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# Promising Thermocatalytic Processes for Refining of Brown and Sapropelite Coal into Synthetic Fuels, Binding and Carbon Materials

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## Abstract

The article summarizes the results of the studies performed at the Institute of Chemistry and Chemical Technology of the SB RAS from 1998 to 2014 in the area of thermocatalytic transformations of brown and sapropelite coal into gaseous and liquid fuels, binding and carbon materials. The fundamentals were developed for the autothermal process of brown coal carbonization in a fluidized bed of catalyst with obtaining semi-coke and carbon sorbents. Additionally, the simultaneous preparation of fuel gas and syngas based on parallel operation of two fluidized bed reactors that are pyrolyser and gasifier was studied. Due to the use of a fluidized bed of catalyst particles during oxidative carbonization of brown coal, we managed to combine in one apparatus the processes of combustion and thermal treatment of coal. Metallurgical slags capable of oxidizing volatile substances released from coal were used as catalysts at elevated temperatures. The developed method allowed regulating the degree of coal carbonisation and, respectively, the properties of the resulting carbon products by changing the consumption coefficients of powdery coal and air fed to the reactor. Herewith, the depth of thermal treatment of coal and such characteristics of the resulting carbon product, as the heat of combustion, a content of volatile substances, its chemical composition and porosity were changed. Only the most reactive part of fuels was gasified in a catalytic boiling layer in a mode of partial gasification of coal and the porous carbon product was formed, the latter could be used as a sorbent. It was proposed to produce syngas by using a pyrolyser-gasifier. Semi-coke formed during brown coal carbonization in a pyrolyser was raw materials for steam gasification. Since the major part of volatile substances was already removed from semi-coke, the release of resinous products did not accompany its gasification. Therefore, the product gas did not require expensive purification from impurities before its use in synthesis processes. New methods for the preparation of liquid fuels and road binders were proposed. They were based on the process of hydrogenation of brown coal and its mixtures with oil residues and synthetic polymers in the presence of mechanically activated iron-ore catalysts in the environment of hydrogen donor solvents. Products of joint refining of brown coal, oil residues and synthetic polymers wastes were used to obtain road binders, and it was proposed to obtain modifiers for paving asphalt based on oil-resistant rubbers and liquid coal products. The optimum conditions for thermal refining of sapropelite coal in a fluidized bed reactor were selected. They provided the increased yield of liquid products in comparison with the known processes of semicoking of coal. The composition of the products allowed their refining by standard oil refining technologies.

**Keywords:** coals, brown, sapropelite, thermocatalytic refining, products, synthetic fuels, solid, gaseous, liquid, binding and carbon materials, properties, use

## INTRODUCTION

Coal is environmentally more hazardous energy raw material compare to other types of fos-

sil fuels. Reducing damage to the environment from coal energetics is achieved by using less environmentally hazardous gaseous and liquid fuels obtained by thermochemical refining of coal [1].

To increase the efficiency of processes of deep refining of coal it is advisable to use catalysts that intensify the process, increase the yield of target products and reduce the formation of hazardous emissions [2, 3].

Unlike processes of conversion of liquid and gaseous hydrocarbons, the use of catalysts in refining of fossil coals is currently limited in scope. This is related to difficulties of the developed surface of contact of the catalyst with solid raw materials required for the efficient catalytic effect for process underway, and also to the need to address catalyst deactivation problems by various impurities contained in coal and issues of catalysts regeneration [4].

Various approaches were used to overcome these problems. This review considers some of them developed under the direction of the authors on an example of thermocatalytic processes for obtaining synthetic fuels, binding and sorption materials from brown and sapropelite coal that are promising for industrial use.

#### OBTAINING SOLID FUELS AND CARBON SORBENTS FROM BROWN COAL

Refined or clean coal, synthetic gaseous and liquid fuels obtained by chemical refining of coal refer to environmentally friendly fuels of coal origin. Emission of harmful substances during combustion of these synthetic fuels is much lower than when using raw coal.

Refined solid fuel (RSF) has a higher heat of combustion than that of brown coal. There are specific user requirements that allow distinguishing several varieties of RSF. Thus, fuel for power boilers with a pulverized-coal combustion system is better ignited and burns at a high content of volatile substances and increased hydrogen/carbon ratio. On the contrary, these indicators should be minimum for process fuel designed for use in metallurgy.

The use of fine raw materials lifts some diffusion restrictions on heat and mass transfer and substantially increases the performance of

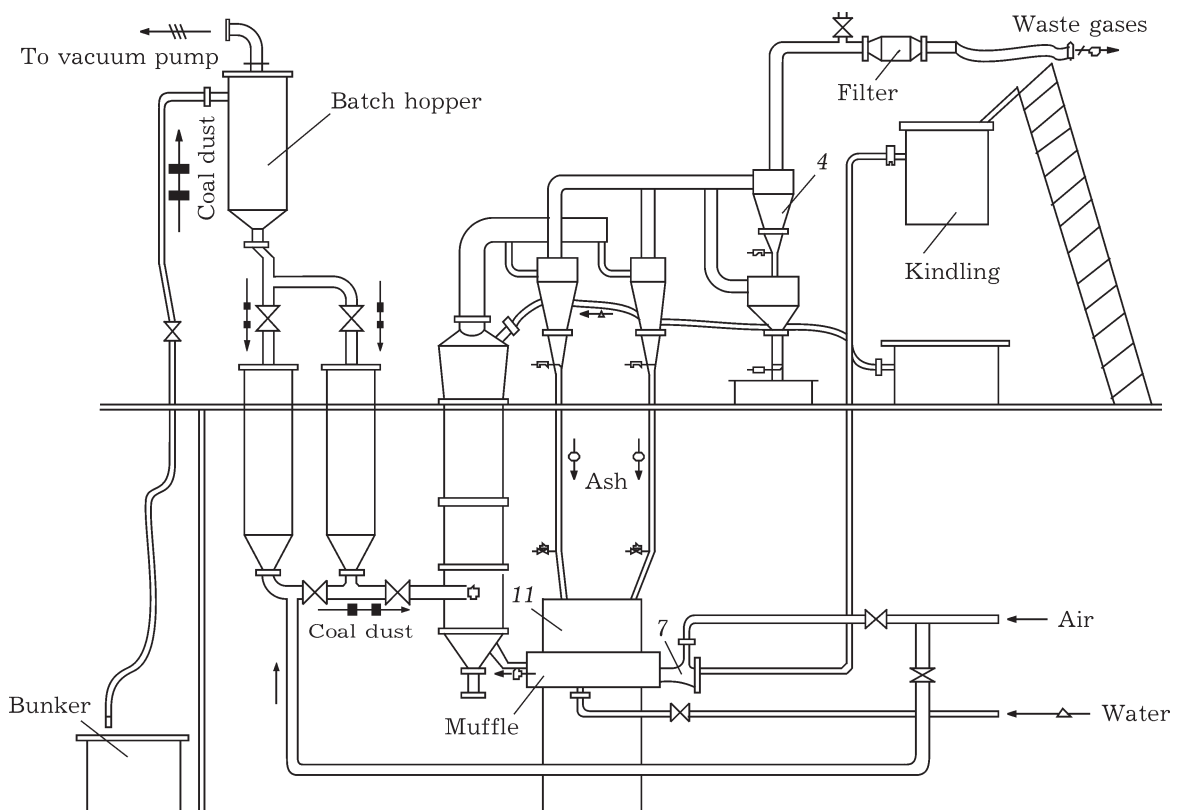


Fig. 1. Scheme of pilot setup for autothermal carbonization of pulverized coal.

TABLE 1  
Change of semi-coke characteristics by fractions

Fractional composition, mm	Ash content $A^d$ , %	Total porosity, $\text{cm}^3/\text{g}$	Iodine activity, %
0–0.063	31.62	0.30	9.40
0.063–0.090	20.63	0.33	10.64
0.090–0.140	12.98	0.36	13.09
0.140–0.200	11.43	0.38	12.76
0.200–0.315	11.02	0.38	22.88
0.315–0.400	10.97	0.31	17.36
Polydisperse semi-coke	18.60	–	18.20

Note. Semi-coke was obtained under the following conditions: 810 °C, treatment time of 0.16 s, treatment depth of 0.4 s, initial coal concentration of 0.94  $\text{kg}/\text{m}^3$ .

setups. With all the variety of technological methods used in these technologies, all of them are based on the allothermic principle of treatment of raw materials. Heat to maintain the process is obtained in the furnace due to combustion of a part of products of thermal decomposition of coal. This is often used for warming up a heat carrier (solid or gaseous) that is later transported to apparatuses for thermal decomposition of coal, where heat is transferred to the processed raw materials.

The process of autothermal oxidative carbonization of brown coal being developed at the Institute of Chemistry and Chemical Technology SB RAS is an example of autothermal technology of obtaining RSF [5]. We managed to combine in one apparatus processes of combustion and thermal treatment of coal due to using a fluidized bed of catalyst particles (Fig. 1).

Dried coal dust is supplied to an apparatus with a fluidized bed of a catalytically active material. Metallurgical slags that at elevated temperatures have a catalytic activity in reactions of oxidation of volatile substances released from coal are used as this material. Fine fuel enters into the lower part of a preheated fluidized bed of slag, passes through it in the upward flow of air. Herewith, coal is heated and emits volatile substances that are oxidized on the surface of catalytically active slag. Heat released during catalytic oxidation of volatile substances allows ensuring proceeding the process of thermal treatment of coal in autothermal mode.

This method allows regulating the degree of carbonation of fuel and, accordingly, RSF properties by a change in discharge coefficients of sup-

plied crushed coal and air. Herewith, the depth of thermal treatment of coal and such characteristics of the resulting solid product as heat of combustion, the content of volatile substances, its chemical composition and texture are changed.

Different fractions of lignite semi-coke obtained by autothermal carbonization in co-current flow were characterized by different properties of porosity and sorption activity (Table 1).

Experimental results demonstrated that separation of a fine fraction of semi-coke (less than 0.090 mm) enabled to significantly reduce ash content in the target product. Carrying out this technical solution allows obtaining about 9 % of the main fraction of semi-coke (0.090–0.350 mm) with ash content of 10.4–11.2 % during thermal treatment of coal with initial ash content of about 9 %. Ash content of initial polydisperse semi-coke obtained at the same parameters is 18.6 %. It is known that the formation of the porous structure of brown coal proceeds in two

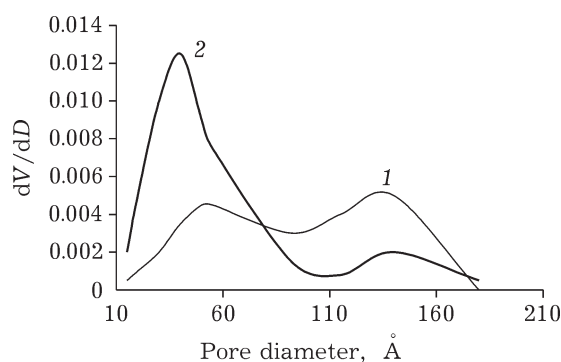


Fig. 2. Effect of the composition of gas medium on pore size distribution: 1 – flue gases from combustion of diesel fuel, 2 – the same with addition of up to 40 vol. % of water vapour.

stages: the formation of macro/mesoporous structures occurs at the first stage resulting from pyrolysis under conditions of thermal shock for the time about 0.1 s, the development of micropores resulting from the interaction with the gaseous reactants present in the reaction zone happens at the second stage, the duration of which is several seconds [6].

The effect of the composition of gas medium on the pore-size distribution in lignite semi-coke obtained in the co-current flow passing through a fluidized bed of catalyst illustrate these data given in Fig. 2.

A significant increase in pore volume with a size of about 5 nm happens in the gas phase for quite a short time of thermal treatment (1.2 s) during an increase in the concentration of water vapour, while the proportion of larger pores (12–15 nm) decreases. Therefore, the introduction of an additional amount of water vapour into the reaction medium and an increase in treatment time to several seconds improves indicators of the porous structure of semi-coke.

A distinguishing feature of carbonized products obtained by this technology is high reactivity towards oxidation with air oxygen and water vapour, which is driven by their porosity and less ordered structure in comparison with lignite semi-cokes obtained by traditional technologies.

A pilot batch of RSF of Kansk-Achinsk brown coal (KAC) was tested as boiler fuel. In comparison with initial KAC, combustion of RSF proceeded more fully under similar conditions. Chemical and mechanical underburning dropped significantly. The heat of combustion of RSF was 1.6 times higher than that of ordinary brown coal.

High-performance technology of combined pyrolysis and activation process in a fluidized bed of brown coal with obtaining inexpensive granular and powdery carbon sorbents was developed in a pilot installation. Pilot batches of brown coal sorbents demonstrated high efficiency in purifying waste water from phenols and heavy metals, and also in capturing nitrogen oxides from flue gases [7, 8].

The study of sorption of nitrogen oxides by brown coal adsorbents was performed under dynamic conditions for mixtures that are models of gas emissions of energy enterprises.

When changing the  $\text{NO}_x$  partial pressure in an inert atmosphere from 5.7 to 169 Pa

( $\text{NO}_x$  content – from 73 to 2157  $\text{mg}/\text{m}^3$ ), the dynamic adsorption capacity increases from 0.2 to 1.8  $\text{mg}/\text{g}$  of sorbent. The latter increases from 4.6 to 8.3  $\text{mg}/\text{g}$  during the introduction of oxygen into the gas phase in an amount from 2 to 6 vol. % and the  $\text{NO}_x$  partial pressure from 26 to 151 Pa ( $\text{NO}_x$  content from 335 to 1925  $\text{mg}/\text{m}^3$ ).

Thus, brown coal sorbents obtained by means of simultaneous pyrolysis and activation can be successfully used for purification of waste gases of power units operating on organic fuel.

Cooling of water used at thermal power objects is often performed in open water reservoirs, where it becomes contaminated with humic substances. To remove the latter combined purification methods are used including coagulation, filtration, electrochemical oxidation, adsorption by activated carbon, membrane treatment [9, 10]. The need to use combined technologies is driven by the complex and heterogeneous chemical composition of humic substances, which does not allow reaching a high degree of their removal using one-step purification processes.

Experiments for combined water treatment from humic substances were carried out in a laboratory flow-through installation modelling the purification process under real conditions. The concentration of humic substances was selected close to real for the Berezovskaya GRES Power Plant in summer – 7.5  $\text{mg}/\text{L}$ .

It was found that brown coal sorbent obtained of coal from the Borodino deposit by thermal treatment with a mixture of flue gases and water vapour in an apparatus with a fluidized bed was superior to the industrial sorbent BAU by its sorption activity during water purification from aluminum cations and humic substances.

Methods of thermo-alkaline activation of brown coal allow obtaining porous carbon materials (PCM) with a well-developed microporous structure [11]. These PCM may demonstrate high selectivity to sorption of low molecular mass gases [12] that enables their use in gas-separation processes.

The formation of a porous structure of carbon materials obtained by the method of thermocatalytic activation in a melt of alkalis was studied on an example of brown coal of Berezovskoye (BBC) and Irbeyskoye (IBC) deposits.

The results of physical chemical studies for the products of activation of brown coal with

TABLE 2

Characteristics of PCM obtained by alkaline activation of brown coal in an atmosphere of argon at 800 °C

Samples	Coal/alkali ratio	Specific surface, m <sup>2</sup> /g	Pore volume, cm <sup>3</sup> /g
BBC/KOH	1 : 3	1134	0.54
BBC/KOH	1 : 5	2680	2.12
BBC/NaOH	1 : 5	1259	0.72
IBC/KOH	1 : 3	2003	0.86
IBC/KOH	1 : 5	2250	1.45

alkalis at 600 °C demonstrated that high specific surface and total pore volume depended on the nature of alkali used and its content in the initial mixture. It was found that specific surface and pore volume of activated BBC samples reached a maximum with a ratio of brown coal/KOH of 1 : 5 (1565 and 0.78 cm<sup>3</sup>/g, respectively). The detected dependencies remained during the interaction of BBC with NaOH, however, indicators of specific surface and total pore volume were lower (1240 and 0.56 cm<sup>3</sup>/g, respectively).

Similar dependencies were also found during the activation of IBC samples, however, PCM with lower specific surface and total pore volume were obtained during the activation of IBC samples, KOH and NaOH.

It was determined that The total pore volume and PCM specific surface increased during an increase of activation temperature from 600 to 800 °C and the amount of the introduced activating agent, as established.

An increase in specific surface with a rise of the ratio from 1 : 1 to 1 : 5 was typical for all BC/alkali systems, herewith, this amount reached the maximum value of 2680 and 2250 m<sup>2</sup>/g, respectively, for BBC/KOH and IBC/KOH samples. Specific surface for NaOH-modified coal was 1259 m<sup>2</sup>/g under similar conditions (Table 2). A subsequent increase in the amount of alkali introduced into coal up to a ratio of 1 : 7 caused a decrease in specific surface of the PCM.

Thus, thermocatalytic activation of brown coal in the presence of the alkali hydroxides allowed obtaining carbon sorption-active materials with high specific surface (to 2700 m<sup>2</sup>/g) and significant pore volume (1.5–2.1 cm<sup>3</sup>/g).

#### OBTAINING GASEOUS FUELS FROM BROWN COAL

Three major areas of using gasification products of solid raw materials could be distinguished [13]:

- obtaining synthetic analogue of natural gas mainly consisting of methane;
- production of industrial fuel gas containing H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub> and a significant amount of nitrogen;
- generation of syngas consisting of hydrogen and carbon monoxide in various proportions.

Some gasification technologies provide for combustion in a gasifier of a certain part of solid raw materials to compensate energy costs to carry out endothermic gasification reactions. This allows carrying out the gasification process in the autothermal mode, *i. e.* without heat supply to a gas generator. The Lurgi, Winkler and Koppers–Totzek processes currently used to obtain syngas/fuel gas on an industrial scale in some countries are well known in the world practice.

Heat supply to compensate endothermal reactions at allothermic methods is performed using a heat carrier supplied to the gas generator or through the reactor walls, due to which there is no need to burn a part of raw materials in a gasifier for heat generation.

The use of catalysts offers new opportunities on regulating the composition of the produced gas and compensation of energy costs for endothermal reactions of carbon with water vapour, methanation, and carbon monoxide conversion [14].

Simplifying the stage of the introduction of the catalyst into the reaction medium, addressing issues of deactivation of catalysts and their isolation for reuse could be distinguished as relevant problems of the practical development of catalytic coal gasification. Many of these prob-



lems could be solved during pulverized-coal gasification in a boiling layer of catalyst particles [2].

A comprehensive solution for the problem of catalyst deactivation is the use of inexpensive catalytically active materials, regeneration of which is inadvisable [4]. The materials can be used in the gasification process until they wear-out. Some natural minerals (*e. g.*,  $\text{CaCO}_3$ ) and ore catalysts (*e. g.*, metallurgical slag) containing elements (Fe, Ni, Mn, *etc.*) able to accelerate oxidation reactions, conversion of CO and hydrocarbons, methanation could be used as such materials. A Cu-Cr/ $\text{Al}_2\text{O}_3$  catalyst (IC-12-70) had the highest catalytic activity. Out of slags, electro steel melting of smelting of stainless steel and marten final are more active. Electro steel melting oxidation and marten slags are the best ones by this criterion.

The brown coal gasification process in a fluidized bed of catalyst is under development and has been performed in a pilot installation [13, 15]. A gas generator represented a vertical tube of stainless steel with an inside cut of  $0.22 \times 0.22$  m and a height of 4.2 m, at the lower part of which an air diffusion grill with a free section of 3 % was placed. Process steam heated to 150 °C and air were fed into the reactor under this grill, and a mixture of pulverized coal and air – above it.

Coal of Borodino mine of the Kansk-Achinsk basin (KAB) was used in gasification experiments. The particle size of crushed coal was identical to that of pulverized coal for industrial power boilers. Martin slag that is inexpensive and easily accessible has high thermal and mechanical resistance was used as filler for a fluidized bed.

Catalytically active catalyst particles may accelerate conversions of volatile compounds released during pyrolysis of coal. They do not have direct effect on conversion of solid carbonated products but intensify heat and mass transfer processes. Catalytic effect appears in release of additional heat due to acceleration of exothermal oxidation reactions of volatile substances.

Only the most reactive part of fuel is gasified in a fluidized bed of catalyst in the mode of partial gasification of brown coal, and porous carbon residue that can be used as a sorbent is formed.

A certain temperature is established depending on the ratio of the initial reagents (coal/

air/vapour). To produce fuel gas, it is recommended to maintain temperature at a level of 900–950 °C with the maximum intensity of the process. Herewith, crude gas of the following composition is formed (vol. %): CO 8–13,  $\text{N}_2$  45–60,  $\text{CO}_2$  12–15,  $\text{CH}_4$  1.5–3.5,  $\text{H}_2$  7–12, and  $\text{H}_2\text{O}$  11–15. Its heat of combustion is 3–4.5 MJ/m<sup>3</sup>. The degree of coal conversion increased in the studied range of parameters of the gasification process with an increase in the length of stay of fuel particles in a fluidized bed of slag particles.

Stricter requirements were imposed on syngas for production of chemical products than those to fuel gas. Syngas generation was proposed to carry out by joint use of parallel operation of two reactors with a fluidized bed that are pyrolyser and gasifier [15]. Semi-coke formed during carbonization of brown coal in a pyrolyser was raw materials for gasification in a process under development. Since the major part of volatile substances had already been removed from semi-coke, the release of resins and other hydrocarbons did not accompany its gasification; therefore, the product gas did not require expensive treatment before use in synthesis.

A mixture of air and pulverized fuel in the pyrolyser reactor was fed from the bottom up through a fluidized bed of catalytically active particles of Martin slag. Experiments proved that the degree of coal conversion at a temperature of  $(950 \pm 50)$  °C was 40–70 %, depending on the length of stay of fuel particles in the reaction zone. Only the most reactive part of fuel was gasified in this case. Porous semi-coke having high specific surface and reactivity was formed from the residue.

Semi-coke particles formed in the pyrolyser reactor were separated from a gas flow in a hot cyclone. Unreacted semi-coke constantly recycled between a gasifier and a pyrolyser. Thus, the endothermal process of vapour gasification was provided with heat transferred by semi-coke from a pyrolyser into a gasifier.

Selection of concerted technological modes for pyrolysis and gasification reactors that make possible synchronization of these stages was to ensure sufficiently intense heat transfer into the gasifier. This task was resolved by increasing the circulation rate of solid heat carrier between pyrolysis and gasification reactors and a rise in temperature in the pyrolyser reactor.

There are almost no resins, oils, and phenols in the condensate after gasification. Experimental data testify that obtaining synthetic gas without use of oxygen is possible and this gas does not contain undesirable organic impurities.

#### OBTAINING LIQUID FUELS FROM BROWN COAL

The complexity of the chemical composition and the diversity of the different types of chemical bonds available in the organic mass of coal (OMC) complicate the study of coal liquefaction processes that are the result of flowing of many consecutive and competing reactions. Breaking of and saturation with hydrogen of C=C, C=O, C=S and C=N bonds, hydrogenation of aromatic rings may happen during the hydrogenation process, isomerization, condensation, and dehydrogenation reactions may flow.

It is most likely that hydrogenation and liquefaction of coal primarily begin with breaking of donor-acceptor bonds between macromolecules and homolytic thermal decompositions of alkyl bridges of benzyl  $\text{ArCH}_2\text{CH}_2\text{Ar}$  and ether  $\text{ArCH}_2\text{OAr}$  groups. The resulting free radicals are stabilized by hydrogen atoms or recombine with the formation of high molecular mass substances.

Catalysts are required to carry out deep hydrogenation and liquefaction of coal [5, 16, 17]. The primary role of hydrogenation catalysts consists in molecular hydrogen activation or acceleration of hydrogenation of the solvent that becomes a hydrogen carrier.

A closer contact between the catalyst and the coal, and the intermediates was reached when applying salts of metal catalysts onto initial coal. Herewith, deeper conversion of OMC in high yields of liquid products, lower gas formation and decreased hydrogen consumption was observed.

Applied bifunctional catalysts comprising sufficiently acid and hydrogenating functions are especially active. For example, Lewis acid catalysts, in particular,  $\text{ZnCl}_2$ ,  $\text{SnCl}_2$ , etc. are active catalysts for coal liquefaction. Their ability to penetrate the finest pores in coal is an advantage of solutions of these salts.

To intensify coal liquefaction processes various techniques were used, including:

- selection of inexpensive and efficient catalysts for coal hydrogenation;

- selection of organic solvents able to donate hydrogen to the coal;
- activated carbon treatment;
- joint processing with various organic wastes (oil residues, hydrolysis lignin, synthetic polymer wastes).

Literature analysis demonstrates that molybdenum-based catalytic systems have a high activity but are rapidly deactivated. Since molybdenum catalysts are expensive, they must be regenerated, which significantly complicates and increases the cost of the coal hydrogenation process.

These problems may be eliminated, when iron compounds including ore materials incorporating in their composition iron derivatives are used as catalysts (Fig. 3). These materials are easily accessible; therefore, they are used without regeneration.

The need to add ore materials to coal in large amounts (10 mass %) complicates their use in coal hydrogenation processes. Therefore, application prospect of iron ore materials as catalysts in industrial technologies of coal hydrogenation is related to the development of effective methods of their activation and modification to reduce catalyst concentration in the reaction mixture and increase their selectivity for liquid products

An effective method for activation of catalysts of ore origin is their treatment in activator mills. Mechanical activation leads not only to material grinding but also to crystal structure deformation, initiating decomposition reactions of a sub-

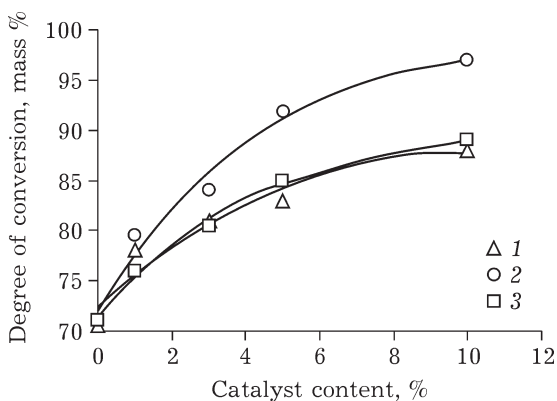


Fig. 3. Effect of the number of added ore samples containing hematite (1), magnetite (2) and pyrite (3) as basic crystal faze on the degree of conversion of Kansk-Achinsk basin coal into liquid and gaseous products during its hydrogenation in tetralin at 430 °C, 5.0 MPa initial hydrogen pressure.

stance or its interaction reactions with the medium where the activation happens.

Specific surface of various iron ores dramatically increased during their treatment in an AGO-2 centrifugal-planetary mill activator reaching the maximum values at the optimum length of activation, and then is either decreased (for samples containing hematite and magnetite), or remained unchanged (samples containing pyrite and pyrrhotite).

It was found that water additives during mechanochemical activation in an amount up to 100 % relatively to samples of ore origin resulted in a significant increase in their specific surface (Table 3). The maximum increase (from 7.9 to 53 m<sup>2</sup>/g) was reached for a sample containing magnetite. Perhaps, water passivates sintering and aggregation of small particles in activated samples.

Correlation between the value of catalyst specific surface and coal conversion degree was found [18, 19]. It was demonstrated that mechanochemical treatment of iron-ore catalysts in a mixture with elementary sulphur led to an increase of their catalytic activity in hydrogenation of Kansk-Achinsk brown coal. The use of an activated catalyst containing pyrite during coal hydrogenation in tetralin allowed reaching a complete conversion of OMC into liquid and gaseous products.

Addition of synthetic polymers to coal in its liquefaction processes is regarded as a promis-

ing method for increasing the yield and quality of the liquid products and simultaneous refining of polymer wastes [20].

Thermal decomposition of low-metamorphosed brown coal happened at temperatures lower than thermal decomposition temperature of both bituminous coal and polyolefins. Probably, this effect was related to the increased number of C–O bonds in low-metamorphosed coal, thermally less stable than C–C chemical bonds that dominated in polyolefins and bituminous coal. It may be assumed that radical fragments of thermal destruction of organic matter in brown coal will initiate depolymerisation of polyolefin macromolecules.

Thus, the presence of bonds with the increased reactivity allows performing the chemical interaction between the products of decomposition of brown coal and polymer macromolecules, contributing to destruction of the latter.

Products of joint refining of brown coal, oil residues and synthetic polymers were used to obtain road binders [21], and it was proposed to obtain modifiers for paving asphalt based on oil-resistant rubbers and liquid coal products [22].

It was demonstrated [23] that ore-originated iron catalysts modified by mechanochemical treatment increased the degree of conversion of coal/polymer mixture by 10–13 mass %, the yield of a fraction of liquid products boiling out to 180 °C – in 1.4–1.6 times and the yield of a fraction boiling out in a range of 180–350 °C – in 1.2–1.4 times.

TABLE 3

Effect of water additives during mechanochemical activation on specific surface value of ore catalysts (mechanical treatment duration: 40 min for samples containing pyrite and pyrrhotite, 30 min – magnetite and 10 min – hematite)

Samples, major crystal phase	Amount of added water, mass %	Specific surface, m <sup>2</sup> /g
Hematite	0	26
	20	47
	100	75
Magnetite	0	8
	20	52
	100	82
Pyrrhotite	0	7
	20	40
	100	55
Pyrite	0	6
	20	30
	100	45



Liquid distillate products of joint thermal conversion of brown coal and polyolefin polymers mainly consisted of paraffins and olefins. The chemical structure of these substances was determined by the type of the polymer used. Mainly linear hydrocarbons are formed during decomposition of coal/polyethylene mixtures. A high content of skeletal isomers and cyclic hydrocarbons was observed in products derived from coal/propylene mixture. The content of aromatic hydrocarbons in these products increased with coal concentration in the initial raw materials.

High molecular mass fractions of liquid products of joint thermal conversion of coal and polyolefin polymers were characterized by the complex composition. Infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy demonstrated the presence of various oxygen-containing, aromatic, and aliphatic compounds.

The use of catalysts during joint thermal conversion of coal and polyolefin polymers allowed not only increasing the yield of distillate products but also significantly decreasing the content of olefin and polycyclic hydrocarbons.

Products derived from polymers based on synthetic rubbers and primarily used car tires constitute a separate group of polymer materials, large-tonnage wastes of which appear promising for joint refining with coal.

Thermal dissolution of a mixture of brown coal and rubber [24] in the residue of oil distillation at 350–380 °C and pressure not exceeding 0.5 MPa was studied. The hydrocarbon fraction boiling above 350 °C is the main transformation product. It was demonstrated that high-boiling products after their oxidative modification with water vapour over iron oxides could be used as paving asphalt. Herewith, there is no need in separation of the products obtained from the unreacted coal, coal ash, mineral components and soot contained in rubber. Selection of process technological parameters that allow obtaining bitumen with the yield up to 62 mass % and distillate hydrocarbon products with the yield up to 23 mass % was implemented.

Additives of polyethylene, polypropylene, rubber based on butyl resin in amount of 25 mass % at the stage of thermal dissolution of coal allow increasing the yield and substantially improving the major characteristics of bi-

tumens. The resulting bitumens match the State Standard (GOST) requirements for high-quality oil bitumens on the major characteristics, and the composition of distillate products allows considering them as raw materials for production of motor fuels and organic solvents [24].

#### PREPARATION OF LIQUID PRODUCTS FROM SAPROPELITE COAL

Sapropelite coal is characterized by a high yield of volatile substances and increased hydrogen content (up to 12 % calculating for the mass of the organic part of coal) [25]. There are almost no aromatic structural fragments in the structure of organic substances of sapropel, and naphthenic rings containing 2–3 cycles are the basis of the carbon skeleton. Thus, by the structure of the organic mass, sapropelite coal is found closer to coal than humic. These peculiarities of the structure and composition allow suggesting that they can be converted into liquid products with smaller hydrogen consumption and under softer conditions than humic coal.

The Budagovo deposit of sapropelite (Irkutsk Region) and the Barzas deposit of sapromixite (Kemerovo Region) with proven reserves of sapropelites of 20–30 mln t in each were recognized as most promising when assessing the resources of sapropelite coal [26].

The yield of the primary resin during semicoking of sapropelites was 3–5 times higher than that from brown and bituminous coal [27, 28]. Baltic shales that are quite efficiently recycled by the semicoking method now give the yield comparable with that of sapropelites; however, sapropelite coal is distinguished by a significantly lower ash content, in comparison with shales, which simplifies and makes more efficient their refining.

The most common industrial process of semicoking of combustible fossils is carried out in apparatuses with internal heating by a gaseous heat carrier [26–29].

The process of semicoking of sapropelites from the Barzas deposit was studied in a flow laboratory setup under autoclave conditions in various gas media that were argon, hydrogen, and syngas [30–32].

The purpose of research consisted in selection of conditions for the process of thermal treatment of sapropelite coal ensuring the maximum yield of liquid organic products.

The maximum yield of resins in an inert medium (32.4 % per coal organic mass) was observed at temperatures of about 450 °C, in a flow of hydrogen – 36.4 % at a temperature of 700 °C, and in a flow of syngas – 39.2 % at 650 °C. The composition of the gas mixture had a significant effect not only on the yield but the dynamics of resin formation. The maximum yield of resins in a medium of hydrogen and syngas shifts to high temperature region. The yield of resins obtained a flow of syngas and hydrogen at 650 °C was 1.5 times higher than in those obtained in a flow of argon.

An increase in the yield of liquid products during thermal treatment a flow of hydrogen and syngas was probably driven by secondary reactions proceeding with participation of coal volatile matter.

The process of thermal decomposition of the organic mass of sapromixite can be presented as a scheme given in Fig. 4. From the experimental data obtained, it follows that the type of semicoking gas does not have a significant effect on stages 3 and 5. The observed increase in the yield of liquid organic products in reductive gases is reached due to a decrease in the yield of pyrolysis gases that hydrogen and syngas inhibit reactions of decomposition of primary liquid products at stage 4.

An increase in the yield of resins in a medium of hydrogen and syngas can be explained by the fact that these gases act as inhibitors of free-radical reactions of liquid product destruction, which leads to a rise in the yield of the latter and a shift in the maximum of their formation to high temperature region.

Based on the experimental data obtained, the method of semicoking of solid fuel that provides the increased yield of liquid products in comparison with the traditional process was developed [33]. The substance of the process consists in the fact that thermal treatment of coal proceeds in the upper layer of the reactor that is subjected to fluidization by hot products of gasification containing hydrogen and carbon monoxide. The semi-coke generated in this stage overflows into in the lower fluidized layer where it is gasified by a mixture of air and water vapour. The resulting hot gas is used for fluidization and thermal treatment of coal in the upper layer. Thus, the process flows continuously and autothermally.

The resulting excess of combustible gases is withdrawn from an apparatus and burned in the boiler-utilizer providing the process with water vapour.

Calculations of the yield of the major marketable products obtained during semicoking of Barzas sapromixite by the given scheme demonstrated that about 200 kg of resin might be obtained from 1 t of raw coal. Intermediates formed in the process and used as fuels are the following: gas with the heat of combustion of about 12 MJ/m<sup>3</sup> in amount of 160–180 m<sup>3</sup> per ton of raw coal and semi-coke in amount of 450–490 kg with the heat of combustion of 19 MJ/kg and ash content of about 50 %.

The composition and content of individual substances in light-boiling (initial boiling point of 180 °C) fractions of products by hydrogenation and hydrolysis of sapromixite from the Barzas deposit were determined. The indicated

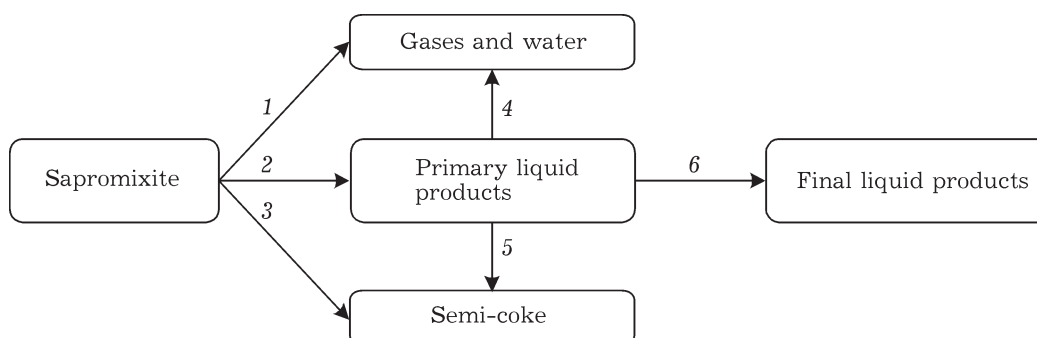


Fig. 4. Scheme of the process for thermal decomposition of the organic mass of sapromixite: 1–6 – stages of the process.

fractions obtained by hydropyrolysis more than 50 mass % consist of normal paraffins, at the same time, like hydrogenation products, are characterized by the increased content of cyclic hydrocarbons and isoparaffins. The content of aromatic hydrocarbons in these fractions does not exceed 14 mass %.

It was found by IR and NMR spectroscopy that fractions of products by hydrogenation and hydropyrolysis of sapromixite boiling out in a range of 180–350 °C mainly contained aliphatic fragments and were close by composition to products of oil origin.

The use of a mechanically activated iron-ore catalyst in processes of hydrogenation and hydropyrolysis of sapromixite led to an increase in the content of distillate fractions formed in liquid products and hydrocarbons with a low molecular mass in a low-boiling fraction (IBP-180 °C).

## CONCLUSIONS

New data on thermocatalytic transformations of brown and sapropelite coal were obtained resulting from research carried out at the Institute of Chemistry and Chemical Technology of the SB RAS.

The fundamentals were developed for the process of autothermal oxidative carbonization of brown coal in a fluidized bed of catalyst with obtaining refined solid fuels (RSF) with a given degree of thermal treatment.

It was demonstrated that a distinguishing feature of carbonized products obtained by this technology was high reactivity towards oxidation with air oxygen and water vapour, which was driven by their higher porosity and less ordered structure in comparison with lignite semi-cokes obtained by traditional technologies.

The heat of combustion of refined solid fuel from Kansk-Achinsk brown coal was 1.6 times higher than that in raw coal.

Pilot batches of brown coal sorbents obtained by parallel processes of pyrolysis and activation in a fluidized bed demonstrated high efficiency in purifying waste water from phenols and heavy metals, as well as in capturing nitrogen oxides from flue gases.

Selection of conditions for alkaline thermal activation of brown coal from the Berezovskoye

(BBC) and Irbeyskoye (IBC) deposits providing preparation of nanoporous carbon materials with specific surface above 2500 m<sup>2</sup>/g was carried out.

The scientific basis was developed for the process of simultaneous generation of syngas and fuel gas from brown coal based on parallel operation of two fluidized bed reactors that were pyrolyser and gasifier.

An advantage of the proposed technology is reduction of oxygen consumption for syngas generation in 5–7 times in comparison with traditional technologies based on the Lurgi, Winkler and Koppers-Totzek processes due to integrating into a single technological cycle of oxidative pyrolysis of pulverized coal in a fluidized bed of catalytically active slag with gasification of the resulting semi-coke with water vapour. Continuous recirculation of hot semi-coke between pyrolyser and gasifier provides additional heat to the gasification process. Additionally, the use of oxidative pyrolysis in the first stage of refining of coal, allows removing a significant part of resins from raw materials, which gives an opportunity to obtain clean syngas in the next stage.

Selection of harmonized operating regimes of pyrolyser and gasifier providing autothermal gasification of brown coal into syngas and fuel gas was carried out.

Improved techniques for producing liquid fuels from brown coal were proposed. The methods were based on hydrogenation processes in the presence of activated iron-ore catalysts. It was demonstrated that a high degree of conversion of the organic mass of coal (OMC, to 95 mass %) and the yield of distillate products (to 58 mass % calculating for OMC) were reached when combining the optimum methods of mechanical activation of iron-ore catalysts with high hydrogen-donor activity.

A nonadditive increase in the degree of conversion of the mixture and the yield of low-boiling hydrocarbons happened during the joint thermal transformations of brown coal and synthetic polymers, as established.

Activated iron samples of ore origin showed catalytic activity during hydropyrolysis of coal/synthetic polymer mixtures leading to an increase in the yield of low-boiling hydrocarbons in 1.4–1.6 times, there is a sharp decrease (from

20 to 3 mass %) olefins, in their composition, and significantly reduced contents of polycyclic aromatic compounds in high-boiling fractions.

The obtained indicators on the yield and quality of distillate products of brown coal hydrogenation in the presence of iron-ore catalysts corresponded to characteristics for the best foreign coal liquefaction processes, in which expensive synthetic catalysts were used.

The yield of light hydrocarbons in pyrolysis and hydrolysis processes of Barzas sapropelites was 7 times higher than in case of thermal transformations of brown coal. The liquid hydrocarbon fraction boiling above 200 °C was the predominant product of thermal transformation, as established.

The optimum conditions of the process that provides the increased yield of liquid products in comparison with the known technologies of semicoking of sapropelite coal were selected. This choice was based on the results of the study on the effect of thermal treatment of Barzas sapropelites (argon, hydrogen, syngas) and treatment conditions (temperature, length).

Liquid products of thermal treatment of sapropelite coal can successfully be recycled into motor fuels and traditional petrochemicals using standard oil refining technologies.

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