

# Supercritical ethanol as an enhanced medium for lignocellulosic biomass liquefaction: Influence of physical process parameters



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## ABSTRACT

In this study, the influence of various physical process parameters on the liquefaction of lignocellulosic biomass (pine wood) in supercritical ethanol was investigated. The parameters include reaction temperature (280–400 °C), initial nitrogen pressure (0.4–7.5 MPa), reaction time (0–240 min), and biomass-to-solvent ratio (0.06–0.25 g/g). The reaction temperature and residence time were found to have a more significant effect on biomass conversion and product yield than pressure and biomass-to-solvent ratio had; conversion in the range 34.0–98.1% and biocrude yield in the range 15.8–59.9 wt% were observed depending on the process parameters. Despite the absence of catalysts and external hydrogen source, solid biomass to liquid and gaseous products conversion of 98.1%, and a high biocrude yield of approximately 65.8 wt% were achieved at 400 °C, 120 min, and a biomass-to-solvent ratio of 0.06 g/g. Moreover, the biocrude contained considerably lower amounts of oxygen and higher amounts of carbon and hydrogen, resulting in a substantially higher heating value (>30 MJ/kg) as compared to raw feedstock (20.4 MJ/kg). A comparison with sub- or supercritical water-based liquefaction revealed that supercritical ethanol produced biocrude with a lower molecular weight and much better yield. Finally, a new biomass liquefaction reaction mechanism associated with supercritical ethanol is proposed.

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## 1. Introduction

Extensive efforts are being made to develop renewable and sustainable energy sources, and cost-effective energy processes, owing to concerns regarding global warming and fossil fuel depletion [1]. Biomass is considered as one of the most promising renewable energy resources as it is carbon neutral and abundant. Several thermochemical conversion technologies such as fast pyrolysis, liquefaction, and gasification followed by Fischer–Tropsch synthesis (or biomass-to-liquid, BTL) have been investigated to

convert biomass into liquid fuels and valuable platform chemicals. In a typical BTL process, biomass is first gasified at high temperatures of 600–1300 °C to produce syngas (CO and H<sub>2</sub>) and then the syngas is converted to mostly straight chain alkanes using Co-, Fe- or Ru-based catalysts. Fast pyrolysis and liquefaction generate multicomponent oxygenated hydrocarbon mixtures called “bio-oils” or “biocrude.” Fast pyrolysis and liquefaction are similar but not identical processes with many differences in reaction parameters and product characteristics. Fast pyrolysis is the thermal degradation of organic matter in the absence of oxygen at atmospheric pressure. The high heating rate combined with short residence time (both few seconds) and the medium operating temperatures (450–650 °C) associated with fast pyrolysis convert biomass into oxygenated hydrocarbons. Subsequent rapid quenching of produced organic vapors results in high-yield bio-oil. The bio-oil produced in fast pyrolysis, however, typically has less desirable physicochemical properties such as, higher oxygen

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(~36 wt%) and moisture content (~25 wt%), lower calorific value (~23 MJ/kg), higher acidity and corrosiveness, and faster aging properties compared to liquefaction (oxygen content, ~12 wt%; moisture content, ~5 wt%; calorific value, ~36 MJ/kg), its advantages over liquefaction including a shorter reaction time and lower capital costs notwithstanding [2–4]. The liquefaction process for lignocellulosic biomass is still in its developing stage. Liquefaction is the thermal degradation of lignocelluloses and other organic materials in a solvent under intermediate temperature (250–400 °C) and high pressure (5–4 MPa) conditions. One of major advantages of liquefaction is that the cost intensive drying of biomass prior to conversion is not required. Table 1 presents comparison of the three thermochemical conversion technologies.

In addition to decomposition and transformation of biomass from a solid substrate to liquid fuel, another criterion for biomass liquefaction includes removal of oxygen via chemical reactions such as dehydration, decarbonylation, decarboxylation, and hydrodeoxygenation, in order to obtain fuels suitable for use in transportation. This is essential since biomass has a high oxygen content (40–50 wt%) that significantly lowers its heating value. In liquefaction, the solvent generally plays a critical role in obtaining desirable biocrude yields and properties. Besides sub- or supercritical water (subH<sub>2</sub>O or scH<sub>2</sub>O), the most widely used liquefaction solvent, various organic solvents such as alcohols (methanol, ethanol, propanol, and isopropyl alcohol), phenol, acetone, ethylene glycol, ethylene carbonate, tetralin and toluene have also been examined as potential liquefaction media [5–9].

Supercritical alcohol has the following advantages compared to subH<sub>2</sub>O/scH<sub>2</sub>O for biomass liquefaction:

- 1. Better solubility:** Alcohols are better solvents of biocrude compared to water. The solubility of organic liquids in water in ambient conditions is fairly low, but increases with temperature as a result of a strong decrease in its dielectric constant from 80 to 10–30 when heated to the sub- or supercritical region [10]. Once cooled down, water loses its solvent properties in the mixture of water and biocrude, which consequently segregates and forms condensates of biocrude compounds on the surface of solid residues. In contrast, the dielectric constant of alcohol is much lower than that of water, making it a better solvent for biocrude at both ambient and supercritical conditions; e.g., the dielectric constant of ethanol in ambient conditions is approximately 25 and decreases to below 4 at supercritical conditions [11].
- 2. Easier product separation:** Product separation is a critical issue in liquefaction because of the variety and complexity of chemical species in biocrude that include acids, aldehydes, ketones, esters, and phenols. The liquid products in sub/scH<sub>2</sub>O-based liquefaction split up into water soluble and insoluble fraction. Recovery of bio-oil from the water phase requires either liquid–liquid extraction using an organic solvent such as ethyl acetate and subsequent evaporation of solvent, or a highly energy-intensive water evaporation [12]. In addition, organic

**Table 1**  
Comparison of the thermochemical conversion of biomass routes to produce liquid fuels and platform chemicals [2].

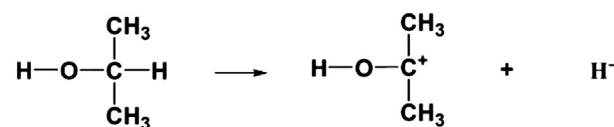
	Temperature (°C)	Pressure (MPa)	Catalyst	Drying
Gasification	600–1300	0.1	Essential in Fischer–Tropsch synthesis	Necessary
Fast pyrolysis	450–650	0.1–0.5	Not required	Necessary
Liquefaction	250–400	5–40	Not essential	Not necessary

solvents such as acetone are required to recover heavy oil deposited on the solid residue. Conversely, the liquid product in supercritical alcohol liquefaction can form a single liquid phase whereby biocrude can be recovered by simple alcohol drying.

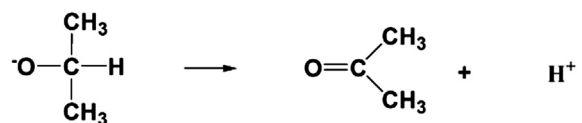
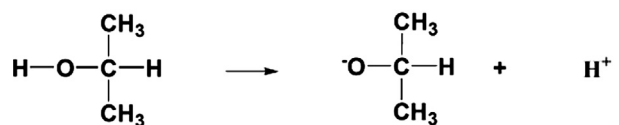
- 3. Lower corrosivity:** SubH<sub>2</sub>O is highly corrosive resulting in higher capital and process costs [13]. However, in the use of supercritical alcohols as liquefaction media, corrosion is not a significant factor.
- 4. Properties as a hydrogen donor and hydroxylalkylation agent:** Supercritical alcohol acts not only as a solvent but also as a reactant, since it is a hydrogen donor and a hydroxylalkylation agent [14–19]. The hydrogen generated from supercritical alcohol serves as a hydrogenolysis agent—to depolymerize biomass, a deoxygenation agent—to remove oxygen from biomass via H<sub>2</sub>O formation, and a radical quenching agent—to retard repolymerization and formation of char/tar. As shown in Scheme 1, hydrogen donation mechanisms in supercritical alcohol have been reported in literature [16,17]. The first mechanism proposes the initial donation of  $\alpha$ -hydrogen in hydride form, and the formation of an electron-deficient hydroxylalkylation species. The second mechanism, resembling the Meerwein–Ponndorf reduction, consists of alcohol reduction which leads to alkoxide ion and proton transfer, followed by  $\alpha$ -hydrogen donation and ketone formation.

Previous studies reported in literature have utilized the advantages of supercritical alcohol in the liquefaction of various types of biomass including lignocellulose, lignin, cellulose, sewage sludge, and microalgae [8,14,20–28]. Some major drawbacks in the various studies conducted thus far have been discrepancies in experimental procedures and the exploration of a variety of process parameters with different reaction systems, leading to contradictions in reported results [29]. In addition, there is disparity between reaction setups in various studies; for example, reactor volumes vary from 5 ml to 1.8 L, which may result in heating rate differences by approximately two orders in magnitude [30–32].

The aim of this study is to investigate the influence of physical process parameters on product distribution and the energy content in scEtOH (supercritical ethanol)-based biomass liquefaction. The



Nakagawa et al. [16]



Ross et al. [17]

**Scheme 1.** Hydrogen donation and hydroxylalkylation mechanisms proposed and reported in literature [16,17].

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