Polymerisation behaviour of water hyacinth-based bio-oil during heating up in the presence of oxygen-containing compounds

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Abstract. Bio-oil is susceptible to repolymerisation due to its high content of reactive oxygen-containing compounds. In this work, the polymerisation of the bio-oil produced from fast pyrolysis of water hyacinth was investigated during heating-up at various temperatures (50-95°C) in the presence of extra oxygen-containing model compounds (methanol and sucrose) with various concentration (10-50 wt%). The coke formed during the heating was quantified. The stability and reactivity of the hyacinth-based bio-oil for 48-h storage in the presence and the absence of the oxygen-containing compounds was also evaluated. This study showed that the presence of methanol in the bio-oil during heating up could suppress the repolymerisation leading to coke formation even at a higher temperature. In contrast, coke formation was severe (18.94 wt%) during the bio-oil heating up in the presence of sucrose at higher temperature (95°C). The presence of sucrose in the bio-oil could possibly promote the repolymerisation leading to coke formation. The repolymerisation possibly continued to occur during storage indicated by the increase in the viscosity, density and coke propensity of the bio-oil with added 50 wt% of sucrose compared to a negligible change in those properties of that with added methanol.

1. Introduction

The importance of exploring renewable energy resources is highly increasing due to the depletion of fossil-based fuels [1] and environmental issue [2]. Thermal conversion of invasive aquatic plants-based biomass such as water hyacinth [3-4] to e.g. bio-oil through a fast pyrolysis is one of the most promising techniques in the technology to obtain a new renewable liquid fuel [5-6]. However, the bio-oil produced from a fast pyrolysis could not directly used as a fuel for vehicles with high technology engines due to its undesirable properties such as high acidity leading to high corrosive property, viscosity, instability due to its relatively high oxygen content, and water content resulting in low calorific value [7-8].

The presence of high amount of oxygen (approximately 35-40 wt%) in bio-oil distributed in more than 300 compounds [9] resulted in an increase in the bio-oil reactivity and susceptibility to undergo repolymerisation leading to the formation of coke [10]. This behaviour would be accelerated by a thermal treatment at a longer storage time [11-12]. The formation of coke during heating up a real bio-oil [13-14] as well as model compounds [15-17] in the presence of acid catalysts has been reported.
However, the behaviour of the real bio-oil components itself during heating up and how repolymerisation would be promoted by the presence of reactive oxygen-containing compounds were not clearly explained. The presence of a catalyst could provide a bias information on how the bio-oil behaves during storage and/or heating up. The interaction of water hyacinth-based bio-oil during heating up in the presence of extra oxygenated compounds was investigated in this study, and the effect of prolonged storage at room temperature (30°C) on its repolymerisation behaviour was evaluated.

2. Methods
The bio-oil in this study was produced from a fast pyrolysis of water hyacinth using a fixed-bed type pyrolyser as reported elsewhere [8]. Dried water hyacinth with a particle size of 350-850 μm was used as the biomass feedstock. The pyrolysis was conducted at 550°C at an atmospheric pressure. The reactivity of the bio-oil during heating up in the presence of oxygen-containing model compounds, i.e. methanol and sucrose, was investigated at a temperature range of 50-95°C and an atmospheric pressure. A set of reflux apparatus was used in the experiments. The coke formed due to heating in the presence of methanol or sucrose was quantified. The tendency of the bio-oil to undergo a further repolymerisation after heating up in the presence of those compounds was also studied during storage for 0-48 h. The viscosity and density of the bio-oil in the presence of methanol and sucrose upon heating up and storage were measured and compared to those upon heating up only. The coke propensity of the bio-oil upon heating up in the presence of methanol and sucrose was evaluated by using the thermo-gravimetric analyser and compared as well to those upon heating up only. The change in the chemical structures of the bio-oil components was investigated by using an FTIR spectrophotometer.

3. Results and Discussion
3.1. The characteristics of water hyacinth-based bio-oil
The pyrolysis of water hyacinth in this study used no carrier gas and yielded 36.72 wt% bio-oil and 35.82 wt% biochar. The appearance of the water hyacinth feedstock, the produced bio-oil and biochar through the fast pyrolysis is presented in Figure 1. The gaseous product was determined by difference due to the low possibility to capture and quantify the product during the pyrolysis.

![Figure 1. Physical appearance of (a) dried water hyacinth with a particle size of (350-850 μm), (b) bio-oil produced through a fast pyrolysis at 550°C and (c) biochar as a byproduct.](image)

The bio-oil produced from the pyrolysis of water hyacinth in this study had a dark brown color with a typical odor. The viscosity and the density of the produced bio-oil were 1.56 cP and 1.10 g/mL, respectively, indicating a totally flowing liquid and showing a good characteristic as a fuel candidate [18]. The bio-oil contained various oxygen-containing compounds detected by the gas chromatograph as listed in Table 1.

The most abundant GC-detectable compounds in the bio-oil produced from water hyacinth was acetic acid (ca 32.43 %). Acetic acid was possibly formed from the break-down of hemicellulose component
of water hyacinth through the cleavage of the acetylate groups at a relatively mild condition [19]. 2,2-Dimethoxy propane and 1-hydroxy-2-propanone were the second and third most abundant compounds in the GC-detectable components of the bio-oil. Those two compounds were possibly produced from the decomposition of lignin’s aromatic C-O bonds and depolymerization of cellulose via the creation of oxygenated moieties, i.e. carbonyl groups, respectively [19].

Table 1. The GC-detectable components the bio-oil produced from the pyrolysis of water hyacinth— with a particle size of 350-850 μm using a fixed-bed pyrolyser at 550°C.

| GC-detectable compound                                  | Relative abundance (%) |
|--------------------------------------------------------|------------------------|
| n-Hexane                                               | 3.55                   |
| 2,2-dimethoxy propane                                  | 16.32                  |
| Acetic acid                                            | 32.43                  |
| 1,1-bibicyclo(2,2,2)oktil-4-carboxyl                   | 1.88                   |
| 1,2,5-Oxadiozol                                        | 2.82                   |
| Ethylbenzene                                           | 5.44                   |
| 1-hydroxy-2-propanone                                  | 11.50                  |
| 2-cyclopentene                                         | 2.20                   |
| 4- hydroxy-4-methyl-2-pentanone                        | 9.10                   |
| 1,4-diacetic-2,3-dimethylbutane                        | 5.12                   |
| Propanoic acid                                         | 1.05                   |
| Trans-caryophyllene                                    | 3.24                   |
| 2(3H)-furanone                                         | 0.63                   |
| 2-Furannethanol                                        | 3.77                   |
| Phenol                                                 | 0.94                   |

3.2. The behaviour of the bio-oil during heating up in the presence of oxygen-containing model compounds

Figure 2. Density and viscosity (with apostrophe signs) of (a) bio-oil with added 10-50wt% methanol and (b) bio-oil with added 10-50wt% sucrose. A and A’ refers to density and viscosity of the bio-oil. B and B’ refers to those of the bio-oil with added 10wt% methanol or sucrose. C and C’ refers to those of the bio-oil with added 50wt% methanol or sucrose.

Density and viscosity are the easy-measured parameters in describing the compatibility of fuel candidates. The density and viscosity of the bio-oil upon heating up in the presence and absence of
simple oxygenated compounds, i.e. sucrose and methanol were evaluated and presented in Figure 2. The presence of methanol could preserve the density and viscosity of the bio-oil during thermal treatment (Figure 2(a)). Methanol could possibly obstruct the repolymerisation of the reactive components in the bio-oil, due to the domination of methanolysis [20].

In contrast, the addition of sucrose in the bio-oil caused a significant increase in the viscosity of the bio-oil, particularly during thermal treatment at a higher temperature and more added sucrose (Figure 2(b)). Sucrose could decompose to form glucose and fructose, especially in the presence of acids [21]. Glucose was reported to play a key role in promoting polymerisation due to its decomposition to form compounds with carbonyl groups [20] that showed higher tendency in polymerisation leading to coke formation [22]. This was also supported by the data in Table 2 showing the extremely high coke yield of the bio-oil with added more sucrose (50wt%) upon heating up at a higher temperature.

**Table 2.** The coke yields during the thermal treatment of the bio-oil in the presence of different amount of methanol and sucrose.

| Extra compound added | Amount of added compound (wt%) | T of thermal treatment (°C) | Coke yield (wt%) |
|----------------------|--------------------------------|-----------------------------|-----------------|
| NA                   | 0                              | 80                          | 0.11            |
| Methanol             | 10                             | 80                          | 0.12            |
| Methanol             | 10                             | 90                          | 0.10            |
| Methanol             | 50                             | 50                          | 0.01            |
| Methanol             | 50                             | 78                          | 0.05            |
| Sucrose              | 10                             | 80                          | 0.23            |
| Sucrose              | 10                             | 94                          | 4.07            |
| Sucrose              | 50                             | 80                          | 0.76            |
| Sucrose              | 50                             | 95                          | 18.94           |

**Figure 3.** TGA curves of (A) fresh bio-oil, (B) aged bio-oil for 48 h, (C) bio-oil heated at 95°C and aged for 48 h, (D) bio-oil with added 50wt% methanol (E) bio-oil with added 50wt% methanol heated at 78°C and aged for 48 h, (F) bio-oil with added 50wt% sucrose, and (G) bio-oil with added 50wt% sucrose heated 95°C and aged for 48 h.

**Figure 4.** IR spectra of (A) fresh bio-oil, (B) aged bio-oil for 48 h, (C) bio-oil heated at 95°C and aged for 48 h, (D) bio-oil with added 50wt% methanol (E) bio-oil with added 50wt% methanol heated at 78°C and aged for 48 h, (F) bio-oil with added 50wt% sucrose, (G) bio-oil with added 50wt% sucrose heated 95°C and (H) bio-oil with added 50wt% sucrose heated 95°C aged for 48 h.
3.3. The effect of the length of storage on the repolymerisation tendency

Further polymerisation phenomenon was investigated through an aging process at various length of time towards the bio-oil after heating up in the presence (and absence) of added methanol and sucrose. The coking tendency was measured (as indicated by TGA curves in Figure 3) and the change in the functional groups in the bio-oil was evaluated (as showed by the IR spectra in Figure 4).

The coking propensity of the bio-oil and the bio-oil with added methanol was negligible (see Figure 3A-E). A quite significant coke propensity (11.34%) was observed for the bio-oil with the added sucrose upon heating up and storage for 48 h. This data supported the indication of the role of sucrose (with a reactive carbonyl group) in promoting polymerisation leading to coke formation. Moreover, a disappearance of some functional groups at wavenumbers of 1750-500 cm\(^{-1}\) also indicated the repolymerization and/coke formation of the bio-oil during heating up in the presence of added sucrose. It was important to note that the effect of heating temperature was likely more predominant compared to the extent of added oxygen-containing compounds and to the length of storage time. The three factors would be promoting the polymerisation and/or coke formation if synergetically employed.

4. Conclusion

Polymerisation behaviour of water hyacinth-based bio-oil was promoted by the presence of compounds with a reactive carbonyl group. It was indicated by the significant coke formation in the thermal treatment of the bio-oil in the presence of sucrose. The change in the density and viscosity of the bio-oil upon heating in the presence of sucrose also supported this claim. A higher coke propensity as well as the disappearance of some functional groups of the bio-oil with added sucrose upon heating were another supporting evidence. In contrast, methanol could suppress the polymerisation of the bio-oil during heating up, indicated by insignificant change in the density and viscosity of the bio-oil. Moreover, no coke propensity was observed in this case.

Upon different storage time, there was no significant change in the properties of the bio-oil with and without addition of oxygen-containing compounds. It was likely that heating the bio-oil at a higher temperature was the main factor affecting the polymerisation behaviour of the bio-oil. When the temperature was kept low, the polymerisation and/or coke formation was likely possible to be prevented even in the presence of reactive carbonyl groups during the treatment.

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