

THE FEATURES OF AROMATIC HYDROCARBONS IN LIQUID PRODUCTS OF CATALYTIC OXYCRACKING OF VACUUM GAS OIL

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Abstract

While studying the structural and group composition of aromatic hydrocarbons in liquid fractions of the products of catalytic oxycracking of vacuum gas oil, as well as their molecular weight distribution, it was revealed that monocyclic aromatic hydrocarbons predominate in their composition. Their concentration is lower than in the traditional catalytic cracking sample and decreases in 1% OCC > CC > 2% OCC. Among the identified polyaromatic hydrocarbons, naphthalene and its homologs dominate at 1% oxycracking, and phenanthrene and its homologs dominate at 2% oxycracking; at a 1% degree of oxidation, the amount of naphthalene exceeds the indicators of traditional catalytic cracking by almost 2 times, while at a 2% degree of oxidation, this figure decreases by 4 times, which is the smallest among the studied samples. The cresol content also increased significantly. The concentration of fluorene, phenanthrene, and anthracene decreases, but only slightly. In oxycracking products at a 2% degree of oxidation, the content of all PAH groups is the lowest among the samples under consideration. The trend towards a drop in benzo-containing PAHs, noted for traditional catalytic cracking products, is also true for this sample.

Keywords: catalytic oxycracking, vacuum gas oil, aromatic hydrocarbons, naphthalene, cresol, phenanthrene

I. Introduction

The concentration of aromatic hydrocarbons (AHC) is successfully used instead of individual lower homologs of benzene (toluene, xylenes) as solvents for varnishes, enamels, and paints [1-4]. Aromatic solvents are produced: light with the content of C9-C10 arenes - 98% (wt.), medium with 97.3% (wt.) arenes of the naphtha fraction and heavy, containing 87.6% (wt.) of the arenes of the kerosene fraction. Various areas of use of arenes and aromatic solvents correspond to the boiling limits of gasoline-naphtha fractions. The authors noted that one of the most large-scale areas of use of aromatic hydrocarbons (except for the organic synthesis industry) and their mixtures are solvents, primarily for paints and varnishes. The global solvent market consumes about 15 million tons/year for these purposes, of which 36%, i.e. 5.4 million tons/year, are hydrocarbons [1]. According to Hildebrand solubility parameters, aromatic solvents occupy an intermediate position between paraffin-naphthenic and polar solvents [1]. Therefore, aromatic solvents exhibit high dissolving ability towards both non-polar and polar compounds and polymers.

Another large-scale area for the use of aromatic solvents is the oil production industry - mainly in drilling and cementing wells, stimulating oil flow. Aromatic hydrocarbon solvents are used to displace oil, influence the bottom hole formation zone, and inhibit and remove asphaltene-resin-paraffin deposits.

Aromatic solvents increase the effectiveness of de-emulsifiers during dehydration and desalting of oils. Increasing the concentration of arenes in the absorbent of hydrocarbons from natural gas, for example, replacing the hydrocarbon fraction with a boiling point of about 238 °C and an average molar mass of 180 with mesitylene, led to an increase in the degree of propane extraction from 37.1 to 60.2% [1]. The introduction of arenes (0.01-0.04 mol/l) helps to accelerate radical copolymerization processes, for example, methyl methacrylate with vinyl butyl ether, and increases the proportion of vinyl butyl ether units in the copolymer.

One of the most important areas of use of arenes of middle distillate petroleum fractions is the production of detergents based on both linear alkylbenzenes - n-alkyl-benzenesulfonates, characterized by high biodegradability - and alkylbenzenes with branched alkyl chains. Extracts of aromatic hydrocarbons are used as a softener for rubber compounds, to produce carbon black, etc.

Of interest is the method of intensifying the process of distillation of petroleum residues in the presence of aromatic concentrates [5-8]. Thus, adding 3% (wt.) of the extract of the oil fraction 350-420°C to the vacuum residue of West Siberian oil leads to an increase in the distillate yield by 11.5% (wt.). Various explanations for this effect have been proposed: an increase in the degree of dispersion of the oil system, a change in the degree of solvation of dispersed particles; and increasing the thermal stability of the system, which allows increasing the final temperature of the rectification process. Arene derivatives - alkyl arylsulfonates, Petrov's contact, alkylbenzene synthetic oils, sulfonate additives, and antioxidants - are also widely used.

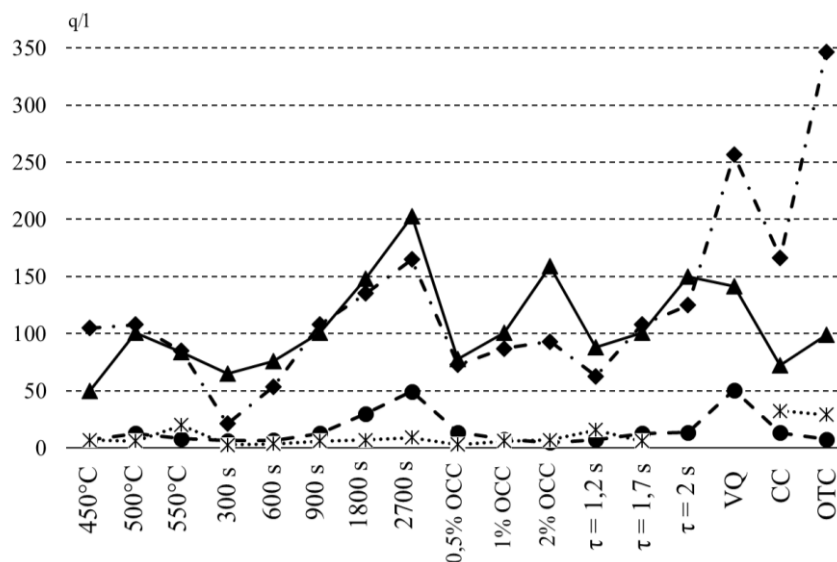
During our previous studies [9-11] of the process of catalytic oxycracking of vacuum gas oil (OCC VG), it was found that increased temperature conditions and high duration and contact time contribute to the formation of a product of a heavy fractional composition. In this regard, studies of the distribution and nature of ArHc are of particular interest for understanding the characteristics of the progression of OCC of VG.

II. Methods

Studies of the oxycracking process [9-11] were carried out in a flow-through installation at atmospheric pressure, at temperatures of 450, 500, and 550°C, with a catalyst volume of 5 cm³. To obtain data on the dependence of quantitative and qualitative indicators of the oxycracking process on technological parameters, it was carried out at 500°C with varying contact time (1.2, 1.7 and 2 s), process duration (300, 600, 900, 1800 and 2700 s), and 0.5, 1 and 2.0% degree of oxidation of the raw material - vacuum gas oil (VG). During the research, experiments of three types were carried out: catalytic oxycracking (OCC) itself, to determine the contribution of the catalyst-non-catalytic oxidative thermal cracking (OTC), as well as a series of experiments of traditional catalytic cracking (CC) under conditions identical to OCC and OTC. The VG OCC process was carried out in the presence of an industrial microspherical cracking catalyst OMNIKAT-210P (manufactured by Grace). The catalyst formed during the experiments was a mixture of both target fractions and unconverted raw materials. Quantitative analysis of hydrocarbons was carried out in a complex consisting of an Agilent 6890N gas chromatograph equipped with a skin with a highly efficient mass selective detector Agilent 5975. Correlation analysis was carried out by calibration with standard reference solutions. A mixture of deuterated polycyclic aromatic hydrocarbons was used as an internal standard: naphthalene-d₈, phenanthrene-d₁₀, pyrene-d₁₀, cresol-d₁₂ and perylene-d₁₂ (Cambridge Isotope Laboratories, Inc., Andover, USA). The calculation was carried out based on an external calibration curve. A mixture of 16 polycyclic aromatic hydrocarbons (TCL PAH MIX, Supelco, USA) was used as a standard reference solution.

III. Results

Based on the corresponding characteristic masses of ions, mass fragmentograms of mono-, bi-, and poly ArHc were obtained and the content of the corresponding classes of compounds in VG oxycracking catalysates was determined depending on the process conditions (Fig. 1). The quality of the initial oil fraction, as well as the catalyzer obtained at 500°C for 900 s with a contact time of 1.7 s under conditions during traditional QC and the liquid QC product, is also shown in Fig. 1 and Table 1.



Picture 1: The influence of OCC process conditions on the individual content in fraction 1 (alkyl-ArH (dotted line)) and fraction 2 (mono-ArHc (dashed line), alkyl-ArHc (solid line) and PaHc (dot-dash)).

Based on the ArHc content in fraction I (standard gasoline), the catalysates selected at temperatures of 450 and 500°C, OCC duration up to 30 minutes, oxidation degree of 0.5 and 1%, contact time 1.7 s can be classified as types of gasoline with an average ArHc content (3-9%); and under conditions of elevated temperatures - 550°C, durations of 30 and 45 minutes, and contact time of 1.2 seconds - to gasoline with a high ArHc content (>9%). Comparative results of the group hydrocarbon composition of fractions I obtained under the conditions of traditional catalytic and oxidative thermal cracking, presented in the figure, indicate that these gasoline components also belong to highly aromatic products.

In the composition of fraction II of oxycracking samples, a relatively high content of aromatic hydrocarbons is observed (from 24.6 to 59.6% relative to 17.8% in CC), represented by mono-, bi-, and polycyclic structures.

We studied in detail the influence of the OCC process parameters on their nature and distribution due to the high content of ARC in this fraction. Due to the influence of a large number of factors on the content of aromatic hydrocarbons in the oxycracking catalyst, it is almost impossible to unambiguously predict any trend in their formation without describing experimental studies. The highest ArHc content is characteristic of samples obtained under conditions of maximum temperature, oxycracking duration, and contact time. In contrast to these parameters, the degree of oxidation does not have such a significant impact on this indicator. The data obtained indicate the contribution of the catalyst to the formation of ARC under OCC conditions, partly as a result of the same reactions as during traditional catalytic cracking (hydrogen transfer, dehydrogenation of naphthenes and dealkylation of alkyl aromatic hydrocarbons, dehydrogenation and cyclization of olefin hydrocarbons, decomposition of

naphthoaromatic hydrocarbons [12-14]), but mainly due to oxidative dehydrogenation and oxidative dehydrocyclization.

Table 1: Influence of technological parameters of the oxycracking process on the content of ArHc groups

Nomination	BF	Content in catalyst, %															
		°Degree oxidation%			Temperature °C			°Duration, s				Contact time, s		°OTK	°KK		
		0,5	1,0	2,0	450	*	550	300	600	*	1800	2700	1,2	*	2,0		
Aromatic hydrocarbons, incl.	35,70	30,89	27,44	27,85	24,58		35,69	36,12	28,12		45,14	59,58	30,05		42,34	46,03	17,84
mono-, alkyl-ArU	11,26	11,50	11,06	16,63	6,17		10,78	14,49	9,61		21,71	25,05	21,19		10,82	10,05	5,13
ind PAH	4,03	2,19	1,30	0,57	0,88		0,99	0,96	0,92		3,98	5,88	1,94		0,92	0,78	0,94
2-6 ring alkyl PAHs	20,40	17,21	15,07	10,65	17,53		23,91	20,67	17,59		19,45	28,66	19,20		18,32	35,20	11,77
ΣPAH/mono-	2,17	1,69	1,48	0,67	2,99		2,31	1,49	1,93		1,08	1,38	0,99		1,78	3,58	2,48

¹ process conditions: duration 900 s; temperature 500°C; contact time 1.7 s.

² process conditions: duration 900 s; oxidation degree 1%; contact time 1.7 s.

³ process conditions: temperature 500°C; oxidation degree 1%; contact time 1.7 s.

⁴ process conditions: duration 900 s; temperature 500°C; oxidation degree 1%.

⁵ thermal oxidative cracking, process conditions: duration 900 s; temperature 500°C; oxidation degree 1%.

⁶ traditional catalytic cracking, process conditions: duration 900 s; temperature 500°C; contact time 1.7 s.

* Experimental conditions: duration 900 s; temperature 500°C; contact time 1.7 s, oxidation degree 1%.

When comparing the data obtained, it is also clear that each of the technological parameters individually has a specific effect on the nature of the distribution of mono- and poly-ArHc: with an increase in the degree of oxidation, the content of mono increases against the background of a decrease in poly- ArHc; at 2% the TCC of mono-ArK is absolute majority; with increasing temperature, both types of compounds gradually increase; the process duration of 600-900 s is the interval in which the resulting catalyst has a minimum content of ArHc of both types; An increase in contact time mainly promotes the formation of mono-ArK ArHc

The ratio of the total content of poly-ArHc as products of condensation and the addition of mono ArHc to the content of the latter can indirectly indicate the nature of the ongoing reactions: condensation, addition on the one hand, or isomerization reactions, hydrogen transfer, transalkylation of aromatic hydrocarbons and cyclization, on the other. For comparison, OTK products, being the most aromatized, in which this ratio is 3.58, are probably formed as a result of addition reactions of fused rings, while KK products, in which the poly-/mono- ratio is 2.58, are cyclization, alkylation [13, 14] .

The results obtained indicate that OCC conditions generally favor isomerization, hydrogen transfer, transalkylation, and cyclization reactions. Whereas low-temperature conditions and large oxycracking contacts slightly increase the contribution of condensation reactions of aromatic hydrocarbons.

Chromato-mass spectrometric analysis, which showed the presence of valuable petrochemical products, such as: acenaphthalene, phenanthrene, fluoranthene, etc., determined the concentrations of individual PAHc in oxycracking catalysts (Table 2). A detailed analysis of the distribution of individual PAHc indicates that in the raw materials, the following 5 components dominate: fluorene, phenanthrene, anthracene, benzo(a)anthracene, and cresol. In traditional CC

products, the amount of fluorene and anthracene increased by 40% and 17%, respectively, cresol decreased by 60%, and phenanthracene remained virtually unchanged. The main difference was a more than 6-fold increase in the concentration of naphthalene and a decrease in all benzo-containing PAHs without exception.

Table 2: The influence of technological parameters of the oxycracking process on the concentration of individual PAHc

PAH	Concentration depending on process parameters, µg																
	VG	¹ Oxidation state, %			² Temperature, °C			³ Duration, s					⁴ Time contact with, s			⁵ OTK	⁶ KK
		0,5	1,0	2,0	450	*	550	300	600	1800	*	2700	1,2	*	2,0		
Naftalin	12.4	13.0	148.8	34.4	24.5		38.9	49.7	74.9	50.3		17.7	53.3		15.4	14.9	79.6
Acenaftilen	6.9	1.4	5.5	2.0	3.2		3.4	1.8	3.5	3.9		1.8	2.2		3.3	1.5	6.3
Acenaften	16.5	3.5	26.7	9.1	9.8		10.9	10.3	12.9	12.3		10.3	12.1		10.5	7.6	21.8
Fluoren	128.2	30.1	143.0	84.3	96.0		103.3	99.9	103.3	108.4		107.	113.6		106.7	78.8	179.5
Fenantren	737.8	96.1	654.5	389.2	511.5		533.3	468.4	490.8	570.7		539.5	549.7		543.9	417.1	743.2
Antrasen	58.3	13.4	63.3	37.0	38.4		39.7	36.9	32.7	43.5		42.5	39.0		40.3	32.0	68.2
Fluoranten	22.7	8.5	22.3	12.2	18.6		18.6	14.8	16.4	17.2		19.2	17.8		16.4	16.4	26.9
Piren	48.2	21.3	41.0	23.2	38.4		32.5	27.9	35.7	38.0		36.1	34.4		34.5	31.2	44.5
Benzantrasen	53.4	30.4	47.2	21.1	32.8		32.2	29.1	30.9	35.6		38.2	27.7		28.9	32.4	44.7
Krizen	239.6	100	178.3	72.6	106.5		97.1	85.8	96.4	98.5		104.9	99.6		97.6	107.2	97.9
Benzfluonten	20.3	15.7	16.1	5.4	11.8		9.9	8.72	10.2	9.6		9.7	10.5		9.1	14.6	12.2
Benz(a)piren	13.4	7.7	4.1	1.3	3.1		3.8	2.61	3.1	2.8		2.6	3.0		2.6	4.0	4.1
Indenpiren	5.2	3.1	2.5	0.2	2.2		1.2	0.98	1.2	0.8		1.5	1.5		1.2	2.2	1.1
Benzperilen	2.9	5.2	0.9	0.7	2.1		1.3	1.19	1.4	1.1		1.6	1.6		1.4	3.4	1.7
Dibenzatrcen	2.9	7.3	6.0	1.3	3.1		3.6	2.4	3.1	3.6		3.1	2.4		2.7	6.2	1.7

¹ process conditions: duration 900 s; temperature 500°C; contact time 1.7 s.

² process conditions: duration 900 s; oxidation degree 1%; contact time 1.7 s.

³ process conditions: temperature 500°C; oxidation degree 1%; contact time 1.7 s.

⁴ process conditions: duration 900 s; temperature 500°C; oxidation degree 1%.

⁵ thermal oxidative cracking, process conditions: duration 900 s; temperature 500°C; oxidation degree 1%.

⁶ traditional catalytic cracking, process conditions: duration 900 s; temperature 500°C; contact time 1.7 s.

* Experimental conditions: duration 900 s; temperature 500°C; contact time 1.7 s, oxidation degree 1%.

IV. Discussion

Consideration of the results of the distribution of individual PAHc in oxycracking products made it possible to identify several distinctive features in comparison with the indicators of traditional catalytic cracking. The composition of raw materials - VG, as well as liquid products of its oxycracking and traditional catalytic cracking, includes the same homologous series of aromatic hydrocarbons, monocyclic aromatic hydrocarbons predominate; concentration changes of monocyclic aromatic hydrocarbons: 1% OCC > CC > 2% OCC ; Among the identified polyaromatic hydrocarbons, naphthalene and its homologues dominate at 1% oxycracking, and phenanthrene and its homologs dominate at 2% oxycracking; in oxycracking samples the concentration of ArHc is lower than in traditional catalytic cracking.

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