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Fast hydrothermal liquefaction of native and torrefied wood

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Abstract

The work presented in this paper aimed to examine the effect of heating rate on the bio-crude yield of wood hydrothermal liquefaction. Three different heating methods were developed, resulting in heating rates ranging from 66°C/min to 179°C/min. The experiments were conducted using Norway spruce wood as feedstock at an operation temperature of 350°C and with a total reaction time of 15 minutes. The bio-crude product was collected and separated using dichloromethane (DCM) as solvent and a centrifugal separator. The results confirm that heating rate has a clear positive effect on the bio-crude oil yield, increasing from 18.9 wt% for the lower heating rate of 66°C/min to 35.8 wt% for the higher heating rate of 179°C/min. It is also shown that the effect of feedstock pre-treatment via torrefaction on the bio-crude yield is negative.

Keyword: Hydrothermal liquefaction; Fast HTL; Bio-oil; Bio-crude; Biomass

1. Introduction

Hydrothermal liquefaction (HTL) is a thermo-chemical conversion method that can directly convert non-food crop biomass such as algae, black liquor, forest and agricultural residues to liquid fuel (bio-crude or bio-oil). HTL involves the use of compressed water at elevated temperatures, often close to the critical point (374ᵒC). Therefore, HTL requires no pre-drying of the feedstock, which would otherwise reduce the overall energy efficiency as the fast pyrolysis does to do the same job of producing bio-oil from biomass. The correlation between heating rate and oil yield in fast pyrolysis is well established. However, little attention has been paid to studying this correlation during HTL. There have been even contradictory observations on this. A negative effect of faster heating on oil yield for example has been reported [1]. On the other hand, it is suggested that moderate heating rates may be sufficient to obtain a positive effects on oil yield [2]. Recently, fast heating has been reported to be a key point for achieving

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high bio-oil yield in several papers [3-7].

In fact, the effect of heating rate on the oil yield is dependent on other parameters, such as temperature, retention time and the feedstock used, which may explain the contradictory results. Kamio et al. [1] observed a negative impact on the bio-oil yield when increasing the heating rate from 1ºC/min to 10ºC/min for HTL of cellulose at relative low temperatures between 170ºC and 280ºC. Later, Brand et al. [5] studied HTL of pine saw dust at temperatures within 250-350ºC, employing two different heating rates of 2ºC/min and 20ºC/min. They found that the higher heating rate did have a clear positive effect on the oil yield of HTL at relatively higher temperatures between 315ºC and 350ºC, whereas it was not the case at lower HTL temperatures of 250-280ºC.

The studies by Brand et al. and Kamio et al. employed relatively low heating rates under 20ºC /min for their HTL experiments. Zhang et al. [6] demonstrated that for HTL of grassland perennials, the liquefaction yield (aqueous and oily phase) is increased when increasing the heating rate from 5ºC/min to 140ºC/min. Knezevic et al. [8] achieved a bio-oil oil yield of 58 wt% for HTL of wood, employing a heating rate of 140ºC/min. Bach et al. [3, 7] confirmed positive effects of heating rates when increased the heating rate even higher to the range from 136ºC/min to 585ºC/min, using macro-alga *Laminaria Saccharina* as feedstock. However, no study has examined HTL of woody biomass, employing heating rates above 140ºC /min. Therefore, the study reported in this present paper was carried out. The objective of this study is to verify the effect of heating rate on HTL oil yield. The same experimental set-up reported by Bach et al. [3] was employed. Possible errors of using organic solvents for oil extraction and separation was taken into consideration in the experiment. In addition, the effect of feedstock pre-treatment via torrefaction on HTL oil yield was also investigated since it was reported that torrefaction enhanced fast pyrolysis of biomass [9].

2. Methods

2.1 Feedstock preparation and characterization

Table 1: Proximate and ultimate analysis for raw and torrefed samples

Sample	Proximate analysis				Ultimate analysis					
	Moisture[a]	VM[b]	FC[b]	Ash[b]	C[b]	H[b]	O[b]	N[b]	S[b]	HHV[c]
Raw spruce	6.23	86.34	13.43	0.23	50.1	6.36	43.52	0.07	0.05	20.45
Torrefied spruce	4.8	75.77	23.89	0.34	56.04	5.66	38.17	0.008	0.05	22.28

VM: volatile matter, FC: fixed carbon, HHV: higher heating value. [a]wt%. [b]wt%, dry basis. [c]MJ/kg

Spruce wood (*Picea abies*) samples were obtained from local sources in Trondheim Norway. Part of the raw samples was torrefied with a residence time of 1 hour and torrefaction temperature of 275°C. Both the raw and torrefied samples were ground down to a particle size between 63-125µm. A proximate analysis for the spruce wood was conducted according to the ASTM standards ASTM E871, ASTM E872, and ASTM D1102 for moisture content, volatile matter, and ash content, respectively. The ASTM 1762-84 standard methods, applicable to charcoal powders, were applied to conduct the proximate analysiss of the torrefied spruce. The result from proximate and ultimate analyses for the raw and torrefied spruce is given in Table 1.

2.2 Reactors and experiment method

Sealed quartz capillaries were used as the HTL reactors. The reactor length is 200 mm and its inner diameter is 2 mm, resulting in an inner volume of 0.63 ml. Two different wall thicknesses of 1mm and 2mm were used for differentiating heating rates. Prior to loading, one end of the quartz reactor was sealed using an acetylene torch. The feedstock and water were introduced to the reactor, measured by weight

difference, so that the biomass/water weight ratio was 1/10. The loaded reactor was purged carefully with nitrogen through a long needle for 2 minutes. This step is to minimize the contamination risk, due to the possibility of combustion products from the acetylene flame entering the reactor. The reactor was then quickly sealed at the other end and left for at least 20 hours for the mixture to reach equilibrium before the HTL experiments. The small reactor sizes enable generally high heating rates. A disadvantage of the quartz reactors is the limited mechanical strength of the thin walls, which may lead to explosions during the experiments if the internal pressure is too high and/or the sealing operation is not good. The risk of explosion increases with the amount of biomass, which limits the amount of biomass for each experiment. As a result, only 10 mg of biomass was used for each experiment. Three different heating methods were employed for studying the effect of heating rate on the bio-oil yield at 350°C: i) The quartz reactor of 1mm thick wall heated in a preheated sand bath (high heating rate); ii) The quartz reactor of 2 mm thick wall heated in a preheated sand bath (medium heating rate); and iii) The quartz reactor of 2 mm thick wall heated in air in a preheated muffle furnace (low heating rate).

2.3 Products collection and separation

The products collection and separation procedure reported by Bach et al. [3] was adapted for the present study, with a slight modification of prolonged evaporation time for the mixture of bio-oil and dichloromethane (DCM) used as extraction solvent. After the test was finished, the reacted and cooled quartz reactor was opened and injected with DCM using an adjustable volume pipette (10-100 μl Finnpipiette). The mixture of DCM and HTL products was extracted from the reactor using a syringe and transferred to a plastic cup. To minimize possible mass losses, this operation was repeated 5 times, using proximately 1300 μl of DCM in total for each reactor. The products were then separated using a centrifugal separator (MSE Minor Centrifuge), operated at 5000 rpm for 3 minutes, leaving the products in 3 different layers: An aqueous phase on top, bio-oil dissolved in DCM (also referred to as oily phase) in the middle, and solids at the bottom. Next, the aqueous and oily phase (the liquid products) were extracted and filtered through a 0.1 μm filter to remove any solid products from the liquid products. Finally, the layers of the oily and aqueous phase were separated into two plastic cups. The gaseous products were calculated by difference.

2.4 Calculation of product yields

Bio-oil in this study is defined as the organic compounds soluble in DCM, and $m_{bio-oil}$ is the mass of bio-oil (g) after solvent evaporation. $m_{biomass}$ is the mass of the initial dry feedstock (g), $m_{aqueous\ phases}$ is the mass of the dry aqueous products (g) and $m_{solid\ residue}$ is the mass of the dry solid products (g). The remaining mass from the mass balance is referred to as gas product.

$$Bio-oil\ (wt\%) = \frac{m_{bio-oil}}{m_{biomass} \times (100 - Ash\% - Moisture\%)} \cdot 100\% \qquad (1)$$

$$Aqueous\ phase\ (wt\%) = \frac{m_{aqueous\ phase}}{m_{biomass} \times (100 - Moisture\%)} \cdot 100\% \qquad (2)$$

$$Solids\ (wt\%) = \frac{m_{solid\ residue}}{m_{biomass} \times (100 - Moisture\%)} \cdot 100\% \qquad (3)$$

3. Results and Discussion

3.1 Measurement and estimation of heating rate

Two different methods were employed to estimate the thermal behavior in the quartz reactors during HTL: (i) with air inside the reactor, neglecting possible effects the real slurry biomass solution may have on the heating rate. (ii) with a heating oil, Duratherm 630, inside the reactor to simulate the slurry solution. Given the experimental set-up, the heat transfer in the reactor is obviously governed by the

conduction mechanism, of which the rate is very low as the temperature inside the reactor approaches the target temperature or the driving force approaches to zero. Therefore, an important question is what temperature would be used for estimating the heating rate. One method is based on the heating time being defined as the time needed for the reactor to reach 95% of the heating media temperature [10, 11]. This definition is adopted for this study. The heating rate is calculated using Eq. (4):

$$Heating\ rate\ = \frac{(T_{ftnal} - T_{start}) * 0.95}{Heating\ time} \qquad (4)$$

For this study, the reaction time, defined as the total time the reactor is placed in the preheated heating media, is 15 minutes for all cases with different heating methods. In addition, the holding time is defined as the difference between the reaction time and heating time. With these definitions, the properties for the different heating methods and a comparison between the two heating estimations methods are given in Table 2.

Table 2: The heating rate (HR) and holding time for the three different heating methods

Heating method	Heating time	Holding time	HR estimation, air in reactor	HR estimation, oil in reactor
2mm wall, air heating	4.75 min	10.25 min	66°C/min	66°C/min
2mm wall in sand bath	3.5 min	11.5 min	99°C/min	89°C/min
1mm wall in sand bath	1.75 min	13.25 min	376°C/min	179°C/min

3.2 Solvent evaporation and collection of bio-oil product

In the present study, the added DCM was naturally evaporated in a fume cupboard at room temperature. The results showed that after 17 days no significant mass change was observed for all of the samples, although 90% of the mass change was observed within the first 5 hours. It should be noted that DCM evaporation might not have been the only factor responsible for the observed mass changes. Some of the light volatiles of the bio-oil presumably evaporates during the evaporation of DCM [12, 13]. Low boiling point compounds may become volatile during long evaporation processes and continue to evaporate after days of exposure to the circulating air in the fume cupboard [14]. Some mass losses may also have been due to moisture content evaporating, as typically the water content in bio-oil is in the range between 2-13% [15]. Based on the experimental observation, it was decided to take 17 days as the evaporation time for the present study. This is to avoid overestimation of the oil yield. The extensive evaporation time in fact had a big impact on the calculated bio-oil yield. In the case of the highest heating rate for example, the calculated bio-oil yield is about 60, 45, and 36% for the evaporation time of 24 hours, after 4 days, and 17 days, respectively.

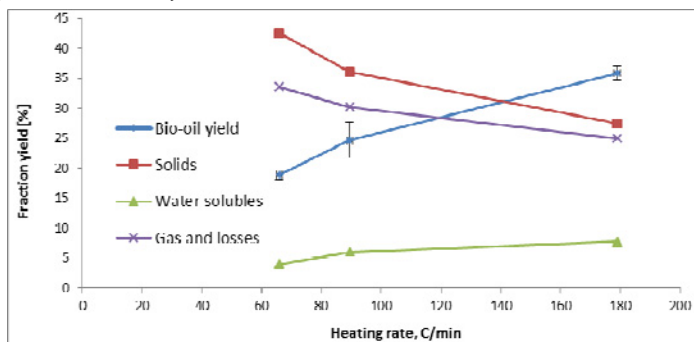### 3.3 Effect of heating rate on bio-oil yield

Figure 1. The effect of heating rate on the product yield.

Fig.1 shows the average values of the different HTL products based on between 4 to 7 replicates, using raw spruce as feedstock. The bio-oil results had relative good reproducibility, with the exception of the results from the medium heating rate. From the low heating rate of 66 °C/min to the high heating rate of 179 °C/min, the bio-oil yield almost doubled from 18.9 wt% to 35.8 wt%. The solid yield, however, decreased from 43% to 27% from the lowest to highest heating rate. The clear increase of bio-oil from the medium to the high heating rate indicates that very high heating rates are beneficial, and that for spruce wood the positive effect may continue well above 179 °C/min.

The trend of bio-oil yield increase with higher heating rates in the present study is in agreement with the observation reported by Bach et al. [3]. Both studies show a somewhat larger increase in bio-oil yield from the low to medium heating rate, than from the medium to high heating rate. Bach et al. [3] used a heating rate estimation with only air inside the reactor, and so temperature data obtained from the same method should be applied when comparing results to these experiments. As shown in Table 2, this would mean that the high heating rate achieved in the present project was 376°C/min instead of 179°C/min.

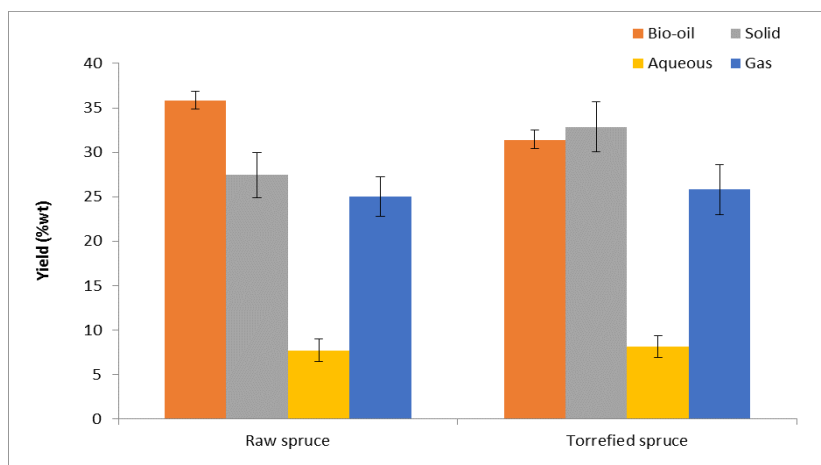*3.4 Effect of feedstock torrefaction on bio-oil yield*

Fig. 2 Products yields for HTL of raw and torrefied spruce (high heating rate)

The effect of feedstock torrefaction on the oil-yield was studied at the high heating rate of 179°C/min. The results of product yields in comparison those of torrefied spruce samples are shown in Fig. 2. The bio-oil yield for the torrefied spruce wood is 31.37 wt%, 4.5 wt% lower than that for the raw spruce, while the solid yield is affected in an opposite direction, i.e. increased by almost the same mass percentage of 4.5 wt% from the raw to the torrefied samples. On the other hand, the aqueous and gas yields remain unchanged.

4. Conclusion

The effect of heating rate on the oil yield of Norway spruce HTL was experimentally studied at the reaction temperature of 350°C and the reaction time of 15 minutes, employing sealed capillary quartz reactors of 0.63 ml. Three heating rates of 66 °C /min, 89 °C /min, and 179 °C /min were measured and estimated using the quartz reactor sealed at one end and filled with Duratherm 630 heating oil to simulate the biomass slurry solution in the real sealed reactor. These heating rates are equivalent to 66°C/min, 99°C/min ad 376°C/min, respectively, when the heating oil was replaced with air. The results confirm the positive effect of the heating rate on the bio-oil yield, with a bio-oil yield increased from 18.9 wt% for the low heating rate to 35.8 wt% for the high heating rate. In addition, the effect of torrefaction on oil yield

was also studied, comparing raw and torrefied spruce. It appeared that the torrefaction has a negative impact on the oil yield, i.e. decreased from 35.8% to 31.37% for the raw and torrefied spruce samples, respectively.

Acknowledgements

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