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RESEARCH

PRODUCTS FROM HYDROGENATION OF VACUUM RESID AS A RAW MATERIAL FOR OBTAINING AROMATIC HYDROCARBONS

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In order to study in any depth the process of destructive catalytic hydrogenation of vacuum resid in a medium of carbon monoxide and water vapor (steam) to produce motor fuels, information is needed on the individual composition of the liquid products from the hydrogenation operation.

In this article we present results from a study of the chemical composition of products obtained in the hydrogenation of a vacuum resid having the following elemental composition (in %): C 85.4, H 10.3, S_{tot} 2.3. This vacuum resid contained 8.1% asphaltenes, 11.2% resins, and 80.7% oils. The hydrogenation was performed with an initial pressure of 4 MPa at a temperature of 425°C. In this work we used STK-1-1 commercial catalyst, normally used for medium-temperature conversion of carbon monoxide [1], and iron sulfide systems (pyrite, pyrrhotite) [2, 3]. The liquid product from the hydrogenation was distilled to obtain IBP-180°C and 180-350°C fractions. The group composition of the hydrogenated products was investigated by ^{13}C and ^{1}H NMR spectrometry. The results from these studies are presented in Table 1 and Fig. 1. The contents of paraffinic, naphthenic, and aromatic hydrocarbons were determined by the ASTM D 2140 method [4].

^{13}C NMR spectrometry identifies different types of atoms directly; from such data, the contents of paraffinic, naphthenic, and aromatic hydrocarbons can be determined accurately. In the present work, we recorded the spectra of 50% solutions of the test samples in $CDCl_3$, using a Tesla B-567 Fourier spectrometer in the pulse mode with a holdup of 4 sec between pulses, with a working frequency of 25.142 MHz. In this operating mode, the time required to measure the spectral lines is minimized.

The contents of aromatic hydrocarbons were calculated from the integral intensities in the 110-160 ppm interval. The contents of paraffins were calculated from the sum of the integral intensities of all resolved signals in the 25-60 ppm interval and the total intensity in the 0-25 ppm interval (by greatly expanding the spectra in the vertical and horizontal directions, we were able to integrate the areas pertaining to the paraffinic hydrocarbons). The content of naphthenes was calculated as the difference between the contents of aromatic and paraffinic hydrocarbons.

For samples 1, 3, and 5 (Table 1), which had significant contents of olefins, we were unable to determine the ratio of aromatic and olefinic hydrocarbons from the ^{13}C NMR spectra, owing to overlap of the signals. This ratio can be found from ^{1}H NMR spectra, since the signals of the aromatic protons lie in the 6.7-7.3 ppm interval, while the signals of protons at multiple bonds lie in the 4-6 ppm interval.

The paraffinic hydrocarbons have a straight-chain structure, as indicated by the fact that in their spectra (Fig. 1), all signals have a triplet structure — other than the signal of the terminal methyl group at 14 ppm, which gives a quartet. Alkylaromatics with short side chains on the ring give a ^{1}H NMR signal at 2.25 ppm, close to a quartet.

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TABLE 1

Sample No.	Fraction, °C	Contents of hydrocarbons, %			
		aromatics	olefins	paraffins	naphthenes
		Without catalyst			
1	Below 180	5	6	54	35
2	180–350	18	–	55	27
		Over STK-1-1 catalyst [1]			
3	Below 180	4	4	59	33
4	180–350	15	–	56	29
		Over iron sulfide system [2]			
5	Below 180	4,6	5	54	36,4
6	180–350	14,0	–	47	39

TABLE 2

Peak number on chromatogram (see Fig. 2)	Aromatic hydrocarbons	Content, %
1	Benzene	0,33
2	Toluene	2,25
3	Ethylbenzene	0,90
4	p-Xylene	2,33
5	m-Xylene	
6	o-Xylene	1,30
7	Isopropylbenzene	0,32
8	n-Propylbenzene	0,3
9	1-Methyl-3-ethylbenzene and 1-methyl-4-ethylbenzene	0,96
10	1,3,5-Trimethylbenzene	0,51
11	1,2,4-Trimethylbenzene	0,61
12	1-Methyl-3-isopropylbenzene	0,01

TABLE 3

Hydrocarbons	Content in hydrotreated IBP-200°C fraction, %
Paraffins	42,87
straight-chain	20,10
monoalkyl-substituted	15,14
dialkyl-substituted	7,63
Naphthenes	42,12
cyclopentanes	17,34
cyclopentane	0,90
monoalkyl-substituted	2,06
dialkyl-substituted	6,51
trialkyl-substituted	7,87
cyclohexanes	24,78
cyclohexane	0,89
monoalkyl-substituted	1,76
dialkyl-substituted	2,01
trialkyl-substituted	2,78

Our analysis of the IBP-180°C and 180-350°C fractions by means of ^{13}C and ^{1}H NMR shows that the products of hydrogenation over iron sulfide catalytic systems [2, 3] are distinguished by smaller contents of aromatic and olefinic hydrocarbons and total sulfur (0.13% and 0.27%, respectively). These data indicate that the products of the hydrogenation will be easier to upgrade in the subsequent processing stages.

A wide fraction of the product of hydrogenation (IBP-350°C) was hydrotreated at 400°C with a hydrogen pressure of 6 MPa, over alumina—cobalt—molybdenum catalyst. The individual hydrocarbon composition of the hydrotreated fraction distilling below 200°C was determined by gas—liquid chromatography in a glass capillary column (length 50 m, diameter 0.25 mm) with OV-101 mobile phase, programming the temperature from 50°C at a rate of 4°C/min (Fig. 2). The hydrotreated 200-350°C fraction was analyzed by the fluorescence indicator method.

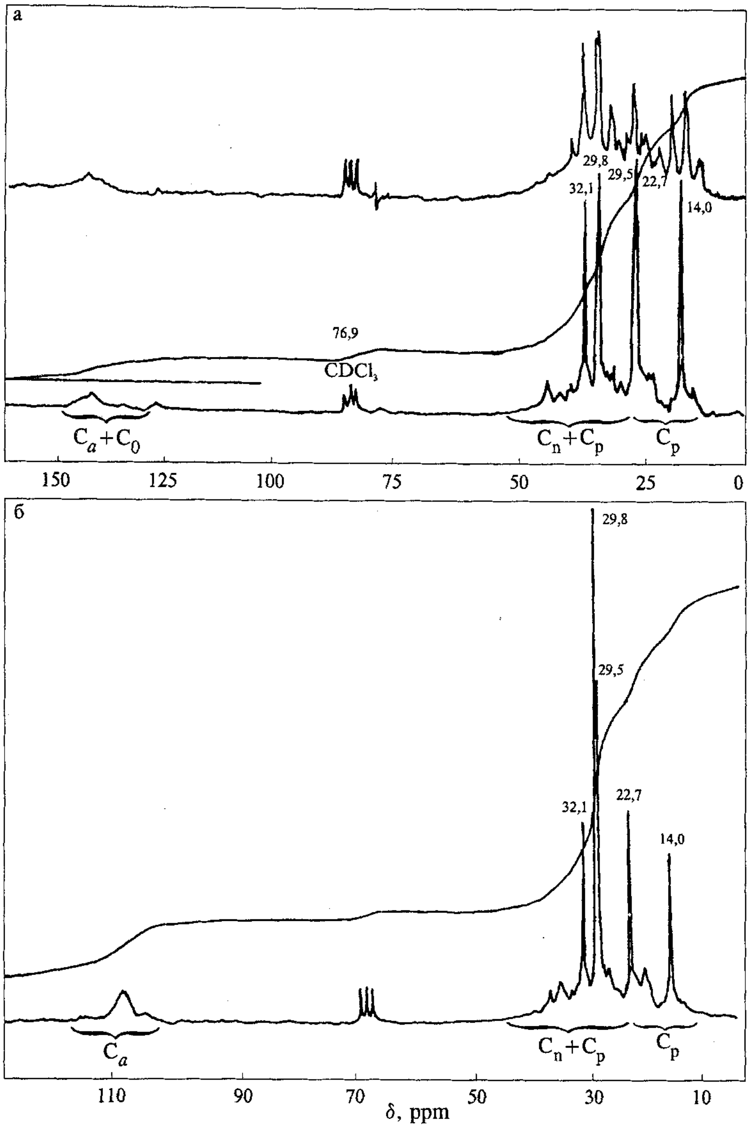

Fig. 1. ^{13}C NMR spectra of light fraction (a) and middle fraction (b).

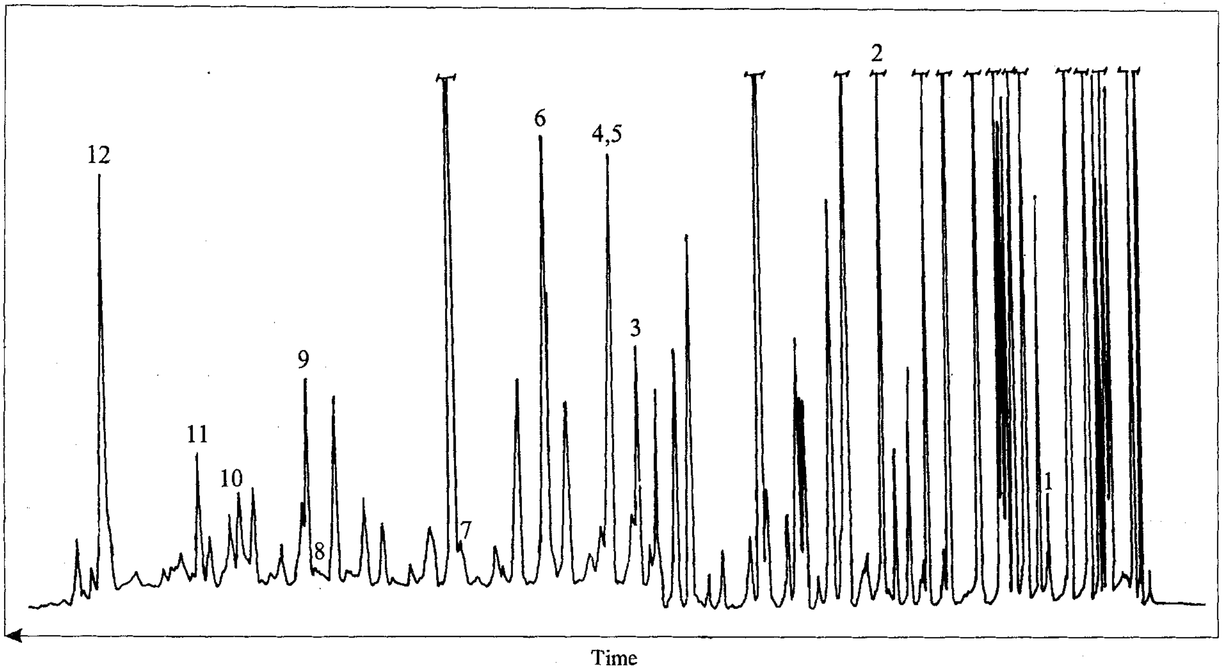

Fig. 2. Chromatogram of light fraction (IBP-200°C). Deciphering of peaks is given in Table 2.

In the IBP-200°C fraction, the n-paraffins consist largely of hexane and heptane, with respective contents of 6.32% and 8.16%. This fraction contains a large amount of naphthenes. Among the aromatic hydrocarbons, toluene and xylenes predominate (Table 2). The ratio of paraffins to naphthenes is close to 2 (Table 3), which is characteristic for the naphtha fractions of paraffinic—naphthenic crudes. The hydrocarbon group composition of the middle fraction (200-350°C) is as follows: paraffins + naphthenes 52.5%, olefins 1.8%, aromatics 45.7%.

Thus, the liquid products from hydrogenation of vacuum resid in a medium of carbon monoxide and water vapor, over an iron sulfide catalyst system, are completely analogous to commercial products in their chemical composition. The products from vacuum resid hydrogenation can be used for the production of aromatic hydrocarbons.

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