

## Optimizing catalytic pyrolysis of rubber seed oil for light aromatics and anti-deactivation of ZSM-5



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### ABSTRACT

The ex-situ catalytic pyrolysis of rubber seed oil (RSO) with ZSM-5 catalyst on fixed bed reactor was conducted. Catalysis temperature, pyrolysis temperature, nitrogen flow rate, and weight hourly space velocity (WHSV) were investigated to optimize the conditions for BTX (benzene, toluene, and xylenes). The optimal bio-oil which contained 99.56% total aromatics and 78.68% BTX, was obtained when nitrogen flow rate and WHSV were respectively 150 mL min<sup>-1</sup> and 5.48 at catalysis temperature 550 °C and pyrolysis temperature 550 °C. In order to prolong the lifetime of the catalyst, an alkali treatment resulted in enlarged pores of ZSM-5 and inhibited deactivation with slight reduction of BTX in products.

### 1. Introduction

With the continuous growth of the global population and drastic development of industrialization, fossil fuels hardly satisfy our demand. What is more, excessive depletion of fossil fuels induced the negative impact on environment, such as atmospheric pollution and global warming [1]. The environmental issues and contradiction between increasing demand with limited fossil fuel promoted the development of renewable fuels [2–4]. Bio-oil obtained from biomass pyrolysis was considered as a potential candidate for power production because of its high energy density compared to raw biomass, convenient transportation, convenient use and de-coupling of conversion and utilization processes [5,6]. Bio-oil has been successfully carried out in combustion tests; however, when it was applied in engines, several problems arose, for instance, char blocking in filters and atomizers, high viscosity, phase separation and acid corrosive [7]. Therefore, the Bio-oil is badly in need of further upgrading.

Biomass catalytic pyrolysis upgrades Bio-oil by deoxygenation and aromatization in the presence of zeolite catalysts. Catalytic pyrolysis could be conducted by two methods: in-situ and ex-situ. In-situ process occurs in single reactor after biomass feedstock mixed with catalyst, while ex-situ process provides two reactors respectively carrying out pyrolysis reaction of biomass and catalysis reaction of pyrolysis vapors [8–10]. Compared with in-situ process, in the ex-situ process vapors

contacts more significantly with catalysts; moreover, ex-situ has flexibility to control the pyrolysis and catalysis conditions [11]. Gamlie et al. [8] compared in-situ and ex-situ catalytic pyrolysis using micro-system, and concluded that ex-situ process showed higher selectivity to permanent gas and yielded aromatics in Bio-oil. In the research of Luo et al., in-situ and ex-situ catalytic pyrolysis of beetle-killed trees were investigated, the results noted that two processes yielded similar contents of aromatic volatiles and solid residues. However, the in-situ process obtained more xylenes and aromatics with nine carbons, while the ex-situ upgrading exhibited higher selectivity to benzene and toluene [10].

Pyrolysis of vegetable oil, including edible soybean oil [12–15], palm oil [16], and buriti oil [17] has drawn lots of attention of researchers. RSO is non-edible oil, which is extracted from waste rubber seeds with low cost, has a bright prospect for Bio-fuels [18,19].

Aromatic hydrocarbon with high octane is a kind of significant chemical. It could be used as additive to raise the octane value of gasoline [20]. Especially, monocyclic aromatics mainly including BTX, are raw chemicals for organic chemicals, plastic resins, synthetic fibers, pesticides, dyes and solvents [21]. The primary source of BTX is refinement of petroleum; however, the green and renewable way is catalytic pyrolysis of biomass [22–24]. The relative amount of aromatics in Bio-oil strongly relies on the condition of catalytic pyrolysis, for instance, pyrolysis temperature, heating rate, weight hourly space

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velocity (WHSV) and catalyst [8,25,26]. Zeolite catalyst plays a distinct role in catalytic pyrolysis of biomass [27]. Among zeolite, ZSM-5 was considered as the optimal one for the production of aromatic hydrocarbon, especially monocyclic aromatics [28–30]. Brønsted acidic sites and crystalline pore structure are the major factors for aromatics production [31]. In order to resolve coke deposition which leads to catalyst deactivation, adjusting pore structure and active sites is necessary [27]. Alkaline treatment is an effective method to weaken coke deposition [32,33]. It could enlarge the pore size by desilication, and the decrease of Si/Al ratio would change the Brønsted acidic sites. Li et al. [34] studied the influence of desilication of ZSM-5 using NaOH solution during catalytic fast pyrolysis of lignocellulosic biomass, and proved that proper desilication promoted the conversion of lignocellulose to valuable aromatics and restrained the formation of undesired coke.

The object of this work was to determine the optimal condition for production of light aromatics in Bio-oil, mainly BTX, during ex-situ catalytic pyrolysis of RSO. The effect of catalysis temperature, pyrolysis temperature, nitrogen flow rate, and WHSV on aromatics were systematically studied. For enhancing deactivation of ZSM-5, the alkali treatment was researched.

## 2. Experimental

### 2.1. Materials

RSO was purchased from Xishuangbanna Huakun Biotechnology Co., LTD, China. The distribution of fatty acids was the following: linoleic acid 56.95%, linolenic acid 40.28%, oleic acid 2.77%. ZSM-5 with white rod shape was obtained commercially from the Catalyst Plant of Nankai University, China. Before the experiment was conducted, the ZSM-5 was first ground manually and sieved into 0.420–0.840 mm size range. High purity nitrogen was provided by Kunming Messer Gas Products Co., LTD, China.

To prepare the alkali treated ZSM-5, the method adopted derived from related research [34]. ZSM-5 firstly was mixed with NaOH solution ( $0.1 \text{ mol L}^{-1}$ ,  $0.2 \text{ mol L}^{-1}$ ,  $0.3 \text{ mol L}^{-1}$ ,  $0.4 \text{ mol L}^{-1}$  and  $0.5 \text{ mol L}^{-1}$ ) in  $70^\circ\text{C}$  for 2 h, with mixture ratio 1 g ZSM-5/10 mL solution. After that the catalyst was washed to neutral and dried at  $110^\circ\text{C}$  for 12 h. Then the catalyst was ion-exchanged with  $\text{NH}_3\text{NO}_3$  for 3 times at  $80^\circ\text{C}$ . Finally, catalyst was dried at  $110^\circ\text{C}$  for 12 h and calcinated at  $550^\circ\text{C}$  for 10 h.

### 2.2. Characterizations of catalysts

The X-Ray powder diffraction (XRD) was used for characterizing catalysts. The spectra of X-ray diffractometer (TTR III) were scanned at a rate of  $10.0^\circ \text{ min}^{-1}$  in the range  $2\theta = 5.0^\circ\text{--}45.0^\circ$ . The textural parameters of catalysts were analyzed by  $\text{N}_2$  absorption/desorption isotherm with TriStar II 3020 at  $-195.85^\circ\text{C}$ . Before measurement catalyst was degassed under a vacuum at  $300^\circ\text{C}$  for 10 h. The BET surface area was calculated from the linear portion of BET plot. The micropore volume and external surface areas were calculated by t-plot method while the pore size distribution was determined by the BJH model.

### 2.3. Pyrolysis and catalytic pyrolysis of RSO

The pyrolysis and catalytic pyrolysis of RSO were conducted in a fixed-bed reactor, which was designed specially. Experimental apparatus mainly consisted of pyrolysis reaction part, catalysis reaction part, and condensation part, as shown in Fig. 1. The furnace in fixed-bed reactor was heated electrically and the temperature was measured inside by a thermocouple. The pyrolysis reaction and catalytic pyrolysis reaction took place in the reactor, a stainless steel pipe with 1 cm diameter and 55 cm length, which was inserted through pyrolysis furnace and catalysis furnace. High-purity nitrogen and RSO were introduced from the top of the reactor while the bottom was connected to

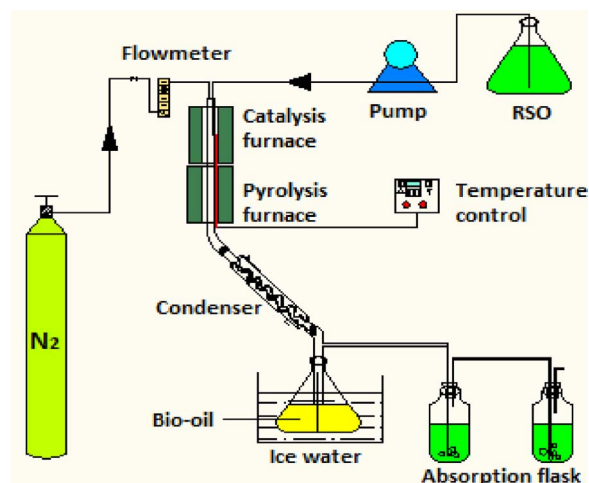


Fig. 1. Apparatus of pyrolysis and catalytic pyrolysis of RSO.

condenser. Firstly, dry glass fiber was inserted into reactor for loading catalysts, and 4 g catalyst was introduced. Then the pyrolysis furnace and catalysis furnace were heated to a setting temperature. The high-purity nitrogen was used as carrier gas to purge oxygen in reactor. As soon as wriggle pump drew liquid RSO into reactor at pyrolysis part, the experiment of catalytic pyrolysis began and lasted 15 min. Finally, the Bio-oil was obtained in collecting bottle.

For optimizing the Bio-oil, the catalysis temperature, pyrolysis temperature, nitrogen flow rate, WHSV, and alkali treatment of ZSM-5 were studied respectively. The best condition depended on the contents of total aromatics and BTX in Bio-oil. In addition, the deactivation and regeneration of catalyst were researched. After catalysts were used continuously for 3 times, each one was regenerated at  $550^\circ\text{C}$  for 8 h in the presence of air. After regeneration, the catalysts were applied in catalytic pyrolysis of RSO.

### 2.4. The compounds of bio-oil

Compounds of the Bio-oil were identified by Clarus 600 GC–MS (PerkinElmer). The  $1 \mu\text{L}$  of Bio-oil dissolved in methanol was injected into the instrument. The capillary chromatographic column was a HP-5MS ( $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$ ); the temperature of the injector was  $260^\circ\text{C}$ , and the split ratio of the carrier gas was 1:10. The carrying gas used was high-purity helium. The oven temperature program proceeded as follows: first, the temperature was held at  $50^\circ\text{C}$  for 1 min; then, the temperature was increased from  $50^\circ\text{C}$  to  $260^\circ\text{C}$  at  $5^\circ\text{C min}^{-1}$ , and held at  $260^\circ\text{C}$  for 3 min. For the MS condition, the ionization parameters were as follows: ionization methods, EI; ionization energy, 70 eV; scan per second over range electron ( $m/z$ ), 30–500 amu; ion source temperature,  $230^\circ\text{C}$ . The relative contents of compounds in Bio-oil were calculated based on the peak areas from GC.

## 3. Results

In the presence of a catalyst, the compositions in Bio-oil mainly are hydrocarbons. For comparison of catalytic performance, the compositions of Bio-oil were divided into three groups: BTX (benzene, toluene, xylenes), alkyl benzenes (ethyl benzene, *m*-ethyltoluene), and polycyclic aromatics (naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, 2,6-dimethylnaphthalene). A blank experiment was also conducted, and the result showed that in the absence of a catalyst, the RSO was mainly converted into liquid product containing 9-Hexadecenoic acid (41.09%), fatty acid methyl ester (17.34), light aromatics (15.3%) and aliphatic hydrocarbons (9.68%).

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