



Preparation of jet fuel range hydrocarbons by catalytic transformation of bio-oil derived from fast pyrolysis of straw stalk



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ABSTRACT

The growing demand of commercial jet fuels, in combination with the strict environmental legislations, has led to immense interest in developing aviation biofuels. This work demonstrated that the bio-oil derived from fast pyrolysis of straw stalk was able to be converted into the jet and diesel fuel range hydrocarbons by a designed transformation route. This transformation included three reaction steps: (i) the catalytic cracking of bio-oil into low-carbon aromatics and light olefins, (ii) the synthesis of C₈–C₁₅ aromatic hydrocarbons by the alkylation of low-carbon aromatics with light olefins, and (iii) the production of C₈–C₁₅ cyclic alkanes by the hydrogenation of C₈–C₁₅ aromatics. It was also demonstrated that the production of the desired C₈–C₁₅ aromatics with a high selectivity of 88.4% was achieved by the low temperature alkylation reactions of the bio-oil-derived aromatics using the ionic liquid of [bmim]Cl–2AlCl₃ (1-butyl-3-methylimidazolium chloroaluminate). The synthetic biofuels basically met the main technical specifications of jet fuels based on the combustion heat, viscosity, freeze point and other characteristics of fuels.

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1. Introduction

Today, the most commonly used commercial and military aviation fuels are jet fuels like Jet A-1, Jet A and JP-8, which are mainly produced from petroleum refining [1,2]. The growing demand of commercial transportation fuels, in combination with strict environmental legislations, has led to immense interest in developing new generation hydrocarbon biofuels, with a particular focus on green aviation biofuels [1,3–6]. Jet fuels must meet very stringent international specifications, which makes it more difficult to develop an alternative fuel for aviation turbine fuels than for automobile applications [7]. Several promising routes such as hydrotreating of lipids (triglycerides and free fatty acids etc.) from animal and vegetable oils [4–12], Fischer Tropsch synthesis using the biomass-based syngas [1,3,13–15], and aqueous-phase catalytic transformation of soluble sugars [16,17], have been developed with the aim of producing bio-jet fuels from various biomass feedstocks.

Hydrotreating of triglyceride-based vegetable oils, animal fats and recycled grease can produce liquid linear alkanes, which are particularly suitable for the applications of diesel and/or jet fuels. Numerous researches on the hydrotreating of various edible and non-edible vegetable oils like soybean oil, sunflower oil, Jatropha oil, algae oil and waste restaurant oils have been reported [4–12]. After the oils were extracted from the feedstocks, triglycerides in the extracted oils are subsequently hydrotreated under high hydrogen pressures over noble metals supported or metal sulfides supported catalysts. The hydrotreating of triglycerides into hydrocarbons mainly involves: (i) the hydrogenation saturation of the olefinic bonds in triglycerides, (ii) the formation of free fatty acids via breaking the C–O bonds in the saturated triglycerides, and (iii) forming n-alkanes by the hydrodeoxygenation of free fatty acids. Low temperature hydrogenation of vegetable oils (typically at 300–350 °C) usually generates straight-chain alkanes in the diesel range from C₁₅ to C₁₈. To produce jet range fuels (mainly C₈–C₁₅ hydrocarbons), the cracking and isomerization of longer chain alkanes are required (typically at higher temperatures of 350–450 °C), which can offer higher yield of iso-alkanes in the kerosene range [7,12]. So far, the

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SPKs (synthetic paraffinic kerosenes) derived from triglycerides have been approved for use as the commercial aviation fuels up to a 50/50 blend of SPKs with petroleum derived jet fuels [4,18,19]. The most prominent advantage for producing hydrocarbon fuels by the triglycerides-based hydrotreating technologies would be high yield of bio-fuels, since vegetable oils typically contain a considerable number of C₁₆–C₁₈ fatty acids, which are suitable for the production of diesel and/or jet fuels. However, there are some adverse factors for the hydrotreating of vegetable oils, such as limited resource as compared with richer lignocellulosic biomass, high hydrogen consumption and low yields of cyclic alkanes and aromatics which are also required for commercial jet fuels [6,20].

Another important route, FTS (Fischer–Tropsch synthesis), has been highly developed and technically proven process to transform lignocellulose biomass into liquid alkanes suitable for gasoline, diesel and jet fuel applications [1,3,13–15]. Producing liquid hydrocarbon fuels by the FTS routes generally includes four main steps: (i) the production of synthesis gas by biomass gasification, (ii) cleaning and adjusting crude bio-syngas, (iii) FT synthesis typically using iron or cobalt-based catalysts and (iv) subsequent upgrading of liquid fuels. Typically, the FTS-derived liquid products are complex spectra, mainly consisting of the five families of hydrocarbon groups (paraffins, iso-paraffins, olefins, aromatics and naphthenes) alone with oxygenates, which depend on reaction conditions and catalyst types [1,3,13–15]. For the preparation of jet range biofuels, the raw FTS fuels (mainly straight chain hydrocarbons) should be further upgraded to the acceptable synthetic paraffinic kerosene (SPK jet fuels) by subsequent hydrotreating (hydrocracking and isomerizing) and distilling [1,3,13]. To meet the specific requirement of commercial and military aviation fuels, aromatics and naphthenes should be increased in the FTS-derived fractions, since most of the liquid hydrocarbons derived from FTS are paraffins and olefins alone with a lower yield of cycloparaffins and aromatics [14,15,20,21]. Moreover, soluble sugars or hemicellulose-derived xyloses, produced by hydrolysis of lignocellulose, can be transformed into gasoline, diesel and jet fuels by means of aqueous-phase catalytic routes, which mainly involve the C–C coupling reactions and hydrodeoxygenation [16,17].

Bio-oil, a black oxygenated organic liquid derived from fast pyrolysis of lignocellulosic biomass, is considered to be a promising platform chemical for producing renewable bio-fuels or chemicals [22–30]. Compared with solid biomass as the raw material, bio-oil may offer the advantages of more convenient storage and transportation of raw material, together with equipments sharing with already existent petroleum refining infrastructures. However, the crude bio-oil has some unfavorable properties such as high viscosity and acidity, alone with low stability and heating value due to its high oxygen content. Thereby, it is required to upgrade the oxygenated compounds in bio-oil to liquid hydrocarbon bio-fuels to meet the requirements of the conventional transportation fuels. Two main routes for upgrading bio-oil into high grade biofuels (hydrodeoxygenation and catalytic cracking) have been widely investigated [30–33]. Hydrotreatment of bio-oil is a good technology to improve its heating value and stability by efficiently removing oxygen in bio-oil. Typically, the upgrading of bio-oil by the HDO (hydrodeoxygenation) is operated under high hydrogen pressures over noble metals supported or metal sulfides supported catalysts. The most prominent advantage for HDO upgrading would be high yield of bio-fuels [34]. Alternatively, the catalytic cracking of bio-oil is regarded as a cheaper route for converting the oxygenated compounds of bio-oil to hydrocarbons, since this process is typically conducted using cheaper catalysts like zeolites under the atmospheric pressure, along with

free of external hydrogen consumption. The co-feeding of bio-oil with conventional petroleum streams using an already existent fluid catalytic cracking refinery infrastructure can further decrease capital expenditures [31]. However, main hydrocarbon products derived from the catalytic cracking of bio-oil are typically low carbon hydrocarbons which do not meet the specific requirement of jet fuels [25]. Thus, new or improved technologies are required to meet the challenges associated with producing bio-jet fuels using bio-oil.

At the present time, bioethanol and biodiesel are the most widely used liquid biofuels, which have been successfully implemented in the transportation sector as alternatives to petrol-based gasoline and diesel, respectively [6,35,36]. However, these bio-fuels used for the hydrocarbon-based transport infrastructure may face serious energy-density and compatibility issues [6]. Generally, the commercial or military jet fuel is a mixture of three main components including alkanes, cyclic alkanes and aromatic hydrocarbons [20,21,37,38]. As mentioned above, synthetic paraffinic kerosene, produced by the hydrotreating of triglycerides or FTS using bio-syngas, are currently being utilized as alkane component in conventional jet fuels. However, another two main chemical compositions, cyclic alkanes and aromatics in the kerosene range, could be difficult to be generated from the developed hydrotreating of vegetable oils [6,7,20] or FTS processes [14,15,20,21].

The purpose of this work is to transform bio-oil into jet or diesel fuel range hydrocarbons, including production of C₈–C₁₅ aromatics and C₈–C₁₅ cycloparaffins using the straw stalk-derived bio-oil. ILs (Ionic liquids) have attracted wide interest in organic synthesis, catalysis, separation, extraction, electrochemistry, polymerization reactions as well as hydrolysis of cellulose to sugars or biomass platform chemical, due to the unique properties of ILs like having low vapor pressures, high thermal and chemical stability, nonflammability and Bronsted and Lewis acidity in some cases [39–43]. Present work also demonstrated that the key reaction step, the production of the desired C₈–C₁₅ aromatics from the bio-oil was able to be realized by the low temperature alkylation reactions of low carbon aromatics using the [bmim]Cl–2AlCl₃ ionic liquid, and the end products are close to the main requirements of the conventional jet fuels.

2. Materials and methods

2.1. Materials and chemicals

Bio-oil was produced by the fast pyrolysis of straw stalk in a circulating fluidized bed with a capacity of 120 kg h⁻¹ oil at our Lab [24–29]. The classified chemical composition of the bio-oil along with the elemental composition of the bio oil used was given in Table 1. Conventional chemicals with AR grade were purchased from Sinopharm Chemical Reagent Company Limited (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 NH₄⁺ exchange procedure, followed by calcination in air at 550 °C for 4 h. For the preparation of the [bmim]Cl–2AlCl₃ (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-

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