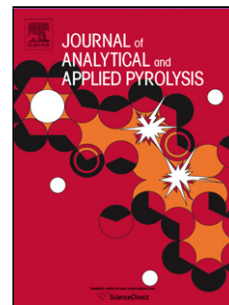


Accepted Manuscript

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PII: S0165-2370(15)30238-2
DOI: <http://dx.doi.org/doi:10.1016/j.jaap.2016.03.004>
Reference: JAAP 3681

To appear in: *J. Anal. Appl. Pyrolysis*

Received date: 6-10-2015
Revised date: 20-2-2016
Accepted date: 4-3-2016

Please cite this article as: Khairuddin Md Isa, Colin E.Snape, Clement Uguna, Will Meredith, Hui Deng, Pyrolysis oil upgrading in high conversions using sub- and supercritical water above 400^{circ}C, Journal of Analytical and Applied Pyrolysis <http://dx.doi.org/10.1016/j.jaap.2016.03.004>

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

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Highlights

- Pyrolysis oil upgrading in near supercritical and supercritical water above 400°C
- The highest feedstock conversion of 90 wt. %
- Produced heavy oil with relatively low oxygen content (~15 %).
- The utilisation of water hydrogen in pyrolysis oil upgrading (*Ca* 0.30 %).

Abstract

The upgrading of pyrolysis oil to bio-fuel was investigated using sub- and supercritical water at 410 and 450°C, 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 410°C, 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 410°C. No further cracking of the heavy oil was observed for experiments at 450°C, and an increase of 10 wt. % in the gas yield was observed when the temperature was increased to 450°C (33 wt. %) from 410°C (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 450°C), 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 450°C 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

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

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

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

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

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

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°C, 450°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 cool down. Once the reactor was cooled to room temperature, the gas inside the reactor was transferred into a sampling bag using a gas syringe and the volume collected was recorded.

The reacted products (solid and liquid) were washed with approximately 150 ml toluene and transferred into the round bottom flask. Heavy oil can be defined as the oil product from oil upgrading process which has a density of greater than one, whilst light oil has a density less than one which either floated on the water or was on the reactor walls after the experiments. A Dean-Stark apparatus was used to separate water from reacted products (toluene solubles and char) for the anhydrous runs. For the hydrous runs, water was first pipetted out from the reactor and the remaining was distilled to

remove water using the Dean-Stark apparatus. The flask was heated by a heating mantle at 110°C for 12 h. After reflux, the products in the round bottom flask (toluene solubles and char) were allowed to cool, and the volume of generated water from the reaction was recorded (water for anhydrous).

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

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

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

2.3. Analyses

The gases were analysed using a Clarus 580 gas chromatograph (GC) fitted with a FID and TCD detectors operating at 200°C. 5 ml of sample of gas introduced to the GC for hydrocarbon and non-hydrocarbon analysis. Hydrocarbon (HC) gas was determined by FID by injecting 100 µl of gas samples (split ratio 10:1) at 250°C with separation performed on an alumina plot fused silica 30 m x 0.32 mm x 5 µm column, with helium as the carrier gas. The oven temperature was programmed from 60°C (13 min hold) to 180°C (12 min hold) at 10°C/min. Individual gas yields were determined quantitatively in relation to methane as an external gas standard, and the total yield of the generated

gases calculated using the total volume of gas collected in relation to the aliquot volume of gas introduced to the FID. Non-hydrocarbon (NHC) gas was determined by TCD by injecting 500 μl of sample of gas at 165°C with the CO_2 , CO and H_2 yields being calculated using the external gas standard.

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

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

3. Results and discussion

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

The pyrolysis oil upgrading experiments to investigate the effect of the mass ratio of pyrolysis oil to water were conducted using various ratios, namely R1:3.5, R1:5.5, R1:7.9, and supercritical water conditions with R1:9.3. The protocol used to obtain the supercritical water conditions was the same as described in a previous study [44]. A series of blank runs with water (20, 22 and 24 ml) using the 75 ml vessel were conducted to determine the baseline data for subcritical and supercritical conditions. Experiments were conducted at 375°C for 1 h, giving measured water pressures of 206 bar (20 ml), 212 bar (22 ml) and 218 bar (24 ml). Therefore, to reach supercritical conditions, an amount of >24 ml water must be loaded in the 75 ml vessel with temperature of 374°C or higher ($T_c > 374^\circ\text{C}$, $P_c > 221$ bar).

The experiments were conducted for 1 h using 75 ml reactor. The pressures recorded for these experiments were 260-320 bar. Adding more water into the reactor gave increasing conversions with experiments in the supercritical water (SCW) condition giving the highest conversion of ~89-91 wt. % (Fig. 1). 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. %). Coal conversion in SCW has been reported to be higher than in supercritical toluene [45]. Han et al. (2008) reported SCW can promote the conversion of coal-tar pitch to maltene and retard the formation of gas and char [46]. There have been no previous reports on the pyrolysis oil upgrading in direct liquefaction (without catalyst) via sub- and supercritical water conditions.

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

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

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

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.

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. Experiments were designed using pyrolysis oil to water mass ratio of 1:5.5 with pressure controlled at 290-300 bar. 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. 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.

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°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°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°C obtained (23 wt. %).

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 CO₂ 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 CO₂) 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).

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 CH₄, H₂ and CO₂ increased from R1:3.5 to R1:5.5, and levelled off afterwards. The CH₄ yield increased from 1.26 wt. % (R1:3.5) to 1.62 wt. % (R1:5.5). The H₂ yield rose to 0.15 (SCW) from 0.05 at R1:3.5. It was observed that CO₂ 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 CO₂ 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 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].

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.

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 CO₂ generated suggests that small amounts water hydrogen are being utilised. This is significantly lower than for tetralin but sinks for oxygen other than CO₂ 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.
7. The findings demonstrate that near supercritical and supercritical water can be an effective reaction medium at temperatures above 400°C for converting pyrolysis oil in high yields to oils with reduced oxygen contents.

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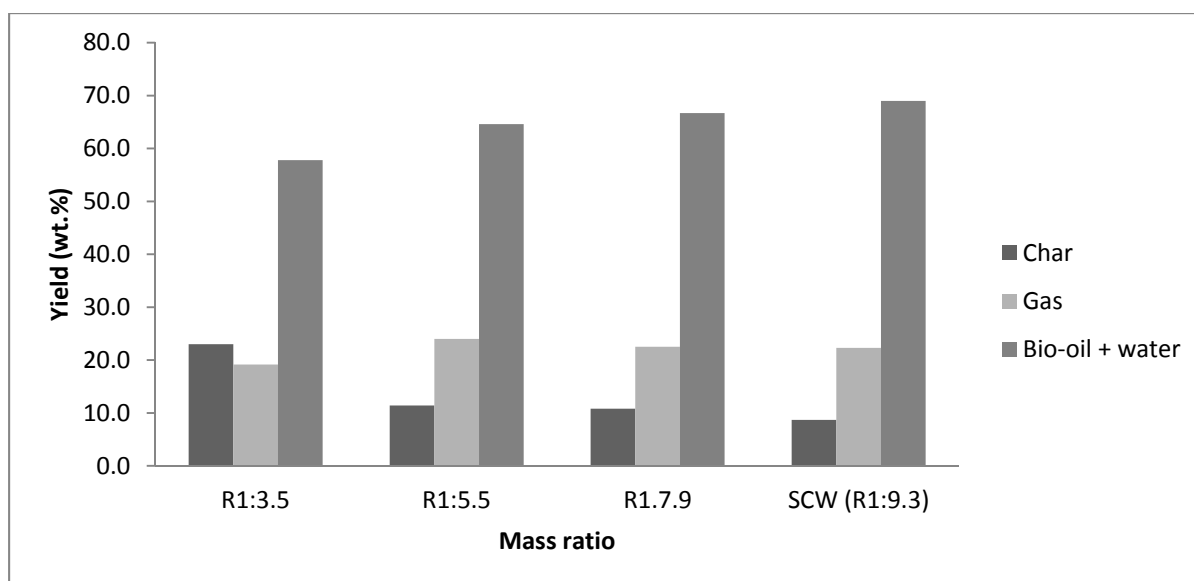


Fig. 1. Pyrolysis oil upgrading with hydrous pyrolysis (various mass ratios of sample to water and supercritical water (SCW)) using the 75 ml reactor at 410°C for 1 h.

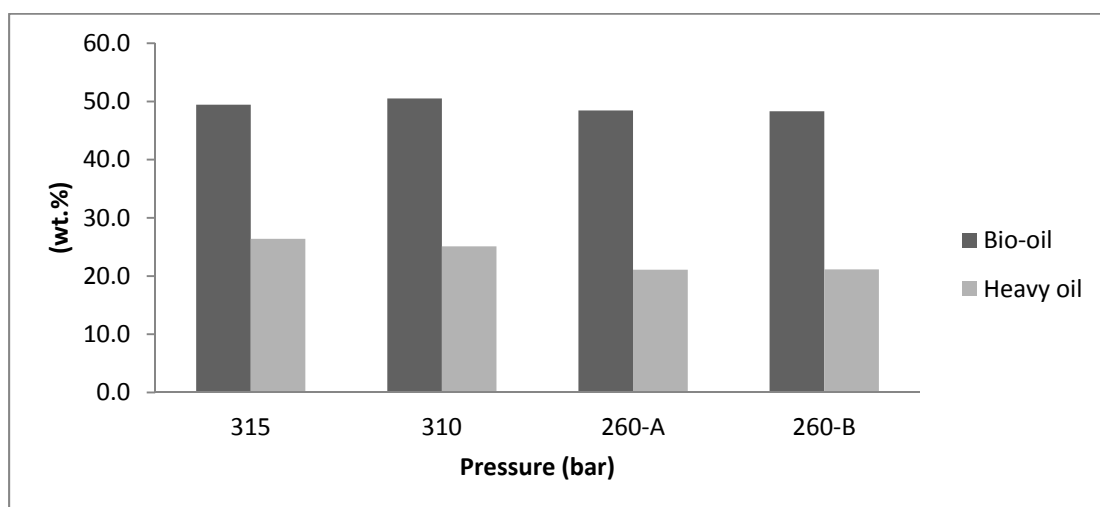


Fig. 2. Heavy oil and bio-oil (total oil) yields (DAF) from hydrous runs of pyrolysis oil at different reaction pressure conducted using the 75 ml reactor at 410°C for 1 h.

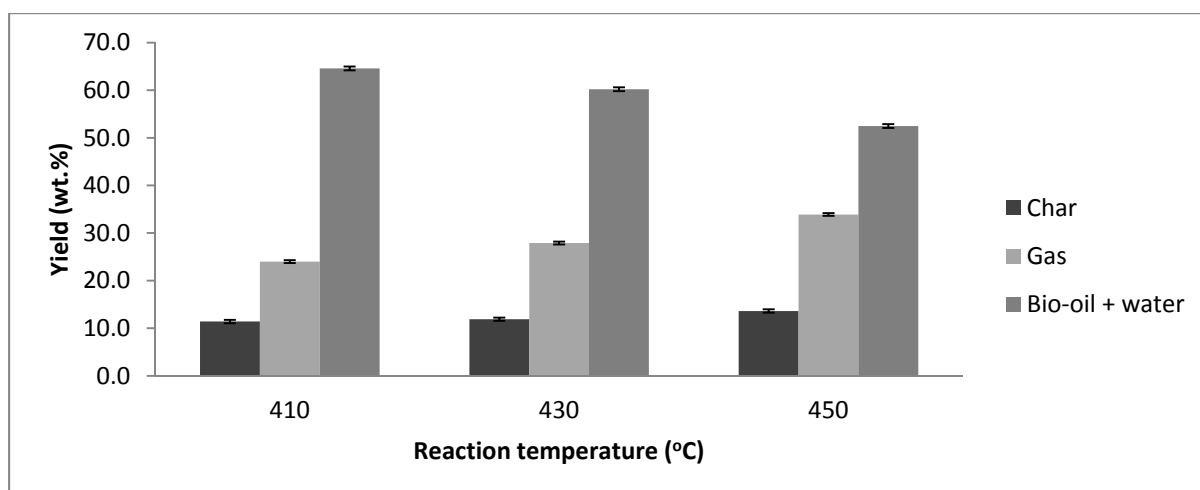


Fig. 3. Yield of products (DAF) in pyrolysis oil upgrading at different reaction temperatures with R1:5.5 using the 75 ml reactor for 1 h. (std deviation ≤ 0.4 ; 4 times replication).

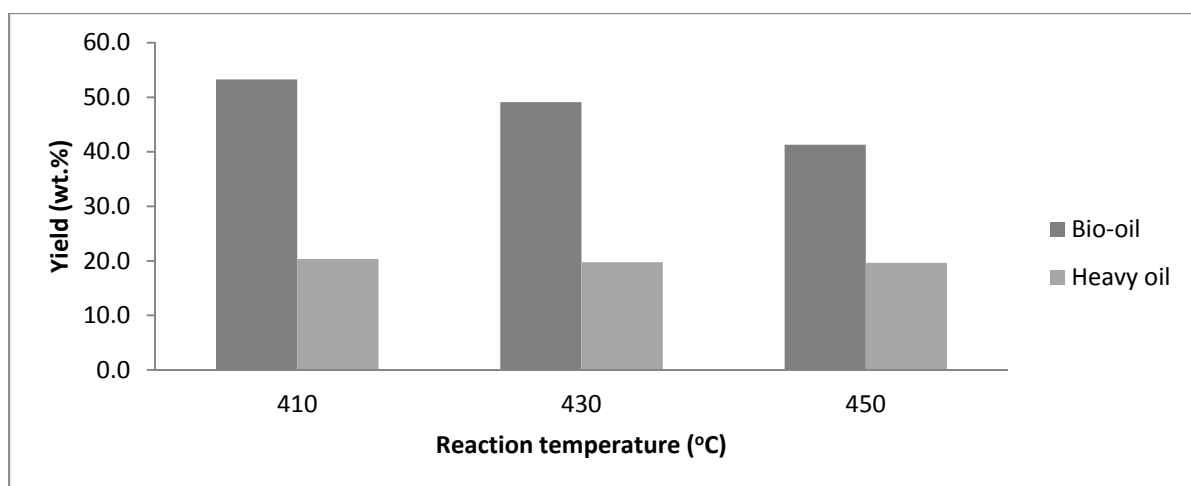


Fig. 4. Heavy oil and bio-oil yields (DAF) in pyrolysis oil upgrading at different reaction temperatures with R1:5.5 conducted using the 75 ml reactor for 1 h.

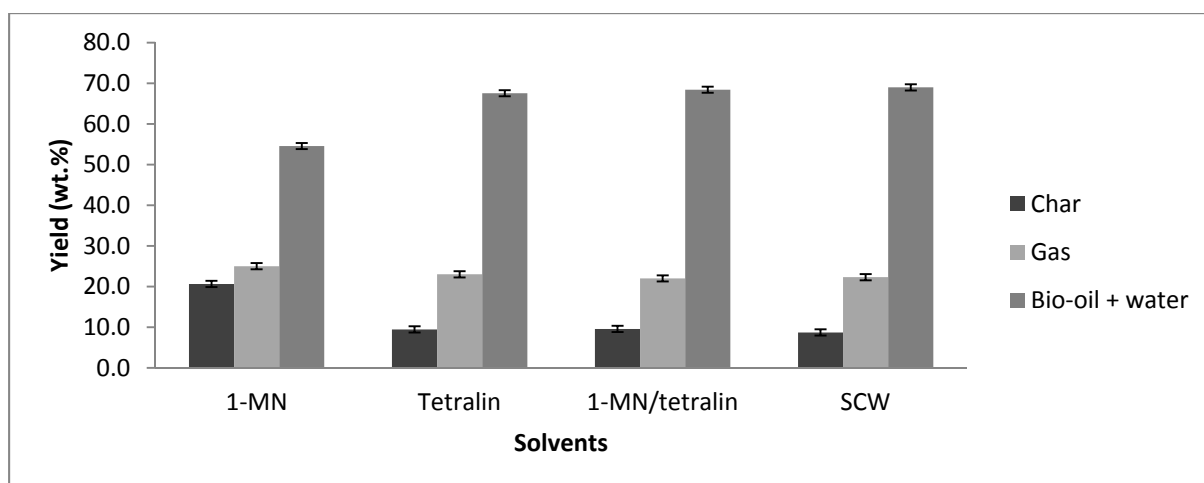


Fig. 5. Pyrolysis oil upgrading with different solvents using the 75 ml reactor at 410°C and 1 h. (std deviation ≤ 0.8 ; high conversion experiment in SCW included; 4 times replication).

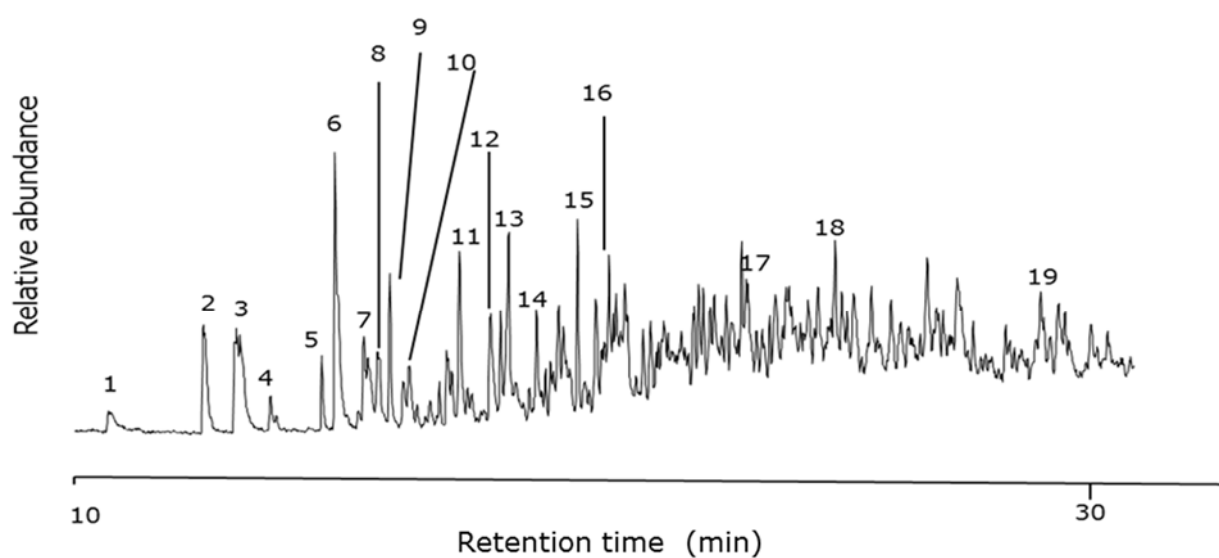


Fig. 6. Compound identification (for Table 9) from the TIC for the heavy oil in the pyrolysis oil upgrading experiment using supercritical water at 410°C for 1 h.

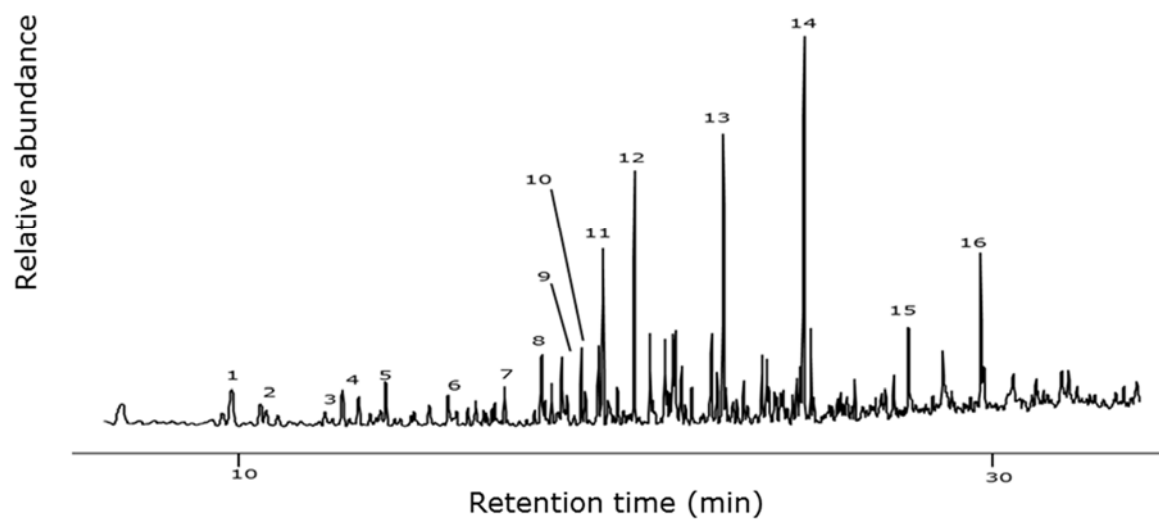


Fig. 7. Compound identification (Table 10) from the TIC for the light oil in pyrolysis oil upgrading experiment using supercritical water at 410°C for 1 h.

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

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

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

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

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

Table 4 Oxygen balance to calculate the water generated from pyrolysis oil upgrading with supercritical water at 410°C for 1 h.

	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

Table 6 Hydrocarbon gas (C₁-C₄) 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)
<i>Gas yields (wt. % DAF)</i>				
CH ₄	1.25	1.61	1.43	1.50
C ₂ H ₄	0.09	0.11	0.12	0.10
C ₂ H ₆	0.49	0.57	0.41	0.51
C ₃ H ₆	0.23	0.31	0.29	0.34
C ₃ H ₈	0.34	0.38	0.37	0.37
C ₄ H 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 CO₂ ~0.14-0.25; 4 times replication

Table 7 Hydrogen consumed in pyrolysis oil upgrading with subcritical and supercritical water conditions at 410°C and 450°C (all as a % DAF basis).

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

	(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 ₂ H ₄				0.001	0.18
C ₂ H ₆				0.007	0.83
C ₃ H ₆				0.005	0.61
C ₃ H ₈				0.005	0.63
C ₄ H ₁₀				0.002	0.28
Total gas				0.153	18.9
			Total (g)	0.646	
			Carbon conversion (wt. %)		79.2

Table 9 Compounds from GC-MS analysis for heavy oil produced from the pyrolysis oil upgrading experiment using supercritical water at 410°C for 1 h.

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

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

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