Thermal destruction of the components of high-sulfur vacuum residues

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Abstract. The problem of processing vacuum residues is relevant due to the enhancement of heavy crude oil recovery. The processing of fuel oil and vacuum residues is complicated due to the high content of resins and asphaltenes present in them. In order to develop new approaches to the processing of vacuum residues, it is necessary to comprehend the mechanisms of thermal degradation of high-molecular-weight oil components. Three samples of high-sulfur vacuum residues are cracked at a temperature of 500 °C and with a various process duration. The characteristic changes in the material and fractional composition of the products of the vacuum residue cracking depending on the process conditions are shown. It is found that the ratio of light to medium distillates in the composition of the products depends on the duration of cracking.

1. Introduction

Due to the wider demands in motor fuels and a simultaneous decrease in light oil reserves, the need for advanced processing of heavy oil residues (vacuum residue, fuel oil) into light fractions (gasoline, diesel) increases [1-4]. Due to the enhancement of heavy crude oil recovery, it is necessary to develop processes based on the destruction of the structures of high-molecular compounds, in particular asphaltenes, with the formation of components of distillate fractions [5, 6]. Asphaltenes, which are contained in significant quantities in oil residues, are mainly responsible for the formation of coke and the deactivation of the catalyst during their processing. The development of thermo-destructive methods for upgrading heavy oil residues will make it possible to reduce the rate of secondary compaction reactions, to achieve a higher degree of feedstock conversion and lower coke formation [7-10]. The aim of the work was to study the patterns of cracking of the components of high-sulfur vacuum residues of different composition.

2. Experimental section

2.1. Objects of study

The objects of study were the vacuum residues of the Novokuibyshevsk refinery, the Omsk refinery, and the vacuum residue obtained from the oil sampled at the Zyuzeyevskoye oil field. Vacuum residues contain a high amount of resin-asphalene substances; hence, the content of resins reaches 37.8 wt%, while that of asphaltenes – 20.5 wt%. It should also be noted that the vacuum residues are high-sulfur with a low atomic H/C ratio, which characterizes them as unsuitable feed stocks for the
production of distillate fractions by the method of catalytic cracking. The main physico-chemical characteristics of the objects of study are presented in Table 1.

| Parameter                  | Novokuibyshevsk vacuum residue (NVR) | Zyuzeyevsk vacuum residue (ZVR) | Omsk vacuum residue (OVR) |
|----------------------------|-------------------------------------|---------------------------------|---------------------------|
| Elemental composition (wt%)| Carbon 82.28                        | 81.56                           | 85.49                     |
|                            | Hydrogen 10.73                       | 9.58                            | 10.99                     |
|                            | Sulfur 3.04                          | 6.43                            | 1.8                       |
|                            | Nitrogen 0.19                        | 0.84                            | 0.56                      |
|                            | Oxygen 3.76                          | 1.59                            | 1.16                      |
|                            | H/C 1.56                             | 1.41                            | 1.54                      |
| Coking behavior            | 13.59                                | 24.15                           | 14.02                     |
| Fractional composition (wt%)| T<sub>bp</sub> 343.0                 | 474.0                           | 224.0                     |
|                            | 200-360                              | 1.4                             | 0.0                       |
|                            | 360-500                              | 77.9                            | 0.0                       |
|                            | >500                                 | 20.7                            | 100                       |
| Material composition (wt%) | Oil components 60.7                  | 41.7                            | 65.8                      |
|                            | Resins 33.6                          | 37.8                            | 33.1                      |
|                            | Asphaltenes 5.7                      | 20.5                            | 1.1                       |
| Molecular mass (a.m.u.)    | Oil components 600                   | 639                             |
|                            | Resins 718                           | 1552                            |
|                            | Asphaltenes 2142                     |                                 |

2.2. Thermal cracking of vacuum residues
Cracking was carried out in 12 cm<sup>3</sup> autoclave reactors at 500 °C for 15-60 minutes. The weight of vacuum residue sample was 7 g. During the experiment, the mass of the empty reactor and the mass of the reactor with the sample were recorded. Upon completion of feedstock heat treatment, the yield in gaseous cracking products was determined from the mass loss of the reactor with the sample after degassing. Then the reactor was washed with chloroform and weighed. The obtained difference between the reactor mass before and after the experiment was determined as coke.

2.3. Determination of the material composition
The material composition of vacuum residues and cracking products was established according to the standard scheme. First, the content of asphaltenes in the sample was determined by the ‘cold’ Golde method. Next, the content of oils and resins in the resulted malties was determined by the adsorption method. For this purpose the sample under analysis was applied on the activated ASC silica gel and the mixture was placed in a Soxhlet extractor for sequential elution of hydrocarbon components. The oil components were extracted with n-hexane, while resins – with ethanol-benzene mixture in the ratio 1:1.

2.4. Determination of fractional composition
The fractional composition of the liquid cracking products was determined by gas-liquid chromatography. Gas-liquid chromatography (GLC) was performed using a Kristall 2000M chromatograph with a quartz capillary column (30 m × 0.22 mm), and a stationary phase SE-54. Helium was used as a carrier gas. The device was equipped with a flame ionization detector (FID).
The linear temperature increase ranged from 80 to 290 °C and the heating rate of the column thermostat was 15 deg/min. The identification of hydrocarbons and the separation of chromatogram segments into gasoline (bp – 200 °C) and diesel (200-360 °C) fractions were performed according to the retention times of n-alkanes (hexane and hexadecane), pristane, and phytane.

2.5. Gas chromatographic analysis

The determination of the hydrocarbon composition of the gaseous products of the cracking of vacuum residues was carried out by the gas chromatographic method using a Kristall 5000 chromatograph according to GOST 31371.3-2008. The detection of hydrogen, oxygen, and nitrogen was carried out using a column filled with NaX molecular sieves (fraction 80-100 mesh., column length 3 m, internal diameter 2 mm). The velocity of the carrier gas (argon) was 30 ml/min. The separation of C1-C6 hydrocarbons was performed on a column filled with Porapak R polymer sorbent (fraction 80-100 mesh, Column length 3 m, internal diameter 2 mm). The velocity of the carrier gas (helium) was 30 ml/min. The analysis was carried out in the mode of temperature programming simultaneously on two columns from 35 to 170 °C with heating rate 5 °C/min.

3. Results and discussion

To determine the thermal stability of vacuum residue components, the cracking was carried out at 500 °C. The time of process was 15, 30, 45 and 60 minutes (Table 2). It was found out that during the thermal treatment of the objects of study, the destruction involving mainly resins results in the formation of petroleum coke and gas [11]. At the initial stage of cracking of the vacuum residues from the Novokuibyshevsk refinery (15 min.), the content of asphaltenes in liquid cracking products increases, which is explained by the predominance of the rate of formation of asphaltenes from resins over the rate of condensation of asphaltenes to coke. An increase in the cracking time from 15 to 60 minutes leads to a decrease in the yield of liquid products due to the intensification of gas and coke formation processes. The amount of resin-asphaltene substances in the composition of cracking products decreases: the content of resins by 76 %, and that of asphaltenes – by 86 rel.% (compared with the initial vacuum residue). This is due to the prevalence of reactions of condensation of resin-asphaltene components to coke. The sulfur content in oils increases due to transition of low molecular weight sulfur-containing fragments into the oil fraction [12]. An increase in the cracking time also contributes to a slight increase in the content of sulfur compounds in the composition of liquid products. This is probably due to the predominance of the rate of condensation of sulfur-free components to a solid product and, as a consequence, the concentration of sulfur-containing compounds in the liquid cracking products.

It was found that the initial vacuum residue, extracted from the Zuzeyevsk oil, contains the highest amount of resin-asphaltene substances: resins – 37.8 wt% and asphaltenes – 20.5 wt%, which greatly simplifies the process of their condensation. For the time of cracking 15 minutes, the content of oils in liquid products increases due to the destruction of resins resulted in the formation of low molecular weight components and gaseous products. If the cracking lasts for 60 minutes, the yield in gas and coke exceeds 58 wt%. The content of asphaltenes is reduced by 98% and that of resins – by 82 rel.% compared with the initial vacuum residue as a result of their condensation to solid products of cracking. The amount of sulfur in liquid products decreased by 72 rel.%. It is shown that at the initial stage of cracking (0-15 min) of the vacuum residue from the Omsk refinery the reactions of resin condensation with the formation of significant amounts of newly formed asphaltenes and coke prevail. A further increase in the time of process leads to an intensification of the reactions of destruction of oil components and, as a result, gas formation increases. The content of resins in liquid products is significantly reduced (the residual amount is 24 % relative to their initial content in the vacuum residue).
Table 2. Composition of the products of vacuum residue cracking.

| Time   | Gas     | Liquid (S<sub>total</sub>) | Coke   | Oils (S<sub>total</sub>) | Resins | Asphaltenes |
|--------|---------|---------------------------|--------|--------------------------|--------|-------------|
|        | Content, wt% |                |        |                          |        |             |
| NVR    | Initial  | 0                     | 100 (3.04) | 0                      | 60.70 (1.36) | 33.6 | 5.7         |
|        | 15 min   | 18.38                 | 81.33 (2.41) | 0.29               | 58.63 (1.36) | 16.46 | 6.24        |
|        | 30 min   | 19.70                 | 75.06  | 5.24                     | 56.70  | 13.5 | 4.86        |
|        | 45 min   | 22.48                 | 65.78  | 11.74                    | 53.69 (1.13) | 8.62 | 3.47        |
|        | 60 min   | 26.20                 | 57.80 (2.84) | 16.00               | 48.00 (1.86) | 9.0  | 0.8         |
| ZVR    | Initial  | 0                     | 100 (6.43) | 0                      | 41.70 (1.82) | 37.8 | 20.5        |
|        | 15 min   | 10.40                 | 72.10 (3.74) | 17.50             | 53.50 (1.80) | 9.9  | 8.7         |
|        | 30 min   | 13.70                 | 61.80 (2.67) | 24.50             | 52.00 (2.24) | 8.3  | 1.5         |
|        | 45 min   | 14.70                 | 60.00 (2.34) | 25.30             | 50.20 (2.17) | 9.1  | 0.7         |
|        | 60 min   | 20.70                 | 41.40 (1.78) | 37.90             | 34.00 (1.54) | 6.8  | 0.6         |
| OVR    | Initial  | 0                     | 100 (1.80) | 0                      | 64.90 (0.67) | 34.0 | 1.1         |
|        | 15 min   | 7.90                  | 87.10 (1.05) | 5.00             | 66.90 (0.53) | 14.9 | 5.3         |
|        | 30 min   | 10.90                 | 78.60  | 10.50                    | 59.40  | 15.3 | 3.9         |
|        | 45 min   | 11.80                 | 77.10  | 11.10                    | 59.10  | 15.1 | 2.9         |
|        | 60 min   | 31.60                 | 49.50  | 18.90                    | 40.70  | 8.1  | 0.7         |

Table 3. Fractional composition of liquid products of vacuum residue cracking.

| Time   | Content (wt%) |
|--------|----------------|
|        | B.p. – 200 200 – 360 |
| NVR    |                |
| Initial | 0.0           | 1.4 |
| 15 min  | 13.2           | 29.4 |
| 30 min  | 27.9           | 23.4 |
| 45 min  | 27.2           | 20.3 |
| 60 min  | 30.6           | 16.9 |
| ZVR    |                |
| Initial | 0.0           | 0.0 |
| 15 min  | 18.8           | 26.3 |
| 30 min  | 19.2           | 24.7 |
| 45 min  | 20.1           | 22.9 |
| 60 min  | 16.0           | 15.0 |
| OVR    |                |
| Initial | 0.0           | 25.9 |
| 15 min  | 13.6           | 39.1 |
| 30 min  | 21.3           | 32.8 |
| 45 min  | 24.6           | 31.8 |
| 60 min  | 12.5           | 27.1 |

The fractional composition of the liquid products of the cracking of vacuum residues is presented in Table 3. It was found that the formation of components of gasoline and diesel fractions occurs at the initial stage of the process. Probably, the fraction bp-200 °C is formed due to cracking of the oil components, while the formation of the fraction 200-360 °C occurs during resin cracking. With an increase in the time of process, the content of resins decreases and, as a result, the rate of formation of
components of the fraction 200–360 °C becomes lower than the rate of their cracking. This leads to a 
decrease in the content of the fraction 200-360 °C in cracking products and an increase in the yield of 
the fraction bp=200 °C. If cracking of Omsk vacuum residue (OVR) and Zuzeyevsk vacuum residue 
(ZVR) lasts 45-60 min, the yield in the bp-200 °C fraction decreases. This is probably due to 
autocatalytic reactions occurring on the surface of coke, which to this time becomes sufficient to 
initiate the reaction of gasoline cracking on its surface [13].

The analysis of gaseous products showed that the cracking of vacuum residues results in the 
formation of C1-C4 hydrocarbons predominantly (Table 4), while iso- and n-pentanes, carbon dioxide 
are also present. The main gaseous cracking products are methane and ethane (~ 85 rel.% of the total 
amount of all gases). An increase in time of the process leads to an increase in the content of C1–C3 
hydrocarbons in the composition of cracking gases of all the objects of study. The content of C4–C5 
hydrocarbons remains the same, being less than 1 wt%.

Table 4. Composition of gaseous products of cracking of vacuum residues.

| Gases     | Content, wt% |
|-----------|--------------|
|           | OVR 15 | OVR 30 | OVR 45 | OVR 60 | ZVR 15 | ZVR 30 | ZVR 45 | ZVR 60 | NVR 15 | NVR 30 | NVR 45 | NVR 60 |
| H2        | 0.23   | 0.39  | 0.67  | 0.94  | 0.49  | 0.70  | 0.57  | 0.45  | 1.07  | 0.79  | 0.53  | 0.82  |
| CH4       | 4.52   | 7.26  | 8.48  | 21.42 | 6.50  | 8.58  | 10.04 | 14.46 | 12.11 | 14.28 | 17.28 | 17.31 |
| CO2       | 0.17   | 0.06  | 0.08  | 0.24  | 0.29  | 0.37  | 0.28  | 0.36  | 0.58  | 0.34  | 0.42  | 0.26  |
| C2H6      | 0.02   | 0.01  | 0.01  | 0.01  | 0.01  | 0.01  | 0.00  | 0.04  | 0.01  | 0.01  | 0.01  | 0.01  |
| C3H8      | 1.50   | 2.05  | 1.68  | 6.49  | 1.96  | 2.52  | 2.52  | 3.61  | 2.97  | 2.88  | 4.54  | 4.88  |
| C4H10     | 0.96   | 0.82  | 0.61  | 1.36  | 0.79  | 1.06  | 0.91  | 1.32  | 1.19  | 1.02  | 1.78  | 1.92  |
| i-C4H10   | 0.12   | 0.08  | 0.06  | 0.26  | 0.09  | 0.12  | 0.10  | 0.14  | 0.12  | 0.11  | 0.19  | 0.19  |
| n-C4H10   | 0.27   | 0.17  | 0.14  | 0.66  | 0.19  | 0.24  | 0.19  | 0.28  | 0.23  | 0.20  | 0.52  | 0.41  |
| i-C5H12   | 0.05   | 0.03  | 0.11  | 0.04  | 0.05  | 0.04  | 0.04  | 0.04  | 0.03  | 0.01  | 0.09  | 0.07  |
| n-C5H12   | 0.06   | 0.03  | 0.15  | 0.04  | 0.05  | 0.04  | 0.04  | 0.03  | 0.04  | 0.02  | 0.12  | 0.08  |
| Σgas      | 7.90   | 10.90 | 11.80 | 31.60 | 10.40 | 13.70 | 14.70 | 20.70 | 18.38 | 19.70 | 25.48 | 26.20 |

4. Conclusion
It has been found out that resins prevail in the composition of initial resins (33–38 wt.%). The 
dependence of the degree of conversion of the components of vacuum residues on the duration of 
cracking has been revealed. It has been shown that the reactions of condensation of resins to 
asphaltenes and coke readily run at the initial stage of the process (0–15 min). With an increase in the 
duration of cracking, reactions of destruction of oil and resin components with the formation of 
distillate fractions begin to proceed, and gas and coke formation also increases.

The content of distillate fractions in liquid products of vacuum residue cracking can reach 50 wt%.
At the initial stage of cracking, accumulation of the fraction 200-360 °C occurs in the composition of 
products. The increase in the time of process results in cracking of this fraction and the accumulation 
of distillate (boiling point 200 °C) in the liquid cracking products.

Acknowledgements
The work was carried out as a part of project No. V.46.2.2 of the Program for Basic Scientific 
Research of State Academies of Sciences.

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