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MODELING OF THE COKING PROCESS

Abstract: The article is devoted to the modeling of coking as the most common conversion process of vacuum residue in oil refineries. The main parameters of the process and the impact of the products on the product and characteristics are taken into account. The main features of each process (chemistry, kinetics and thermal decomposition of asphalts) are summarized. Some dependencies published in the literature are evaluated and used to predict the yield and properties of coke products.

Key words: Coking process, kinetic parameters, oil, atmospheric residue, resin, asphalten.

Language: English

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Introduction

At present, the gradual coking of all technologies for the processing of heavy crude oil with the depletion of carbon has a special place, because it is very economically viable for refineries. The purpose of coking is to convert residual raw materials (residues of oil distillation in the atmosphere and vacuum column) into lighter and more valuable products, including gases, gasoline fractions, light and heavy gas oil, as well as solid products - petroleum coke. During coking, long hydrocarbon molecules break down into shorter ones under thermal conditions.

This process is called "gradual coking" because the cracking reaction takes place in the coking chambers, where the heated raw material has a longer shelf life, rather than in the kiln's snake tubes. Failure to do so may result in coking of the pipes and premature shutdown of the unit. The heat given off by the kiln to the raw material is sufficient for destructive distillation, but without the raw material entering the coke chamber, the coke is not delivered to initiate recovery reactions. In other words, heating in the furnace only initiates cracking reactions, which are completed in the coking chambers [1-4].

Method

Oil refineries with coking facilities are often referred to as continuous refineries. The advantage of coking is the inherent flexibility of the conversion process of various raw materials, which allows to solve the problem of reducing the demand for heavy oil by switching to the production of more expensive and lighter products.

One of the goals of the coking process may be the production of different types of coke. Coking can produce several types of coke, depending on the characteristics of the raw material, the design of the plant and the operating conditions [2]. Fuel coke, anode coke, needle coke.

By changing the operating parameters, it is possible to change the quality and productivity of coke products in accordance with the goals set by the refinery. The variable parameters in the coking plant are:

- Heat when leaving the furnace and at the entrance to the coking chambers. Heat is the main parameter that determines the coking conditions. Heat determines the quality of coke;

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- Pressure in the coking chamber. The coking output decreases with decreasing pressure in the coking chambers;

- Recycling ratio of raw materials;
- composition of raw materials;

Results

Kinetics of coking reactions

The kinetic parameters of coking and pyrolysis reactions can be determined by conducting TGA at different temperatures. Based on isoconversion methods, Schuker (1983) obtained a number of activation energies for pyrolysis depending on the evaporated part of the asphalt. At higher conversion rates, the activation energy was higher. On the other hand, Shikh and Son [3] found that the rate of

conversion of activation energy is almost constant for different values.

Using the direct dependence of Arrhenius, Park, and co-authors [4], he found that the activation energy in the decomposition region of carbonaceous materials at 350–600 °C was in the range of 146–246 kJ / mol. mol. The area where the evaporation of light organic substances occurs (50-350 °C), the activation energy is less (19-23 kJ / mol). Separation of atmospheric residues

Different fractions of atmospheric distillation residues of heavy oil were isolated by chromatographic separation. The properties of the oil and the atmospheric distillation residue are given in the table.

Table 1. Properties of heavy oil and its atmospheric distillation residue

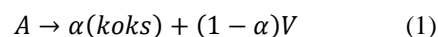
Property	Oil	atmospheric residue
Density, °API	12	5,6
Sulfur content,% by weight .	5,29	6,08
Amount of metals mg / kg: Ni		
V	89	97
Elemental composition,% by mass:		
C	83,98	82,56.
H	10,28	10,56
N	0,40	0,74
Ingredients,% by weight:		
Saturated hydrocarbons are aromatic	15,83	11,75
hydrocarbons	36,74	23,66
resins	18,61	34,27
asphaltenes	28,82	30,32

After separation of saturated and aromatic hydrocarbons, resins and asphaltenes, TGA was carried out for each part, as well as for atmospheric residues. The temperature was changed from room temperature to 800 °C. To determine the kinetic parameters of coke formation, all fractions and atmospheric residues (excluding saturated hydrocarbons) were analyzed at three different temperatures: 8.12 and 16 °C / min. Thermogravimetric analysis of the saturated hydrocarbon fraction was performed only at a single value of the temperature (8 °C / min) as it is prone to early thermal decomposition.

Non-isothermal kinetics

Kinetic parameters of pyrolysis of asphalts were determined by non-isothermal method. TGA data were analyzed by the Friedman method and the kinetics were calculated for the first-order reaction. The method is based on the comparison of data

obtained at different linear heating rates. When the form of the kinetic equation is unknown, it can be used to find the activation energy of a number of processes. According to Shuker and Keveshan (1980), the thermal decomposition of heavy components can be described as follows



where A is the reagent; V - volatile fraction; α is the stoichiometric coefficient for coke.

The following kinetic expression for volatile products can be obtained from this equation:

$$\frac{1}{v_0} \cdot \frac{dv}{dt} = k_0 e^{-E_A/RT} \left[1 - \frac{V}{v_0} \right] \quad (2)$$

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where V_0 is the total amount of evaporated substance. The linear transformation of equation (2) gives the following expression:

$$\ln \left[\frac{dx}{dt} \right] = \ln [k_0(1-x)] - \frac{EA}{RT} \quad (3)$$

where $x = V / V_0$ is part of the volatile fraction, corresponding to the degree of transformation of asphalts during thermal decomposition.

Equation (3) is used by substituting different values of the degree of transformation x ranging from 0.1 to 0.8. The first derivatives of the TGA curves were used to determine the dx/dt and T values for all values of the conversion rate obtained at different temperature rates (8, 12, 16 °C / min). The linear regression of formula (3) gave a number of values of

activation energy (E) and previous exponential factors (k_0) depending on the degree of conversion of the asphalts.

Results

Thermal decomposition

Figure 1 shows the results of the TGA analysis of atmospheric residues and other fractions

- Atmospheric residue. The mass varies between 100 and 500 °C. Initially, evaporation is mainly due to the distillation of light alkanes and lasts up to 350 oC. At temperatures between 350 and 500 °C, showing the decomposition of heavy fractions - asphalt and resin rapid evaporation occurs. Evaporation between 500 and 800 ° is low and continues at an almost constant rate, with coke output from the atmospheric residue at 16.3 ms. %.

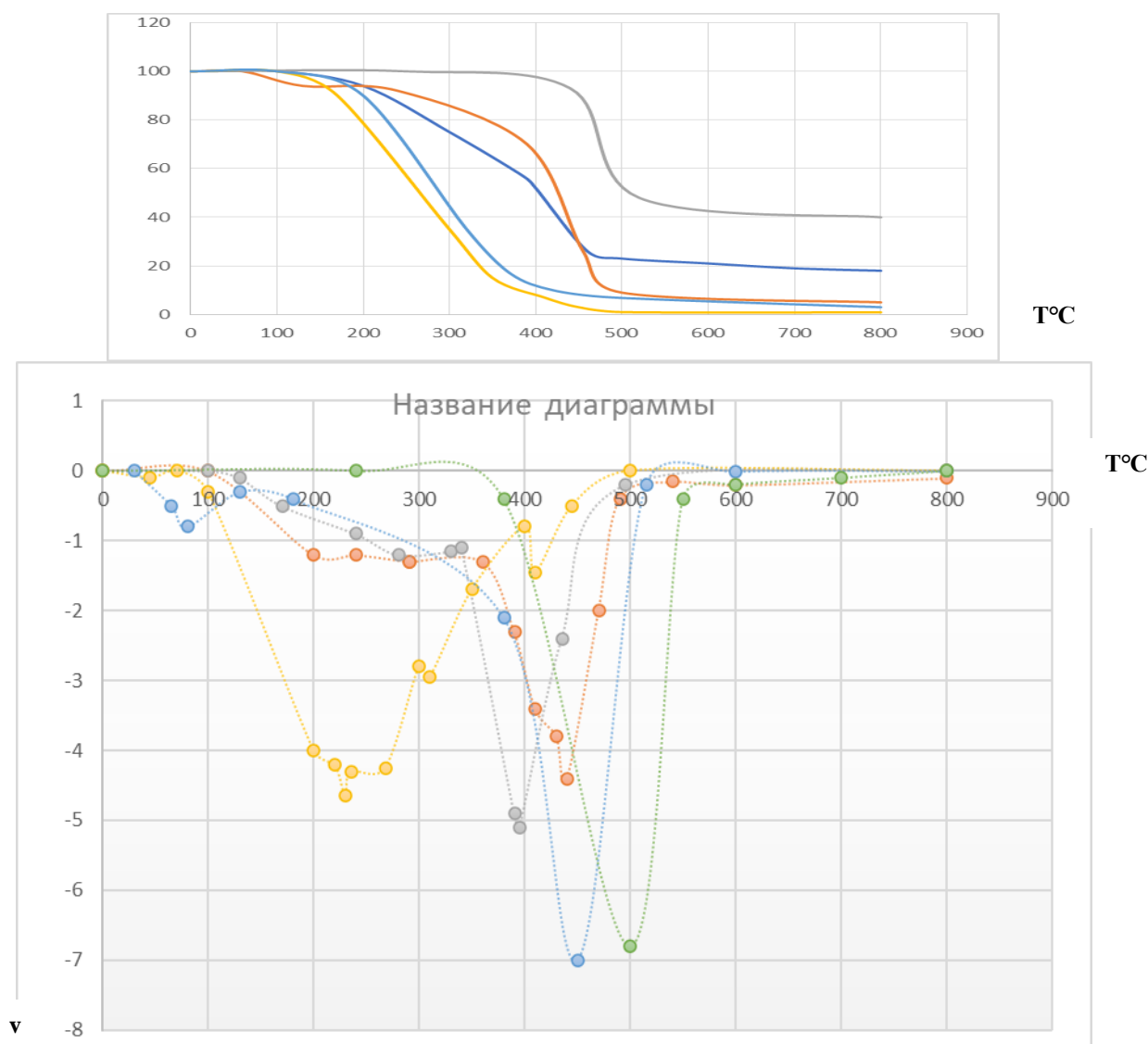


Figure 1. Thermograms and curves of the rate of change of mass of atmospheric residue and its fractions when heated in nitrogen atmosphere at 8oS / min

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Asphaltenes. Evaporation from room temperature to 350 ° C corresponds to a conversion of almost 10%. [5] reported that changes observed at temperatures of about 350 ° C could be explained by the removal of alkyl groups of asphaltene structures from peripheral areas.

The most significant mass loss is observed in the temperature range between 430 and 550 ° C, where intermolecular and chemical bonds are expected to be broken, including sulfur bridges and C-C bonds. At this stage, asphalts can be converted into gases and valuable components, ie oils. As pyrolysis takes place between 550 and 800 ° C, asphalts undergo condensation reactions to form coke as a final product. In the range of 600 to 800 ° C, the coke product obtained from the asphalt part remains practically stable (43.1kut.%).

- Resins. Reflecting this fraction gives a 7% mass loss in the range of 50 to 150 ° C, which is light reflects the evaporation of alkanes. Distillation continues between 150 and 350 ° C. Between 350 and 500 ° C, mass loss is accelerated by the reactions of the cracking process. During this period, almost 80% of the resin mass is thermally decomposed. The pyrolysis interval of resins is the widest compared to other fractions. A possible explanation for this is that during pyrolysis, resins can participate in condensation reactions with the formation of heavier molecules, such as asphaltenes [6]. Weakly bound alkyl groups form free radicals that tend to neutralize and condense into larger molecules. After evaporation of most of the light compounds from the initial stages of heating, the remaining large molecules of resin and asphalt formed as a result of thickening evaporate, which explains the extent of pyrolysis of resins. Coke from resins makes up 4.6% of the mass.

- Aromatic hydrocarbons. No significant mass loss occurs at temperatures up to 100 ° C. In the range

of 100 to 320 ° C, the most variable is the evaporation of mono-, di-, tri- and higher polycyclic compounds. In the range of 320-480 ° C, resins undergo cracking reactions. . Coke output is 3.8 blunt. About% of aromatic hydrocarbons are very close to resins.

- Saturated hydrocarbons. All compounds of this fraction give very small amounts of coke (0.3 kg.%) Due to complete evaporation. Saturated hydrocarbons are practically not involved in cracking reactions: all changes occur in the distillation phase.

- Thermograms of asphalts and atmospheric residues behave similarly at temperatures below 400 ° C; Between 450 and 800 ° C, it is practically the same. This may indicate that the behavior of atmospheric residues in this range is generally determined by reactions involving heavy fractions such as asphalt.

Figure 1 separately shows the rate of change in the mass of each fraction and atmospheric residue. The maximum rate of change in the mass of asphalts and resins is observed at 467 and 455 oC, respectively. The point of the maximum mass loss ratio of asphalts (467 ° C) is very close to that obtained by other researchers]. At relatively low temperatures (below 350 ° C) the thermal decomposition of asphaltenes continues with the elimination of peripheral groups. At temperatures above 350o C, asphalt structures are significantly reduced in size. In the early stages of pyrolysis, low-molecular compounds are distilled, but it is also possible for larger molecules to break down with the formation of volatile fragments with increasing temperature.

Initially, gases are released as a result of breaking the alkyl chains, but at fairly high temperatures (above 450 ° C) the decomposition of asphalts breaks stronger chemical bonds and breaks down skeletons, increasing the amount of gases released.

Table 2. Values of activation energy and exponential stress depending on the degree of conversion

X	Atmospheric residue			Asphaltenes			Resins			Aromatic hydrocarbons		
	E _A	k ₀	r	E _A	k ₀	r	E _A	k ₀	r	E _A	k ₀	r
0,1	11,5	4,1 · 10 ⁵	0,989	41,0	1,4·10 ¹⁴	0,978	10,8	4,4·10 ⁴	0,992	10,8	6,7·10 ⁷	0,991
0,2	15,3	4,4·10 ⁶	0,999	54,9	1,8 · 10 ¹⁸	0,998	14,8	5,9·10 ⁵	0,998	14,5	7,8·10 ⁹	0,997
0,3	12,4	1,0·10 ⁵	0,995	56,7	4,2·10 ¹⁸	0,996	21,1	3,9·10 ⁷	0,999	14,2	1,7·10 ⁹	0,991
0,4	12,7	4,8·10 ⁴	0,991	52,8	1,6·10 ¹⁷	0,993	35,8	1,3·10 ¹²	0,999	17,6	4,6·10 ¹⁰	0,992
0,5	20,1	9,5·10 ⁶	0,985	58,6	6,7·10 ¹⁸	0,995	45,9	1,2·10 ¹⁵	0,996	17,9	1,3·10 ¹⁰	0,990
0,6	24,8	1,2·10 ⁸	0,994	52,1	4,6·10 ¹⁶	0,998	49,8	1,3·10 ¹⁶	0,998	21,6	1,1·10 ¹¹	0,992
0,7	27,8	2,7·10 ⁸	0,994	53,1	5,9·10 ¹⁶	0,999	47,5	1,7·10 ¹⁵	0,994	19,8	8,9·10 ¹⁰	0,994
0,8	30,0	2,4·10 ⁸	0,980	58,6	8,1·10 ¹⁷	0,987	48,9	2,6·10 ¹⁵	0,999	19,2	1,2 · 10 ¹⁰	0,994

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The most significant conversion of asphalts occurs in the range of approximately 430 to 550 ° C. Compared to atmospheric residues and other fractions, this is the narrowest range in which fission reactions predominate. Coke yield was the same at all temperatures (43.1% by weight) and the activation energy increased to peak values at the conversion levels of 0.5 and 0.8. Asphalt has a higher activation energy than atmospheric residues and other fractions can be associated with. free radicals in the reaction.fracture operations.

. Atmospheric residue is formed by the distillation of lighter components, resulting in the concentration of heavy components in heavy fractions; The only significant reaction to cracking under these conditions.

Evaporation of the resins is completed at about 500 ° C. The coke output is the same at all three values of heating rate (4.6 kg.%). With the increase in the conversion rate, the activation energy changes and reaches the highest values between 0.4 and 0.8. This process can be the result of the decomposition of resins with the formation of free radicals condensing in the form of coke.

The evaporation curve and the Arrhenius area for aromatic hydrocarbons are not shown; for them only

the values of the activation energy, the pre-reading factor and the correlation coefficient are given in Table 2. The activation energy of this fraction is less than that of asphalt and resins; is approximately the same as atmospheric residues at low conversion rates. Thermogravimetric data show that asphalts contribute the most to the formation of odors; they are followed by resins and aromatic hydrocarbons. In terms of activation energy, the atmospheric residue occupies an intermediate position between aromatic hydrocarbons and resins.

RESULTS

The results show that asphalt is the main coke-forming part. It accounted for 43.1% of the asphalt coke mass. Decomposition reactions should be expected to convert asphalts to gases, oils and resins. Resins and aromatic hydrocarbons produce almost the same amount of coke, but the activation energy of resins is slightly higher. Saturated hydrocarbons evaporate almost completely. Atmospheric residue indicates that the activation energy increases with increasing conversion rate. This indicates that in the first stages of heating, the light components evaporate, and then the heavy fractions - resins and asphalts - begin to break down.

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