



# Pyrolysis and catalytic upgrading of pine wood in a combination of auger reactor and fixed bed



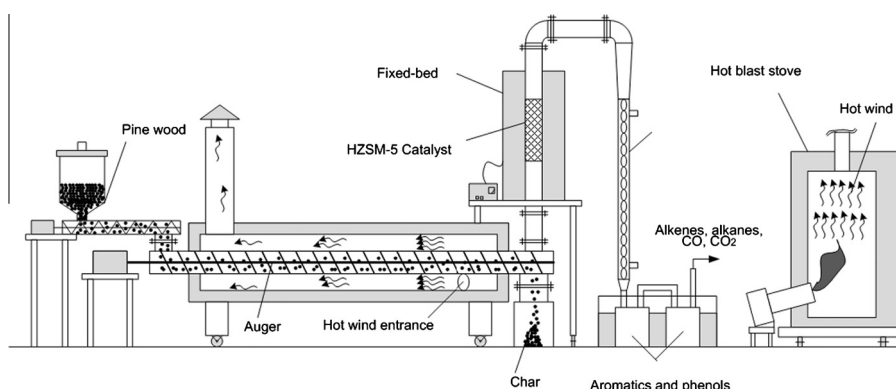
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## HIGHLIGHTS

- Pyrolysis and catalytic upgrading of pine wood was studied in a combined system.
- The system included an auger pyrolysis reactor and a fixed-bed catalytic reactor.
- HZSM-5 catalyst was evaluated for catalytic cracking.
- HZSM-5 was suitable for converting pine wood to phenols and aromatics.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A combined system of auger pyrolysis reactor and fixed-bed catalytic reactor was designed and used for continuous pyrolysis and catalytic upgrading of pine wood in this paper. HZSM-5 (Si/Al = 38) catalyst was evaluated for catalytic cracking. The distributions of liquid and gaseous products at the pyrolysis temperatures of 400–600 °C and the catalytic cracking temperatures of 450–650 °C were determined. The results showed that HZSM-5 catalyst, at a catalytic temperature of 650 °C, was suitable for converting pine wood to phenols, aromatics and gaseous hydrocarbons. The phenols and aromatics increased from 6% (peak area) for non-catalytic pyrolysis to 41%. The decrease in oxygen content of bio-oil and the increase in alkenes and alkanes of gaseous products are desirable for the pyrolysis and catalytic upgrading of biomass.

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## 1. Introduction

The development of renewable energy as replacements for fossil-based fuels is rapidly progressing. Lignocellulosic biomass is being studied worldwide as a feedstock for producing liquid fuels and chemicals to replace petroleum because of its renewability and large availability [1–3]. Pyrolysis is one of the main methods

from biomass to bio-oil production, and it has caused great attention and sparked interest extensively in recent years. However, bio-oil from biomass pyrolysis, is a mixture of more than 200 highly oxygenated compounds. Bio-oil is thermally unstable and must be upgraded if to be used as fuels.

Various approaches have been applied to the improvement of bio-oil quality, including hydrodeoxygenation [4,5], catalytic cracking [6,7], emulsification [8,9], steam reforming [10], esterification [11], etc. One option for bio-oil upgrading is to use biomass-derived feedstocks in a petroleum refinery, such as catalytic cracking.

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Catalytic cracking of bio-oil is an upgrading process of deoxygenation, which can improve the quality of bio-oil. Various types of zeolite catalysts have been studied in the catalytic cracking of biomass in the past 20 years, such as ZSM-5, Beta, Y, Al-MCM-41, and SBA-15. Catalysts for bio-oil upgrading have been well reviewed by many researchers [12,13]. Among these catalysts, HZSM-5 performs as a good catalyst for catalytic conversion of biomass due to its moderate internal pore space and steric hindrance [14]. It has been found to dramatically change the composition of bio-oils by both reducing the amounts of oxygenated compounds via deoxygenation reactions and simultaneously increasing the aromatic species, producing a lighter fraction, while decreasing the bio-oil molecular weight [15].

Several types of reactors have been used in catalytic pyrolysis/upgrading of biomass [16–18]. In bench-scale reactors, currently only bubbling fluidized beds (BFBs) and circulating fluidized beds (CFBs) can be applied to continuous production, and there is mixing of solid biomass with the solid catalyst. There are two drawbacks on fluidized bed reactors. (1) The fluidized beds need large volumes of inert carrier gases, which dilute the pyrolytic gases and reduce the thermal efficiency of the process. (2) The presence of char (especially the ash in char) in the catalyst reduces the capability of the catalyst.

Auger pyrolysis reactors, with/without the use of sand as a heat carrier, are among the most popular reactors being evaluated today [19,20]. These reactors do not require large volumes of carrier gases, and can produce pyrolysis vapors continuously. If a catalytic bed is connected to the auger pyrolysis reactors, the pyrolysis vapors will pass through the catalyst and there is no mixing of solid biomass with the solid catalyst, which called catalytic upgrading of pyrolysis vapors. Thus, the combined system of auger pyrolysis reactor and fixed-bed catalytic reactor can overcome the drawbacks of fluidized bed systems.

In this paper, a combined system of auger pyrolysis reactor and fixed-bed catalytic reactor was applied to achieve biomass continuous pyrolysis and catalytic upgrading of pyrolysis vapors. HZSM-5 zeolite was evaluated for catalysis cracking upgrading using pine wood as feedstock. The reaction parameters were optimized with a focus on the effects of reaction temperatures. Furthermore, the properties and components were investigated before and after upgrading.

## 2. Experimental

### 2.1. Characterization of feedstock and catalysts

The pine wood feedstock was from Guangdong province, China. Feedstock was ground and sieved to a particle size <1 mm. The pine wood samples were oven-dried overnight to 6–8% moisture content at 105 °C before tests. Elemental analyses of pine wood samples were carried out using a Vario EL cube. The ash content was determined according to ASTM D-482. Thermogravimetry (TG) analysis of feedstock was carried out under a nitrogen flow rate of 30 ml/min with STA 449 °C thermal analyzer (NETZSCH, Germany) by using 10 mg samples and a 30 °C/min temperature increase.

HZSM-5 zeolite catalyst with a Si/Al ratio of 38 was from the Nankai University Catalyst Co. Ltd. (Tianjin, China). The shape of catalysts was cylindrical with the diameter of 3 mm and the length of 10 mm. Before using, the catalysts were calcined at 550 °C for 6 h in air. NH<sub>3</sub> temperature-programmed desorption (NH<sub>3</sub>-TPD) analysis was carried out in a quartz tube reactor with a thermal conductivity detector (TCD). 200 mg of catalyst was pretreated in a flow of helium (25 ml/min) at 500 °C for 1 h, and after cooling to 120 °C, ammonia adsorption was carried out. Subsequently, excessive physisorbed ammonia was removed by purging with he-

lium at 100 °C for 1 h. Tests were carried out by increasing the temperature from 100 to 700 °C at a rate of 10 °C/min and a helium flow rate of 25 ml/min.

### 2.2. Pyrolysis and catalytic cracking upgrading

Pine wood was pyrolysed and catalytic cracking upgrading using a combined system of auger pyrolysis reactor and fixed-bed catalytic reactor as shown in Fig. 1. The dried biomass was introduced into the hopper of the feeder and fed into the auger reactor at a feeding rate of 25 kg/h. The pine wood was pushed through the hot zone of the reactor with an auger screw driven by a 1.5 kW variable speed motor. All the tests were conducted at auger speeds of 5 rpm which corresponds to a solid residence time inside the reactor of 8 min. Outside the auger screw, a stainless-steel tube with a length of 300 cm (heating zone was 240 cm) and a diameter of 16 cm was heated by a hot blast stove. A diesel burner (Riello 40 G3, Italy) was the heat resource of the hot blast stove. The temperature of the external wall in the pyrolysis reactor was recorded and maintained at set temperatures. The temperature of the pine wood sample pyrolysed was also quantified. Due to the structure of the reactor and the blowing direction of hot wind, the varied temperature values existed along the reactor's axis. Owing to the relatively low heat transfer coefficient between the wall and the biomass moving bed, a significant temperature gradient was established between the biomass bed and the wall of the reactor. Fig. 2 shows the time–temperature profile for the pyrolysis of pine wood and the wall of the reactor. After pyrolysis, the charred particles were collected, left to cool for 2 h and weighed in a char pot. The pyrolysis vapors were sucked into a fixed-bed catalytic reactor which was loaded zeolite catalysts. The fixed-bed catalytic reactor (a stainless-steel tube with a length of 130 cm and a diameter of 78 cm) was heated by an electrical furnace to the desired temperature (450–650 °C) before experiments. After upgrading, the pyrolysis vapors were condensed in two condensation units. The first unit was a vertical tube with cooling water coils where pyrolysis vapors were cooled to approximately 25 °C. The second condensation unit consisted of two traps in series immersed in water cooled by ice. The pressure inside the reactor was kept by a Roots vacuum pump with a frequency converter. The Roots vacuum pump with a frequency converter to regulate the suction had two purposes: (1) helping to suck the pyrolysis vapors from the reactor, and (2) controlling the velocity of flow to adjust the residence time of vapors inside the pyrolysis reactor and catalyst bed. The yield of liquid was determined by weighing the first condenser and the traps. The non-condensable gases were calculated by difference.

### 2.3. Product analysis

Gas chromatography mass spectroscopy (GC/MS) analysis of bio-oil was performed on a gas chromatograph (7890A, Agilent Technologies, USA) coupled with a mass spectrometer (5975C, Agilent Technologies, USA). A HP-INNOWax capillary column was used for the chromatographic separation of chemical components in bio-oil. The injector temperature was 260 °C, and a split ratio 20:1 was used. The GC oven temperature program was 2 min at 60 °C, and to 240 °C in a rate of 10 °C/min with a dwell time of 10 min. The mass spectrometer was operated in the electron impact mode at 70 eV. After a solvent delay of 2.8 min, full scan mass spectra were acquired from 12 to 500 m/z. The identification of the main peaks was made from NIST11 MS Library and previously published literatures.

The water content of the bio-oil was determined by Karl Fischer titration (ASTM D 1744) with a Metrohm 787 KF Titrino. The analysis was carried out three times to confirm the

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