



From lignin to cycloparaffins and aromatics: Directional synthesis of jet and diesel fuel range biofuels using biomass



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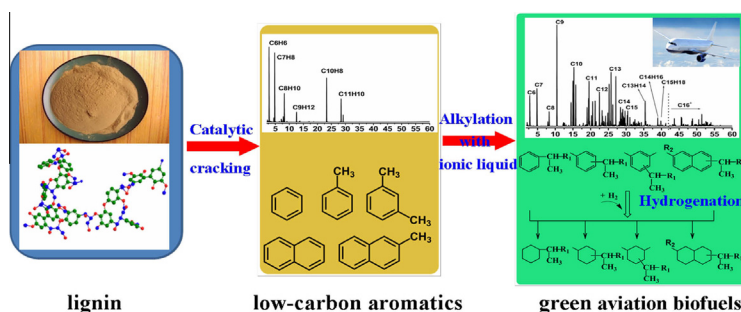
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HIGHLIGHTS

- A controllable transformation of lignin into green bio-jet fuels was demonstrated.
- Production of C8–C15 hydrocarbons was achieved by alkylation using ionic liquid.
- Lignin-derived biofuels basically met main technical requirements of jet fuels.

GRAPHICAL ABSTRACT

A novel controllable transformation of lignin into C8–C15 cycloparaffins and aromatics in the jet and diesel fuel range by catalytic depolymerization of lignin into low carbon aromatics coupled with alkylation of aromatics using ionic liquid.



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ABSTRACT

The continual growth in commercial aviation fuels and more strict environmental legislations have led to immense interest in developing green aviation fuels from biomass. This paper demonstrated a controllable transformation of lignin into jet and diesel fuel range hydrocarbons, involving directional production of C8–C15 aromatics by the catalytic depolymerization of lignin into C6–C8 low carbon aromatic monomers coupled with the alkylation of aromatics, and the directional production of C8–C15 cycloparaffins by the hydrogenation of aromatics. The key step, the production of the desired C8–C15 aromatics with the selectivity up to 94.3%, was achieved by the low temperature alkylation reactions of the lignin-derived monomers using ionic liquid. The synthetic biofuels basically met the main technical requirements of conventional jet fuels. The transformation potentially provides a useful way for the development of cycloparaffinic and aromatic components in jet fuels using renewable lignocellulose biomass.

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1. Introduction

The increased demand for commercial traffic fuels combined with potential environmental benefits have accelerated advances

in developing new generation (hydrocarbon) bio-fuels, with a particular focus on aviation biofuels from renewable biomass (Daroch et al., 2013; Valle et al., 2012; Yan et al., 2013; Wang et al., 2012). Aviation fuel is a specific type of fuel oils designed for use in aircraft and the most commonly used commercial aviation fuels are jet fuels which are currently produced from petroleum refining (Liu et al., 2013). The development of aviation biofuels can help

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reduce our dependence on the fossil energy and particularly release the environmental pressure. In this sense, new or improved technologies are required to meet the challenges associated with producing bio-jet fuels from biomass or biomass-derived feedstocks.

Jet fuels must meet very stringent specifications, which makes it much more difficult to develop an alternative fuel for the use of aviation than for automobile applications (Verma et al., 2011). Several promising routes, especially, hydrotreating of vegetable oils (Bezergianni et al., 2009; Robota et al., 2013; Wang et al., 2012), and Fischer Tropsch synthesis (Kumabe et al., 2010; Liu et al., 2013; Naik et al., 2011; Yan et al., 2013), have been developed with the aim of producing aviation biofuels from various biomass feedstocks. Numerous feedstocks of edible and non-edible vegetable oils like soybean oil, Jatropha oil, algae oil and waste restaurant oils have been intensively investigated for producing hydrocarbon fuels by the hydrotreating technologies, showing great potential for the production of alkanes particularly suitable for diesel and/or jet fuels applications. The synthetic feedstocks of triglycerides extracted from plant or animal oils are typically hydrotreated under high hydrogen pressure over noble metals or metal sulfides supported catalysts. The hydrotreating of triglycerides into hydrocarbons mainly involves the following processes: (i) the hydrogenation of the unsaturated olefinic bonds in triglycerides; (ii) the formation of free fatty acids along with propane through breaking the C–O bonds in the saturated triglycerides; (iii) the formation of linear n-alkanes by hydrodeoxygenation, decarbonylation and decarboxylation of free fatty acids; and (iv) the formation of lighter iso-alkanes by hydrogenation cracking and isomerization. The most representative vegetable oils are essentially composed of C16 and C18 fatty acids, and consequently, the typical products obtained from the hydroprocessing of vegetable oils at lower temperatures of 300–350 °C are C15–C18 alkanes in the diesel range. To produce jet range biofuels (typically C8–C15 hydrocarbons), the cracking and isomerization at higher temperatures are generally required (Verma et al., 2011). So far, American Society for Testing and Materials (ASTM) have adopted a new specification D7566-14a for a 50:50 blend of the synthetic paraffinic kerosene's (SPKs) produced from triglyceride-based vegetable oils with conventional jet fuels (ASTM D7566-14a). The hydrotreating of vegetable oils can offer higher yield of diesel or jet fuels, which could benefit from the fact that triglycerides contain saturated fatty acids with a moderate chain length of C16–C18 together with higher H/C ratio.

Fischer–Tropsch synthesis (FTS) is a highly developed and technically proven route to transform lignocellulose biomass into liquid biofuels (particularly alkanes) (Kumabe et al., 2010; Liu et al., 2013; Naik et al., 2011; Yan et al., 2013). The biomass-based FTS process generally includes four main steps: (i) the production of bio-syngas by means of biomass gasification, (ii) cleaning and conditioning of crude syngas, (iii) high pressure FT synthesis and (iv) subsequent upgrading of crude fuels for gasoline, diesel and jet fuel applications. The liquid products from FTS are commonly complex compounds, mainly consisting of the five families of hydrocarbon groups (n-paraffins, iso-paraffins, olefins, aromatics and naphthenes) alone with oxygenates, which depend on reaction conditions and catalyst types. The raw FTS fuels must be further upgraded to the acceptable jet range fuels by subsequent hydrocracking, isomerizing and distilling (Liu et al., 2013; Yan et al., 2013). Most of the liquid hydrocarbons from FTS are paraffins and olefins, and thereby, aromatics and naphthenes should be increased in the FTS-derived fractions to meet the specific requirement of jet fuels (Corporan et al., 2011; Dupain et al., 2005; Huber et al., 2006). FTS-derived SPKs have been also approved for a 50/50 blend with petroleum-derived jet fuels (ASTM D7566-14a (2014); Corporan et al., 2011; Lobo et al., 2011). Chemically, main compo-

sitions of commercial and military jet fuels can be described as paraffins, naphthenes and aromatics (Vukadinovic et al., 2013; Yan et al., 2013). As mentioned above, triglycerides- or FTS-derived SPKs are currently being utilized as the component of alkanes in commercial jet-fuels. However, another two main compositions (cyclic alkanes and aromatics) required for the commercial and military jet fuels seem to be difficult to get from the well developed hydrotreating of vegetable oils or FTS process (Corporan et al., 2011; Dupain et al., 2005; Robota et al., 2013).

Lignin, a main constituent of lignocellulosic biomass, has been proven to potentially produce aromatic chemicals and biofuels by means of various strategies like hydrogenation, oxidation, pyrolysis, and catalytic pyrolysis (Deng et al., 2010; Jiang et al., 2014; Lou et al., 2010; Mullen and Boateng, 2010; Olcese et al., 2013; Pandey and Kim, 2011; Shen et al., 2010; Zakzeski et al., 2010). In view of its structure characteristics (three dimensional amorphous polymer containing phenylpropane units), lignin, potentially, can serve as a plentiful renewable resource for producing aromatics and cyclic alkanes.

Here, we demonstrate the directional transformation of lignin into jet or diesel fuel range hydrocarbons by a novel route, including directional production of C8–C15 aromatics by the catalytic depolymerization of lignin into C6–C8 low carbon aromatics coupled with the alkylation of aromatics, and the production of C8–C15 cycloparaffins by the hydrogenation of C8–C15 aromatics. Owing to the unique properties of ionic liquids (ILs) like having low vapor pressures, high thermal and chemical stability, non-flammability and Brønsted and Lewis acidity in some cases, ILs have attracted wide interest in organic synthesis, catalysis, separation, extraction, electrochemistry, polymerization reactions (Blanco et al., 2006; Corma and García, 2003; Han and Row, 2010; Olivier-Bourbigou et al., 2010) as well as hydrolysis of cellulose to sugars or biomass platform chemical (Liu et al., 2012). Present work also demonstrated that the key step, the selective production of the desired C8–C15 aromatics from lignin was able to be realized by the low temperature alkylation reactions of the biomass-derived monomers using ionic liquid, and the end products meet the basic requirements of the conventional jet fuels.

2. Methods

2.1. Materials

The raw material of lignin, purchased from Lanxu Biotechnology Co. Ltd. (Hefei, China), was a brown and sulfur-free lignin powder manufactured from wheat straw. The dried lignin contained 63.46 wt.% carbon, 5.61 wt.% hydrogen, 29.23 wt.% oxygen and 1.70 wt.% nitrogen, which were determined by the elemental analysis with an elemental analyzer (Vario EL-III, Elementar, Germany). All analytical reagents used were purchased from Sinopharm Chemical Reagent Company Limited (Shanghai, China).

2.2. Catalyst preparation and characterization

The HZSM-5 zeolite with the Si/Al ratio of 25 used for the catalytic cracking of lignin was prepared by the conversion of the sodium form supplied by Nankai University catalyst Co., Ltd. (Tianjin, China) to the protonated form via NH_4^+ exchange procedure, followed by calcination in air at 550 °C for 4 h. For preparation of the [bmim]Cl-2AlCl₃ (1-butyl-3-methylimidazolium chloroaluminate) ionic liquid (used for alkylation of lignin-derived aromatics), 1-butyl-3-methylimidazolium chloride ([bmim]Cl) was first prepared by the following procedures: dried and redistilled N-methylimidazolium and 1-chlorobutane were placed into a dry round-bottomed flask equipped with a reflux cooler and a magnet-

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