellulosic biomass. *Chemical Society Reviews* **2014,** 43, (22), 7594-7623.

588 (3) Mihalcik, D. J.; Mullen, C. A.; Boateng, A. A., Screening acidic zeolites for catalytic

589 fast pyrolysis of biomass and its components. *Journal of Analytical and Applied*

590 *Pyrolysis* **2011,** 92, (1), 224-232.

591 (4) Yang, H.; Coolman, R.; Karanjkar, P.; Wang, H.; Dornath, P.; Chen, H.; Fan, W.;

592 Conner, W. C.; Mountziaris, T.; Huber, G., The effects of contact time and coking on the

593 catalytic fast pyrolysis of cellulose. *Green Chemistry* **2017,** 19, (1), 286-297.

594 (5) Dickerson, T.; Soria, J., Catalytic Fast Pyrolysis: A Review. *Energies* **2013,** 6, (1),

595 514-538.

596 (6) Zhang, H.; Shao, S.; Xiao, R.; Shen, D.; Zeng, J., Characterization of coke

597 deposition in the catalytic fast pyrolysis of biomass derivates. *Energy Fuels* **2013,** 28,

598 (1), 52-57.

599   (7) Williams, P. T.; Nugranad, N., Comparison of products from the pyrolysis and

600   catalytic pyrolysis of rice husks. *Energy* **2000,** 25, (6), 493-513.

601   (8) Aho, A.; Kumar, N.; Eränen, K.; Salmi, T.; Hupa, M.; Murzin, D. Y., Catalytic

602   pyrolysis of woody biomass in a fluidized bed reactor: Influence of the zeolite structure.

603   *Fuel* **2008,** 87, (12), 2493-2501.

604   (9) Yildiz, G.; Ronsse, F.; van Duren, R.; Prins, W., Challenges in the design and

605   operation of processes for catalytic fast pyrolysis of woody biomass. *Renewable and*

606   *Sustainable Energy Reviews* **2016,** 57, 1596-1610.

607   (10) Vasalos, I.; Lappas, A.; Kopalidou, E.; Kalogiannis, K., Biomass catalytic pyrolysis:

608   process design and economic analysis. *Wiley Interdisciplinary Reviews: Energy and*

609   *Environment* **2016,** 5, (3), 370-383.

610   (11) Cerqueira, H.; Caeiro, G.; Costa, L.; Ribeiro, F. R., Deactivation of FCC catalysts.

611   *Journal of Molecular Catalysis A: Chemical* **2008,** 292, (1), 1-13.

612   (12) Vitolo, S.; Bresci, B.; Seggiani, M.; Gallo, M., Catalytic upgrading of pyrolytic oils

613   over HZSM-5 zeolite: behaviour of the catalyst when used in repeated upgrading–

614   regenerating cycles. *Fuel* **2001,** 80, (1), 17-26.

615   (13) Paasikallio, V.; Lindfors, C.; Kuoppala, E.; Solantausta, Y.; Oasmaa, A.; Lehto, J.;

616   Lehtonen, J., Product quality and catalyst deactivation in a four day catalytic fast

617   pyrolysis production run. *Green Chemistry* **2014,** 16, (7), 3549-3559.

618   (14) Mullen, C. A.; Boateng, A. A., Accumulation of Inorganic Impurities on HZSM-5

619   Zeolites during Catalytic Fast Pyrolysis of Switchgrass. *Industrial & Engineering*

620   *Chemistry Research* **2013,** 52, (48), 17156-17161.

621   (15) Jae, J.; Coolman, R.; Mountziaris, T. J.; Huber, G. W., Catalytic fast pyrolysis of

622   lignocellulosic biomass in a process development unit with continual catalyst addition

623   and removal. *Chemical Engineering Science* **2014,** 108, 33-46.

624   (16) Wang, K.; Zhang, J.; Shanks, B. H.; Brown, R. C., The deleterious effect of

625   inorganic salts on hydrocarbon yields from catalytic pyrolysis of lignocellulosic biomass

626   and its mitigation. *Applied energy* **2015,** 148, 115-120.

627   (17) Carpenter, D.; Westover, T. L.; Czernik, S.; Jablonski, W., Biomass feedstocks for

628   renewable fuel production: a review of the impacts of feedstock and pretreatment on the

629   yield and product distribution of fast pyrolysis bio-oils and vapors. *Green Chemistry*

630   **2014,** 16, (2), 384-406.

631   (18) Neupane, S.; Adhikari, S.; Wang, Z.; Ragauskas, A. J.; Pu, Y., Effect of torrefaction

632   on biomass structure and hydrocarbon production from fast pyrolysis. *Green Chemistry*

633   **2015,** 17, (4), 2406-2417.

634   (19) Zheng, A.; Jiang, L.; Zhao, Z.; Huang, Z.; Zhao, K.; Wei, G.; Wang, X.; He, F.; Li,

635   H., Impact of Torrefaction on the Chemical Structure and Catalytic Fast Pyrolysis

636   Behavior of Hemicellulose, Lignin, and Cellulose. *Energy & Fuels* **2015,** 29, (12), 8027-

637   8034.

638   (20) Qiao, X.; Zhao, C.; Shao, Q.; Hassan, M. J. E.; fuels, Structural characterization of

639   corn stover lignin after hydrogen peroxide presoaking prior to ammonia fiber expansion

640   pretreatment. **2018,** 32, (5), 6022-6030.

641   (21) Zhao, C.; Qiao, X.; Cao, Y.; Shao, Q. J. F., Application of hydrogen peroxide

642   presoaking prior to ammonia fiber expansion pretreatment of energy crops. **2017,** 205,

643   184-191.

644   (22) Wigley, T.; Yip, A. C. K.; Pang, S., The use of demineralisation and torrefaction to

645   improve the properties of biomass intended as a feedstock for fast pyrolysis. *Journal of*

646   *Analytical and Applied Pyrolysis* **2015,** 113, 296-306.

41

647   (23) Saha, B. C.; Qureshi, N.; Kennedy, G. J.; Cotta, M. A. J. I. B.; Biodegradation,

648   Biological pretreatment of corn stover with white-rot fungus for improved enzymatic

649   hydrolysis. **2016,** 109, 29-35.

650   (24) Yang, X.; Zeng, Y.; Ma, F.; Zhang, X.; Yu, H. J. B. t., Effect of biopretreatment on

651   thermogravimetric and chemical characteristics of corn stover by different white-rot

652   fungi. **2010,** 101, (14), 5475-5479.

653   (25) Oudenhoven, S. R. G.; Westerhof, R. J. M.; Kersten, S. R. A., Fast pyrolysis of

654   organic acid leached wood, straw, hay and bagasse: Improved oil and sugar yields.

655   *Journal of Analytical and Applied Pyrolysis* **2015,** 116, 253-262.

656   (26) Xin, X.; Torr, K. M.; De Miguel Mercader, F.; Pang, S., Insights into Preventing

657   Fluidized Bed Material Agglomeration in Fast Pyrolysis of Acid-leached Pine Wood.

658   *Energy & Fuels* 2019, 33, (5), 4254-4263.

659   (27) Yildiz, G.; Ronsse, F.; Venderbosch, R.; van Duren, R.; Kersten, S. R.; Prins, W.,

660   Effect of biomass ash in catalytic fast pyrolysis of pine wood. *Applied Catalysis B:*

661   *Environmental* **2015,** 168, 203-211.

662   (28) Hernando, H.; Jiménez-Sánchez, S.; Fermoso, J.; Pizarro, P.; Coronado, J.;

663   Serrano, D., Assessing biomass catalytic pyrolysis in terms of deoxygenation pathways

664   and energy yields for the efficient production of advanced biofuels. *Catalysis Science &*

665   *Technology* **2016,** 6, (8), 2829-2843.

666   (29) Xin, X.; Pang, S.; de Miguel Mercader, F.; Torr, K. M., The effect of biomass

667   pretreatment on catalytic pyrolysis products of pine wood by Py-GC/MS and principal

668   component analysis. *Journal of Analytical and Applied Pyrolysis* **2019,** 138, 145-153.

669   (30) Persson, H.; Yang, W. J. F., Catalytic pyrolysis of demineralized lignocellulosic

670   biomass. **2019,** 252, 200-209.

671   (31) Oudenhoven, S. R. G.; Lievens, C.; Westerhof, R. J. M.; Kersten, S. R. A., Effect of

672   temperature on the fast pyrolysis of organic-acid leached pinewood; the potential of low

673   temperature pyrolysis. *Biomass and Bioenergy* **2016,** 89, 78-90.

674   (32) Persson, H.; Han, T.; Sandström, L.; Xia, W.; Evangelopoulos, P.; Yang, W. J. E.,

675   Fractionation of liquid products from pyrolysis of lignocellulosic biomass by stepwise

676   thermal treatment. **2018,** 154, 346-351.

677 (33) Wigley, T.; Yip, A. C. K.; Pang, S., Pretreating biomass via demineralisation and

678 torrefaction to improve the quality of crude pyrolysis oil. *Energy* **2016,** 109, 481-494.

679 (34) Zheng, A.; Zhao, Z.; Huang, Z.; Zhao, K.; Wei, G.; Wang, X.; He, F.; Li, H.,

680 Catalytic Fast Pyrolysis of Biomass Pretreated by Torrefaction with Varying Severity.

681 *Energy & Fuels* **2014,** 28, (9), 5804-5811.

682 (35) Adhikari, S.; Srinivasan, V.; Fasina, O., Catalytic pyrolysis of raw and thermally

683 treated lignin using different acidic zeolites. *Energy & Fuels* **2014,** 28, (7), 4532-4538.

684 (36) Srinivasan, V.; Adhikari, S.; Chattanathan, S. A.; Tu, M.; Park, S., Catalytic

685 pyrolysis of raw and thermally treated cellulose using different acidic zeolites. *BioEnergy*

686 *Research* **2014,** 7, (3), 867-875.

687 (37) Mahadevan, R.; Adhikari, S.; Shakya, R.; Wang, K.; Dayton, D. C.; Li, M.; Pu, Y.;

688 Ragauskas, A. J., Effect of torrefaction temperature on lignin macromolecule and

689 product distribution from HZSM-5 catalytic pyrolysis. *Journal of Analytical and Applied*

690 *Pyrolysis* **2016,** 122, 95-105.

691   (38) Wigley, T.; Yip, A. C.; Pang, S., A detailed product analysis of bio-oil from fast

692   pyrolysis of demineralised and torrefied biomass. *Journal of Analytical and Applied*

693   *Pyrolysis* **2017,** 123, 194-203.

694   (39) Zeng, K.; He, X.; Yang, H.; Wang, X.; Chen, H., The effect of combined

695   pretreatments on the pyrolysis of corn stalk. *Bioresour. Technol.* **2019,** 281, 309-317.

696   (40) Chen, D.; Mei, J.; Li, H.; Li, Y.; Lu, M.; Ma, T.; Ma, Z., Combined pretreatment with

697   torrefaction and washing using torrefaction liquid products to yield upgraded biomass

698   and pyrolysis products. *Bioresour. Technol.* **2017,** 228, 62-68.

699   (41) Zhang, S.; Zhu, S.; Zhang, H.; Chen, T.; Xiong, Y., Catalytic fast pyrolysis of rice

700   husk: Effect of coupling leaching with torrefaction pretreatment. *J. Anal. Appl. Pyrolysis*

701   **2018,** 133, 91-96.

702   (42) Oudenhoven, S. R. G.; Westerhof, R. J. M.; Aldenkamp, N.; Brilman, D. W. F.;

703   Kersten, S. R. A., Demineralization of wood using wood-derived acid: Towards a

704   selective pyrolysis process for fuel and chemicals production. *Journal of Analytical and*

705   *Applied Pyrolysis* **2013,** 103, 112-118.

706 (43) Mullen, C. A.; Strahan, G. D.; Boateng, A. A., Characterization of various fast-

707 pyrolysis bio-oils by NMR spectroscopy†. *Energy & Fuels* **2009,** 23, (5), 2707-2718.

708 (44) Carlson, T. R.; Jae, J.; Lin, Y.-C.; Tompsett, G. A.; Huber, G. W., Catalytic fast

709 pyrolysis of glucose with HZSM-5: the combined homogeneous and heterogeneous

710 reactions. *Journal of Catalysis* **2010,** 270, (1), 110-124.

711 (45) Meng, J.; Park, J.; Tilotta, D.; Park, S., The effect of torrefaction on the chemistry of

712 fast-pyrolysis bio-oil. *Bioresource Technology* **2012,** 111, 439-446.

713 (46) Srinivasan, V.; Adhikari, S.; Chattanathan, S. A.; Park, S., Catalytic Pyrolysis of

714 Torrefied Biomass for Hydrocarbons Production. *Energy & Fuels* **2012,** 26, (12), 7347-

715 7353.

716 (47) Griffin, M. B.; Iisa, K.; Wang, H.; Dutta, A.; Orton, K. A.; French, R. J.; Santosa, D.

717 M.; Wilson, N.; Christensen, E.; Nash, C., Driving towards cost-competitive biofuels

718 through catalytic fast pyrolysis by rethinking catalyst selection and reactor configuration.

719 *Energy Environ. Sci.* **2018,** 11, (10), 2904-2918.

720

721

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
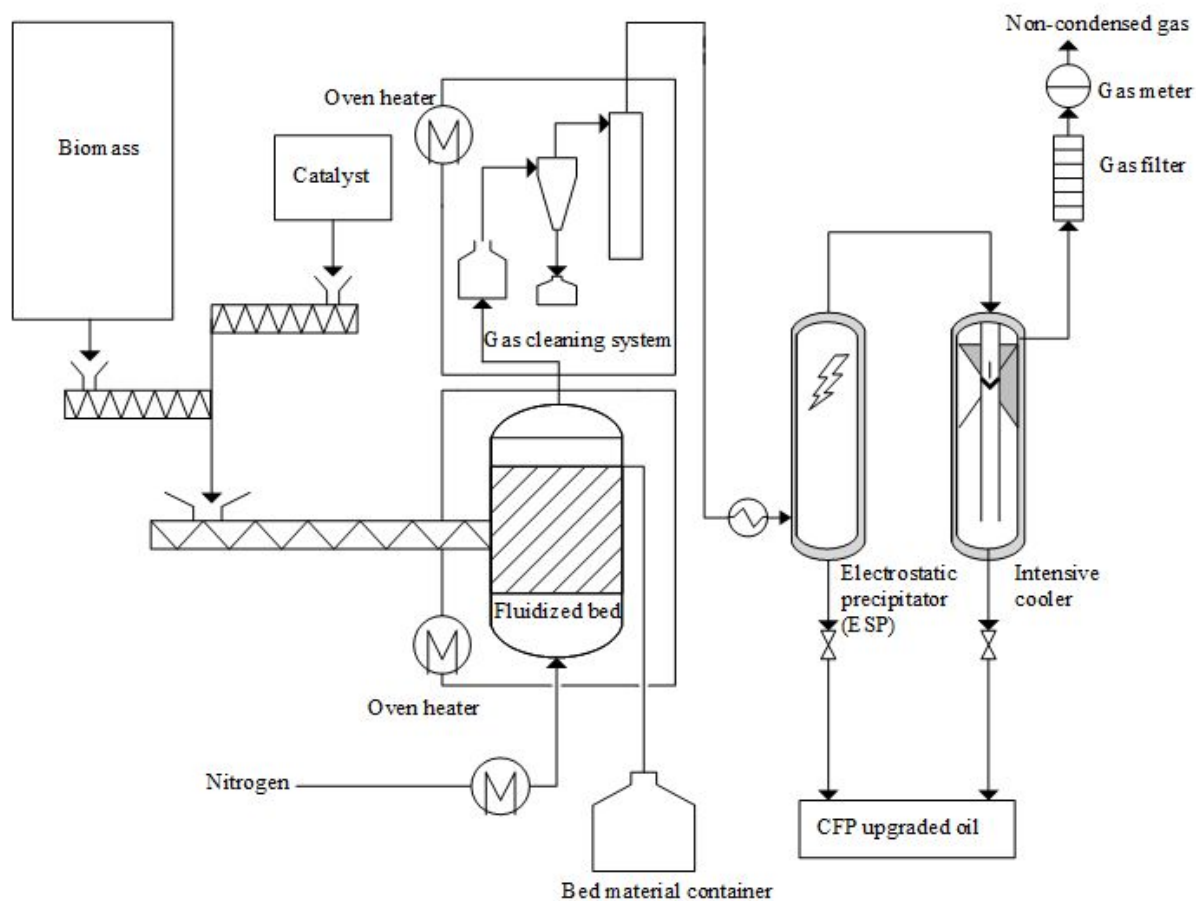
722

723 **Figure 1.** Schematic diagram of the bubbling fluidized bed reactor system.

724

Figure 2. SEM images of char products mixed with used catalyst collected from catalytic

fast pyrolysis experiments, AL360L (A), AL450L (B) and AL500L (C).

729 **Table 1.** A summary of catalytic fast pyrolysis experiments.

Wood sample	Code	Temperature (°C)	C/B ratio	Bed agglomeration
Rwood	R500L*	500	2.5	false
	R500M	500	4	false
	R500H	500	6	false
	R450L	450	2.5	false
	R360L	360	2.5	false
ALwood	AL500L	500	2.5	true
	AL500M	500	4	true
	AL500H	500	6	false
	AL450L	450	2.5	false
	AL360L	360	2.5	false
Twood	T500L	500	2.5	false
	T500M	500	4	false
	T500H	500	6	false
ALTwood	ALT500L	500	2.5	false
	ALT500M	500	4	false
	ALT500H	500	6	false

730 *Reproducibility.

731   **Table 2.** Experimental results from catalytic fast pyrolysis of ALwood and Rwood.

	AL500H	R500H	AL450L	R450L	AL360L	R360L
Biomass	ALwood	Rwood	ALwood	Rwood	ALwood	Rwood
Temperature, °C	500	500	450	450	360	360
C/B ratio, wt/wt	6	6	2.5	2.5	2.5	2.5
Product yield, wt.% [a, b]						
Upgraded bio-oil	9	9	12	10	11	8
Aqueous-phase organics	<1	<1	2	1	8	4
Produced water	23	21	24	23	18	21
Char/coke [c]	29	29	27	27	37	43
CO	27	22	21	20	11	13
CO_2	7	13	10	12	6	8
CH_4	1	1	1	1	0.2	0
C_2H_4	1	2	1	1	0.1	0.3
C_3H_6	1	2	1	2	0.3	0.4
Elemental composition of upgraded bio-oil , wt.% [d]						
C	77.8 ± 1.2	81.5 ± 1.3	74.2 ± 0.7	76.6 ± 1.4	69.2 ± 1.0	71.9 ± 0.6
H	6.6 ± 0.2	7.0 ± 0.04	6.4 ± 0.1	6.6 ± 0.3	6.3 ± 0.3	6.6 ± 0.02
O	16	12	19	17	25	22
O/C (mol/mol)	0.15	0.11	0.20	0.16	0.27	0.22
GC/MS results of upgraded bio-oil, peak area % [e]						
Aromatics	73 ± 0.2	80 ± 0.0	69 ± 0.1	73 ± 0.1	38 ± 0.0	53 ± 0.2
Phenols	15 ± 0.1	12 ± 0.0	16 ± 0.0	14 ± 0.0	14 ± 0.1	11 ± 0.1
Oxygenated aromatics	10 ± 0.1	8 ± 0.0	11 ± 0.1	11 ± 0.1	15 ± 0.1	14 ± 0.1
Guaiacols	0.2 ± 0.0	0.2 ± 0.0	1.2 ± 0.0	0.7 ± 0.0	17 ± 0.1	12 ± 0.0
Ketones	0.7 ± 0.0	0.3 ± 0.0	2 ± 0.0	0.8 ± 0.0	10 ± 0.1	7 ± 0.1
Furans	0.4 ± 0.0	0.3 ± 0.0	0.5 ± 0.0	0.5 ± 0.0	5 ± 0.0	1 ± 0.0
Catechols	0.1 ± 0.0	0 ± 0.0	0.9 ± 0.0	0.4 ± 0.0	2 ± 0.0	2 ± 0.0

732   [a] Dry raw wood basis; [b] The yields of H_2, C_2H_6 and C_3H_8 were $\leq$ 0.1, 0.3 and 0.3 wt.%, respectively; [c] The

733   yields of char and coke are reported together; [d] Average values of triplicate analyses calculated on dry

734   basis $\pm$ one standard deviation, oxygen content calculated by difference to 2 significant figures; [e] Average

735   values of duplicate analyses $\pm$ one standard deviation, details are shown in Supporting Information (Table

736   S2).

737 **Table 3.** Experimental results from catalytic fast pyrolysis of Twood and Rwood.

	T500L	R500L	T500M	R500M	T500H	R500H[a]
Biomass	Twood	Rwood	Twood	Rwood	Twood	Rwood
Temperature, °C	500	500	500	500	500	500
C/B ratio, wt/wt	2.5	2.5	4	4	6	6
Product yield, wt.% [b, c]						
Upgraded bio-oil	13 (11)	8.5 ± 0.2	8 (7)	8	8 (7)	9
Produced water	16 (13)	22.8 ± 0.9	17 (14)	23	16 (13)	21
Char/coke [d]	32 (27)	24.0 ± 0.2	34 (28)	25	40 (33)	29
CO	20 (17)	21.6 ± 0.4	20 (17)	20	20 (17)	22
CO_2	11 (9)	12.0 ± 0.2	11 (7)	12	10 (8)	13
CH_4	1	1.1 ± 0.03	1	1	1	1
C_2H_4	2	1.6 ± 0.02	2	2	2	2
C_3H_6	2	1.8 ± 0.06	2	2	2	2
Elemental composition of upgraded bio-oil, wt.% [e]						
C	78.4 ± 1.4	79.8 ± 1.0	80.0 ± 0.6	80.6 ± 1.1	79.6 ± 1.1	81.5 ± 1.3
H	6.7 ± 0.3	7.0 ± 0.3	6.6 ± 0.3	7.0 ± 0.2	6.8 ± 0.4	7.0 ± 0.04
O	15	13	13	12	14	12
O/C (mol/mol)	0.14	0.12	0.13	0.12	0.13	0.11
GC/MS results of upgraded bio-oil, peak area % [f]						
Aromatics	77 ± 0.1	76 ± 0.9	75 ± 0.2	79 ± 0.1	78 ± 0.1	80 ± 0.0
Phenols	13 ± 0.2	13 ± 0.3	15 ± 0.0	11 ± 0.1	13 ± 0.1	12 ± 0.0
Oxygenated aromatics	9 ± 0.1	10 ± 0.2	8 ± 0.1	9 ± 0.0	7 ± 0.0	8 ± 0.0
Guaiacols	0.6 ± 0.0	0.2 ± 0.0	0.6 ± 0.0	0.2 ± 0.0	0.4 ± 0.0	0.2 ± 0.0
Ketones	0.5 ± 0.0	0.3 ± 0.0	0.4 ± 0.0	0.2 ± 0.0	0.4 ± 0.0	0.3 ± 0.0
Furans	0.2 ± 0.0	0.2 ± 0.0	0.3 ± 0.0	0.2 ± 0.0	0.2 ± 0.0	0.3 ± 0.0
Catechols	0.3 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0 ± 0.0	0.1 ± 0.0	0 ± 0.0

738 [a] Included from Table 2 for ease of comparison; [b] Reported on dry torrefied wood basis with corrected

739 yields on dry raw wood in parentheses; Product yields were reported ± one standard deviation for the

740 three R500L experiments; [c] The yields of H_2, C_2H_6 and C_3H_8 were ≤ 0.1, 0.3 and 0.3 wt.%, respectively; [d]

741 The yields of char and coke were reported together; [e] Average values of triplicate analyses calculated on

742 dry basis ± one standard deviation, oxygen calculated by difference to 2 significant figures; [f] Average

743 values of duplicate analyses ± one standard deviation, details are shown in Supporting Information (Table

744 S2).

745   **Table 4.** Experimental results from catalytic fast pyrolysis of ALTwood.

	ALT500L	R500L[a]	ALT500M	ALT500H
Biomass	ALTwood	Rwood	ALTwood	ALTwood
Pyrolysis temperature, ^{o}C	500	500	500	500
Catalyst/biomass ratio, wt/wt	2.5	2.5	4	6
Product yield, wt.% [b, c]				
Upgraded bio-oil	10 (9)	8.5 ± 0.2	7 (6)	7 (6)
Produced water	18 (15)	22.8 ± 0.9	19 (16)	17 (15)
Char/coke [d]	29 (25)	24.0 ± 0.2	33 (28)	37 (32)
CO	22 (19)	21.6 ± 0.4	23 (20)	22 (19)
CO_2	10 (9)	12.0 ± 0.2	10 (9)	10 (9)
CH_4	1	1.1 ± 0.03	1	1
C_2H_4	1	1.6 ± 0.02	1	1
C_3H_6	2	1.8 ± 0.06	1	2
Elemental composition of upgraded bio-oil, wt.% [e]				
C	79.6 ± 1.4	79.8 ± 1.0	80.7 ± 0.5	80.7 ± 1.5
H	6.8 ± 0.2	7.0 ± 0.3	6.3 ± 0.04	5.9 ± 0.2
O	14	13	13	13
O/C (mol/mol)	0.13	0.12	0.12	0.12
GC/MS results of upgraded bio-oil, peak area % [f]				
Aromatics	76 ± 0.5	76 ± 0.9	73 ± 0.2	77 ± 0.3
Phenols	14 ± 0.1	13 ± 0.3	17 ± 0.0	14 ± 0.0
Oxygenated aromatics	8 ± 0.6	10 ± 0.2	9 ± 0.2	8 ± 0.2
Guaiacols	0.6 ± 0.0	0.2 ± 0.0	0.6 ± 0.0	0.4 ± 0.0
Ketones	0.6 ± 0.0	0.3 ± 0.0	0.8 ± 0.0	0.6 ± 0.0
Furans	0.2 ± 0.0	0.2 ± 0.0	0.3 ± 0.0	0.2 ± 0.0
Catechols	0.2 ± 0.0	0.1 ± 0.0	0.2 ± 0.0	0.1 ± 0.0

746   [a] Included from Table 3 for ease of comparison; [b] Reported on the basis of dry acid-leached and torrefied

747   wood with corrected yields on dry raw wood in parentheses; [c] The yields of H_2, C_2H_6 and C_3H_8 were ≤ 0.1,

748   0.3 and 0.3 wt.%, respectively; [d] The yields of char and coke were reported together ; [e] Average values of

749   triplicate analyses calculated on dry basis $\pm$ one standard deviation, oxygen content calculated by

750   difference to 2 significant figures; [f] Average values of duplicate analyses, details are shown in Supporting
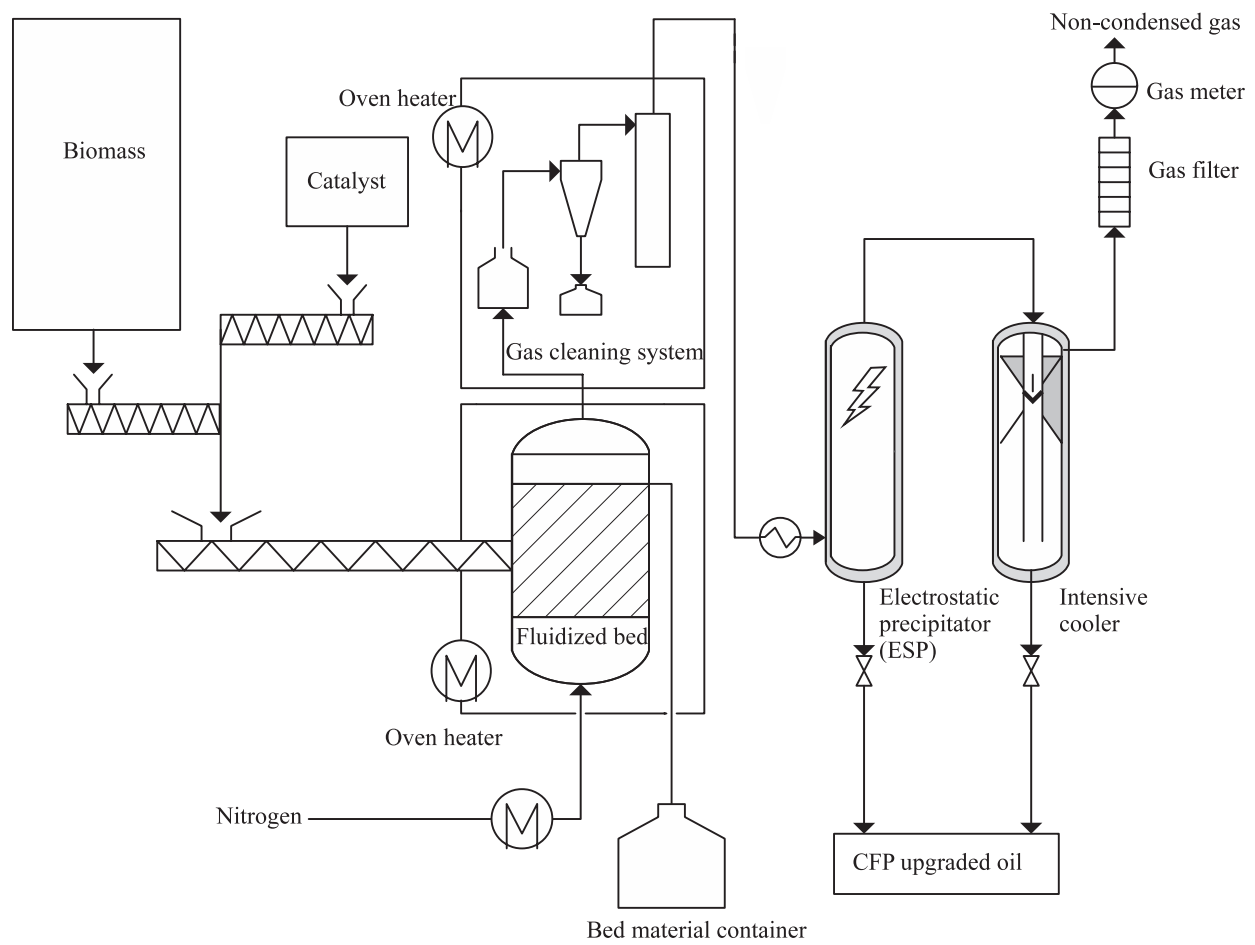
751   Information (Table S2).

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Biomass

Catalyst

Oven heater

Gas cleaning system

Fluidized bed

Oven heater

Nitrogen

Bed material container

Non-condensed gas

Gas meter

Gas filter

Electrostatic
precipitator
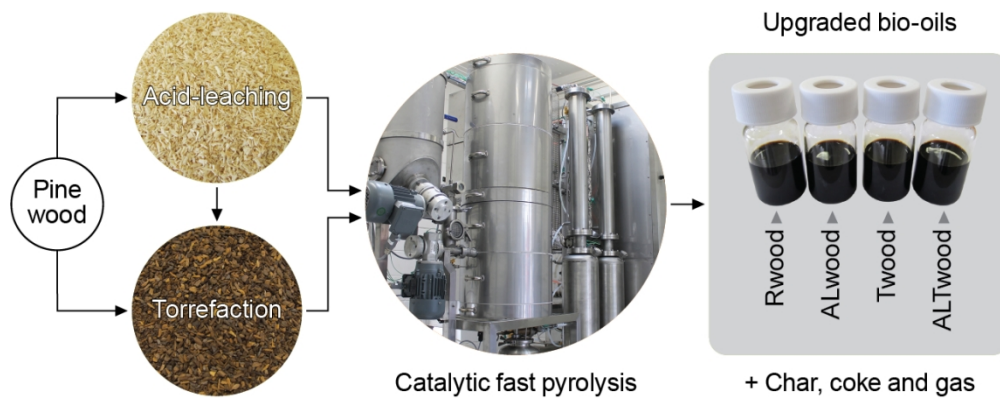(ESP)

Intensive
cooler

CFP upgraded oil

Figure 2. SEM images of char products mixed with used catalyst collected from catalytic fast pyrolysis experiments, AL360L (A), AL450L (B) and AL500L (C).

Upgraded bio-oils

Catalytic fast pyrolysis

+ Char, coke and gas

Graphical abstract