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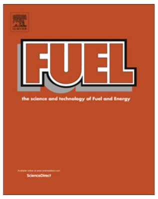


Full Length Article

Liquefaction of oil palm empty fruit bunch using sub- and supercritical tetralin, *n*-dodecane, and their mixture

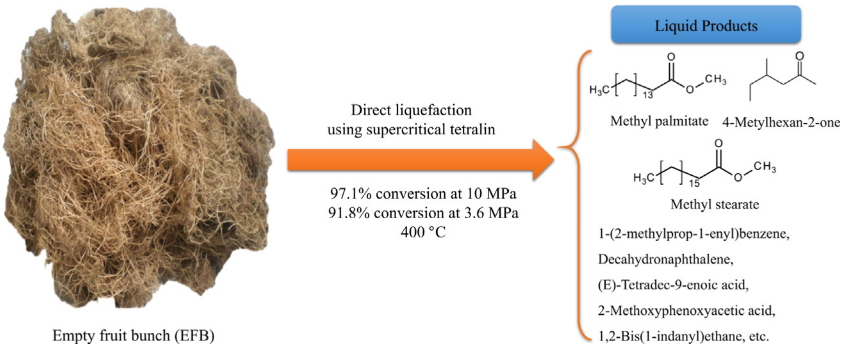
Anton Koriakin [1], Seunghyun Moon [1], Doo-Wook Kim, Chang-Ha Lee *

Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul, Republic of Korea

HIGHLIGHTS

- Supercritical tetralin achieved higher conversion than *n*-dodecane at lower pressure.
- EFB conversion at 400 °C in tetralin reached 97.1% with the addition of Fe_3O_4 and H_2.
- Higher temperature at 400 °C led to increasing gas product yield in both solvents.
- Activated solid residue after liquefaction showed good adsorption capacity for CO_2.

GRAPHICAL ABSTRACT



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ABSTRACT

The direct thermochemical liquefaction of oil palm empty fruit bunch (EFB) was performed using sub- and supercritical solvents. The total feedstock conversion at 400 °C in tetralin reached 91.8%, and 97.1% with the addition of Fe_3O_4 and H_2. Increasing the reaction temperature to 450 °C with *n*-dodecane present led to a slight increase in the total feedstock conversion. At 400 and 450 °C in *n*-dodecane, the liquefaction reaction afforded almost identical feedstock conversions (>77%) and high liquid product yields; however, the reaction pressure exceeded 10 MPa. The variations of the reaction performance in the *n*-dodecane/tetralin mixture were correlated to the quantity of tetralin. Tetralin was an ideal solvent that promoted an efficient EFB liquefaction process and suppressed char formation. The solid residues collected after the liquefaction reaction were thermally activated, and some of them showed good CO_2 adsorption capacity when compared to activated carbons.

1. Introduction

Producing liquid fuels and chemicals from wood biomass is one of many promising solutions that could potentially address modern day environmental and energy challenges such as climate change and fossil fuel depletion [1]. Moreover, it has been reported that wood biomass can be used as a good source of low-cost adsorbent for CO_2 adsorption [2,3]. In order to fully utilize biomass resources such as wood sludge, wood waste, as well as forestry and agricultural residues, it is important to develop efficient technologies that can be used to convert biomass into biofuels or valuable fine chemicals [4].

Biomass can be liquefied into biofuels via thermochemical or biological processes [5]. For competitive biomass-based products, it is vital to demonstrate that biofuels or fine chemicals can be effectively mass-produced from biomass. It has been suggested that thermochemical liquefaction is far more attractive compared to biological liquefaction because it affords high product conver-

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* Corresponding author.
E-mail address: leech@yonsei.ac.kr (C.-H. Lee).

[1] A. Koriakin and S. Moon contributed equally to the paper as first authors.

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sion, is compatible with various feedstocks, and can be feasibly used for large-scale applications [6]. Recently, it has been studied that co-liquefaction of biomass feedstocks and petrochemical feedstocks can have a great potential to improve the quality of oil products [7]. In addition, liquid products from biomass feedstock, as a liquefaction medium, could be directly combined with petrochemical streamlines in residual treating or blending processes without separation [8,9].

Lignocellulosic biomass has become the most potential renewable feedstock for the chemicals and fuels production. The dominant components in lignocellulosic biomass are cellulose, hemicellulose, and lignin, which are all oxygen-rich macromolecules. A significant difficulty encountered during biomass liquefaction is the depolymerization of lignin and crystalline cellulose, which often causes a significant coking issue [10,11]. Another important challenge is to minimize the amount of oxygen content in the liquid products, and convert the biomass feedstock used into a fuel that has appropriate combustion and thermochemical properties [12,13]. To obtain more deoxygenated biofuels, the hydrotreating process has recently received much attention [12].

The hydrotreating process is typically carried out under high pressure (over 20 MPa) at temperatures up to 400 °C. However, the use of direct hydroliquefaction for biomass processing appears to be an attractive option as it can eliminate an extraneous process step. It has been reported that the combination of cellulose hydrolysis and hydrogenation could significantly improve total product conversion and increase the yields of the desired compounds [14]. A typical high-pressure direct liquefaction process works in the temperature and pressure range of 200–450 °C and 5–20 MPa, respectively. A wide range of reaction times (from 10 min to 24 h) and solvents (*e.g.*, water, alcohols, acetone, etc.) have also been reported previously [15,16].

In direct liquefaction processes, the reaction medium plays an important role as the solvent can promote the degradation of the molecular structure of the lignocellulosic biomass, and influence the final product yield, as well as the types and numbers of resulting components [17–20]. Supercritical fluids have been widely used in various chemical processes owing to their ability to improve the phase behavior, decrease mass transfer limitations, and promote reaction rates [21–23]. Therefore, supercritical fluid-based technologies have gained a great deal of attention among the proponents of direct liquefaction methods [19,20,24].

Supercritical or hot-compressed water is the most widely used solvent for liquefaction. It is not only an environmentally friendly solvent, but it also facilitates the recycling of the inorganic components of biomass as fertilizers. However, liquefaction using supercritical or hot-compressed water has disadvantages such as challenging operating conditions, low yield of water-insoluble bio-oil and low-combustion values of the resulting bio-oil. Alternatively, using organic solvents with lower critical points as the reaction medium has a number of advantages over water as the reaction requires milder operation conditions, affords greater yields of water-insoluble products, and produces final bio-fuel products with less oxygen content but greater combustion value [25]. Furthermore, the addition of hydrogen (to enrich the H/C ratio) into subcritical or supercritical organic solvents significantly affects the product conversion [26,27].

Another important concern in the practical application of biomass conversion lies with the operating pressure and temperature of the chosen methods as harsh conditions may not be economically competitive for actual production-driven processes. Using the reaction conditions of petrochemical processes as guidelines, a pressure of less than 10 MPa at high reaction temperatures may be desirable for biomass conversion owing to process reliability factors; however, the choice of reaction solvent can be limited under such circumstances.

Comparing the liquefaction process of pinewood using water, acetone, and ethanol in the reaction temperature range of 250–450 °C, aprotic acetone is a better solvent in terms of product conversion, while the highest oil yield is afforded by ethanol (26.5%) at 400 °C [28]. However, owing to their great vapor pressures, the operating pressures for the corresponding reaction are very high. The pyrolysis of cellulose in sulfolane, an aprotic polar solvent with a high boiling point of 285 °C, gives a simple reaction product under relatively low pressure [29,30].

Alternatively, the use of hydrogen-donor solvents for biomass liquefaction has increasingly gained attention as they have been widely used for gaseous hydrogenation in previous studies of biomass liquefaction [9,31]. Hydrogen-donor solvents not only donate hydrogen atoms, but also improve the hydrogen transport mechanism during the process of biomass conversion. Hence, using hydrogen-donor solvents could offer a greater liquefaction efficiency compared to other kinds of solvents.

As a representative hydrogen-donor solvent, tetralin has been widely studied for coal liquefaction. However, due to the high utilization cost of tetralin, it actually uses distillation products (*e.g.* mid-cuts) from coal liquefaction instead [32]. In the early 1990s, tetralin has been studied as a solvent for biomass liquefaction [33]. Also, liquefaction using tetralin under H_2 pressure has been studied, and it was found that the hydrogen-donor effect of tetralin becomes evident only when liquefaction occurs at the higher temperature of 300–450 °C [17]. In addition, the previous studies reported that tetralin imparts a positive effect on product conversion and enhances the yields of liquid oil and gases compared to toluene (a non-hydrogen donor solvent) in a biomass liquefaction process [34].

In this study, we investigated the feasibility of the integrated process for both lignocellulosic biomass liquefaction and heavy oil upgrading using an organic solvent. Oil palm empty fruit bunch (EFB) was selected as a feedstock because it consists of approximately 20.4% of the total oil palm biomass [6]. *n*-dodecane was used as a representative hydrocarbon in the streamlines of actual petrochemical processes (*e.g.*, mid-cuts, recycled oil. etc.), and tetralin was used as a hydrogen-donor solvent in EFB liquefaction. The efficiency of EFB liquefaction and char suppression using sub- and supercritical tetralin, *n*-dodecane, and their mixture was evaluated under various reaction conditions by varying the reaction temperature (400 and 450 °C), hydrogen content, and the amount of the Fe_3O_4 nano-catalyst used. In addition, the solids obtained after the reaction were treated by simple thermal activation (300 and 600 °C), and their adsorption capacity as a porous adsorbent for CO_2 was evaluated at 30 °C and 1 bar.

Since oil refinery generally operates the upgrading units for heavy oils and the streamlines of petrochemical processes which contain hydrogen-donor hydrocarbons including tetralin [32], the results of this study can contribute to evaluating the feasibility of co-processing of conventional petroleum feedstocks directly combined with biomass products pre-treated by organic solvents.

2. Materials and methods

2.1. Materials and reagents

Oil palm empty fruit bunch (EFB) fibers, with an average fiber size of 5–10 mm, were used directly without any pretreatment. The composition analysis of the EFB fibers was performed using the standard method for determining carbohydrates by high-performance liquid chromatography (HPLC, ASTM E1758-01) [35]. The EFB fibers contain 28.3 wt% of lignin, 36.3 wt% of glucan, 21.4 wt% of xylan, 6.0 wt% of ash, and 8 wt% of moisture. As the EFB fibers contain 6.0 wt% of ash, it is inevitable that some solids are