Investigation of Coke Formation During Thermal Treatment and Hydrocracking of Liaohe Vacuum Residue

Wang Zongxian, Aijun Guo, and Guohe Que, University of Petroleum-East China Dongying, Shandong, China

Abstract

Coke formation has long been a concern of petroleum refiners and researchers as it leads to fouling coils and catalyst-beds, and deactivating catalysts during breaking and catalytic processing of vacuum resid. Hence, the study of coke formation is significant in searching for coke inhibition procedures. The purpose of this paper to make some efforts to understand the early stage of coke formation, and to characterize using microscopy and FTIR techniques. The study looked at coke formed at different process severities during thermal treatment and slurry bed catalytic hydrocracking of Liaohe vacuum resid (VR). Results show that the propensity of coke formation was related not only to reaction conditions, but also the chemical and physical properties of vacuum resid. With increasing processing severity, the coke formed in the bulk of reaction system changed from fine dispersed particulate to coke clusters. Initially-formed coke seemed to promote coke formation and growth of coke clusters, especially during thermal treatment under low pressure. The on-set of coke formation was quite closely related to the ability of the reaction system to peptize coke precursors.

Introduction

China's crude oils are relatively heavy, and at present can not fully meet domestic demand. Import of crude oil is estimated to reach 50 million tons per year by the year by the year 2000.[1] Therefore, it is critically important for China to make full use of all of our crude oil resource and to further the process of heavy oil/vacuum residues to meet the demand for lighter petroleum products. Of the available heavy oil resources, Liaohe heavy oil is currently the largest volume produced and is of relatively poor quality. Its VR is high in nitrogen, heavy metals, carbon residue and acidity. If used as a coking feedstock, the VR may produce large amounts of byproducts such as dry gas and inferior green coke. Obviously, it is not a good resid fluid catalytic cracker RFCC feedstock. Its fixed-bed catalytic hydrotreating products are not desirable.[2-4] Therefore, Liaohe VR is a plentiful heavy oil resource with special characteristics, and problems that make it worthy of further study.

Most processes for petroleum residue conversion are limited by the formation of a solid coke by-product. This limitation is very severe in the cases of visbreaking, catalytic hydrotreating and catalytic hydrocracking, in which no appreciable amount of coke can be tolerated because of the need to flow freely through coils or catalyst-bed and the need to keep the catalyst active. In the FCC, RFCC or slurry-bed catalytic hydrocracking (SBCH) processes, coke formation may deactivate catalysts and decrease the depth of upgrading. Even delayed-coking would be limited by coke formation in heating coils. Coke formation is one of key factors influencing petroleum residue upgrading. In addition to processing conditions, the physical and chemical properties and structural composition of petroleum residues dictate the action of coke formation.[5-8] A VR with low H/C atomic ratio and high carbon residue may have a high propensity to produce large amounts of coke. The inducing period of coke formation is not only related to carbon residue value but to the miscibility of residue sub-fractions and particularly to the ability of the vacuum resid system to peptize its asphaltene and coke precursors.[9-12] A long induction period of coke formation is relevant to visbreaking and hydrotreating processes. Therefore, the study of coke formation is significant in searching for coke inhibition procedures. This work is intended to take Liaohe vacuum residue as an example for study, and to investigate coke formation during thermal and hydrothermal conversion in slurry-bed catalytic hydrocracking.

Experimental

Sample

Liaohe vacuum residue was collected from Liaohe Petrochemical Plant in March 1996. Gudao VR was collected from Shengli Oil Refinery. Their general properties are listed in Table 1.

Analytical Procedures

"Isolation of six sub-fractions"

Three grams of VR were fractionated into asphaltenes (nC5–At) and pentane-soluble fraction (maltene) by n-pentane.

Then, the maltene was chromatographically separated into five fractions on a neutral alumina (about 220g, 100–200mesh, 5 wt% water) column (1.8×180cm), using the solvent system: n-pentane (300m1), n-pentane/benzene(85/15, v/v, 300ml), n-pentane/benzene (50/50,v/v, 300m1), benzene (300m1), benzene /ethanol (50/50,v/v, 150m1) and ethanol(150m1) as successive eluents. Thus, the corresponding six fractions, i.e., light oil (F1), heavy aromatic fraction (F2), light resin (F3), middle resin (F4), heavy resin (F5) and n-pentane asphaltenes (F6) were obtained.

"Ultimate analysis and molecular weight measurement"

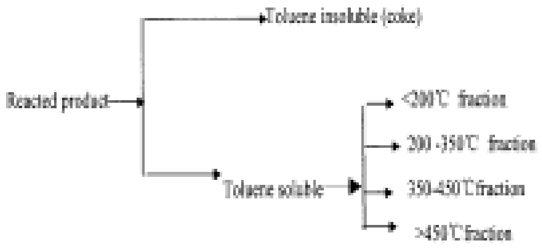
A Carlo Erba 1160 elemental analyzer was used for C, H, N analysis. An atomic absorption was used to determine Ni, V, Fe and Ca content of the fractions. Average molecular weight was measured by using vapor pressure osmit VPO method (benzene as solvent, 45^{o}C) with Knauer molecular weight analyzer.

"FTIR and microscopic characterization of petroleum coke"

FTIR analysis of coke was conducted with a Nicolet Magna 750 IR analyzer. An OLYMPIAN HS-2 microscope was used to visualize the coke formed in the bulk of the reaction system.

"Liaohe VR thermal and hydrothermal conversion and catalytic hydrocracking"

Experiments were carried in a 100ml FDW-0l stirred autoclave reactor. Initial pressure was 5.0Mpa N_2 for thermal conversion and 7.0Mpa H_2 for hydrothermal conversion and catalytic hydrocracking. The catalyst used in hydrocracking reaction was Mo-based oil soluble additive (ca.200 PPM Mo in reaction feed), and was pre-sulfurized by elemental sulfur at 320^{o}C for 30 minutes after mixing with Liaohe VR (S/Mo atomic ratio=3/1). Reaction temperature (430^{o}C) was reached within 25 minutes from room temperature. After 1 hr. reaction time, the reactor was quenched (cooled) to room temperature. The reactor gas was vented, and toluene slurry was prepared from the reactor contents. Any solids adhering to the reactor walls or internals were carefully scraped off. The slurry was then centrifuged and the toluene insoluble (TI or coke) separated and washed (extracted) with boiling toluene by using quantitative filter paper. The solids were dried and weighed. The toluene soluble material was distilled into several fractions. The distillation scheme is as follows.



Results and Discussion

Relation Between Feed Properties and Cokes Formation

For the purpose of comparison, Gudao VR (the feed to VRDS unit in Shengli Refinery) was also studied for its properties and composition. The data in Table 1 shows that Liaohe VR, in contrast to Gudao VR, is high in viscosity, CCR, heavy metals, nitrogen content, aromaticity (f_A), and the ratio of aromatic ring number to naphthenic ring number (R_A/R_N). This indicates that Liaohe VR will generate more coke than Gudao VR under high processing severity (e.g. delayed coking and RFCC). The fact that its sulfur content, H/C ratio, paraffinicity (f_P) and naphthenicity (f_N) are much lower than Gudao VRs indicates Liaohe VR has poor cracking conversion.

However, the SARA analysis (group compositions) are similar for the both VRs. For example, the oil fractions (saturates+aromatics) are 47.7% and 49.3% for Liaohe VR and Gudao VR, respectively. Even the n-heptane asphaltene (nC7-At) content of Liaohe VR is less than that of Gudao VR. The properties of oil fractions in Liaohe VR are even better than those of Liaohe Oil fraction (Table 2). In contrast to Gudao VR oil fraction, Liaohe VR oil fraction has lower density, viscosity, pour point, CCR, sulfur, nitrogen and metal content.

Therefore, it can be inferred that the qualities of resin and asphaltene fractions of Liaohe VR must be much inferior to those of Gudao VR. It is verified by further analysis of six sub-fractions of these two VRs (Table 3). The nitrogen, nickel and CCR in the heavy resin and asphaltene fractions account for 69.1%, 78.6%, and 74.1% respectively of total N, Ni and CCR in Liaohe VR, while the corresponding values for Guado VR are only 61.0%, 61.0%, and 63.0%. The aromaticity and R_A/R_N ratio of Liaohe resin and asphaltene are much higher than those of Gudao resin and asphaltene, indicating that the cracking performance of Liaohe resin and asphaltene fractions is quite poor. If used as a feedstock for fixed-bed catalytic hydrocracking process, Liaohe VR would lead to heavy coke and metal deposition on catalyst-bed and deactivation of the catalysts.

A great difference exists in molecular weight distribution in six Liaohe VR sub-fractions. The ratio of asphaltene molecular weight to oil molecular weight for Liaohe VR is about 9.5, while that for Gudao is only about 4.6. The gap between properties of oil fraction and resin-asphaltene fraction of Liaohe VR is much wider than that of Gudao VR, which implies that the system of Liaohe VR is not homogeneous, its uniformity is low and its colloidal stability must be low. All the above properties show that Liaohe VR is an inferior heavy oil; the propensity to coke formation is much higher than Gudao VR during processing. A preliminary thermal treatment test has shown that the induction period of coke formation of Liaohe VR is shorter than that of Gudao VR.

The Distribution of Products in Thermal Treatment and Hydrocracking of Liaohe VR

Table 4 lists properties of the <450^{o}C fraction, >450^{o}C cracked residue, coke content in reaction products, and pentane asphaltene content in cracked residue. As the reaction temperature is increased, the <450^{o}C fraction yields increases for all three series of reactions, and the increment is the highest for thermal reaction and the least for catalytic hydrocracking with Mo-based catalyst. But the conversion to light products is the highest for the latter process under unit coke formation conditions. Under the reaction condition of 430^{o}C and reaction time 1 hr, coke formation is less than 1% and conversion reaches up to 50% for the latter process. Coke formation is much greater than 1% as conversion reaches 50% for the other two series of reactions of Liaohe VR. Coke formation increases rapidly with temperature for thermal treatment of Liaohe VR, but quite slowly for catalytic hydrocracking. The asphaltene content in the three reaction systems are similar to cracked residue proportions. The molecular weight of asphaltene decreases with increasing reaction temperature for all three reaction systems. The decrease of asphaltene molecular weight under thermal treatment is pronounced.

The Characterization of Coke Formation by Microscopic Analysis

Reacted materials were sampled from the bulk of reaction system using thin glass plates as the samplers and then visualized by using an Olympas HS-2 microscope. Three series of microphotographs (10x40x3.3) were taken of reacted materials from three series of reaction systems. These are shown in Figures 1, 2, and 3 corresponding to Liaohe VR reacted under thermal treatment, hydro-thermal treatment, and catalytic hydrocracking respectively. It can be seen that there is yet little coke at 420^{o}C for hydrocracking system. As the temperature, increased coke formed in the bulk of reaction system was changed from fine dispersed particles to small clusters (0.1–0.2% coke), as seen in Figures l, 2, and 3 at 425°, 415°, and 400^{o}C, and then to coke clusters as seen in Figures l, 2, and 3 at 430°, 420°, 415^{o}C. The description of coke formation in Figures 1, 2, and 3 was the only result observed at ambient temperature. The coke formed in a reactor system at high temperature may be quite different and can be observed by using a hot-stage microscope; this will be discussed in another topic.

The Characterization of Coke by FTIR

Fourier Transform Infrared spectrometry (FTIR) is a useful technique for characterizing functional groups of organic substances. It is used to characterize the coke formed in a reaction system and to describe the changes of different organic functional groups, such as aromatic carbon, and paraffinic carbon, and the substitution extent on aromatic rings reaction severity in coke formation progresses. Aromatic C=C double bond vibrates at 1600 cm^{-1} and aromatic C-H bond vibrates at 3030 cm^{-1}, 750 cm^{-1}, 810 cm^{-1}, and 870 cm^{-1}. Paraffinic C-H vibrates at 2920 cm^{-1}, 2860 cm^{-1}, 1460 cm^{-1}, and 1380 cm^{-1} due to contributions by methyl C-H bond. Here, the relative vibrating strength (Ax'), i.e., the ratio of vibrating strength (Ax) of functional groups to C=C vibrating strength (A1600), was used to describe the relative changes of coke functional groups and to reveal the way in which chemical structures change. The relative vibrating strengths of several organic functional groups of coke formed at different temperatures in Liaohe VR reaction systems are tabulated in Table 5. With increasing temperature, A_{2920} and A_{2860} was gradually decreasing, showing that paraffinic portion of coke decreased, aromaticity was increasing. A_{870}, A_{810}, and A_{750} increased with temperature, showing that condensation of the aromatic ring was decreasing and side chain cracking occurred. The FTIR data indicated that the aromaticity of coke formed in hydrocracking process was less than that of coke formed in thermal treatment process. Therefore FTIR is an effective means for characterization of coke formation during VR processing.

Analysis of Reactor Wall Coke and the Bulk Coke

In order to clarify the difference between the reactor wall coke and the coke in the bulk of reaction system and to reveal the mechanism of two kinds of coke formation, the reactor wall coke and the bulk coke were separately collected from the Liaohe VR catalytic hydrocracking system. Then, these two kinds of coke were floated with water to separate light wall coke (w-coke), heavy wall coke (w-coke2), light bulk coke (b-coke) and heavy bulk coke (b-coke2). The analysis is listed in Table 6. The H/C atomic ratio of w-coke was less than that of b-coke. This was consistent with their FTIR data; the A_{2920} and A_{2860} of w-coke were less than those of b-coke, its A_{870}, A_{810} and A_{750} were greater than those of b-coke, showing that the wall coke underwent stronger cracking/condensation reaction. The fact that wall coke was higher than bulk coke in Mo, Ni, and Fe contents showed that wall coke could strongly concentrate heavy metals.

The Mechanism of Initial Coke Formation and Its Effect

Vacuum residue is a colloidal system with asphaltene and heavy resins as the dispersed phase and an oil fraction and light resins as the medi.[9,10] If physical and chemical properties of the dispersed phase were much different from those of the media constituents, the media would not properly peptize the asphaltene, and the colloidal system would not be stable. For example, asphaltenes can be precipitated by n-pentane because pentane dilutes the colloidal system and makes the media less aromatic, and of low average molecular weight and polarity. When heating disturbs vacuum residue system, the molecules move fast, the micelles made up of asphaltenes and media become loose and some asphaltene molecules may bump off the micelle cage and coalesce. The vacuum residue colloidal system can also be disturbed by fine, solid, polar particles due to the adsorption of asphaltene molecules on these particles. At high heating severity, some weak bonds in asphaltene molecules may crack. Asphaltene micelles may break apart; some asphaltene molecules may physically coalesce or chemically interact to form large molecules. At the same time, the ability for media to peptize asphaltene molecules becomes lower due to light fractions increasing, thus causing asphaltene molecules to coalesce and be precipitated. All these factors can account for the initial coke formation of VR reaction systems. In fact, initial coke is the physical-chemically-coalescent phase of asphaltene molecules, whose properties are very similar to those of a asphaltene—coke precursor. Hence, initial coke may have a high affinity for asphaltene molecules and promote coalescence of asphaltene molecules and coke formation.

In order to test the effect of the initial coke on the reaction system, Liaohe VR with some pre-added coke powders was subjected to thermal treatment and hydrocracking tests. The results were tabulated in Table 7. The thermal treatment under atmospheric nitrogen gas was conducted in a quartz tube reactor (30 ml) heated by an electric tin bath; other tests were carried out in an autoclave of 100 ml under 7MPa hydrogen gas. Coke formation was about 0.73% for Liaohe VR thermal treatment under conditions of 406^{o}C, 2hr reaction time and nitrogen atmosphere. When 0.5% coke was pre-added in the thermal treatment system, total coke was about 1.93%, net coke formation was 1.20%, net coke increment was about 0.47% in contrast to a virgin test without pre-added coke; 1% pre-added coke promoted 1.22% net coke formation compared with the virgin thermal treatment. It was obvious that initial coke could promote coke formation during thermal treatment of vacuum residue under low pressure. In hydrothermal treatment of VR, it seemed, that pre-added coke had little influence on coke formation. In fact, the Ni, and Fe in pre-added coke might act as hydrocracking catalysts. The active catalytic hydrogen could saturate the coke precursor free radicals and inhibit the chemical condensation of these free radicals, thus inhibit the coke formation. The counteraction between the coke promotion by initial coke and the coke inhibition by heavy metals in the coke makes total coke formation similar to the coke formation in virgin hydrothermal treatment. In the catalytic hydrocracking process, pre-added coke could markedly inhibit net coke formation. In addition to activating hydrogen, the pre-added coke and Mo sulfide solid particles were of high affinity for asphaltene free radicals, and absorbed these coke precursor radicals adsorbed around them. Thus, the active hydrogen on catalysts could instantly terminate coke precursor radicals; thus, the coke inhibition efficiency was enhanced. The performance for catalyst particles to enrich asphaltene-coke precursors around them and to promote utilization of hydrogen may be an important factor for slurry-bed catalytic hydrocracking of heavy oils to effectively inhibit coke formation.

Conclusions

The SARA group composition of Liaohe VR is similar to that of Gudao VR: the nature of its oil fraction is even better than that of Gudao VR counterpart, but its resin and asphaltene fractions are greatly inferior to those of Gudao VR. The uniformity of Liaohe VR system is lower than that of Gudao VR, its colloidal system is not as stable, and the coke formation tendency is high during further processing.

With processing severity increasing, coke formation in VR reaction system is promoted from dispersed fine particles to coke clusters. FTIR technique can effectively characterize the evolution of aromatic part and paraffinic part of the coke formed at different severities. The aromaticity and heavy metal contents of reactor wall coke are greater than those of coke formed in the bulk of reaction system.

The initial coke can promote coke formation, especially during low-pressure thermal treatment of VR. During hydrothermal and hydrocracking treatments, pre-added coke seems to promote catalytic function.

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Property	Liaohe VR	Gudao VR
Density (20^{o}C), g./cm^3	0.9976	0.9998
Viscosity (100^{o}C)/mm^2.s^{-1}	3375	1710
Pour point, ^{o}C	42	41
Flash point, ^{o}C	312	327
Carbon residue, %	19.0	15.6
Elemental composition		
C, %	87.0	85.4
H, %	11.4	11.4
S, %	0.43	2.52
N, %	1.08	0.80
H/C (Atomic ratio)	1.50	1.60
Total Metal/PPM	258.6	131.6
Ni, PPM	122.6	48.0
V, PPM	2.9	2.2
Fe, PPM	37.5	13.8
Ca, PPM	95.6	33.8
Ash, %	0.056	0.026
SARA fractions:		
Saturates, %	17.1	14.5
Aromatics, %	30.3	34.8
Resins, %	50.2	47.2
nC7-Asphaltene, %	2.1	3.5
Structural Parameters		
F_A	0.267	0.181
F_N	0.258	0.330
R_A/R_N	0.93	0.47

Table 1: Properties of Liaohe and Gudao Vacuum Residue (VR)

Properties	Oil fraction of Liaohe VR	Oil Fraction of Gudao VR
Density (20 ^{o}C) g/cm^{3}	0.9392	0.9558
Viscosity (100^{o}C), mm^{2}.s^{-1}	84.1	103.0
Pour point, ^{o}C	36.0	39.0
Carbon residue, %	3.5	5.8
MW	630	860
Elemental composition		
C, %	87.2	85.0
H, %	12.3	11.9
S, %	0.34	2.0
N, %	0.33	0.45
H/C(Atomic ratio)	1.68	1.67
Metals		
Ni, PPM	1.3	6.0
V, PPM	2.4	/
Ca, PPM	1.1	19.8

Table 2: Properties of Oil Fraction of Liaohe VR and Gudao VR

Property	F1	F2	F3	F4	F5	nC5-At
Liaohe VR:						
Yield/%	36.1	11.6	16.8	9.0	12.3	14.2
MW	590	810	1050	1380	2240	5970
f_A	/	/	0.329	0.357	0.371	0.509
f_N	/	/	0.201	0.153	0.151	0.082
R_A/R_N	/	/	1.5	2.2	2.4	6.2
H/C	1.75	1.48	1.44	1.41	1.38	1.19
N/%	0.16	0.85	1.42	1.70	1.78	1.96
N_f/N_T, %	2.1	10.8	18.0	21.6	22.6	24.9
Ni/PPM	3		197.3	225.2		502.3
Ni_f/Ni_T, %	0.2		21.3	24.3		54.3
CCR, %	3.5		23.2	31.1		45.3
CCR_f/CCR_T, %	3.4		22.5	30.2		43.9
Gudao VR:						
Yield, %	34.9	14.2	15.6	7.9	8.8	15.9
MW	800	1000	1370	1760	2430	3920
f_A	/	/	0.285	0.290	0.297	0.437
f_N	/	/	0.149	0.182	0.166	0.128
R_A/R_N	/	/	1.8	1.5	1.7	3.3
H/C	1.83	1.50	1.51	1.49	1.48	1.29
N, %	0.10	0.75	1.17	1.37	1.43	1.48
N_f/N_T, %	4.2	12.9	21.9	13.0	19.7	28.3
Ni, PPM	0.6	9.7	109.1	43.7	49.6	127.3
Ni_f/Ni_T, %	0.4	2.9	35.7	7.2	12.0	41.8
CCR, %	2.4	15.9	21.7	23.6	21.7	41.8
CCR_f/CCR_T, %	4.8	12.9	19.3	10.6	14.5	37.9

MW — molecular weigh t. N_f/N_T — the ratio of nitrogen in fraction to total nitrogen in VR

Ni_f/Ni_T — the ratio of nickel in fraction to total nickel in VR

CCR_f/CCR_T — the ratio of carbon residue of fraction to total carbon residue in VR

Table 3: Properties and Composition of Six Fractions of Liaohe VR

Reaction Condition		<450°C Product, %	>450°C cracked residue, %	Coke, %	nC5-At in cracked residue	
					%	MW
N2 5MPa	400°C	37.7	62.2	0.1	/	/
	410°C	44.4	54.2	1.4	24.6	3349
	420°C	67.1	32.9	10.9	15.8	2829
	430°C	62.8	17.7	19.5	9.2	1499
H2 7MPa	400°C	28.27	71.68	0.05	/	/
	410°C	40.90	59.00	0.10	23.1	3837
	420°C	50.20	46.60	3.20	17.9	2989
	430°C	61.40	30.78	7.92	13.3	1979
H2 7MPa Mo 200ppm	400°C	18.95	81.00	0.05	/	/
	410°C	25.60	74.31	0.09	/	/
	420°C	35.54	64.24	0.22	15.8	3477
	430°C	50.19	49.13	0.68	14.8	2932
	440°C	53.79	42.0	4.21	12.2	2063

Table 4: Yields of Conversion Products Under Three Series of Reaction Conditions (Reaction time 1hr)

Coke Samples	A_{2920}	A_{2860}	A_{3030}	A_{870}	A_{810}	A_{750}
N2						
410°C	0.780	0.493	0.060	0.271	0.206	0.185
420°C	0.650	0.426	0.095	0.283	0.243	0.241
430°C	0.273	0.210	0.098	0.349	0.312	0.294
H_2, Mo200ppm						
425°C	0.574	0.385	0.068	0.280	0.152	0.149
430°C	0.375	0.256	0.058	0.278	0.210	0.184
435°C	0.265	0.176	0.060	0.214	0.215	0.196
440°C	0.183	0.155	0.030	0.390	0.422	0.406

Table 5: Relations Between Coke FTIR Data and Reaction Conditions

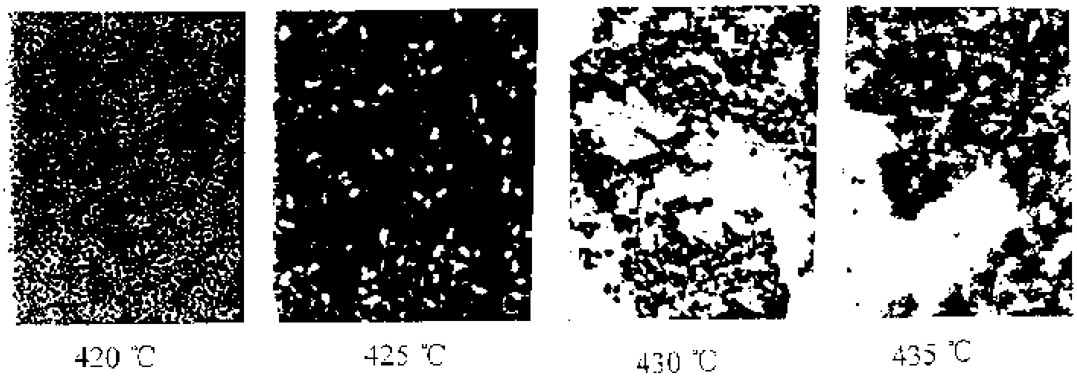
Coke Samples	C%	H%	N%	H/C	Mo, PPM	Ni, PPM	Fe, PPM
w-coke1	77.44	4.67	3.53	0.72	16305	2174.0	3609.0
w-coke2	79.28	4.64	3.24	0.70	17509	2479.6	5148.1
b-coke1	80.9	5.01	3.71	0.75	10890	2147.0	2354.0
b-coke2	80.96	4.90	3.74	0.73	12135	2133.3	3067.5

Table 6: Elemental Composition of the Coke Collected from the Internal Wall of Reactor and the Bulk of Reaction System

Reaction Condition	Sample	<450°C Product, %	>450°C Cracked Residue, %	Coke, %	Coke/% Increment/%
N_2 (blowing), 2hr, *					
406°C	LHVR	/	/	0.73	0.73
406°C	LHVR+0.5% coke	/	/	1.93	1.20
406°C	LHVR+l.0% coke	/	/	2.45	1.95
H_2, 7MPa, 2hr					
412°C	LHVR	53.37	43.70	2.93	2.93
412°C	LHVR+0.5% coke	54.06	42.50	3.44	2.94
H_2, 7Mpa, 2hr					
Mo, 200ppm					
425°C	LHVR	56.87	41.50	1.63	1.63
425°C	LHVR0.5% coke	52.96	45.40	1.64	1.14

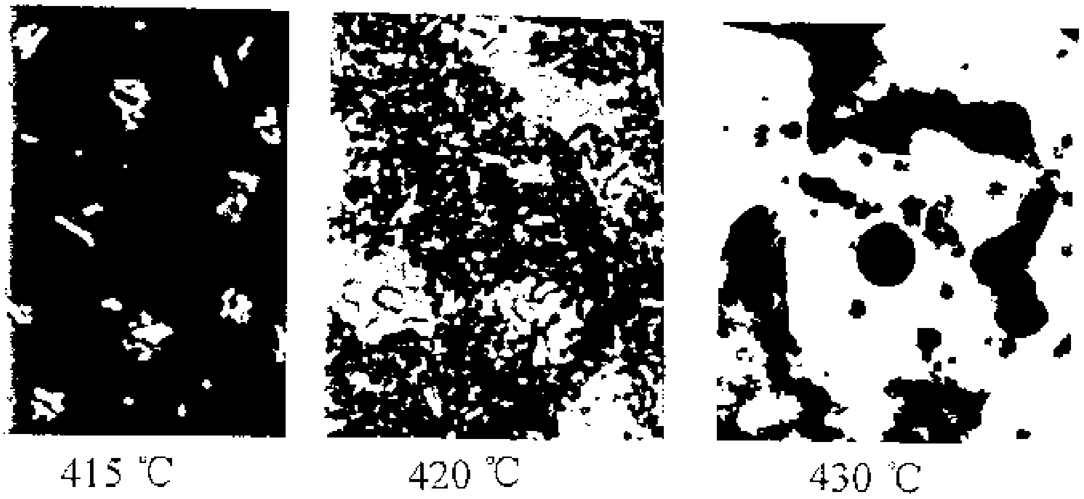
Conducted by using a quartz tube reactor with N2 as a blowing gas

Table 7: Effect of Initial Coke on Coke Formation of Reaction System



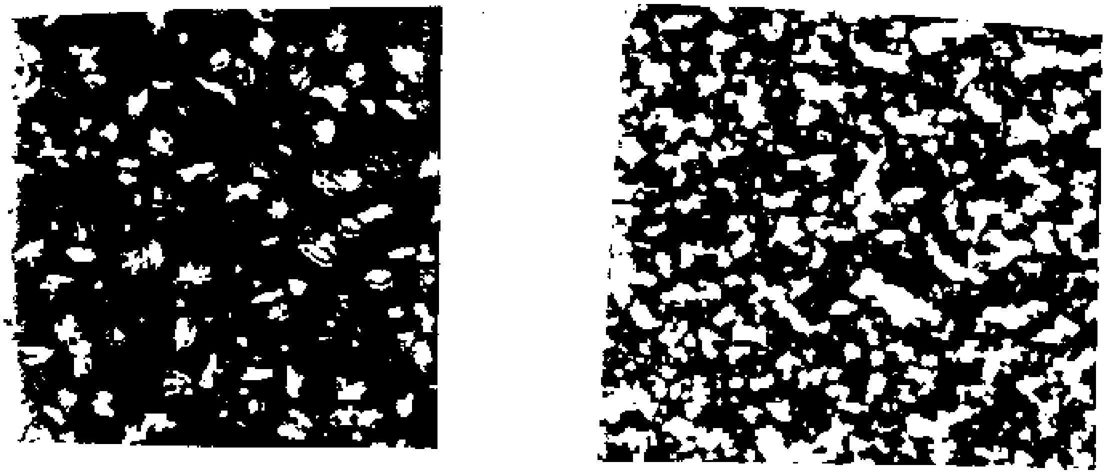
420 ℃ 425 ℃ 430 ℃ 435 ℃

Figure 1: Micrographes of Liaohe VR Catalytic Hydrocracking System



415 ℃ 420 ℃ 430 ℃

Figure 2: Micrographes of Thermally Treated Liaohe VR System (Under H_2 Atmosphere)



400 ℃

415 ℃

Figure 3: Micrographes of Thermally Treated Liaohe VR System (Under N_2 Atmosphere)