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Bio-oil production from sequential two-step catalytic fast microwave-assisted biomass pyrolysis

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HIGHLIGHTS

- Sequential two-step catalytic fast microwave-assisted pyrolysis of corn stover was studied.
- The pyrolysis and catalytic cracking and upgrading processes can be flexibly and independently controlled.
- High selectivity of aromatic hydrocarbons was obtained by small catalyst loading.
- HZSM-5 catalyst has good stability in the catalytic upgrading process.

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ABSTRACT

A sequential two-step fast microwave-assisted pyrolysis (fMAP) for high quality bio-oil production was investigated. In the process, fMAP was followed by catalytic cracking and upgrading using a packed bed catalyst reactor with HZSM-5 as the catalyst. Effects of pyrolysis temperature, catalyst loading, and catalyst bed temperature on the product distribution were investigated. Results showed that maximum bio-oil and aromatic hydrocarbons yields were obtained when pyrolysis temperature reached 550 °C With the increase in the catalyst loading, the bio-oil yield decreased linearly while the aromatic hydrocarbons yield increased. The catalyst bed temperature also has a significant effect on the product chemical profiles. The aromatic hydrocarbons proportion of the bio-oil was found to increase with increasing catalyst bed temperature and reached its maximum of 26.20% at 425 °C. In addition, coke yield increased with increasing catalyst to biomass ratio and decreasing catalyst bed temperature.

1. Introduction

Biomass is considered as an alternative feedstock for liquid biofuel due to its abundance and renewable nature [1–3]. Pyrolysis has been around for several decades. In the process, biomass is exposed to high temperature (450–600 °C) at a high heating rate in an inert atmosphere, and is converted into a liquid known as bio-oil, and bio-char and non-condensable gases. However, bio-oil is a complex mixture of chemical compounds, such as acids, alcohols, esters, sugars, phenols, and furans [4,5]. Its direct use as an alternative to conventional fuels is limited due to its poor quality, such as high water content, poor thermal stability, high oxygen content and corrosiveness [6]. The high amount of oxygenated compounds renders the bio-oil only half of the heating value of the petroleum fuel equivalents.

The properties of bio-oil produced from biomass pyrolysis are affected by a number factors including heating characteristics. Bio-oil crude may be catalytically upgraded to high quality fuels. Microwave-assisted pyrolysis employs microwave heating, which offers relatively uniform internal heating of feedstock particles [7–10]. A fast microwave heating method employing microwave absorbents was recently developed [11–13], making fast microwave assisted pyrolysis (fMAP) possible. The present study was to evaluate a sequential two-step catalytic pyrolysis and upgrading method for improving the quality of bio-oil from fMAP of corn stover.

Catalytic fast pyrolysis is a key approach for removing the oxygenated components in order to upgrade bio-oil to improve the

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bio-oil quality and stability. Up to now, most studies in the literature have been focused on one-step catalytic fast pyrolysis where the catalysts are mixed with the feedstock in the pyrolysis reactor. A two-step process, where the upgrading catalyst is separate from the pyrolysis vicinity, has been studied to a less degree. The major disadvantages of the one-step process include fixed cracking and catalytic upgrading temperature, and high coke formation on the catalyst causing the rapid catalyst deactivation, etc. These advantages can be overcome by using the two-step process. Zhang et al. from our lab investigated two-step fast microwave-assisted pyrolysis [14], in which the catalyst bed was placed right above the microwave absorbent inside microwave cavity. In this kind of set-up, there is no need for separate heating for pyrolysis and catalytic upgrading and the pyrolysis temperature and upgrading temperature were assumed the same. Since the optimal temperature for pyrolysis and catalytic upgrading may often differ, there would be advantages if the temperature of two processes could be controlled independently. In the present study, the catalyst bed is placed between the pyrolysis and condensation process outside of the microwave cavity. The advantages of this new two-step catalytic fMAP include not only providing the ability to control the cracking and catalytic upgrading independently for optimum pyrolysis condition and catalytic upgrading conditions but also allowing the bio-char to be removed to avoid contaminating the catalyst, and to be easily separated and collected as the valuable byproduct. In addition, the catalysts life can be significantly extended, and can be recycled and regenerated more easily, therefore reducing the cost. Gungor et al. [15] compared one-step and two-step catalytic fast pyrolysis of pine bark on a semi-batch fixed bed reactor using ReUS-Y catalyst. They reported that oxygen content was found to be reduced in the two-step pyrolysis but not in the one-step pyrolysis. Wang et al. [16] investigated the two-step (ex situ) catalytic pyrolysis of biomass of Douglas fir sawdust pellets on a microwave-assisted reactor with Zn/ZSM-5 catalyst and found that product yield and bio-oil composition were significantly affected by catalyst bed temperature and $(WHSV)^{-1}$. Recently, many catalysts [17–19] were screened and analyzed, such as soluble inorganics, metal oxides, microporous materials and mesoporous materials [20], and HZSM-5 has been most extensively studied due to its shape selectivity for aromatic hydrocarbons [21,22]. Due to the three-dimensional structure of HZSM-5 with intermediate pore size (0.54×0.56 nm), only the small molecules are allowed to enter into the micropores and folded to aromatic hydrocarbons.

A newly developed sequential two-step catalytic fast microwave-assisted pyrolysis of biomass through a packed-bed HZSM-5 catalyst for high quality bio-oil production was researched. The effects of pyrolysis temperature, catalyst loading and catalyst bed temperature on product yields and chemical properties were analyzed. The relevant optimized conditions for high aromatic hydrocarbons production were determined. In addition, X-ray Diffraction (XRD) analysis was conducted on the fresh, spent and regenerated HZSM-5 catalyst samples to examine their stability during-catalytic upgrading process.

2. Materials and methods

2.1. Materials

Corn stover, which was obtained from local farm field in Saint Paul, Minnesota, USA, was used as feedstock. Prior to experiments, feedstock was dried in air and pulverized mechanically and sieved to less than 2 mm before pyrolysis. Proximate analysis of corn stover (wt.%, on dry basis) was 3.90 wt.% moisture, 3.45 wt.% ash, 90.95 wt.% volatile matter and 1.70 wt.% fixed carbon. Elemental analysis of corn stover (wt.%, on dry basis) was 44.91 wt.% C, 6.00 wt.% H, 1.58 wt.% N and 44.07 wt.% O (by difference). Based on the previous study from our lab [23], composition analysis of corn stover (wt.%, on dry ash-free basis) was 37 wt.% cellulose, 27 wt.% hemicellulose, 18 wt.% lignin and 18 wt.% extractives.

Zeolite powders (Si/Al = 80, Surface Area = 425m^2/g) used in this study were obtained from Zeolyst International (Conshohocken, PA). Prior to use, ZSM-5 catalyst was calcined at 500 °C in air for 5 h to make it become hydrogen form HZSM-5.

2.2. Sequential Two-Step catalytic fMAP system

Microwave oven (MAX, CEM Corporation) was operated with power of 750 W and a frequency of 2450 MHz. Pyrolysis process and catalytic process arranged in tandem, both of which can be independently controlled in temperature. The schematic diagram of sequential two-step catalytic microwave-assisted pyrolysis system is shown in Fig. 1. The experimental apparatus is composed of: (1) biomass feeder; (2) biomass feedstock; (3) quartz connector; (4) oven; (5) control panel; (6) quartz reactor; (7) SiC bed; (8) thermocouple (K-type); (9) heater; (10) catalyst bed; (11) quartz wool; (12) outlet quartz connectors; (13) liquid fraction collectors; (14) condenser; (15) connection for vacuum pump.

Experiments in three sections were conducted in this study. The aim of the first section was to determine the effect of pyrolysis temperature on two-step catalytic fMAP product distribution and selectivity. At the fixed catalyst bed temperature and loading, pyrolysis was carried out at different temperature severities 450 °C, 500 °C, 550 °C, 600 °C and 650 °C respectively. After the optimum pyrolysis temperature was determined, the effects of catalyst bed temperature and catalyst loading on product distribution and selectivity were investigated at the optimum

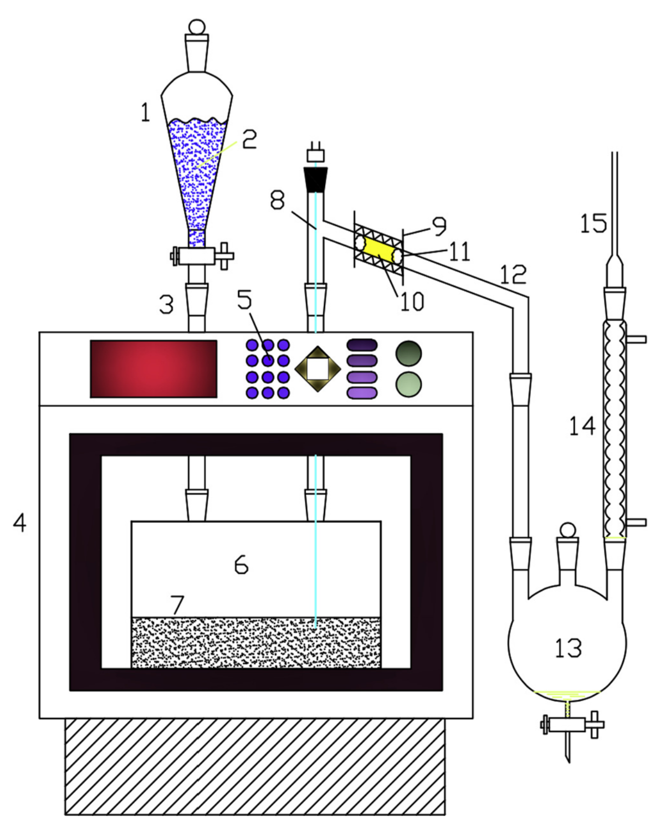

Fig. 1. Schematic diagram of sequential two-step catalytic microwave-assisted pyrolysis system.