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Studies on catalytic pyrolysis of heavy oils: Reaction behaviors and mechanistic pathways

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Abstract

Catalytic pyrolysis of heavy oils on various catalysts was investigated in a confined fluidized bed reactor. As for catalytic pyrolysis of Chinese Daqing atmospheric residue (Daqing AR) on catalyst CEP-1, reaction temperature, residence time, weight ratios of catalyst-to-oil, steam-to-oil and feed properties have significant influence on product yields and product distribution. The optimal laboratory operating conditions are as follows: reaction temperature is within 650–680 °C, residence time within 2.0–4.0 s and catalyst-to-oil weight ratio within 13–18. The catalytic pyrolysis ability becomes better and the yields of light olefins become higher with the larger H/C mol ratio and the lower aromatic carbon content of feedstocks. After the cracking mechanisms of hydrocarbons are analyzed and the thermal pyrolysis of Daqing AR is investigated, a mechanism parameter R_M is proposed to study the mechanistic pathways of heavy oil catalytic pyrolysis. As for the processes of Daqing AR catalytic pyrolysis on catalysts LCM-5 and CEP-1, the relative acting percentage of the free radical mechanism and that of the carbonium ion mechanism are obtained.

Keywords: Catalytic pyrolysis; Heavy oil; Reaction behavior; Mechanistic pathway; Ethylene; Propylene

1. Introduction

Catalytic pyrolysis, a promising technology for the production of light olefins, is usually conducted at high temperature over special catalysts. Compared with conventional steam pyrolysis, catalytic pyrolysis can not only reduce reaction temperature and energy cost, but also allow one to flexibly adjust product distribution. Catalytic pyrolysis can also produce light olefins from a wide range of lower quality feedstocks, such as heavy oils.

Studies of catalytic pyrolysis on heavy oil have been carried out since the 1960s, but these studies did not attract great interest until the 1980s. Up to now, many technologies of heavy oil catalytic pyrolysis have been studied and developed, together with pyrolyzing catalysts [1]. Experimental research shows that both product yields and the effects of operating conditions on product distribution vary greatly with both catalyst properties and feed properties, indicating that the processes of hydrocarbon catalytic pyrolysis are very complicated [2–4].

One of the most important aspects in understanding heavy oil catalytic pyrolysis is its mechanistic pathway. But unfortunately, there has not been a uniform viewpoint that could be accepted by all researchers so far. The majority of researchers think that hydrocarbon catalytic pyrolysis follows the free radical mechanism [5–7], while others consider that pyrolyzing reactions on acidic molecular sieve catalysts proceed by the carbonium ion mechanism [8,9], and still another group of researchers believes that pyrolyzing reactions on acidic molecular sieve catalysts (especially for the catalysts of catalytic pyrolysis process (CPP) technology) proceed by both the carbonium ion and the free radical mechanisms [10,11].

It is reported that the reaction mechanisms of catalytic pyrolysis vary with catalysts and technologies. Generally, catalytic pyrolysis involves catalytic cracking reactions and thermal cracking reactions, following both the carbonium

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ion mechanism and the free radical mechanism. As for catalytic pyrolysis processes on metal oxide catalysts at high temperature, the free radical mechanism plays a leading role; as for those on acidic molecular sieve catalysts at low temperature, the carbonium ion mechanism plays a primary part; and as for those on zeolite molecular sieve catalysts with double acidic centers, both the free radial mechanism and the carbonium ion mechanism play important roles [1]. However, as far as a concrete catalytic pyrolysis process is concerned, the percentage contributions of the two reaction mechanisms are still unknown.

In the present work, we investigate the reaction behaviors of heavy oil catalytic pyrolysis over catalyst CEP-1, and then introduce a mechanism parameter R_M, which is used to study the mechanistic pathways of hydrocarbon catalytic pyrolysis.

2. Experimental

2.1. Feedstocks and catalysts

In this study, Chinese Daqing AR, Chinese Daqing vacuum gas oil (Daqing VGO), Chinese Daqing vacuum residue (Daqing VR) and Chinese Huabei atmospheric residue (Huabei AR) were used as feedstocks; the main properties of each type are given in Table 1. The catalysts were CEP-1 (used for CPP technology), LCM-5 (used for heavy-oil contact cracking (HCC) technology) and AKZO (used for FCC technology), and their primary properties are listed in Table 2.

2.2. Apparatus

In experiments of heavy oil catalytic pyrolysis, a confined fluidized bed reactor was used; the schematic diagram can be seen in references [12,13]. It is comprised of five sections: oil and steam input mechanisms, a reaction zone, temperature control system and a product separation and collection system. A variable amount of distilled water was pumped into a furnace to form steam, and then mixed with the feedstock pumped simultaneously by another pump at the outlet of a constant temperature box. The mixture was heated to approximately 500 °C in a pre-heater, and then entered into the reactor with an effective volume of about 580 ml.

Table 1
Properties of pyrolysis feedstocks

	Feedstocks			
	Daqing AR	Daqing VR	Daqing VGO	Huabei AR
Density (20 °C) g/cm^3	0.9069	0.9221	0.8011	0.9162
Viscosity (100 °C) mm^2/s	28.9	106	7.2	43.3
Carbon residue (wt%)	4.3	8.8	0.05	8.9
Molecular weight	577	895	426	608
Hydrogen (wt%)	13.11	12.78	13.58	12.87
Carbon (wt%)	86.52	86.93	86.36	86.51
H/C mol ratio	1.82	1.76	1.89	1.79
Aromatic carbon (wt%)	10.90	13.76	6.84	13.00
Group analysis (wt%)				
Saturates	57.08	42.91	85.39	56.80
Aromatics	27.61	34.53	11.98	22.65
Resin and asphaltene	15.31	22.56	2.63	20.55

Table 2
Properties of pyrolysis catalysts

	Catalysts		
	CEP-1	LCM-5	AKZO
Micro-activity index	70	3	57
Pore volume (cm^3/g)	0.19	0.11	0.092
Surface area (m^2/g)	80	38	76.61
Packing density (g/cm^3)	0.97	1.20	0.91
Particle density (g/cm^3)	1.5	–	–
Particle size distribution (wt%)			
0–20 (μm)	1.2	2.0	1.4
20–40 (μm)	13.4	18.8	10.6
40–80 (μm)	55.9	56.1	49
>80 (μm)	29.5	24.1	39

2.3. Operating conditions

The operating conditions for the main catalytic pyrolysis tests are summarized in Table 3.

2.4. Analytical methods

Catalytic pyrolysis products include pyrolysis gas, pyrolysis liquid and coke. An Agilent 6890 gas chromatograph with Chem Station software was used to measure the volume percentage of components in pyrolysis gas. The equation of state for ideal gases converts the data to mass percentages. The pyrolysis liquid was analyzed with a simulated distillation gas chromatogram to get the weight percentage of gasoline, diesel oil and heavy oil. Coke content on catalysts was measured with a coke analyzer.

3. Reaction behaviors of heavy oil catalytic pyrolysis

For heavy oil catalytic pyrolysis on CEP-1, the influences of operating conditions and feed properties on product yields and product distribution were investigated.

Table 3
Operating conditions for main pyrolysis tests

Item	Value
Temperature of reactor (°C)	600–716
Temperature of steam furnace (°C)	300
Temperature of pre-heater (°C)	500
Water inflow (ml/min)	1.0–6.0
Oil inflow (g/min)	2–10
Catalyst loaded (g)	20–80
Residence time (s)	1.5–4.5
Catalyst-to-oil weight ratio	6–27
Steam-to-oil weight ratio	0.2–1.6