



Production of renewable jet fuel range alkanes and aromatics via integrated catalytic processes of intact biomass



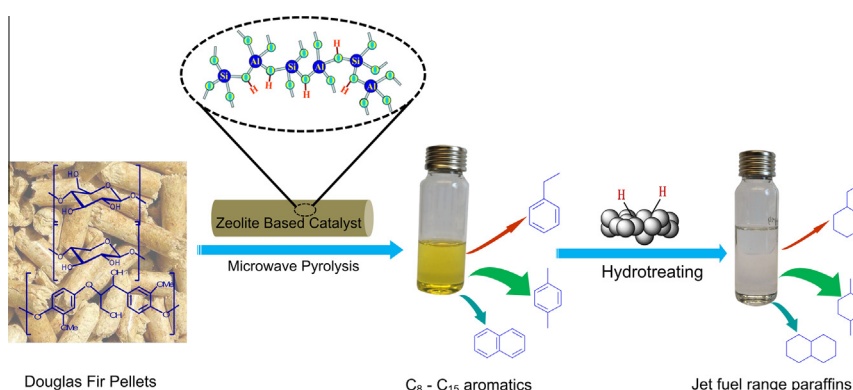
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HIGHLIGHTS

- Integrated catalytic processes were employed to produce paraffins and aromatics.
- Hydrotreating reactions were conducted at mild conditions.
- Inexpensive catalyst (Raney nickel) was first used in the integrated processes.
- Maximum yield (12.63%) of jet fuel range cycloalkanes was gained.
- The process paves a new route for commercial development of jet fuels from biomass.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel pathway was investigated to produce jet fuel range paraffins (alkanes) and aromatics by catalytic microwave-induced pyrolysis of intact biomass (Douglas fir) integrated with the hydrotreating upgrading process. The proof-of-principle for the consecutive two-step process for converting lignocellulosic biomass into jet fuel range paraffins and aromatics involves the use of the well-promoted ZSM-5 in the process of catalytic microwave pyrolysis and Raney nickel in the hydrotreating process. The production of desired C₈-C₁₅ aromatics was achieved from catalytic depolymerization of intact biomass at 375 °C. Up to 12.63% selectivity of C₈-C₁₅ paraffins and 19.48% selectivity of hydro-aromatic hydrocarbons were obtained from the hydrotreating of parent oil under a low-severity condition (for 2 h). A central composite experimental design (CCD) was employed to investigate the effects of reaction temperatures and initial pressures on the composition of hydrotreated oils. We observed that increasing reaction temperature and initial pressure with prolonged time could enhance the hydrogenation and hydrogenolysis reactions to form jet fuel range paraffins and aromatics. Gaseous fraction mainly consisted of unreacted hydrogen, carbon dioxide, and methane. Integrating catalytic processes of lignocellulosic biomass potentially paves a new way for the development of jet fuels over inexpensive catalysts under the mild condition.

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1. Introduction

Growing concerns about global climate change and rapid diminishing fossil-based petroleum reserves have spurred

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immense interest in the utilization of renewable resources for developing new generation (hydrocarbon) biofuels, with a particular focus on green aviation fuels [1,2]. The commonly commercial aviation fuels designed for use in aircraft are jet fuels, which are exclusively derived from petroleum refining [3]. In order to reduce dependence on fossil sources, the development of alternative fuels for aviation received more attention. Lignocellulosic biomass is a ubiquitous and sustainable source of carbon that displays promising potential in the manufacture of hydrocarbon transportation fuels and versatile chemicals [4,5]. Furthermore, renewable hydrocarbons based fuels will become drop-in replacements for petroleum-derived jet fuels if current technological innovations contribute to competitive production costs [6].

In fact, it is much tougher to develop renewable alternative fuels for utilization in aviation than automobile application owing to the stringent specifications of jet fuels [7]. To produce green jet fuels (typically C₈–C₁₅ hydrocarbons), Dumesic and co-workers have discovered a new route by aldol condensation of furfural and acetone to synthesize the long carbon chain intermediates of C₈–C₁₆ [8,9]. The hydrodeoxygenation process was stepwise introduced to obtain the branched alkanes with high thermal stability and energy density, which could be used as alternative aviation fuels [8]. Moreover, other studies emphasized on biomass-derived techniques to manufacture jet fuel range cyclic alkanes from the lignocellulose-derived platform compounds [10–13]. However, these aforementioned techniques necessitate expensive acetone or pinenes as the reactant and noble metal catalysts, resulting in infeasible commercialization in biorefineries, comparing with commercial formulations based on petroleum derived jet fuels. Other promising pathways such as hydrotreating of vegetable oils and Fischer Tropsch synthesis have been intensively investigated with the aim of producing bio-jet fuels [5]. Although these technologies show promising potential in the manufacture of jet fuel range alkanes, the synthetic feedstocks extracted from plant or animal oils are commonly upgraded under high hydrogen pressure in the presence of noble metals catalysts or sulfide-based catalysts [14].

Instead, fast pyrolysis has received special recognition because it is one of the viable process options to convert lignocellulosic biomass to liquid product [15,16]. The raw liquid product is unable for use as a transportation fuel because of detrimental properties, including a much lower energy density than petroleum fuels, poor thermal and chemical stabilities, and high viscosity [17,18]. To circumvent these problems, raw bio-oil has to be upgraded to eliminate total or partial oxygenates and unsaturated degree prior to its practical application as transportation fuel [19]. Among the upgrading approaches for jet fuels, hydrodeoxygenation (HDO) is deemed to be a promising and effective process [20]. This process normally removes the oxygen content under high-pressure hydrogen with a catalyst [21,22]. Most hydrodeoxygenation researches have concentrated on sulfide Co–Mo and Ni–Mo supported on γ -Al₂O₃ catalyst [19]. Such conventional sulfide-based catalyst, however, are not satisfactory for hydrotreating raw bio-oil since the introduction of sulfur-containing compounds (H₂S or thiophene) with the purpose of maintaining the catalysts at the active status, which gives rise to increasing contamination risk of liquid products [23]. Alumina (Al₂O₃) support with the catalysts is well known to be rapidly deactivated by coke deposition and potentially poisoned by water exist in bio-oils [16,24]. Noble-based catalysts can also be employed in the processes, which significantly raise cost for catalysts.

In addition, the HDO process conditions are rather severe (300–400 °C, 80–300 bar H₂ pressure) [17,18]. Since advanced jet fuels from HDO process are expected to be enlarged in a biorefinery scale, high capital costs caused by tolerance of severe condition and low selectivity of liquid products render these processes

uneconomical [25,26]. Accordingly, the production of jet fuels from renewable biomass resources calls for ideal technologies with efficient solid-phase catalysts to make the processes economically feasible under a mild reaction condition. It is more reasonable to use Ni-based catalysts for hydrotreating bio-oil because of their high activity of hydrogenation and low cost. Raney-type nickel is widely used as a versatile catalyst in such a hydrotreating process for reductive transformations of organic compounds [27]. Moreover, Raney-type nickel is utilized in other widespread fields for fine chemical manufacturing owing to its good catalytic performance [18]. In addition to catalyzing liquid products, costly hydrogen derived from aqueous-phase reforming could also be obtained over a tin-promoted Raney-nickel catalyst by Huber and his colleagues [28].

Typically the commercial and military jet fuels are comprised of paraffins, naphthenes and aromatics [2]. Nonetheless, two main compositions of cyclic paraffins and aromatics in commercial military jet fuels are hard to attain from well-developed hydrotreating of vegetables or Fischer–Tropsch synthesis [14]. On the other hand, it is widely known that oxygen content of bio-oil can be partially or even completely eliminated by zeolite cracking during fast pyrolysis of biomass [29]. Carlson et al. have reported that biomass-derived carbohydrates can be directly converted into aromatics with ZSM-5 as catalyst in a single catalytic pyrolysis step [30]. Lei and his colleagues have focused on the production of aromatic hydrocarbons through catalytic microwave-induced pyrolysis of Douglas fir sawdust [31]. Up to 92.60% selectivity of the liquid organics obtained was jet fuel range (C₈–C₁₅) aromatic hydrocarbons. In this sense, these aromatics in the bio-oils with low oxygen content can be hydrogenated into cyclic paraffins and olefins.

Based on aforementioned consideration, the directional conversion of lignocellulosic biomass into jet fuels production by integrated processes are proposed: (1) lignocellulosic biomass is firstly converted into jet fuel range (C₈–C₁₅) aromatics by catalytic microwave pyrolysis over well-promoted ZSM-5 and (2) the bio-oil derived from catalytic microwave pyrolysis is hydrotreated into desired C₈–C₁₅ hydrocarbons (including paraffins and minor aromatics) which satisfy basic requirements of conventional jet fuels by using Raney nickel as the catalyst. Since the coupling of two steps (catalytic microwave pyrolysis and downstream bio-oil hydrotreating) over regular catalysts has not been previously studied, this study demonstrates proof-of-principle of a novel consecutive two-step process to produce jet fuels from intact biomass.

2. Experimental section

2.1. Materials

The feedstock used was Douglas fir sawdust pellets (Bear Mountain Forest Products Inc., USA) which were approximately 7 mm in diameter and 15 mm in length with a moisture content of 8 wt%. Proximate and elemental analysis of raw Douglas fir sawdust pellets were described in Table S1. Parent ZSM-5(SiO₂/Al₂O₃ Mole Ratio: 50) was purchased from Zeolyst International, USA. Raney Ni 4200 (slurry in water) in an activated form was supplied by Sigma–Aldrich Corporation (St. Louis, MO, USA). Phenol (99%), *p*-cresol (99%), *o*-cresol (98%), guaiacol (98%), toluene (99.7%), *p*-xylene (99%), creosol (98%), ethylbenzene (99%), 1H-indene (97%), indane (95%), naphthalene (99.6%), tetralin (97%), 1-methylnaphthalene (96%), *n*-undecane (99%), and *n*-dodecane (99%) were used as purchased from Alfa Aesar (Ward Hill, MA, USA). Ethylcyclohexane (99%), 1,2,4-trimethylbenzene (98%), 1,2,4-trimethylcyclohexane (97%), propylcyclohexane (99%), and 1H-Indene,octahydro (99%) were supplied by Sigma–Aldrich Corporation (St. Louis, MO, USA).

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