



Sustainable production of aromatics from bio-oils through combined catalytic upgrading with *in situ* generated hydrogen



Fengbo Li^{a,*}, Yin Yuan^{b,a}, Zhijun Huang^a, Bingfeng Chen^a, Fosong Wang^{a,**}

^a Beijing National Laboratory of Molecular Science, Key Laboratory of Green Printing, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P.R. China

^b University of Chinese Academy of Sciences, Beijing, 100049, P. R. China

ARTICLE INFO

Article history:

Received 5 August 2014

Received in revised form 16 October 2014

Accepted 20 October 2014

Available online 28 October 2014

Keywords:

Sustainable chemistry

Renewables

Catalytic upgrading

Bio-oils

Aromatics.

ABSTRACT

Pyrolysis liquids or bio-oils from rice husks are selectively converted into aromatics through a combined catalytic process, which includes two sequent steps: reforming and upgrading. Hydrogen from methanol and low-weight molecules in bio-oil is *in situ* generated in the reforming reactor. Methanol (16 wt% of total bio-oils) is added not only as the hydrogen donor, but also as polar solvent for homogenizing bio-oil and reducing its viscosity. Structured nickel nets are used as both the reforming catalyst and heating grid for gasifying high-boiling-point components of bio-oil. In the upgrading reactor, the combination of Co–Ru–Zr/silica with Pt-ZSM-5 gives the highest yield of aromatics (53.7%) and the lowest coke deposition (7.1%). Hydrogen for deoxygenation is generated from reforming of added methanol and low-weight molecules in bio-oil. Coke formation during fixed-bed upgrading can be significantly suppressed through the combined catalytic process.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Pyrolysis liquids or bio-oils are carbon-rich liquids produced from fast pyrolysis of lignocellulosic biomass [1]. There are three thermal processes for converting biomass into more useful energy forms—pyrolysis, gasification and combustion [2]. Fast pyrolysis is the only process to give high yield of liquids (up to 75 wt%), which are considered as inexpensive renewable feedstocks for liquid fuel and chemicals [3]. However, there are several fundamental challenges of converting bio-oil into transport fuels and value-added chemicals. Firstly, bio-oils are low-quality fuels with high oxygen content of up to 60 wt% and immiscible with conventional hydrocarbon fuels. They cannot be directly used in gasoline and diesel engines. Secondly, bio-oils are acidic and unstable mixtures that have a water content of around 30 wt%. Polymerization and phase separation take place during storage. Thirdly, the complexity of biomass feedstocks and conversion processes results in lack of detailed models of describing physicochemical properties of bio-oil [4]. Despite these drawbacks, it is feasible to upgrade bio-oil to hydrocarbon fuels and chemicals through deoxygenation and zeolite cracking over well-designed catalysts [5–7].

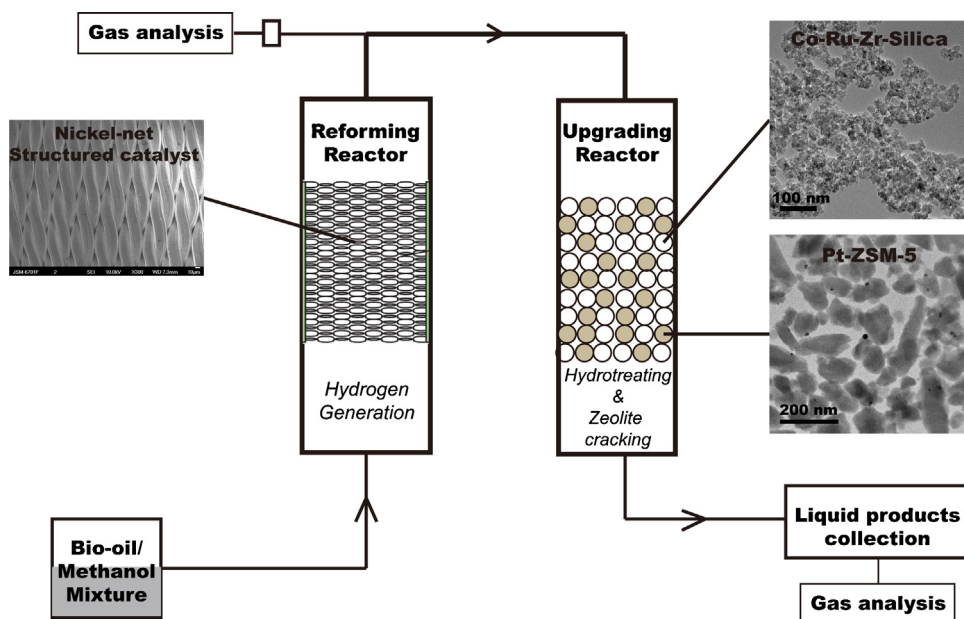
There are three main methods for upgrading bio-oils—physical treatment, catalytic upgrading and chemical conversion [8]. Physical treatments include filtration to remove char microparticles, solvent addition to reduce the viscosity and emulsion to improve the miscibility with hydrocarbon fuels [9,10]. Catalytic upgrading of bio-oils is the most efficient way. Catalytic cracking and hydrotreating can deoxygenate bio-oils and give hydrocarbon mixtures with properties close to conventional transport fuels [11–17]. Oxygen of bio-oil can be reduced by zeolite cracking [18–21]. Catalytic reforming of bio-oils in vapor or liquid phases produces clean gaseous energy forms—hydrogen and syngas [22]. Chemical conversions, such as esterification and reactive distillation, are less common methods for upgrading bio-oils because of their high cost and relatively low efficiency [23–25]. The rapidly emerging research in improving bio-oil properties may increase its potential for bio-fuel and chemical production. However, the upgrading efficiency is relatively low and most of the research is performed over model compounds and catalysts only for fundamental purposes. Actually, more sophisticated catalytic systems are required to be developed from a practical angle to prove the feasibility and reliability of bio-oil upgrading.

Integrated catalytic upgrading processes can be divided into two types: catalytic pyrolysis to improve the quality of bio-oil and integrating different catalytic models in bio-oil upgrading process. Regalbuto [26] recently gave a perspective about several routes developed to directly convert biomass into hydrocarbon.

* Corresponding author. Tel.: +86 10 62634920; fax: +86 10 62559373.

** Corresponding author.

E-mail addresses: lifb@iccas.ac.cn (F. Li), fswang@iccas.ac.cn (F. Wang).



Scheme 1. Schematic illustration of the proposed combined catalytic upgrading of rice husks' pyrolysis oils.

However, there are several inherent problems in the catalytic pyrolysis—coking, catalyst regeneration and the reactor design for efficient mass and heat transfer. Vispute et al. [27] recently reported a breakthrough in converting bio-oils into aromatics and olefins with the carbon yield above 60% using an integrated catalytic approach that combines hydroprocessing with zeolite catalysis. Bio-oils are first incompletely deoxygenated with hydrogen at a moderate temperature and further processed over a zeolite catalyst in a fluidized bed reactor to produce aromatics and olefins. As pointed out by the authors, the integrated catalytic approach avoids the use of the large amount of expensive hydrogen and heavy coke deposition over the catalysts.

In this work, a well-designed integrated catalytic process is established for improving the quality of bio-oils. Bio-oils used in our research are manufactured from rice husks in a 100 ton/day pilot plant of YMB New Energy Co. (Jilin, China) (Fig. S1). The process includes two sequent steps in separate reactors: a reforming reactor and an upgrading reactor (as shown in Scheme 1). The function of reforming reactor is *in situ* generation of hydrogen from added hydrogen donors and low-weight molecules in bio-oil and no exterior hydrogen is introduced into the system. Methanol is not only the added hydrogen donor, but also polar solvent for homogenizing bio-oil and reducing its viscosity. The upgrading step combines hydrotreating catalysts and zeolite catalysts in one single reactor. Coke formation during fixed-bed upgrading can be significantly suppressed through the combined catalytic process. Two types of catalysts are packed in the reactor through a physical-mixture model. The mixture from the reforming reactor is directly led into the upgrading reactor to produce aromatic-enriched liquids.

Bio-oil of rice husk has a high oxygen content of approximately 50 wt%, which gives bio-oil a low energy density. Oxygen-containing compounds such as organic acids and other active molecules contribute to corrosiveness, phase separation and polymerization of bio-oil. The economic removal of oxygen from bio-oil is crucial to its successful application as an alternative to petroleum-derived hydrocarbon feedstocks and fuels. Oxygen can be rejected as water through hydrotreating with pure hydrogen or as carbon dioxide through zeolite cracking. The high oxygen content of bio-oil requires a large amount of hydrogen to

achieve complete hydrodeoxygenation. Active molecules in bio-oil are prone to thermal polymerization and heavy coke deposition during zeolite cracking causes sharp degradation of the catalyst. Hydrogenation of these active compounds to alcohols can markedly suppress coke formation over zeolite catalysts [27].

Hydrogen is a tight and expensive resource. In the present industrial system, it is produced through costly and energy-intensive processes. The most commonly used route is SMR (steam-methane-reforming)–WGS (water-gas-shift)–PSA (pressure-swing-adsorption) [28]. A huge amount of CO₂ is released with hydrogen production from fossil feedstocks and fuels for generation of energy to drive the process. In China, coal is the main feedstock for steam reforming, which outlet sulfur and nitrogen oxide pollutants to the atmosphere. When considering environmental and economic cost of hydrogen production, sustainability of hydrogen-intensive conversion of bio-oil to hydrocarbons is doubtful. In this work, hydrogen for upgrading is generated from added methanol and light-weight organics of bio-oil. Bio-oils have been widely considered as renewable feedstocks for hydrogen production through catalytic reforming [7,22,29,30]. Water-soluble, small molecules are relatively easy to be reformed and partially supply hydrogen for further upgrading. Methanol is used as added hydrogen donor, which is safer and cheaper than pure hydrogen. Another advantage is that the addition of methanol homogenizes bio-oil and reduces its viscosity. This makes the injection proceed smoothly. Nickel catalysts have been extensively investigated as reforming catalysts for methanol and oxygenates reforming [31–34].

2. Experimental

2.1. Feedstock: bio-oil properties

Bio-oils (YMB-BO) used in our research were produced from rice husks in a 100 ton/day pilot plant of YMB New Energy Co. (Jilin, China) (Fig. S1). Fine char particles in the crude bio-oil were removed through a high-speed centrifuge. Basic properties of bio-oil were listed in Table 1 and its detailed chemical compositions were provided in Table S1. A well-calculated amount of methanol (16 wt%) was added into bio-oil to homogenize the mixture and

Download English Version:

<https://daneshyari.com/en/article/45586>

Download Persian Version:

<https://daneshyari.com/article/45586>

[Daneshyari.com](https://daneshyari.com)