

Hydrocarbon composition of liquid products of catalytic oxy-cracking of vacuum gasoil

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Abstract. The hydrocarbon composition of liquid products of oxycracking of vacuum gas oil obtained in the presence of a zeolite-containing catalyst has been studied. It has been established that the group hydrocarbon composition of the liquid oxycracking catalyzate is significantly affected by the process parameters. When considering the influence of the process temperature, it was found that the concentration of C₅-C₉ and C₁₀₊ alkanes has an opposite temperature dependence: the C₅-C₉ yield passes through a maximum at a temperature of 500°C, while for C₁₀₊ it is a minimum temperature; there is a linear relationship between the temperature and the yield of unsaturated; the yield of naphthenes gradually decreases with increasing temperature; elevated temperatures contribute to an increase in the total yield of aromatic hydrocarbons. When varying the duration of the process, it was revealed: within 900 seconds from the beginning of the process, the most significant decrease in concentration was noted for aromatic hydrocarbons. The low oxidation state of 0.5% contributes to the intensive conversion of high molecular weight alkanes and aromatic hydrocarbons with long side chains; the concentration of oxygen-containing compounds raises with an increase in the degree of oxidation to 1%, passing through a maximum. The contact time with the catalyst had a complex effect on the hydrocarbon composition of the liquid products of vacuum gas oil oxycracking: a short contact time contributes to a decrease in the concentration of high molecular weight paraffinic and naphthenic hydrocarbons and an increase in aromatic hydrocarbons; with a subsequent increase to 2 s, it drops sharply. The obtained data made it possible to establish the fundamental distinguishing features of the catalytic oxycracking of vacuum gas oil from the traditional catalytic and non-catalytic oxidative ones, and also to propose a list of reactions occurring during the catalytic oxycracking of vacuum gas oil.

1 Introduction

Processing of petroleum hydrocarbons remains one of the most intensively developing scientific areas. First of all, this is due to the need to fully use the potential of oil feedstock, especially heavy oil fractions, to obtain various types of feedstock for the petrochemical

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industry. Another factor is related to a certain level of technological "exhaustion" of well-known technological solutions.

From its inception in 1942 to the present day, the catalytic cracking process has proven itself to be the main tool for increasing the profitability of oil refining. This is predetermined by its ability to convert low-value oil residues (vacuum gas oil, etc.) into high-value gasoline, diesel fuel, unsaturated C₃-C₄. Despite its uniqueness, the development of the catalytic cracking process was mainly associated with the evolution of the catalyst and, judging by the data of the periodical literature, it reached a certain level of saturation [1-3].

A fundamentally new approach to the processing of liquid heavy oil fractions can be oxidative catalytic cracking - oxycracking based on the oxidation of heavy oil fractions with oxygen [4-6]. It is a complex of catalytic thermochemical transformations of hydrocarbons in the presence of oxygen, resulting in a process of cracking and oxidation reactions occurring simultaneously and affecting each other. The predominance of one or another process, their mutual influence affects the process indicators (qualitative and quantitative composition of products).

As we have shown in previous works [4-6], one of the main advantages of oxycracking in comparison with traditional catalytic cracking is an increase in conversion by almost 10% (69.42% under oxycracking conditions at 500°, 1% oxidation state, contact time 1.7 sec, 900 sec duration versus 61.3% with the traditional one), which is attractive from an economic point of view, since it is known that an increase in this indicator by every 1% leads to an increase in profit by \$0.10 per barrel of raw materials at [7-10].

In this regard, it is of interest to study the features of the hydrocarbon composition, the concentration limits of liquid products of catalytic oxycracking of vacuum gas oil, and the influence of process parameters on them.

2 Methods

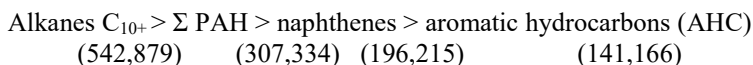
Vacuum gas oil was chosen as the object of research (start of boiling 270 – end of boiling 500°C) as the most typical feedstock for catalytic cracking units. Physico-chemical characteristics of vacuum gas oil corresponding to TY 38.1011304-2004 are shown in Table. The industrial microspherical zeolite-containing catalyst OMNICAT-210 manufactured by Grace was chosen as a catalyst. The process of traditional, oxidative thermal and oxidative catalytic cracking was carried out on a flow unit at atmospheric pressure at 500°C and in the temperature range of 450-550°C, respectively; catalyst volume was 5 sm³.

The yield of cracking gas was determined by its volume and density, the yield of coke was determined by the gravimetric method by the adsorption of ascarite dioxide, and the quantitative yield of liquid products (gasoline fraction (start of boiling) - 195 °C, light gas oil 195 - 350 °C and heavy gas oil - residue > 350 °C) was determined by the according to the results of distillation (fractionation). Determination of the fractional composition, products of traditional and oxidative catalytic cracking was carried out in accordance with GOST 2177-99. Quantitative hydrocarbon analysis was carried out in a system consisting of an Agilent 6890N gas chromatograph interfaced with an Agilent 5975 high-performance mass selective detector (Agilent Technologies, USA). Conditions for chromatographic analysis are given in [4-6]. WILLEY and NIST libraries were used as spectral databases.

3 Results

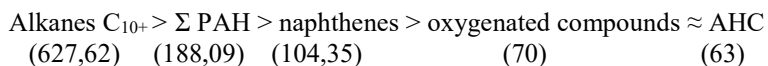
Since the influence of the main technological parameters on the yield and quality of the products obtained is more convenient to consider in relation to a specific type of oxycracking feedstock, we initially studied the group hydrocarbon composition, including in the context

of concentrations, the composition of vacuum gas oil (table.). The analysis of the individual composition of vacuum gas oil is difficult due to the large number of hybrid hydrocarbons. Analysis of the group chemical composition by modern physical and chemical methods showed that the main component of the vacuum distillate are alkanes. In addition, along with paraffins in vacuum gas oil, there are also monocyclic naphthenes and hydrocarbons of the benzene series, as well as bi- and polycyclic - naphthenic, aromatic, including polycyclic aromatic (PAH) and naphtheno-aromatic hydrocarbons. In general, the group hydrocarbon composition of vacuum gas oil is represented by the following decreasing sequence of concentrations (g/l) (table):

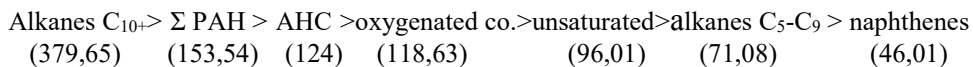


As you can see, aromatic hydrocarbons are the second main component of vacuum gas oil. Basically, these are mono-, bi- and tricyclic hydrocarbons, as well as hydrocarbons, the molecules of which contain more than four rings.

In the catalyzate obtained at a low temperature oxycracking (450°C), the first 3 components remain in their original places, but aromatic hydrocarbons are replaced by unsaturated ones (Table):



On the example of an oxycracking sample obtained at 500°C, 1% oxidation state, contact time 1.7 sec, duration 900 sec, the order of arrangement of hydrocarbon groups in the liquid oxycracking catalyst according to decreasing concentration (g/l) is the following sequence (table):



As follows from the presented data, compared with the initial vacuum gas oil, the concentration of C_{10+} alkanes in the liquid catalyzate in the presence of oxygen decreased by 1.4 (against 0.8 in catalytic cracking), naphthenes by 4.3 (against 8.9 in catalytic cracking). The content of individual aromatic, polyaromatic carbohydrates, as well as 2-6 ring polyaromatic carbohydrates decreased by 1.1 times (against an almost 2-fold decrease with catalytic cracking), 3.5 times (against 3.8 with catalytic cracking) and 1.5 times (vs. 1.5-fold reduction in catalytic cracking), respectively. The same sequence is also typical for 550°C (with a slight difference in concentrations: C_5-C_9 alkanes, naphthenes and oxygen-containing compounds decrease by an average of 2-3 times, while C_{10+} alkanes, unsaturated and, mono- and poly-aromatic, on the contrary, increase).

With a constant high content of C_{10+} alkanes and polyaromatic carbohydrates, the effect of duration on the concentration of other groups of hydrocarbons is as follows: the maximum amount of C_5-C_9 alkanes is observed up to 900 s, unsaturated - 1800 sec, oxygen-containing compounds - at 900 s. the concentration of C_{10+} alkanes and all aromatics grows symbatically with the duration of the process. The concentration of the latter exceeds the initial value in the raw material and indicates the high aromaticity of the liquid catalyzate. The minimum amount of C_{10+} alkanes was found in the 900 sec oxycracking sample; it decreased by 1.5 times compared to the initial one, which indicated a high degree of cracking of this group of hydrocarbons.

A low degree of oxidation contributes to the highest degree of conversion of C₁₀₊ alkanes (their concentration decreased by a factor of 3.2 compared to vacuum gas oil), a high degree of oxidation contributes to the maximum formation of C₅-C₉.

Table 1. Effect of Oxycracking Conditions on the Concentration of Hydrocarbon Groups in the Liquid Catalyst.

№ experience	Oxycracking mode	Concentration, g/l								concentration of all hydrocarbons, g/l
		alkanes C ₅ -C ₉	alkanes C ₁₀₊	naphthenes	unsaturated	oxygenated compounds	aromatic hydrocarbon	Individual PAH	2-6 ring PAH	
Temperature effect										
1	450 °C	50	627.6	104.4	70	63.1	63	9.0	179.059	1021.5
2	500 °C	72	379.7	46	136	118.6	124	14.6	168.935	1120.8
3	550 °C	22	642.9	12	169	50.3	101	9.3	223.982	936.6
Effect of duration, sec										
4	300 s	35	434.7	179	38	71.0	127	8.4	181.777	876.4
5	600 s	52	586.2	112	112	79.6	96	9.2	175.74	999.2
2*	900 s	72	379.7	46	96	118.6	124	14.6	168.935	1120.8
6	1800 s	31	555.3	65	218	66.1	218	39.9	195.243	1004.0
7	2700 s	19	769.2	78	148	48.1	253	59.4	289.534	1010.2
Effect of oxidation state, %										
8	0,5%	57	169.9	162	58	108.7	124	23.5	185.613	1078.6
2*	1%	72	379.7	46	96	118.6	124	14.6	168.935	1120.8
9	2%	104	430.8	17	312	85.0	203	6.9	129.995	1220.5
Influence of contact time, sec										
10	1.2 s	106	589.3	102	204	151.0	108	9.2	182.9	998.5
2*	1.7 s	72	379.7	46	96	118.6	124	14.6	168.9	1120
11	2 s	-	312.3	20	119	41.2	215	19.7	194.8	1014
VGO	-	-	542.9	196.2	-	11.4	141	50.7	256.6	1257
CC	500°C	120	643.2	21.9	59.1	12.1	72.5	13.3	166.4	1413
OTC	500 °C	18,3	312.6	126.2	254	76.8	98.9	7.7	346.6	984.7

VGO - Vacuum gas oil

CC - Catalytic cracking

OTC - Oxidative thermal cracking

Consideration of the concentration data of the group hydrocarbon composition of samples of liquid oxycracking catalyzate makes it possible to establish the nature of the effect of process parameters. In particular, the influence of temperature can be represented as follows: the concentration of C₅-C₉ and C₁₀₊ alkanes has an opposite temperature dependence: the yield of C₅-C₉, like oxygen-containing compounds, passes through a maximum at a temperature of 500°C, while for C₁₀₊ - this is a minimum temperature; there is a linear relationship between the temperature and the yield of unsaturated; the yield of naphthenes gradually decreases with increasing temperature; elevated temperatures contribute to an increase in the total yield of aromatic hydrocarbons, and especially for individual aromatic hydrocarbons and polycyclic aromatic hydrocarbons; at a temperature of 550°C, the increase in the total yield of aromatic hydrocarbons continues against the background of a sharp drop in the yield of individual, especially polycyclic aromatic hydrocarbons.

It should be noted that the duration of the process has the following effect: within 900 seconds from the start of the process, the most significant decrease in concentration was noted for aromatic hydrocarbons, which is apparently due to the fact that they undergo oxidation of attached alkyl groups, oxidative destruction of aromatic rings with the formation of a series of carboxylic acids or the oxidation of hydrogen bound in the aromatic cycle to carbonyl oxygen (these reactions relate primarily to aromatic hydrocarbons with long side chains), it was during this time period that an intensive increase in the concentration of oxygen-containing compounds was noted; with an increase in the duration of the process over 900 seconds, a redistribution of hydrocarbon groups was recorded - the concentration of mainly high-molecular saturated and aromatic hydrocarbons increased, which indicates the occurrence of condensation reactions, additions, resulting in the products entering into compaction reactions; these data are in good agreement with the results presented earlier [6] on the increase in the amount of polycyclic aromatic hydrocarbons with an increase in the duration of the process - unsaturated hydrocarbons enter into condensation reactions with aromatic hydrocarbons with the formation of high-molecular surface compaction products.

Comparison of the data presented in the table also made it possible to establish that the depth of change in the qualitative group composition of the liquid oxy-cracking catalyzate depends, first of all, also on the degree of oxidation - this is one of the determining factors affecting the rate of reactions of oxidation, polymerization, polycondensation, oxidative dehydrogenation, dehydrogenation of various hydrocarbon groups components of vacuum gas oil, and to the greatest extent will determine the qualitative characteristics of the products obtained: at a low oxidation state of 0.5%, high-molecular alkanes and aromatic hydrocarbons with long side chains are most intensively converted; the concentration of oxygen-containing compounds with an increase in the degree of oxidation to 1% increases, passing through a maximum.

Consideration of the data obtained depending on the contact time allows us to conclude that a short contact time contributes to a decrease in the concentration of high molecular weight paraffinic and naphthenic hydrocarbons and an increase in aromatic hydrocarbons; the selectivity for oxygen-containing compounds increases with a contact time in the range from 1.2 to 1.7 s, with a subsequent increase to 2 s, it drops sharply. The maximum concentration of unsaturated was noted under conditions of elevated temperatures and a high degree of oxidation.

The comparative composition of liquid products obtained in the process of catalytic cracking of vacuum gas oil at 500°C is also presented in the table. As can be seen, the content of hydrocarbon components of the liquid catalytic cracking obtained at a temperature of 500°C is presented in the form of the following series in decreasing concentration:

Alkanes C₁₀₊ > Σ PAH > alkanes C₅-C₉ > AHC > unsaturated > naphthenes
 (643,17) (179,69) (120,05) (72,46) (59,12) (21,87)

The observed change in the distribution of hydrocarbon groups is associated with intensive cracking of high molecular weight paraffin's and de-alkylation of alkyl aromatic hydrocarbons with long chains into lower molecular weight paraffinic, olefin and alkyl aromatic hydrocarbons with short side chains, naphthenic into alkyl naphthenic or alkyl aromatic, then into unsaturated, cracking and redistribution of hydrogen in the latter, isomerization, polymerization, condensation, coking, etc. The order of arrangement of hydrocarbon groups according to the degree of their reactivity in accordance with the change in concentration relative to the feedstock is the sequence: naphthenic hydrocarbons > alkylated polycyclic aromatic hydrocarbons, aromatic hydrocarbons > paraffinic hydrocarbons, which is in good agreement with the data available in the literature [11-13] on stability different classes of hydrocarbons to catalytic splitting. The absence of a catalyst

under OTC conditions is characterized by the following sequence of distribution of hydrocarbons in the liquid catalyze in descending order of concentration:

Σ PAH > Alkanes C₁₀₊ > unsaturated > AHC > oxygenated co. > naphthenes > alkanes C₅-C₉
(346,58) (312,62) (254,26) (98,93) (76,81) (166,15) (18,31)

The nature of the resulting hydrocarbons, which is different compared to traditional catalytic cracking and oxy-cracking, is a consequence of the high-temperature oxidative processes occurring exclusively by the radical chain mechanism [14–17]. Oxygen, reacting with an organic compound, splits off hydrogen or is introduced into a molecule, or both at the same time. This process results in the formation of free radicals and hydro-peroxides as intermediates. Chain reaction starts. Chain termination occurs as a result of radical recombination. A stationary equilibrium concentration of free radicals is quickly established in the system. Other possible reactions also proceed simultaneously: oxidative dehydrogenation; oxidative polymerization; de-alkylation; poly-condensation; cracking, followed by compaction of its products, etc.

The high concentration of PAHs indicates the dehydrogenation nature of the reactions taking place and the high degree of oxidation. A characteristic feature of OTC products is also the highest content of C₁₀₊ alkanes (as we will see below, these are n-alkanes and iso-alkanes with the number of carbon atoms from 30 and more). The main part of atmospheric oxygen in the OTC goes to the formation of water and carbon dioxide, an insignificant part - to the formation of organic substances containing oxygen. Oxidative transformations are accompanied by the formation of a small amount of oxygen-containing substances, in which oxygen is in the form of carbonyl and ester groups, which are further converted into resins – hetero-aromatic cycles, the content of which is in the OTC catalyze.

4 Conclusion

The features of the hydrocarbon composition of liquid products of catalytic oxycracking of vacuum gas oil and the influence of process parameters on them have been studied. The results of the concentration dependences of hydrocarbon groups showed that the complex of ongoing reactions is fundamentally different from traditional catalytic and oxidative thermal cracking. Comparison of the quantitative hydrocarbon composition of the liquid catalyze indicates that the main processes occurring during the oxidation of vacuum gas oil are destruction, dehydrogenation of paraffins, dehydrogenation of naphthenes, oxidative dehydrogenation of hydrocarbons with a decrease in molecular weight and the formation of unsaturated and oxygen-containing compounds, dealkylation of alkyl substituents of aromatic compounds. An analysis of the dynamics of changes in the hydrocarbon composition of liquid products of oxycracking made it possible to establish the direction of the reactions: the conversion of C₁₀₊ alkanes is facilitated by a long contact time, a low degree of oxidation, a short duration of the process, and a medium temperature regime; the conversion of naphthenes, on the contrary - a short contact time, a high degree of oxidation, a long process time and a high temperature regime; the formation of unsaturated - high temperature, oxidation state and duration of the process, but short contact time; accumulation of oxygen-containing compounds - average temperature, duration and degree of oxidation, but short contact time; aromatic hydrocarbons - high contact time, oxidation state and duration of the process, but medium temperature regime. The obtained data on the nature of the occurring reactions and changes in the group composition of liquid catalyze samples depending on the process parameters will contribute to the formation of a theoretical basis.

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