

Influence of Catalyst Type and Regeneration on Upgrading of Crude Bio-oil through Catalytical Thermal Cracking

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Abstract : Catalysts, such as HZSM-5(Si/Al=50), HZSM-5(25), zeolite 5A, CaHZSM-5(50), ZnHZSM-5(50), and Kaolin were used in upgrading of crude biomass oil from pyrolysis in a fixed-bed reactor under atmospheric pressure, in order to investigate the effects of catalyst type on the yield of desired product. A blank test was carried out in a bed of inert packings to determine the extent of non-catalytical thermal cracking. The gas produced in the reaction was analyzed by the chemical absorption method. Among those catalysts, HZSM-5(50) gave the highest yield of the desired organic distillate while Kaolin gave the least formation of coke. Regeneration of deactivated HZSM-5(50) was studied. In terms of yield of organic distillate and formation rate of coke, the catalytic activity did not change much during the first 3 times of regeneration.

Key words : catalytic cracking; biomass; catalyst; regeneration

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1 INTRODUCTION

The development of bio-energy has drawn great attention of researchers since the early 1980's and upgrading of crude bio-oil from pyrolysis of biomass to prepare fuel oil of high quality has become now an area attracting more R&D efforts. Fuel from biomass contains less amount of sulfur and nitrogen and therefore reduces greatly SO_2 and NO_x in emission, and on the other hand, the total CO_2 in emission is equal to that plants take in from atmosphere. Bio-oil, directly derived from various processes, e.g., flash pyrolysis^[1], vacuum pyrolysis^[2] or microwave pyrolysis^[3], is usually of low quality and with high viscosity, high oxygenate components, low stability and low heat value. Upgrading is necessary to improve its quality by reducing the content of oxygenates.

The current research on upgrading^[4-6] focuses on two technological routes, i.e., catalytic hydrogenation and catalytic cracking. Catalytic hydrogenation refers to the process in which crude bio-oil is hydrotreated under hydrogen pressure (10~20 MPa) in the hydrogen-donor solution. Catalytical thermal cracking is, on the other hand, a process in which crude bio-oil is thermally treated in a gas-solid phase at atmospheric pressure without hydrogen. Compared with catalytic hydrogenation, though catalytical thermal cracking proceeds at atmospheric pressure, disadvantages are however low yield (14%~22.5%, ω), easy coking (26.1%~38.5%)^[5] and thus shorter life of catalyst. In this paper, different types of catalyst were used in catalytic cracking to investigate their effects on yield and coking.

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2 EXPERIMENTAL

2.1 Materials

The crude bio-oil, used as the experimental material, was a viscous black liquid obtained from pyrolysis of sawdust in a spouting fluidized-bed reactor^[7]. The analysis data in Table 1 shows that deficiency of hydrogen and high content of oxygen are two main factors that cause low quality of crude bio-oil^[8]. Reduction of oxygenated amount and cracking of the big molecules into small ones are the main purposes of upgrading. The oxygen is removed in the form of CO, CO₂ or H₂O.

Table 1 Properties of crude bio-oil

Density (kg/L)	Viscosity (50°C) (Pa·s)	Element analysis (%)			
		C	H	O	N and S
1.12	2.53×10^8	50.30	6.93	41.84	0.96

2.2 Preparation of Catalysts

Three types of catalysts were prepared: Group 1 (HZSM-5, CaHZSM-5 and ZnHZSM-5), Group 2 (zeolite 5A) and Group 3 (Kaolin).

In Group 1, CaHZSM-5 and ZnHZSM-5 were prepared from powders of NH₄HZSM-5, HZSM-5 directly from the chemical store. The above three types of catalysts were blended with Kaolin powders at weight ratio 1:1. Pellets were dried at 120°C for 10 h, followed by calcination at the heating rate of 3~4°C/min until at 500°C for 1 h.

Zeolite 5A was crushed to the size of 2~3 mm and treated with either 0.1 mol/L HCl or 0.1 mol/L H₂SO₄ for 12 h in a reflux operation.

Pellets of Kaolin were thermally treated through the same procedures as the catalyst in Group 1 experienced. Catalyst pellets were sieved to the size of 2~3 mm as desired.

Data of characterization of the catalysts are listed in Table 2.

Table 2 Properties of catalysts

Catalyst	BET surface area (m ² /g)	Average pore size (nm)	Si/Al	Pore volume PV _{Hg} (cm ³ /g)	Acid intensity ^[9]	Acid quantity (mmol/g)
HZSM-5(50)	381.9	0.56	50	0.1729	+0.8<H ₀ <+3.3	1.20
HZSM-5(25)	387.9	0.51	25	0.1698	+0.8<H ₀ <+3.3	1.92
CaHZSM-5	360.1	0.62	50	0.1742	+1.2<H ₀ <+3.3	0.91
ZnHZSM-5	368.7	0.65	50	0.1751	+1.2<H ₀ <+3.3	0.87
Kaolin	56.8	13.6	2	0.2418	+1.2<H ₀ <+3.3	0.22
5Aa	216.9	0.47	2	0.1492	+3.3<H ₀ <+4.8	
5Ab	210.8	0.50	2	0.1527	+2.0<H ₀ <+3.3	0.08

2.3 Experimental Setup

The setup, as indicated in Fig.1, consists of such parts as a tubular fixed-bed reactor, feeding device, electric heater, temperature controller, condenser and liquid product collector. The reactor was made from a stainless steel tube (20 mm in diameter, 750 mm in length), with an inside casing for thermocouple moving longitudinally. Heat supplied from an electric heater was controlled so that the maximum operation temperature (700°C) could be maintained. Between the top and the

bottom inert packings, the fixed bed was 60 mm in height with 10 g of solid catalyst. A metering pump fed continually crude bio-oil into the reactor.

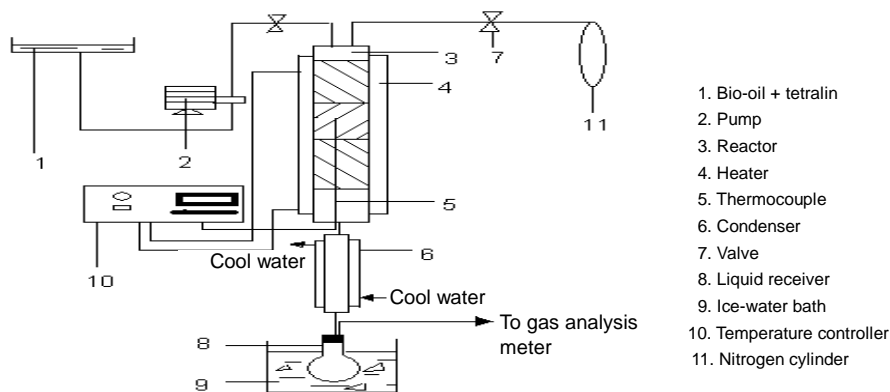


Fig.1 Flowsheet of the experimental setup

2.4 Experimental Method

The bed was preheated while nitrogen flowed as carrying gas through the reactor. As the temperature reached the desired one, feeding started. Gaseous product out of the reactor was partially condensed; the condensate was collected in the container and the gas product was sampled for analysis. Regeneration of the deactivated catalyst was carried out at 600°C for 12 h with atmospheric air.

The liquid product from thermal cracking, was separated through vacuum distillation (135 Pa, 150°C), and it settled to two immiscible phases, i.e., organic phase and water phase. The residue left from distillation was counted as the unconverted bio-oil. The wall of the reactor tube, the catalyst bed and the packing were all rinsed by solvent acetone. The washed-off tar oil was recovered from acetone. Coke was determined by weight difference of the catalyst and the packing before and after the rinsing.

Gaseous product amount was obtained from the final weight difference between feed and the sum of those, such as coke, tar oil, water, oil residue and the organic phase.

3 RESULTS AND DISCUSSION

All tests were carried out at the temperature of 380°C for 50 min with the weight space velocity of 3.1 h⁻¹. The yield of the product is defined as

$$Y = \left(\frac{m}{\text{feed}} \right) \times 100\% (\omega),$$

where m is the weight of a product.

Conversion is defined as

$$X = \frac{\text{feed} - \text{residue oil}}{\text{feed}} \times 100\% (\omega).$$

Weight space velocity WHSV is defined as

$$\text{WHSV} = \frac{\text{feeding rate (g/h)}}{\text{catalyst (g)}} (\text{h}^{-1}).$$

3.1 Effects of Catalyst Types

Yield of the organic phase from the thermal cracking is an important benchmark to evaluate the employed catalysts, and closely related to the acid intensity of catalyst, total amount of acid, ratio of Si/Al, and the micro-structure of the solid. They in turn affect the distribution of activity sites. In general, the higher the ratio of Si/Al is, the greater the activity and stability of the catalyst are; the stronger the acidity, the greater the activity and selectivity. Though tests were carried out under the same operation conditions, catalysts of different types affected the results differently.

Table 3 Effect of catalyst type on the yield of products (% , ω)

Catalyst type	Organic distillate	Coke	Tar	Aqueous phase	Residue oil	Conversion	Gas
	6.7	53.3	4.8	16.7	15.3	84.7	3.2
HZSM-5(50)	23.8	33.4	4.5	25.3	3.4	96.6	9.6
HZSM-5(25)	22.1	31.7	5.8	25.1	4.1	95.9	11.2
Kaolin	19.9	25.6	5.7	28.1	7.8	92.2	12.9
Zeolite 5Aa	18.3	39.2	3.6	25.1	9.2	90.8	6.6
Zeolite 5Ab	19.5	39.1	4.3	23.6	9.1	90.9	6.4
CaHZSM-5(50)	17.7	34.7	5.7	27.7	7.3	92.7	7.9
ZnHZSM-5(50)	18.7	33.9	4.9	26.1	8.5	91.5	7.9

The test results in Table 3 show that most of the bio-oil under thermal cracking turned into coke without the presence of catalyst and resulted in a low yield of organic phase. The presence of catalysts increased the yields of organic phase and reduced coke formation to a different degree. Of all the tested catalysts, HZSM-5(50) had the most positive effect on the yield of organic phase as high as 23.8% (ω). Zeolite 5A, as compared with catalysts CaHZSM-5 and ZnHZSM-5, had a better effect on the yield of organic phase, though not as good as HZSM-5.

Catalyst Kaolin resulted in the lowest coke formation with a medium yield of organic phase. Zeolite 5A caused severe coking.

The presence of catalysts increased the conversion of bio-oil from 84.7% (without catalyst) to 96.6% in average and led to the increasing formation of water indiscriminately.

The gas product (Table 4) mainly consisted of CO₂, CO, C₂H₄, CH₄ and H₂. Because of the deficiency of hydrogen in crude bio-oil, the formation of CO₂ and CO is a desirable route to remove oxygen rather than formation of H₂O.

Table 4 Effect of catalyst type on gas composition (% , ω)

Catalyst type	CO ₂	CO	C ₂ H ₄	CH ₄	H ₂	N ₂ and other component
	5.6	8.7	15.6	2.8	4.1	63.2
HZSM-5(50)	10.6	14.8	8.3	3.6	5.7	57.0
HZSM-5(25)	10.2	14.7	8.5	3.9	5.8	56.9
Kaolin	9.6	13.9	10.5	3.1	6.2	56.7
Zeolite 5Aa	9.9	14.4	9.2	3.9	6.0	56.6
Zeolite 5Ab	9.1	14.2	9.1	3.7	5.9	58.0
CaHZSM-5	11.1	14.6	8.1	3.5	5.6	57.1
ZnHZSM-5	10.5	14.9	8.7	3.0	5.8	57.1

3.2 Effect of Regeneration

The effect of regeneration of deactivated catalyst HZSM-5(50) on the results of catalytical thermal cracking was investigated. The deactivated catalyst was regenerated in air atmosphere at 600°C for 12 h.

The catalyst was tested and regenerated for 5 times. Activity fell with regeneration: the yield of organic phase fell from 23.8% to 20.6% (ω), coke formation rose and conversion decreased from 96.6% to 93.7% (ω) (Table 5). As to the gas product, there was no evident change in composition except a slight decrease in the content of C₂H₄ and CH₄ (Table 6).

Table 5 Effect of catalyst regeneration on the yield of products (% , ω)

	Organic distillate	Coke	Aqueous phase	Tar	Gas	Conversion
Fresh HZSM-5(50)	23.8	33.4	25.3	4.5	9.6	96.6
1R HZSM-5(50)	23.9	32.8	25.9	3.8	10.5	96.9
2R HZSM-5(50)	23.5	33.7	24.7	4.2	9.8	95.4
3R HZSM-5(50)	23.2	33.9	24.9	4.5	9.3	95.8
4R HZSM-5(50)	22.1	35.1	22.8	4.6	8.7	93.3
5R HZSM-5(50)	20.6	39.4	20.7	4.4	8.5	93.7

Table 6 Effect of catalyst regeneration on gas composition (% , ω)

	CO ₂	CO	C ₂ H ₄	CH ₄	H ₂	N ₂ and others
Fresh HZSM-5(50)	10.6	14.8	8.3	3.6	5.7	57.0
1R HZSM-5(50)	10.5	14.1	8.0	3.5	5.8	58.1
2R HZSM-5(50)	11.1	14.5	7.9	3.5	5.3	57.7
3R HZSM-5(50)	10.3	13.9	7.9	3.4	5.1	59.4
4R HZSM-5(50)	10.7	14.7	7.5	3.3	5.4	58.4
5R HZSM-5(50)	10.9	14.2	7.1	3.0	5.2	59.6

The data in Tables 5 and 6 indicate that with repeated regeneration of catalyst, the yield of coke rose while that of gas fell, but the gas composition did not change significantly. This phenomenon implies that deactivation by coke blocking pores led to the decrease in the amount of exposed activity sites while the thermal cracking did not change its mechanism.

The analysis of organic phase on the instrument Vario EL III indicates, as shown in Table 7, that fresh catalyst HZSM-5(50) resulted in relatively efficient removal of oxygen from bio-oil, i.e., oxygen content fell from 41.84% to 21.01% (ω). However, the increase in oxygen content from 21.01% to 30.22% (ω) in the upgraded oil verified the gradual loss of activity with regeneration.

Table 7 Effect of catalyst regeneration on composition of organic phase (% , ω)

	C	H	O		C	H	O
Bio-oil	50.30	6.93	41.84	3R HZSM-5(50)	69.79	7.11	23.00
Fresh HZSM-5(50)	71.81	7.08	21.01	4R HZSM-5(50)	66.20	6.95	26.75
1R HZSM-5(50)	70.97	7.06	21.87	5R HZSM-5(50)	62.77	7.01	30.22
2R HZSM-5(50)	71.23	7.02	21.65				

4 CONCLUSIONS

(1) Catalysts HZSM-5(50), HZSM-5(25), zeolite 5A, CaHZSM-5, ZnHZSM-5, Kaolin were employed in catalytical thermal cracking of bio-oil to improve the yield of organic phase and reduce coking. They affected the results to a different degree.

(2) Of all the six catalysts, the presence of catalyst HZSM-5(50) in upgrading resulted in the highest yield of organic phase, efficient removal of oxygen from bio-oil in the form of CO₂ and CO.

(3) Coking is the main problem in catalytical thermal cracking, which may cause deactivation and short life of catalysts.

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