



Full Length Article

Production of hydrocarbon fuels from heavy fraction of bio-oil through hydrodeoxygenative upgrading with Ru-based catalyst

Xinghua Zhang^{a,b,c,*}, Wenwu Tang^{a,b,c}, Qi Zhang^{a,b,c}, Yuping Li^{a,b,c}, Lungang Chen^{a,b,c}, Ying Xu^{a,b,c}, Chenguang Wang^{a,b,c}, Longlong Ma^{a,b,c,*}

^a Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, PR China

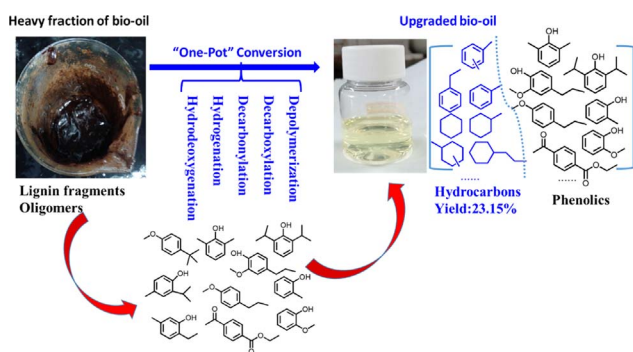
^b CAS Key Laboratory of Renewable Energy, Guangzhou 510640, PR China

^c Guangdong Provincial Key Laboratory of New and Renewable Energy Research and Development, Guangzhou 510640, PR China



GRAPHICAL ABSTRACT

An efficient catalytic process for utilization of bottom-layer oil was proposed with Ru/ α -Al₂O₃ catalyst and ethanol solvent. Depolymerization, decarboxylation, decarbonylation, hydrogenation and hydrodeoxygenation took place simultaneously in one-pot, obtaining hydrocarbon fuels with yield of 23.15%.



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ABSTRACT

Heavy fraction of bio-oil, the bottom-layer of biomass fast pyrolysis oil, is hard to be directly used due to its high molecular weight, complex components and deteriorate thermal stability. Here, a novel catalytic hydrotreating process for the heavy fraction of bio-oil, including depolymerization, decarboxylation, decarbonylation, hydrogenation and hydrodeoxygenation (HDO), is proposed with Ru/ α -Al₂O₃ catalyst and super/subcritical ethanol. Results demonstrated that heavy fraction of bio-oil was depolymerized into monomeric phenolic compounds, and then was converted to hydrocarbons by hydrodeoxygenation in one-pot. The average molecular weight (M_w) of upgraded oil decreased drastically from 8941 g/mol to 937 g/mol during the catalytic hydrotreating process, and the formation of coke is suppressed. Under the optimal conditions, the total yield of hydrocarbons, which were comprised of alkyl-substituted cyclohexane and alkyl-substituted benzene, could be up to 23.15%. These hydrocarbons have a high octane number, would be the desirable components for fungible liquid transportation fuel. Furthermore, Ru/ α -Al₂O₃ catalyst can be regenerated by calcination in the presence of O₂. These results indicated high quality fuels could be obtained from heavy fraction of bio-oil over suitable catalytic system.

* Corresponding authors at: Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, PR China.

E-mail addresses: zhangxh@ms.giec.ac.cn (X. Zhang), mall@ms.giec.ac.cn (L. Ma).

1. Introduction

Bio-oil, a renewable liquid fuel derived from fast pyrolysis of biomass, is highly regarded as substitutes of petroleum fuels. Since 1990s, several research organizations have successfully established large-scale fast pyrolysis plants [1,2]. However, bio-oils are totally different from petroleum fuels, which contain carboxylic acids, aldehydes, ketones, sugars, phenols and lignin-derived oligomers. It was reported that more than 300 compounds had been identified in bio-oil [3]. Generally, apart from water, bio-oils can be globally represented as GC-detectable compounds (around 40 wt%), non-volatile HPLC detectable compounds (around 15 wt%) and high molar mass non-detectable compounds (around 15 wt%) [4,5].

Bio-oil can be easily separated into two fractions (namely “upper-layer” and “bottom-layer”) by simply adding water in bio-oil due to the differences in water solubility [6,7]. Heavy fraction, the bottom-layer of biomass fast pyrolysis oil, includes glucan, phenols, macromolecular aromatics (usually present as lignin-derived oligomers), and pyrolytic lignin etc. Compared with the whole bio-oil, heavy fraction of bio-oil has lower content of water, acidity and oxygen, high carbon content and high heating values. However, the heavy fraction of bio-oil is unstable because of the polymerization with reactive monomers (such as unsaturated carbon-carbon bonds) and other oligomers under heated environment. In addition, heavy fractions tend to settle at the bottom of the storage tank, adhere to the pipe wall, and the block strainer [8]. These deteriorated properties make bio-oil utilization rather difficult.

Although a lot of work had been done to upgrade bio-oils [9–12], few works had been done to convert heavy fraction of bio-oil to chemicals and high-quality fuels. The possible reasons are the low yield of upgraded bio-oil and fast deactivation of the catalysts resulted from the re-polymerization of the heavy fraction of bio-oil. These drawbacks result in poor economic efficiency for the use of heavy fraction of bio-oil. For example, more than 40 wt% cokes were observed when pyrolytic lignin derived from bio-oil was catalytic pyrolysis over ZSM-5 and MCM-41 catalysts [13]. The hydrotreatment of high-boiling fraction of bio-oil (obtained by distillation) was also explored in supercritical methanol with bifunctional Pt-based catalysts [14]. However, high selectivity for coke was observed because re-polymerization of pyrolytic lignin and lignin-derived oligomers occurred during the hydrotreatment process [13–18]. Normally, higher acidity in the reaction system tended to promote the repolymerization of pyrolytic lignin, obtaining more solid residues [14,19]. In addition, the conventional solid acid, such as γ - Al_2O_3 and molecular sieve, is unstable under hydrothermal environment [20]. Structural collapse and phase change usually occurred under during the hydrotreatment process, resulting in a difficult to regenerate the catalyst. Therefore, one of the alternatives to this issue is to develop new catalytic materials for the successful utilization of the heavy fraction of bio-oil.

The solvent also has important influence on the hydrotreatment of bio-oil heavy fraction. Ethanol is an environmentally benign solvent and can be obtained directly from the renewable lignocelluloses [21,22]. Super/subcritical ethanol (243.1 °C, 6.3 MPa) is a super solvent, providing a single-phase environment for reactions. Moreover, super/subcritical ethanol usually serves as a hydrogen donor solvent, providing a high concentration hydrogen-atmosphere in the process of hydrogenation. In our previous work, super/subcritical ethanol had been used for the upgrading of bio-oil. The results showed that the formation of coke was successfully suppressed during the upgrading process [23].

In this study, super/subcritical ethanol and Ru/ α - Al_2O_3 catalyst were employed to convert heavy fraction of bio-oil. The focus is to produce hydrocarbon fuels from pyrolytic lignin via catalytic depolymerization and hydrodeoxygenation (HDO) in one pot method. Ru was selected due to its high hydrogenation and hydrocracking capabilities. It was reported that Ru catalyst exhibited excellent catalytic activity for the hydrocracking of heavy fraction of bio-oil. Most of the pyrolytic

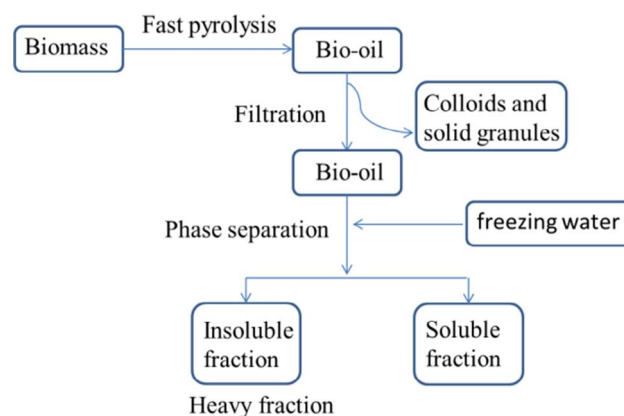


Fig. 1. Procedure schematic for preparation of the heavy fraction of bio-oil.

lignin was depolymerized into liquid fuel consisting of stable organic compounds with a heating value as high as 34.93 MJ/kg, while the amount of tar or coke decreased significantly [24]. α - Al_2O_3 was chosen as the catalyst support because its excellent hydrothermal stability [25]. Moreover, α - Al_2O_3 is mesoporous material which could reduce the pore blocking caused by the macromolecular of the heavy fraction of bio-oil. For comparison purposes, the catalysts Ru/ γ - Al_2O_3 and Ru/C were also employed in this work.

2. Experimental section

2.1. Materials

The typical schematic of the experimental procedure for the preparation of heavy fraction was given in Fig. 1. The bio-oil used in this study was obtained through the fast pyrolysis of rice husks according to the literature [26]. Bio-oil was filtered through the filter paper with mesh size of 45 μm in order to remove colloids and solid granules. Heavy fraction of the bio-oil was prepared through dropwise addition of freezing water into bio-oil with vigorous stirring in ice-water bath (3–5 °C). Detailed procedure had been reported in literature [27]. The main physiochemical properties for the obtained heavy fraction of bio-oil were exhibited in Table 1.

2.2. Catalyst preparation and characterization

The catalysts Ru/ α - Al_2O_3 and Ru/ γ - Al_2O_3 with 5 wt% Ru loadings were prepared by an incipient-wetness impregnation method using $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ as Ru precursor. Support materials α - Al_2O_3 , γ - Al_2O_3 and the catalyst Ru/C were commercialized products and purchased in the market. All catalysts were reduced at 400 °C for 4 h in a flow of reducing gas (5% H_2 + 95% N_2) before use.

The BET surface area, average pore diameter and pore volume of the catalysts were determined by the N_2 adsorption–desorption isotherms

Table 1
Physiochemical properties of heavy fraction of bio-oil.

Property	Heavy fraction of bio-oil
Density (g/mL)	1.19 ± 0.02
Water content (wt.%)	15.2 ± 0.32
High heating value (MJ/kg)	28.3 ± 1.2 (dry basis)
Ash (wt.%)	0.19 ± 0.04
<i>Element composition (wt.%)</i>	
C	61.89 ± 0.41
H	6.12 ± 0.28
N	0.80 ± 0.06
S	0.02 ± 0.01
O (by difference)	31.17 ± 0.33

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