CHEMICAL STRUCTURE CHANGE OF RECYCLING VACUUM BOTTOM RESIDUE FROM SLURRY-BED HYDROCRACKING OF KARAMAY ATMOSPHERIC RESIDUE IN THE PILOT PLANT

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INTRODUCTION

Since the early 1980s, slurry-bed hydrocracking of residue has been developed for upgrading poor-quality residue, which may be high content of sulfur, metal and Conrason carbon residue, to produce distillate product(1). Conventionally slurry bed hydrocracking of residue is achieved by once-through heating residue in a high-pressure hydrogen atmosphere in the presence of a dispersed and disposable catalyst (2). However, once-through hydrocracking mode dependent on different reaction conditions can give 60%~80 % conversion (<524^{o}C). To achieve higher conversion of residue and keep coke formation low and the operation successful at the same time, some hydrocracking modes can be adopted such as cracked vacuum residue recycling, cracked atmospheric residue recycling and cracked vacuum gas oil recycling. Generally cracked atmospheric residue recycling model can achieve higher conversion and get more distillate products than the other three models at the same reaction conditions. The objective of this study is to investigate chemical structure change of cracked atmospheric residue recycling from slurry-bed hydrocracking and to evaluate the subfractions change in the cracked atmospheric residue recycling.

EXPERIMENTAL

The feed was chosen as Karamay atmospheric residue and obtained from Karamay Petrochemical Complex, Xingjiang, China. The property of Karamay atmospheric residue (>360^{o}C) and its vacuum residue (>500^{o}C) was presented in Table 1. Keeping the total VSHL is 1h^{-1}, Karamay atmospheric residue was hydrocracked in the presence of about 1000 ppm multi-metal dispersed catalyst, under 10MPa H_2, 445 ^{o}C,in an pilot plant of 120 kg/d and the products were fractionated into gases, naphtha (C_5~180^{o}C), AGO (180~360 ^{o}C) and atmospheric bottom residue (>360^{o}C). Some atmospheric bottom residue (about 5wt%) was thrown off, and the other atmospheric bottom residue was pumped back intermittently and mixed with the fresh feed for recycled hydrocracking (the ratio is 1:1). Thus we can obtain non-recycled atmospheric bottom residue, which is the once-through atmospheric bottom residue (ABR#), the first-time recycled atmospheric bottom residue (first-ABR), the second-time recycled atmospheric bottom residue (Sec-ABR), the third-time recycled atmospheric bottom residue (Third-ABR). The atmospheric bottom residues(>360^{o}C) were distillated into the corresponding vacuum bottom residues(>500^{o}C), which include fresh VBR(VBR), the once-through vacuum bottom residue (VBR#), the first-time recycled vacuum bottom residue(first-VBR), the second -time recycled vacuum bottom residue(Sec-VBR), the third-time recycled vacuum bottom residue(Third-VBR) and these VBRs were precipitated using n-pentane. The pentane-solubles were separated into fraction 1 (mixture of saturates, light and middle aromatics), fraction 2 (heavy aromatics), fraction 3(light resins), fraction 4 (middle resins) and fraction 5 (heavy resins) by the alumina chromatography column with 5% water. The separation scheme is shown in Figure1. The contents of H, C and average molecular weights of all subfractions were determined by Shimazsu Element Analyzer and Knauer analyzer by VPO, respectively. Structural parameters of fractions for all VBRs were calculated based on Density Method and the calculation program was shown in the appendix (2).

Table 1. Properties of Karamay atmospheric residue and Karamay Vacuum Residue

Sample	AR	VR
Density, d_4^{20}	0.9442	0.9613
Viscosity (100°C), mm^2·s^{-1}	109	1115
Molecular weight (VPO)	470	950
CCR, wt%	7.0	11.0
C, wt%	86.6	87.1
H, wt%	12.5	11.9
H/C atomic Ratio	1.73	1.62
N, wt%	0.13	0.63
S, wt%	0.13	0.24
Ni, ug·g^{-1}	11.8	21.6
V, ug·g^{-1}	0.35	0.65
Ca, ug·g^{-1}	346	460
Fe, ug·g^{-1}	10.2	20.4
Saturate wt%	50.4	35.3
Aromatic	22.2	25.6
Resin	27.2	38.3
n-C_7 Insoluble	0.2	0.8

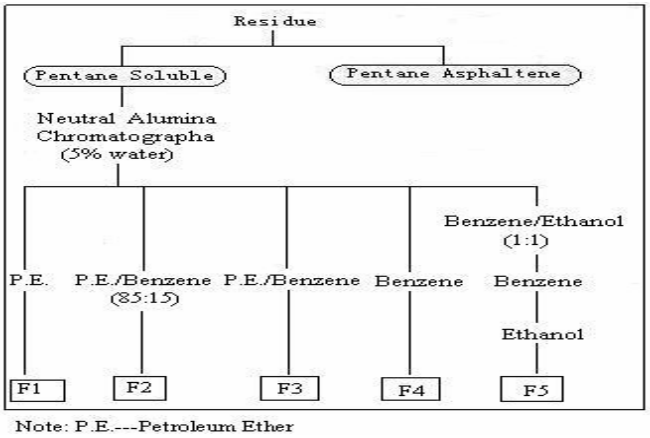

Figure1 Separation of six subfractions in residue

RESULTS AND DISCUSSION

Change of Six Fraction Yields. From Table2, it is clear that the VGO and vacuum bottom residue yields of AR have been greatly changed after slurry-bed hydrocracking. Before reaction, VGO and VBR in Karamay atmospheric residue were 41.02%, 58.98% and after hydrocracking, they were 61.77%, 38.23%. When cracked atmospheric residue was recycled from slurry bed hydrocracking(recycling ratio 1:1) , the decrease of VGO in AR and the increase of VBRs depended on different recycling times. The more recycling times were, the less yields of VGO were and the more yield of VBRs were. It shows that the recycled AR is the more refractory with the recycling times.

Tables 2 yields for different recycle times of VGO and vacuum bottom residue

	VGO(*W*/%)	VBR(*W*/%)
ABR	41.02	58.98
ABR#	61.77	38.23
First- recycled ABR	58.31	41.69
Second- recycled ABR	55.71	44.29
Third- recycled ABR	31.92	68.08

Tables 3 Subfractions yields for feed and different times recycled VBRs

	VBR	VBR#	First-VBR	Sec-VBR	Third-VBR
F1(*W*/%)	54.53	42.58	42.09	41.84	41.47
F2(*W*/%)	9.98	9.27	9.64	9.10	8.77
F3(*W*/%)	13.28	13.27	13.76	13.83	12.80
F4(*W*/%)	7.26	6.13	6.40	7.20	7.29
F5(*W*/%)	8.42	6.65	5.98	6.95	6.18
F6(*W*/%)	6.53	22.11	22.12	21.08	18.88
Coke(*W*/%)	0	1.80	2.45	2.89	4.57
F1+F2(*W*/%)	61.51	51.85	51.67	50.94	50.24
F3+F4+F5(*W*/%)	28.96	26.05	26.14	27.98	26.27

From Table3, it is clear that the yields of six sub fractions in fresh vacuum residue and residues from once-through operation and the recycling-operation have been changed, although F1+F2 (saturates and aromatics) was the main fraction of fresh VBR and hydrocracked VBRs. Among six sub fractions, F1 and F6 have considerably changed after slurry-bed hydrocracking, On the one hand, F1 in VBR decreased sharply, while F6 and coke increased sharply. On the other hand, with recycling-operation times increasing, the yields of six fractions in recycled VBRs have changed smooth. It is clear that the biggest change happened in the once-through hydrocracking operation. It is shown that it is in the first time hydrocracking process (the once-through hydrocracking process) that the cracking and condensation reaction of fresh feed was the most obvious in all processes. Although the increasing cracking yields could be achieved through recycling operation of cracked atmospheric residue, increasing degree of that was limited since cracking reaction of ABR had almost been finished. On the contrary, the degree of increasing of condensation reaction was very clear depended on the recycling-operation times.

H/C and average molecular weight of six fraction. From Table 4, H/C of six subfractions for feed and different times recycled VBR show different change. H/C of F1 hardly changed and the H/C of F2, F3, F4 and F5 decreased a little. However, H/C of F6 decreased sharply. Tables 5 give out the average molecular weight (VPO) of six subfractions for feed and different times recycled vacuum bottom residue. It is obvious that average molecular weight of all six subfractions decreased after once-through hydrocracking and different ABR recycling times hydrocracking. Among six subfractions, the decreasing trends of F6, F5 and F4 were very clear, especially for F6. It is shown that in the hydrocracking and different cracked ABR recycling hydrocracking, the moleculars of six subfractions have experienced different degree cracking reactions. On the other hand, the more complex molecular (F6, F5 and F4) have gone through the more considerable cracking reactions. In addition, the de-aggregation reaction of C_5-asphaltene can be important in the hydrocracking based on the three-time sharp change of average molecular weight before and after once -through reaction.

Tables 4 H/C of fractions for feed and different times recycled VBRs

H/C	VBR	VBR#	First-VBR	Sec-VBR	Third-VBR
F1	1.76	1.75	1.72	1.73	1.76
F2	1.51	1.43	1.31	1.31	1.35
F3	1.49	1.27	1.16	1.17	1.19
F4	1.44	1.28	1.23	1.17	1.19
F5	1.41	1.43	1.34	1.32	1.28
F6	1.38	0.88	0.84	0.83	0.86

Tables 5 Average molecular weight (VPO) of fractions for VBR and different-time recycled VBRs

	VBR	VBR#	First-VBR	Sec-VBR	Third-VBR
F1	730	682	637	614	608
F2	880	718	549	518	550
F3	1160	871	781	708	704
F4	1485	988	894	695	699
F5	1484	791	733	798	909
F6	7879	2545	2247	2330	1684

Structural parameters of subfractions for VBR and different-time recycled VBRs. From Table 6-9**,** Structural parameters of fractions for VBR and different-time recycled VBR have different degree change in the once-through hydrocracking and recycled hydrocracking process. After once-through hydrocracking, structural parameters including Condesation Index, aromaticty, C_T, C_A, R_A, R_T of six fractions have changed greatly compared to the corresponding of feed. Then after ABR recycling hydrocracking, structural parameters of six fractions have changed smooth deepened on the recycling times and the changing trend show Condesation Index, aromaticty, C_T, C_A, R_A, R_T of six fractions have more change to a smooth limit while more recycling times go on. It is shown that the substantial chemical structure change happened in the first hydrocracking. For F_6, F_5 and F_4, the important change can be more obvious

CONCLUSION:

1. Saturates and aromatics were the main subfractions of fresh VBR and all hydrocracked VBRs
2. Structural parameters of six fractions after once-through hydrocracking have changed greatly compared to the corresponding of feed. It is shown that the substantial chemical structure change happened in the first-time hydrocracking.
3. Structural parameters of six fractions have changed smooth deepened on the recycling times. After different times recycling hydrocracking, the average molecular weights of six subfractions decrease and the content of saturates decreases obviously, while asphaltene and resins increase sharply, C/H, aromaticity and Condensation Index of the asphaltene increase.

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Tables 6 Structural parameters of fractions for VBR and different-time recycled VBRs

		F1	F2	F3	F4	F5	F6
VBR	Conden. Index	0.136	0.217	0.223	0.240	0.242	0.245
	C_T	47.0	63.7	84.4	107.0	104.7	528.6
	C_A	4. 9	17.4	24.2	34.5	36.2	198.0
	R_T	4.2	7.9	10	14	14	65.8
	R_A	0.7	3.9	5.6	8.1	8.5	49.0
	R_N	3.5	4.0	4.8	5.5	5.1	16.8
VBR#	Conden. Index	0.140	0.242	0.281	0.278	0.229	0.360
	C_T	49.0	52.8	64.3	71.9	51.7	184.8
	C_A	5.6	17.6	28.6	31.8	17.4	141.1
	R_T	4.4	7.4	10.0	11.0	6.9	34.3
	R_A	0.9	3.9	6.7	7.4	3.8	34.8
	R_N	3.6	3.5	3.4	3.6	3.1	-0.5
First-times recycled VBR	Conden. Index	0.149	0.271	0.308	0.288	0.259	0.371
	C_T	46.0	40.5	57.9	64.7	50.7	166.5
	C_A	6.0	16.8	30.8	30.8	20.5	132
	R_T	4.4	6.5	9.9	10	7.6	31.9
	R_A	1.0	3.7	7.2	7.2	4.6	32.5
	R_N	3.4	2.8	2.7	3.1	2.9	-0.7
Second-times recycled VBR	Conden. Index	0.146	0.273	0.306	0.302	0.265	0.372
	C_T	44.4	38.2	52.6	50.32	56.0	172.3
	C_A	5.5	16.1	27.5	26.4	23. 4	138.0
	R_T	4.2	6.2	9.0	8.6	8.4	33.0
	R_A	0.9	3.5	6.4	6.1	5.3	34.0
	R_N	3.4	2.7	2.7	2.5	3.1	-1.0
Third-times recycled VBR	Conden. Index	0.136	0.263	0.302	0.300	0.275	0.368
	C_T	43.7	40.6	52.3	51.1	64.3	125.1
	C_A	4. 6	15.8	26.6	26.2	28.6	97.1
	R_T	4.0	6.3	8.9	8.7	9.8	24.0
	R_A	0.6	3.5	6.2	6.0	6.6	23.8
	R_N	3.3	2.9	2.7	2.6	3.2	0.2

Tables 7 Aromacity of subfractions for VBR and different-time recycled VBRs

f_a (%)	VBR	VBR#	First-VBR	Sec-VBR	Third-VBR
F1	10.37	11.28	12.96	12.41	10.51
F2	27.33	33.34	41.5	42.12	38.97
F3	28.69	44.51	53.24	52.32	50.87
F4	32.19	44.19	47.7	52.6	51.23
F5	34.56	33.6	40.42	41.74	44.56
F6	37.45	76.36	79.34	80.13	77.61

Tables8 R_T of subfractions for VBR and different-time recycled VBRs

R_T	VBR	VBR#	First-VBR	Sec-VBR	Third-VBR
F1	4.2	4.4	4.4	4.2	4.0
F2	7.9	7.4	6.5	6.2	6.3
F3	10.0	10.0	9.9	9.0	8.9
F4	14.0	11.0	10	8.6	8.7
F5	14.0	6.9	7.6	8.4	9.8
F6	65.8	34.3	31.9	33.0	24.0

Tables9 R_A of subfractions for VBR and different-time recycled VBRs

R_A	VBR	VBR#	First-VBR	Sec-VBR	Third-VBR
F1	0.7	0.9	1.0	0.9	0.6
F2	3.9	3.9	3.7	3.5	3.5
F3	5.6	6.7	7.2	6.4	6.2
F4	8.1	7.4	7.2	6.1	6.0
F5	8.5	3.8	4.6	5.3	6.6
F6	49.0	34.8	32.5	34.0	23.8

Appendix:

Density Method for calculating structural parameters of subfractions in residue is as follows:

1.Relative density: $D_4^{20}=1.4673-0.04.31\times H\%$

2.Ratio of H/C atom: $H/C =11.92\times H\%/C\%$

3.Mc/d: $Mc/d=Mc/(D_4^{20} \times C\%)$

4.Corrected Mc/d: $(Mc/d)c= Mc/d-6.0(1- C\% - H\%)/ C\%$

5.Aromaticity in an average molecular: $fa=0.09(Mc/d)c-1.15\ H/C +0.77$

6.Condesation Index in an average molecular: $C.I=2-H/C-fa$

7.Total carbon atom in an average molecular: $C_T=(C\%\times M)/12.01$

8.Aromatic carbon atom in an average molecular: $C_a= C_T \times fa$

9.Total rings in an average molecular: $R_T=[C_a\times(C.I)/2]+1$

10.Aromatic rings in an average molecular: $R_A=(C_a -2)/4$

11.naphthenic rings in an average molecular: $R_N=R_T-R_A$

Note: M refers to average molecular weight