



# Effect of heating rate on biomass liquefaction: Differences between subcritical water and supercritical ethanol



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## ABSTRACT

This study investigates the influence of heating and cooling rate on liquefaction of lignocellulosic biomass in subH<sub>2</sub>O (subcritical water) or in scEtOH (supercritical ethanol), in dependency of final reaction temperatures (250–350 °C) and residence times (1–40 min). The heating rate has been identified as a crucial parameter in the subH<sub>2</sub>O-based liquefaction, whereas it has marginal influence in the scEtOH-based liquefaction. Detailed characterization of gas, liquid and solid products enables to identify the individual reaction steps, which results in a new insight into the reaction mechanisms, depending on the liquefaction solvents and conditions. Similar to fast pyrolysis, hydrothermal liquefaction consists of beneficial primary reactions (pyrolytic & hydrolytic degradation) and non-beneficial secondary reactions i.e. recombination and secondary cracking. In scEtOH, biomass was decomposed by pyrolysis and alcoholysis at relatively high reaction temperatures while the recombination of reaction intermediates are retarded by the unique reactions of scEtOH such as hydrogen donation and hydroxylalkylation.

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## 1. Introduction

Biomass is one of the most promising renewable energy resources in the current context of rising energy demand and fossil fuel depletion. In particular, lignocelluloses are naturally abundant worldwide and their conversion into fuels and value-added chemicals by thermochemical processes is considered to be carbon neutral due to zero net emissions of green house gases (e.g., CO<sub>2</sub>). In fact, this is only true in case that most of energy required for harvest, transportation and conversion of the biomass is derived from renewable sources as well. Fast pyrolysis and liquefaction are the two major thermochemical processes that produce liquid bio-oil/bio-crude production from lignocelluloses in a single step. These processes are often compared and related to each other due to their similarity of process conditions and products [1–5]. A comparison between fast pyrolysis and liquefaction is summarized in Table S1.

The unique properties of water in sub- and supercritical conditions (subH<sub>2</sub>O (subcritical water) or scH<sub>2</sub>O (supercritical water)) has been recognized and explored over the past few decades in various applications including extraction and supercritical water oxidation [6]. In the field of bioenergy, subH<sub>2</sub>O or scH<sub>2</sub>O is widely used to produce biochar through carbonization, biocrude through liquefaction, and hydrogen through gasification [1,7]. Recently, supercritical alcohols have been explored as an alternative solvent in biomass liquefaction due to their advantages including higher bio-crude yields, better solubility of organic intermediates, hydrogen donor properties, and easier separation due to their low boiling points [8–11].

Many studies have been published in recent years in the field of hydrothermal liquefaction [2,12–16]. The influence of reaction parameters and their optimization for high biocrude yield has been the main target of these studies. It is well-known that the biooil yield in fast pyrolysis can be maximized through a combination of fast heating rate to a mid-range temperature, a very short residence time, and immediate quenching of the organic vapors that retard secondary reactions such as condensation and secondary cracking [17]. In fast pyrolysis, the heating rate is one of the most crucial parameters to obtain high biocrude yields. Similarly to the case of

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fast pyrolysis, knowledge of the heating rate effect on biomass liquefaction is necessary in order to understand the decomposition behavior of woody biomass and to optimize the process for achieving high conversion and biocrude yield, or to develop a kinetic model that would enable the tuning of selectivity for producing fine chemicals. However, to date, only a few works have addressed the heating rate issue and in some cases, contradictory results have been reported. Nelson et al. investigated the liquefaction process as an alternative to biological biomass conversion technologies with aiming to produce biomass derived adhesives or asphalt substitutes [18]. The utilization of two different reactor sizes (3 and 300 ml) may give an insight into the effect of heating rate, since the larger reactor required much longer time to reach the reaction temperature. Their liquefaction results suggested that faster heating rates would be useful to reduce the inevitable degradation and recombination of the initial products. Zhang et al. (2008) performed hydrothermal liquefaction experiments using aspen wood chips and a corn stover in a 75 ml batch reactor equipped with an inductive heating system [19]. They found that there was a linear relationship between the heating rate and conversion for both of the feedstocks; when the heating rate increased from 5 to 140 °C/min, the liquid biocrude yield increased from ca. 50 wt% to ca. 70 wt% with a simultaneous decrease in gaseous and solid products. The cooling rate appeared to have no significant effect on product distribution. The heating rate was found to have no impact on the chemical composition of the biocrude. Kamio et al. (2008) tested the effect of heating rate on cellulose decomposition in subH<sub>2</sub>O under the relatively narrow range of 1–10 °C/min [20]. In contrast to the results from Zhang et al., the slow heating rate appeared to be beneficial for high conversion and high biocrude yield. The heating rate impact was clearly presented, but the strength was strongly dependent on final temperature. At 250 °C, a considerable difference in biomass conversion was observed under different heating rate conditions; results showed high conversion of over 80% at 1 °C/min and less than 30% conversion at 10 °C/min. A recent review on the effect of process conditions on bio-oil yield in hydrothermal liquefaction of biomass suggested that moderate heating rates would be enough to overcome heat transfer limitations for producing high liquid oil yield [21]. In addition to the contradictory conversion results of the previous studies, the role of heating rate and its influence on reaction mechanisms have not been understood thus far in hydrothermal liquefaction. In supercritical alcohol-based liquefaction, the effects of heating rate on biomass conversion, biocrude yield, and properties of gas/liquid/solid products have not yet been explored.

In the literature, many different reactor designs and heat sources have been applied for biomass liquefaction [15,16,22–26]. Reactor volumes in the range of 5–1800 ml have been used which can be heated relatively rapidly by fluidized sand, molten tin, and oil bathes or relatively slowly by external electric heaters. The reported heating rates were between 3 and 360 °C/min. Table 1 illustrates the differences in the reaction setup reported in selected references. The comparability of the previous experimental results, produced with different reactor volumes and heat sources, needs to be questioned in case that the heating rate would have a significant influence on the reaction mechanism and the products.

This study investigates the influence of the heating rate on conversion, product yields, and reaction mechanism in biomass liquefaction using subH<sub>2</sub>O and scEtOH (supercritical ethanol) as solvents. The tested heating rate was in the range of 2–20 °C/min, with final reaction temperatures of 250–350 °C and residence times of 1–40 min. The gas/liquid/solid products obtained by varying the process conditions and solvents were characterized in detail. Based on product yields and characterization results, different reaction schemes for the subH<sub>2</sub>O-based and the scEtOH-

**Table 1**  
Comparison of selected batch reactor systems reported in the literature.

Reactor volume [ml]	Heat source	Heating rate (°C/min)	Cooling method	References
1800	Electrical furnace	3	Internal coil	[26]
250	Electrical furnace	ca. 6	Fan	[15]
200	Electrical furnace	3	Fan	[22]
75	Electrical furnace	10	Wet cloth	[16]
20	Oil bath	ca. 300	Water bath	[23]
14	Fluidized sand bath	360	N.A. <sup>a</sup>	[24]
5	Molten tin bath	ca. 300	water bath	[25]

<sup>a</sup> N.A. = not available.

based liquefaction that describe the impact of heating rate, final temperature, and residence time in liquefaction were proposed.

## 2. Materials and methods

### 2.1. Materials

The biomass feedstocks used in this study were red pine sawdust obtained from Nutrapharm Co. (Seoul, Korea) and  $\alpha$ -cellulose (>99.5%) purchased from Sigma Aldrich (St Louis, MO, USA). The biomass samples were sieved to a particle size smaller than 40 mesh (<0.42 mm) and dried overnight at 105 °C prior to each experiment. The results of structural and elemental analyses of the feedstock are listed in Table S2.

Ethanol (99.5%), acetone (99.9%), ethyl acetate (99.9%), and THF (tetrahydrofuran, 99.9%) were purchased from Sigma Aldrich and used as received. High purity nitrogen (99.99%) was purchased from Shinyang Sanso Company (Seoul, Korea). DDI (distilled and deionized) water was prepared using a Milli-Q ultrapure water purification system with a 0.22  $\mu$ m filter (Billerica, MA, USA).

### 2.2. Liquefaction process and product separation

Liquefaction experiments were performed in a 160 ml batch reactor (Inconel 625) equipped with a magnetic stirrer. A detailed description of the apparatus is given in a previous paper [11]. For each experiment, 6 g of biomass (sawdust or cellulose) and 60 ml of solvent (ethanol or DDI water) were placed in the reactor. After the reactor was sealed, the air in the reactor was displaced with nitrogen. The reactor was then heated to a desired temperature by an electrical furnace and, when fast heating rates were required, it was additionally heated by four cartridge heaters that were placed inside the reactor wall. The stirring rate was set to 400 rpm. After the experimentally desired reaction time, the reactor was cooled by quenching in a water bucket and an electrical fan. The produced gas was collected in Teflon sampling bags (0.5 L) using a gas sampling line and was then analyzed. The reactor was then opened and the product mixture was collected by rinsing with DDI water (in water experiments) or acetone (in ethanol experiments). After hydrothermal liquefaction, a small amount of water insoluble, bio-crude was coated on the reactor wall and the stirrer. This oily product was recovered by scratching with a metal spoon, and added to the product suspension prior to filtration. The product was then filtered using vacuum filtration with a pre-weighted Whatman Nr. 5 filter paper. The details on the separation steps have been described elsewhere [11]. Briefly, the filtrate from the water experiments was extracted using ethyl acetate, followed by solvent evaporation. The product was designed as WSO (water soluble oil). The filter cake was extracted using acetone in a soxhlet for at least 12 h. The extract was obtained following solvent evaporation using a rotary evaporator; the extract is designed as a HO (heavy oil) or biocrude. The extracted solid residue was dried in a vacuum oven overnight

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