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Production of jet and diesel biofuels from renewable lignocellulosic biomass

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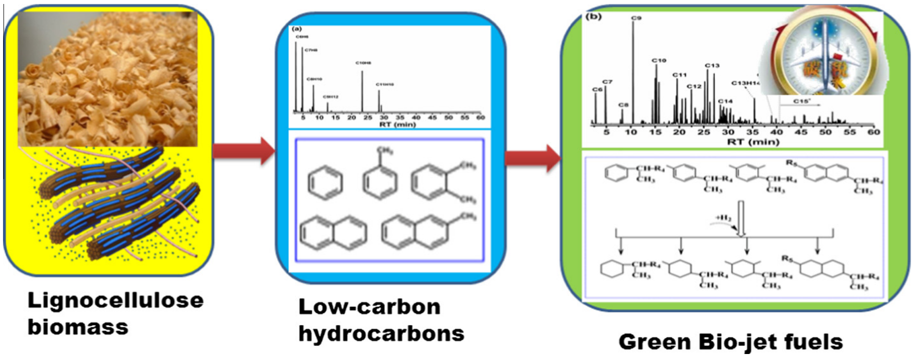
HIGHLIGHTS

- A novel controllable transformation of biomass into bio-jet fuels was demonstrated.
- Production of C8–C15 hydrocarbons was achieved by alkylation using ion liquid.
- Sawdust-derived biofuels basically met main technical requirements of jet fuels.

GRAPHICAL ABSTRACT

A new controlled conversion of lignocellulose biomass to bio-jet and diesel fuels by catalytic pyrolysis of biomass into low carbon hydrocarbons coupled with alkylation of aromatics.



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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 renewable lignocellulosic biomass. This work demonstrated a novel transformation of biomass into bio-jet and diesel fuels. The transformation included following three reaction steps: (i) the catalytic pyrolysis of sawdust into low-carbon aromatics, (ii) the production of C8–C15 aromatics by the aromatic alkylation and (iii) the production of C8–C15 cyclic alkanes by the hydrogenation of C8–C15 aromatics. The production of the desired C8–C15 aromatics with the highest selectivity of 92.4% was achieved by the low temperature alkylation reactions of the low carbon aromatics using the ionic liquid of [bmim]Cl–2AlCl$_3$ (1-butyl-3-methylimidazolium chloroaluminate). The biofuels derived from sawdust basically met the main specifications of jet fuels. This transformation potentially provides a useful avenue for the development of green aviation biofuels utilizing lignocellulose biomass.

1. Introduction

Jet fuel or aviation turbine fuel is a type of aviation fuel designed for use in aircraft powered by the gas-turbine engines.

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The most commonly used fuels for commercial aviation are produced from petroleum refining with the standardized international specifications [1]. Over the past decade, the development of new generation hydrocarbon biofuels from renewable biomass has stimulated significant interest because of the continual growth in commercial traffic fuels and their potential environmental benefits [1–8].

To meet the challenges associated with producing bio-jet fuels from biomass, new or improved technologies are needed. Two representative technologies, catalytic hydrotreating of vegetable oils [3,5,6,9–14] and Fischer Tropsch synthesis using biomass-derived syngas [1,4,15–20], have been developed for producing green aviation bio-fuels. Catalytic hydrotreating of vegetable oils and related feedstocks can transform the triglycerides-based oils into liquid alkanes in the diesel and/or jet fuel ranges. Generally, triglycerides extracted from plant or animal oils are hydrotreated over noble metal supported or metal sulfide supported catalysts under high hydrogen pressures. Such transformation typically involves the formation of free fatty acids (FFA) by breaking the C–O bonds of the triglycerides, followed by the deoxygenation of FFA to form linear n-alkanes and the formation of lighter iso-alkanes by isomerization or cracking. The low-temperature hydrotreating (typically at 300–350 °C) mainly produce C15–C18 alkanes in the diesel range, and the cracking and isomerization at higher temperatures are generally required to improve the yield of iso-alkanes in the kerosene range [3,5,12]. So far, the synthetic paraffinic kerosenes (SPKs) produced from triglyceride-based vegetable oils have been approved for use in commercial aircraft in a 50/50 blend with petroleum-derived jet fuels [5].

Alternatively, Fischer–Tropsch synthesis (FTS) is a highly developed route to convert lignocellulose biomass into liquid alkanes used as transportation fuels [1,4,15–20]. The production of biofuels by FTS generally includes the preparation of synthesis gas by biomass gasification, cleaning and conditioning of crude bio-syngas, Fischer–Tropsch synthesis and subsequent upgrading of fuels [1,4]. The liquid products derived from FTS primarily consist of the five families of hydrocarbon groups (paraffins, iso-paraffins, olefins, aromatics and naphthenes) alone with oxygenates [1,4,15–20]. To produce acceptable jet range fuels, the raw FTS fuels must be further upgraded by subsequent hydrocracking, isomerizing and distillating [1,4,15]. Since most of the liquid hydrocarbons produced by FTS are paraffins and olefins, naphthenes and aromatics should be increased in the FTS-derived fractions to meet the specific requirement of jet fuels [16–20]. Currently, FTS-derived SPKs have been also approved for a 50/50 blend of SPKs with petroleum derived jet fuels [1,18–19].

Chemically, main compositions of commercial and military jet fuels can be described as paraffins, cyclic alkanes and aromatics, typically ranging from C8 to C15 hydrocarbons [4,15,19,21]. As mentioned above, triglycerides or FTS derived SPKs are currently utilized as the component of alkanes in commercial jet-fuels. Recently, the aromatization of propane obtained from triglycerides hydrogenolysis has been proposed to supply aromatics for blending issues in renewable jet fuels production from vegetable and algal oil [22,23]. However, directional transformation of lignocellulose biomass into C8–C15 cyclic alkanes and aromatics is still a challenging task. For example, the liquid products produced by pyrolysis of lignocellulosic biomass are generally dominated by oxygenated organics (named as bio-oils), which are not suitable for engine applications due to high viscosity, high acidity, low stability and heating value in bio-oils [24–27]. Even though the catalytic pyrolysis of lignocellulose biomass over zeolites is regarded as a cheaper route for converting biomass to hydrocarbons, main products formed from this process are typically low carbon hydrocarbons which do not meet the specific requirement of jet fuels [28,29].

The purpose of this work is to transform sawdust into jet and diesel fuels range hydrocarbons. This transform includes the production of C8–C15 aromatics by the catalytic pyrolysis of biomass coupled with the alkylation of aromatics, and the production of C8–C15 cycloparaffins by the hydrogenation of aromatics. Owing to the unique properties of ionic liquids (ILs) like low vapor pressure, high stability, nonflammability and having Bronsted and Lewis acid, ILs have attracted wide interest in organic synthesis, catalysis, separation, extraction, electrochemistry and polymerization reactions [30–34]. Present work also demonstrated that the production of the desired C8–C15 aromatics from sawdust can be achieved by the low temperature alkylation of aromatics using the [bmim]Cl–2$AlCl_3$ ionic liquid.

2. Materials and methods

2.1. Materials

The biomass material (sawdust), purchased from Anhui Yineng Bio-energy Co. Ltd. (Hefei, China), was sieved to obtain particle sizes <0.3 mm. The elemental compositions in the dried and ash free biomass mainly consists of 46.20 wt% carbon, 6.02 wt% hydrogen, 47.30 wt% oxygen and 0.48 wt% nitrogen, measured by an elemental analyzer (Vario EL-III, Elementar, Germany). All analytical reagents used were purchased from Sinopharm Chemical Reagent Company (Shanghai, China).

2.2. Catalyst preparation and characterization

The HZSM-5 zeolite with Si/Al ratio of 25 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 the preparation of the [bmim]Cl–2$AlCl_3$ (1-butyl-3-methylimidazolium chloroaluminate) ionic liquid, 1-butyl-3-methylimidazolium chloride ([bmim]Cl) was first prepared by the following procedures. The dried and redistilled N-methylimidazolium and 1-chlorobutane were placed into a dry round-bottomed flask equipped with a reflux cooler and a magnetic agitator. The mixture was heated and reacted under the temperature of 80–85 °C for 24 h. Then the mixture was cooled to room temperature, and the unreacted reactants were removed using a rotary evaporator. The resulting imidazolium salt was washed using acetonitrile as solvent, and dried in a vacuum drying box to remove the residual solvent and water. Finally, the [bmim]Cl–2$AlCl_3$ ionic liquid was prepared by slowly adding the dried aluminum chloride to the imidazolium salt with a molar ratio of 2.0 between $AlCl_3$ and [bmim]Cl and stirring overnight at room temperature. The Pd/AC catalyst used for the hydrogenation of aromatics was prepared by the incipient wetness impregnation of the HNO_3-treated AC (active carbon) with the H_2PdCl_4 solution ($PdCl_2$ dissolved in HCl solution). The impregnated product was dried at 120 °C for 24 h, and finally reduced by H_2 (60 mL/min) at 280 °C for 8 h.

Acidity characterizations of the ionic liquid were conducted by infrared spectroscopy (Bruker Tensor 27 FT-IR spectrometer) using pyridine as a probe molecule of Lewis and Bronsted acid at room temperature. The samples were prepared by mixing pyridine and the ionic liquids in the volume ratio of 5:1, and then smeared into the liquid films on the KBr windows. The FT-IR spectrum was acquired at 1 cm^{-1} resolution using 16 scans for each sample. The NMR measurements were carried out on a high-resolution liquid nuclear magnetic resonance spectrometer (Bruker Avance 300 MHz). The HZSM-5 catalyst was characterized by NH_3-TPD (temperature programmed desorption of ammonia), XRD (X-ray