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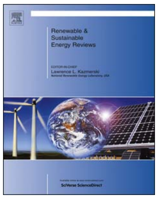

Producing jet fuel from biomass lignin: Potential pathways to alkylbenzenes and cycloalkanes

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ABSTRACT

Jet turbine fuels have not been completely replaced by biomass-derived fuels due, in part, to the lack of the aromatic and cycloalkane hydrocarbons in bio-jet fuels. Such molecules play a critical role in traditional jet fuels for combustion characteristics and material compatibility. To date, this problem has been addressed by blending bio-jet fuel with traditional petroleum-based oils. In order to produce a 100% biomass-derived jet fuel, a suitable bioresource is needed for synthesizing aromatic and cycloalkane fuel compounds. Lignin, the only biomass component rich in aromatic benzene ring structures, is currently underutilized for low-value heat or treated as process waste because of its high chemical resistance. In this review, a four-step pathway of pretreatment, depolymerization, hydrodeoxygenation (HDO), and alkylation to convert lignin into jet-fuel-range aromatic hydrocarbons and cycloalkanes is explored. While many studies about these processes can be found in the literature for biomass and bio-derived molecules, the purposes of those studies were often for something other than lignin valorization. For example, pretreatment processes focus on cellulose and hemicellulose as desired products while lignin is handled as a waste. Most HDO studies focus on the upper phase of bio-oil which contains primarily water and phenolic monomers, ignoring the bottom phase which contains the larger, main components from depolymerization. Many alkylation studies used single, pure components; by comparison, the feedstocks from HDO of lignin-derived bio-oil are mixtures of varying complexity. This review of each process can be used to guide pathway integration and optimization.

1. Introduction: the case for making jet fuel from lignin

Decreasing accessibility to crude oil, combined with increasing world populations and concerns about global climate change, has led to increased interest in alternative energy sources such as solar, hydro, and biomass [1,2]. Some of these renewable energy sources are not supported by current infrastructure, meaning that they will need significant time to become technically and economically feasible. Biomass-derived liquid fuels can have similar properties to their fossil-derived counterparts, so few changes to existing infrastructure are needed [3]. The U.S. Department of Agriculture and the U.S. Department of Energy have a long-term goal to obtain 20% of transportation fuels from biomass by 2030 [4]. Furthermore, the U.S. Energy Information Administration predicts that the yield of biomass-derived fuels will increase rapidly in the next three decades, regardless of the fluctuation of crude oil prices [5].

Biomass is a renewable carbon source [6,7] from which we can produce liquid and gaseous fuels, electricity [8], and a variety of chemicals. In 2005, approximately 14% of the total world energy consumption [9] and over 3% of the total U.S. energy consumption was supplied by biomass, exceeding hydroelectric power as the most dominant renewable energy source [4]. Biomass-derived fuel is nearly sulfur-free and CO_2-neutral, and thus has the potential to mitigate some of the negative effects from fossil fuel combustion such as greenhouse (CO_2) and acid gas (NO_x, SO_x) emissions [10–14].

Lignocellulose is the most promising form of biomass for transportation fuels production due to its abundance, non-food nature, and lower costs. More than 1.37 billion dry tons per year of biomass can be accessible from agricultural and forest lands in the U.S, respectively [4]. To prevent conflict with food production, research has increased focus on forest residues, agricultural wastes such as bagasse and corn stover, and non-edible fuel crops from marginal lands [15,16]. Biomass is composed of various sugars (starch), triglycerides (oils), and lignocellulose (cellulose, hemicellulose, and lignin [10]). More expen-

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Abbreviations: BTX, benzene, toluene, and xylene; GHG, greenhouse gas; HDO, hydrodeoxygenation; HEFA, hydroprocessed esters and fatty acids; HHV, higher heating value; HTL, hydrothermal liquefaction; IL, ionic liquid; MCH, methyl-cyclohexane; MWL, milled wood lignin; SCW, supercritical water; TMC, transition metal carbide; TMN, transition metal nitride; TMP, transition metal phosphide; TMB, tri-methyl-benzene; TSI, threshold soot index; YSI, yield soot index

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Nomenclature

Zeolites

HZSM-5	hydrogen-type zeolite Socony Mobil-5
MCM	Mobil Crystalline Materials
SBA	Santa Barbara Amorphous
USY	ultra-stable Y
ZSM-5	zeolite Socony Mobil-5

Ionic liquids

[amim]Cl	1-allyl-3-methyl-imidazolium chloride
[bmim][CH_3COO]	1-butyl-3-methylimidazolium acetate
[bmim]Cl	1-butyl-3-methylimidazolium chloride
[emim]$MeSO_3$	1-ethyl-3-methylimidazolium methanesulfonate
[emim]$EtSO_3$	1-ethyl-3-methylimidazolium ethylsulfonate
[emim]CF_3SO_3	1-ethyl-3-methylimidazolium trifluoromethanesulfonate
[mmim]$MeSO_4$	dimethylimidazolium methyl sulfate
[Ch][Gly]	cholinium glycine
[Ch][Phe]	cholinium phenylalaninate
[Ch][Lys]	cholinium lysinate
[emim]Cl	1-ethyl-3-methylimidazolium chloride
[emim]OTf	1-ethyl-3-methylimidazolium triflate
[emim][CH_3COO]	1-ethyl-3-methylimidazolium acetate

sive feedstocks like oils, terpenes, and sugars are generally utilized for high-value fine chemicals [17], while low-value fuels are produced from lignocellulose [18–20].

Lignin is the second most abundant component in lignocellulose and the most underutilized. Lignin is a natural amorphous hydrophobic polymer that includes three major phenyl-propanoid units: *p*-coumaril, coniferyl and sinapyl alcohols, shown in Fig. 1. Most lignin-derived compounds partition into a non-polar phase due to their lower oxygen content [10,21], leading to more thermally stable [22,23] and higher energy density [24,25] liquid fuels compared to fuels derived from other biomass components. Yet there is relatively little research focused on valorization of lignin relative to cellulose or hemicellulose [17,26–29], especially on the conversion of lignin to the liquid transportation fuels [30]. Lignin production from the pulp and paper industry largely surpasses the demand from existing lignin product markets, such that only 2% of lignin from the paper industry is commercially utilized [31–34].

Airplanes are much less energy source flexible than stationary and mobile energy users. For example, ships can depend on wind or nuclear power as alternatives to diesel or heavy fuel oil; cars can depend on oxygenated liquid fuels, hydrogen, solar power or electricity as alternatives to gasoline. Airplanes, however, need fuel with high energy density, low freezing point, turbine-compatible combustion characteristics, high degrees of consistency from one batch to another, and low levels of contaminants—after all, the consequences of engine failure at high altitudes are much more severe than the consequences of engine failure on the ground. This means that the aviation industry is and will remain sensitive to hydrocarbon fuel price volatility and concerns about long-term supply sustainability. U.S aviation is responsible for approximately 11% of global transportation greenhouse gas (GHG) emissions [35]. The International Air Transport Association predicts that 10% alternative fuel will be utilized by 2017, carbon cycle balance will be achieved by 2020, and emissions from aviation will decrease 50% compared with 2005 levels by 2050 [36]. One study indicates that biomass-derived jet fuel can lower the GHG emission to 85% of petroleum-derived jet fuel [37]. Pressure to reduce GHG emissions has stimulated research into using bio-jet fuels to replace fossil fuels [38]. Several renewable alternatives have been developed and implemented with varying degrees of success: 1) Fischer-Tropsch synthetic paraffinic kerosenes (FT-SPKs) [39], 2) biomass-derived synthetic paraffinic kerosenes (bio-SPKs) produced from camelina, jatropha, or algae [40], and 3) hydroprocessed esters and fatty acids (HEFA) derived from animal fats or plant oils [41].

A major hurdle to commercialization of bio-jet fuels is the need to replicate the physical and chemical properties of petroleum jet fuels. Conventional jet fuel consists of *n*-paraffins (20%), *iso*-paraffins (40%), and cycloalkanes (20%), and 20% by volume of aromatic hydrocarbons (i.e. naphthalenes) [42,43], with a carbon range of about C_9-C_{16} [44]. There are maximum limitations for aromatics (25 vol% [43]), sulfur (3000 ppm [45]), and olefins (5 vol% [46]) in jet fuel to control the freezing point, sulfur oxide emissions, and formation of gums and sediments during storage [44]. Current bio-jet fuels have, generally, higher freezing points, lower thermal stability in engines, and lower long-term storage stability, meaning that bio-jet fuels need to be tailored for regular use in commercial jet airplanes [47]. The most significant difference between petroleum-derived jet fuels and renewable jet fuels is that most renewable jet fuels contain no aromatics [48] while petroleum-derived fuels contain up to 25% by volume [40]. These aromatics play a vital role in jet fuel quality and safety, specifically the fuel's elastomeric swelling, material compatibility, and lubricity characteristics [42]. To ensure that alternative jet fuels meet quality and performance standards, the most recent technical specification, ASTM D7566-14a, requires that renewable/synthetic jet fuels be blended with conventional fuels such that the blend contains no more than 50 vol% renewable fuel. A minimum aromatics content of 8 vol% is required in the blended fuels [49].

To produce 100% alternative jet fuels compatible with ASTM D7566 and ASTM D1655, researchers have studied the influence of aromatics on various fuel characteristics (thermal-oxidative stability, emissions, material compatibility, etc.) and have found that adding target aromatic compounds to renewable jet fuels would make it possible to produce a fully synthetic jet fuel (FSJF) [50,51]. Low molecular weight alkyl-benzenes, such as di- and tri-methyl-benzene, ethyl-benzene, and iso-propyl-benzene, were identified as desirable aromatic compounds for FSJF as they cause less soot formation upon combustion in the engine than other aromatic compounds.

Such alkyl-benzenes could be produced through fast pyrolysis of lignin-rich biomass followed by lignin-derived bio-oil upgrading. The reasons for selecting lignin as the alkyl-benzene feedstock are that 1) lignin is composed of aromatic compounds [34], which can be more easily transformed into aromatic hydrocarbons than other biomass components; 2) lignin, from the pulp and paper industry and the cellulosic ethanol industry, is abundant and currently underutilized (2% for chemicals production [52] and the rest for heat and power [31]); 3) fast pyrolysis is a potentially economical approach for converting biomass into fuels and chemicals; and 4) demands for stationary energy can be met through other renewable sources (solar,

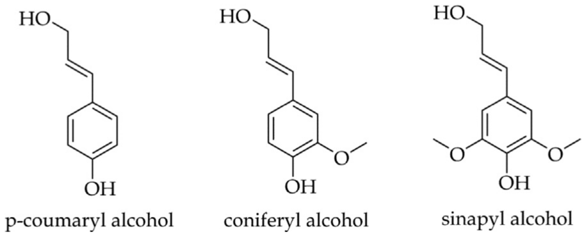

Fig. 1. Three phenols derived from lignin [54].