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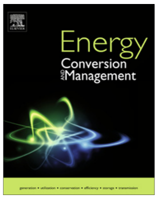

Pyrolysis oil upgrading using supercritical water, with tetralin and 1-methylnaphtalene as a baseline study

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ABSTRACT

The upgrading of pyrolysis oil to bio-fuel in high conversion was investigated using supercritical water (SCW) above 400 °C with the 75 mL reactor for 1 h. Tetralin and 1-methylnaphtalene provided a baseline product conversion as a good hydrogen donor and non-hydrogen donor (eventhough with much lower mass to solvent mass ratio). Experiments under SCW indicate that conversions increased with increasing pyrolysis oil to water mass ratio at high water ratio, these giving 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. Tetralin runs gave similar product conversion of 90 wt.% but with lower sample to solvent mass ratio (1:2), and 1-methylnaphtalene yielded much lower conversion 70 wt.% using the same sample to solvent mass ratio. A combination of 1-methylnaphtalene/tetralin gave the same feedstock conversion (90 wt.%), suggesting that only a small amount of hydrogen needed to produce high conversion. The oxygen contents of the heavy oil recovered were 16% for SCW, with H/C atomic ratios of 1.1. The heating value of upgraded oil was increased to 33 MJ/kg compared to 18.5 MJ/kg of initial pyrolysis oil. The heavy oil with similar product conversion (90 wt.%) using tetralin and much lower solvent to oil ratios had slightly lower oxygen content (14%), and the H content was increased from 7.0 wt.% to 7.3 wt.%.

1. Introduction

Thermochemical processes have been employed for converting biomass into alternative energy and chemicals by researchers worldwide [1–7]. Thermal degradation process is 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 oxidized to produce syngas), and pyrolysis (a thermal degradation in the absence of oxygen to produce liquid products) [8,9]. Substantial research is being conducted within the field of energy to seek alternative fuels for gasoline and diesel.

Fast pyrolysis of biomass is a simple way to obtain bio-oil with high yield. Fast and slow pyrolysis can be conducted depending on the types of products desired. Many 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 [10–17]. The oil palm empty-fruit-bunch has been pyrolysed to produce bio-oil and chemicals [18–20]. Maize stalk has been fast pyrolysed to produce bio-oil [21,22].

Although pyrolysis techniques have demonstrated a promising route to produce liquid fuels (approximately 70–80%), the product can be unstable due to its high content of alcohols, aldehydes, ketones, esters, acids, aromatics, furans, phenols, sugars, guaiacols, and water [23]. Pyrolysis oil requires post treatment to improve its quality [24]. Pyrolysis oils contain a high oxygen content (approximately 40%) and 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 contains high water content derived from the original moisture in the feedstock, and also due to dehydration of sugars to produce furfurals and other chemical routes. 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 in the range from 2 to 3 [7]. There are a few methods which can be employed to improve the quality of bio-oil,

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such as hydrodeoxygenation, catalytic cracking, emulsification and steam reforming [27].

In order to decrease the oxygen content and to increase the stability of the pyrolysis oil, catalytic hydrodeoxygenation (HDO) is one of the most promising upgrading methods, which can provide a combustible mixture with a higher heating value and stronger to resemblance to fossil fuels. A number of experiments on the hydrodeoxygenation of pyrolysis oils derived from biomass catalytic pyrolysis have been conducted [28–30]. Xu et al. claimed 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% [29]. Wang et al. reported 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]. However, molecular hydrogen is needed in HDO and requires additional cost.

Water can simultaneously act as both a reactant and a catalyst [31], and has received extensive attention because it is inexpensive and easy to recycle reaction medium for converting wet and dry biomass into crude bio-oils with or without a catalyst [32]. Hydrothermal liquefaction (also known as a 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 [33]. 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 [34]. By moving from subcritical to supercritical temperatures (374 °C) at pressures above Pc (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 [33].

Supercritical water (SCW) has been used in previous fuel processing studies, especially for the upgrading of feedstocks such as heavy oils and coal tar [35,36]. Although SCW requires elevated pressures compared to some competitive technologies, it has potential advantages in terms of process intensity, process energy balance, water recovery, and product distribution [37]. In-situ hydrogen generation promoting hydrogenation in liquefaction of biomass [38] and upgrading of heavy oil [39] has been reported. Isa et al. reported the performance of SCW as a weak hydrogen donor in liquefaction of biomass [38]. Reduced CO and increased CO_2 yields suggested that water hydrogen was utilised but the estimated amounts of ca. 0.5% under SCW condition were considerably lower than with hydrogen donor solvent [38]. However, in the absence of sulphur the "hydrogen donating capability" of water is highly questionable [31]. Kida et al. reported that water plays at least three important roles in the SCW decomposition of alkyl sulphides: as a reactant in a hydrolysis of thioaldehyde, as the source of many H atoms needed for desulfurization, and as an H-transfer catalyst [31].

Tetralin is a good model to describe an effective hydrogen-donor capability. Tetralin has been shown to undergo thermal dehydrogenation to naphthalene and rearrangement to methylindan in either the absence or presence of free radical acceptors [40]. In the case of biomass liquefaction, the hydrogen transfer from the hydrogen-donor solvents stabilises the free radical of fragmented biomass [41]. The free-radical mechanism occurs when the heated-biomass cleaves into free-radical and seeks stabilisation depending on the energy requirements. Furthermore, hydrogen donor solvents can have a dual-function to donate hydrogen to stabilise fragments and assisting thermal cleavage [42]. Tetralin is a hydrogen-donor solvent which gives high conversions by reacting with free radicals producing more lower molecular weight products as reported previously [41–43]. Tetralin as a solvent in biomass conversion gives rise to high feedstock conversion (90 wt.%), as a result of the hydrogen donated from the solvent [44].

Pyrolysis oil upgrading using supercritical water was examined in this study, with the aim to identify the best conditions required to upgrade the pyrolysis oil at high conversion and high liquid yield. Heavy oils with low oxygen content were produced and routes of oxygen removal were reported (via water generation and decarboxylation). As in our previous study [38], hydrogen donation from both water and tetralin, and the effect on oxygen removal was reported. The same approach was used for pyrolysis oil upgrading to ascertain the differences and similarities compared to biomass. Tetralin and 1-methylnaphtalene provided a baseline product conversion as a good hydrogen donor and non-hydrogen donor (eventhough with much lower sample to solvent mass ratio). The performance of tetralin and 1-methylnaphtalene were compared with SCW (a weak hydrogen donor).

2. Materials and methods

2.1. Materials

Pyrolysis oil from biomass conversion was supplied by BP (UK) and kept refrigerated until used. 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. Pyrolysis 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 pressure vessel (75 ml cylindrical) at pre-set temperatures (410 °C) for 1 h (Table 2). In the upgrading experiments, the distilled water used was first de-gassed by bubbling nitrogen gas through it for approximately 30 min, after which the required amounts of water (total water) and sample (pyrolysis oil) for the experiment were measured and loaded into the vessel. After sealing the vessel and attaching the pressure gauge, it was purged 20 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 fluidized 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 the container to mix the sand, providing a uniform temperature inside the sand bath. As soon as the experiment was finished, the reactor was removed from the sand bath and left overnight to cool. Once the reactor was cooled to room temperature, the gas inside the reactor was transferred into

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