

UDC 622.74 : 662.75

Composition of Coals from Northern Fields of the Lena Coal Basin Estimating the Conversion into Liquid Fuel

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(Received July 4, 2008; revised September 12, 2008)

Abstract

The composition of coals from new northern fields of the Lena coal basin and their reactivity in the processes of thermal dissolution and hydrogenation were studied. It has been established that the content of rare-earth elements in the coals under investigation in some cases is 5–10 times higher than industrially significant parameters. Results of coal thermochemical conversion into liquid substances have been investigated. Quantitative relationships between the conversion level in the process of thermal dissolution and the data of coal technical analysis such as hydrogen concentration and the yield of volatile substances have been determined. Suitability of Lena coal basin application for obtaining liquid fuel employing the method of catalytic hydrogenation is grounded. It is noted that complex coal processing with rare-earth concentrate obtaining is quite appropriate.

Key words: coal, composition, rare-earth elements, processing, liquid fuel, gasoline

INTRODUCTION

The hypothetical resources of the Lena basin, the largest in Russia with respect to coal reserves are amounting to more than 756 billion ton [1]. The Lena coal basin is located within middle and lower reach of the Lena River basin siding with the Laptev Sea shore. In pool allocate eight carboniferous regions are considered therein, those are mainly presented by humus coals of a wide metamorphic range from lignites up to anthracites. Low-ash and low-sulphur kinds of coal at low stage of metamorphism are prevailing, such as brown coals and jet black coals. As a whole, the Lena coal basin is poorly known, the balance coal reserve determined amounts only 6.775 billion ton, *i.e.* less than 1 % hypothetical resources [1]. Purposeful complex studies on coal technological properties were not carried out up till now, the most comprehensive investigation were performed concerning only medium-ash low-sulphur brown coal from a large-scale Kangalas coalfield 40 km ranging along the left river-

side of the Lena River. Coal is developed employing a cheap open-pit method on small scale; it is used for power-plant purposes (as fuel for municipal and household needs). According to the technological properties this coal represents a valuable raw material for obtaining the products of different purpose such as liquid fuel, carbon materials, *etc.* [2–8].

It should be noted that in the northern provinces of the Lena coal basin there are also sapropelite, sapropelite-humulite and humito-sapropelite coal deposits occurring within the layers of humus coals and in the form of a separate ingress, which sapropelite, sapropelite-humulite and humito-sapropelite coal serve as a high-quality raw material for chemical conversion into liquid fuel and valuable organic substances [1, 9, 10]. Considerable deposits of boghead coals with bed thickness up to 1.0 m are found out in the Taymylyr field in the Oleknek coal area, where 1.049 million ton are taken into account by the State list of resources. Remaining boghead coal ingresses do not represent any industrial importance owing to in-

significant resources and insignificant bed thickness. Nevertheless, there are certain geological preconditions for discovering new boghead ingresses in the Oleknek coal area, since coal layers have been revealed therein within the sediment that represent a stratigraphic analogue of horizons whereto the Taymylyr and other sapropelite coal fields here are timed.

Fossil coals represent naturally occurring concentrators of chemical elements (about 70 chemical elements of the Mendeleev Periodic Table) [11]. With the increase in scale of coal output and use, the presence of chemical elements therein gives rise to a number of scientific, technological and environmental problems. Coal fields of the Lena basin are unique not only due to the resources, but also due to increased metalliferous features [12–14]. In some cases the content of metals in the Lena basin coals is so great that the coals could be considered to be a promising source of valuable metals such as, scandium, yttrium, lanthanum, niobium, lanthanoids, *etc.* and germanium, whose significant part in the world is traditionally produced from coals. There are significant concentration of valuable rare-earth elements (REE) found out in brown coals of the Kangalas coalfield [12, 13]. Abnormally high concentrations of Y, Yb, Sc, Zr, Cr, Ni, V, Co, Sr and some other valuable metals with the total content up to 15 kg/t of ashes [12, 13] are revealed in near-top and near-bottom layers of the Zhigansk coalfield.

Large-scale reserves as well as a wide range of grade composition allow one to consider the coals of the Lena coal basin to be not only a power-plant fuel, but also a valuable raw material for deep complex chemical conversion into the products of various purposes. However, the development of metalliferous deposits requires for solving the problem of the isolation of valuable mineral components [11, 15, 16].

One of the efficient directions for utilizing the coals of the Lena basin consists in their joint processing with the residues of petroleum refining, whose prospective fields have been explored within the bounds of the Lena coal basin [17–19]. Such an approach allows one to optimally involve the coal in chemical processing and simultaneously to increase petroleum refining level with obtaining an additional amount of top (light fractions).

Earlier in the course of exploration work researchers investigated carboniferous sediment

within the Salga-Talabakh area of the Oleknek carboniferous region at the northern part of the Lena basin. Data have been obtained concerning geological and tectonic structure, carboniferous features of sediments, coal quality, mining and geological bedding conditions. Coal seams with an increased thickness have been revealed for open-pit development. Sapropelite coal seams have been found out within separate areas.

This work presents the results of the studies on the composition of coals from new coalfields of the north of the Lena coal basin and the estimation of their suitability for the processing in order to obtain liquid fuel.

EXPERIMENTAL

Representative samples of coals were taken from wells, ditches and bore pits in the course of geological exploration of the Salga-Talabakh area. The samples were grinded and dried in a vacuum drying oven at 85 °C. The general technical and elemental analyses were carried out using standard methods. The content of mineral components was determined using spectral analysis methods by means of strewing coal samples with the help of a DFS-8 spectrometer as well as with the use of leaching solutions with the help of an Optima-3100RL spectrometer employing inductively coupled plasma assay. The petrography analysis was performed according to polished-section briquettes prepared.

The reactivity of coals was estimated in processes of thermal dissolution and hydrogenation in the media of solvents within autoclaves of 80 and 500 mL capacity. Gaseous products after the completion of the reaction were sampled and analyzed using a chromatograph with a heat conductivity detector. The contents of the autoclave was withdrawn, liquid products obtained were filtered. The residue remained on the filter was extracted by petroleum-ether (or toluene) in a Soxhlet apparatus. The conversion level of coal was determined according to the loss of its organic mass after the extraction and according to the ash level of the initial coal and the insoluble residue. In separate experiments the liquid products after the extraction of phenols and bases therefrom were subjected to fractionation. A petrol fraction was

analyzed using a chromatography assay employing a chromatograph with a capillary column and a flame ionization detector. The identification of chromatographic peaks was carried out with use of individual hydrocarbons and Kovac indices.

RESULTS AND DISCUSSION

The data of technical and elemental analysis of the coals sampled are presented in Table 1. One can see that the content of ash-forming substances in the samples ranges from 7.8 to 34.3 %. All the samples contain insignificant amount of sulphur-containing and nitrogen-containing compounds (less than 0.65 and 1.10 %, respectively). The highest content of hydrogen (5.1 to 5.5 %) is inherent in coal samples UYa5, UYa9 and UYa11. Coal samples UYa8, UYa9 and UYa11 are distinguished by the yield of volatile substances (47.4–52.1 %).

The petrographic structure of all samples is presented mainly by the components of the vitrinite group (ranging from 74 to 94 %), as well as liptinite (ranging from 1 to 10 %) and inertinite (from 6 to 22 %). Mineral inclusions contain mainly quartz, kaolinite and carbonates. According to spectral analysis data, in the composition of the ash residue there are silicon, calcium, aluminium and iron compounds prevailing (Table 2). According to the composition the ashes in conformity with [20] could be referred to mid-melting ashes with the softening beginning temperature values of 1240–1480

TABLE 2

Ash composition for the coals under investigation

Samples	Content, mass %				
	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃
UYa1	46.1	15.6	26.9	0.5	6.9
UYa2	61.4	5.4	15.4	0.2	13.6
UYa3	60.8	8.2	17.2	0.7	9.1
UYa4	23.6	27.8	33.4	0.6	10.6
UYa5	50.4	38.8	4.5	0.2	2.3
UYa6	39.6	18.9	32.7	0.5	4.3
UYa7	24.3	22.8	38.0	0.7	10.2
UYa8	46.3	40.5	3.7	0.7	5.0
UYa9	27.4	20.2	44.6	0.6	3.5
UYa10	53.6	26.8	1.9	0.5	13.3
UYa11	48.6	21.4	13.5	1.20	8.1

°C, the temperature of fluidity beginning amounting to 1270–1680 °C, the temperature of normal slag-tap removal ranging within 1320–1750 °C.

The spectral analysis of coal microelemental composition has demonstrated the presence of the majority of rare, transition and other metals. The content of the main toxic elements (Be, V, Co, Ni, Cd, Mn, As, Pb, Se, Sb, Ta, Zn, F, and Cr) did not exceed significantly the level of toxicity and coal clarkes. A considerable excess with respect to coal clarkes was observed for the majority or rare-earth elements. Especially high concentrations of REE are found out in the sediment of the bottom Lukumay series. On the average the content of some REE in coal samples amounted to (g/t

TABLE 1

Data of the technical and elemental analysis of coals

Samples	W _t ^f , %	A ^d , %	V ^{daf} , %	Content, mass % daf				
				C	H	S	N	O
UYa1	13.4	18.6	34.6	75.9	3.7	0.21	0.92	19.2
UYa2	8.8	34.3	36.1	76.2	4.0	0.16	1.10	18.5
UYa3	15.7	23.5	35.7	74.4	3.8	0.22	0.79	20.7
UYa4	15.4	7.8	32.7	76.8	3.6	0.16	0.79	18.6
UYa5	14.4	21.6	39.1	70.2	5.3	0.37	0.94	23.1
UYa6	16.4	8.0	42.0	73.2	4.9	0.65	0.94	20.3
UYa7	16.8	12.9	37.8	68.3	3.4	0.23	0.80	27.2
UYa8	17.3	24.2	47.4	68.4	4.6	0.23	1.00	25.7
UYa9	13.5	8.1	52.1	74.6	5.1	0.43	0.85	19.0
UYa10	8.9	48.3	37.9	72.5	3.8	0.10	0.79	22.7
UYa11	12.0	13.5	49.8	73.2	5.5	0.53	0.89	19.9

TABLE 3
Content of some rare-earth elements in coal samples

Elements	Content*, g/t		
	average all over the world [21]	commercially in samples significant [22]	
Yttrium	7.0	15	183–210
Ytterbium	0.9	1.5	14–15
Scandium	(10)	10	45–49
Cerium	(70)	–	339–517
Neodymium	–	–	173–249
Praseodymium	–	–	155
Lanthanum	(29)	150	156–374
Samarium	–	–	25–51
Berillium	2.4	5	18–25

*Parenthetically are specified approximate values.

of coal): Y 183–210, Yb 14–15, Sc 45–49. The data obtained are 5 to 10 times higher than industrially significant parameters of REE content in coal (Table 3), which should be taken into account in the development of technologies for coal chemical processing.

The reactivity of coals with respect to the formation of liquid products was estimated for the process of thermal dissolution in the medium of a hydrogen-donating solvent such as tetraline with no use of molecular hydrogen at 430 °C. The autoclave tests have demonstrated that the level of conversion into hexane-soluble substances (oils) and gaseous products for different samples of coal ranged from 32.3 to 69.7 %. A high conversion level (58.0–69.7 %) is demonstrated by samples UYa5, UYa8, UYa9, UYa11 those are characterized by an increased content of hydrogen and increased yield of volatile substances. On the contrary, coals with low hydrogen content and low yield of volatile substances exhibited low reactivity. For all the series of samples under investigation we have established correlation relationships between the conversion level (X) under thermal dissolution and the content of hydrogen as well as the yield of volatile substances, with linear correlation coefficient $R = 0.93$ and 0.85 , respectively (Fig. 1):

$$X, \% = -16.05 + 14.82[H^{\text{daf}}]$$

$$X, \% = -167.4 + 8.88V^{\text{daf}} - 0.08V^{\text{(daf)2}}$$

At the significance level value $\alpha = 0.95$ the above mentioned equations adequately describe

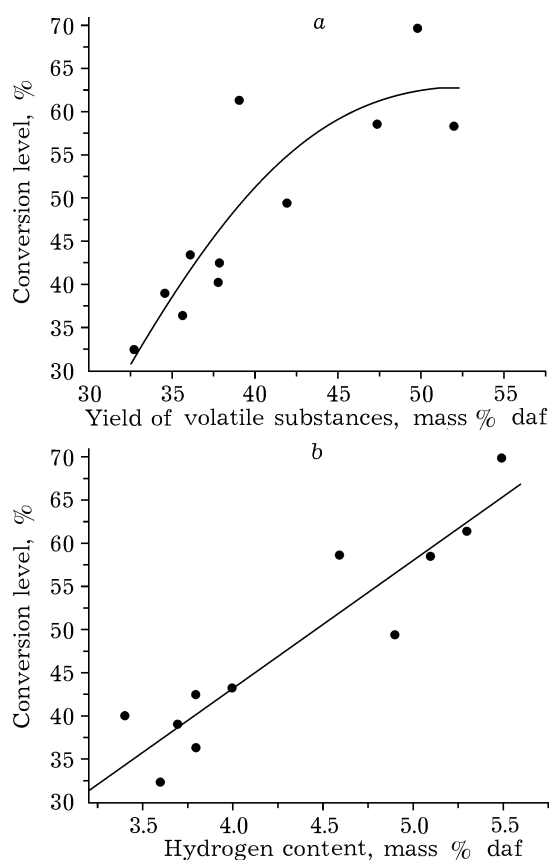


Fig. 1. Coal conversion level (resulting from thermal dissolution in tetraline) depending on the yield of volatile substances (a) and hydrogen content therein (b).

the experimental data obtained. Hence, basing on the results of technical analysis one could estimate the reactivity of coals in the process of thermochemical conversion into liquid and gaseous products.

In the process of thermal dissolution, the highest activity is exhibited by sample UYa11 with the content of hydrogen equal to 5.5 % and the yield of volatile substances amounting to 49.8 % having the following petrographic composition, %: vitrinite 87, liptinite 12, inertinite ~1. This sample was tested in the process of hydrogenation together with naphtha residue; the latter was chosen to be M100 technical mazout (with the mass fraction of sulphur equal to 1.3 %). The experiments have demonstrated that the hydrogenation in the mazout paste-forming agent did not result in achieving any high conversion level. At 430 °C and initial hydrogen pressure of 5 MPa the conversion level into toluene-soluble substances and gas was equal to 34.9 % only, whereas in the

TABLE 4

Process parameters for coal hydrogenation in various solvents at the temperature of 430 °C (coal/solvent = 1 : 1.5, pressure 5 MPa, reaction time 1 h)

Solvents	Catalyst	Conversion level, %	Yield of products, mass %	
			Liquids	Gases
Tetraline	–	86.0	71.9	14.1
Mazout	–	34.9	19.9	15.0
Mazout + 25 % tetraline	3 % RKG-1 + 3 %*	87.4*	65.5	21.9

*Reaction time 2 h.

tetraline medium under the same conditions this value amounted up to 86.0 % at the yield of toluene-soluble substances equal to 74.9 % (Table 4). A low decomposition level of coal could be connected with the absence of active hydrogen donors in the mazout composition those promote coal conversion into low-molecular liquid substances.

In order to efficiently realize the process of coal hydrogenation the paste-forming agent is usually added with a small amount of hydroaromatic hydrocarbons those play the role of hydrogen donors. So, in the process developed at the Fossil Fuels Institute (Moscow), researchers use for these purposes partly hydrogenated middle fractions of liquefaction products [3]. In our autoclave experiments, a high conversion level of coal was achieved due to adding mazout with a small amount of tetraline (up to 30 %) as a hydrogen-donating component and a superfine ferriferous catalyst developed earlier with elemental sulphur (3 %) [23, 24]. At the temperature of 430 °C and the reaction time amounting to 2 h the conversion level of coal amounted to 87.4 % with the yield of toluene-soluble liquid products and gases equal to 65.5 and 21.9 %, respectively. Among gaseous products there were hydrocarbons prevailing: their content amounted to 75.0 % (mainly methane with the content of 44.5 %); the fraction of carbon oxides was equal to 25.0 %.

The liquid hydrogenate obtained was filtered from solid residue. The filtrate obtained was treated by dilute solutions of alkali and acid in order to remove phenols and bases. The hydrocarbonic fraction isolated was subjected to fractionation. As far as the liquid hydrogenate is concerned, the content of petrol (gasoline) fraction with the boiling beginning temperature (BB) of 180 °C was equal to 17.5 %,

the content of the fraction with BB of 180–350 °C amounted to 46 %, and that of a high-boiling fraction was of 36.5 %.

The petrol fraction contained an insignificant amount of sulphur-containing compounds (0.14 %). The chromatographic analysis of its composition have resulted in revealing about 170 components among those prevailed alkanes with normal structure including *n*-hexane (1.56 %), *n*-heptane (4.83 %), *n*-octane (6.81 %), *n*-nonane (6.37 %), *n*-decane (4.75 %). Isoalkanes are basically presented by monomethyl isomers: so, the octane fraction exhibited the content 2- and 3-methylheptanes equal to 2.57 and 0.77 %, respectively, whereas the content of more branched 2,2,3-trimethylpentane and 2,3,4-trimethylpentane amounted to 0.67 % only. As far as naphthene hydrocarbons are concerned, a high content was observed for methylcyclohexane (0.90 %), ethylcyclopentane (0.76 %) and *n*-butylcyclopentane (0.52 %). Aromatic hydrocarbons are presented basically by toluene (2.25 %), *m*-xylene (2.26 %), *o*-xylene (1.85 %), *p*-xylene (0.84 %), ethylbenzene (1.3 %) and various methylethylbenzenes (1.92 %).

Table 5 presents data concerning the group hydrocarbonic composition of the petrol fraction of hydrogenate and the octane level of gasoline calculated according to an additive pattern basing on hydrocarbonic composition. In addition, for comparison there are data presented concerning the group composition of petroleum gasoline fractions of oil from large-scale promising fields of the Eastern Siberia (the Yurubcha and Kuyumba oil-and-gas condensate fields, the Sobinka gas condensate field) and of the Yakutia (the Talakan oil-and-gas field). It is seen that the gasoline from hydrogenate contains on the average 2 to 6 times greater amount aromatic hydrocarbons

TABLE 5
Group composition of gasoline fractions obtained from coal and oil

Groups of compounds	Content, mass %				
	from coal	from oil			
		Talakan	Kuyumba	Yurubcha	Sobinka
Aromatic HC	20.0	7.5–12.5	3.6	5.8–3.7	3.7
Naphtenes	16.7	9.2–20.6	15.7	16.7–14.4	12.2
Isoparaffins	21.3	72.7–81.8	34.5	36.0–31.6	33.2
Normal paraffins	30.3		46.0	41.4–47.1	48.1
Unsaturated HC	2.9	–	–	–	–
Non-identified	8.8	–	–	–	–
Sulphur-containing compounds	0.14	–	0.08	0.03	–
Octane level	60	–	–	40	–

Note. The octane level for gasoline obtained from coal was determined using an investigation method, whereas for gasoline obtained from the Yurubcha oil this parameter was determined using a motor method.

and much less amount of isoparaffins as compared to oil gasoline. For the mentioned kinds of oil the relative content of naphtenes and *n*-paraffins is different to a considerable extent (ranging from 12.2 to 16.7 % and from 41.4 to 48.1 %, respectively), which is inherent in oil [25]. For gasoline obtained from hydrogenate the content of naphtenes amounts to 16.7 % and that of *n*-paraffins is equal to 30.3 %, *i. e.* these parameters are close to their content in oil gasolines.

From the data presented one could draw a conclusion that in order to obtain high-octane gasolines from the petrol fraction of hydrogenate it should be subjected to catalytic processing, in particular, *via* hydrorefining, reforming and isomerization according to known technologies of petroleum processing. At mini-factories one could obtain high-octane gasoline can be obtained with applying such catalytic processes as zeoforming and zeosyn with no hydrorefining stage [26, 27].

CONCLUSION

The composition and characteristics of a series of coal samples taken from new northern fields of the Lena coal basin during geological research are determined. A significant enrichment of coals with rare-earth elements is established. So, the concentrations of yttrium, niobium and scandium are 5 to 10 times

higher than commercially significant parameters, which open the door to industrial obtaining these elements from such coals.

The reactivity of coals was studied in the process of thermal dissolution in tetraline. Quantitative relationships between the conversion level and technical analysis data have been established.

For the most reactive representative sample of coal, processing availability with employing the method of catalytic hydrogenation to obtain low-sulphur liquid hydrocarbon fuel is vindicated.

Individual and group composition of the petrol fraction of hydrogenate have been studied; a comparison with corresponding data for virgin petrol fractions of petroleum from a number of promising oil fields of Eastern Siberia and Yakutia has been carried out. It is demonstrated that according to the composition the petrol fraction of coal hydrogenate is suitable in order to obtain high-octane components of motor gasoline via traditional methods.

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