Pyrolysis oil upgrading in high conversions using sub- and supercritical water above 400ºC

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Abstract

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

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

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1. Introduction

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

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

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

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

Numerous experiments on the hydrodeoxygenation of pyrolysis oils derived from biomass catalytic pyrolysis has been conducted [27-29]. Wang et al. found that the hydrodeoxygenation of pyrolysis oil 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 $310^{o}C$ [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 $400^{o}C$ 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 $370^{o}C$, 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 ($374^{o}C$) at pressures above Pc (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

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

2. Materials and methods

2.1. Materials

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

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

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

2.2. Oil upgrading experiments

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

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 $200^{o}C$. 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 $250^{o}C$ 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 $60^{o}C$ (13 min hold) to $180^{o}C$ (12 min hold) at $10^{o}C/min$. 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 $165^{o}C$ with the CO_2, CO and H_2 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 Quadrapole MS (ionising energy 70 eV, source temperature $280^{o}C$). 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 $50^{o}C$ (2 min) to $300^{o}C$ (28 min)

194 at $5^{o}C/min$. 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 $410^{o}C$*

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 $375^{o}C$ 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 $374^{o}C$ or higher (Tc >$374^{o}C$, Pc > 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.
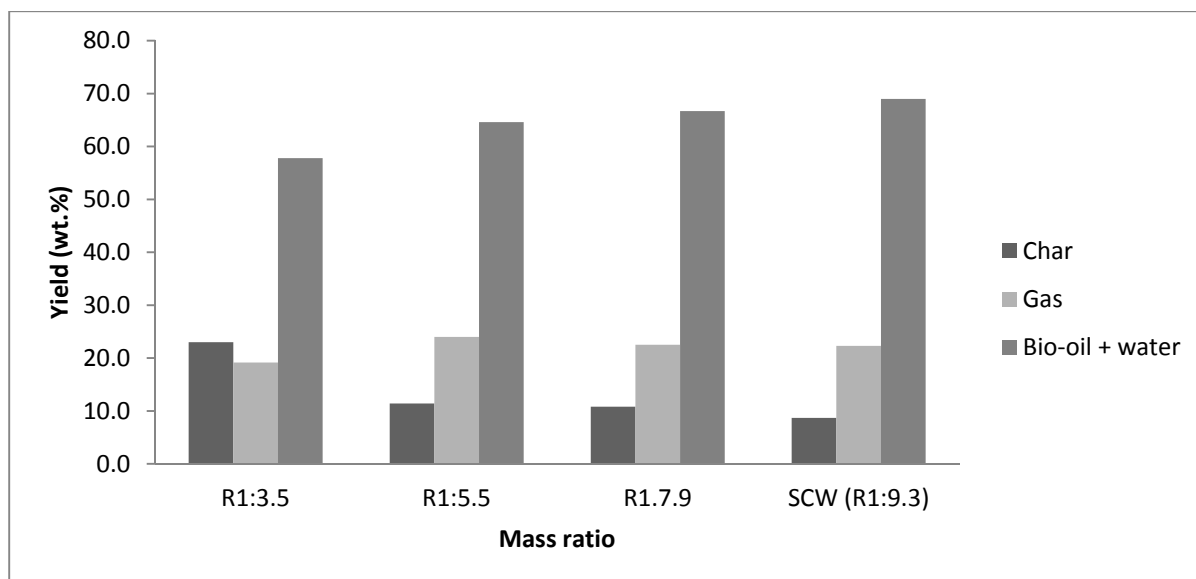
224

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 $410^{o}C$ as compared to supercritical water at $410^{o}C$. 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].

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

Table 2

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

3.2 The effect of reaction pressure

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

Increasing oil yield with escalating pressure has been reported in a previous study [48], with Yang reporting that the bio-oil yield increased in hydrothermal *Sedum plumbizincicola* from 2.84 % to 4.28 % when the pressure was raised to 250 bar from 210 bar at 370°C. The dependency of total oil yields on the pressure of the system did show a clear trend in this study. Higher pressure is known to increase the solvent density and solubility of the target components, allowing solvent to penetrate more efficiently into the molecular structure, enhancing the extraction of bio-oil components, and yielding greater amounts of heavy oil [47] whilst at the same time possibly suppressing cracking to lighter oil.
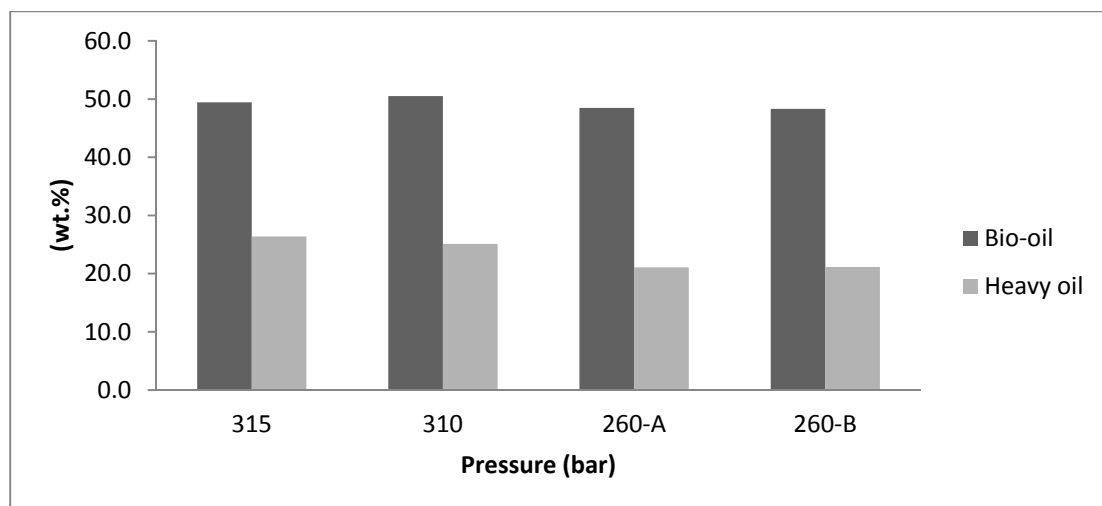
Fig. 2. Heavy oil and bio-oil (total oil) yields (DAF) from hydrous runs of pyrolysis oil at different reaction pressure conducted using the 75 ml reactor at 410°C for 1 h.
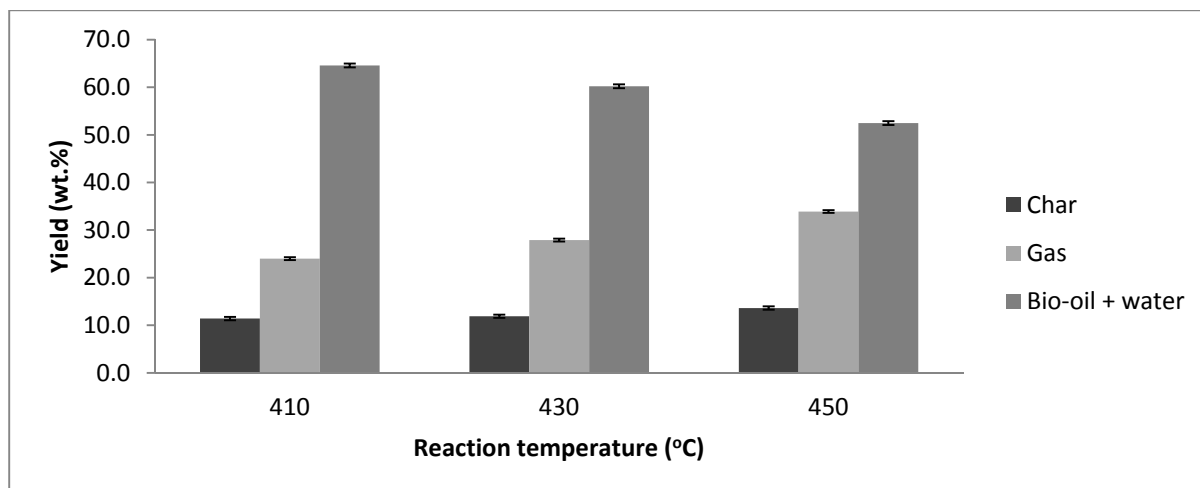
3.3 The effect of reaction temperature

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

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

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


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

Fig. 4 shows the heavy oil and bio-oil yields from experiments in pyrolysis oil upgrading at 410, 430 and 450°C for 1 h. It can clearly be seen that the bio-oil yields decreased with increasing temperature from ~52 wt. % (410°C) to ~48 wt. % (430°C) and rapidly decreased to ~41 wt. % at 450°C. However, the heavy oil yields were the same at ~20 wt. % for all experiments. The results show at higher temperature the breakdown of the light ends started to occur to form gas products while the heavy products remain unchanged, suggesting no cracking occurred.
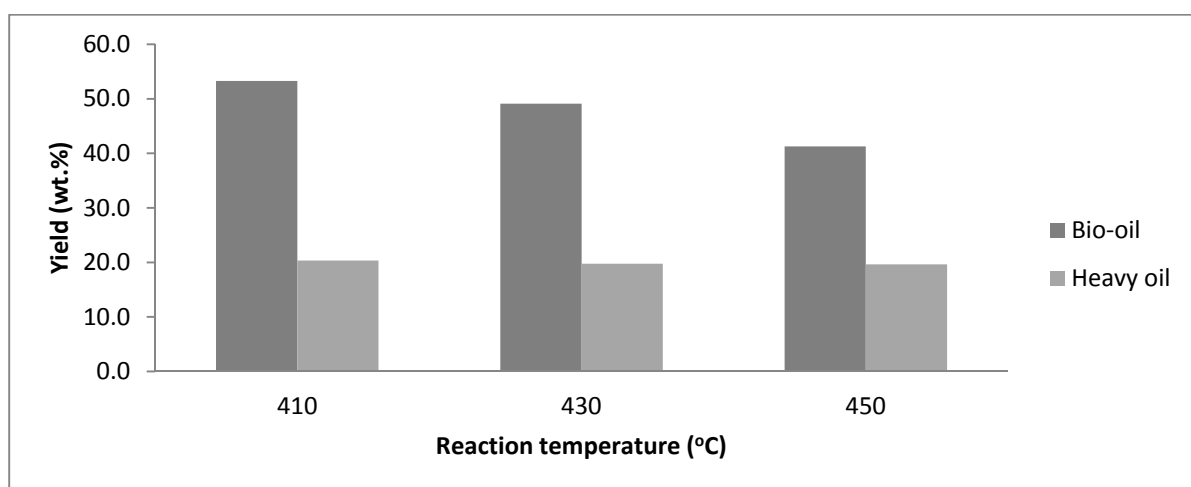
Fig. 4. Heavy oil and bio-oil yields (DAF) in pyrolysis oil upgrading at different reaction temperatures with R1:5.5 conducted using the 75 ml reactor for 1 h.

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3.4. The effect of other solvents

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

The presence of tetralin favours the molecular rearrangement and stabilization of free radicals produced by pyrolysis and hydrolysis of bio-oil through hydrogen donors [50]. Experiments with 1-MN gave ~80 wt. %, ~53 wt. % of bio-oil plus water yields and 25 wt. % gas yields. By using 1-MN-tetralin (mass ratio 80 % : 20 %) gave the same product conversion as the runs with tetralin ~90 wt. %. This is in agreement with Deng et al., 1-MN becomes a good shuttle to carry hydrogen to stabilise the free radicals. The upgrading of bio-oil with tetralin was performed at $360^{o}C$ for 30 mins, and reported 75 % conversion was obtained [51]. However, the authors did not specify the mass ratio used in this experiment.
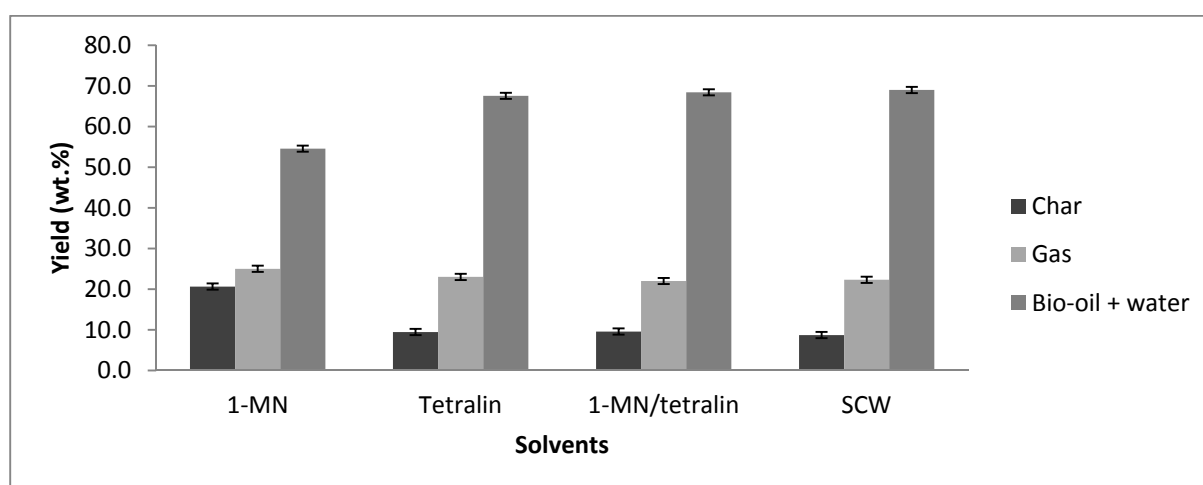
Comparing water and tetralin, although supercritical water gives a higher conversion, tetralin gives a higher yield of heavy oil (40 wt.%) and fewer light products. A similar amount of gas yields in bio-oil upgrading using tetralin and supercritical water at $410^{o}C$ obtained (23 wt. %).

Fig. 5. Pyrolysis oil upgrading with different solvents using the 75 ml reactor at $410^{o}C$ and 1 h. (std deviation ≤0.8; high conversion experiment in SCW included; 4 times replication).

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3.5. Elemental analysis and product recovery

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Table 3 gives the elemental compositions (average base on four times replication) of the heavy oil from pyrolysis oil upgrading at 410^oC. 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_2 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^oC 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^oC) did not promote oxygen removal. Compared with tetralin which produced similar overall conversions (at 410^oC R1:2), the heavy oil have slightly lower oxygen contents (~14 %).

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The H/C and O/C gave 1.1 and 0.2 respectively, for the analysed heavy oil (at 410^oC), 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.

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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^oC produced 11.3% of water. Table 4 gives the oxygen balances carried out on the products (heavy oil, char, CO and CO_2) for the test under supercritical conditions.

358

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).

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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

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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_2				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

Table 5

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

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

*corrected value

3.5. Gas composition and utilisation of water hydrogen

Table 6 gives the gas yields for the experiments that investigated the effect of the mass ratio of
pyrolysis oil:water. It was observed that individual gases like CH_4, H_2 and CO_2 increased from R1:3.5
to R1:5.5, and levelled off afterwards. The CH_4 yield increased from 1.26 wt. % (R1:3.5) to 1.62 wt.
% (R1:5.5). The H_2 yield rose to 0.15 (SCW) from 0.05 at R1:3.5. It was observed that CO_2 increased
by 3 wt. % from R1:3.5 (~12 wt. %) to R1:5.5 (~15 wt. %).

One of the advantages of hydrothermal conversion using subcritical and supercritical water is the
significant removal of oxygen via decarboxylation, which is the optimal way of deoxygenation from
an energetic point of view [49]. Knezevic and co-workers reported the gas produced consisted of more
than 70 wt. % at 350°C (230 bar) for 10 mins. In this study, the yield of CO_2 produced approximately
68 wt. % from the total gas in subcritical water conditions at 410°C for 1 h, in agreement with the
trend reported [49].

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

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

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

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

Table 6

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

	R1:3.5	R1:5.5	R1:7.9	R1:9.3 (SCW)
Gas yields (wt. % DAF)				
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

Std deviation for CO_2 ~0.14-0.25; 4 times replication

Table 7

Hydrogen consumed in pyrolysis oil upgrading with subcritical and supercritical water conditions at $410^{\circ}C$ and $450^{\circ}C$ (all as a % DAF basis).

	% of H donated	
	$410^{\circ}C$	$450^{\circ}C$
Mass ratio		
R1:4 (high pressure-315 bar)	0.21	
Supercritical water (R1:9.3)	<0.01	
R1:5.5		0.34

Table 8 lists the carbon balance for pyrolysis oil upgrading from the experiment under supercritical water conditions. The total carbon balance was found to be ~79.2 wt. % with oil, char and CO_2 contributing the predominant weight of C, giving 45, 15 and 9 wt. % respectively. In the carbon balance, the 20.8 wt. % product loss is assumed to be light oil giving a total oil yield of *ca*. 66 wt. % of the total carbon compared to ca. 42 wt. % on a mass basis. The light oil mass loss experiment was performed in our previous study [44].

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_2				0.074	9.09
CO				0.036	4.46
CH_4				0.023	2.81
C_2H_4				0.001	0.18
C_2H_6				0.007	0.83
C_3H_6				0.005	0.61
C_3H_8				0.005	0.63
C_4H_{10}				0.002	0.28
Total gas				0.153	18.9
			Total (g)	0.646	
			Carbon conversion (wt. %)		79.2

3.6. Oil composition

The total ion chromatograms (TIC) from the heavy oil generated by pyrolysis oil upgrading under supercritical water at 410°C are shown in Fig. 6, and Table 9 lists the main compounds identified. Alkyl phenol is seen to form the majority of the compounds that have been identified. The C_6-C_{12} phenols and small amounts of benzenes account for all the constituents listed. The *m/z* 108, 122 and 136 mass chromatograms show the presence of methyl, dimethyl and ethyl and C_3-phenols.

The compounds identification for the light oil from the pyrolysis oil upgrading experiments using supercritical water at 410°C and 1 h is given in Fig. 7 and the compounds are listed in Table 10. The majority of the compounds are alkyl-substituted benzenes with phenols also present. The C_8-C_{10} benzenes and phenols account for all the constituents listed. The mass chromatograms at *m/z* 105 show the C_3-benzene at peaks 4, 5 and 6.
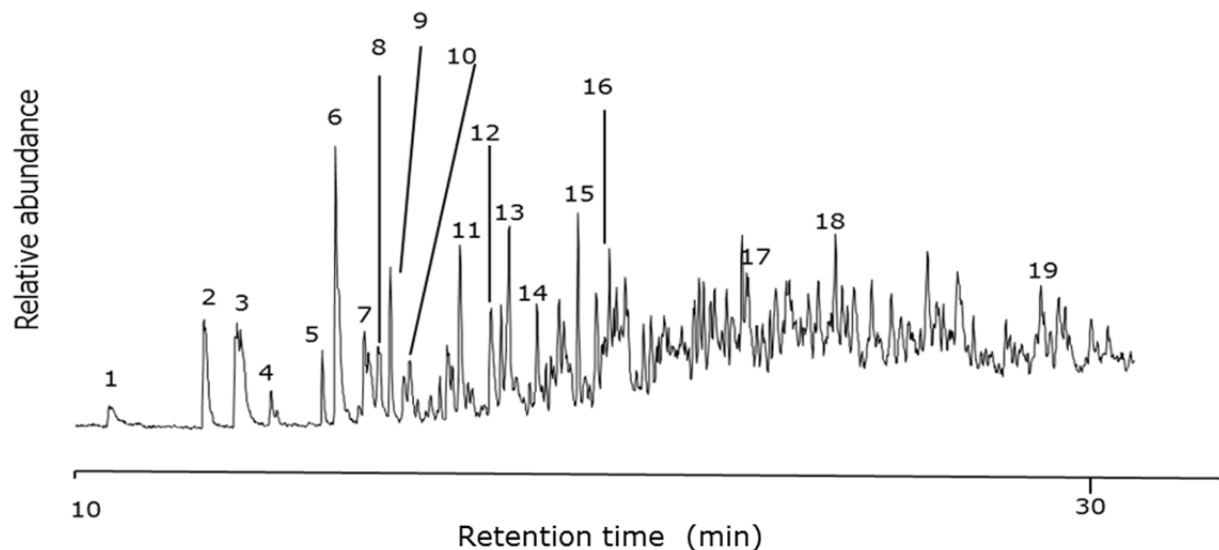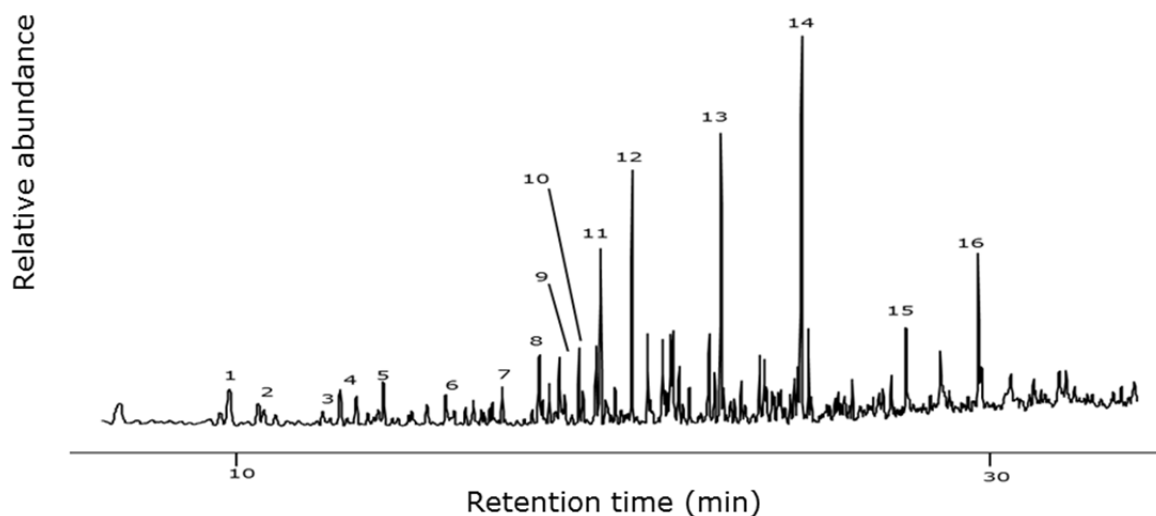
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492 Fig. 6. Compound identification (for Table 9) from the TIC for the heavy oil in the pyrolysis oil

493 upgrading experiment using supercritical water at 410°C for 1 h.

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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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3.7. Comparison of bio-oil upgrading with biomass pyrolysis

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

4. Conclusions

1. The liquefaction of pyrolysis oil with high water mass ratios under supercritical and supercritical water above 400°C gives high overall conversions of up to ~90 wt. % DAF. The highest heavy oil yield was obtained under supercritical water (R1:9.3) at 410°C for 1 h, with 28 wt. % DAF of heavy oil recovered.

2. The gas products increased at 450°C for 1 h. However the addition of more water (more than R1:5.5-biomass to water mass ratio) into the reactor at 410°C did not increase the gas yield.

3. Approximately 13-14 wt.% DAF of light oil were produced with supercritical water at 410°C for 1 h. The GC-MS analysis shows the majority of the compounds present are aromatic, while alkyl phenols are found to be the majority in the heavy oils.

4. The product conversion was observed to decrease slightly when the temperature was raised to 450°C. This shows that combination reactions occur at higher temperature to form char, hence reducing the product conversion. Experiments at 410, 430 and 450°C gave the same yield of heavy oil, suggesting that heavy products remained unchanged, suggesting no cracking occurred.

5. The amount of ca. 0.3% (DAF biomass) utilised determined from the additional CO_2 generated suggests that small amounts water hydrogen are being utilised. This is significantly lower than for tetralin but sinks for oxygen other than CO_2 cannot be ruled out. .

6. The heavy oils obtained via subcritical and supercritical water had a reduced of O contents of 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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578 **REFERENCES**

579

580 [1. Onay Ö, Beis SH, Koçkar ÖM. Fast pyrolysis of rape seed in a well-swept fixed-bed reactor.
581 *Journal of Analytical and Applied Pyrolysis* 2001,**58–59**:995-1007.
582 2. Beis SH, Onay Ö, Koçkar ÖM. Fixed-bed pyrolysis of safflower seed: influence of pyrolysis
583 parameters on product yields and compositions. *Renewable Energy* 2002,**26**:21-32.
584 3. Onay O, Mete Koçkar O. Fixed-bed pyrolysis of rapeseed (Brassica napus L.). *Biomass and*
585 *Bioenergy* 2004,**26**:289-299.
586 4. Gray KA, Zhao L, Emptage M. Bioethanol. *Current Opinion in Chemical Biology* 2006,**10**:141-
587 146.
588 5. Acikgoz C, Kockar OM. Flash pyrolysis of linseed (Linum usitatissimum L.) for production of
589 liquid fuels. *Journal of Analytical and Applied Pyrolysis* 2007,**78**:406-412.
590 6. Akhtar J, Kuang SK, Amin NS. Liquefaction of empty palm fruit bunch (EPFB) in alkaline hot
591 compressed water. *Renewable Energy* 2010,**35**:1220-1227.
592 7. Isa KM, Daud S, Hamidin N, Ismail K, Saad SA, Kasim FH. Thermogravimetric analysis and the
593 optimisation of bio-oil yield from fixed-bed pyrolysis of rice husk using response surface
594 methodology (RSM). *Industrial Crops and Products* 2011,**33**:481-487.
595 8. Bridgwater AV, Peacocke GVC. Fast pyrolysis processes for biomass. *Renewable and*
596 *Sustainable Energy Reviews* 2000,**4**:1-73.
597 9. Zhang L, Xu C, Champagne P. Overview of recent advances in thermo-chemical conversion of
598 biomass. *Energy Conversion and Management* 2010,**51**:969-982.
599 10. Zhang Y. Hydrothermal liquefaction to convert biomass into crude oil. In: *Biofuels from*
600 *agriculturals wastes and byproducts*. Edited by Hans P. Blaschek, Thaddeus C. Ezeji, Jurgen
601 Scheffran: Blackwell publishing; 2010.
602 11. Predel M, Kaminsky W. Pyrolysis of rape-seed in a fluidised-bed reactor. *Bioresource*
603 *Technology* 1998,**66**:113-117.
604 12. Zhang H, Xiao R, Huang H, Xiao G. Comparison of non-catalytic and catalytic fast pyrolysis of
605 corncob in a fluidized bed reactor. *Bioresource Technology* 2009,**100**:1428-1434.
606 13. Heo HS, Park HJ, Park Y-K, Ryu C, Suh DJ, Suh Y-W*, et al.* Bio-oil production from fast pyrolysis
607 of waste furniture sawdust in a fluidized bed. *Bioresource Technology* 2010,**101**:S91-S96.
608 14. Chen T, Wu C, Liu R, Fei W, Liu S. Effect of hot vapor filtration on the characterization of bio-
609 oil from rice husks with fast pyrolysis in a fluidized-bed reactor. *Bioresource Technology*
610 2011,**102**:6178-6185.
611 15. Pattiya A. Bio-oil production via fast pyrolysis of biomass residues from cassava plants in a
612 fluidised-bed reactor. *Bioresource Technology* 2011,**102**:1959-1967.
613 16. Zhang H, Xiao R, Wang D, He G, Shao S, Zhang J*, et al.* Biomass fast pyrolysis in a fluidized bed
614 reactor under N2, CO2, CO, CH4 and H2 atmospheres. *Bioresource Technology*
615 2011,**102**:4258-4264.
616 17. Pattiya A, Suttibak S. Production of bio-oil via fast pyrolysis of agricultural residues from
617 cassava plantations in a fluidised-bed reactor with a hot vapour filtration unit. *Journal of*
618 *Analytical and Applied Pyrolysis* 2012,**95**:227-235.
619 18. Suttibak S, Sriprateep K, Pattiya A. Production of Bio-oil via Fast Pyrolysis of Cassava Rhizome
620 in a Fluidised-Bed Reactor. *Energy Procedia* 2012,**14**:668-673.
621 19. Abdullah N, Gerhauser H. Bio-oil derived from empty fruit bunches. *Fuel* 2008,**87**:2606-2613.
622 20. Misson M, Haron R, Kamaroddin MFA, Amin NAS. Pretreatment of empty palm fruit bunch
623 for production of chemicals via catalytic pyrolysis. *Bioresource Technology* 2009,**100**:2867-
624 2873.

21. Fan S-P, Zakaria S, Chia C-H, Jamaluddin F, Nabihah S, Liew T-K, *et al.* Comparative studies of products obtained from solvolysis liquefaction of oil palm empty fruit bunch fibres using different solvents. *Bioresource Technology* 2011,**102**:3521-3526.

22. Ji-lu Z. Bio-oil from fast pyrolysis of rice husk: Yields and related properties and improvement of the pyrolysis system. *Journal of Analytical and Applied Pyrolysis* 2007,**80**:30-35.

23. Zheng J-L. Pyrolysis oil from fast pyrolysis of maize stalk. *Journal of Analytical and Applied Pyrolysis* 2008,**83**:205-212.

24. Zhang Q, Chang J, Wang T, Xu Y. Review of biomass pyrolysis oil properties and upgrading research. *Energy Conversion and Management* 2007,**48**:87-92.

25. Bridgwater AV. Review of fast pyrolysis of biomass and product upgrading. *Biomass and Bioenergy* 2012,**38**:68-94.

26. Rezzoug S-A, Capart R. Solvolysis and hydrotreatment of wood to provide fuel. *Biomass and Bioenergy* 1996,**11**:343-352.

27. Wang Y, He T, Liu K, Wu J, Fang Y. From biomass to advanced bio-fuel by catalytic pyrolysis/hydro-processing: Hydrodeoxygenation of bio-oil derived from biomass catalytic pyrolysis. *Bioresource Technology* 2012,**108**:280-284.

28. Xu Y, Wang T, Ma L, Zhang Q, Wang L. Upgrading of liquid fuel from the vacuum pyrolysis of biomass over the Mo–Ni/γ-Al2O3 catalysts. *Biomass and Bioenergy* 2009,**33**:1030-1036.

29. Spadaro L, Palella A, Frusteri F, Arena F. Valorization of crude bio-oil to sustainable energy vector for applications in cars powering and on-board reformers via catalytic hydrogenation. *International Journal of Hydrogen Energy*.

30. Xiu S, Shahbazi A. Bio-oil production and upgrading research: A review. *Renewable and Sustainable Energy Reviews* 2012,**16**:4406-4414.

31. Song C, Hu H, Zhu S, Wang G, Chen G. Nonisothermal catalytic liquefaction of corn stalk in subcritical and supercritical water. *Energy & Fuels* 2004,**18**:90-96.

32. Jin B, Duan P, Zhang C, Xu Y, Zhang L, Wang F. Non-catalytic liquefaction of microalgae in sub- and supercritical acetone. *Chemical Engineering Journal* 2014,**254**:384-392.

33. Zhang J, Chen W-T, Zhang P, Luo Z, Zhang Y. Hydrothermal liquefaction of Chlorella pyrenoidosa in sub- and supercritical ethanol with heterogeneous catalysts. *Bioresource Technology* 2013,**133**:389-397.

34. Brand S, Susanti RF, Kim SK, Lee H-s, Kim J, Sang B-I. Supercritical ethanol as an enhanced medium for lignocellulosic biomass liquefaction: Influence of physical process parameters. *Energy* 2013,**59**:173-182.

35. Li R-d, Li B-s, Yang T-h, Xie Y-h. Liquefaction of rice stalk in sub- and supercritical ethanol. *Journal of Fuel Chemistry and Technology* 2013,**41**:1459-1465.

36. Toor SS, Reddy H, Deng S, Hoffmann J, Spangsmark D, Madsen LB, *et al.* Hydrothermal liquefaction of Spirulina and Nannochloropsis salina under subcritical and supercritical water conditions. *Bioresource Technology* 2013,**131**:413-419.

37. Peterson AA, Frederick Vogel, Russel P Lachance, Morgan Froling, Michael J Antal Jr, Tester JW. Thermochemical biofuel production in hyrothermal media: A review of sub- and supercritical water technologies. *Energy & Environmental Science* 2008,**1**:32-65.

38. Toor SS, Rosendahl L, Rudolf A. Hydrothermal liquefaction of biomass: A review of subcritical water technologies. *Energy* 2011,**36**:2328-2342.

39. Brunner G. Near critical and supercritical water. Part I. Hydrolytic and hydrothermal processes. *The Journal of Supercritical Fluids* 2009,**47**:373-381.

40. Vasilakos NP, Austgen DM. Hydrogen-donor solvents in biomass liquefaction. *Ind. Eng. Chem. Process Des. Dev* 1985,**24**:304-311.

41. Kuznetsov PN, Bimer J, Salbut PD, Korniyets ED, Kuznetsova LI, Snape CE. The nature of the synergistic effect of binary tetralin-alcohol solvents in Kansk-Achinsk brown coal liquefaction. *Fuel Processing Technology* 1997,**50**:139-152.

675 42.   Deng H. Thermally mediated liquid solvent extraction of biomass: University of Nottingham;
676   2013.
677 43.   Deng H, Meredith W, Uguna CN, Snape CE. Impact of solvent type and condition on biomass
678   liquefaction to produce heavy oils in high yield with low oxygen contents. *Journal of*
679   *Analytical and Applied Pyrolysis* 2015.
680 44.   Isa KM, Snape CE, Uguna C, Meredith W. High conversions of miscanthus using sub- and
681   supercritical water above 400 °C. *Journal of Analytical and Applied Pyrolysis*
682   2015,**113**:646-654.
683 45.   Adschiri T, Sato T, Shibuichi H, Fang Z, Okazaki S, Arai K. Extraction of Taiheiyo coal with
684   supercritical water–HCOOH mixture. *Fuel* 2000,**79**:243-248.
685 46.   Han L-n, Zhang R, Bi J-c. Upgrading of coal-tar pitch in supercritical water. *Journal of Fuel*
686   *Chemistry and Technology* 2008,**36**:1-5.
687 47.   Chan YH, Yusup S, Quitain AT, Uemura Y, Sasaki M. Bio-oil production from oil palm biomass
688   via subcritical and supercritical hydrothermal liquefaction. *The Journal of Supercritical Fluids*
689   2014,**95**:407-412.
690 48.   Yang J-g. Heavy metal removal and crude bio-oil upgrading from Sedum plumbizincicola
691   harvest using hydrothermal upgrading process. *Bioresource Technology* 2010,**101**:7653-7657.
692 49.   Knezevic D, van Swaaij WPM, Kersten SRA. Hydrothermal conversion of biomass. II.
693   Conversion of wood, pyrolysis oil, and glucose in hot compressed water. *Ind Eng Chem Res*
694   2010,**49**:104-112.
695 50.   Li Z, Cao J, Huang K, Hong Y, Li C, Zhou X*, et al.* Alkaline pretreatment and the synergic effect
696   of water and tetralin enhances the liquefaction efficiency of bagasse. *Bioresource Technology*
697   2015,**177**:159-168.
698 51.   Zhang S, Yan Y, Li T, Ren Z. Upgrading of liquid fuel from the pyrolysis of biomass. *Bioresource*
699   *Technology* 2005,**96**:545-550.
700 52.   Duan P, Savage PE. Catalytic hydrotreatment of crude algal bio-oil in supercritical water.
701   *Applied Catalysis B: Environmental* 2011,**104**:136-143.
702 53.   Pajak J, Krebs V, Marêché JF, Furdin G. Hydrogen transfer from tetralin and decalin to high-
703   temperature coal tars. Relation with carbon deposit formation. *Fuel Processing Technology*
704   1996,**48**:73-81.
705
706
707
708