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Reaction performance of FCC slurry catalytic cracking

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ABSTRACT

The condensation of heavy hydrocarbon causes the coke formation inside the disengager vessel. Slurry oil is the heaviest component of FCC hydrocarbon products and most likely to be condensed to form coke. Converting slurry to lighter hydrocarbons can alleviate coke formation. The slurry cracking experiments were carried out in a confined fluidized bed reactor. The results showed that the crackability of slurry was lower than that of FCC feedstock, due to the difference of their properties. About 30 wt.% heavy oil remained in the product after the slurry was cracked, but its end point declined and the heavier component decreased. The comparison of slurry cracking results at different reaction temperatures and regenerated catalyst contents indicated that the appropriate operating conditions for slurry conversion were the reaction temperature of 500 °C and the regenerated catalyst content within 25–50 wt.%.

1. Introduction

The fluidized catalytic cracking of hydrocarbons is the main stay process for the production of gasoline and light hydrocarbon products from heavy hydrocarbons such as vacuum gas oils. The resource of the crude oil forces the refiners to process more and more vacuum resid in FCC units [1]. With the use of heavier feedstocks, increasing amounts of coke are found inside fluid catalytic cracking (FCC) disengager vessel [2]. Coke is commonly observed on the surface of the cyclone barrels, disengager dome, and walls [3,4]. Coke deposition in the disengager vessel reduces the operating reliability of FCC unit, due to the constant risk of problems linked to hampered catalyst circulation caused by pieces of coke breaking loose [5,6].

Coke formation has been observed where condensation of hydrocarbon vapors occurs [3]. Heavier boiling components in the cracked products may be very close to their dew point, and they will easily condense and form coke nucleation sites on even slightly cooler surfaces. There are more heavy hydrocarbons in the FCC feedstocks with the increase of the resid blending percentage. It is hard to atomize completely the feedstocks, and the heavy components cannot be fully vaporized and adhere to the surface of the catalyst. The unvaporized heavy hydrocarbons are stripped in the stripping section, and enter the disengager. Passage of stripped hydrocarbons through the cooler area of the disengager vessel, along with their extended residence time inside the vessel, enhances the chance of condensation of the heaviest components of stripped hydrocarbons, which causes coke formation inside the disengager vessel.

In the commercial operation, there are the two basic methods to minimize coking: avoid dead spots and prevent heat losses. An example of the first method is using dome steam or purge steam to sweep out stagnant areas in the disengager [7,8]. An example of the second method is using proper insulation in the disengager vessels [9]. In fact, the essential method to solve coking problems is to prevent heavy hydrocarbons from entering the disengager. In other words, heavy hydrocarbons should be converted to lighter hydrocarbons as completely as possible before they enter the disengager. Therefore, if regenerated catalyst is introduced into the stripping zone and mixed with spent catalyst, the mixture of spent and regenerated catalysts flow downward through the stripper, where the countercurrent stream strips the entrained hydrocarbon from the catalyst mixture. This admixing of spent and regenerated catalyst not only raises the spent catalyst temperature to effect desorption of entrained hydrocarbon, but also improves the catalyst activity to enhance catalytic cracking of the entrained hydrocarbon, thus converting more entrained heavy hydrocarbons to lighter hydrocarbon products. Consequently, the quantity of the heavy hydrocarbons prone to coke is decreased, which reduces subsequent coke formation in the disengager vessel.

Slurry oil is the heaviest component of FCC hydrocarbon products, and it is most likely to be condensed to form coke. Therefore, it should be converted to lighter hydrocarbons as completely as possible. In general, FCC Slurry is mainly used as blending composite for heavy fuel oil [10]. In some commercial FCC unit, the slurry oil can be recycled and cracked along with fresh

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feed. There is, however, limited information in the open literature on the cracking behavior of FCC slurry. So, this study was designed to investigate the catalytic cracking behavior of FCC slurry, and then to determine the appropriate operating conditions to convert slurry in FCC stripping section.

2. Experimental

2.1. Feedstocks and catalysts

The slurry was sampled from the commercial FCC unit of Petrochina Huabei Petrochemical Corporation. The physical properties of slurry oil analyzed were density, molecular weight, carbon residue, and hydrocarbon type. These analyses were tabulated in Table 1. The catalyst was equilibrium LBO-16 sample from the same commercial FCC unit, and its major properties were presented in Table 2. The catalysts used in our experiments included spent catalysts and regenerated catalysts. The coke on spent catalysts was 1.12 wt.%, while the coke on regenerated catalysts was 0.02 wt.%.

2.2. Apparatus

Cracking experiments were carried out in a confined fluidized bed reactor system, shown in Fig. 1. It is comprised of five sections: oil and steam input mechanisms, reaction zone, temperature control system, products 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 in a pre-heater, and then entered into the reactor, where catalytic cracking reactions took place. After reaction, the oil gas was cooled and separated into liquid sample and gas sample.

Table 1
Properties of FCC slurry.

Item	Data
Density (g/cm^3, 20 °C)	0.9668
API	14.3
Carbon residue (wt.%)	5.70
Molecular weight	425
H/C ratio	1.48
Group analysis (wt.%)	
Saturates	50.46
Aromatics	34.85
Resins	9.40
Asphaltenes	5.29

Table 2
Properties of catalyst LBO-16.

Item	Data
Micro-activity index	67
Surface area (m^2/g)	102
Pore volume (cm^3/g)	0.28
Packing density (g/cm^3)	0.90
Component (wt.%)	
Al_2O_3	44.30
Re_2O_3	4.01
Metals content	
Na (wt.%)	0.24
Fe (wt.%)	0.41
Cu (μg/g)	24
Ni (μg/g)	12465
V (μg/g)	431
Particle size distribution (wt.%)	
0–20 μm	0
20–40 μm	5
40–80 μm	51
>80 μm	44

2.3. Analytical methods

Catalytic cracking products include gas, liquid and coke. An Agilent 6890 gas chromatograph with Chem Station software was used to measure the volume percentage of components in the gas product. The equation of state for ideal gases converts the volume data to mass percentages. The liquid product 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.

2.4. Operating conditions

The cracking experiments of slurry oil were carried out over regenerated catalysts sampled from a commercial FCC unit. The

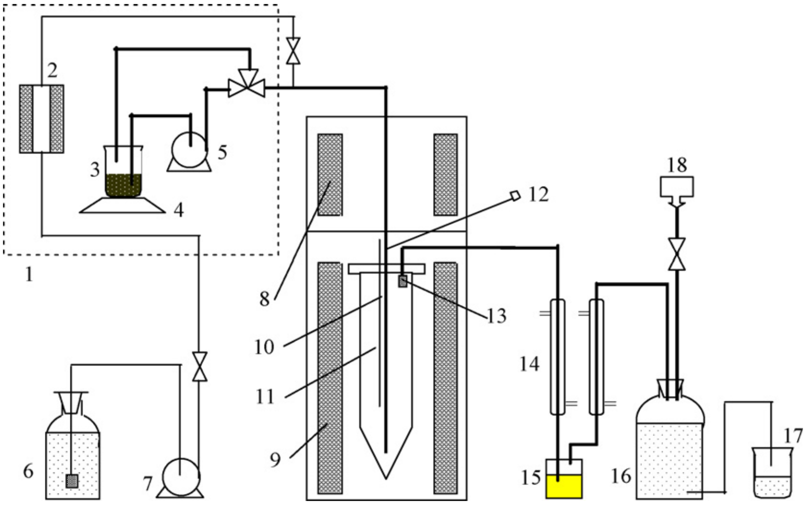

Fig. 1. Schematic diagram of confined fluidized bed reactor unit. (1) Constant temperature box; (2) steam furnace; (3) feedstock; (4) electronic balance; (5) oil pump; (6) water tank; (7) water pump; (8) pre-heater; (9) reactor furnace; (10) thermocouple; (11) reactor; (12) inlet and outlet of catalyst; (13) filter; (14) condenser; (15) collecting bottle for liquid products; (16) gas collection vessel; (17) beaker; (18) gas sample bag.

operating conditions were listed as follows: catalyst loading was 60 g, reaction temperature was 500 °C, catalyst-to-oil weight ratio was 6, and weight hourly space velocity was 20 h^{-1}.

In order to convert slurry oil to lighter hydrocarbons and reduce coke formation in the disengager vessel, regenerated catalysts are introduced into the stripping section to raise reaction temperature and improve catalyst activity. The quantity of the introduced regenerated catalyst and the temperature are key parameters to determine the conversion of slurry. So, we focused on investigating the effect of the two parameters on catalytic cracking of slurry oil. Spent catalysts and regenerated catalysts were mixed in different weight ratios. The content of regenerated catalyst in catalyst mixture varied in the range of 0–100 wt.% and the temperature was within 450–550 °C. Other operating conditions were the same as those in the cracking experiments of slurry oil.

3. Results and discussion

3.1. Catalytic cracking behavior of FCC slurry

Fig. 2 compared the results of cracking FCC slurry and corresponding FCC feedstock with reaction temperature of 500 °C. As expected, a portion of FCC slurry can be converted during catalytic cracking. However, the slurry showed lower conversion. Moreover, the product yields of cracking slurry and FCC feedstock were obviously different. The light oil yield of cracking slurry was only 56% of that of cracking FCC feedstock, and the coke yield was 2.5 times higher than that of cracking FCC feedstock. It is obvious that FCC slurry is more difficult to crack.

The difference in crackability of slurry and feedstock are due to the difference in their properties. Table 3 listed the major properties of corresponding FCC feedstock. The comparison between Tables 1 and 3 showed that slurry oil had much higher density and carbon residue than FCC feedstock, and the ratio of hydrogen to carbon (H/C) of slurry oil was much lower than that of FCC feedstock. Previous work showed that the coke formed in FCC unit was not pure carbon atom, but condensed aromatic, whose H/C ratio was between 0.7 and 1.0 [11]. The H/C ratio of light oil products was approximately 2, and it was higher than 2 for gas products. The H/C ratios of saturates, aromatics, resins and asphaltenes in straightrun heavy oil were about 2.0, 1.5, 1.3 and 1.0, respectively [12]. The H/C ratio of slurry in the present study was 1.48, and between that of aromatics and resins. It was obvious that the hydrogen content in slurry oil was much lower than that in FCC feedstock. The hydrogen added in light oil had to be transformed from coke precursors during slurry catalytic cracking. Hence, from the viewpoint of hydrogen equilibrium, it is impossible to produce a large amount of light oil products. Consequently, light oil yield of cracking slurry was much lower than that of cracking FCC feedstock.

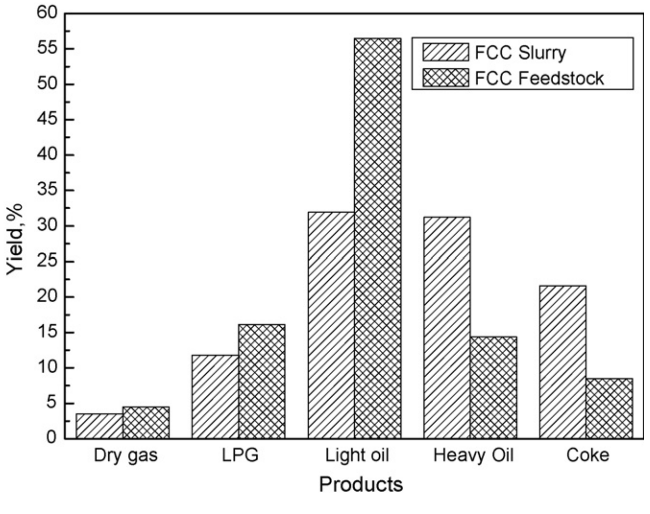

Fig. 2. Cracking results of slurry and corresponding FCC feedstock.

Table 3
Properties of FCC feedstock.

Item	Data
Density (g/cm^3, 20 °C)	0.9004
Carbon residue (wt.%)	4.35
H/C ratio	1.80
Group analysis (wt.%)	
Saturates	60.3
Aromatics	25.0
Resins	14.5
Asphaltenes	0.2

Tables 1 and 3 showed that the aromatic content in slurry oil was 1.4 times higher that in FCC feedstock. The aromatics in slurry were characterized by lower molecular weight, more condensed rings with less and shorter chains in structure. Most of them were mainly trinuclear and tetranuclear aromatics, and therefore evidently different from those in FCC feedstock [13]. Moreover, the slurry contained 10 wt.% resins, which were polar compounds with polynuclear aromatics in structure [14]. In general, the feedstock containing polynuclear aromatics and olefins is more easily to form coke [15]. The characteristic of aromatics and resins in slurry determined that the slurry was harder to be cracked, and converted into coke by hydrogen-transfer and condensation reaction during catalytic cracking. Furthermore, the slurry oil was the cracking product and must contain some olefins. Nevertheless, the group analysis in Table 1 did not include olefins. The olefins also led to form more coke during slurry catalytic cracking.

The content of heavy component in slurry above 550 °C was 22.0 wt.%, indicated that the slurry contains a large amount of heavier components with coking tendency. Whereas, the content of heavy component above 550 °C in slurry cracking products was only 0.7 wt.%, and its end point was 557.8 °C. It was observed that after the slurry was cracked, about 30 wt.% heavy oil remained in the product, but its end point declined and the heavier component also decreased. It implied that the condensation of stripped heavy hydrocarbons in the disengager vessel would decrease, thus reducing subsequent coke formation.

3.2. Effect of reaction temperature and regenerated catalyst content on slurry cracking

The above experiments showed FCC slurry had some crackability at appropriate operating conditions. The sampling in commercial RFCC strippers showed that heavy hydrocarbons carried by catalysts underwent thermal cracking, catalytic cracking and dehydrogenation condensation reactions during stripping [16]. Due to the low temperature and the catalyst was rather inactive, only a little reaction occurred. So, in order to enhance the conversion of heavy hydrocarbons in stripping section, regenerated catalysts should be introduced to raise reaction temperature and therefore improve catalyst activity. The following study was designed to determine the appropriate operating conditions to convert heavy hydrocarbons in FCC stripping section.

The cracking results of slurry oil at different reaction temperatures and regenerated catalyst contents were summarized in Table 4. In this study, the slurry oil conversion was defined as the sum of the yields of dry gas, liquefied petroleum gas (LPG),

Table 4
Cracking results of slurry oil at different reaction temperatures and regenerated catalyst contents.

Reaction temperature (°C)	Regenerated catalyst Content (wt.%)	Product yield (wt.%)					
		Dry gas	LPG	Gasoline	Diesel oil	Heavy Oil	Coke
450	0	3.3	7.8	18.3	11.3	46.2	13.1
	25	3.7	10.8	21.8	11.7	36.2	15.8
	50	3.4	8.8	22.4	12.1	39.4	13.9
	75	2.2	10.8	21.4	12.0	33.4	20.2
	100	2.6	10.2	21.7	10.6	30.8	24.1
475	0	3.4	8.1	19.2	11.0	45.1	13.2
	25	4.0	9.9	20.2	12.0	37.4	16.5
	50	3.7	9.9	20.8	12.0	35.9	17.7
	75	3.5	10.5	22.0	10.4	32.4	21.2
	100	3.3	10.0	19.5	11.4	33.3	22.5
500	0	4.5	10.8	17.1	12.0	38.9	16.7
	25	4.5	13.2	23.5	11.4	29.4	18.0
	50	4.0	11.5	23.7	12.0	31.7	17.1
	75	3.9	11.9	21.5	11.8	31.6	19.3
	100	3.5	11.8	19.6	12.3	31.2	21.6
525	0	5.6	12.0	20.1	11.4	32.3	18.6
	25	4.8	12.9	20.2	11.1	31.6	19.4
	50	6.2	14.8	24.1	10.7	23.8	20.4
	75	4.4	12.4	23.1	11.1	27.9	21.1
	100	3.4	11.2	23.6	10.7	33.3	17.8
550	0	5.1	10.5	17.6	10.0	37.8	19.0
	25	6.7	13.2	22.5	10.9	26.6	20.1
	50	6.7	14.1	22.8	10.4	24.1	21.9
	75	6.6	14.7	21.1	10.1	25.5	22.0
	100	5.5	13.4	22.9	10.4	25.9	21.9

gasoline, diesel oil and coke. Fig. 3 showed the effect of reaction temperature and regenerated catalyst content on the slurry conversion. In experimental tests, the slurry conversion was below 75%, and went up with increasing reaction temperature. The influence of regenerated catalyst content on slurry oil conversion was not monotonic with respect to the quantity of regenerated catalyst. As the regenerated catalyst content was below 50 wt.%, the conversion increased greatly with increasing the quantity of regenerated catalyst. As the regenerated catalyst content was above 50 wt.%, the addition of regenerated catalyst could not evidently improve the conversion of the slurry oil and the conversion decrease a little at high temperature (above 500 °C).

The desirable products of slurry cracking are gasoline and diesel oil. Fig. 4 compared the light oil yield of slurry cracking at different reaction temperatures and regenerated catalyst contents. It was observed that the light oil yield increased evidently with the regenerated catalyst content varied from 0 to 25 wt.%, whereas the regenerated catalyst content had a little influence on light oil yield as the content was above 25 wt.%. The high light oil yield was obtained at 500 °C and the regenerated catalyst content ranging from 25 to 50 wt.%, and increasing further the reaction temperature and regenerated catalyst content was unfavorable for getting more light oil.

As mentioned above, a large amount of coke was formed during slurry cracking. The influence of the reaction temperature and the

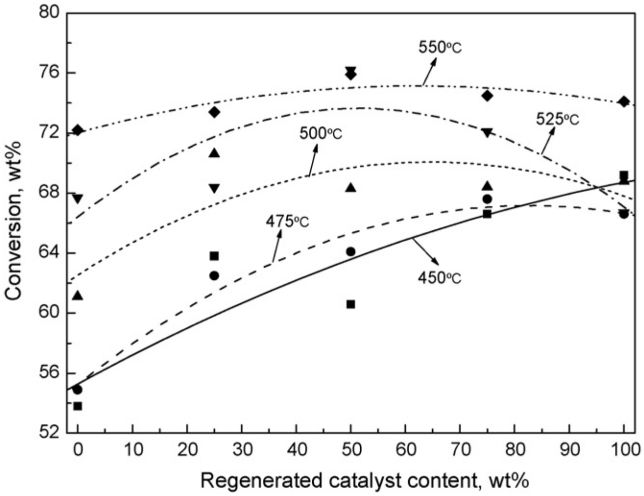

Fig. 3. Effect of reaction temperature and regenerated catalyst content on slurry conversion.

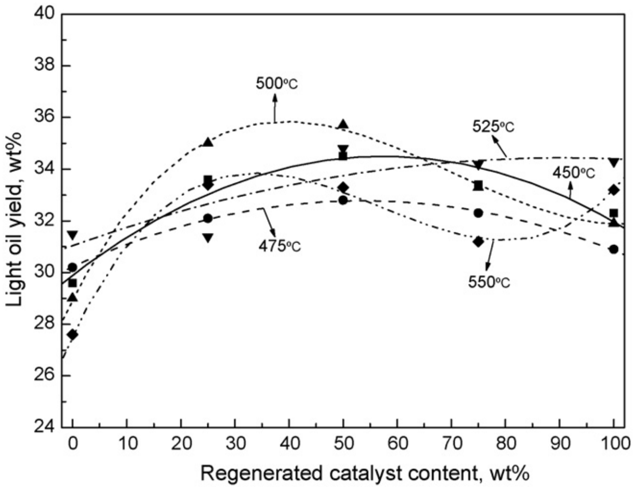

Fig. 4. Effect of reaction temperature and regenerated catalyst content on light oil yield.

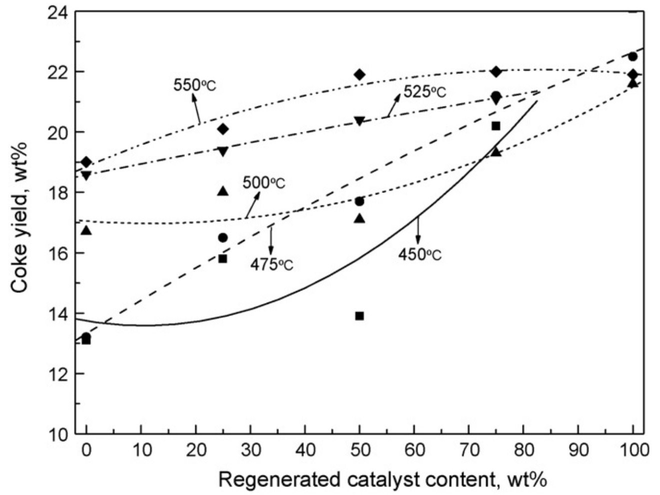

Fig. 5. Effect of reaction temperature and regenerated catalyst content on coke yield.

quantity of regenerated catalyst on coke yield was shown in Fig. 5. The coke yield went up with increasing reaction temperature and regenerated catalyst content. The higher the reaction temperature and the regenerated catalyst content was, the higher activity catalyst possessed. Consequently, the cracking reaction occurred more drastically and more coke was formed.

3.3. Operating conditions to convert slurry in FCC stripping section

The purpose of introducing regenerated catalysts into the stripping section is to convert the entrained heavy hydrocarbons to lighter hydrocarbons as completely as possible. As a high conversion is pursued during slurry cracking, the formation of more light oil and less coke is desirable. The experimental results indicated that higher temperature was favorable for the conversion of slurry oil, which however resulted in more coke deposit on the catalyst. The increase of the deposition of coke on the catalyst can lead to excessive heat generation during catalyst regeneration. The additional heat can create a number of problems, including upsetting the heat balance and damaging the equipment and the catalyst. To reduce the formation of coke, the temperature in stripping section should not be very high. Fig. 4 showed that the light oil yield was higher at the reaction temperature of 500 °C. Taking conversion and the yield of light oil and coke into account, the appropriate operating temperature for slurry cracking was about 500 °C. The results showed that at 500 °C, both the conversion and light oil yield increased initially and then decreased slightly with the increase of the regenerated catalyst content. As the regenerated catalyst content was in the range of 25–50 wt.%, both slurry conversion and light oil yield were satisfied. On the basis of the above research, it can be concluded that, the appropriate operating conditions for slurry conversion are as follows: the reaction temperature is about 500 °C and the content of regenerated catalyst introduced to the stripping section is within 25–50 wt.%.

4. Conclusions

The cracking experiments of slurry oil from a commercial FCC unit over regenerated catalysts from the same FCC unit were carried out in a confined fluidized bed reaction. The results showed that the slurry oil was harder to crack than corresponding FCC feedstock, due to higher density and carbon residue, lower H/C ratio, as well as more polynuclear aromatics and olefins. Hence, more coke formed and light oil yield decreased obviously during slurry cracking. After the slurry was cracked, about 30 wt.% heavy oil remained in the product, but its end point declined and the heavier component also decreased. The reaction temperature and regenerated catalyst content had a profound effect on the slurry conversion, light oil and coke yield. The slurry conversion and the coke yield went up with increasing reaction temperature. As the regenerated catalyst content was below 50 wt.%, the conversion and light oil yield increased with the quantity of regenerated catalyst. As the regenerated catalyst content was above 50 wt.%, the addition of regenerated catalyst could not pronouncedly improve the conversion and furthermore decrease the light oil yield. The appropriate operating conditions for slurry conversion were the reaction temperature of 500 °C and the regenerated catalyst content within 25–50 wt.%.

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