



Reaction Mechanism of Oxygenate Components of Biomass Pyrolysis Oil on HZSM-5 Zeolite

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In this paper, phenol, *m*-cresol and cyclopentanone, chosen as model compounds, were catalyzed upgrading at 500 °C, space velocity 5.0 h⁻¹ and different water content conditions. The results showed that the phenol can't be catalyzed on the phase of zeolite HZSM-5. According to the catalytic pyrolysis products of *m*-cresol and cyclopentanone, simply catalytic reaction pathways were speculated that *m*-cresol cracking included demethylation and isomerization reactions and cyclopentanone cracking was firstly dehydration or decarbonylation and then cyclized to produce cyclocompounds, which provided a theoretical basis for the bio-oil catalytic pyrolysis mechanism research.

Key Words: Bio-oil, Upgrading, Zeolite, Catalytic cracking, Mechanism.

INTRODUCTION

Biomass can be converted to more valuable energy forms via a number of processes including thermal, biological, mechanical or physical processes. Pyrolysis is a most mature technology, which had been applied for thousands of years for charcoal production. However, pyrolysis had been developed rapidly in the last 30 years¹⁻⁴, which was produced at temperatures of around 500 °C and very short reaction times of up to 2s. The pyrolysis technology directly gave high yields of liquids of up to 75 wt. %, however, the liquid products (called bio-oil), which contain high content of oxygen, are of low calorific value and of poor thermal stability; this disadvantage becomes a problem restricting its extensive application and replacement the fossil fuels.

The quality of bio-oil can be improved by the partial or total elimination of the oxygenated functionalities present. Until now, two methods of upgrading bio-oil, which are catalytic cracking and catalytic hydrogenation, have been studied for this purpose⁵⁻⁷. The first technology is a process in which bio-oil is thermally treated over solid acid catalysts at atmospheric pressure without hydrogen, resulting in simultaneous dehydration-decarboxylation. The other technology is a process in which bio-oil is hydro-treated over conventional hydrogen-sulfurization catalysts under pressure (10 MPa-20 MPa) in the hydrogen ambience, for the hydrogenation of unsaturated groups (with elimination of oxygen as water) and hydrogenation hydrocracking of large molecules. Although hydrotreating is extremely effective, techno-economic analyses reveal its

economics to be unfavourable for the production of the fuel-type products it affords⁸.

Many research studied the reactor design, process and catalyst and so on. Some scholars have studied the mechanism of catalytic cracking of bio-oil^{9,10}. However, the mechanism was not described in a simple way. In this paper, the models of bio-oil (phenol, *m*-cresol and cyclopentanone as feedstock) were cracking over zeolite HZSM-5 catalyst at atmospheric pressure in a fixed-bed reactor, the products were condensed in a collector and analyzed by GC/MS. According to the results, the mechanism of catalytic cracking was speculated in a simple way.

EXPERIMENTAL

Experimental installation: The fixed-bed reactor, with dimension of 750 mm in height and 15 mm in diameter, was shown in Fig. 1. The main body of reactor was made up of stainless steel and the catalyst was placed into the middle part of reactor. There was a thermal couple in axial direction of reactor to detect the temperature of catalyst bed. The temperature was controlled by a temperature controller and the heat the reactor demanding was provided by an electric heater. The feeding of material was controlled by a syringe pump and the reaction products were cooled and analyzed by a GC/MS (PerkinElmer Clarus 500) apparatus.

Catalyst: Zeolite HZSM-5 was produced by the catalyst plant of Nankai University. The catalyst must be calcined at 600 °C in a muffle for 5 h, to eliminate the effect of organic film.

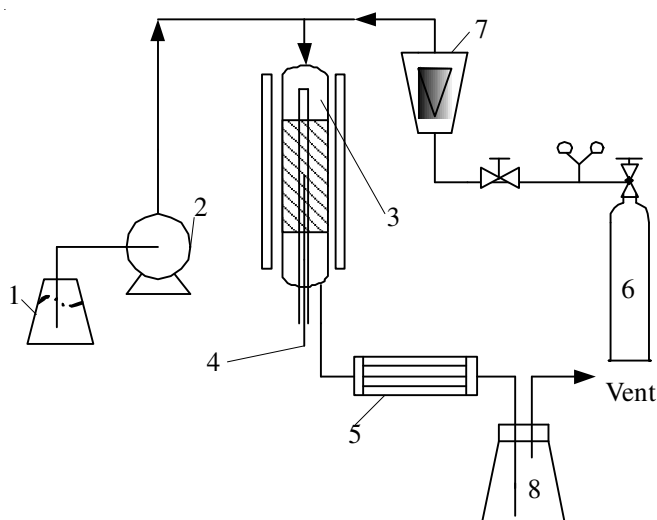


Fig. 1. Schematic of the catalytic cracking process; 1. Raw materials, 2. Syringe pump, 3. Fixed-bed reactor, 4. Thermocouple, 5. Condenser, 6. Cylinder, 7. Flowmeter, 8. Collector

RESULTS AND DISCUSSION

Effect of water on phenol and *m*-cresol cracking: The water content of crude bio-oil was about 15-30 wt %. In order to simulate the real process of catalytic cracking of bio-oil, phenol, *m*-cresol and water were chosen as raw materials for catalytic cracking reaction. The experiments were carried out at 500 °C, WHSV 5.0 h⁻¹ (WHSV was defined as a ratio of the model of bio-oil feed weight flow rate and the weight of the loaded catalyst).

The results showed that phenol can not be catalyzed at 500 °C, WHSV 5.0 h⁻¹. The condensate was analyzed by GC/MS and did not detect other compounds. Due to phenol's benzene ring stable structure, it can't be catalyzed over zeolite HZSM-5.

The results of catalytic cracking of *m*-cresol were list in Table-1.

Products	Products of concentration under different content of water (area%)	Products of concentration under different content of water (area%)			
		30	20	10	0
Phenols	Phenol	11.25	11.34	11.56	11.84
	2-Methyl-Phenol	59.48	60.34	60.80	60.5
	2,3-Dimethyl-Phenol	3.80	3.37	2.54	3.1
	2,5-Dimethyl-phenol	10.11	9.99	10.21	9.92
	2-Ethyl-phenol	5.31	5.71	5.88	5.83
	4-Ethyl-phenol	0.36	0.33	0.29	0.31
	2-(1-Methylethyl)-phenol	0.26	0.2	0.25	0.22
	4-(1-Methylethyl)-phenol	1.38	1.46	1.47	1.4
Total	91.95	92.74	93.00	93.12	
Others	Acetic acid	2.34	2.78	3.01	3.29
	Acetone	4.21	4.02	3.91	3.59
	Naphthalene	1.50	0.46	0.087	0
Total	8.05	7.26	7.01	6.88	

As shown in Table-1, the products of catalytic cracking of *m*-cresol were mainly phenols' compound, which content was up to 91 %. Due to *m*-cresol's benzene ring stable structure,

the products were mainly phenol and its derivative, which indicated that *m*-cresol had only methyl breaking and isomerization reaction over the zeolite HZSM-5 at 500 °C, WHSV 5.0 h⁻¹. Because of complexity of products, the products were classified according to its chemistry property. The results were shown in Fig. 2.

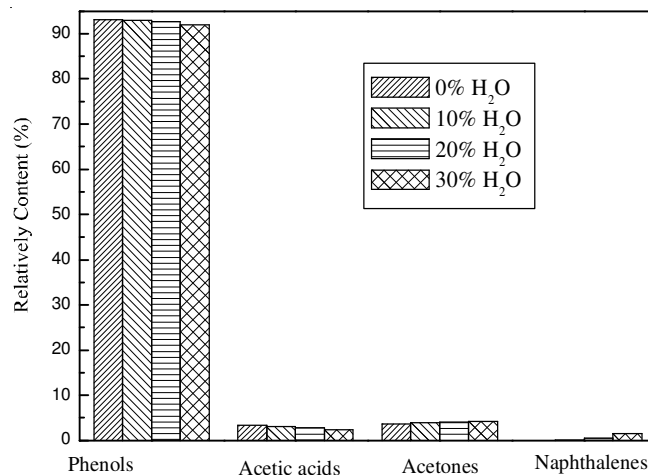


Fig. 2. Products of upgrading *m*-cresol in different content of water

Fig. 2 showed that phenolic compounds and acetic acid content decreased a little while water content increasing, acetone and naphthalene content increased slowly with water content increasing, which indicated that water content had a small effect on the catalytic cracking reactions.

Mechanism of catalytic cracking phenol and *m*-cresol: Table-1 and Fig. 2 showed that the products of catalytic cracking of *m*-cresol were mainly phenol and its derivative, which indicated that *m*-cresol had only methyl breaking and isomerization reactions. In bio-oil, other phenolic compounds had the same mechanism as that of *m*-cresol except phenol. According to the results of experiments, the mechanism of catalytic cracking *m*-cresol was inferred (Fig. 3).

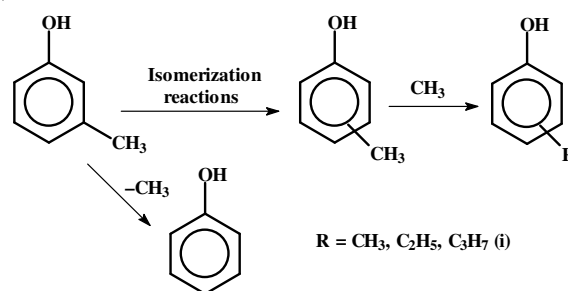


Fig. 3. A possible reaction mechanism of *m*-cresol

Effect of water on cyclopentanone cracking: In this part, cyclopentanone was chose as model of bio-oil. The results of catalytic cracking of cyclopentanone were list in Table-2. The products of catalytic cracking of cyclopentanone included monocyclic ring aromatic compounds (such as toluene, ethyl benzene, xylene, trimethylbenzene), indene and its derivative, naphthalene and its derivative, polycyclic aromatic hydrocarbon (such as fluorine, anthracene, phenanthrene, pyrene, etc.) and didn't contain oxygen compounds, which showed that cyclopentanone deoxidation way was firstly dehydration to

produce cyclopentadiene or decarbonylation to produce butadiene and then cyclopentadiene and butadiene cyclized to produce phenol, indene, naphthalene and their derivatives and polycyclic aromatic hydrocarbon (Fig. 4).

TABLE-2
EFFECT OF WATER CONTENT ON LIQUID
PRODUCT COMPOSITIONS (AREA %)

Products	Products of concentration under different content of water (area %)				
	30	20	10	0	
Phenols	Toluene	2.6	3.55	4.14	5.5
	<i>o</i> -Xylene	1.75	2.07	3.02	3.85
	<i>p</i> -Xylene	2.13	2.15	4.11	5.21
	Ethyl-benzene	3.16	5.96	7.28	10.36
	1,2,3-Trimethyl benzene	1.03	1.89	2.31	3.78
	1,2,5-Trimethyl benzene	1.67	2.43	3.09	4.21
Total	12.34	18.05	23.95	32.89	
Indenes	Indane	3.48	3.28	2.91	2.48
	Indene	5.24	4.51	2.28	1.47
	2-Methyl indane	10.47	10.64	10.11	8.92
	1-Methyl indene	4.97	4.58	3.27	2.97
	Total	24.16	23.01	18.57	15.84
Naphthalenes	Naphthalene	25.13	25.21	24.13	22.88
	1-Methyl naphthalene	8.82	6.56	7.88	7.56
	2-Methyl naphthalene	8.13	8.26	7.17	7
	1,4-Dimethyl naphthalene	7.14	6.21	6.88	5.29
	1,5-Dimethyl naphthalene	7.20	6.86	6.07	4.32
	1,2,6-Trimethyl naphthalene	3.41	2.96	2.37	2.1
	1,2,5,7-Tetramethyl naphthalene	0.15	0.11	0.076	0.011
Total	59.98	56.17	54.576	49.16	
Polycyclic aromatic hydrocarbons	Fluorene	0.11	0.097	0.077	0.073
	Anthracene	0.21	0.17	0.14	0.12
	Phenanthrene	0.45	0.40	0.51	0.36
	1-Methyl phenanthrene	1.38	1.20	1.03	1.01
	2,3-Dimethyl phenanthrene	0.85	0.56	0.42	0.32
	1,2,7-Trimethyl phenanthrene	0.21	0.11	0.087	0.087
	pyrene	0.13	0.093	0.54	0.044
3-Methyl-pyrene	0.18	0.14	0.10	0.087	
Total	3.52	2.77	2.90	2.10	

Fig. 4 indicated that the phenolic compounds content decreased rapidly with water content increasing. Other products increased with water content increasing, in which indene and naphthalene compounds increased rapidly, PAHs compounds increased slowly, which indicated that water content had a greater effect on the catalytic cracking cyclopentanone reactions.

Mechanism of catalytic cracking cyclopentanone:

According to the results of Table-2, a simply mechanism of catalytic cracking cyclopentanone was inferred (Fig. 5).

Fig. 5 showed that the cyclopentanone deoxidation was firstly dehydration to produce cyclopentadiene or decarbonylation to produce butadiene and then cyclopentadiene and butadiene cyclized to produce phenol, indene, naphthalene and

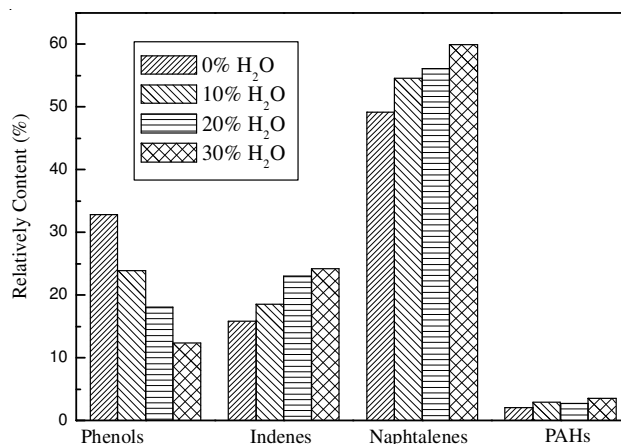


Fig. 4. Products of upgrading cyclopentane in different content of water

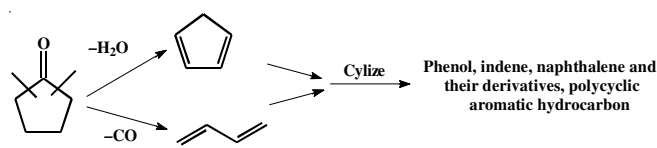


Fig. 5. A possible reaction mechanism of cyclopentanone

their derivatives and polycyclic aromatic hydrocarbon. In bio-oil, other ketone compounds had the same mechanism as that of cyclopentanone.

Conclusion

Phenol can't be catalyzed over zeolite HZSM-5. According to the catalytic pyrolysis products of *m*-cresol and cyclopentanone, simply catalytic reaction pathways were speculated that *m*-cresol cracking included demethylation and isomerization reactions and cyclopentanone cracking was firstly dehydration or decarbonylation and then cyclized to produce cyclopentadiene and butadiene, which provided a theoretical basis for the bio-oil catalytic pyrolysis mechanism.

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