Upgrading of Bio-oil *via* Microwave-assisted Pyrolysis of Corncob over CaO and HZSM-5 Mixed Catalysts to Promote the Formation of Aromatic Hydrocarbons

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Bio-oil upgrading *via* microwave-assisted pyrolysis of corncob over CaO and HZSM-5 mixed catalysts to promote the formation of aromatic hydrocarbon was investigated in this study. Results showed that with an increased ratio of HZSM-5 catalyst, the bio-oil yield was decreased; however, the proportion of aromatic hydrocarbons increased at first and then decreased. The maximum proportion of aromatic hydrocarbons was 35.8%, which was obtained with an optimal ratio of CaO to HZSM-5 of 1:2. This study showed the effects of CaO and HZSM-5 mixed catalysts under microwave-assisted pyrolysis in terms of improving the formation of aromatic hydrocarbons in bio-oil.

Keywords: Upgrading; Bio-oil; Microwave-assisted pyrolysis; CaO and HZSM-5 mixed catalysts; Aromatic hydrocarbons

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INTRODUCTION

Considering its prominent contribution to reducing the dependence on fossil fuels and decreasing serious environmental effects, biomass is one of the most promising alternatives. It is the only renewable and clean energy source that can be converted into several types of fuels, such as bio-oil, char, and gas (Wang *et al.* 2016). Fast pyrolysis is considered as one of the most promising ways to utilize biomass, which converts the biomass to bio-oil (Bridgwater 2012). Bio-oil is considered to be a low quality liquid product due to its high oxygen content from oxygenated compounds such as carboxylic acids, aldehydes, and ketones, which results in acidic, corrosive, and unstable characteristics (Czernik and Bridgwater 2004). These disadvantages of bio-oil significantly restrict its applications. Catalytic pyrolysis of biomass is the most effective way to upgrade the bio-oil (Koike *et al.* 2016). During catalytic pyrolysis process, the primary pyrolysis organic vapors in the presence of catalysts can further react by cracking, reforming, isomerization, and aromatization to reduce or eliminate non-target products and increase selectively target products in bio-oil (Bridgwater 1994). Aromatic hydrocarbons are important chemical platform compounds. The production of aromatic hydrocarbon-rich bio-oil by catalytic pyrolysis of biomass can effectively overcome the existing shortcomings of bio-oil. Many kinds of catalysts have been tested for use in the fast pyrolysis of biomass. These catalysts include microporous (HZSM-5, LOSA-1, *etc.*) (Zhang *et al.* 2009, 2013; Likun *et al.* 2018), mesoporous (MCM-41, SBA-15, Gamma-Al_2O_3, *etc.*) (Adam *et al.* 2005, 2006; Ates and Isikdag 2009), and macroporous catalysts (CaO, MgO, *etc.*) (Lin *et al.* 2010; Lu *et al.* 2010; Zhang *et al.* 2013, 2014). Microporous zeolite catalysts, such as HZSM-5, have been widely used for the catalytic upgrading of pyrolysis bio-oil due to its deoxygenating capacity and its pronounced performance of shape selectivity for aromatics (Zhang *et al*. 2009; Likun *et al*. 2018). However, microporous HZSM-5 catalysts are deactivated by coking, which results in lower aromatic product yields. On the other hand, macroporous catalysts with strong cracking characteristics are used in biomass pyrolysis for cracking heavy compounds. Results by Lin *et al*. (2010) showed that macroporous catalysts cracked heavy compounds into smaller oxygenates. However, these catalysts had no shape-selective catalytic characteristics for aromatic hydrocarbons. A method of using macroporous catalysts to crack the heavy compounds into smaller oxygenates, followed by the microporous catalyst to catalytically convert the small oxygenates into aromatic hydrocarbons has been proposed by Zhang *et al*. (2014). They investigated pine wood catalytic pyrolysis with two mixed catalysts (the microporous catalyst is ZSM-5 and the macroporous catalysts are CaO and MgO) analyzed using thermogravimetry-Fourier transform infrared spectroscopy (TG-FTIR) and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). The TG-FTIR results show that CaO and ZSM-5 mixed catalysts produced more aromatic rings than pure ZSM-5. The Py-GC/MS results show that CaO and MgO mixed with ZSM-5 improved the aromatic yield significantly. The maximum aromatic yield that boosted 30% of that with pure ZSM-5 was obtained with CaO as the additive.

Microwave irradiation heat is a novel biomass pyrolysis method (Miura *et al.* 2004). Compared with convectional heating processes where heat is transferred from the surface to the inside of the material through conduction driven by temperature gradient, microwaves irradiation heat is induced at the molecular level by direct conversion of the electromagnetic energy into heat (Xie *et al.* 2018). Therefore, microwaves pyrolysis can provide uniform internal heating for material particles. However, biomass is a poor microwave absorber. Research by Mamaeva *et al*. (2016), presented the concept of biomass fast microwave-assisted pyrolysis with microwave absorbents. Studies by Wang *et al*. (2017) and Zhou *et al*. (2017) showed that HZSM-5 catalyst in a microwave-assisted pyrolysis of biomass system significantly increased the proportion of aromatics and decreased the oxygen content in bio-oil. Some studies have researched the fast microwave-assisted catalytic co-pyrolysis of biomass with CaO and HZSM-5 or ZSM-5 mixed catalysts. Liu *et al*. (2016) investigated fast microwave-assisted catalytic co-pyrolysis of corn stover and scum for bio-oil production with mixed CaO and HZSM catalysts. Results showed that the maximum yield of aromatic hydrocarbons was obtained when co-pyrolysis temperature, CaO to HZSM-5 ratio, and corn stover to scum ratio were 550 °C, 1:4, and 1:2, respectively. Zhang *et al*. (2017) investigated microwave-assisted catalytic fast co-pyrolysis of *Ageratina adenophora* and kerogen with CaO and ZSM-5 catalysts and studied the effects of reaction temperature and overall effective hydrogen index (EHI) of feedstock. Results showed that the carbon yield of petrochemicals (aromatics + C_2-C_4 olefins + C5 compounds) from co-feeding *Ageratina adenophora* with kerogen was higher than that of two feedstocks under their respective optimal reaction temperatures of 600 °C when EHI is at the range 0f 0.4 to 1.0. *Ageratina adenophora* with kerogen can facilitate aromatics hydrocarbons production. Additionally, it was observed that co-feeding *Ageratina adenophora* with kerogen can facilitate hydrocarbon production. However, a study on the microwave-assisted pyrolysis of biomass over CaO and HZSM-5 mixed catalysts to promote the formation of aromatic hydrocarbons has not been reported. In this study, the upgrading of bio-oil *via* microwave-assisted pyrolysis of corncob using CaO and HZSM-5 mixed catalysts to promote the formation of aromatic hydrocarbons was investigated.

EXPERIMENTAL

Biomass Materials and Reagents

The corncob biomass sample was collected from the Panji District, Huainan (2008). The ultimate analysis of the corncob sample was determined *via* an elemental analyzer (Vario ELIII, Elementar, Langenselbold, Hesse, Germany). The caloric value of the corn cob was measured in an adiabatic bomb calorimeter (C6000, IKA Works Guangzhou, China). Table 1 shows the results of proximate and ultimate analyses of the sample.

Table 1. Ultimate and Proximate Analysis of the Corncob Sample

Ultimate Analysis (ad, wt%)					Proximate Analysis (ad, wt%)				Heating Value (ad, MJ kg^{-1})
C	H	N	S	O	Moisture	Volatile	Ash	Fixed Carbon	
48.85	6.17	0.17	0.09	38.95	7.93	71.72	5.77	14.58	17.86

Note: ad = air dry basis

The CaO catalyst was purchased from Shanghai Jiuyi Chemical Reagent Co., Ltd., Nanjing, Jiangsu, China. The HZSM-5 catalyst (Si/Al = 46, Surface Area = 350 m^2 g^{-1}) was purchased from Nankai University Catalyst Co., Ltd., Wuqing, Tianjin, China. Prior to use, the catalysts were calcined in a muffle furnace at 500 °C under air atmosphere for 5 h. The microwave absorbent, SiC, was purchased from the Shanghai Milling Material & Tool Co. Ltd., Shanghai, China. The particle size of the SiC was approximately 1 mm.

Experimental Procedure

A uniform mixture of 10 g of the corncob and 10 g of SiC with a particle size of 0.5 mm to 1 mm was placed into the lower zone of the quartz reactor (13 cm height and 12 cm inside diameter). A quartz wool was placed into the middle zone of the quartz reactor. The mass ratio of catalyst to biomass was maintained at a constant 1:2 in order to ensure complete pyrolysis of biomass. The total mass of catalyst was set at 20 g. A certain amount of CaO was evenly spread on the quartz wool. Then second layer of quartz wool was placed on the CaO layer. A certain amount of HZSM was placed on the second quartz wool layer, and a third quartz wool layer was placed on top of the HZSM layer. The CaO and HZSM-5 catalysts were used at various mass ratios (CaO only, 2:1, 1:1, 1:2, and HZSM-5 only). Finally, the quartz reactor was placed into the microwave oven. The carrier gas (N_2) with a flow rate of 0.5 L min^{-1} was introduced for 10 min and then was set to 0.3 L min^{-1}. Then, the microwave oven with a maximum power of 2000 W and a frequency of 2450 MHz was turned on and set to 800 W. The pyrolysis reaction was ran for 12 min, then the microwave oven was turned off. After the microwave-assisted pyrolysis, the bio-oil was collected from three flasks, immersed in ice water to condense, and the solid char and SiC were separated *via* sieving based on the difference in their particle size. The bio-oil as well as the solid char yields were calculated from the weight of each fraction. In each experiment, the collected catalysts were calcined at 600 °C for 2 h under air atmosphere to obtain the yield of coke. The gas yield was calculated by the difference based on the mass balance. Each experiment was carried out at least twice in order to ensure its repeatability. The experimental equipment is exhibited in Fig. 1.

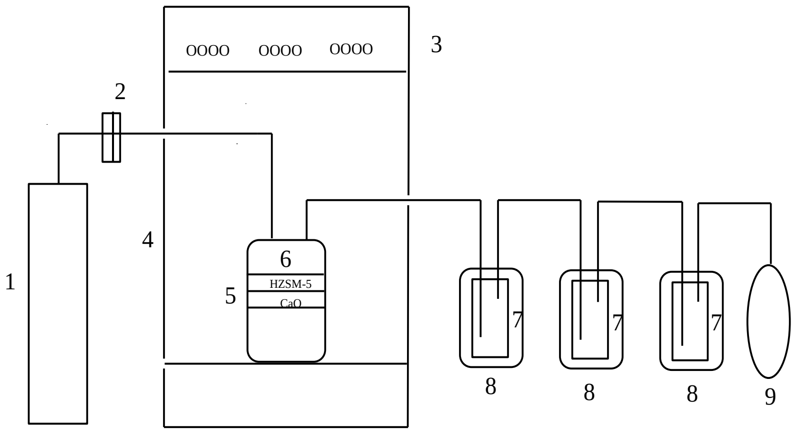

Fig. 1. Schematic diagram of the experimental apparatus: (1) N_2 bottle; (2) flow meter; (3) control system of the microwave oven; (4) microwave oven; (5) quartz reactor; (6) catalysts; (7) condensate bottle; (8) ice water condenser; (9) gas sample bag

The computing formulas to determine the product yields are shown in Eq. 1, Eq. 2, Eq. 3, and Eq. 4,

$$\eta_{\text{Char}} = \frac{m_1}{m_o} \times 100\% \tag{1}$$

$$\eta_{Bio-oil} = \frac{m_2}{m_o} \times 100\% \tag{2}$$

$$\eta_{\text{Coke}} = \frac{m_3}{m_o} \times 100\% \tag{3}$$

$$\eta_{\text{Gas}} = 100\% - \eta_{\text{Char}} - \eta_{\text{Bio-oil}} - \eta_{\text{Coke}} \tag{4}$$

where η_{Char} is the yield of the solid char, $\eta_{Bio\text{-}oil}$ is the yield of the bio-oil, η_{Coke} is the yield of the coke, η_{Gas} is the yield of the gas, m_0 is the weight of the biomass feedstock, m_1 is the weight of the solid char, m_2 is the weight of the bio-oil, and m_3 is the weight of the coke.

Bio-oil Characterization

The analysis of the chemical components of the bio-oil product was performed using a gas chromatography-mass spectrometer (GC/MS-QP5050A, Shimadzu, Nakagyo-ku, Kyoto, Japan) with a DB-5 capillary column (30 m × 0.25 mm i.d. × 0.25 μm) after dehydration using anhydrous sodium sulfate. Acetone was used as a solvent to dilute the dehydrated bio-oil. The solvent cut time was 2 min. Analytical grade Helium (99.999%) was employed as the carrier gas, at a flow rate of 1 mL/min^{-1}. The initial temperature was set to 60 °C for 2 min, then increased to 200 °C at a heating rate of 5 °C/min^{-1} and held for 5 min. After that, the temperature was raised to 280 °C at a heating rate of 10 °C/min^{-1} and held for 5 min. The injection size was 1 μL with a split ratio of 20:1. The interface temperature was set to 280 °C and the ion source temperature was set to 230 °C. The mass spectrometer was utilized for electron ionization (EI), with an ionizing energy of 70 eV mode and a scanning m/z range of 45 amu to 500 amu. The compounds of the bio-oil were identified by comparing the respective mass spectra with those from the National Institute of Standards and Technology mass spectral database. A semi-quantitative method was used to determine the relative content of each component in the bio-oil *via* the calculation of the total ion chromatographic peak area percent.

RESULTS AND DISCUSSION

Effects of the CaO to HZSM-5 Ratio on the Product Yields

The product yields from microwave-assisted pyrolysis with different ratios of CaO to HZSM-5 are given in Fig. 2.

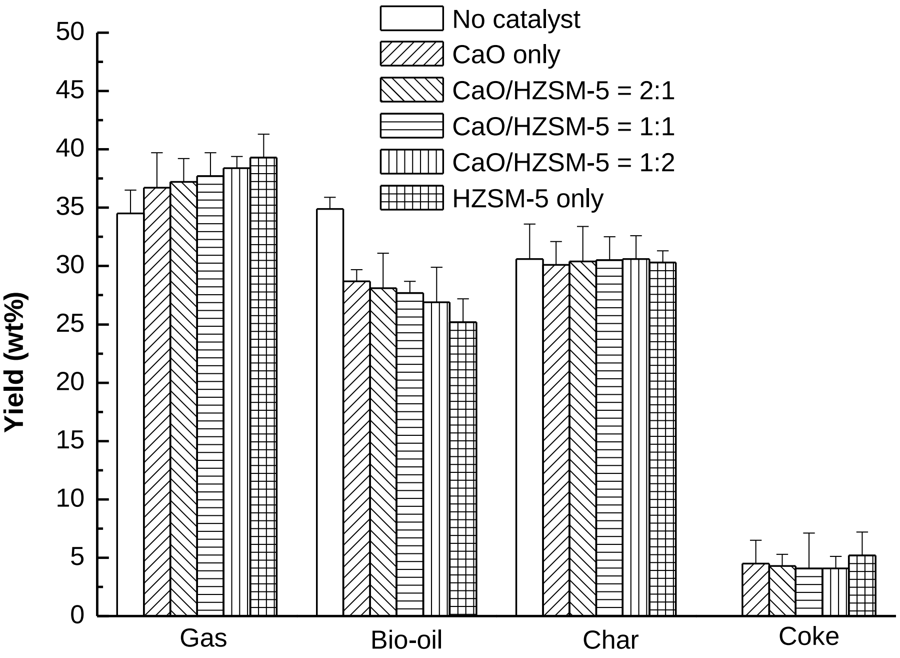

Fig. 2. Effects of the CaO to HZSM-5 ratio on the product yields

The highest bio-oil yield (approximately 35 wt%) was obtained without catalyst. The addition of catalysts decreased the bio-oil yield and increased the gas and coke yields, while the solid char yield had no major change. Because CaO could crack the heavy oxygenated compounds into several light oxygenated compounds (Veses *et al*. 2014). As the microwave-assisted pyrolysis vapors passed through the CaO catalyst layer, the heavy oxygenated were converted to light oxygenated compounds, which passed through the HZSM-5 catalyst layer and converted to light aromatic compounds, as well as light gases, such as CO and CO_2 *via* catalytic cracking, deoxygenation, and aromatization reactions (Vichaphund *et al*. 2015). In terms of the product yields, the bio-oil yield decreased, and the yield of gas increased. However, with an increased ratio of HZSM-5, the coke yield decreased firstly and then increased. The coke yield coming from HZSM-5 catalyst was the higher compared to the other catalysts, which led to the deactivation of the HZSM-5 catalyst due to pore blockage (Liu *et al*. 2016).

Effects of the CaO to HZSM-5 Ratio on the Bio-oil Components

The bio-oil analyzed was a complex mixture of organic compounds. The main chemical compositions identified in the bio-oil mainly included alcohols, aldehydes, ketones, carboxylic acids, phenols, and aromatics. The main components of the bio-oil were classified into three groups: aromatic hydrocarbons (Aromatic H.), oxygen-containing aliphatic compounds (Oxygen-cont. Aliphatic H.), and oxygen-containing aromatic compounds (Oxygen-cont. Aromatic H.). The peak area percentages of the four main chemical components in the bio-oil with different CaO to HZSM-5 ratios are shown in Fig. 3.

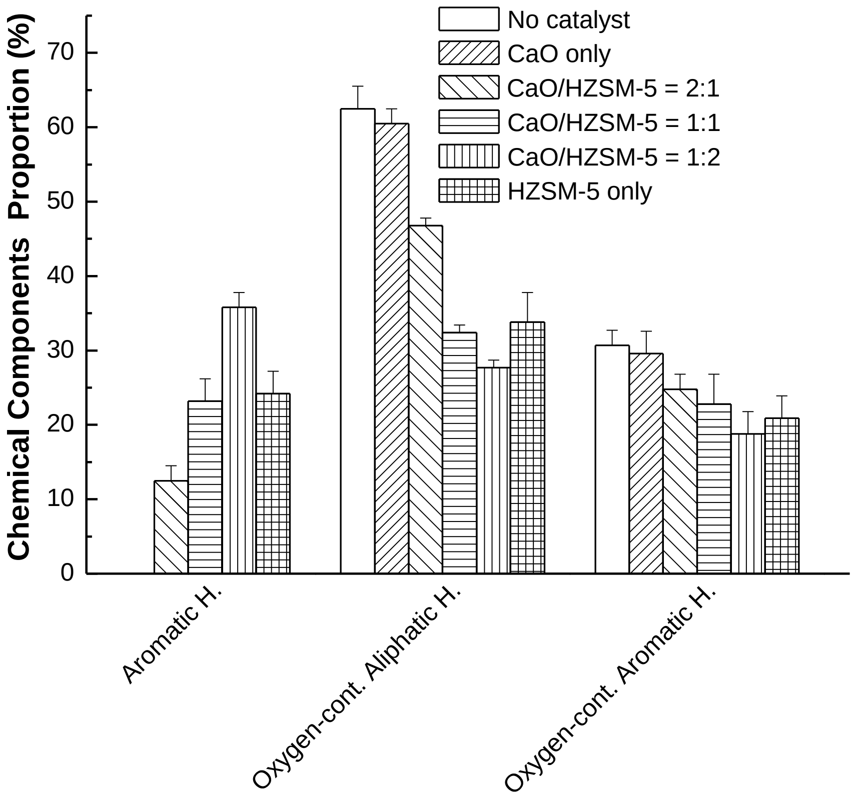

Fig. 3. Effects of CaO to HZSM-5 ratio on chemical components proportion in bio-oil

Bio-oil without catalyst mainly contained the oxygenated compounds (oxygen-containing aliphatic compounds and oxygen-containing aromatic compounds), whose peak area percentages reached about 95%. The aromatic hydrocarbons were not detected The proportion of oxygen-containing compounds was reduced after the addition of the CaO catalyst alone, which showed that the CaO catalyst had a certain deoxygenating capacity. Because CaO catalyst has no shape-selective characteristics for aromatic hydrocarbons, the bio-oil with the CaO catalyst only did not contain aromatic hydrocarbon, while the proportion of oxygen-containing compounds decreased to 90%. The proportion of aromatic hydrocarbons increased with an increase in the ratio of HZSM-5 to CaO and reached a maximum value of 35.8% when the ratio of CaO to HZSM-5 was 1:2, which was 10.6% higher than the value with HZSM-5 only. When the ratio of HZSM-5 to CaO was further increased, the proportion of aromatic hydrocarbons decreased. In addition, the proportion of oxygen-containing compounds decreased with the addition of the HZSM-5 catalyst and reached a minimum value of 46.5% when the CaO to HZSM-5 ratio was 1:2. The reduction in oxygen-containing compounds has a positive effect on the quality of the bio-oil, since oxygen-containing compounds in the bio-oil would cause low heating value and thermal instability, which result in the increase of the viscosity. The peak area percents of the aromatic hydrocarbon are listed in Table 2. When the CaO to HZSM-5 ratio was 1:2, the peak area percents of benzene and toluene reached the maximum value. The xylene content was not significantly changed.

The possible reaction mechanism of the formation of aromatic hydrocarbons is as follows: when the pyrolysis vapors from the biomass microwave-assisted pyrolysis process passed through the mesoporous CaO catalyst, the heavy compounds, such as large phenols and anhydrosugars, were cracked into light oxygenated vapors and defused into the internal pores of the HZSM-5 catalyst, where they formed aromatics and olefins via a series of reactions such as dehydration, decarbonylation, decarboxylation, and aromatization reactions through the hydrocarbon pool (Zhang *et al*. 2017, 2018; Zheng *et al*. 2018; Zhu *et al*. 2018). A simplified schematic diagram of the reaction pathways of the formation of aromatic hydrocarbons from the microwave-assisted pyrolysis of biomass over CaO and HZSM-5 mixed catalysts is presented in Fig. 4.

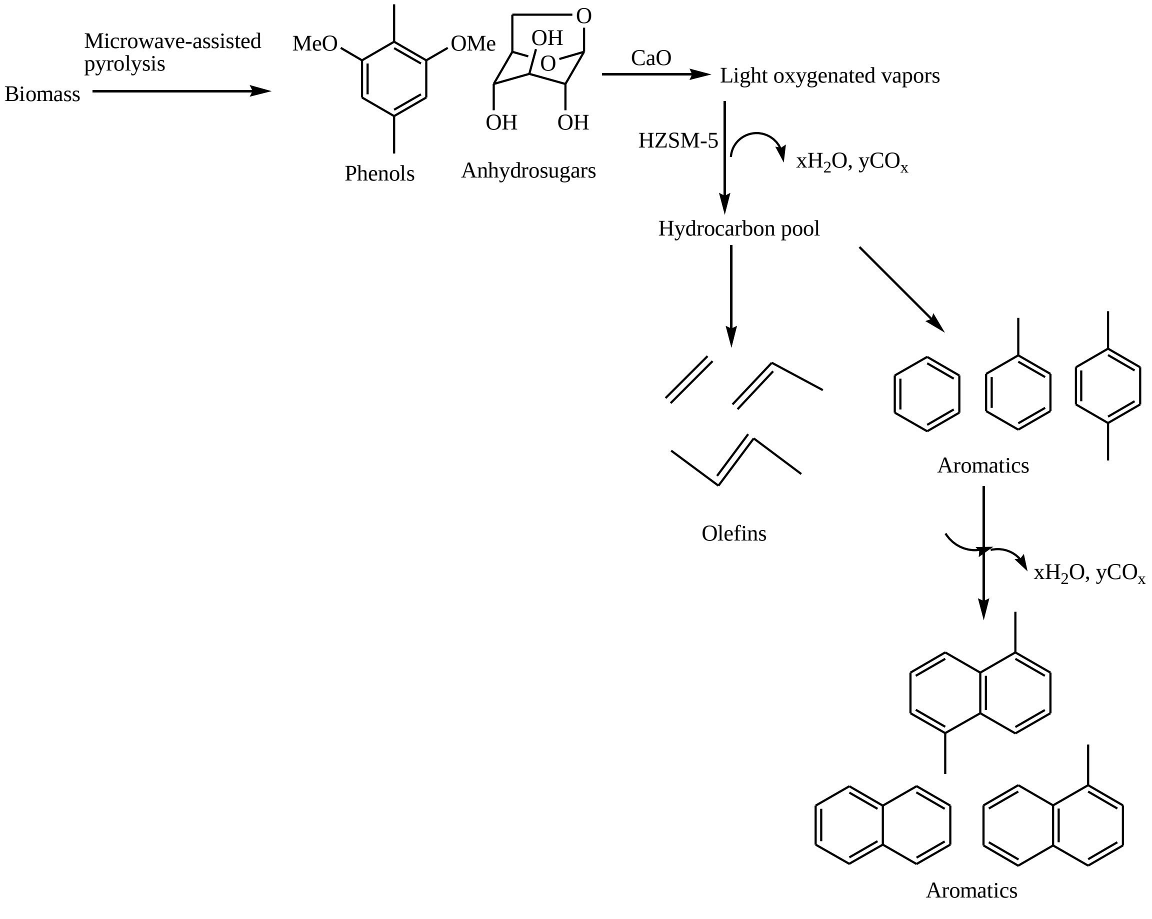

Fig. 4. Reaction pathways of the formation of aromatic hydrocarbons from the microwave-assisted pyrolysis of biomass over CaO and HZSM-5 mixed catalysts

Table 2. Peak Area Percents of the Aromatic Hydrocarbons in Bio-oil

Compound Name	Peak Areas (%)				
	CaO	CaO/HZSM-5= 2:1	CaO/HZSM-5= 1:1	CaO/HZSM-5= 1:2	HZSM-5
Benzene	0	3.4	10.9	10.6	7.9
Toluene	0	4.5	9.1	20.2	12.8
Xylene	0	3.9	3.4	3.3	3.8

These results showed that the microwave-assisted pyrolysis of biomass over CaO and HZSM-5 mixed catalysts was an efficient method to increase the content of aromatic hydrocarbons in bio-oil while decreasing the content of oxygenated compounds for upgrading the bio-oil.

CONCLUSIONS

This study investigated the microwave-assisted pyrolysis of corncob over CaO and HZSM-5 mixed catalysts for improving the yield of aromatic hydrocarbon in bio-oil, and concluded the conclusions as follows:

1. With an increased ratio of HZSM-5 to CaO, the bio-oil yield decreased, while the proportion of aromatic hydrocarbons increased firstly and then decreased.
2. The maximum content of 35.8% of aromatic hydrocarbons in bio-oil was obtained when the ratio of CaO to HZSM-5 was 1:2.

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