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## Production of gasoline fraction from bio-oil under atmospheric conditions by an integrated catalytic transformation process

Zhaoxia Zhang<sup>a, b</sup>, Peiyan Bi<sup>a</sup>, Peiwen Jiang<sup>a</sup>, Minghui Fan<sup>a</sup>, Shumei Deng<sup>a</sup>, Qi Zhai<sup>a</sup>, Quanxin Li<sup>a, \*</sup>

<sup>a</sup> Anhui Key Laboratory of Biomass Clean Energy, Department of Chemical Physics, University of Science & Technology of China, Hefei 230026, PR China

<sup>b</sup> National Engineering Laboratory for Green Chemical Productions of Alcohols-Ethers-Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, PR China

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### ABSTRACT

This work aimed to develop an integrated process for production of gasoline fraction bio-fuels from bio-oil under atmospheric conditions. This novel transformation process included the catalytic cracking of bio-oil to light olefins and the subsequent synthesis of liquid hydrocarbon bio-fuels from light olefins with two reactors in series. The yield of bio-fuel was up to 193.8 g/(kg bio-oil) along with a very low oxygen content, high RONs (research octane numbers), high LHVs (lower heating values) and low benzene content under the optimizing reaction conditions. Coke deposition seems to be the main cause of catalyst deactivation in view of the fact that the deactivated catalysts was almost recovered by on-line treating the used catalyst with oxygen. The integrated transformation potentially provides a useful way for the development of gasoline range hydrocarbon fuels using renewable lignocellulose biomass.

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### 1. Introduction

Energy and environmental issues caused by the strong dependence on the fossil fuels have motivated the world-wide attention on the production of engine fuels using alternative sources [1–3]. Biomass, as an abundant and renewable resource, is a carbon-containing feedstock that can be utilized for the synthesis of engine fuels [1–4]. Bio-oil, a black oxygenated organic liquid derived from fast pyrolysis of lignocellulosic biomass, has been considered to be a promising platform chemical for producing renewable bio-fuels or chemicals [5–10]. However, the raw bio-oil has some unfavorable properties such as high viscosity, high acidity, low stability and low heating value due to its high oxygen content, which impedes its direct utilization as engine fuels [10,11]. Thus, it is needed to upgrade the oxygenated compounds in bio-oil to liquid hydrocarbon bio-fuels to meet the requirements of the conventional transportation fuels. So far, several processes such as bio-oil HDO (hydrodeoxygenation), catalytic cracking of bio-oil, ketonization and steam reforming of bio-oil followed by Fischer–Tropsch synthesis have been developed [10–22].

Among these technologies, the catalytic upgrading of bio-oil by HDO and catalytic cracking has received much attention [10–20]. HDO was regarded as an efficient method to remove oxygen from bio-oil, which are typically conducted under moderate temperatures (300–400 °C) and high hydrogen pressures (80–300 bars) [10–16]. Hydrodeoxygenation of bio-oil could be a hydrogenolysis process that removes oxygen in bio-oil in the presence of hydrogen and a HDO catalyst. Typical HDO catalysts are noble metals supported catalysts, transition metal supported catalysts or metal sulfides catalysts [12,13]. The most prominent advantage for the upgrading of bio-oil by HDO is the high deoxygenation capacity along with a high yield of bio-fuels [10–16]. However, the disadvantage of HDO is the requirement of the presence of high hydrogen pressure and plenty of hydrogen consumption, leading to the increase in capital and production costs. Catalyst deactivation caused by the carbon deposition on catalysts also stood as a problem for the upgrading of bio-oil by HDO [10–13].

Alternatively, the catalytic cracking technology can be used for producing hydrocarbon bio-fuels or chemicals by the deoxygenation of bio-oil *via* decarbonylation, decarboxylation and dehydration [10–13,23–28]. The catalytic cracking of bio-oil seems to be a cheaper route for converting the oxygenated compounds of bio-oil to hydrocarbons, since such processes are typically operated using cheaper catalysts like zeolites under the atmospheric

\* Corresponding author. Tel.: +86 551 63601118; fax: +86 551 63606689.  
E-mail address: liqx@ustc.edu.cn (Q. Li).

pressure, along with free of external hydrogen consumption. In addition, the co-feeding of bio-oil (or biomass) with conventional petroleum streams using a FCC refinery infrastructure has also received attention [18–20]. Nevertheless, the direct use of lignocellulose-derived bio-oils in the FCC process still remained a challenge because of their minor miscibility with hydrocarbons, corrosiveness and high tendency to form coke. As a result, the pretreatment of bio-oil seems to be needed before the co-processing.

Recently, production of light olefins (mainly  $C_2-C_4$ ) from lignocellulosic biomass or bio-oil has attracted great interest [5–8,23–28]. For example, Vispute et al. [6] presented an integrated process involving hydro-processing of bio-oil over supported noble metal catalysts and subsequently catalytic conversion of the refined bio-oil to the renewable chemical commodity including olefins over a ZSM-5 catalyst. Gayubo et al. [26] reported a two-step (thermo-catalytic) process for production of hydrocarbons from crude bio-oil over the Ni/HZSM-5 catalysts. Their results suggested that the co-feeding of bio-oil with methanol was favorable for increasing the selectivity of light olefins and reducing the coke deposition on the catalyst. Zhang et al. [5] investigated the effects of H/C effective ratios of biomass-derived feedstocks on light olefin production. They proved that the feeds with higher H/C ratios favored to increase the yield of light olefins and reduce the coke. Our recent study also shows that light olefins can be selectively produced from bio-oil or biomass over the La-modified zeolites [8,28]. Furthermore, catalytic polymerization of light olefins has been industrially applied in petroleum refineries for producing fuels, and the synthesis fuels using olefins oligomerization could be suitable for utilization as engine fuels due to free of sulfur and other harmful impurities [29–35].

In this work, an integrated catalytic transformation for production of the gasoline range bio-fuels using the bio-oil was demonstrated, which included the catalytic cracking of bio-oil to light olefins followed by the synthesis of liquid hydrocarbon bio-fuels via the oligomerization of light olefins. So far as we know, there is no such report regarding the production of gasoline range bio-fuels from bio-oil with very low contents of oxygen under atmospheric condition. This integrated catalytic transformation potentially provides a new and useful route for the production of green engine fuels from lignocellulosic biomass-derived bio-oil.

## 2. Material and methods

### 2.1. Materials and chemicals

The crude bio-oil was produced by fast pyrolysis of straw stalk in a circulating fluidized bed reactor with a capacity of 120 kg/h oil in our Lab [8]. In present work, the light fraction of the crude bio-oil was used, which was conducted by the distillation of the crude bio-oil up to 373 K at atmospheric pressure. The chemical compositions, elemental compositions and water content of the light bio-oil used were shown in Table 1. The use of the light bio-oil with a high water content can reduce the coke deposition and improve the yield of light olefins during the catalytic cracking of bio-oil, as proved by our previous work [8,36]. All analytical reagents used were purchased from Sinopharm Chemical Reagent Company Limited (Shanghai, China).

### 2.2. Catalyst preparation and characterization

In this work, two zeolite catalysts of La/HZSM-5 and LTG-0, modified with rare earth oxide or transition metal, were selected and used for the catalytic cracking of bio-oil and the oligomerization of light olefins, respectively. ZSM-5 zeolite (Na form, Si/Al

**Table 1**  
Properties of the bio-oil used.<sup>a</sup>

Composition analysis	wt%	Ultimate analysis	wt%
Acids	26.4 ± 3.4	C	42.3 ± 4.6
Aldehydes	14.8 ± 2.3	H	7.5 ± 0.8
Ketones	19.2 ± 3.8	O <sup>b</sup>	50.0 ± 3.9
Alcohols	4.7 ± 1.2	N	0.14 ± 0.1
Phenols	2.7 ± 1.0	S	<0.1
Furans	9.1 ± 1.5		
Nonidentified <sup>b</sup>	23.1		

<sup>a</sup> The crude bio-oil was produced by fast pyrolysis of straw stalk. The light fraction of the crude bio-oil (named as bio-oil) was used in this work, which was conducted by the distillation of the crude bio-oil at 373 K and 1 atm. The water content in the bio-oil used was 72.7 ± 4.9 wt%.

<sup>b</sup> By difference.

ratio = 25) was supplied from Nankai University catalyst Co., Ltd. (Tianjin, China). The proton-type HZSM-5 was obtained via an  $NH_4^+$  exchange procedure followed by calcinating the catalyst at 823 K for 4 h. For the preparation of 6 wt% La/HZSM-5 catalyst, 25 g of HZSM-5 zeolite was impregnated in 0.115 M lanthanum nitrate solution at 298 K overnight, followed by rotary-evaporation at 333 K, drying at 353 K for 6 h and calcinating at 823 K for 5 h. The LTG-0 catalyst was kindly provided from Beijing Huiersanji Green Chem. Co., Ltd. in China. The metallic element contents in the catalysts were determined by ICP/AES (inductively coupled plasma and atomic emission spectroscopy, Atomscan Advantage, Thermo Jarrell Ash Corporation, USA). The catalysts were characterized by XRD (X-ray diffraction),  $N_2$  adsorption/desorption, ammonia temperature-programmed desorption ( $NH_3$ -TPD) and TPO (temperature programmed oxidation) analyses, as the same procedures described in our previous papers [8,36]. Briefly, the XRD patterns of the catalysts were obtained on an X'pert Pro Philips diffractometer (Philips, Netherlands) using a  $Cu K\alpha$  radiation ( $\lambda = 0.15418$  nm). The  $N_2$  adsorption/desorption isotherms of the catalysts were performed at 77 K using the Micromeritics ASAP 2020 V3.00 analyzer. The acidity of the catalysts was measured by  $NH_3$ -TPD from 373 K to 1073 K with a heating rate of 10 K/min. The TPO analyses for determining the carbon content deposited on the used catalysts were conducted in a Q5000IR thermogravimetric analyzer (USA). The samples were heated from room temperature to 1073 K with a heating rate of 10 K/min under the air.

Table 2 shows main physical and chemical properties of the La/HZSM-5 and LTG-0 catalysts. As proved by XRD (Fig. 1), the two catalysts all belong to the type of ZSM-5 zeolite [8]. A small amount of transition metals such as Ni were detected in the LTG-0 catalyst by the ICP/AES analyses. Based on the  $NH_3$ -TPD analyses (Fig. 2), the acidities of the fresh La/HZSM-5 and LTG-0 catalysts were 0.33 mmol  $NH_3/g_{catalyst}$  and 0.38 mmol  $NH_3/g_{catalyst}$ , respectively. The  $NH_3$ -TPD patterns was fitted into two Gaussian components with the centers near 533 K and 723 K, corresponding to the desorption of  $NH_3$  from the weak acid sites and the strong acid sites respectively [8]. For the La/HZSM-5 and LTG-0 catalysts, the ratios of strong acid sites to the weak acid sites were 0.81 and 0.93 respectively. In addition, adding La into the HZSM-5 zeolite can improve the yield of light olefins during the catalytic cracking of bio-oil through adjusting the acidity of the zeolite [8]. The LTG-0 catalyst is a metal oxides-modified ZSM-5 zeolite catalyst, and adding small amount of transition metal oxides into the zeolite can improve the catalytic oligomerization of olefins [37,38].

### 2.3. Experimental setup and product analysis

As shown in Fig. 3, an integrated catalytic transformation process for production of gasoline fraction bio-fuels from the bio-oil

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