

# 1 **Pyrolysis oil upgrading in high conversions using sub- and supercritical water above 400°C**

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12

## 13 **Abstract**

14

15 The upgrading of pyrolysis oil to bio-fuel was investigated using sub- and supercritical water at 410  
16 and 450°C, with a high mass ratio of water to pyrolysis oil to ascertain the maximum yields that could  
17 be achieved. The results indicate that conversions increased with increasing pyrolysis oil to water  
18 mass ratio at high water ratio under supercritical water conditions at 410°C, gave the highest products  
19 conversion of ~91 wt. %, with 28 wt. % heavy oil recovered, ~23 wt. % gas yield, 27 wt. % water  
20 generated and approximately 13-14 wt. % of light oil produced. Similar product conversion was  
21 obtained using biomass as a feedstock with slightly higher water mass ratio added into the reactor  
22 (R1:15), and slightly lower heavy oil yield was recovered (21 wt. %). Gas generation was observed to  
23 reach a maximum and then level off at ~22-23 wt. % in near-supercritical water and supercritical water  
24 experiments at 410°C. No further cracking of the heavy oil was observed for experiments at 450°C,  
25 and an increase of 10 wt. % in the gas yield was observed when the temperature was increased to  
26 450°C (33 wt. %) from 410°C (23 wt. %) with ~7 wt. % of light oil produced and approximately 24 wt.  
27 % of water generated. The oxygen contents of the heavy oil recovered were ~15-16 % (for 410 and  
28 450°C), with H/C atomic ratios of 1.1. Similar overall conversions were achieved using tetralin with  
29 much lower solvent to oil ratios were needed and the liquid products had a slightly lower oxygen  
30 content (14 %). The estimated hydrogen from water was estimated as ca. 0.3 % at 410 and 450°C in  
31 high conversions of pyrolysis oil experiments, and experiments with tetralin/1-methyl naphthalene  
32 provide evidence that a small amount of hydrogen was sufficient to achieve high product conversion,  
33 giving an increase of H element content from 7.0 % to 7.3 %.

34

35 **Keywords:** Pyrolysis oil upgrading, pyrolysis oil, subcritical water, supercritical water, liquefaction

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## 38 1. Introduction

39

40 Thermochemical process has been employed for converting biomass into alternative energy and  
41 chemicals by researchers worldwide [1-7]. Thermal degradation process include; liquefaction (a  
42 process of producing liquid products in which the feedstock macromolecule compounds are  
43 decomposed into fragments of light molecules in the presence of suitable catalyst), gasification (the  
44 first step in indirect liquefaction in which the gasifying coal/biomass is partial oxidised to produce  
45 syngas), and pyrolysis (a combustion process in the absence of oxygen to produce liquid products) [8,  
46 9].

47

48 Hydrothermal liquefaction (HTL) of biomass is a process, where the macromolecular components of  
49 biomass, cellulose, hemi-cellulose and lignin are decomposed in the presence of water to produce  
50 crude oil and other chemicals [10]. Gasification of biomass produces a mixture of hydrogen and  
51 carbon monoxide, commonly called syngas. The syngas is then reformed into liquid oil in the presence  
52 of a catalyst [10]. Fast and slow pyrolysis can be conducted depending on the types of products  
53 desired. Most processes that convert biomass to liquid fuels begin with pyrolysis, followed by catalytic  
54 upgrading of the resulting biocrude liquids [8].

55

56 The pyrolysis of various biomass feedstocks to produce a liquid bio-oil yield and chemicals has been  
57 conducted by numerous researchers [11-18]. The oil palm empty-fruit-bunch has been pyrolysed to  
58 produce bio-oil and chemicals [19-21]. Maize stalk has been fast pyrolysed to produce bio-oil [22, 23].

59

60 Although pyrolysis techniques have demonstrated a promising route to produce liquid fuels  
61 (approximately 70-80 %), the product can be unstable and require post treatment to improve the  
62 quality [24]. Pyrolysis oils contain a high oxygen content (approximately 40 %), which has led to low  
63 heating values [25]. The elemental composition of the pyrolysis oil is about the same as that of the  
64 biomass feedstock [26]. Furthermore, bio-oil can contain high water content derived from the original  
65 moisture in the feedstock. This will lower the heating value and affect the product quality. Pyrolysis  
66 oil is also very corrosive as a result of high acidity with average pH values of 2-3 [7]. There are a few  
67 methods which can be employed to improve the quality of bio-oil, such as hydrodeoxygenation,  
68 catalytic cracking, emulsification and steam reforming.

69

70 Numerous experiments on the hydrodeoxygenation of pyrolysis oils derived from biomass catalytic  
71 pyrolysis has been conducted [27-29]. Wang et al. found that the hydrodeoxygenation of pyrolysis oil  
72 derived from catalytic pyrolysis of biomass was much easier than that from fast pyrolysis of biomass

73 over Pt catalysts [27]. Xu et al. reported that the effects of Ru-loading gave the highest conversion of  
74 acetic acid (30.98%), and the hydrogen content in the pyrolysis oil increased from 6.6 % to 6.9 % [28].

75  
76 Supercritical fluid extraction is becoming widely used in the conversion of biomass. It has been  
77 recently used to improve bio-oil yield and quality, and has demonstrated a great potential for  
78 producing bio-oil with much higher calorific values [30]. Numerous studies using methanol, ethanol  
79 and acetone have been applied in the liquefaction process of biomass [31]. Liquefaction of microalgae  
80 (*Chlorella pyrenoidosa*) in sub and supercritical acetone in the absence of a catalyst, by using a high  
81 pressure bath reactor has been performed and found the highest conversion (~76 %) was obtained at  
82 310°C [32]. Liquefactions of biomass using supercritical ethanol have also been reported [33-35].  
83 Zhang et al. reported a 92 % conversion obtained from liquefaction of *Chlorella pyrenoidosa* in  
84 supercritical ethanol. Li et al. obtained a conversion of 78 % with supercritical ethanol in liquefaction  
85 of rice stalk. In contrast, Brand et al. reported a 98 % conversion of pine wood with supercritical  
86 ethanol at 400°C for 2 h.

87  
88 Water can simultaneously act as both a reactant and a catalyst, and has received extensive attention  
89 because it is clearly an inexpensive and easy to recycle reaction medium for converting wet and dry  
90 biomass into crude bio-oils with or without a catalyst [36]. Hydrothermal liquefaction (also known as  
91 hydrous pyrolysis) using subcritical water occurs generally between 200 and 370°C, with pressures  
92 between 4 and 20 MPa, sufficient to keep the water in a liquid state [37]. At close to the critical point,  
93 water has several properties such as low viscosity and high solubility of organic substances, that  
94 means it can serve as an excellent medium for fast, homogenous and efficient reactions [38]. By  
95 moving from subcritical to supercritical temperatures (374°C) at pressures above  $P_c$  (22 MPa) both the  
96 rate of hydrolysis as well as phase partitioning and solubility of components can be controlled so that  
97 potentially more favourable pathways to gases and liquid biofuels may be realised [37]. Although the  
98 dipole moment decreases with increasing temperature, water in the critical region is still as polar as  
99 acetone [39].

100  
101 Pyrolysis oil upgrading using sub- and supercritical water has been investigated in this study, aimed to  
102 identify conditions required to maximise products conversion and liquid product yield. Experiments  
103 with tetralin (a hydrogen donor solvent) and 1-methylnaphthalene (a non-hydrogen donor solvent)  
104 were conducted to provide comparisons with water at comparable temperatures. Tetralin is a  
105 hydrogen-donor solvent which gives high conversions by reacting with free radicals producing more  
106 lower molecular weight products as reported previously [40-42]. Tetralin as a solvent for biomass  
107 conversion gives rise to high feedstock conversion ~90 wt. %, as a result of the hydrogen donated  
108 from the solvent [43]. As for biomass conversion in our previous study [44], hydrogen donation from

109 both water and tetralin, and the effect on oxygen removal were quantified. The same approach as  
110 previously was used for pyrolysis oil upgrading to ascertain the differences and similarities compared  
111 to biomass.

112

## 113 **2. Materials and methods**

114

### 115 *2.1. Materials*

116

117 Pyrolysis oil from biomass conversion was supplied by BP, UK and kept in the fridge and taken out  
118 prior to each use. The proximate analysis and elemental composition of the pyrolysis oil feedstock are  
119 listed in Table 1. The water content of the pyrolysis oil was determined using the Dean-Stark  
120 apparatus by dissolving 5 g of pyrolysis oil in toluene with the water being distilled and measured.  
121 Experiments were repeated 5 times and an average of 34 wt. % water content was obtained.

122

123 **Table 1** Proximate and ultimate analyses of the pyrolysis oil sample using TGA and EA.

124

Proximate analysis (%) (dry basis)		Elemental composition (%) DAF	
Moisture	13.7	C	48.4
Volatile matter	69.7	H	7.0
Ash	0.1	N	0.2
Fixed carbon	16.5	O (by difference)	44.4

125

### 126 *2.2. Oil upgrading experiments*

127

128 A series of experiments were conducted under anhydrous and hydrous conditions, the latter with  
129 various pyrolysis oil to water mass ratios and also with tetralin and 1-methylnaphthalene (1-MN) as  
130 reference solvents. Experiments were conducted using a Parr 4740 series stainless steel (75 ml  
131 cylindrical) pressure vessel at pre-set temperatures (410°C, 450°C) for 1 h. After sealing the vessel and  
132 attaching the pressure gauge, it was purged 15 times with nitrogen gas to remove the air, and then 2  
133 bar of nitrogen gas was introduced to provide an inert atmosphere. The reactor was heated in a  
134 fluidised sand bath, with experiments repeated 4-5 times to assess reproducibility. Temperature was  
135 monitored by an additional K-type thermocouple, which connected to computer and recorded every 10  
136 s. Compressed air entered into the sand bath from the bottom through a gas distributor and evenly  
137 bubbled inside container to mix the sand, and so evenly distribute the heat through the sand bath. As  
138 soon as the experiment was finished, the reactor was removed from the sand bath and left overnight to

139 cool down. Once the reactor was cooled to room temperature, the gas inside the reactor was  
140 transferred into a sampling bag using a gas syringe and the volume collected was recorded.

141  
142 The reacted products (solid and liquid) were washed with approximately 150 ml toluene and  
143 transferred into the round bottom flask. Heavy oil can be defined as the oil product from oil upgrading  
144 process which has a density of greater than one, whilst light oil has a density less than one which  
145 either floated on the water or was on the reactor walls after the experiments. A Dean-Stark apparatus  
146 was used to separate water from reacted products (toluene solubles and char) for the anhydrous runs.  
147 For the hydrous runs, water was first pipetted out from the reactor and the remaining was distilled to  
148 remove water using the Dean-Stark apparatus. The flask was heated by a heating mantle at 110°C for  
149 12 h. After reflux, the products in the round bottom flask (toluene solubles and char) were allowed to  
150 cool, and the volume of generated water from the reaction was recorded (water for anhydrous).

151  
152 The solid residue then was separated from the heavy oil (toluene-soluble) by filtration using a pre-  
153 weighted 0.5 µm glass fibre filter paper. The residue and filter paper were dried in desiccator using  
154 activated charcoal, and the final dried weight was used to determine the total overall conversion. The  
155 toluene soluble fraction were transferred into a round bottom flask, and a rotary evaporator was used  
156 to remove the toluene and so recover the heavy oil which was then weighed to calculate the yield. For  
157 experiments with tetralin and 1-MN, the vacuum distillation was carried out to distil the solvents and  
158 so recover the heavy oil. In order to recover the light oil product, *n*-pentane was used to wash the  
159 reactor wall, and the floating oil (*n*-pentane soluble) was pipetted from the reactor into a small vial and  
160 refrigerated.

161  
162 The mass ratio used for each experiment is designated by R. The yields of gas were determined using  
163 data from gas chromatography (GC) results. The water yield was recovered/measured using the Dean-  
164 Stark apparatus (for anhydrous and tetralin runs). The confidence interval calculated based on 90 %  
165 confidence level and presented in results and discussion. Total oil (bio-oil yield) consists of heavy oil  
166 and light oil. The yield of each product on a wt. % DAF basis was calculated as follows:

167  
168 Residue yield = (mass toluene insoluble (g)/ initial sample loaded (g) x 100  
169 Total conversion = 100 - residue yield  
170 Total oil and water yield = 100 - (residue yield + gas yield)  
171 Heavy oil yield = (mass heavy oil (g)/initial sample loaded) x 100  
172 Total oil (bio-oil) yield = Liquid yield - estimated water yield  
173 Light oil yield = Total oil (bio-oil yield) - heavy oil yield

174

### 175 2.3. Analyses

176

177 The gases were analysed using a Clarus 580 gas chromatograph (GC) fitted with a FID and TCD  
178 detectors operating at 200°C. 5 ml of sample of gas introduced to the GC for hydrocarbon and non-  
179 hydrocarbon analysis. Hydrocarbon (HC) gas was determined by FID by injecting 100 µl of gas  
180 samples (split ratio 10:1) at 250°C with separation performed on an alumina plot fused silica 30 m x  
181 0.32 mm x 5 µm column, with helium as the carrier gas. The oven temperature was programmed from  
182 60°C (13 min hold) to 180°C (12 min hold) at 10°C/min. Individual gas yields were determined  
183 quantitatively in relation to methane as an external gas standard, and the total yield of the generated  
184 gases calculated using the total volume of gas collected in relation to the aliquot volume of gas  
185 introduced to the FID. Non-hydrocarbon (NHC) gas was determined by TCD by injecting 500 µl of  
186 sample of gas at 165°C with the CO<sub>2</sub>, CO and H<sub>2</sub> yields being calculated using the external gas  
187 standard.

188

189 Gas chromatography-mass spectrometry (GC-MS) analyses of the heavy (1 µl in DCM) and light oils  
190 (1 µl in *n*-pentane) were performed on a Varian Instruments CP 3800 GC interfaced to a 1200  
191 Quadrupole MS (ionising energy 70 eV, source temperature 280°C). Separation was performed on a  
192 fused silica capillary column (50 m x 0.32 mm i.d.) coated with BPX5 phase (0.25 µm thickness).  
193 Helium was used as the carrier gas, with a temperature programme of 50°C (2 min) to 300°C (28 min)  
194 at 5°C/min. Injections were performed in full scan mode with split ratio 100:1.

195

196 The elemental analyses of the heavy oils and chars were determined using Thermo Electron FlashEA  
197 1112 elemental analyser. Vanadium pentoxide was used to determine the sulphur content and found  
198 the amount was too small and negligible for the calculation of this research. The proximate analysis  
199 was performed by thermogravimetric analysis (TA Q500 instrument).

200

## 201 3. Results and discussion

202

### 203 3.1. The effect pyrolysis oil to water mass ratio on conversion at 410°C

204

205 The pyrolysis oil upgrading experiments to investigate the effect of the mass ratio of pyrolysis oil to  
206 water were conducted using various ratios, namely R1:3.5, R1:5.5, R1:7.9, and supercritical water  
207 conditions with R1:9.3. The protocol used to obtain the supercritical water conditions was the same as  
208 described in a previous study [44]. A series of blank runs with water (20, 22 and 24 ml) using the 75  
209 ml vessel were conducted to determine the baseline data for subcritical and supercritical conditions.  
210 Experiments were conducted at 375°C for 1 h, giving measured water pressures of 206 bar (20 ml),

211 212 bar (22 ml) and 218 bar (24 ml). Therefore, to reach supercritical conditions, an amount of >24 ml  
212 water must be loaded in the 75 ml vessel with temperature of 374°C or higher ( $T_c > 374^\circ\text{C}$ ,  $P_c > 221$   
213 bar).

214

215 The experiments were conducted for 1 h using 75 ml reactor. The pressures recorded for these  
216 experiments were 260-320 bar. Adding more water into the reactor gave increasing conversions with  
217 experiments in the supercritical water (SCW) condition giving the highest conversion of ~89-91 wt. %  
218 (Fig. 1). Similar product conversion was obtained using biomass as a feedstock with slightly higher  
219 water mass ratio added into the reactor (R1:15), and slightly lower heavy oil yield was recovered (21  
220 wt. %). Coal conversion in SCW has been reported to be higher than in supercritical toluene [45].  
221 Han et al. (2008) reported SCW can promote the conversion of coal-tar pitch to maltene and retard the  
222 formation of gas and char [46]. There have been no previous reports on the pyrolysis oil upgrading in  
223 direct liquefaction (without catalyst) via sub- and supercritical water conditions.

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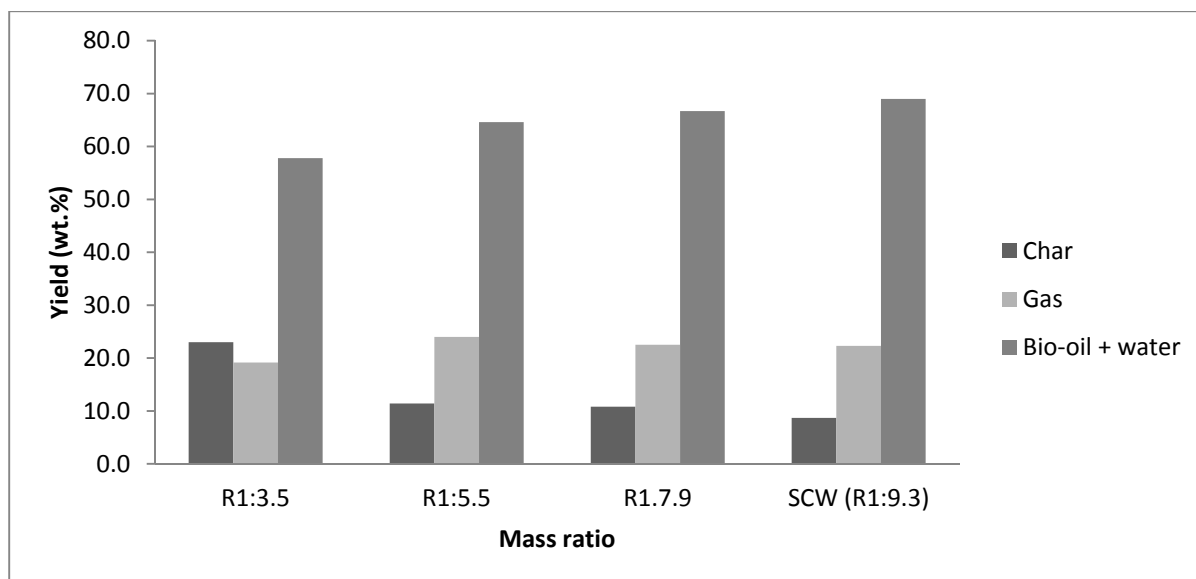
225 An increase in gas yield was observed from R1:3.5 to R1:5.5 (~210 ml to 270 ml). However for  
226 R1:5.5, R1:7.9 and at supercritical water conditions no significant changes for the generated gas were  
227 seen. The condition with supercritical water gave the highest bio-oil plus water yield ~68 wt. % and  
228 the lowest char yield of ~9 wt. %. However, it was observed that for the ratios of R1:5.5, R1:7.9 and at  
229 supercritical water conditions, gas yields were at a maximum and levelled off at ~23 wt. %. It was  
230 found that for pyrolysis oil upgrading experiments, higher water ratios caused hydrolysis to be very  
231 dominant and so prevented repolymerization, which resulted in high bio-oil plus water yields being  
232 obtained.

233

234 The heavy oil yields recovered from the experiments that investigated the effect of mass ratio of  
235 pyrolysis oil to water are shown in Table 2. Increasing the water ratio at supercritical water condition  
236 (R1:9.3) gave the highest heavy oil yield ~28-29 wt. %. The heavy oil yield was slightly lower in  
237 subcritical water (R1:7.9) at 410°C as compared to supercritical water at 410°C. The low density of  
238 supercritical water in this condition leads to high diffusivity and compressibility of water, and hence  
239 water is able to penetrate more efficiently into the tested pyrolysis oil, achieving higher degrees of oil  
240 upgrading [47].

241

242 In addition, the low dielectric constant of supercritical water increases the solvation power of water to  
243 dissolve and extract organic materials which are normally water insoluble, hence supercritical water  
244 has enhanced solubility for organic compounds compared to a conventional liquid or gas solvent [47].



245  
246

247 **Fig. 1.** Pyrolysis oil upgrading with hydrous pyrolysis (various mass ratios of sample to water and  
248 supercritical water (SCW)) using the 75 ml reactor at 410°C for 1 h.

249

250 **Table 2**

251 Yield of heavy oil and bio-oil as a function of sample to water at 410°C for 1 h.

Mass ratio (bio-oil:water)	Anhydrous	Ratio 1:3.5	Ratio 1:5.5	Ratio 1:7.9	Ratio 1:9.3 (SCW)
Pressure (bar)	80	260	285	310	320
Bio-oil yield (wt.%DAF)	23	46.5	53.3	55.4	57.7
Heavy oil yield (wt.%DAF)	10	14.7	20.3	23.6	28.9

252

### 253 3.2 The effect of reaction pressure

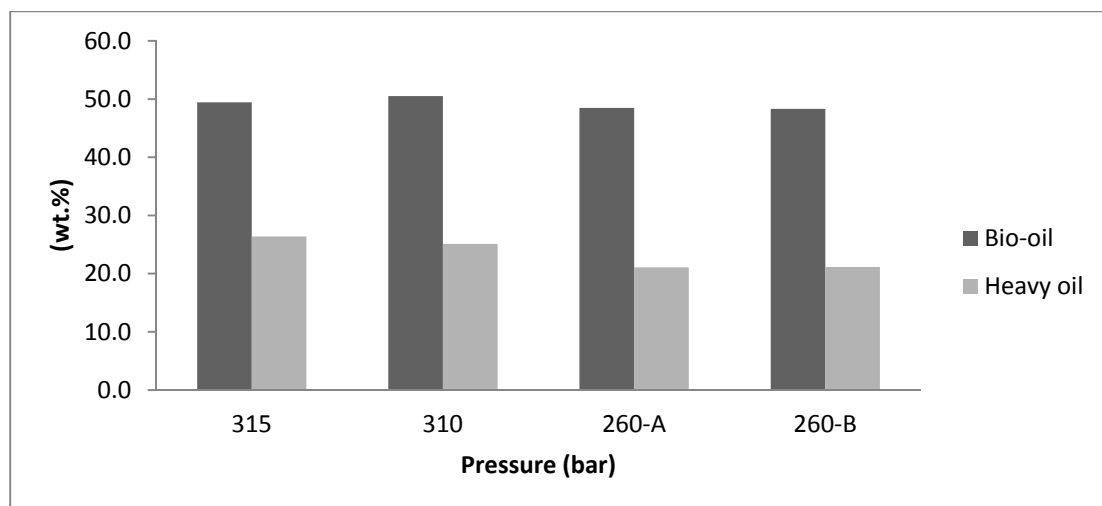
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255 Changing the pyrolysis oil to water ratio affected the pressure of the system. Therefore, experiments  
256 were designed to study the effect of pressure at 310-315 and 260 bar. The effect of pressure on total oil  
257 (bio-oil) and heavy oil yield is given in Fig. 2. It was found that at the higher pressure the proportion  
258 of heavy oil recovered was slightly greater. For the experiments performed with R1:4, at 315 and 310  
259 bar, 25 wt. % of heavy oil was obtained compared to ~20 wt. % at 260 bar. In addition, a slightly  
260 higher total conversion of 85 wt. % compared to 82 wt. % was obtained at the higher pressure (310-  
261 315 bar).

262



263 Increasing oil yield with escalating pressure has been reported in a previous study [48], with Yang  
264 reporting that the bio-oil yield increased in hydrothermal *Sedum plumbizincicola* from 2.84 % to 4.28  
265 % when the pressure was raised to 250 bar from 210 bar at 370°C. The dependency of total oil yields  
266 on the pressure of the system did show a clear trend in this study. Higher pressure is known to increase  
267 the solvent density and solubility of the target components, allowing solvent to penetrate more  
268 efficiently into the molecular structure, enhancing the extraction of bio-oil components, and yielding  
269 greater amounts of heavy oil [47] whilst at the same time possibly suppressing cracking to lighter oil.  
270



271  
272 **Fig. 2.** Heavy oil and bio-oil (total oil) yields (DAF) from hydrous runs of pyrolysis oil at different  
273 reaction pressure conducted using the 75 ml reactor at 410°C for 1 h.

274

### 275 3.3 The effect of reaction temperature

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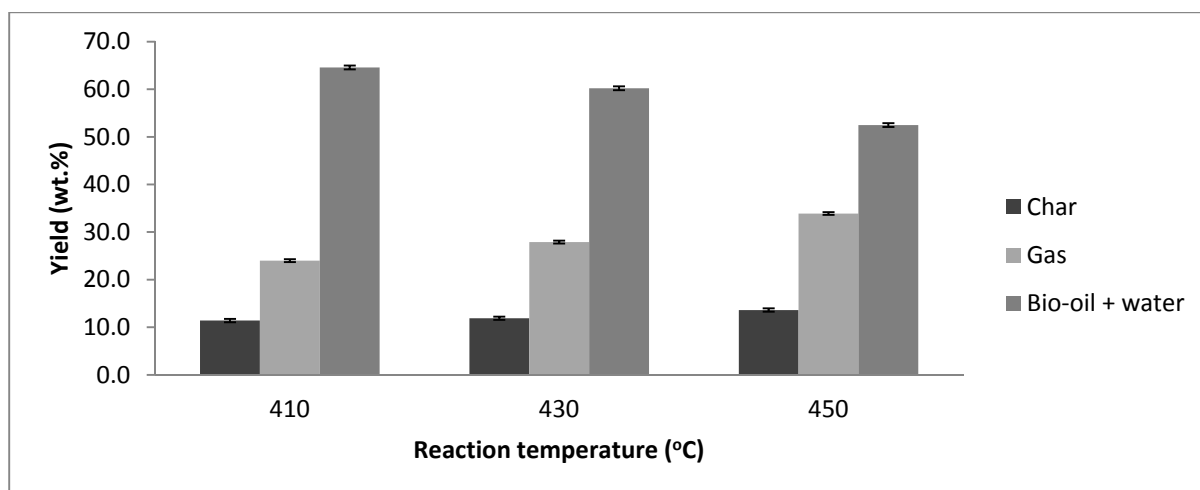
277 The effects of reaction temperature for the experiments on pyrolysis oil upgrading were carried out at  
278 410, 430 and 450°C for 1 h. Samples used in these experiments were 2.4 g bio-oil vs 13.2 water. An  
279 increase in gas yield was observed from 278 ml (410°C) to 346 ml (430°C), and further up to 431 ml  
280 (450°C). Fig. 3 shows the product conversion yields from experiments that investigated the effect of  
281 reaction temperature. The product conversion was observed to decrease slightly from ~88 wt. %  
282 (410°C) to 86 wt. % (450°C). It was observed that the oil+water yield decreased from ~65 wt. % at  
283 410°C to ~60 wt. % at 430°C and further down to 52 wt. % at 450°C.

284

285 As expected gasification required higher temperatures, with the gas yields seen to increase from ~23  
286 wt. % at 410°C to ~28 wt. % at 430°C and then to 33 wt. % at 450°C. With a slight decrease of char  
287 yield, it is suggested the liquid products have been broken down to form gas products at high

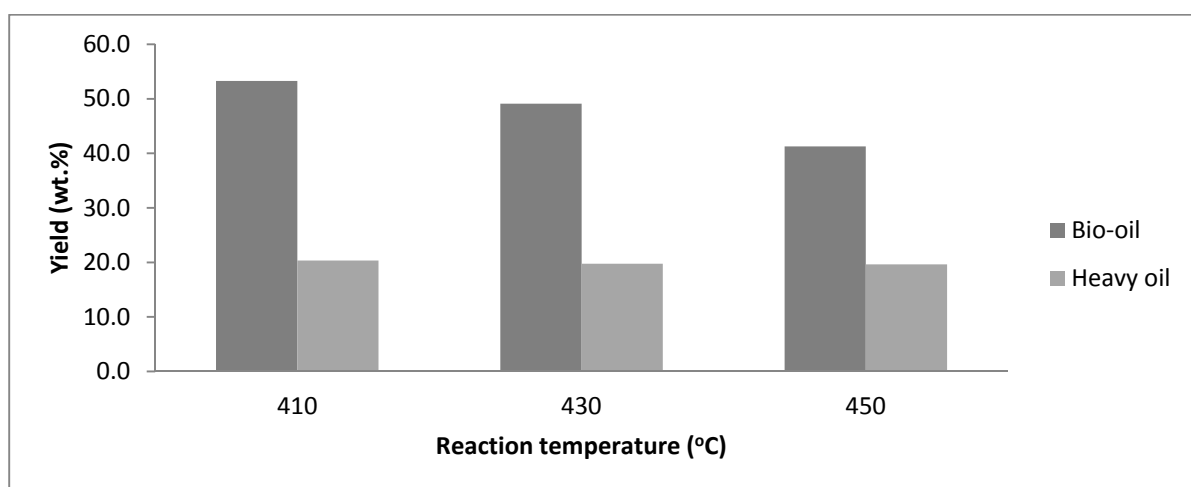
288 temperature. Knezevic et al. reported the possibility of secondary char formation at elevated  
289 temperatures, and also reported that a light oil yield in the range of 20-40 % was obtained [49].  
290 However, the light oil produced in this study is lower, approximately at ~12-14 wt. % (see Section  
291 3.4).

292



293  
294 **Fig. 3.** Yield of products (DAF) in pyrolysis oil upgrading at different reaction temperatures with  
295 R1:5.5 using the 75 ml reactor for 1 h. (std deviation  $\leq 0.4$ ; 4 times replication).

296  
297 Fig. 4 shows the heavy oil and bio-oil yields from experiments in pyrolysis oil upgrading at 410, 430  
298 and 450°C for 1 h. It can clearly be seen that the bio-oil yields decreased with increasing temperature  
299 from ~52 wt. % (410°C) to ~48 wt. % (430°C) and rapidly decreased to ~41 wt. % at 450°C. However,  
300 the heavy oil yields were the same at ~20 wt. % for all experiments. The results show at higher  
301 temperature the breakdown of the light ends started to occur to form gas products while the heavy  
302 products remain unchanged, suggesting no cracking occurred.



303  
304 **Fig. 4.** Heavy oil and bio-oil yields (DAF) in pyrolysis oil upgrading at different reaction temperatures  
305 with R1:5.5 conducted using the 75 ml reactor for 1 h.

306

### 307 3.4. The effect of other solvents

308

309 Experiments with hydrogen donor solvent (tetralin) and non-hydrogen donor solvent were conducted  
310 to provide a baseline conversion to compare with product conversion using supercritical water at  
311 410°C for 1 h. The results are illustrated in Fig. 5. Runs with tetralin gave the highest product  
312 conversion with ~90 wt. %, of which ~68 wt. % was bio-oil plus water yield and ~21-22 wt. % was  
313 gas yield.

314

315 The presence of tetralin favours the molecular rearrangement and stabilization of free radicals  
316 produced by pyrolysis and hydrolysis of bio-oil through hydrogen donors [50]. Experiments with 1-  
317 MN gave ~80 wt. %, ~53 wt. % of bio-oil plus water yields and 25 wt. % gas yields. By using 1-MN-  
318 tetralin (mass ratio 80 % : 20 %) gave the same product conversion as the runs with tetralin ~90 wt. %.  
319 This is in agreement with Deng et al., 1-MN becomes a good shuttle to carry hydrogen to stabilise the  
320 free radicals. The upgrading of bio-oil with tetralin was performed at 360°C for 30 mins, and reported  
321 75 % conversion was obtained [51]. However, the authors did not specify the mass ratio used in this  
322 experiment.

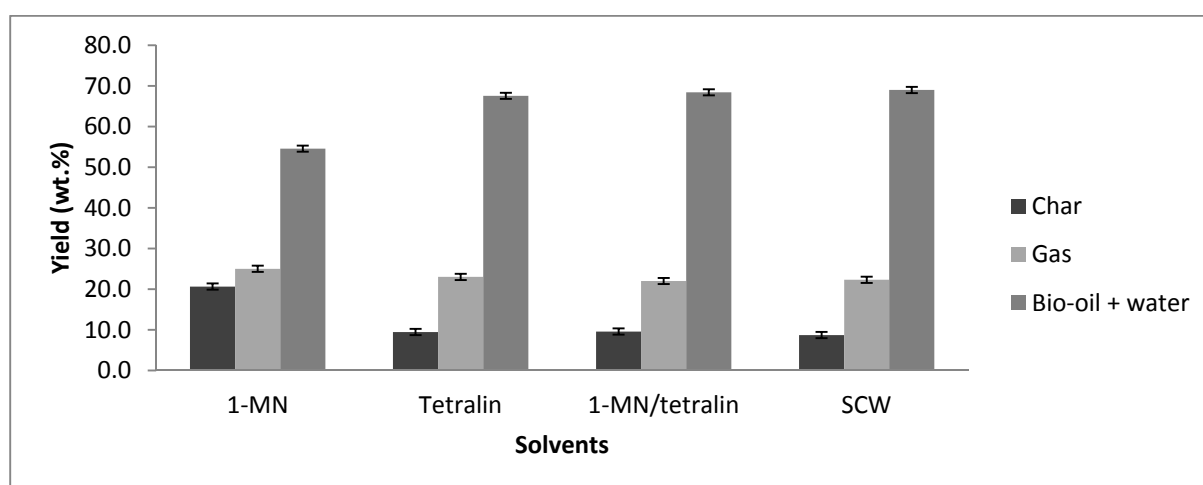
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324 Comparing water and tetralin, although supercritical water gives a higher conversion, tetralin gives a  
325 higher yield of heavy oil (40 wt.%) and fewer light products. A similar amount of gas yields in bio-oil  
326 upgrading using tetralin and supercritical water at 410°C obtained (23 wt. %).

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331 **Fig. 5.** Pyrolysis oil upgrading with different solvents using the 75 ml reactor at 410°C and 1 h. (std  
332 deviation  $\leq 0.8$ ; high conversion experiment in SCW included; 4 times replication).

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### 3.5. *Elemental analysis and product recovery*

Table 3 gives the elemental compositions (average base on four times replication) of the heavy oil from pyrolysis oil upgrading at 410°C. The introduction of a high water ratio increased the oxygen removal going from anhydrous to hydrous conditions. The oxygen content under anhydrous condition was ~25 % and was improved to ~16 % by the addition of more water into the reactor (R1:5.5). Ratios of 1:4 to 1:5.7 yielded almost the same oxygen content (~16-17 %), and the use of supercritical water conditions had a slight effect on oxygen removal which gave ~15 %. These can be explained by low oxygen removal through CO<sub>2</sub> under high conversion experiments. The H element content in the upgraded oil increased from 7 % to 7.3 % under subcritical condition. The elemental compositions at 450°C are also presented (Table 3). Samples with ratio 1:5.5 were tested and gave an oxygen content of ~16-17 wt. %. This shows that for pyrolysis oil upgrading via hydrous pyrolysis, higher temperature (~450°C) did not promote oxygen removal. Compared with tetralin which produced similar overall conversions (at 410°C R1:2), the heavy oil have slightly lower oxygen contents (~14 %).

The H/C and O/C gave 1.1 and 0.2 respectively, for the analysed heavy oil (at 410°C), similar with the heavy oil produced with tetralin (1.1 for H/C). The heating value was also calculated and was increased to ~33 MJ/kg (hydrous) compared to 18.5 MJ/kg for the initial pyrolysis oil.

The yields of water were estimated from oxygen balances to check against the measured value in the case of tetralin and the assumed values of the anhydrous yield for the hydrous experiments as performed in the previous work [44]. The pyrolysis oil upgrading with anhydrous pyrolysis conducted at 410°C produced 11.3% of water. Table 4 gives the oxygen balances carried out on the products (heavy oil, char, CO and CO<sub>2</sub>) for the test under supercritical conditions.

Under supercritical conditions, the oxygen mass balance gave an estimated water yield of ~27 wt.%. The higher water yield estimated for the hydrous experiments is consistent with the lower O contents of the heavy oils, in relation to the anhydrous experiment. Hence, the new bio-oil yield can be calculated and the light oils gave an estimated yield of ~14 wt.% (Table 5).

369 **Table 3**370 Elemental analyses of the chars and heavy oils (DAF basis) from pyrolysis oil upgrading experiments  
371 at 410°C and 450°C for 1 h.

372

Samples	C	H	N	*O
Char (anhydrous)	70.0	3.0	0.2	26.8
Heavy oil (anhydrous)	68.3	7.0	0.1	24.6
Char (R1:4)	78.5	3.5	0.6	17.4
Heavy oil (R1:4)	75.0	7.1	0.5	17.4
Char SCW	82.2	4.2	0.7	12.9
Heavy oil SCW	77.2	6.8	0.4	15.6
Char (R1:5.5)	81.6	4.0	0.5	13.9
Heavy oil (R1:5.5)	76.0	7.3	0.2	16.5
Char (R1:5.7)	81.8	4.1	0.5	13.6
Heavy oil (R1:5.7)	75.5	7.3	0.3	16.9
Char (R1:5.5) at 450	85.0	4.0	0.6	10.4
Heavy oil (R1:5.5) at 450	76.0	7.3	0.4	16.3
Heavy oil (R1:2)-tetralin	78.1	7.3	0.4	14.2

373 \*by difference ; std deviation for O ~0.2-0.3; 4 times replication

374

375

376

377 **Table 4**

378 Oxygen balance to calculate the water generated from pyrolysis oil upgrading with supercritical water at 410°C for 1 h.

379

	O (wt. %)	Yield (wt. %)	Mass DAF (g)	O (g)	O (wt. %)
Initial sample (oil)	44.0		1.7	0.76	
Heavy oil	15.8	29.0	0.5	0.08	10.4
Char	13.0	8.5	0.1	0.02	2.5
CO <sub>2</sub>				0.20	26.4
CO				0.04	5.2
Water				0.17	22.8
			Total	0.51	
			Difference	0.25	
			Total water generated (wt. % DAF)		27.4

380 **Table 5**

381 The corrected mass balance after using the new value for amount of generated water from the  
 382 experiment using supercritical water at 410°C for 1 h.

383

Yields (wt. %)	A	*B
Conversion	91.0	91.0
Liquid (bio-oil + water)	69.0	69.0
Water	11.3	*27.4
Bio-oil	57.7	*41.6
Gas	22.3	22.3
Char	9.0	9.0

384 \*corrected value

385

386 *3.5. Gas composition and utilisation of water hydrogen*

387

388 Table 6 gives the gas yields for the experiments that investigated the effect of the mass ratio of  
 389 pyrolysis oil:water. It was observed that individual gases like CH<sub>4</sub>, H<sub>2</sub> and CO<sub>2</sub> increased from R1:3.5  
 390 to R1:5.5, and levelled off afterwards. The CH<sub>4</sub> yield increased from 1.26 wt. % (R1:3.5) to 1.62 wt.  
 391 % (R1:5.5). The H<sub>2</sub> yield rose to 0.15 (SCW) from 0.05 at R1:3.5. It was observed that CO<sub>2</sub> increased  
 392 by 3 wt. % from R1:3.5 (~12 wt. %) to R1:5.5 (~15 wt. %).

393

394 One of the advantages of hydrothermal conversion using subcritical and supercritical water is the  
 395 significant removal of oxygen via decarboxylation, which is the optimal way of deoxygenation from  
 396 an energetic point of view [49]. Knezevic and co-workers reported the gas produced consisted of more  
 397 than 70 wt. % at 350°C (230 bar) for 10 mins. In this study, the yield of CO<sub>2</sub> produced approximately  
 398 68 wt. % from the total gas in subcritical water conditions at 410°C for 1 h, in agreement with the  
 399 trend reported [49].

400

401 The gas yields of the hydrothermal conversion of wood are higher than those of pyrolysis oil because  
 402 of the amount of gas already released in the pyrolysis process [49]. The same trend was obtained in  
 403 this study where supercritical water conditions produced approximately 22-23 wt. % gas yield (lower  
 404 as compared in biomass conversion).

405

406 The same assumption of hydrogen donation has been made as in the previous study [44]. The  
 407 hydrogen donation in the pyrolysis oil upgrading has been calculated and presented in Table 7. It was

408 suggested that the hydrogen content in treated oil was higher than that of crude feed, suggesting that  
409 water-gas shift reaction may contribute to the in situ generation of hydrogen [52].

410

411 The hydrogen produced with supercritical water condition was low. It is because the higher oxygen  
412 removal occurred via dehydration ( $H_2O \sim 27\%$ ) instead of decarboxylation ( $CO_2 \sim 15\%$ ), with low  
413  $CO_2$  produced gave low  $H_2$  generated, and more hydrogen was removed as water. Approximately 0.3  
414 % of hydrogen donation in the subcritical water runs at 410 and  $450^\circ C$ , considerably lower than in  
415 studies with tetralin as reported by Deng and Pajak et al. [43, 53].

416

417 **Table 6**

418 Hydrocarbon gas ( $C_1-C_4$ ) and non-hydrocarbon gas yields (DAF) in pyrolysis oil upgrading with  
419 different mass ratios of bio-oil to water using the 75 ml reactor at  $410^\circ C$  for 1 h.

420

	R1:3.5	R1:5.5	R1:7.9	R1:9.3 (SCW)
<i>Gas yields (wt. % DAF)</i>				
$CH_4$	1.25	1.61	1.43	1.50
$C_2H_4$	0.09	0.11	0.12	0.10
$C_2H_6$	0.49	0.57	0.41	0.51
$C_3H_6$	0.23	0.31	0.29	0.34
$C_3H_8$	0.34	0.38	0.37	0.37
$C_4H_{10}$	0.13	0.15	0.12	0.16
$H_2$	0.05	0.07	0.14	0.15
$CO_2$	12.57	15.15	15.50	15.11
CO	3.93	5.70	3.50	4.06

421 Std deviation for  $CO_2 \sim 0.14-0.25$ ; 4 times replication

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433 **Table 7**

434 Hydrogen consumed in pyrolysis oil upgrading with subcritical and supercritical water conditions at  
 435 410°C and 450°C (all as a % DAF basis).

436

	% of H donated	
	410°C	450°C
Mass ratio		
R1:4 (high pressure-315 bar)	0.21	
Supercritical water (R1:9.3)	<0.01	
R1:5.5		0.34

437  
 438 Table 8 lists the carbon balance for pyrolysis oil upgrading from the experiment under supercritical  
 439 water conditions. The total carbon balance was found to be ~79.2 wt. % with oil, char and CO<sub>2</sub>  
 440 contributing the predominant weight of C, giving 45, 15 and 9 wt. % respectively. In the carbon  
 441 balance, the 20.8 wt. % product loss is assumed to be light oil giving a total oil yield of *ca.* 66 wt. % of  
 442 the total carbon compared to *ca.* 42 wt. % on a mass basis. The light oil mass loss experiment was  
 443 performed in our previous study [44].

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459 **Table 8**  
 460 Carbon balance for products in pyrolysis oil upgrading under supercritical water conditions at 410°C for 1 h.  
 461

	(wt. %) C	Yield (%)	Mass sample DAF (g)	C (g)	C (%)
Initial sample (sample)	48		1.700	0.816	
Oil	77	28.0	0.476	0.367	44.92
Char	82	9.0	0.153	0.125	15.38
CO <sub>2</sub>				0.074	9.09
CO				0.036	4.46
CH <sub>4</sub>				0.023	2.81
C <sub>2</sub> H <sub>4</sub>				0.001	0.18
C <sub>2</sub> H <sub>6</sub>				0.007	0.83
C <sub>3</sub> H <sub>6</sub>				0.005	0.61
C <sub>3</sub> H <sub>8</sub>				0.005	0.63
C <sub>4</sub> H <sub>10</sub>				0.002	0.28
Total gas				0.153	18.9
			Total (g)	0.646	
			Carbon conversion (wt. %)		79.2

462 3.6. Oil composition

463

464 The total ion chromatograms (TIC) from the heavy oil generated by pyrolysis oil upgrading under  
465 supercritical water at 410°C are shown in Fig. 6, and Table 9 lists the main compounds identified.  
466 Alkyl phenol is seen to form the majority of the compounds that have been identified. The C<sub>6</sub>-C<sub>12</sub>  
467 phenols and small amounts of benzenes account for all the constituents listed. The *m/z* 108, 122 and  
468 136 mass chromatograms show the presence of methyl, dimethyl and ethyl and C<sub>3</sub>-phenols.

469

470 The compounds identification for the light oil from the pyrolysis oil upgrading experiments using  
471 supercritical water at 410°C and 1 h is given in Fig. 7 and the compounds are listed in Table 10. The  
472 majority of the compounds are alkyl-substituted benzenes with phenols also present. The C<sub>8</sub>-C<sub>10</sub>  
473 benzenes and phenols account for all the constituents listed. The mass chromatograms at *m/z* 105 show  
474 the C<sub>3</sub>-benzene at peaks 4, 5 and 6.

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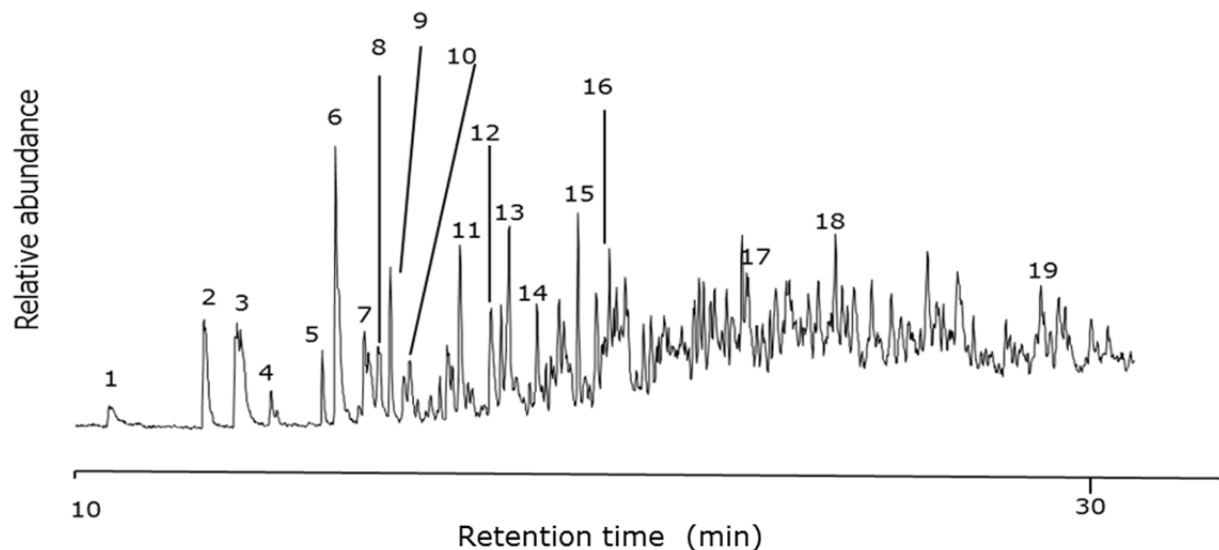
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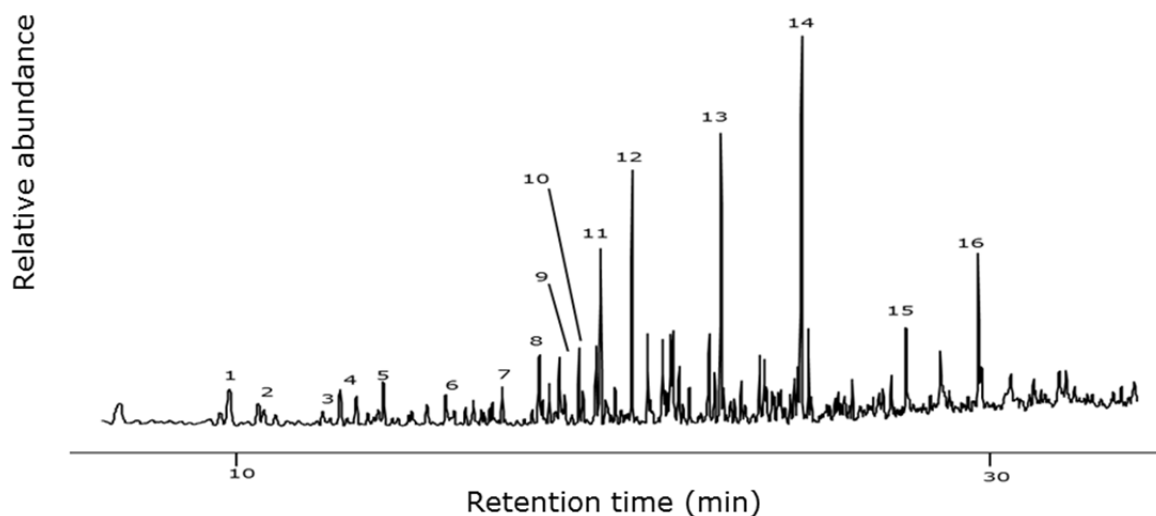
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491  
 492 Fig. 6. Compound identification (for Table 9) from the TIC for the heavy oil in the pyrolysis oil  
 493 upgrading experiment using supercritical water at 410°C for 1 h.  
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495  
 496 Fig. 7. Compound identification (Table 10) from the TIC for the light oil in pyrolysis oil upgrading  
 497 experiment using supercritical water at 410°C for 1 h.  
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503 **Table 9**504 Compounds from GC-MS analysis for heavy oil produced from the pyrolysis oil upgrading experiment  
505 using supercritical water at 410°C for 1 h.

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Peak number	Retention time	Compounds
1	10.6	Phenol
2	12.5	Phenol, 2-methyl
3	13.2	Phenol, 4-methyl
4	13.9	2,4-Dimethylphenol
5	14.9	Phenol, 2-ethyl
6	15.2	Phenol, 2,5-dimethyl
7	15.8	Phenol, 4-ethyl
8	16.1	Phenol, 3,4-dimethyl
9	16.3	1,3-benzenediol, 4-ethyl
10	16.7	Phenol, 2,4,6-trimethyl
11	17.7	Phenol, 2-ethyl-4-methyl
12	18.4	Phenol, 3-propyl
13	18.7	2,4-dimethoxytoluene
14	19.3	1H-indene-1-one,2,3-dihydro-2-methyl
15	20.1	2-methyl-6-propyl-phenol
16	20.8	Phenol, 2-methoxy-6-(1-propenyl)
17	23.6	Phenol, 2-(2-penten-4-yl)-4-methyl
18	25.4	Benzofuran, 5-methoxy-6,7-dimethyl
19	29.5	1-Naphtol, 6,7-dimethyl

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519 **Table 10**520 Compounds from GC-MS analysis for light oil produced from the pyrolysis oil upgrading experiment  
521 using supercritical water at 410°C for 1 h.

522

Peak number	Retention time	Compounds
1	10.1	O-xylene
2	10.9	Cyclopentanone, 2-methyl
3	12.6	4-isopropyl-1,3-cyclohexanedione
4	13.0	Benzene, 1-ethyl-2-methyl
5	14.1	Benzene, 1, 2, 4-trimethyl
6	15.8	Benzene, 1-propenyl
7	17.2	Benzene, 1-ethenyl-4-ethyl
8	18.2	2-hexenoic acid
9	18.7	Benzofuran, 2-methyl
10	19.2	Phenol
11	19.8	Benzene, 1-methyl-2-(2-propenyl)
12	20.6	Phenol, 2-methyl
13	22.9	Phenol, 2,4-dimethyl
14	25.0	1H-Indene, 1-ethylidene
15	27.8	1,2-benzenediol, 4-methyl
16	29.7	1,2-benzenediol

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### 538 3.7. Comparison of bio-oil upgrading with biomass pyrolysis

539

540 The findings for the bio-oil displayed many similar trends to those which have been previously  
541 identified for biomass pyrolysis [44]. Approximately 91 wt.% conversion was obtained for both  
542 samples pyrolysis oil and biomass, however more water was needed (mass water ratio to sample 15:1)  
543 for biomass to obtain the same conversion. The heavy oils obtained via subcritical and supercritical  
544 water had a reduced of O content of 15.5-16 % for pyrolysis oil upgrading, approximately the same as  
545 for those obtained in biomass conversion. For biomass conversion under supercritical water conditions  
546 above 400°C, a greater gas yield was produced (~28-30 wt.%), while for pyrolysis oil upgrading under  
547 the same conditions showed the gas yield reached a maximum of 23 wt.%. The compound  
548 identification showed a similar distribution obtained with methyl, ethyl and C3-phenols found to  
549 comprise the majority of produced oil from both the biomass and pyrolysis oil conversions.

550

551

## 552 4. Conclusions

553

- 554 1. The liquefaction of pyrolysis oil with high water mass ratios under supercritical and  
555 supercritical water above 400°C gives high overall conversions of up to ~90 wt. % DAF. The  
556 highest heavy oil yield was obtained under supercritical water (R1:9.3) at 410°C for 1 h, with  
557 28 wt. % DAF of heavy oil recovered.
- 558 2. The gas products increased at 450°C for 1 h. However the addition of more water (more than  
559 R1:5.5-biomass to water mass ratio) into the reactor at 410°C did not increase the gas yield.
- 560 3. Approximately 13-14 wt.% DAF of light oil were produced with supercritical water at 410°C  
561 for 1 h. The GC-MS analysis shows the majority of the compounds present are aromatic,  
562 while alkyl phenols are found to be the majority in the heavy oils.
- 563 4. The product conversion was observed to decrease slightly when the temperature was raised to  
564 450°C. This shows that combination reactions occur at higher temperature to form char, hence  
565 reducing the product conversion. Experiments at 410, 430 and 450°C gave the same yield of  
566 heavy oil, suggesting that heavy products remained unchanged, suggesting no cracking  
567 occurred.
- 568 5. The amount of ca. 0.3% (DAF biomass) utilised determined from the additional CO<sub>2</sub>  
569 generated suggests that small amounts water hydrogen are being utilised. This is significantly  
570 lower than for tetralin but sinks for oxygen other than CO<sub>2</sub> cannot be ruled out. .
- 571 6. The heavy oils obtained via subcritical and supercritical water had a reduced of O contents of  
572 15.5-16 %, but not as low those obtained with tetralin.

573 7. The findings demonstrate that near supercritical and supercritical water can be an effective  
574 reaction medium at temperatures above 400°C for converting pyrolysis oil in high yields to  
575 oils with reduced oxygen contents.

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