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LIQUEFACTION OF BROWN COALS OF KANSK-ACHINKS FIELD IN CONDITIONS OF HIGH-SPEED HEATING

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Abstract. *In the present work on the basis of results on thermal dissolving of the coals Borodino, Berezovsk and Itatsk deposits of the Kansk-Achinsk field in conditions of high-speed heating and on chemical composition and structure of the manufactured extracts the comparative analysis is carried out and the attempt is made to reveal common relationship of their behaviour in liquefaction process. Such approach will allow predicting efficiency and expediency by using of this method thermotreatment for brown coals of other deposits.*

Key words: *thermal dissolving; high-speed heating; coal extract; organic mass of coal; brown coals; Kansk-Achinsk field; chemical structure; functional groups; structural fragments*

It is obvious, that the prevalence of coal reserves above the other kinds of organic stock (gas, petroleum) allows considering it as the most perspective feedstock for manufacture of gaseous, liquid and solid fuels as well as for base raw to produce of various chemicals and composite materials. Therefore taking into account the decrease of commercial reserves of petroleum; reduction it qualities and increase of the cost of it production there is a very actual problem to develop scientific fundamentals of technologies for coal processing in order to replace petroleum stock on coal one.

One of such processes is coal liquefaction in a protondonor solvent, is known as thermal dissolving or high-temperature extraction by the solvents (so called SRC-process), allowing to isolate from coal substance its organic mass (extract). Using this stock it is possible to produce gasoline, diesel fuel, varnishes, paints, plastics, electrode-coke; bitumen for road construction, mesogenic additives for coking of burdens from weak caking coals and constructional elements.

It is necessary to note, that the coal extracts are very similar to petroleum and heavy petroleum products (bitumen, asphalt, residual fractions) as in chemical composition and structure [1,2], as well in technological procedures and engineering design of their processing (destructive hydrogenation, hydrocracking, reforming etc.). Thus, the research of relationships and structure of products of coal liquefaction represent field of science, which is taking place on joint petroleum and coal chemistry.

One of the features of work is the investigation of coal liquefaction at high-speed heating of reactionary system (120°C/min), that allows in 2-2.5 times intensify process in comparison with „traditional“ heating (2-8°C/min). The development of this direction in solid fuels liquefaction began rather recently, than the limitation of the publications, describing it is explained [3-9].

In the present work on the basis of results on thermal dissolving of the coals Borodino, Berezovsk and Itatsk deposits of the Kansk-Achinsk field in conditions of high-speed heating and on chemical composition and structure of the manufactured extracts [10-12] the comparative analysis is carried out and the attempt is made to reveal common relationship of their behaviour in liquefaction process. Such approach will allow predicting efficiency and expediency by using of this method thermo-treatment for brown coals of other deposits.

Experimental Part

Composite samples of the coals Borodino, Berezovsk and Italsk deposits of Kansk-Achinsk field were investigated, from which on GOST 10742-71 the analytical specimens (Table 1) were prepared. As the solvents tetralin, containing (wt. %): 81.7 of tetralin, 15.7 of decalines (cis- and trans- totally and 2.6 of naphtalene was used. A mass ratio the coal/tetralin was made 0.5.

Thermal dissolving of coals carried out at temperatures 400, 425, 435 and 450 ^{o}C with isothermal exposure τ=0.5, 10 and 15 min. The rate of heating of reactionary system of 120^{o}C/min was achieved with using of the specially designed device [13], which basic unit was micro-autoclave in volume 0.028 l. The operating temperature was maintained accurate to ±3.0^{o}C.

The liquefaction products were separated on gas, liquid products and solid residue, including un-dissolved part of organic matter and mineral components of coal substance. Liquid products were fractionated into a gasoline with boiling point (b.p.) up to 200°C, spent solvent (tetralin) with b.p. 200-230°C and a coal extract with b.p. over 230°C. A confidence interval in determination of conversion as well as yields of the gasoline fraction, extract and solid residue, was ± 3%, and the same value for the gas yield was± 1.9 % (α=0.95; f=2).

The gaseous products of thermal dissolving were analyzed with chromatograph on GOST 14920-79. Hydrocarbon components were divided on a column with n-hexadecane on spherchrom-2, and non-hydrocarbon products and methane on zeolite CaA. The molecular weights of extracts were determined osmometrically, using as the solvent tetrahydofurane. A confidence interval in determination has made 25 units (α=0.95; f=2).

H-NMR-spectra of extracts were recorded on spectrometer „Bruker-200“, using as the solvent $CDCI_3$. The internal standard was tetramethylsilane. From NMR-spectra, according to [14,15],

Table 1. Characteristics of brown coals of Kansk-Achinks field

Deposit	Technical and element analysis, mass %							
	W^a	A^d	V^{daf}	S^{daf}	C^{daf}	H^{daf}	N^{daf}	$O_d{}^{daf}$
Borodino	5.80	6.25	48.51	0.26	73.24	4.85	0.96	20.69
Berezovsk	5.29	4.89	47.37	0.24	72.11	5.19	0.90	21.56
Itatsk	6.23	4.60	46.00	0.22	71.57	4.87	0.73	22.61

Deposit	Petrographic analysis, %					
	V_t	S_v	F	L	M	R
Borodino	88	10	1	1	-	0.36
Berezovsk	89	2	5	2	2	0.35
Itatsk	81	3	15	1	-	0.37

where: W^a - moisture of analytic specimen; A^d – ash content related on dry mass of coal; V^{daf} – yield of volatile matter; daf – related on dry ashless mass of coal; S, C, H, N,O – content of elements; V_t – content of vitrinit; S_v – semivitrinit; F – fusinit; L – liptinit; M – micrinit; R – degree of vitrinit reflection

it was determined the relative contents of hydrogen in the following structural fragments:

- in CH_3-groups of aliphatic compounds, $H^{CH}{}_{3}{}^{,}{}_{aliph}$ (0.5-1.0 ppm);
- in CH_2-groups of aliphatic compounds, $H^{CH}{}_{2}{}^{,}{}_{aliph}$ (0.5-1.0 ppm),

while these structures can be included into composition of aliphatic substitutes at aromatic compounds in β- and γ-positions; in CH_2-groups of naphthenic compounds, $H^{CH}{}_{2}{}^{,\ \circ napht}$ (1.5-1.8 ppm),

in CH_3-groups in α-position to aromatic system, $H^{\alpha}{}_{CH3}$ (2.0-3.0 ppm);

in CH_2-groups in α-position to aromatic system, $H^{\alpha}{}_{CH2}$ (2.5-3.5 ppm);

– in phenol OH-groups, H_{OH} (4.5-5.5 ppm). The reference of singlet in this spectrum area to a phenol proton is based that after dephenolization of extracts, agrees with [16], the signal disappeared;

– in binuclear (H_{bi}) and polynuclear (H_{pol}) aromatics with condensed benzene rings, (7.1-8.3 ppm), while for polynuclear compounds of extracts the number of the condensed rings does not exceed 3. Division of bi- and polynuclear structures on multiplicity carried out according to [17].

A confidence interval in determination of the contents of hydrogen CH_3-groups of aliphatic compounds and in CH_2-groups of aliphatic and naphthenic compounds is equal ±1.2%, and in other groups-±1.0% (α=0.95; f=2).

Results and Discussion

At present the most argued hypothesis [18-23] about a structure of organic mass of coal (OMC) is summarized to the following:

1) Organic mass of coal represents three-dimensional polymer of an irregular structure (rigid skeleton), which includes some monomolecular or oligomeric compounds connected to a polymeric skeleton by weak donor-acceptor interactions or by hydrogen bonding (a mobile phase);

2) Chemical structure OMC contains various on an automatic degree fragments with condensed benzene rings including naphthenes, while these fragments in three dimensions with aliphatic, ester, thioester, imino and so on bridge linkages or their combinations are bonded;

3) The fragments of OMC with condensed benzene and naphthene rings contain both heteroatoms (O, N, S) and various substances and functional groups: alkyl- (less often cycloalkyl), carboxyl-, ester-, carbonyl-, hydroxyl-, mercapto- and amino-. At the same time carbonification (the increase of a metamorphism degree from brown coals to anthracites), conditioned by elimination of CO_2 and H_2O, dehydrogenation, dealkylation and aromatization, occurs reduction of linkage length, increase both aromaticity of coal matter and ordering of the condensed aromatic fragments.

Accepting the stated hypothesis about a structure of OMC as the basis it is possible to predict the main directions and sequence of chemical compounds destruction of coal in system coat - solvent at various temperatures. It is obvious, that at the lowest temperatures of thermal dissolving (350-400°C) at which it is expedient to carry out this process (in our case 400°C), destruction of OMC will proceed mainly on functional groups (-CO, -COOH, -COC, -SH, -NH etc.). At increase of temperature up to 425-450°C decomposition reactions will occur on aliphatic, ester and other bridge bonds as well as heteroatomic ring, and then also aromatic fragments OMC with condensed benzene rings: In this case everyone coal should have characteristics caused by specificity of a structure of its organic mass.

With kinetic point of view destruction of OMC at liquefaction in the solvents proceeds on the mechanism of parallel-successive reactions [24-30]. Conventional is the model, on which at the initial stage of coal matter destruction the most high molecular chemical compounds - preasphaltenes are formed. As a result their destruction leads in formation the easier structures - asphaltenes, at which further decomposition the oils, gasoline and gas are consistently formed: Cracking reactions on the parallel mechanism simultaneously proceed: the formation of oils, gasoline and gas is- direct from chemical structures OMC, destruction of preasphaltenes with formation of ails etc: Schematically it can be presented as follows:

Comparing a structure of OMC and kinetic model it destruction, is possible to believe, that the formation of preasphaltenes and asphaltenes and high molecular structures; containing compounds with condensed benzene rings, is connected to break aliphatic; ester, thioester etc. bridges. In parallel reactions of decomposition of alkyl- and functional groups of OMC; resulting to formation of gas and gasoline, proceed. The formation of oils from organic mass, probably; is connected with isolation of a mobile phase for the account of destruction of its weak bonds with a rigid skeleton. The decomposition of preasphaltenes and asphaltenes up to easier products occurs, apparently; first of all as a result of break of benzene and naphthene rings containing heteroatoms, and at more severe conditions for the account of destruction of aromatic and alicyclic rings in the condensed systems.,

Let's compare the stated rules about a structure of OMC and its decomposition mechanism at thermal dissolving to experimental data.

In Tables 2 and 3 the data on yields of products and composition of gas are given at liquefaction of the coals Borodina; Berezovsk and Itatsk deposits, while in Tables 3, 4, 5 the average values (on times of isothermal exposure) and in Table 2 their complete set are submitted.

Table 2. Conversion and products yields at liquefaction of coals of Kansk-Achinsk field

Deposit	T, °C	Time (τ) min	Products yield, % on dry mass of coal				Conversion %
			Gas	Gasoline	Extract	Solid residue	
1	2	3	4	5	6	7	8
Borodino	400	0	1.1	1.2	3.1	94.8	5.4
		2	2.2	2.4	6.5	88.9	11.1
		5	4.3	2.7	13.0	80.0	20.0
		10	6.5	5.5	13.0	75.0	25.0
		15	9.8	15.3	20.6	54.3	45.7
	425	0	11.8	9.2	20.9	58.1	41.9
		2	13.0	17.2	32.6	37.2	62.8
		5	14.1	21.4	31.6	33.0	67.0
		10	14.1	19.3	33.6	33.0	67.0
		15	15.3	22.8	36.4	25.5	74.5
	435	0	7.5	8.0	23.5	61.0	39.0
		5	10.8	11.5	35.0	42.7	57.3
		10	11.9	13.6	41.2	33.3	66.7
		15	12.7	18.0	35.2	34.1	65.9
	450	0	8.1	17.3	12.3	62.3	37.7
		2	9.5	21.6	23.3	45.6	54.4
		5	10.8	21.2	29.8	38.2	61.8
		10	12.2	20.7	32.5	34.6	65.4
		15	13.5	26.6	28.4	31.5	68.5
Berezovsk	400	0	2.2	1.2	3.3	93.3	6.7
		5	5.3	7.0	20.6	67.1	32.9
		10	4.9	7.6	16.0	71.5	28.5
		15	10.1	8.2	19.0	62.7	37.3
	425	0	3.7	1.2	11.6+15.7	67.8	32.2
		5	7.5	4.9	12.9+29.2	45.5	54.5
		10	11.8	4.6	14.8+31.0	37.8	62.2
		15	12.5	6.2	16.8+29.7	34.8	65.2
	435	0	8.5	6.8	26.0	58.7	41.3
		5	14.2	7.8	42.4	35.6	64.4
		10	15.2	8.4	45.6	30.8	69.2
		15	16.2	5.1	51.7	27.0	73.0
	450	0	6.9	10.0	18.2	64.9	35.1
		5	12.4	11.7	30.7	45.2	54.8
		10	13.8	16.0	29.1	41.1	58.9
		15	15.2	8.3	38.6	37.9	62.1
Itatsk	400	0	1.8	1.2	2.2	94.8	5.2
		5	6.5	4.2	10.8	78.5	21.5
		10	7.1	5.3	14.0	73.6	26.4
		15	6.9	3.1	13.6	76.4	23.6
	425	0	2.6	5.2	10.6	81.6	18.4
		5	7.8	14.7	25.3	52.2	47.8
		10	8.9	10.3	30.8	50.0	50.0
		15	10.8	10.1	37.1	42.0	58.0
	435	0	3.2	6.4	21.6	68.8	31.2
		5	11.0	11.8	42.4	34.8	65.2
		10	15.1	11.4	44.5	29.0	71.0
		15	17.7	8.6	37.1	36.6	63.4
	450	0	2.9	7.7	19.4	70.0	30.0
		5	10.1	15.0	39.0	35.9	64.1
		10	13.9	15.1	41.5	29.5	70.5
		15	16.3	11.9	35.3	36.5	63.5

Table 3. Gas composition at liquefaction of coals of Kansk-Achinsk field

Deposit	T, °C	Gas composition, % mass								
		H_2	CO	CO_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}
Borodino	400	0.2	18.1	73.2	5.7	0.2	1.8	0.2	0.5	0.1
	425	0.6	16.1	66.6	10.7	0.3	3.5	0.3	1.6	0.3
	435	1.2	15.3	65.8	11.6	0.4	3.5	0.3	1.7	0.2
	450	1.3	13.3	67.1	12.6	0.6	3.5	0.3	1.4	0.1
Berezovsk	400	0.2	18.4	72.2	5.8	0.4	1.9	0.2	0.7	0.1
	425	0.6	12.8	59.3	15.1	0.6	7.9	0.5	2.5	0.6
	435	1.6	6.9	65.3	13.3	1.2	8.1	0.6	2.5	0.5
	450	1.3	7.9	63.4	14.4	1.4	7.6	0.6	2.5	0.7
Itatsk	400	0.2	18.6	74.0	5.1	0.1	1.4	0.1	0.3	0.1
	425	0.4	15.2	66.4	12.2	0.1	3.4	0.2	1.5	0.4
	435	1.2	12.5	57.0	20.7	0.4	5.7	0.2	2.0	0.2
	450	1.3	12.4	57.7	18.5	0.2	6.8	0.2	2.2	0.5

Table 4. Relative content of hydrogen in structural fragments of extracts at liquefaction of coals of Kansk-Achinsk field

Deposit	T, °C	Hydrogen content, %							
		$H^{CH}{}_{3}$, alkyl	$H^{CH}{}_{2}$, alkyl	$H^{CH}{}_{2}$, napht	H_{OH}	$H^{\alpha}{}_{CH3}$	$H^{\alpha}{}_{CH2}$	H_{bi}	H_{pol}
Borodino	400	8.5	9.5	7.4	2.2	7.9	5.6	10.8	11.1
	425	7.0	8.5	5.4	2.0	9.6	6.2	14.8	13.0
	435	5.8	8.6	7.8	2.0	7.7	5.8	14.3	20.8
	450	6.1	9.4	6.5	2.4	7.9	5.8	11.3	20.9
Berezovsk	400	11.7	12.9	15.8	2.9	9.6	7.2	13.0	9.7
	425	9.0	11.0	17.0	3.0	10.0	7.0	20.0	9.7
	425^a	5.0	7.0	-	3.5	3.0	6.0	34.1	-
	425^b	4.2	6.6	18.8	3.5	6.4	5.0	-	45.4
	435	10.5	6.6	19.2	3.0	11.7	8.1	18.3	19.0
	450	5.8	7.1	20.6	3.0	13.6	9.7	19.7	11.9
Itatsk	400	11.1	12.1	6.1	2.0	10.8	6.5	12.6	7.4
	425	11.6	11.8	5.7	2.0	11.4	6.5	13.4	8.7
	435	8.0	9.0	6.0	2.5	13.0	7.0	18.0	14.6
	450	7.2	8.3	8.4	2.5	10.5	5.7	14.6	13.0

here and further: ^{a} – b.p. of extract is equal 230-320°C; ^{b} – b.p. of extract is more than 320°C.

Table 5. Content of hydrogen and carbon atoms in structural fragments of extracts, calculated on the basis of NMR ^1H spectroscopy data

Deposit	T, °C		Amount of atoms, units							
			CH_3, aliph.	CH_2, aliph.	CH_2, Napht.	OH	α-CH_3	α-CH_2	Bi	Pol
Borodino	425	H	4.0	4.6	2.9	1.1	5.2	3.4	8.0	7.2
		C	1.3	2.3	1.4		1.7	1.7	10.0	10.1
Berezovsk	425^a	H	3.6	4.4	6.8	1.2	4.0	2.8	8.0	5.0
		C	1.2	2.2	3.4		1.3	1.4	10.0	7.0
	425^b	H	1.5	2.1	-	1.1	4.0	1.8	10.5	-
		C	0.5	1.1	-		1.3	0.9	13.1	-
Itatsk	435	H	3.5	4.0	2.7	1.1	5.8	3.1	8.0	6.5
		C	1.2	2.0	1.3		1.9	1.6	10.0	9.1

It is necessary to note, that the above scheme of coal matter decomposition corresponds to a method of component fractionation of liquefaction products on solubility in the various solvents: preasphaltene are compounds, soluble in tetrahydrofurane, but insoluble in benzene and toluene, asphaltene are chemical compounds, soluble in benzene and toluene, but insoluble in pentane and heptane, oils and gasoline-substance, soluble in pentane and heptane.

In the present work fractional distillation at temperatures of boiling (see Table 2): gasoline -fraction with b.p. up to 200°C, extract - fraction with b.p. > 230°C (oils + asphaltenes + preasphaltenes), solid residue - ash + non-liquefaction part of OMC was used. A fraction with b.p. 200-230°C is used solvent (tetraline), which was recovered from a reactionary mixture.

As follows from Table 2, at temperature of liquefaction 400°C the basic thermal dissolving product is the extract with the yield 20,6%, while the yield of gas does not exceed 10,1 %, and the yield of gasoline only in a case of the coal Borodino deposit achieves 15,3%, whereas for others coals it does not exceed 8,2%. This result, and also composition of the gas (Table 3), confirms a hypothesis about a structure of OMC and sequence of its decomposition.

Probably, at lower temperatures of liquefaction destruction of coal matter proceeds on the mechanism of parallel-successive reactions: on the one hand, there is a consecutive decomposition of OMC up to the heaviest products (preasphaltenes and asphaltenes), that explains a high yield of an extract, and on the other hand, on the parallel mechanism occurs the destruction of functional groups of OMC with formation of gas and petrol fraction. Confirmation it is the composition of gas formed, which at temperature of liquefaction 400°C contains more than 90% (totally) of carbon oxide and dioxide, as its formation occurs at the expense of decomposition of oxygen containing groups (-CO, -COOH, -COC etc.) coal substance.

At increase of thermal dissolving temperature up to 425-450°C it is essential intensified the mechanism of consecutive decomposition of OMC not only up to preasphaltenes and asphaltenes, but also further destruction of these structures up to oils, gasoline and gas, that results in substantial growth of their yield: for gasoline up to 26.6%, and for gas up to 17.7%. The change of gas composition also testifies to it, in which the contents of carbon oxides decreases on 15-25%, and the amount of hydrocarbon components grows (methane in 2.5-5 times, ethane in 2-5 times, propane in 3-7 times, ethylene and propylene in 2-4 times), as the formation of gaseous products begins to proceed at the expense of decomposition of hydrocarbons of gasoline and oil fractions.

Besides the parallel-successive mechanism of OMC destruction, the important feature of liquefaction process of coals is its „reversibility". Together with „direct" reactions of coal matter decomposition with formation liquid and gaseous products, the „reverse" reactions take place. These reactions are condensation, recombination, disproportionation etc. of chemical compounds resulting in formation of high molecular condensed structures, which at separation of products of thermal dissolving transfer in the solid residue.

It is seen from Table 2, that for the coal Borodino deposit the condensation reactions begin to prevail at temperature 435°C, than some reduction of conversion accompanying with essential decrease dissolving transfers in the solid residue. of an yield of gasoline (5-10%) is explained, being the yield of an extract and gas practically does not change. For the coal Berezovsk deposit the reduction of conversion (on the average on 10%) is observed at temperature 450°C, but in this case more, than on 10% the yield of an extract is reduced at practically constant yield of gas and gasoline.

In the case of the coal Itatsk deposit the increase of temperature with 435 up to 450°C practically does not influence on conversion and yield of products. It is possible to believe that at coal liquefaction at temperature 450°C the rate of direct and reverse reactions become rather close.

It is necessary to note, that „reversibility" of thermal dissolving is clearly shown on kinetic dependence's of a yield of products. So, for the coal Borodino deposit at temperature of liquefaction 425°C in an interval of isothermal exposure 5-10 mines, and also at 435°C and τ =10-15 min conversion and the yield of products practically are constant. For the coal Berezovsk deposit at temperature 400°C and τ=5-10 min the reduction of conversion and yield of products are observed, and for the coal Itatsk deposit the similar reactions proceed at temperatures 400, 435 and 450°C at time of exposure 10-15 min.

It is obvious that it will be most effective process of thermal dissolving to proceed at presence of protono-donor solvents containing easily dehydrogenated chemical compounds [31-35]. However, it is possible to believe, that at liquefaction the donor of hydrogen is not only solvent, but also chemical components of coal matter and, in particular, naphthenics which are included in composition of OMC. It proves to be true by changing of the contents of naphthenics ($H^{CH}_{2,napht}$) in extracts (Table 4). The above mentioned reduction of conversion the coal Borodino deposit at passing from 425 to 435°C is accompanied by increase of the contents of naphthenic compounds in extracts from ~5 up to 8 %, while at increase of conversion, the amount of alicyclic structures in extracts is usually reduced (Table 4).

If „reversibility" of thermal dissolving is shown at liquefaction of all investigated coals, only from the coal Berezovsk deposit at 425°C an extract with initial b.p. 230°C is received, whereas all extracts others investigated coals, among them Berezovsk deposit, received at 400, 435 and 450°C, have initial b.p. 290-295°C. In this connection for an extract of the coal Berezovsk deposit, received at 425°C, the yields of fractions with b.p. 230-320 and above 320°C are estimated. Therefore in Table 2 for this coal, the yield of an extract is resulted as sum from the marked fractions; which are separately illustrated in Tables 4 and 5.

Difference of fractional composition of an extract from the coal Berezovsk deposit, probably, is connected with petrographic composition of coals studied. As it is seen from TabIe 1, the coal Borodino deposit contains 88% of vitrinite and 14% of semivitrinite, which are the most easy Iiquceficated petrographic components [19,21]. By it is explained that at thermal dissolving of this coal the maximal conversion (74.5%) is achieved at 425°C (lowest for investigated coals). In this case the yield of easy products, gas and petrol, consists 15.3 and 22.8%, respectively (Table 2); whereas the yield of heavy liquid product (extract) makes only 36.4%:

At the same time the coal Itatsk deposit contains only 84% (totally) of vitrinite and semivitrinite as well as 15% fusinite, being on the most difficult liquceficated petrographic components (the coal Borodino deposit there is only 1% of fusinite).

In this connection; the maximal conversion at thermal dissolving of this coal (71.0%) corresponds to temperature of 435°C while the yield of gas consists ~16% and of petrol - only ~11%, but the yield of an extract achieves 44.5%.

The coal Berezovsk deposit has intermediate position: it contains 89% of vitrinite, 2% semivitrinite and 5% of fusinite. Increased content of it; in comparison with the coal Borodino deposit, leads to that the greatest conversion (73.0%) corresponds to higher temperature - 435°C. In this case the yield of gas practically is the same as at others coals (~15%) and the yield of petrol is lower in ~2.5 times than at the coal Borodino deposit and in ~0.5 times in comparison with the coal Itatsk deposit, while an yield of extract is maximal - 51.7%. It is apparently that the increase of fusinite content in OMC results to increase of temperature; at which the maximal conversion- is achieved: for the coal Borodino deposit - 425, for the coal Berezovsk deposit - 435 and for the coal Itatsk deposit – 435-450°C. Therefore, petrographic composition essentially influences an the yield of products: at thermal dissolving of vitrinitic coals should be expected high yields of gas and petrol, so far as increase of the fusinite content - increase of an extract yield.

However, above-mentioned rule though reflects the basic regularities of coals liquefaction, but also has the certain exceptions. In particular; at liquefaction of the coal Berezovsk deposit, contained in 3 times there is less of fusinite, than the coal Itatsk deposit, the yield of heavy liquid products is higher, and the gasoline are lower; that is: by the reason of formation of an extract with b.p. above 230°C. Probably at liquefaction of the coal Berezovsk deposit at 425°C essential destruction of chemical structures of an extract with formation of a gasoline fraction does not proceed.

If on the basis of data (Table 4) to estimate contents of carbon in CH_3,- and CH_2-groups in aliphatic compounds of extracts as $H^{CH}_{3,aliph}/3$ and $H^{CH}_{2,aliph}/2$, the formed ratio $C^{CH}_{2,\ aliph}/C^{CH}_{3,\ aliph}$, will characterize the length of their chains and isomerization degree. The higher is this ratio, the longer is the main chain and the less is the side chains in molecules, in that case this hydrocarbon is more thermal stable. It is found, that for extracts from the coal Berezovsk deposit this ratio average for each of temperature from 400 up to 450°C makes 1.53, 1.94, 1.10 and 1.60, while for extracts from the coal Borodino deposit it is equal 1.54-1.63, and for the coal Itatsk deposit 1.3-1.49.

Hence, the destruction of OMC of Berezovsk deposit at 425°C is accompanied by formation of the most thermal stable aliphatic hydrocarbons, which decomposition up to gasoline fraction procced much less, than at others coals (see the yields of gasoline in Table 2), therefore they remain in extract with formation a fraction with b.p. above 230°C. The maximal ratio $C^{CH}_{2,\ aliph}/C^{CH}_{3,aliph}$ at 425°C, probably, is explained that at 400°C reactions of OMC destruction proceed not enough deeply, and at higher temperatures they so increase, that begin essentially to affect and these hydrocarbons.

The data of H^1 NMR-spectroscopy for fractions of an extract from the coal Berezovsk deposit are significant interest. As follows from Table 4, the fraction of an extract with b.p. 230-320°C does not contain naphthenic and polynuclear aromatic compounds. Absence last is explained to that temperature of their boiling is higher 320°C for anthtracene - 354°C, for phenanthrene - 340,2°C and so on. Apparently, and naphthenic compounds which are included in extracts composition, boil out above 320°C. In such case they should contain 14 and more carbon atoms, or, that is quite possible, to have a structure of adamantine, which in proton spectra gives singlet, as well as in our case (Figure 1), at δ=1,782 ppm. This assumption is quite justified, as adamantine and its derivatives are identified in coals, oils and in products them processing [31,37].

At the same time in a fraction of an extract with b.p. is higher 320°C binuclear aromatic compounds are absent (Table 4). From here follows, that these chemical structures of extracts contain no more than 5 carbon atoms in available at them of methyl and alkyl substitutes, as, for example, such compound as 1,6-dimethyl-4-isopropylnaphthalene (cadalene) has b.p. 315°C. However, the presence in extracts an aromatic compounds with such long chain alkyl substituents, as propyl is improbable, as the conditions of liquefaction is severe enough (400-450°C).

At present a number of methods is offered for calculation of structural-group composition of oil and coal refining products (hydrogenizates, extracts, bitumens, asphalts e.t.c.) on the basis of the H^1 NMP-data [38-41]I, using various systems of assumptions and postulates. In that work, in which received spectra have enough high degree of resolution (Figure 1), the attempt of account of absolute number of protons in various chemical structures of extracts is made by one of the standard methods, used for proton spectra of individual compounds [42,43].

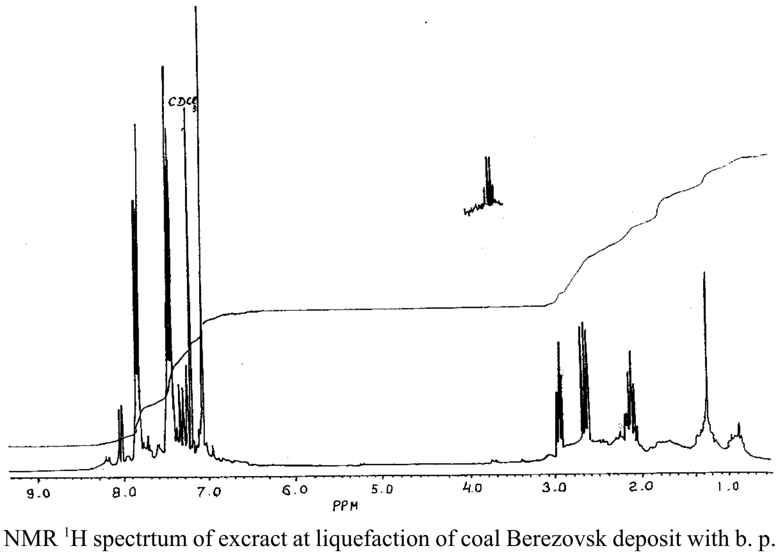

Figure 1. NMR ^{1}H spectrtum of excract at liquefaction of coal Berezovsk deposit with b. p. > 230 °C

The essence is the next: if any line of a spectrum corresponds obviously known number of protons, that, having divided a height of integral curve this line on number of protons we receive coefficient of proportionality, which can be applied to any .part of the given spectrum. In our case it is advisable to use those lines of spectra, where are shown protons of binuclear aromatic compounds giving two clear quadruplets (Figure 1), each of others corresponds to 4 protons.

In Table 5 are given results of such accounts, on basis of its the amount of hydrogen and carbon atoms in hypothetic molecules of extracts was obtained. The content of carbon atoms in CH_3- and CH_2 -groups was determined by division of number of hydrogen atoms by 3 and 2; respectively; and in di- and polynuclear aromatic compounds by multiplication - by 1.25 and 1.40 accordingly.

Table 6. Elemental analysis and molecular mass (M) of extracts by liquefaction of coals of Kansk-Achinsk field

Deposit	T, °C	Elemental analysis, mass %					M, unit
		C	H	N	S	O	
Borodino	400	84.66	7.10	0.73	0.19	7.32	415
	425	84.55	7.13	0.64	0.17	7.51	407
	435	85.80	6.77	0.83	0.17	6.43	370
	450	84.97	7.08	0.68	0.15	7.12	392
Berezovsk	400	85.40	7.53	0.80	0.30	5.97	367
	425	86.48	7.01	0.85	0.23	5.43	376
	425[a]	84.26	7.47	0.55	0.15	7.57	223
	425[b]	88.66	5.93	1.17	0.12	4.12	552
	435	86.98	6.80	1.02	0.19	5.01	371
	450	86.57	6.90	1.08	0.13	5.32	368
Itatsk	400	84.67	7.29	0.46	0.41	7.17	348
	425	84.81	7.86	0.34	0.20	6.79	393
	435	86.14	7.35	0.61	0.12	5.76	364
	450	85.87	6.81	0.53	0.20	6.59	387

Table 7. Experimental (E) and calculated (C) data for molecules of extracts from coals of Kansk-Achinsk field

Parameters	Borodino		Berezovsk				Itatsk	
	E	C	E	C	E	C	E	C
Formula	$C_{28,6}$ $H_{29,0}$ $O_{1,91}$ $S_{0,02}$ $N_{0,19}$	$C_{28,4}$ $H_{35,3}$ $O_{1,0}$	$C_{27,1}$ $H_{26,4}$ $O_{1,26}$ $S_{0,03}$ $N_{0,23}$	$C_{26,5}$ $H_{34,6}$ $O_{1,0}$	$C_{15,7}$ $H_{16,7}$ $O_{1,05}$ $S_{0,01}$ $N_{0,09}$	$C_{16,9}$ $H_{19,9}$ $O_{1,0}$	$C_{26,1}$ $H_{26,7}$ $O_{1,31}$ $S_{0,01}$ $N_{0,16}$	$C_{27,1}$ $H_{33,6}$ $O_{1,0}$
Mol. mass	407	392	376	369	223	239	364	375
f	0.69	0.71	0.68	0.64	0.77	0.77	0.73	0.70

Further on the basis of experimental data (Table 6) and obtained from H^1 NMR-spectra (Table 5) the formula of extracts, their molecular weights and its aromaticity (f) were calculated, which are given in Table 7. As it is seen, the convergence of the received results is good, though the content of hydrogen in the estimated formulas is a little above. Probably, it is explained to that such products of coal processing as extracts, asphaltenes etc. have enough high -reaction ability, that is shown, in tendency to condensation and recombination processes, especially, if they are received in conditions of high-speed heating [6,8]. In the present work the analysis of extracts was performed so, that H^1 NMR-spectra were recorder within 1-3 days after their receiving, and element analysis carried out after 10-20 days, than, probably, and is explained the more high contents of hydrogen in the estimated formulas.

It is necessary to note; that offered in the given work the method of calculation of proton spectra of extracts allowing to receive good convergence with experiment, has certain advantages before traditional [38-41], as does not require any assumptions, in some cases rather disputable. In particular, practically in all works the formulas for calculation of average lengths of a chain of the substituents at aromatic compounds are given and never this parameter does not connect with conditions of production researched compounds: However, it is obvious, that products received at high temperature processes (coking, pyrolysis); will have the more short chain alkyl substituents; or in general only methyl, rather than products of thermal dissolving; hydrogenization or extraction.

In the present work for determination of this parameter it is possible to use experimental results and H^1 NMR-spectroscopy data. It was earlier shown that the number of carbon atoms: in alkyl and methyl substituents at aromatic compounds of extracts did not exceed 5. For example, for a molecule of an extract from the coal Itatsk deposit (Table 5) it is visible; that aromatic compounds which are included in its structure, have 2 methyl substituents (α-CH_3 = 1.9 and 1-alkyl substituent (α-CH_2 = 1.6), which can to be either ethyl or propyl a radical; that is maximal the number of carbon atoms in alkyl groups is equal 3. However, as referred to above, the presence of so long-chain substituents is unlikely; therefore it is possible that the average number of carbon atoms in alkyl groups at aromatic compounds of extracts is equal 2, though the presence at them C_3-substituents also does not cause doubts.

On the basis of stated data it was calculated two structural formulas, representing a fragment from 4 molecules of an extract from the coal Berezovsk deposit with b.p. > 230°C ($C_{26,5}H_{34,5}C_{1,0}$)~ given in Figure 2. The essential distinctions in these structures, each of which has the right on subsistence, consists in the following: at first, naphthenes in structure (a) are presented wíth cyclotetradecane; and in (b) - adamantane, a possibility of which presence in, coals and in products of their processing it was marked earlier, Secondly, in formula (b) methylene bridges are presenting, which occurrence in products of rather high-temperature process of thermal dissolving (400-450°C) is quite doubtful.

However, as shown in works [44,45]; thermal stability of similar compounds is high enough: diphenylmethane at 400°C practically is not decomposed during 18 hours, and at 400°C the rate constant of it destruction makes $3x10^{-3}$ min^{-1}. Though the stability of methylene bridges in real coal products is lower, than in modeling compounds, their presence in extracts it is rather probable, as thermal dissolving carried out in a conditions of high-speed heating with short residence time and fast cooling of system (~2,5 min up to 100°C): Besides, in proton spectra of extracts (Figure 1), in the field of display of rnethylene bridges (CH_2-) between aromatic compounds (3,5-4,5 ppm), there is a very weak signal at $\delta = 3.72$ ppm, which practically is not shown on an integrated curve and consequently do not take into account at analysis of spectra.

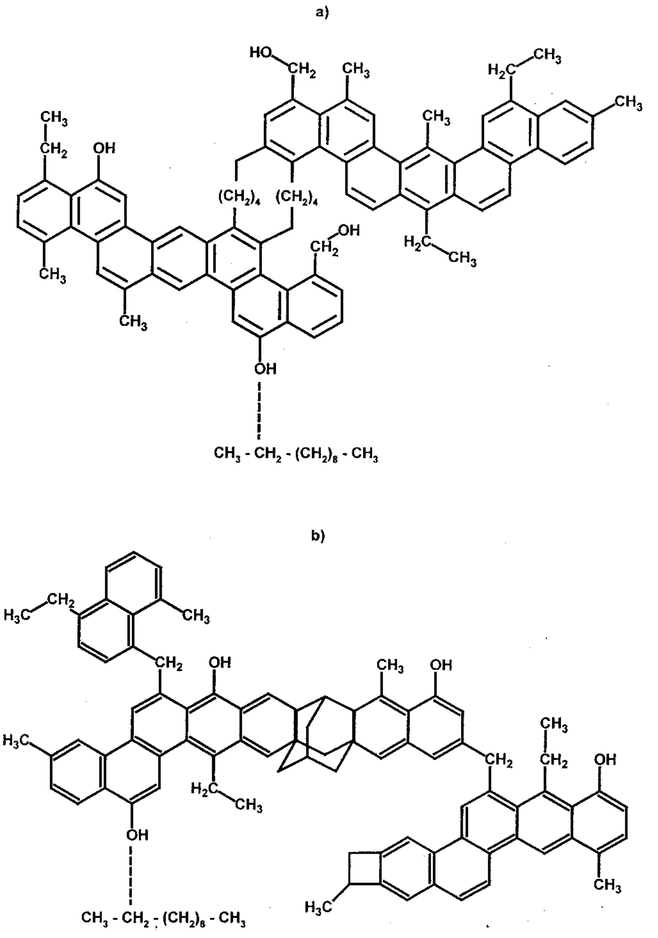

Figure 2. Structure formulas including four molecules of extract at liquefaction of coal Berezovsk deposit with fragment: cyclotetradecane (a) and adamantane (b)

The offered earlier hypothesis about a structure of OMC; provides the presence in it of mobile phase, connected to a rigid skeleton with weak donor-acceptor bonds. In brown coals to mobile phase it is possible to refer, first-of all, paraffin hydrocarbons; contents of its achieves 10-12 % on OMC [21]; and which naturally in that or other kind, should be present at extracts. In our case the paraffin fragment is presented by undecane (Figure 2).

Conclusion

The carried out analysis of results of thermal dissolving and data on composition and structure of products obtained at liquefaction of brown coals of Kansk-Achinsk field, convincingly enough confirms the theory, in which OMC is considered as three-dimensional polymer irregular structure. This polymer contain monomolecular compounds, connected with polymeric skeleton by weak donor-acceptor bonds while the chemical structure of OMC includes fragments with condensed benzene and naphthene rings, which are bonded by aliphatic ether and so-on bridge linkages.

It is established, that destruction of OMC at liquefaction of coals proceeds on to the mechanism of parallel-successive reactions, thus is considered a sequence of decomposition of functional groups and chemical bonds in coal substance at various temperatures.

It is found; that at thermal dissolving of coals along with reactions of OMC destruction the reactions of condensation (recombination and etc.) of formed coal fragments are proceeding, and for various coals it occurs at different temperatures and residence times. These conditions are defined, mainly, by petrography composition of solid fuel that has also essential influence on yield and structure of products.

It is shown, that the proton spectra of exctracts it is possible to interpret without introduction of any assumptions, receiving thus results well agreed with experiment. On the basis of the data H^1 NMR-spectroscopy the chemical structure of extracts molecules was calculated and 2 structural formulas including till 4 molecules of an extract from the coat of Berezovsk deposit were suggested. It is visible, that obtained coal products on composition and structure are close enough to heavy oil products (petroleum residue; gasoils and so on) [1,2]. Therefore they can be used as feedstock for catalytic hydroprocessing into motor and diesel fuels; and, in contrast them, they practically not contain such catalytic poisons, as sulfur and heavy metals.

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