

Hydropyrolysis and Hydrogenation Liquid Products of Sapromixite from Barzas Deposit

V. I. SHARYPOV¹, B. N. KUZNETSOV¹, N. G. BEREGOVTSOVA¹, N. YU. VASILIEVA², V. A. SOKOLENKO¹, N. I. PAVLENKO¹, A. N. STARTSEV³ and V. N. PARMON³

¹*Institute of Chemistry and Chemical Technology, Siberian Branch of the Russian Academy of Sciences, Ul. K. Marksa 42, Krasnoyarsk 660049 (Russia)*

E-mail: sharypov@icct.ru

²*Krasnoyarsk State University, Pr. Svobodny 79, Krasnoyarsk 660049 (Russia)*

³*Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 5, Novosibirsk 630090 (Russia)*

(Received January 21, 2005; in revised form August 1, 2005)

Abstract

Liquid products of the autoclave hydrogenation and hydropyrolysis of the Barzas sapromixite were studied. Chromatomass spectrometry was used to determine the content of individual substances in the low boiling fractions. Hydropyrolysis product appears to consist of normal paraffins by more than 50 mass %. Hydrogenation products is characterized by a higher content of cyclic and structure isomerized paraffins. Aromatics content in both products does not exceed 14.1 mass %. IR and NMR spectroscopy show that fractions boiling above 180 °C contain mostly aliphatic fragments. Hydropyrolysis products composition is similar to that of oil, while hydrogenation product is characterized by more aromatic and shorter aliphatic fragments per statistically average molecule. If mechanically activated iron ore catalyst is used at the sapromixite hydrogenation and hydropyrolysis, the contribution of distillate fractions increases, and low boiling (boiling start 180 °C) fractions contain more low molecular mass hydrocarbons.

INTRODUCTION

By composition and structure, sapropelic coals are considered as a promising alternative raw for the production of liquid hydrocarbons. It is well known, that using quite simple thermal methods, one may obtain liquid and gas phase products from sapropelic coals of various carbon index (see *e.g.* [1–4]). Products composition and properties essentially depend on the coal type, processing conditions, *etc.*

Earlier the heavy fraction (boiling above 220 °C) of Budagovo sapropelite was thermally dissolved in tetralin, which is a well known solvent and hydrogen donor [5]. The obtained fraction (dissolving temperature being 370–390 °C) was found to have the following composition, mass %: paraffins and naphthenes – 10–13,

asphaltenes – 19–50, monoaromatic compounds – up to 30, polyaromatic compounds – up to 16.

Kuznetsk sapromixite dissolving in regenerated solvent (boiling point 200–300 °C) yielded product boiling above 350 °C, its composition being as follows, mass %: paraffins and naphthenes – 33, asphaltenes – 25, low aromatics resins – 19 [6].

At the Budagovo sapropelite autoclave pyrolysis at elevated hydrogen pressure high boiling fraction ($T_{\text{boil}} > 300$ °C) consists mainly of aliphatic compounds of normal structure. However, no data are given related to the distillate composition [7].

Earlier we studied thermal transformations of sapromixite from the Barzas deposit at its pyrolysis in inert atmosphere, hydropyrolysis in hydrogen, and at its thermal dissolving in

oil distillation residue, used as hydrogenation solvent [8]. We have found that using all above mentioned processes one can convert sapromixite into liquid hydrocarbons with a high enough yield. The best sapromixite conversion into liquid products was attained at its pyrolysis in hydrogen (78–97 mass %) at 400–430 °C in the presence of mechanically activated iron ore catalyst.

In the present work we study the composition of liquid products obtained *via* the Barzas sapromixite autoclave pyrolysis and hydrogenation.

EXPERIMENTAL

Liquid products were obtained by the autoclave hydrolysis and hydrogenation. Unoxidized sapromixite, taken from a shaft near Barzas (Kemerovo Region, Russia), served as a raw material. Sol content in the sample was 27.3 mass % [9]. Elemental composition was as follows, mass %: C 77.9, H 7.5, N 0.7, S 0.6, O 13.3 (balance).

Sapromixite hydrogenation and hydrolysis were performed in autoclaves under hydrogen working pressure 7.0 MPa at 430 °C.

West Siberia oil distillation residue (boiling start 350 °C) was used as a solvent at hydrogenation (mass ratio coal : solvent = 1 : 1). Distillation residue composition was as follows, mass %: C 85.4, H 12.5, N 0.2, S 0.9, O 1.0 (balance).

Iron ore concentrate (preliminarily activated in activator mill AGO-2) was used as a catalyst. Activation method and catalyst composition are presented in [10].

Liquid products boiling below 180 °C (fraction I) was distilled out of autoclave under vacuum. Compounds were condensed in a trap cooled by liquid nitrogen. Then remaining autoclave content was extracted by benzene. After benzene removal extract was fractionated under vacuum into products boiling at 180–350 °C (fraction II) and distillation residue boiling above 350 °C (fraction III).

Individual hydrocarbons in fraction I were identified with the liquid chromatomass spectrometry at full ion current registering using a Varian Saturn 2100D GC/MS. Products were separated in methylphenylsilicone capillary column SE-52 (60 m long). Temperature was

programmed in a range of 50–300 °C, temperature raising rate being 5 °C/min. Hydrocarbons were automatically identified *via* their spectra comparison with the reference data from database NIST98.

Liquid products in fraction II and III were studied with a Vektor 22 Fourier transform IR spectrometer and Bruker Avance 200 NMR spectrometer. Samples for NMR spectra were dissolved in CDCl₃.

RESULTS AND DISCUSSION

We have found that liquid products from hydrogenation and hydrolysis essentially differ by their fraction composition. Hydrolysis products obtained without catalyst contain mainly fraction III, while distillate fractions I and II in sum are less than 40 % (Fig. 1). On the contrary, at hydrogenation distillate fractions exceed 60 mass % in total.

Catalyst addition in amount of 5% *versus* sapromixite mass has the following effect. At hydrolysis distillate fractions increase by

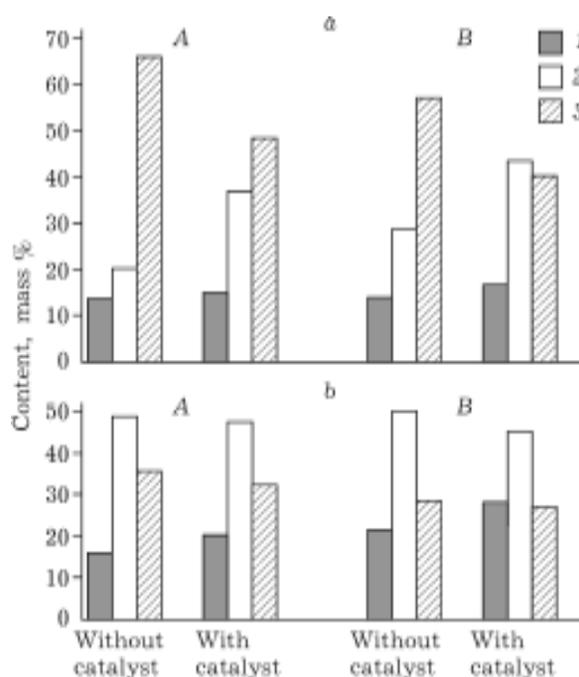


Fig. 1. Composition of liquid organic products yielding from sapromixite hydrolysis (a) and hydrogenation (b): 1 – fraction I (boiling below 180 °C), 2 – fraction II (boiling out at 180–350 °C), 3 – fraction III (boiling out above 350 °C). A, B – thermal treatment at 400 °C and 430 °C, respectively.

TABLE 1

Composition of fraction I (boiling below 180 °C) yielding from the thermal catalytic processing of sapromixite

Compounds	Content, mass %, in the low boiling product of	
	hydrogenation	hydropyrolysis
Butane	2.31	0.16
Butane, 2-methyl	2.88	0.43
Pentane	7.53	4.12
2-Pentene	0.13	0.00
Pentane, 2-methyl	5.57	1.98
Pentane, 3-methyl	1.57	0.52
Hexane	8.32	8.54
3-Hexene	0.11	0.31
Cyclopentane, methyl	3.54	2.78
Benzene	2.49	2.48
Hexane, 2-methyl	1.75	0.00
Hexane, 3-methyl	2.06	0.28
Cyclopentane, dimethyl	3.32	1.21
Heptane	8.34	10.20
3-Heptene	0.11	0.25
Cyclohexane, methyl	3.40	2.43
Cyclopentane, ethyl	1.56	1.42
Cyclopentane, trimethyl	1.17	0.78
Toluene	2.40	3.59
Heptane, 2-methyl	3.68	1.13
Heptane, 3-methyl	0.84	0.38
Cyclohexane, 1,2-dimethyl	2.03	1.62
Octane	6.59	11.99
Cyclohexane, dimethyl	0.66	0.35
Heptane, 2,6-dimethyl	1.14	0.25
Cyclohexane, ethyl	1.14	0.65
Cyclopentane, propyl	1.17	0.72
Benzene, ethyl	1.80	1.40
Benzene, dimethyl	2.02	1.03
Octane, 3-methyl	1.05	1.96
Nonane	3.76	9.27
Benzene, trimethyl	1.50	3.03
Phenol	0.10	0.32
Decane	1.72	5.98
Indan	0.13	0.40
Benzene, methylpropyl	0.06	0.20
Benzene, tetramethyl	0.18	0.20
Phenol, methyl	0.06	0.30
Indan, methyl	0.22	0.44
Undecane	0.75	2.74
Naphthalene	0.11	0.40
Dodecane	0.39	1.09

17–19 mass %. At hydrogenation low boiling fraction in liquid product attains 27 % at the temperature of sapromixite conversion (430 °C). We have already shown that higher hydrogenation temperature is not reasonable, since liquid products start decomposing producing gas, and liquid product yield decreases [8].

Using chromatographic mass spectrometry we identified 42 individual compounds in the low boiling liquid fraction, mass content of each component being higher than 0.1% (Table 1). As a rule, identification probability exceeded 90 %. Table 1 lists the contents of individual hydrocarbons in the low boiling products obtained via both hydrogenation and hydrolysis at 430 °C. Apparently, products are characterized by the low content of olefins and of molecules containing heteroatoms. Normal structure paraffins are the main products of hydrolysis, while structure isomerized and cyclic paraffins dominate after hydrogenation. Most likely, cyclic compounds yield from the thermal conversion of oil residue used as solvent.

Aromatic hydrocarbons are presented mainly by the alkyl-substituted benzenes. Their content in the low boiling product of hydrogenation ranges within 10.5–11.9 mass %, and within 12.3–14.1 mass % – at hydrolysis. Let us note that hydrolysis yielding fraction contains phenol, indan, methyl indan and naphthalene in noticeable amounts. Among the similar product of hydrogenation their content is 23 times lower. This means that above mentioned compounds are the products of sapromixite conversion, and as fragments they enter a statistically average coal macromolecule.

Figure 2 shows the distribution of individual compounds in the low boiling fraction with respect to the number of carbon atoms in their molecules. Apparently, this distribution goes through a maximum, characterizing compounds with 7–8 carbon atoms. Catalyst operation in the processes of sapromixite thermal conversion shifts this maximum towards smaller molecular masses as referred to fraction I. This is most likely caused by the partial hydrogenolysis of hydrocarbons.

Fractions II and III resulting from the sapromixite conversion are characterized by elemental composition independent of the process condition (temperature, catalyst,

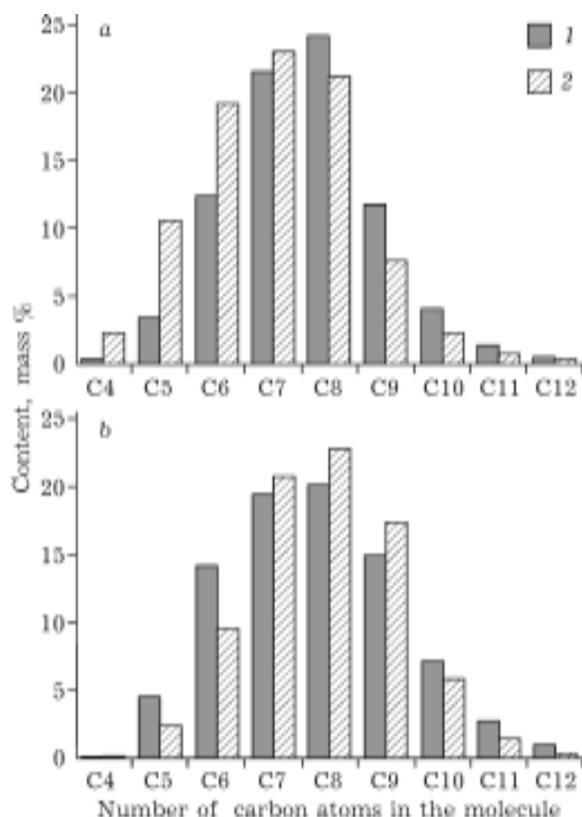


Fig. 2. Hydrocarbons distribution in fraction I at coal hydrogenation (a) and hydroxyprolysis (b) versus the number of carbon atom in the molecule (process temperature 430 °C): 1 – hydrocarbons obtained without catalyst, 2 – with the catalyst.

heating duration, etc.), but is determined by the process type (hydrogenation or hydroxyprolysis). Table 2 shows that products are characterized by a low content of heteroatoms. Oxygen maximum mass content in fractions II and III is 1.8 %, which is 7-fold lower than in the starting sapromixite. Hydrogen content in the hydroxyprolysis product is noticeably higher than that in the hydrogenation product, and attains 13.1 mass % for fraction II, which is 1.7-fold higher in comparison to that in the raw sapromixite. Atomic ratio H/C, *i.e.* the number of hydrogen atoms per one carbon atom in statistically averaged molecule, is 1.9 for this fraction. Therefore, fraction II contains many aliphatic hydrocarbons.

Figure 3 shows the FTIR spectra of above-mentioned fractions. These spectra are characterized by a high intensity of the valence vibrations related to bonds C–H (2800–3000 cm^{-1}) and of deformation vibrations related to aliphatic groups $-\text{CH}_2$, $-\text{CH}_3$ (1460 and 1379

TABLE 2

Elemental composition of products yielding from the catalyst assisted sapromixite thermal conversion at 430 °C

Conversion method	Content, mass %					H/C
	C	H	N	S	O*	
<i>Fraction II</i>						
Hydrogenation	86.0	11.3	0.5	1.0	1.2	1.6
Hydroxyprolysis	84.3	13.1	0.4	0.4	1.8	1.9
<i>Fraction III</i>						
Hydrogenation	86.8	10.2	0.6	1.0	1.4	1.4
Hydroxyprolysis	85.9	12.5	0.4	0.6	0.6	1.7

Note. Here and in Table 3: fraction II – products boiling out at 180–350 °C, fraction III – products boiling out at temperatures higher than 350 °C.

*Oxygen content is determined by difference: total mass (100 %) minus summed mass portions of C, H, N, S.

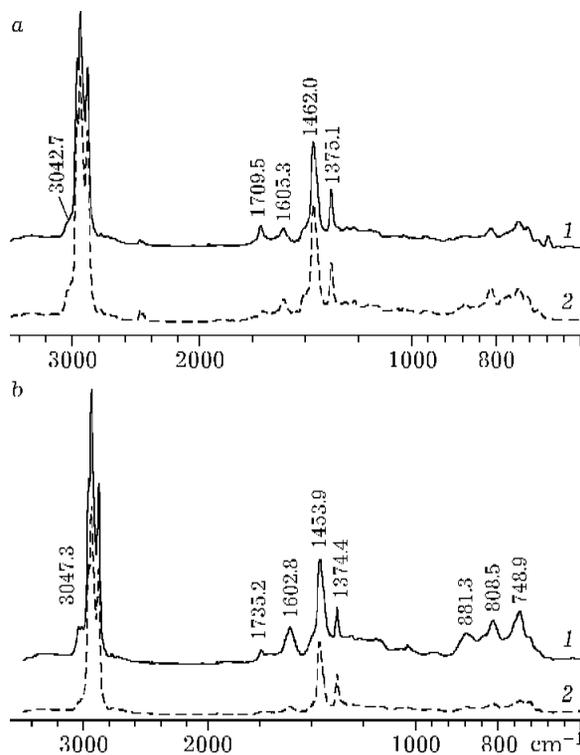


Fig. 3. FTIR spectra of fraction II (a) and III (b) obtained at the Barzas sapromixite hydrogenation (1) and hydroxyprolysis (2).

cm^{-1}). Let us note, that intensities of bands at 3050 cm^{-1} (C–H bonds oscillation in the aromatic ring) and at 1600 cm^{-1} (C–C bonds in the aromatic ring) are essentially higher as referred to hydrogenation product in comparison with the hydroxyprolysis one. Moreover, spectra of fraction III from hydrogenation show absorption bands at 748,

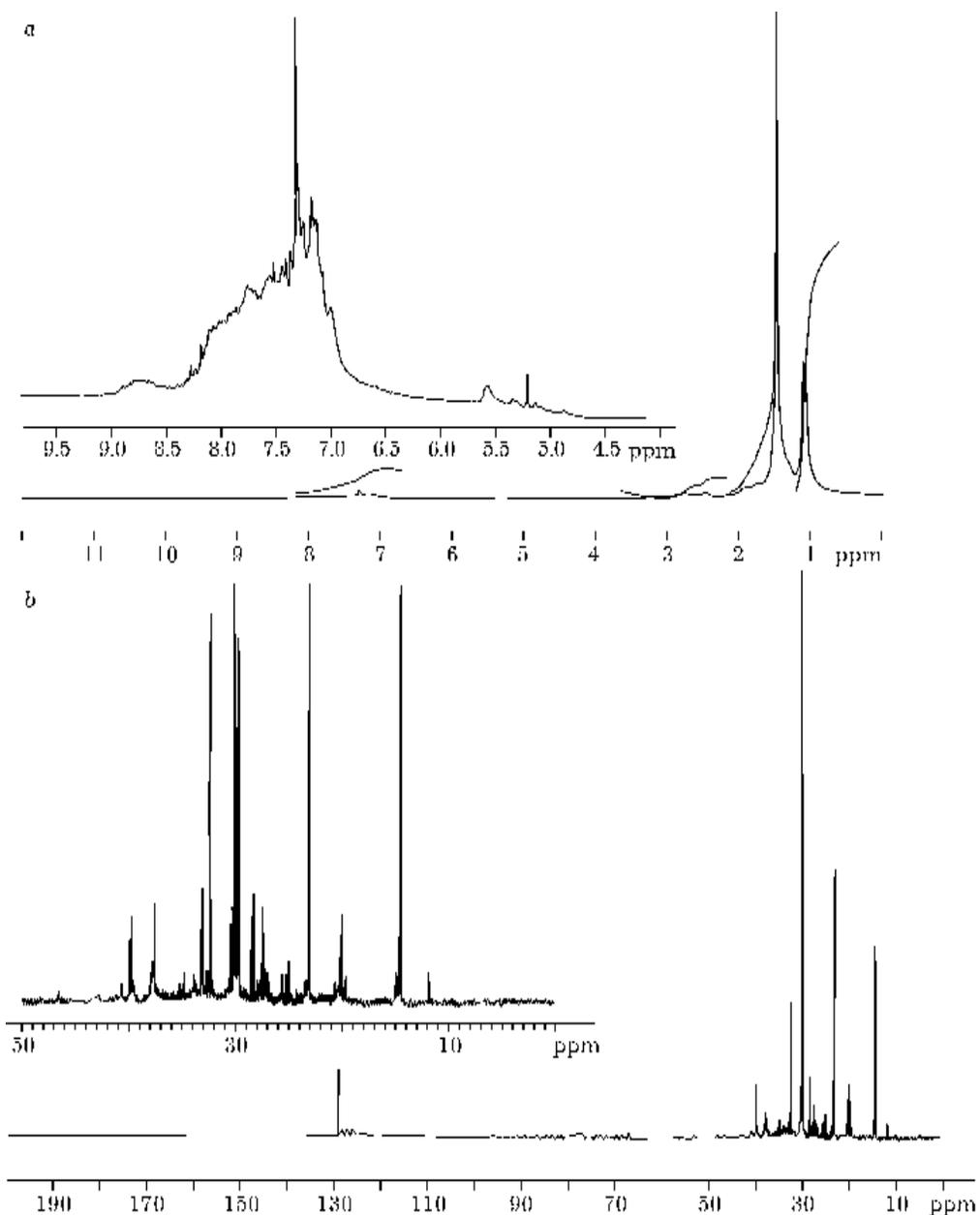


Fig. 4. ^1H NMR spectra (a) and ^{13}C NMR spectra (b) of fraction II yielding from sapromixite hydropyrolysis.

809, and 881 cm^{-1} , typical for the out of plane deformation vibrations of C–H bonds in the aromatic rings characterized by various substitution degree. FTIR data analysis related to the oil distillation residue shows essentially lower intensity of the same bands.

According to the NMR spectroscopy data fractions II and III from both hydropyrolysis and hydrogenation contain mainly aliphatic protons in positions β and γ (Fig. 4, a and Table 3). PMR spectra show a low intensity of signal in a range of 6.0–4.5 ppm, characterizing protons

at double C=C bonds. Therefore, most likely a weak ^{13}C NMR signal within 140–114 ppm refers to the aromatic ring (see Fig. 4, b). ^{13}C NMR spectra at 50–10 ppm show hydropyrolysis product to contain mostly aliphatic hydrocarbons with 14–16 carbon atoms.

Structure parameters, related to various type protons and carbon atoms calculated from ^1H NMR and ^{13}C NMR, are listed in Table 3. For comparison we give the same data for the oil distillation residue used as solvent at hydrogenation. These data confirm that

TABLE 3

Structure parameters of hydrogenation and hydropyrolysis products as calculated from the ^1H NMR and ^{13}C NMR spectra

Products	Protons content					n^*
	H_{arom}	H_{α}	$\text{H}_{\beta\gamma}$	C_{arom}	C_{aliph}	
Oil residue	0.05	0.11	0.84	0.15	0.85	8.6
<i>Sapromixite hydrogenation</i>						
Fraction II	0.07	0.12	0.81	0.24	0.76	7.8
Fraction III	0.21	0.18	0.61	0.42	0.58	4.4
<i>Sapromixite hydropyrolysis</i>						
Fraction II	0.06	0.08	0.86	0.16	0.84	11.8
Fraction III	0.04	0.9	0.9	0.17	0.83	16.0

Note. For designation see Table 2.

* n is length of aliphatic fragment of statistically-average molecule equal to $(\text{H}_{\alpha} + \text{H}_{\beta\gamma})/\text{H}_{\beta}$.

sapromixite hydrogenation and hydropyrolysis products differ by their composition. Hydropyrolysis product is indeed characterized by the low mass content of aromatic carbon comparable with the same parameter for the oil residue (boiling above 350 °C). However, statistically average length of aliphatic fragments in the hydropyrolysis product attains 16 carbon atoms, which is twice longer than that in the oil residue. On the contrary, hydrogenation product contains more aromatic compounds, especially fraction III. Meanwhile average aliphatic fragment in this product is twice shorter than that in the oil residue.

Therefore, liquid products at sapromixite hydropyrolysis and hydrogenation form due to the thermal destruction of oxygen containing groups, elimination of mostly normal structure aliphatic fragments, and intermediates hydrogenation. The proof is the high content of normal paraffins, low content of olefins, essentially lower oxygen content (in comparison to initial sapromixite), and higher hydrogen content. IR and NMR detected differences, characterizing hydropyrolysis and hydrogenation products, are most likely caused by the following reasons:

1. Sapromixite hydrogenation fractions contain the transformed products of oil distillation used as solvent.

2. Additional fraction III (in comparison to hydropyrolysis product), obtained at hydroge-

nation and then extracted by oil residue, contains quite a lot of aromatic fragments.

It has been shown [8] that under comparable conditions (temperature, hydrogen pressure, thermal treatment duration) sapromixite conversion at hydrogenation is by 12–14 mass % higher than at hydropyrolysis.

Let us note that sapromixite hydropyrolysis and hydrogenation give products differing by their composition from those obtained from humic coals [11]. Products yielding from humic coals contain mainly aromatic (including polycyclic) hydrocarbons.

The aliphatic character of products obtained from sapromixite is not peculiar to the products of humic coals processing, but resembles the oil-originated product. Moreover, the low content of heteroatoms in the sapromixite conversion products allows their further successful transformation to motor fuels and other products using conventional oil processing technologies. It is of importance that far less energy is spent on sapromixite hydropyrolysis and hydrogenation than at the same coal processing but through gasification.

CONCLUSIONS

1. We have determined the composition of fractionated (boiling below 180 °C) products obtained *via* the hydropyrolysis and hydrogenation of Barzas sapromixite. Individual components in these products have been identified, and their content has been determined. Above mentioned fractions, obtained by hydropyrolysis, consist of normal paraffins by more than 50 mass %, while hydrogenation product is characterized by the higher content of cyclic and structure isomerized hydrocarbons. The content of aromatic hydrocarbons in these fractions does not exceed 14.1 mass %.

2. IR and NMR spectroscopy were used to investigate the composition of hydropyrolysis and hydrogenation fractions, boiling at at 180–350 °C, and of distillation residue boiling above 350 °C. All fractions contain mostly aliphatic hydrocarbons. By composition hydropyrolysis product is similar to that of oil originating products, while hydrogenation product contains

more aromatic compounds, and by the less length of aliphatic fragment as estimated for statistically-average molecule.

3. It has been shown that using mechanically and chemically activated iron ore catalyst at sapromixite hydrogenation and hydrolysis, one increases the content of distillate fractions in the liquid products, and also the content of low mass hydrocarbons in the low boiling fractions.

Acknowledgements

Authors are grateful to V. A. Utkin (Boreskov Institute of Catalysis, SB RAS) for chromatography mass spectrometry analysis of liquid products.

REFERENCES

- 1 Goryuchiye slantsy, in T. F. Jen (Ed.), Nedra, Leningrad, 1980.
- 2 Yu. F. Patrakov, S. V. Denisov, *Goryuchiye Slantsy*, 7 (1990) 272.
- 3 L. P. Noskova, Z. V. Semenova, V. V. Tuturina *et al.*, *Khim. Tv. Tela*, 6 (1987) 54.
- 4 N. V. Bodoev, Sapropelitovye ugli, in B. N. Kuznetsov (Ed.), Nauka, Novosibirsk, 1991.
- 5 S. N. Evstafyev, Osobennosti genezisa, sostava i svoystv gumusovykh i sapropelitovykh ugley (Chemical Sciences Doctoral Dissertation), Irkutsk, 1993.
- 6 A. B. Vol-Epstein, B. G. Tryasunov, M. B. Spielberg *et al.*, *Khim. Tv. Tela*, 3 (1986) 77.
- 7 S. N. Evstafyev, O. I. Shmidt, V. V. Tuturina, *Ibid.*, 1 (1987) 83.
- 8 V. I. Sharypov, B. N. Kuznetsov, N. G. Beregovtsova *et al.*, *Chem. Sust. Dev.*, 12, 6 (2004) 719. <http://www.sibran.ru/English/csdw.htm>
- 9 All-Union State Standard 11022-75 ST SEV 1461-78. Ugli burye, kmennye, antratsit i slantsy goryuchiye. Metod opredeleniya zol'nosti, Moscow, 1986.
- 10 V. I. Sharypov, B. N. Kuznetsov, N. G. Beregovtsova *et al.*, *Fuel*, 1 (1996) 39.
- 11 V. I. Sharypov, N. G. Beregovtsova, S. V. Baryshnikov, B. N. Kuznetsov, *Novye metody intensivatsii protsessov polucheniya zhidkikh produktov iz burykh ugley* (Treatises), Krasnoyarsk, 2001, pp. 229-242.