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Microwave-assisted catalytic pyrolysis of Chinese tallow kernel oil for aromatic production in a downdraft reactor

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ABSTRACT

Microwave-assisted pyrolysis of Chinese tallow kernel oil with silicon carbide (SiC)-foamed ceramic catalyst in a downdraft reactor was carried out in this study. In this paper, we studied the influence of catalytic temperature, catalyst-to-feed ratio, and feeding rate on product distribution and chemical components of bio-oil. The aromatic proportion reached a maximum value of 89.707 wt% when catalytic conditions were set as follows: 300 °C catalytic temperature, 1:2 catalyst/feedstock ratio, and 1 ml/min feed rate. Fourier-transform infrared spectra were consistent with the results obtained from gas chromatography–mass spectrometry. Their outstanding thermal stability allowed SiC-foamed ceramics to perform well in five cycles of repeated experiments under optimal conditions. These results indicate that the SiC-foamed ceramics are promising catalysts for aromatic production in microwave-assisted pyrolysis of Chinese tallow kernel oil in a downdraft reactor. This pathway can also improve the application prospects of microwave pyrolysis technology.

1. Introduction

Owing to the increasing consciousness of environment protection and the decreasing petroleum reserves, seeking for renewable and environment-friendly resources have gained attention [1]. Chinese tallow kernel oil (*Triadica sebifera* L.) is recognized as a promising feedstock for obtaining renewable fuels or chemicals due to its high yield and low cost [2,3].

Pyrolysis refers to the thermal decomposition of materials using heat and chemical catalysts, and it has been confirmed as an effective method for gaining energy resources. In the absence of oxygen and at high temperatures of 450 °C to 600 °C, biomass is converted into char residue, bio-oil, and gas [4]. As a volumetric heating technology, microwave heating has been widely applied in bio-oil production via pyrolysis [5]. In contrast to conventional pyrolysis, microwave-assisted pyrolysis can reduce the processing cost, save operation time, and increase oil yields [6,7]. In terms of product distribution, microwave-assisted pyrolysis produces higher gas and lower solid fraction yields [8,9]. In conclusion, microwave-assisted pyrolysis serves as a suitable technology for converting biomass into a useful energy source.

Catalyst, another way of improving the quantities of product oil, attracts wide attention recently. The commonly used catalysts include the well-known HZSM-5 [10–12], the economical carbonaceous materials [13,14], and alkaline compounds, such as NaOH and Na_2CO_3 [15,16]. Researchers discovered that HZSM-5 promotes dehydration, deoxygenation, and denitrogenation during chemical reactions and favors the formation of aromatic hydrocarbons [11,17]. Addition of activated carbon as catalyst can reduce oxidation compounds and increase phenols and phenolics in bio-oil [13]. Investigations have confirmed that alkaline catalysts can combine with carboxylic acids in pyrolysis products. Carboxylates can be decomposed by pyrolysis temperature to form alkanes and olefins [15,16,18]. However, Fernada et al. mentioned that different types of catalyst was necessary to be used to improve bio-oil characteristics [19]. The sponge-like SiC-foamed ceramics have extraordinary characteristics in serving as catalyst like high thermal conductivity, high microwave absorption, high critical breakdown field and stable catalytic activity[20,21]. Considerable research have used SiC-foamed ceramics as composite catalyst support because it can clean biomass-derived syngas and improve the reforming performance of structures [20]. However, studies rarely used SiC-foamed ceramics to aid the catalytic reforming of pyrolysis vapors into the desired products. In this study, SiC-foamed ceramics will be used as

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catalyst to investigate their influence on bio-oil characteristics, service life, and stability.

During experiments, we observed that the main difference between oil pyrolysis and biomass pyrolysis lies on two factors, namely, whether the raw material will completely decompose, and whether pyrolysis vapors will flow into the condensing system with the reaction product. Improvements have been made on the reaction system to overcome these defects. The pyrolysis gas exits the reactor from the bottom of the quartz tube by employing the downdraft system to avoid the direct flow of unreacted oil vapors into the condenser via the upper ex-situ tube.

In this study, three sets of pyrolysis experiments have been conducted using the downdraft reactor to determine the effects of temperature (250 °C, 300 °C, 350 °C, 400 °C, and 450 °C), catalyst ratio (0:4, 1:4, 1:2, 1:1, and 2:1), and feed rate (0.5, 1, 1.5, 2, and 2.5 ml/min) on product yield and chemical composition of bio-oil. The chemical composition and functional group variations were determined using gas chromatography–mass spectrometry (GC—MS) and Fourier-transform infrared (FTIR) spectroscopy, respectively. Optimal conditions were maintained to investigate the stability of catalysts upon repeated use.

2. Methods

2.1. Materials

Chinese tallow kernel oil, the pyrolysis material of the fast microwave-assisted pyrolysis, was purchased from Jiujiang City, Jiangxi Province. Elemental analysis was conducted using an elemental analyzer (Vario EL III, Elementar, Germany) to determine the carbon, hydrogen, nitrogen, and oxygen contents of the sample. Saponification value was determined according to the procedures stated in standard ISO 3657:2002. Fatty acid composition was analyzed using GC–MS after methyl esterification. Table 1 presents the main characteristics of Chinese tallow kernel oil. SiC particles with a size of approximately 5 mm as a reaction bed can absorb microwave and conduct heat. It was supplied by Shenzhen Yike Abrasive Materials Co., Ltd. In the current study, the catalyst SiC-foamed ceramics used were obtained from Yi Fang Manufacturing (Laiwu, Shandong, China).

2.2. Experimental procedure

The microwave-assisted catalytic fast pyrolysis system uses a microwave oven (MAX, CEM Corporation) operating with a frequency of 2450 MHz and a constant power input of 1000 W. External catalytic pyrolysis reactions were conducted on the microwave system shown in Fig. 1. The effects of catalytic temperature (250 °C, 300 °C, 350 °C, 400 °C, and 450 °C), catalyst: Chinese tallow kernel oil ratio (0:4, 1:4, 1:2, 1:1, and 2:1), and feed rate (0.5, 1, 1.5, 2, and 2.5 ml/min) on product distribution and chemical composition of bio-oil were studied. Approximately 500 g of SiC particles were poured into the pyrolysis reactor (100 mm × 120 mm) to absorb microwaves. Prior to pyrolysis, nitrogen gas was pumped into the reaction system at a flow rate of 1 l/min for 2 min to expel air from the reaction system. In a typical run, 10 g of Chinese tallow kernel oil was added to the downdraft reactor with a specified flow rate when the reaction bed reached the target temperature of 550 °C. The steady pyrolysis temperature was retained for 30 min by turning the microwave power on and off to ensure complete pyrolysis in each run. After the reaction, nitrogen gas was passed over with the same flow rate and time to discharge the pyrolysis gas. The condensed components (bio-oil) collected from the U-type vessels in the 2 °C ice bath were used for subsequent analysis. Each run of the experiment was conducted in triplicates. The weight change in the quality of the quartz bottle before and after the reaction is the char weight. The quantitative difference between fresh and used catalyst corresponds to the amount of coke produced. Bio-oil, coke and char yield were calculated based on actual weight. The yield of gaseous fraction was calculated by mass balance.

Table 1
Characteristic of Chinese tallow kernel oil.

Properties	Tallow kernel oil
Acid value(AV)/(mg KOH/g oil)	3.969
Saponification value/(mg KOH/g oil)	209.31
Moisture content/wt%	1.447
Viscosity(25 °C,mPa·s)	46.89
molecular mass(g/mol)	831
Density at 20 °C (g/cm3)	0.941
Elemental analysis(wt%)	
Carbon	43.02
Oxygen	44.83
Hydrogen	5.34
Nitrogen	2.56
Fatty acid content(wt%)	
$C_{10}H_{16}O_2$	2.16
$C_{16}H_{32}O_2$	7.72
$C_{18}H_{32}O_2$	50.57
$C_{18}H_{30}O_2$	38.53
Other fatty acids	1.02

2.3. Characterization of bio-oil

Characterization of bio-oil was carried out by using GC–MS and FTIR spectroscopy. The chemical composition of bio-oil was tested using Aligent GC–MS 7890B. The chromatographic column used was an HP-5 ms column (30 m × 0.25 mm × 0.25 μm). The recommended GC–MS working condition was provided for reference in this study [5]. Bio-oil components were identified using the National Institute of Standards and Technology data library. The chromatographic area percentage was used to calculate the relative content of each component in the semi-quantitative method.

FTIR analysis was carried out by using Nicolet iS5 FTIR spectrometer with a resolution of 4 cm^{-1} and 16 scans to observe wave changes in bio-oil.

2.4. Stability of catalyst in repeated experiments

After completion of the reaction, the optimal conditions (1 ml/min feed rate, 1:2 catalyst/ feedstock ratio, and 300 °C catalytic temperature) were used to investigate the service life and stability of the catalyst. The experiment was repeated five times. The same amount of Chinese tallow kernel oil was added in the experiment for each run. The bio-oil yield and aromatic contents of bio-oil were the criteria for assessing the stability of catalyst.

3. Results and discussion

3.1. Analysis of pyrolysis product distribution

Fig. 2(a) presents the product yields under different catalytic temperatures (250 °C, 300 °C, 350 °C, 400 °C, and 450 °C) with a 1 ml/min feed rate and 1:2 catalyst-to-feed ratio. No change in the quality of the quartz bottle was observed before and after the reaction, indicating that char was not produced during the reaction. Fig. 2(a) shows that coke yield reduced from 4.65% to 0.52% with increasing temperature from 250 °C to 450 °C. This phenomenon resulted from the increased coke conversion at high catalytic temperatures, thus decreasing coke yield [22,23]. Bio-oil yield first increased from 66.50 wt% (250 °C) to 69.11 wt% (300 °C) and then a decrease tendency gradually appeared as the further increase in temperature. As the temperature grew up, the catalytic activity of the catalyst increased which caused the material converting into bio-oil. However, the bio-oil yield decreased when the temperature continued increasing. This phenomenon was mainly due to secondary cracking at higher catalytic temperature, leading to decreased bio-oil production. This phenomenon also observed in others'