

Investigation of Thermal Transformations of the Barzas Sapromixite under Autoclave Conditions

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(Received January 10, 2004; in revised form February 26, 2004)

Abstract

Thermal transformations of sapromixite from the Barzas deposit are investigated under the conditions of pyrolysis processes in an inert atmosphere, hydrolysis in the atmosphere of hydrogen, thermal dissolution in the residue from oil refining and catalytic hydrogenation. It is shown that sapromixite can be transformed with a high yield into liquid hydrocarbon products. The main products of this transformation is the fraction of liquid hydrocarbons with boiling point above 180 °C; its yield from sapromixite is substantially (up to 7.7 times during pyrolysis) higher than the corresponding value for brown coal. The highest degree of sapromixite conversion into liquid and gaseous products was achieved for its pyrolysis in the atmosphere of hydrogen and for hydrogenation in the presence of mechanically activated iron-ore catalyst. For hydrogenation, maximal conversion of sapromixite reaches 94–97 mass % at a temperature within 400–430 °C. For hydrolysis of sapromixite, the degree of conversion increases with an increase in the process temperature and reaches 78–80 mass % at 430–460 °C. Further temperature rise causes a sharp increase in the amount of gas formed and a decrease in the yield of liquid products. The application of iron-ore catalyst during hydrogenation allows one to increase the sapromixite conversion degree by 21–23 % and to achieve total yield of liquid products of hydrolysis up to 58 mass % with rather low gas formation.

INTRODUCTION

Scarcity of oil resources stimulates the research aimed at the development of up-to-date technologies of obtaining organic products and petrol from natural coal. Sapropelites, being the products of coalification of algae, plankton, as well as spores and pollen of plants, are of special interest for this purpose. Unlike humus coal, they are characterized by the high yield of volatile substances and increased hydrogen content, which is up to 12 mass %. Sapropelite coal is more similar to oil than the humus coal [1], so the former can be transformed into liquid products with lower hydrogen consumption and under more gentle conditions than brown coal which is usually consid-

ered as an alternative to oil raw material for the production of petrol.

At present, sapropelite coal does not find application in power engineering and is not used to obtain traditional products of humus coal processing, *i. e.*, reducing agents and sorbents, because of the absence of the developed thick seams of sapropelite coal. Estimation of the resources of this coal as a potential raw material for the production of synthetic liquid fuel (SLF) was carried out in the first half of the 20th century. At the territory of Siberia, the deposits recognized as promising were the Budagovo deposit of sapropelites (Irkutsk Region) and the Barzas deposit of sapromixite, that is, liptobolite coal (Kemerovo Region); the confirmed resources were 20–30 mln t each.

Later exploration work showed that the number of deposits with enormous resources of sapropelite coal can be much larger. For instance, as calculated by the Krasnoyarskgeologiya Company in 1979, the predicted resources of humus and sapropelite coal in the Kansk-Achinsk Coal Basin are approximately estimated to be 3.2 billion tons, including 200 mln t of the Pasheno deposit, the most promising one from the viewpoint of organization of SLF production [2].

It is known that sapropelite coal of different types can be transformed into liquid products using the conventional processes of petrol production from humus coal. The highest yield of these products was achieved for boghead, highly metamorphized representative of sapropelite characterized by the highest hydrogen content (up to 12 mass %) and the yield of semi-coking tar (>70 mass %) among the types of fossil coal [2–5]. For instance, according to the data reported in [5], during hydrogenation of the Matagan boghead in the presence of MoS_2 catalyst in mixture with the paste-forming agent (1 : 1), which was recirculating fraction of high-boiling liquid products, the oil yield of 84.8 mass % was achieved, as calculated for total organic coal mass (OCM) and the mass of paste-forming agent.

In the process of thermal dissolution of the Barzas sapromixite in recirculating paste-forming agent in the flow set-up, the degree of coal conversion into gaseous and liquid products achieved 79 mass % [6]. However, the major part of liquid products was represented by high-boiling fractions which were assumed to be used as a substitute of oil asphalt. Investigation of thermal dissolution of this coal in tetralin under non-isothermal conditions showed that within the dissolution temperature range 350–425 °C high-molecular components (asphaltenes) are prevailing in the products (60–70 mass %); the degree of coal conversion is 59–71 mass % [4]. Comparing the above-reported data with the data on thermal dissolution of sapropelite coal from a number of other deposits [7] we see decreased reactivity of sapromixite.

Investigation of hydrogenation of the Budagovo sapropelite [8] under the autoclave conditions with the working hydrogen pressure

of 8.0 MPa showed that the degree of conversion achieves the maximal value (97 mass %) at 410 °C. Liquid products mainly boiling at a temperature above 300 °C are formed. The use of a mixture of ferric sulphate and ammonium *para*-molybdate as a catalyst (mass concentrations of iron and molybdenum per OCM being 1 and 0.2 %, respectively) does not cause any substantial changes in the process characteristics. The oil yield of 95.6 % per OCM in the absence of a catalyst and a solvent was achieved by means of hydrogenation of the Arctic boghead (Olenek Bay) at a higher hydrogen pressure (63.5 MPa) [9].

In thermal processing of humus coal, substantially interesting aspect is the use of cheap catalysts based on iron-containing ores or the products of their processing. We showed previously [12] that the products of enrichment of iron ores subjected to mechanochemical activation can be used as efficient catalysts of hydrogenation of the brown Kansk-Achinsk coal. Optimal activation conditions and parameters of hydrogenation were determined to achieve high conversion of coal into liquid and gaseous products (over 90 mass %).

The aim of this work is to study thermal transformations of Barzas sapromixite during pyrolysis in an inert atmosphere, hydropyrolysis in a hydrogen atmosphere, thermal dissolution, and catalytic hydrogenation in residues from oil distillation.

EXPERIMENTAL

Two sapromixite samples were collected from different sites and different bore pits around the Barzas village and were used in this work together with B-2 brown coal from the Borodinsk deposit of the Kansk-Achinsk basin. Table 1 lists some characteristics of the samples.

Thermal transformations of coals were conducted in 0.25 l rotating autoclaves. An autoclave was charged with coal (10 g; particles less than 0.1 mm) dried at 100 °C until the humidity level was <1 mass %. In some experiments, solvent (10 g) and catalyst (5 g) additions were used. For the solvent we chose the residue obtained from distillation of West Siberian oil (boiling point 350 °C; composition, mass %:

TABLE 1

Characteristics of coal samples under investigation

Sample type	Ash content, mass %	Elemental composition, % per mass of the dry ash-free coal				
		C	H	N	S	O
Sapromixite of the Barzas deposit, sample 1	30.8	70.0	6.6	0.6	0.5	22.3
The same, sample 2	27.3	77.9	7.5	0.7	0.6	13.3
Brown coal from the Borodinskoye deposit	8.3	67.6	5.1	0.7	0.2	26.4

Notes. 1. Ash content was determined according to the State Standard (GOST) 11022-75 [13]. 2. The concentration of oxygen was determined as a difference $100\% - \text{concentration of C, H, N, S}$.

C 85.4, H 12.5, N 0.2, S 0.9, O 1.0). For the catalyst we employed ore-dressing concentrate preliminarily treated in an AGO-2 mill using the procedure of [10]. Specific surface of the sample, m^2/g : 1.8 for the starting sample, 82.0 for the mechanically activated sample. The element composition and mass fractions of elements in the sample are given below, %:

Fe	43.0
S	1.4
Cu	0.03
Ni	0.009
Co	0.017
Zn	0.025
Pb	0.011

Prior to the start of experiment, the autoclave was cleaned by blowing with argon to remove air. During pyrolysis and thermal dissolution of coals, initial argon pressure was 0.3 MPa; hydropyrolyses and hydrogenations were conducted at a hydrogen pressure of 3.0 MPa. The working pressure in the autoclave was 1.0 and 7.0 MPa, respectively (reaction temperature 400 °C). The heated autoclave was kept at the reaction temperature for 1 h. After the experiment, the volume of gaseous products was determined. The composition of the gases was determined on a chromatograph with a heat conductivity detector and columns filled with zeolite (to analyze CH_4 and CO) and with porapak PQ (to analyze CO_2 and hydrocarbons). Liquid products boiling below 180 °C were collected by freezing with liquid nitrogen in a trap under vacuum, then the contents of the autoclave was extracted with benzene. After evaporating

the solvent, the extract was dried to a constant mass under vacuum at room temperature. The yield of the extract was determined by means of gravimetric method. The extract contained mainly the fractions of liquid products with boiling points above 200 °C. The degree of OCM transformation was calculated using the amount of the benzene-insoluble solid residue taking into account changes in the mass of its mineral part as a result of burning and calcination of the solid residue when determining the ash content.

RESULTS AND DISCUSSION

Pyrolysis and hydropyrolysis of coal

Investigations showed that for the pyrolysis in an inert atmosphere the degree of transformation of sample 2 of the Barzas sapromixite into liquid and gaseous products reaches a maximal value (63–64 mass %) at a temperature within 430–460 °C (Fig. 1), sample 1 – at 430 °C. The obtained values are almost twice as large as the corresponding parameter for the brown coal. Further increase in the pyrolysis temperature causes a substantial decrease in the degree of sapromixite conversion, which is likely to be due to an increase in the contribution from condensation reactions.

For hydropyrolysis of sapromixite in the atmosphere of hydrogen, the degree of conversion of its organic mass into liquid and gaseous products increases linearly with an increase in temperature from 400 to 500 °C reaching

76 mass % at 500 °C. Under these conditions, the addition of mechanochemically activated iron-ore catalyst causes an increase in the degree of coal conversion by about 10 mass %.

The data on the yield of products formed in pyrolysis of sapromixite and brown coal in the inert atmosphere are shown in Table 2. The main products of sapromixite transformation are the substances extracted with benzene (the fraction with boiling point above 180 °C); their yield only slightly depends on the process temperature and varies within the range 42–45 mass %. Under comparable conditions, the yield of this fraction from brown coal is 7.7 times lower, while the yield of gaseous products is 2.4 times higher. The differences between sapromixite and brown coal in the yields of aqueous and easily boiling hydrocarbon fractions are less substantial.

The indicated differences are due to the features of chemical composition of the coal samples under investigation. Increased oxygen content of the organic mass of brown coal (see Table 1), the major part of which is present as carbonyl and carboxyl functional groups [15], determines high yield of the gaseous products of pyrolysis, which are composed of carbon oxides by more than 90 mass % (Table 3). Unlike brown coal containing aromatic fragments, the organic mass of sapropelite coal is composed of aliphatic hydrocarbons with the chain length up to 33 carbon atoms which are connected with each other by heteroatomic bonds in macromolecules. The presence of ether bonds [7, 9, 14] characterized by low thermal stability determines increased (in comparison with

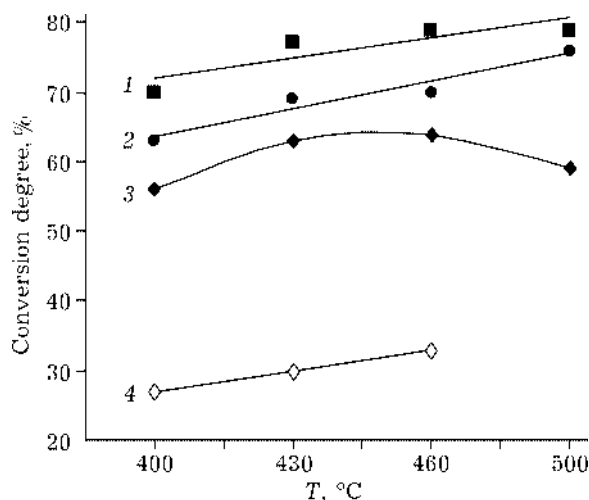


Fig. 1. Effect of the process temperature on the degree of conversion of the Barzas sapromixite (sample 2, see Table 1) during its hydrolysis with the catalyst (1) and without a catalyst (2), during pyrolysis in argon (3), and brown coal from the Kansk-Achinsk Basin during pyrolysis in argon (4).

brown coal) conversion degree and the yield of liquid products during pyrolysis.

For hydrolysis within the temperature range 400–460 °C, the degree of sapromixite transformation increases in comparison with the corresponding characteristics for pyrolysis in the inert atmosphere by 5–10 mass % and reaches 70 mass %. The major product of transformation is the fraction boiling above 180 °C. However, unlike for pyrolysis in the inert atmosphere, its yield decreases substantially with the rise of the process temperature from 400 to 500 °C. At the same time, the yield of gases increases sharply up to 31 mass % at 500 °C (see Fig. 2). With an increase in the temperature of hydrolysis, the concentration of C₂–C₄ hydrocarbon gases in the gaseous products increases intensively; this is likely to be due to cracking of the organic mass of sapromixite and a part of the formed liquid products (Table 4).

TABLE 2

Yield of products of coal pyrolysis in the atmosphere of argon

Temperature, °C	Yield of fractions, mass %			
	Aqueous	<180 °C	>180 °C	Gas
<i>Sapromixite, sample 2</i>				
400	7.0	2.0	42.8	4.2
430	6.0	3.5	45.9	6.6
460	6.0	4.5	43.0	10.5
<i>Sapromixite, sample 1</i>				
430	6.5	3.8	46.6	7.1
<i>Brown coal</i>				
430	4.0	2.0	5.8	18.2

TABLE 3

Composition of gaseous products of pyrolysis of coal in the atmosphere of argon at 430 °C

Coal type	Composition, mass %					
	CO	CO ₂	CH ₄	C ₂	C ₃	C ₄
Brown coal	20.5	71.5	1.8	3.9	2.0	0.3
Sapromixite, sample 2	2.1	54.1	9.5	11.4	17.5	5.4

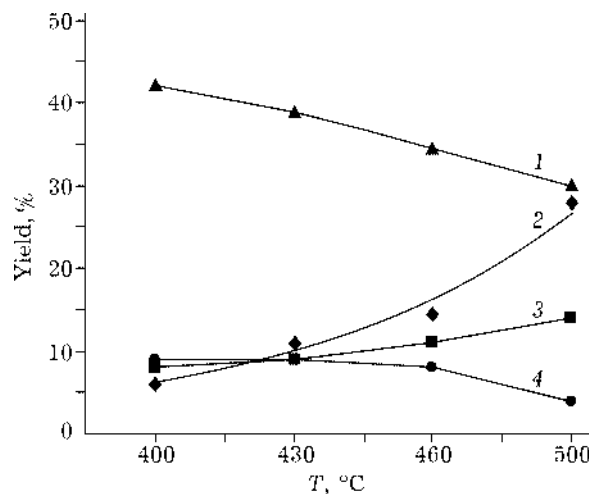


Fig. 2. Yield of products formed in hydropyrolysis of the Barzas sapromixite (sample 2, see Table 1): 1 - fraction with boiling point above 180 °C, 2 - gaseous products, 3 - fraction boiling below 180 °C, 4 - aqueous fraction.

The addition of the iron-ore catalyst during hydropyrolysis causes an increase in the yield of high-boiling fraction; the maximal yield is 51 mass % at a temperature of 430 °C (Fig. 3). Under these conditions, total yield of the liquid hydrocarbon products is 58 mass %. It should be stressed that the catalyst has only slight effect on the yield of gases and aqueous fraction.

Hydrogenation and thermal dissolution of coal in the residue of oil distillation

The most frequent solvents in the process of thermal dissolution and hydrogenation, which are under development for obtaining liquid products from humus coal, are high-boiling fractions of the liquid products of the process, that is, recycling of the solvent is carried out [15]. It is known that alkanes are pre-

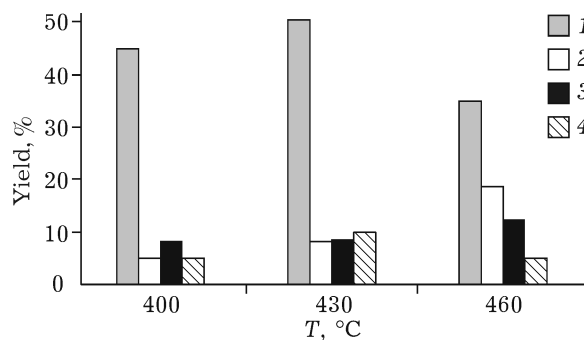


Fig. 3. Yield of the products of hydropyrolysis of the Barzas sapromixite (sample 2, see Table 1) in the presence of the iron-containing catalyst activated mechanochemically (mass concentration 5 %): 1 - the fraction with boiling point above 180 °C, 2 - gaseous products, 3 - fraction boiling below 180 °C, 4 - aqueous fraction.

dominant in the neutral part of liquid products of thermal transformation of sapropelites [4, 8]. Because of this, the solvent modeling the recycling fraction was chosen to be the residue of distillation of the West Siberian oil with boiling point above 350 °C which was added to the coal at a ratio of 1 : 1.

Investigation of the effect of temperature on the characteristics of thermal dissolution of sapromixite showed that the maximal conversion of the OCM 59–60 mass % is observed within temperature range 400–430 °C (Fig. 4). These values almost coincide with the data obtained for sapromixite pyrolysis in inert atmosphere (see Fig. 1). At the same time, it is necessary to note increased yield (in comparison with the pyrolysis in an inert atmosphere) of low-boiling products; at a temperature of 460 °C, it is 11 % of the mass of a mixture of sapromixite and the oil residue. For thermal dissolution of the brown coal from Kansk-Achinsk basin, under comparable conditions the degree of its conversion was 1.5 times lower and the yield of low-boiling fraction was more than 2 times lower than that in the case of sapromixite.

Changes in the conversion degree of sapromixite under variation of temperature of its hydrogenation are shown in Fig. 5. For comparison, the same Figure shows the corresponding results obtained for the case without catalyst. Similarly to thermal dissolution, the max-

TABLE 4

Effect of temperature of sapromixite pyrolysis (sample 2) on the composition of gaseous products

Process temperature, °C	Composition of the gaseous products, mass %					
	CO	CO ₂	CH ₄	C ₂	C ₃	C ₄
400	2.0	59.7	12.6	14.3	9.7	1.7
430	4.4	56.5	11.4	14.7	10.4	2.6
460	6.94	5.2	15.7	18.8	10.5	2.9
500	5.6	29.9	14.8	23.8	22.3	3.6

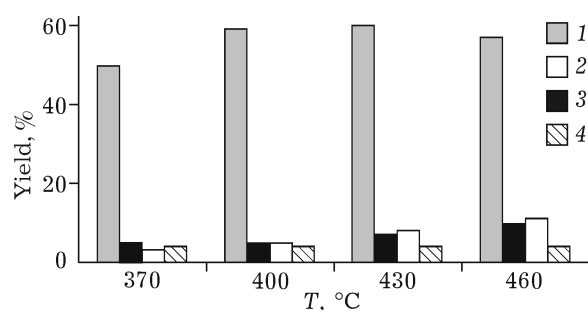


Fig. 4. Effect of temperature of thermal dissolution of sapromixite (sample 1, see Table 1) on the degree of conversion (1), the yield of gaseous products (2), hydrocarbon fraction boiling below 180 °C (3), aqueous fraction (4).

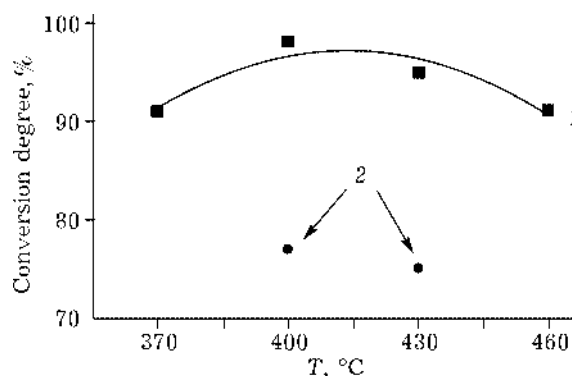


Fig. 5. Effect of temperature of sapromixite hydrogenation (sample 1, see Table 1) on the degree of its conversion in the presence of iron-containing catalyst activated mechanochemically (1), without the catalyst (2). The solvent : coal ratio is 1 : 1, initial hydrogen pressure is 3.0 MPa.

imal conversion of the OCM reaching 94–97 mass % is observed for hydropyrolysis within temperature range 400–430 °C. Under these conditions, the iron-ore catalyst (mass concentration 5 %) causes an increase in sapromixite conversion rate by 21–23 mass %.

The use of hydrogenation allows obtaining the highest yield of liquid products among the processes investigated in the present work (Table 5). The yield of the low-boiling hydrocarbon fraction reaches 21.3 % of the mass of mixture (sapromixite + oil residue) or 42.6 % as calculated for the mass of the charged coal at hydrogenation temperature of 460 °C. The yield of gaseous products does not exceed 10 mass %; within the temperature range providing maximal conversion (400–430 °C) it is 6.1–7.2 mass %.

Comparison of these results with the data obtained previously [10, 16] for catalytic hydrogenation of the brown Kansk-Achinsk coal shows that the yield of low-boiling liquid products from sapromixite is 1.5–1.8 times higher than that from the brown coal. It is important that hydrogenation of brown coal was carried out at higher working pressure of hydrogen (11.0–11.5 MPa) than that for the case of sapropelite coal.

The promoting action of iron-containing catalyst during hydrogenation of sapromixite is likely to be connected with the acceleration of hydrogenation of unsaturated hydrocarbons or radical fragments of thermal destruction of OCM, which prevents their polymerization with

the formation of high-molecular compounds and coke, and promotes an increase in coal conversion degree (see Fig. 5) and the yield of liquid products (see Table 5). It is necessary to note that the ore catalyst exhibits noticeable activity in OCM cracking reactions, which is evidenced by an increase, under the action of the catalyst, in the yield of low-boiling hydrocarbon fractions, gases (see Table 5) and the concentrations of methane, ethane and ethylene in the gaseous products (Table 6).

CONCLUSIONS

It is shown that sapromixite of the Barzas deposit can be transformed into liquid hydrocarbon products with a high yield using the following thermal processes: pyrolysis in an inert atmosphere, pyrolysis in the atmosphere of

TABLE 5
Effect of temperature of sapromixite hydrogenation (sample 1) on the yield of the products

Temperature, °C	Yield of fractions, mass %			
	Aqueous	<180 °C	>180 °C	Gas
<i>With the catalyst</i>				
370	4.3	75.4	10.5	5.3
400	5.0	73.8	14.1	6.1
430	5.6	64.7	20.2	7.2
460	5.5	58.9	21.3	9.8
<i>Without the catalyst</i>				
400	5.2	56.2	11.4	4.2

TABLE 6

Effect of temperature of sapromixite hydrogenation (sample 1) on the composition of gaseous products

Temperature, °C	Composition of gaseous products, mass %					
	CO	CO ₂	CH ₄	C ₂	C ₃	C ₄
<i>With the catalyst</i>						
370	3.0	65.8	11.5	12.0	72	0.5
400	4.3	50.4	19.4	17.7	7.5	0.7
430	5.4	35.6	27.4	20.1	9.6	1.9
<i>Without the catalyst</i>						
400	4.5	63.8	10.6	12.4	8.2	0.5

hydrogen, hydrogenation, and thermal dissolution in the oil distillation residue. The main product of transformation is the liquid hydrocarbon fraction with boiling point >180 °C; its yield from the Barzas sapromixite is substantially (up to 7 times for pyrolysis) higher than the corresponding parameter for brown coal.

The highest degree of sapromixite conversion into liquid and gaseous products was achieved during its hydropyrolysis, pyrolysis and hydrogenation in the presence of mechanochemically activated iron-ore catalyst.

During hydrogenation of sapromixite coal, the degree of its conversion reaches 94–97 mass % at a temperature within 400–430 °C. During hydropyrolysis of sapromixite, the degree of its conversion increases with an increase in the process temperature and reaches 78–80 mass % at 430–460 °C. Further temperature rise causes a sharp increase in the amount of gas formed and to a decrease in the yield of liquid products.

The iron ore concentrate activated mechanochemically exhibits high catalytic activity in

hydrogenation and hydropyrolysis of sapromixite. The use of this catalyst for hydrogenation increases the degree of sapromixite conversion by 21–23 mass %, gas formation being not high.

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