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Heat Treatment Condition Influence on Novokuibyshevsk Vacuum Residue Component Composition

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Abstract

The article presents the information about thermal degradation of Novokuibyshevsk vacuum residue and change of products composition during this process. The optimal conditions for the thermal destruction of vacuum residue components were established. The regularities of material balance composition change, $S_{general}$ were determined depending on cracking conditions. The basic directions of resin-asphaltene component transformations were identified, changes in their structural-group parameters in the process of initiated cracking were analyzed. Conducting of Novokuibyshevsk vacuum residue thermolysis leads to deep resins-asphaltenes average molecules structure characteristic changes. Developed alkyl and naphthenic moieties, which are presented in initial molecule, undergo degradation, amount of structural blocks in resins and asphaltenes molecules reduces, their average size decreases. Also the reduction in total content of the rings (saturated and aromatic) was established in average structural unit, at the same time decrease of rings substitution and length of the aliphatic fragments can be observed. In general the process of vacuum residue thermal cracking causes partial degradation of saturated (aliphatic and naphthenic) fragments and, partially, aromatic rings, which contain heteroatomic elements.

1. Introduction

Nowadays in the world there is a tendency of permanent increase in motor fuels demand tightening the environmental requirements for oil products in conjunction with the steady decline in the share of light oils produced. Decrease in reserves and low viscosity light oils output in many oil producing regions of the world

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including Russia results in involving relatively new for refining hydrocarbon sources, e.g. heavy oils and petroleum residues, in economic turnover[1]. This leads to covering the shortage by means of heavy sulfur oil production. All these trends as well as the need to increase oil output cause the development of new ways of processing heavy hydrocarbon feedstock. These processes should be aimed to obtaining distillate fractions for subsequent production of motor fuels and oils. It results in the increase of vacuum distillates and residual fractions enriched with sulfur-containing compound in overall balance of petroleum products[2,3]. These compounds have a high molecular weight, tend to condense and coke formation during the processing, deactivate the catalyst. Nowadays research of resins-asphaltenes components destruction methods with simultaneous sulfur containing components removal would allow obtaining high content of low-boiling fractions oil with low heteroatomic component amount[4]. For this reason it becomes relevant to develop new high effective refinery technologies of high boiling vacuum distillates, which would combine increase of motor fuel yields with decrease in amount of sulfur to the level which will comply with Euro – 3 ÷ 5[5,6]. Therefore, the aim of work is to establish main hydrocarbon and sulfur compounds transformations directions which are parts of high molecular Novokuibyshevskiy vacuum residue components in process of initiated thermocracking.

2. **Experimental**

2.1. *Reagents and samples*

As an object of research Novokuibyshevsk vacuum residue has been taken. Physicochemical object characteristics are shown in Table 1. Residue is heavy hydrocarbon material, which has already been heat treated in the process of commercial oil distillation, resins-asphaltenes vacuum residue components have thermal stability higher than that of initial raw materials. According to the obtained data (Table 1) vacuum residue has high resins content - 33.6 %, asphaltenes- 5.7% wt.

Table 1 Physicochemical Novocuibyshevsk vacuum residue characteristics

Index	
Material composition, % wt.:	
Oil	60.7
Resins	33.6
Asphaltenes	5.7
Molecularweight, a.m.u.	
Resins	600
Asphaltenes	718

Oil content is 60.7 % wt. by weight. Novokuibyshevsk vacuum residue is sour (3.08 % wt.), which makes it unsuitable material for gasoline and diesel fuels production. Low atomic H/C ratio of residue (1.56) indicates that components are highly aromatic. IBP – 343 °C, > 360 ° C fractions content in it is 98.6 wt %.

Table 2 shows the results of liquid-solid chromatography of initial vacuum residue oil. More than half of it is saturated compounds (35.02 %), content of biaromatic and triaromatic compounds is smaller (5.22 % wt.). The smallest part of sulfur is in biaromatic compounds (0.15 %) and the highest is in saturated ones (0.56 % wt.)

Thermal cracking experiments of heavy hydrocarbon material are carried out in an autoclave, the volume of which is 12 cm^3. Sample weight is 5 g. Thermal cracking experiments with vacuum residue are carried out at temperature 400 – 500 °C, the process time is from 40 to 120 min in air. In the experiment the reactor mass is

recorded without and with sample, prepared for thermolysis. After heat treatment of vacuum residue, yields of gas products is defined by weight loss of reactor after removal of gas from reactor.

Table 2 SulfurcontentinNovokuibyshevskrefineryvacuumresiduecomponents

Components	Yield, % wt.	$S_{depending\ on\ component}$, % wt.	S_{genera}, % wt.	$\sum S_{general}$, % wt.
Hydrocarbons				
Saturated	35.02	0.56	1.60	
Monoaromatic	14.69	0.51	3.49	
Biaromatic	5.22	0.15	3.01	3.04
Three+Poliaromatic	5.65	0.17	3.14	
High molecule compounds				
Resins	33.60	1.37	4.07	
Asphaltenes	5.70	0.28	4.93	

Resulting difference between reactor mass before and after the experiment is determined as coke.

2.2. Material composition determination

Initial vacuum residue group composition and its thermolysis products are established using traditional scheme: firstly, the content of asphaltenes in the sample is determined by the Golde "cold" method. The asphaltene content is found by diluting the sample with n-hexane in solvent with ratio 1:40. After keeping this mixture for 1 day, the precipitate is filtered. The resulting precipitate is placed in paper cartridge and desorbed in Soxhlet device with hexane, and then it is washed away from asphaltenes with chloroform and benzene. Next step is to distill solvent off and dry to the constant weight of asphaltenes. Hexane mixture is added to the deasphaltenized sample. Then, resins and oil concentration is established in obtained maltenes by the adsorption method giving off the product which need to be analyzed on silica gel, placing the mixture in extractor and, subsequently, desorbing hydrocarbon oil components by n-hexane and resins by ethanol-benzene mixture 1:1 at boiling points of this solvents.

2.3. Structure-group parameters and elemental composition determination

Resin and asphaltene structural-group parameters isolated from the original vacuum residue and its cracking products under different conditions are calculated by the method developed in the IPC SB RAS which is based on sharing the results of the elemental composition, average molecular weights and PMR spectroscopy data[7].

3. Results and discussions

To determine Novokuibyshevsk vacuum residue components thermal stability cracking is carried out at temperatures 400, 450 and 500 °C. Vacuum residue thermolysis products components composition data is presented in Table 3. It is found that initial Novokuibyshevsk vacuum residue contains significant amount of resin-asphaltene components in its composition. At temperature below 450 °C high molecule component amount changes insignificantly. At temperature above 450 °C oil formation reactions prevail (content increased by 8.5 % wt.), also, resins destruction reactions take place to form coke and gas. Resins concentration extremum indicates

that reaction direction changes resulting in accumulation of intermediates, destruction of which gives off additional oil and light fraction yields.

Table 3 Novokuibyshevsk vacuum residue cracking product composition

Sample	Content, % wt.			Liquid products composition, % wt.		
	Gas	Liquid	Coke	Oil	Resins	Asphaltenes
Initial vacuum residue	0.0	100.0	0.0	60.7	33.6	5.7
400 °C 60 min	0.9	97.7	1.4	56.2	33.7	7.8
450 °C 60 min	2.1	96.5	1.4	42.8	44.6	9.1
90 min	4.0	92.8	3.2	65.6	18.7	8.6
120 min	5.8	89.2	5.0	69.2	15.2	4.8
500 °C 30 min	8.3	81.3	10.4	54.7	16.1	10.5
60 min	13.6	71.6	14.9	46.5	13.1	12.0
90 min	29.7	49.0	21.3	31.8	8.9	8.3

Vacuum residue cracking at temperature 450 °C with 60 min process duration results in increase of resin amount by 11 % wt. Longer cracking leads to destruction of resins, the content of which drops to 18.7 % and 15.2 % wt. for 90 and 120 min, respectively, with oil, gas, and coke formation. During vacuum residue thermolysis the following regularities can be observed: at relatively low temperature (450 °C) the amount of resins increase, low amounts of coke and gas products form. After heat treatment at all temperatures the amount of asphaltenes increases.

Table 4 Novokuibyshevsk vacuum residue $S_{general}$ content in cracking products

Sample	Conversion on the sulfur amount in the component, % wt.			$\sum S_{general}$, % wt.
	$S_{general}$ Oil	$S_{general}$ Resins	$S_{general}$ Asphaltenes	
Initial vacuum residue	1.39	1.37	0.28	3.04
400 °C 60 min	1.14	1.26	0.39	2.79
450 °C 60 min	0.98	1.23	0.41	2.62
90 min	1.40	0.66	0.41	2.47
120 min	1.69	0.44	0.16	2.29
500 °C 30 min	1.25	0.60	0.47	2.32
60 min	1.04	0.45	0.53	2.02
90 min	0.80	0.29	0.32	1.41

Vacuum residue cracking results in decrease of $S_{general}$ amount at temperature 450 °C in liquid products (Table 4). Wherein with cracking duration increase (from 60 to 120 min) the proportion of S in oil increase, sulphur content in resins and asphaltenes decrease almost 3 times, which is likely to be a consequence of partial S transformation to the composition of coke and gas. Resins degradation increase leads to penetration of low molecular weight fragments in oil composition, which explains increase of oil in liquid product composition and

proportion of S in them. Vacuum residue in severe conditions (500 °C 30 – 90 min) results in a significant decrease of both liquid product yield and S content in oil and resins (43 % and 51.7 %, respectively).

The structural parameters of initial and its thermolysis products of vacuum residue resins and asphaltenes are shown in Table 5. It is established that resin and asphaltene molecules contain huge amount of sulfur and oxygen atoms. Average resin and asphaltene molecules (ARM and ASM) are calculated with the help of program developed by IPC SB RAS, the algorithm of which is described in details in[8]. Initial vacuum residue resin molecule (molecule weight is 600 a.m.u.) is formed mostly from aliphatic fragments, 3 aromatic and 3 naphthenic rings and has allow aromatic factor. Atomic ratio of C/H is sufficiently small – 1.41, which is a consequence of high molecule cyclisation and significant amount of heteroatoms in molecule.

Table5.Novokuibyshevskvacuum residue thermolysis product resin molecule structural-group parameters

Sample		Resins			Asphaltenes		
Index		Initial	Resins 450 °C,120 min	Resins 500 °C,60 min	Initial	Asphaltenes 450 °C, 120 min	Asphaltenes 500 °C, 60 min
MW	a.m.u.	600	370	359	718	690	635
Elemental composition	C	81.66	78.23	82.87	82.91	79.52	79.45
	H	9.64	5.49	7.95	7.14	5.49	5.41
	N	1.29	0.99	1.72	1.74	0.99	1.67
	S	4.07	3.34	3.46	4.93	3.34	4.43
	O	3.33	10.66	4.00	3.28	10.66	9.04
Blocks in molecule	m_a	1.51	1.30	1.45	2.03	2.07	2.03
Ring's structure	$K_{overall}$	6.35	9.56	5.09	13.39	14.18	12.67
	$K_{aromatic}$	3.07	2.14	2.85	5.59	5.93	6.05
	$K_{saturated}$	3.27	7.41	2.24	7.80	8.25	6.63
Aromatic factor	f_a	14.50	39.16	51.28	46.45	53.94	58.62

According to the structural-group analysis data the initial vacuum residue of ASM has molecular weight 718 a.m.u., and consists of a two block molecule. Half of initial vacuum residue of ASM consist of aromatic structures (aromatic factor f_a = 46.45), has a high substitution degree (σ_a = 0,48). Average structural molecule block has 13 rings including 5 aromatic and 8 naphthenic rings. Atomic ratio of H/C is only 1,03. It is known that such structures can be easily influenced by reactions of cyclization and dehydrogenation in condition of heat treatment forming condensed polyaromatic structures. During this process the separation of low molecular fragments takes place, which form additional yields of fractions IBP – 360 °C[9]. It is stated that thermal destruction has a significant influence on structural-group resins-asphaltens molecule parameters (Table 5, Figure 1). Resins and asphaltens molecule weight decrease (to 359 and 635 a.m.u., respectively). The number of structural units in ARM decreases, but, at the same time, the substitution degree of aromatic nuclei increases, aromatic factor increases threefold and increases further with temperature. Sulfur eliminates from average molecule structure.

Vacuum residue cracking results in significant structural blocks densification, increase in substitution degree of aromatic nuclei in ASM, which leads to increase in aromatic factor (for 16 % relatively), rings amount remains constant. It should be noted that H/C ratio decrease in ASM that can be explained by the large molecular sealing

and change in their structure from archipelago type to the continental (Figure 1). In cracking process asphaltens molecular mass reduces in comparison with initial one.
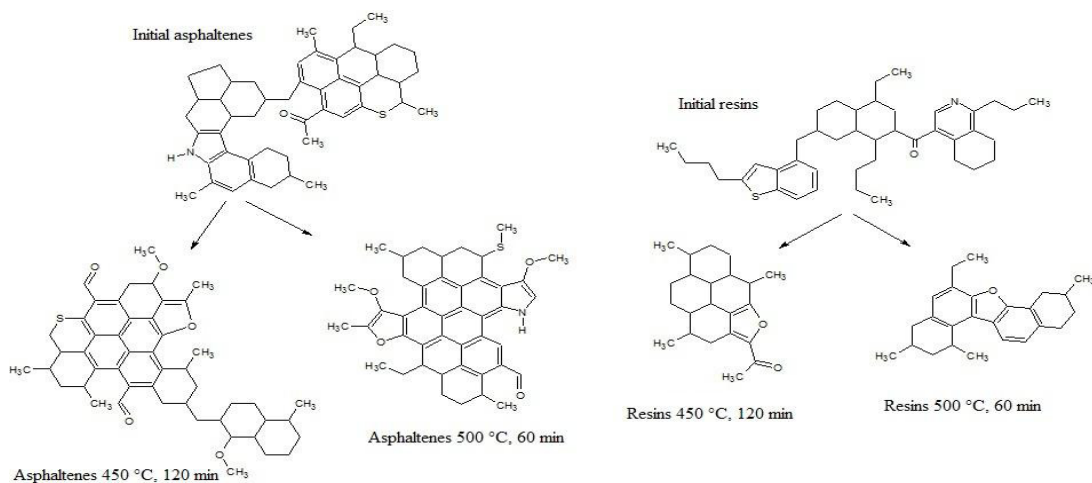

Figure 1 Resins and asphaltenes molecules transforamtion scheme during cracking process in different conditions

Summary

Novokuibyshevsk vacuum residue thermolysis results in deep structural-group characteristic changes of ASM and ARM. Developed alkyl and naphthenic fragments forming the initial molecules, undergo to degradation, the number of structural molecule blocks of resins and asphaltenes decreases, their average size reduces. The total number of rings also decreases (saturated and aromatic) in average structural block, ring substitution degree is reduced decreasing the length of the aliphatic fragments. In general, thermal cracking process causes partial degradation of saturated (aliphatic and naphthenic) fragments and part of aromatic rings containing heteroatoms.

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