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The Effect of Iron-Containing Powders on Chemical Compositions of Oils

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Abstract

The effect of a composite material based on micron iron powder, modified with cobalt and nickel ions on the composition of oils with different contents of heteroatoms and resin-asphaltene components (a mixture of West Siberian light oils and Usinskaya heavy oil) is studied. It is shown using analytical methods, including elemental and structural group analysis, GC-MS, IR and ^{1}H-NMR - spectroscopy that a composite based on micron sized iron powder modified with cobalt and nickel ions could be used for pretreatment of hydrocarbon feedstock with high content of heteroatom components. It is found out during treatment of the mixture of light West Siberian oil that its qualitative composition remains virtually invariable. Heavy oil treatment from the Usinskoye oil field using composite results in a decreased concentration of nitrogen and organic sulfur compounds.

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Keywords: Oil, heterorganic compounds, metal powders;

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1. Introduction

The most important task for refineries is the production of high quality motor fuels. The quality of the produced oil products depends to a certain extent on the content of high molecular (asphaltenes and resins) and low molecular heteroatomic compounds (HAC) in an initial hydrocarbon feedstock. Their presence in the oils has a negative impact on the refinery processes, the quality of fuels and lubricants, and environmental safety of production[1-3].

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Existing regulations on the HAC content in petroleum products stimulate the search for new approaches to pre-treatment of raw materials supplied to the refineries in order to improve their compositions[4,5]. The treatment of oil with materials containing metal powders could be considered as one of these approaches[6]. It is well known that metals such as copper, silver, iron, nickel and cobalt can form complex compounds with heteroatom components[7-9]. This makes them attractive for the use as part of the composite materials intended for reducing HAC in oils. In recent years much attention has been paid also to resin-asphaltene substances (RAS)[10-15], but there is virtually no information on changes in their composition and structure in the presence of metals. Hence, the acquisition and generalization of data on the behavior of oil disperse systems in the presence of metals both during pre-treatment and directly in the course of thermal and catalytic processes are of interest to solve problems related to the production of petroleum products meeting modern requirements.

The purpose of this investigation is to study the effect of composite materials based on micron iron powders on the chemical composition of oils with different contents of heteroatoms and resin-asphaltene substances.

2. Materials and methods

The objects of investigation are a mixture of light and average oils from the West Siberian oil fields (sample 1) and a heavy oil from the Usinskoye oil field (sample 2) (Table 1). This choice is determined by the fact that the reserves and production volumes of low-viscosity light oils have been reduced recently and oils with a high content of RAS and heteroatoms are extensively used for refining.

The oils were treated by a composite based on iron powder, modified with divalent nickel and cobalt ions. It was found out at the stage of pilot study that the treatment of oil with micron sized powders of copper, iron, and nickel without modifiers has no significant effect on the qualitative composition of the oils and quantitative content of their components. The iron powder was prepared by the method of iron wires electrical explosion in argon gas medium according to the procedure described in[16]. According to the electron microscopy data the shape of these powder particles is nearly spherical ranging in size from 1 to 3 micrometers. It was modified with Ni^{2+} and Co^{2+} ions from saturated sodium chlorides of the respective metals. A 0.5 g sample of the metal powder was put in a 50 g oil sample and then stirred with a magnetic stir bar in a glass reactor at 35 °C for 2 hours. The resulted slurries had been settled for at least 2 hours at room temperature and then separated by filtration through a filter paper. The treatment of the oils under study with a composite resulted in liquid products – sample 1.1 and sample 2.1.

A comparative analysis of the composition of original oils and the products of their treatment was performed on the basis of elemental analysis, IR- Fourier and 1H NMR spectroscopy, structural group analysis, and gas chromatography-spectrometry.

The oils were separated to components (asphaltenes, resins, and oils) in accordance with a standard operating procedure[17]. Molecular weights of resins and asphaltenes were measured via cryoscopy in benzene in accordance with a procedure described in[17].

The elemental composition of the samples was determined using 'Vario EL Cube' CHNS-analyzer.

IR spectra were recorded in the range of 4000-400 cm^{-1} using Nicolet 5700 FT-IR spectrometer in order to calculate spectral coefficients, which are the ratios of the optical densities of absorption bands at frequencies 1710, 1600, 1465, 1380, 1030 and 720 cm^{-1} representing, respectively, the relative content in aromatic structural fragments (C_1), carbonyl (C_2) and sulfoxide (C_5) functional groups, and the fraction of aliphatic structural fragments (C_4) and their branching (C_3). The values of spectral coefficients were as follows: $C_1 = D_{1600}/D_{720}$, $C_2 = D_{1710}/D_{1465}$, $C_3 = D_{1380}/D_{1465}$, $C_4 = D_{720}+D_{1380}/D_{1600}$, and $C_5 = D_{1030}/D_{1465}$[18].

Resins and asphaltenes were subjected to a structural group analysis (SGA) in accordance with a procedure described in[19], which is based on sharing of the data on molecular weights, elemental composition, and distribution of protons between different moieties of their molecules determined using ^1H NMR spectroscopy. This approach allowed us to calculate the average structural characteristics of molecules of the components under study. The assumption that their structure contains a single central aromatic polycyclic unit was also taken into account. The following parameters were calculated: the number of carbon atoms in aromatic C_a, paraffinic C_p and naphthenic C_n structural moieties (in an average molecule, in the α-position with respect to aromatic rings C_α, and in the terminal methyl groups (C_γ) not linked with aromatic rings), the fractions of carbon atoms in the aromatic, naphthenic and paraffinic structural moieties, f_a, f_n, f_p, the total number, K_t, the number of aromatic, K_a, and naphthenic, K_n, cycles in an average molecule, and, m_a, the number of aromatic units in an average molecule.

^{1}H NMR spectra were registered using a Bruker AVANCE AV Fourier 300 NMR spectrometer at 300 MHz in $CDCl_3$ solutions. The chemical shifts are measured with respect to tetramethylsilane at a room temperature. The relative content of protons in different structural moieties was determined by the peak area of signals in the respective spectrum regions: H_{ar} is the fraction of protons contained in aromatic structures – 6.6-8.5 ppm., H_α is the fraction of protons for the carbon atom in α-position of aliphatic substituents of aromatic structures – 2.2-4.0 ppm., H_β and H_γ is the fraction of protons in the methylene and methyl end groups of aliphatic moieties of molecules, respectively, – 1.1-2.1 ppm and 0.3-1.1 ppm.

GC-MS analysis (GC-MS) was performed using a magnetic *DFS* spectrometer GC («*Thermo Scientific*», Germany). Conditions for registration of spectra, their treatment and approaches to the identification of compounds are given in[20].

IR, ^{1}H NMR, and GC-MS spectra were recorded using the equipment of Tomsk Regional Joint-Use Center of Tomsk Scientific Center of the Siberian Branch of the Russian Academy of Sciences.

3. Results and discussion

The investigation revealed that the treatment of a mixture of West Siberian light oils with metal powder does not result in any significant change in its elemental composition (Table 1). Its qualitative composition remains also virtually unchanged. The IR spectra of samples 1 and 1.1 exhibit the same set of characteristic absorption bands. However, the treated oil differs from the original oil by higher values of spectral indices demonstrating the relative content of aromatic C_1 and aliphatic C_4 structural moieties and carbonyl C_2 functional groups (Table 2). The values of parameters characterizing the content of sulfoxide functional group C_2 and the branching of aliphatic structural moieties C_3 remain unchanged.

Table 1. Characteristics of the oils under study and the products of their treatment.

Sample	Content, wt.%					H/C_{at}
	RAS	C	H	S	N	
sample 1	14.8	83.93	12.01	1.42	0.34	1.72
sample 1.1	20.4	81.97	11.66	1.63	0.39	1.71
sample 2	27.3	84.10	10.65	1.97	0.64	1.52
sample 2.1	21.7	83.90	11.42	1.27	0.41	1.63

A significant reduction in content of sulfur and nitrogen was observed for the untreated oil from the Usinskoye oil field (Table 1). However, the set of characteristic absorption bands registered in the IR spectra of the samples 2 and 2.1 is similar to that registered for the West Siberian oil. At the same time, the values of the spectral indices for these samples are different. The most significant changes are demonstrated by indices of aromaticity C_1 and sulfurization C_5. For the sample of oil from the Usinskoye oil field the aromaticity increased after the treatment with iron-containing powder while the sulfurization on the contrary decreased (Table 2).

Table 2. Spectral characteristics of oils and their components.

Sample	Spectral indices				
	C_1	C_2	C_3	C_4	C_5
sample 1	0.74	0.053	0.50	5.85	0.119
sample 1.1	0.78	0.062	0.50	5.59	0.118
sample 2	0.93	0.072	0.51	4.85	0.141
sample 2.1	0.98	0.073	0.50	4.82	0.129

The treatment with iron-containing powder causes changes in the quantitative content of components in the oils under study. For sample 1.1 an increase in total content of RAS from 15 to 20% is observed, while for the sample 2.1 the content of resins and asphaltenes is observed to decrease from 27 to 22% (Table 1).

The high molecular weight components of both oils concentrate in their compositions heteroatomic compounds (Table 3). Thus, RAS in the mixture of West Siberian oils accumulate 52% of sulfur atoms and 27% of nitrogen atoms present in these oils, while the resins and asphaltenes of the Usinskaya oil − 49% and 45% nitrogen and sulfur atoms, respectively. The asphaltenes of both oils are enriched with heteroatoms more than their resins. In addition, the asphaltene components are characterized by higher measured values of average molecular weights (Table 3). On the other hand, the average molecular weights for asphaltenes and resins of the Usinskaya oil are 2.3 and 2.6 times higher than for the same components of the West Siberian oil.

The data about the size and structure of molecules, composition and quantity of various structural groups of RAS obtained by the method of structural group analysis[19] show that the oils under study differ in average structural parameters of molecules of resins and asphaltenes (table 3). The average molecules of asphaltenes of the Usinskaya oil contain more of carbon atoms (C = 93.60) than those of West Siberian oil (C = 42.8) mainly due to a higher number of these atoms in the aromatic (C_a = 38.9 versus 14.5) and naphthenic (C_h = 49.7 vs. 26.1) cycles. Most carbon atoms in the molecules of asphaltenes in both samples (66.12 and 58.48% for samples 1 and 2, respectively) are contained in saturated moieties ($f_n + f_p$). The carbon fractions in aromatic moieties (f_a) in the average molecules of asphaltenes of West Siberian and Usinskaya oils are 33.88 and 41.52%, respectively. It should be noted that carbon atoms form three (m_a = 3.0) structural units in the average asphaltene molecules of the Usinskaya oil, while only two (m_a = 1.6) in those of the West Siberian oil.

However, the general cyclicity of structural units of asphaltenes in samples 1 and 2 is virtually the same (K_o* = 7.5 and 8.0). In Sample 1 the arene nucleus consisting of two homo- and heterocycles (K_a* = 2.1) is conjugated with five saturated rings (K_n* = 5.4). In sample 2 five saturated rings (K_n* = 4.7) are condensed with three arene rings (K_a* = 3.3). The alkyl substituents in the structural units of asphaltenes of samples 1 and 2 are represented by methyl groups (C_p* = C_γ* = 1.4 and 1.7) only. In sample 1, four methyl groups (C_α = 4.0) and in sample 2 five methyl groups (C* = 4.9) are connected directly to the aromatic nucleus.

The average molecules of resins of both oils contain fewer carbon atoms than do asphaltenes extracted from the respective oils. The resins of the Usinskaya oil contain more carbon atoms (C = 59.3) than the resins of the West Siberian oil (C = 21.8). A larger number of carbon atoms in the average molecules of the Usinskaya oil is due to the fact that the number of carbon atoms in aromatic C_a and naphthenic C_n cycles in the resins of sample 2 is higher (4.3 and 2.6 times, respectively) than that in an average resin molecule of sample 1. The fraction of saturated carbons in the average molecules of resins in both samples is higher than that of asphaltenes extracted from the above oils. The sum of the relative contents of carbon atoms in naphthenic and paraffinic structural moieties in average molecules of resins of the West Siberian oil is higher (f_n+f_p = 81.74%) than in those of the Usinskaya oil (f_n+f_p = 70.88%). The fraction of aromatic carbon in average molecules of resins of the Sample 1 is lower (f_a = 18.26%) than in those of the sample 2 (f_a = 29.12%) and lower than in the relative asphaltenes. The average molecules of the resins of samples 1 and 2 differ from each other and from those of asphaltenes by the number of structural units m_a. Unlike asphaltenes the resins contain less of structural units and the resins of the West Siberian oil contain them less than the resins of Usinskaya oil. The numerical values of parameter m_a suggest that an average molecule of resins of sample 1 consists of a single structural unit (m_a = 0.9) and an average resin molecule of sample 2 – two structural units (m_a = 1.8). The structural units of resins differ in their total cyclicity. The structural unit of resins from sample 1 consists of three or four cycles (K_o* = 3.4), two or three of them falling within the saturated (K_n* = 2.4) and one the aromatic (K_a* = 1.0) rings. The structural unit of resins of sample 2 consists of two or three homo- and heterocycles (K_a* = 2.4) with a predominance (54%) of bicyclic fragments. Each arene nucleus has K_n* = 3.1 saturated rings, thus the total number of cycles in a structural unit is K_o* = 5.5. The aliphatic moieties in the structural units of resins in both samples have about 11 carbon atoms (C_p*) each. Most of paraffinic carbon atoms are linked with the alkyl substituents located on the periphery of aromatic nuclei (C_α* = 3.2 and 4.6 for samples 1 and 2, respectively), no more than 24% (C_γ*/C_p* • 100) as terminal methyl groups. Thus, the calculated parameters characterizing the average structural unit of resins and asphaltenes of the Usinskaya oil are higher than the respective parameters for the RAS molecules of the mixture of West Siberian oils.

Table 3. Structural parameters of oil components.

Parameters	compounds			
	samples 1		samples 2	
	asphaltens	resins	asphaltens	resins
Average molecular weight	619	340	1405	877
Element structure, wt.%				
C	83.03	76.95	79.92	81.14
H	7.87	10.28	7.07	9.45
N	0.92	0.57	1.23	1.08
S	2.14	1.54	3.77	2.96
O	5.04	6.86	8.01	5.37
Quantity of atoms in a medium molecule				
C	42.8	21.8	93.6	59.3
H	48.3	34.7	98.6	82.2
N	0.41	0.14	1.23	0.68
S	0.41	0.16	1.66	0.81
O	1.95	1.46	7.03	2.94
H/C	1.13	1.59	1.05	1.39
Ring composition				
$K_о$	11.9	3.0	23.8	23.8
$K_а$	3.4	0.9	9.8	9.8
$K_н$	8.5	2.1	14.0	14.0
Fraction of carbon atoms in structural moieties, %				
$f_а$	33.88	18.26	41.52	29.12
$f_н$	61.0	40.15	53.08	38.21
$f_п$	5.12	41.59	5.40	32.67
Quantity of carbon atoms of different type in a medium molecule				
$C_а$	14.5	4.0	38.9	17.3
$C_н$	26.1	8.8	49.7	22.7
$C_п$	2.2	9.1	5.1	19.4
C_α	6.4	2.8	14.7	8.2
C_γ	2.2	2.1	5.1	4.6
Parameters of average structural units (* - denotes a structural unit)				
$m_а$	1.6	0.9	3.0	1.8
$K_о$*	7.5	3.4	8.0	5.5
$K_а$*	2.1	1.0	3.3	2.4
$K_н$*	5.4	2.4	4.7	3.1
C*	27.1	24.6	31.4	33.2
$C_а$*	9.1	4.4	13.0	9.7
$C_н$*	16.3	9.8	16.7	12.9
$C_п$*	1.4	10.2	1.7	10.8
C_α*	4.0	3.2	4.9	4.6
C_γ*	1.4	2.4	1.7	2.6

Taking into account the changes in the content of RAS in the oils under study after their treatment with the iron-containing powder (Table 1), the content of average molecules of resins and asphaltenes would thus be expected to increase by 1.3 times in the treated West Siberian oil and to decrease 1.3 times in Usinskaya oil. In this case, the average resin molecules of the treated West Siberian oil would increasingly be presented as tricyclic fragments with one aromatic nucleus associated with two or three naphthenic rings. Their aliphatic substituents with linear or lightly branched structure contain 10 carbon atoms. The constituents of average asphaltene molecules of this oil would be larger bicyclic aromatic nuclei, condensed with five or six naphthenic rings, whose aliphatic substituents are represented by methyl substituents only.

The fraction of fragments containing bi- or tricyclic aromatic nucleus conjugated with three naphthenic rings and having rather developed but slightly branched aliphatic substitution would be decreased in the average resin molecules of Usinskaya oil. In the structure of the average asphaltene molecules of this oil a decrease in the fraction of fragments consisting of tricyclic aromatic nuclei condensed with five naphthenic rings and methyl substituents only would be observed.

It should be noted that a concentration of sulfur and nitrogen compounds is significantly reduced in the treated heavy Usinskaya oil (Table 1). A comparative GC-MS analysis of heteroatomic components of the original oil and treated oils revealed similarities and differences in their composition. It was found out that nitrogen and sulfur compounds in both samples are represented by complex mixture of aromatic heterocyclic components. The alkylated C_2-C_5 benzothiophenes, unsubstituted dibenzo- and naphtobenzothiophenes, and their alkylhomologs from C_1 to C_4 and from C_1 to C_2 have been, respectively, identified in a composition of sulfur compounds. The C_1 and C_2-alkyldibenzothiophenes prevail while among the nitrogen compounds the neutral and basic substances are observed.

Among the neutral nitrogen compounds carbazole and its C_1-C_5 alkylhomologues with prevalence of C_3-carbazoles have been found out. Among the nitrogenous bases such alkyl derivatives as (C_4-C_9)-quinolines, (C_1-C_8)-benzo- and (C_1-C_7)-dibenzoquinolines, (C_2-C_8)-thiophenoquinolines, (C_1-C_7)-benzo- and (C_1-C_5)-dibenzothiophenoquinolines have been identified. Most of them are C_3-C_4 alkylhomologues of benzoquinoline and thiophenoquinoline.

The treatment with a composite based on iron powder modified with nickel and cobalt ions resulted in a decrease in the fraction of alkyl-substituted benzothiophenes, quinolines, thiophenoquinolines, and carbazoles among heteroatomic components.

The activity of iron powder modified with cobalt and nickel ions in respect to heteroatomic components is confirmed by the results of previous GC-MS investigation of the mixture of light West Siberian oils[21]. It has been found out that the content of dibenzothiophene compounds and alkyl derivatives of benzenes, naphthalenes, and phenanthrenes decreases in the treated oil.

4. Conclusion

It has been established that the micron-sized iron powder modified with cobalt and nickel ions has different effects on the chemical composition of oils with different contents of RAS and heteroatoms. It has also been found out that a treatment of the mixture of light West Siberian oils with a composite is accompanied by an increase in the total content of RAS and by the changes in structural-group characteristics of average molecules of their asphaltenes and resins. In the treated heavy oil from the Usinskoye oil field, the content of high molecular components and the concentration of sulfur and nitrogen compounds have been observed to decrease. The fraction of alkyl derivatives of benzothiophenes, quinolines, thiophenoquinolines and carbazoles in the latter is also smaller.

Thus, the composites based on the micron-scale iron powders could be used for preliminary upgrading of the heavy hydrocarbon feedstock with a high content of heteroatomic components.

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