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The International Journal

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VOLUME 59 SEPTEMBER 15, 2013

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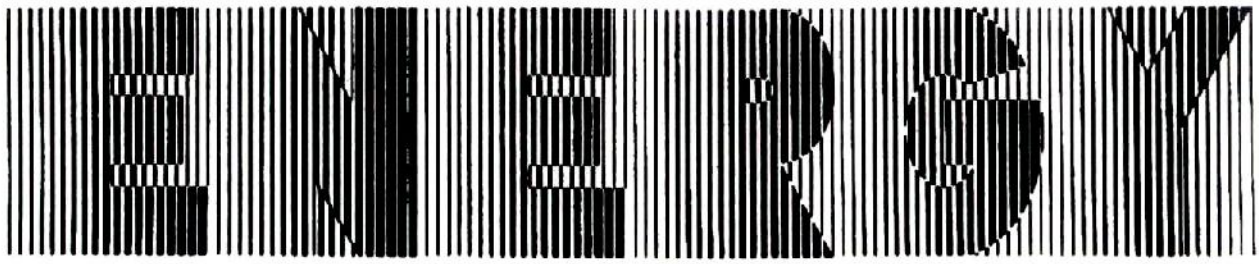

IMPACT . CONSERVATION . MANAGEMENT . POLICY

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

Steffen Brand [a,b], Ratna Frida Susanti [a,b,c], Seok Ki Kim [a], Hong-shik Lee [a], Jaehoon Kim [d,e,*], Byung-In Sang [f,**]

[a] Clean Energy Research Center, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 136-791, Republic of Korea
[b] Department of Clean Energy and Chemical Engineering, University of Science and Technology, 113 Gwahangno, Yuseong-gu, Daejeon 305-333, Republic of Korea
[c] Chemical Engineering Department, Industrial Technology Faculty, Parahyangan Catholic University, Ciumbuleuit 94 Bandung, West Java 40141, Indonesia
[d] School of Mechanical Engineering, Sungkyunkwan University, 2066, Sebu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 440-746, Republic of Korea
[e] Sungkyun Advanced Institute of Nano Technology (SAINT), 2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 440-746, Republic of Korea
[f] Department of Chemical Engineering, Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul 133-791, Republic of Korea

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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.


## 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 $H_2$) 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

* Corresponding author. School of Mechanical Engineering, Sungkyunkwan University, 2066, Sebu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 440-746, Republic of Korea. Tel.: +82 31 299 4843; fax: +82 31 290 5889.
** Corresponding author. Tel.: +82 22 220 2328; fax: +82 22 220 4716.
*E-mail addresses:* jaehoonkim@skku.edu, kjh0508@gmail.com (J. Kim), biosang@hanyang.ac.kr (B.-I. Sang).

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