Chemistry for Sustainable Development **18** (2010) 239–251

UDC 662.6:662.7

Processing of the Kansk-Achinsk Brown Coal into Synthetic Fuel

B. N. KUZNETSOV[1,2], M. L. SHCHIPKO[1] and V. I. SHARYPOV[1]

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

E-mail: bnk@icct.ru

[2]*Siberian Federal University,*
Prospekt Svobodny 79, Krasnoyarsk 660041 (Russia)

Abstract

Results of investigations carried out at the Institute of Chemistry and Chemical Technology in the area of mastering the technologies for obtaining synthetic solid, gaseous and liquid fuel from the brown Kansk-Achinsk coal are generalized. The technologies under development are based on the processes of autothermal pyrolysis and gasification of brown coal in the reactors with the boiling bed of catalytically active slag, and on the processes of thermal dissolution of coal and its mixtures with carbon-containing wastes in the presence of activated iron ore catalysts that provide obtaining liquid fuel and binders for road construction.

Key words: brown coal, processes of pyrolysis, gasification, thermal dissolution, iron-containing catalysts, synthetic solid, gaseous and liquid fuel

INTRODUCTION

Enormous resources of natural organic raw material are concentrated at the Krasnoyarsk Territory. Unique Kansk-Achinsk basin (KAB), in which it is possible to produce up to 1 milliard t of coal per year using the cheap open-pit method, is situated at this territory. The amount of transportation of the Kansk-Achinsk coal to the neighbouring regions and for export is limited by the high transportation expenses. It is more reasonable from the economic viewpoint to develop deep coal processing into the assortment of important products with the low transportation component in their cost [1]. At present, the Kansk-Achinsk coal is used almost exclusively for power engineering, though it is a promising raw material for processing into synthetic fuel and chemical products due to the physicochemical characteristics and high reactivity of coal.

On the basis of this deposit, the Kansk-Achinsk Fuel and Energy Complex (KAFEC) started to form 25 years ago, to provide large-scale production of electric power, synthetic fuel and chemical products from brown coal [2]. At the same time, efforts aimed at the investigation of pyrolysis, gasification and hydrogenation of brown coal gained development at the Institute of Chemistry and Chemical Technology (ICCT), SB RAS. The goal of these investigations has become to lay the scientific foundations of the technologies intended for obtaining transportable solid fuel (coal char), fuel gas and synthesis gas, liquid fuel and small-scale products (sorbents, humic substances *etc.*) from the coal of the KAB.

Industrial development of the known technologies of deep processing of coal is restricted by their low productivity in comparison with the processes involved in oil processing, and by the high investment [3, 4].

The possibilities to improve the technological and economical parameters of coal processing technologies by rising temperature and pressure, and modifying the instrumentation, are close to exhaustion. Because of this, many new developments in the area of deep processing of coal are based on the use of efficient catalysts. Some examples of the successful use of catalytic processes in chemical processing of fossil coal and wood raw material were considered in a number of reviews published previously [5–8].

Selection of catalysts for deep processing of solid fossil raw material is complicated due to a number of factors connected with the topochemical nature of chemical transformations, increased deactivation of catalysts by impurities present in the raw material, difficulties in catalyst regeneration. Some of these problems can be solved by choosing cheap catalytically active materials, for example iron-containing ores and slag [9, 10].

In the present work we describe the results of investigations performed during the recent years at the ICCT, SB RAS, and aimed at improvement of the processes of obtaining synthetic fuel from the Kansk-Achinsk brown coal.

OBTAINING REFINED SOLID AND GASEOUS FUEL FROM BROWN COAL

Among all the kinds of fossil fuel, coal is the most dangerous energy raw material from the ecological viewpoint because of increased emission of hazardous substances from its combustion. Reduction of environmental harm from coal power engineering can be achieved by passing to the use of ecologically safe fuel originating from coal. These kinds of fuel include refined or pure coal, synthetic gaseous and liquid fuel obtained by chemical processing of coal. Emission of hazardous substances from the combustion of these synthetic kinds of fuel is much lower than that from raw coal.

Synthetic solid fuel (SSF) is represented by a wide range of refined (improved) kinds of fuel including pure coal, coal briquettes, coal char, thermocoal, autoclaved coal. SSF with improved characteristics is obtained from brown coal using different methods, depending on the kinds of raw material and the assumed area of SSF application.

Improvement of the quality of brown coal having low combustion heat due to the high content of moisture and oxygen is usually achieved by refining during pyrolysis. Thermal treatment of brown coal not only increases the heat of combustion of the resulting coal char but also decreases the emission of SO_2 and NO_x. Coal char is a good domestic fuel and is used as a reducing agent in ferroalloy industry and other areas, as the raw material for gasification.

Promising technologies of processing Kansk-Achinsk coal into SSF are based on using fine raw material, which decreases the role of diffusion limitations for heat and mass transfer and causes a substantial increase in the process productivity. An example of the technologies developed in our country may be the achievements of the Energy Institute (ETKh and TKKU) and the Institute of Fossil Fuel (thermocoal) [11–13].

At the ICCT we developed the foundations of more economical version of obtaining refined solid fuel – autothermal carbonization of brown coal in pseudo-fluidized layer of oxidation catalyst or catalytically active slag. Unlike for conventional allothermic pyrolysis technologies, all the stages of thermal treatment are combined in the same reaction volume, which substantially decreases metal consumption in the technology and enhances its energy efficiency [14]. Volatile substances evolved from coal are oxidized at the catalyst, so this technology excludes the formation of pyrolysis tar, and the concentration of benzo[a]pyrene in gaseous products is sharply decreased. By varying the technological parameters, it is possible to control the properties of resulting solid products within a broad range. The process was mastered at the pilot plant in the ICCT with the productivity up to 200 kg of coal per hour.

The solid products of autothermal pyrolysis were successfully tested as the refined energy fuel, additive to mixtures for coking, single-use sorbents for water purification from oil products [14–17].

Other promising directions of the use of dust-like coal char from Kansk-Achinsk coal are injection into blast furnaces for the purpose of saving expensive coke, replacement of fuel oil in the production of alumina, and obtaining synthesis gas.

The described autothermal method of obtaining SSF was used in the development of different versions of brown coal gasification in the pseudo-fluidized layer apparatuses.

The shortcomings of the majority of industrial gasification technologies are due to the necessity of high temperatures, pure oxygen, increased pressure and high investment. The most relevant process is obtaining a mixture of hydrogen and carbon monoxide (synthesis gas) through the interaction of water vapour with carbon according to reaction

$$C + H_2O = CO + H_2 \quad \Delta H = 118.5 \text{ kJ/mol}$$

Because this reaction is endothermic, it is necessary to use technological approaches based on the combustion of a part of fuel and recirculation of the solid heat carrier.

One of the methods to solve this problem is to combine the gasifying reactor with another reactor in which the heat is formed due to the combustion of a part of the products of thermal decomposition of fuel and heating of the solid recirculating heat carrier [17–19].

The advantages of the technologies under development involving steam-driven gasification in fluidized bed reactors are substantial: there is no necessity to use pure oxygen, investment decreases due to the use of cheaper materials for reactors and communications, the concentration of hydrogen in the produced gas increases. Because of this, the attention to the investigation of solid fuel gasification using two apparatuses with fluidized bed in increasing during the recent years [20, 21].

At the ICCT we studied the features of gasification of brown Kansk-Achinsk coal in a set-up with two fluidized bed reactors. In the first reactor, oxidative carbonization of finely dispersed raw material in the fluidized bed of open-hearth slag exhibiting catalytic activity in the oxidation of volatile substances was carried out. At the second stage, gasification of carbonized fuel with water vapour was carried out. The heat was supplied to the gasifying unit by the flow of open-hearth slag and coal char; this flow was recirculating between the carbonizing unit and the gasifying unit.

The features of autothermal carbonization of fine fuel, corresponding to the performance conditions in the first reactor, were considered in previous publications. In the present work we pay the major attention to the second stage of the process, *i. e.* gasification of coal char with water vapour. The characteristics of the raw material used in the process are listed in Table 1.

Experiments were carried out with the set-up described in [22]. The reactor for pyrolysis is a vertical tube made of stainless steel with the inner cross section of 0.048 m^2 and the height of 4.2 m. An air distributing grill with the free area of 3 % is mounted in the lower part of the reactor. The major part of the air is supplied into the reactor under the distributing grill. The gasifying unit has a similar design, and its height is 1.5 m. In the first reactor, the fluidized layer is composed of the particles of open-hearth slag 0.5–1.5 mm in size. In the second reactor the fluidized layer is composed of a mixture of relatively small particles of open-hearth slag and thermally treated raw material (coal char). Dust-like raw material (coal, hydrolysis lignin) is supplied in compressed air flow above the distributing grill into the lower part of fluidized layer. The raw material with poor looseness (birch chips) is loaded into the reactor with the help of an auger feeder through which the same amount of the air is passed as that used for pneumatic transportation of dust-like fuel.

Two fractions of open-hearth slag (0.8–1.2 and 0.10–0.25 mm) were loaded into the pyrolysis unit. The coarse fraction was in the fluidized state during the operation of the reactor, while the fine fraction was carried out of the reactor with a flow of gaseous products and entered gasifying unit together with the particles of carbonized fuel. The major components of the slag are, mass %: SiO_2 19.4, CaO 38.6, MgO 14.3, MnO 5.7, Fe 6.7. The material used is cheap and readily available; it has high thermal and mechanical stability.

The data on the effect of the temperature of fluidized bed on the yield of the products of gasification of different kinds of solid fuel are presented in Table 2.

Under gasification of brown coal char and charcoal in the fluidized bed of catalytically

TABLE 1

Characterization of the raw material used for gasification (calculated per working mass), mass %

Raw materials	Humidity	Ash content	Yield of volatiles	C	H	N	S	O
Borodino coal	9.6	8.7	39.2	57.8	3.9	0.8	0.3	18.9
Birch chips	42.2	0.7	–	32.4	3.4	0.1	0.0	21.2
Hydrolytic lignin	12.3	2.5	41.3	59.7	5.4	0.1	0.5	19.5

TABLE 2

Effect of fluidized bed temperature on the yield of the products of gasification of carbon raw material with water vapour

Raw materials	Temperature, °C	Concentration of hydrogenin dry gas, vol. %	Tar content in dry gas, g/nm^3	Low heat value, MJ/nm^3
Brown coal (char)	670–750	50–60	Traces	10.5–11.1
Birch coal	620–710	58–65	1.0	10.2–10.8
Hydrolytic coal	670–780	52–59	Traces	10.2–10.5

active slag, the volume fraction of hydrogen in the produced gas reaches 60–65 %; tarry matter is almost completely absent from the resulting gas.

It should be stressed that the temperature in the gasifying unit is determined by a number of factors among which the most important are the rate of recirculation of heat carrier between the reactor of autothermal carbonization (pyrolyzing unit) and the gasifying unit, as well as the ratio of steam and raw material fed to the gasifying unit. The heat carrier is a mixture of open-hearth slag (fraction 0.1–0.25 mm) with coal char. Its recirculation rate is determined by the intensity of carry-off of these particles from the reactor of autothermal carbonization, and it is a function of the linear velocity of gases in this apparatus. The velocity of gases in the upper part of the apparatus was determined experimentally assuming the equality of the amounts of nitrogen fed into the reactor and passing out of it, on the basis of equation

$W = \{G^a[N_2]^a/([N_2]^g S)\}T_c$

where W is the linear velocity of gases at the outlet of the reactor of autothermal carbonization, m/s; G^a is air flow rate at the inlet, m^3/s; $[N_2]^b$ is the volume fraction of nitrogen in the blast (0.78 in the case under consideration), $[N_2]^g$ is the volume fraction of nitrogen in the gases passing out of the reactor; S is the free area of the apparatus in its upper part equal to 0.048 m^2; T_c is temperature coefficient taking into account the change of gas volume due to the difference of temperatures at the reactor inlet and outlet.

Results characterizing the effect of gas velocity in carbonization apparatus on a number of important process parameters are presented in Fig. 1. Experiments were carried out with brown coal at the temperature of autothermal carbonization equal to (840±10) °C.

It follows from the data obtained that gas velocity has an essential impact on the recirculation of heat carrier within the whole parameter range studied. However, temperature in the gasifying unit changes only when gas velocity varies up to 6.5 m/s. Further increase in gas velocity and in the rate of recirculation of heat carrier causes almost zero increase in temperature. So, it may be stated that the maximal temperature in the gasifying unit of the set-up is about 100 °C lower than temperature in the fire chamber.

A linear dependence observed for the rate of output of the organic mass of coal char from the carbonizing reactor (see Fig. 1, curve *3*) may be explained by the fact that, in order to provide constant temperature in the carbonizing unit, in parallel to an increase in air flow rate, we had to increase also the consumption of fuel.

At the reasonable (from the viewpoint of heat transfer efficiency) gas velocity in the

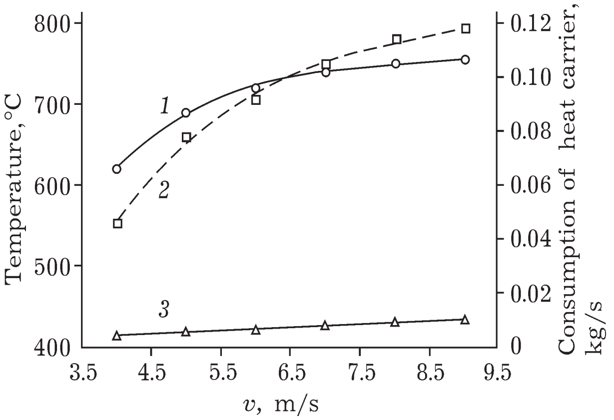

Fig. 1. Effect of gas velocity in the carbonizing reactor (v) on temperature in the gasifying unit (*1*) and the rate of recirculation of heat carrier (*2*, *3*): *2*, *3* – consumption of heat carrier (open-hearth slag + coal char) at the outlet of carbonizing reactor (*2*) and consumption of coal char calculated for the organic mass, at the outlet of carbonizing reactor (*3*).

carbonizing unit equal to 6.5 m/s, the consumption of the organic mass is about 0.008 kg/s. A comparison of this value with the data on the yield of carbon-containing gases from the gasifying unit points to the fact that the amount of coal char arriving from the carbonizing unit is substantially (2–6 times) larger than the amount of coal char having enough time to undergo gasification. So, the velocity of gases in the free area of carbonizing unit, approximately equal to 6.5 m/s, is acceptable from all the viewpoints.

The second important parameter determining the process temperature is the ratio of vapour to coal raw material entering the gasifying unit. Its effect on the efficiency of gasification processes has been studied rather thoroughly within the range 0.2–2.0 [23, 24]. However, in the technology under development, the ratios of vapour to coal raw material below 0.8 are of no practical interest because low vapour consumption does not provide fluidization of the particles of open-hearth slag. The data on the effect of vapour/coal char ratio on the performance of the gasifying unit are shown in Fig. 2. It is necessary to stress that the amount of the organic mass of coal char taken for calculations was determined from the yield of coal-containing components in the produced gas. Experimental conditions: brown coal, temperature at the stage of carbonization (820±10) °C, gas velocity in the upper part of carbonizing unit 5 m/s, temperature of vapour fed into the gas generator was equal to 460 °C, pressure 0.16 MPa.

It should be stressed that the vapour entering the gas generator should be heated to the temperature of fluidized layer, which requires substantial energy consumption. In addition, with an increase in vapour / fuel ratio the degree of H_2O transformation in the gas generator decreases progressively (see Fig. 2, curve *2*). These two facts, as well as the comparison with literature data, pointing to the efficiency of vapour consumption in these systems at a level of 10 % [23, 24], unambiguously prove the reasonability of choosing the minimal vapour flow rate admissible according to the technical specifications of the process.

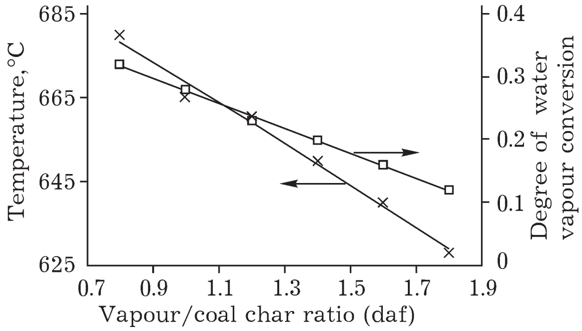

Fig. 2. Effect of the ratio of water vapour to the organic mass of reacted coal char on the degree of vapour conversion and process temperature.

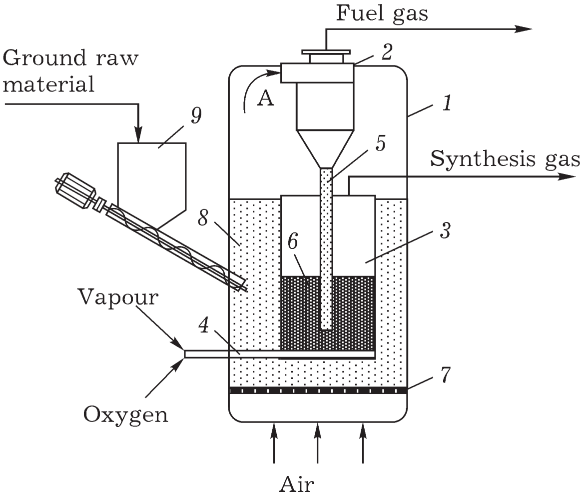

Fig. 3. Scheme of the gasifying unit for simultaneous formation of fuel and synthesis gas: *1* – reactor of oxidative carbonization, *2* – built-in cyclone; *3* – reactor for obtaining synthesis gas; *4* – injector for gasifying agent; *5* – overflow pipe; *6* – fluidized bed of coal char; *7* – air distributing grill; *8* – fluidized bed of slag; *9* – feeding bunker. Arrow A indicates the direction in which carbonization products move (a mixture of gases, tar and solid carbonized fuel).

Another version of gasification process developed at the ICCT [2] is based on the use of an apparatus of special design [25] providing simultaneous formation of fuel and synthesis gases (Fig. 3).

A specific feature of the process is decreased oxygen consumption in comparison with analogs. In the developed method, the ground solid fuel is fed into the air-fluidized bed of thermally stable heat carrying material, for example open-hearth slag, where the fuel undergoes carbon-ization at a temperature of 800–1000 °C. The formed carbonization products are separated into fuel gas and the solid residue. The fuel gas is carried out of the process, while the solid residue undergoes gasification with a mixture of water vapour and oxygen, resulting in the synthesis gas (a mixture of H_2 and CO); synthesis gas is passed from the reactor in a separate flow. Device *2* and gasifying unit *3* are connected with a vertical tube *5* which provides the arrival of solid coal char particles *6* into the gasifying unit. The length of vertical tube *5* and the degree of filling it with carbonized fuel are chosen so that the gases formed in the gasifying unit do not get into cyclone *2*.

Air flow fed under grill *7* provides fluidization of the heat carrying material and partial combustion of entering fuel. The heat evolved during the combustion provides autothermal character of carbonization process. Intense mixing characteristic of the particles in the fluidized bed allows uniform distribution of fuel coming from dosing bunker *9* and heat evolved in its partial combustion over the section of external vessel *1*.

The major part of solid particles gets separated from the flow in cyclone *2*. Under the action of gravity, these solid particles go down vertical tube *5* and pas into gasifying unit *3*. The vapour and gas mixture with the residual smallest particles of carbonized fuel is led out of the process and burnt out in the boiler (not shown in the scheme). The heat generated in the boiler can be used to generate the vapour to be fed into the gasifying unit *3*, and/or to be directed to exterior consumers (in particular, to produce electricity).

Carbonized fuel entering the gasifying unit *3* gets fluidized and gasified in the mixture of water vapour and oxygen. A part of the heat necessary to maintain endothermic reactions of gasification is fed from the zone of oxidative carbonization *8* (fluidized bed of heat carrier material) through the wall of gasifying unit *3* into gasification zone *6* (fluidized bed of carbonized fuel). Due to this, the demand for oxygen decreases. The characteristics of typical gasification modes are listed in Table 3.

One can see that with the same raw material (low-calorie brown coal) the consumption of oxygen for the production of synthesis gas is 3.5 times smaller than its consumption in the conventional Winkler process. The productivity of the installation with respect to synthesis gas in the new process is about 10–15 % higher.

Investigation of the features of gasification of different kinds of raw material revealed substantial differences at the first stage of the process, which is autothermal carbonization of the initial raw material. The second stage, which is the formation of synthesis gas, differs insignificantly for different kinds of raw material, which is perhaps due to the use of relatively unified fuel, namely coal char.

It should also be stressed that the productivity of the first and the second stages of the process with respect to the gas are linked through the inverse relationship. For instance, the yield of fuel gas in the heat equivalent (353 MJ/h) corresponds to experiment No. 5 (see Table 3); the productivity with respect to synthesis gas is minimal. Quite contrary, the maximal productivity with respect to the synthesis

TABLE 3

Process parameters for different gasification modes

Experiment No.	Raw materials	Air flow rate, nm^3/h	Temperature in carbonization zone, °C	Oxygen consumption, nm^3/nm^3 of synthesis gas	Yield of synthesis gas, nm^3/h	Yield of fuel gas*, MJ/h
1**	Brown coal (char)	–	–	0.32	8.9	–
2	Birch chips	52	820	0.17	9.2	303.1
3	Hydrolytic lignin	60	890	0.12	9.8	292.7
4	Brown coal	66	1000	0.09	10.3	284.1
5	Undersized coal ($A^d = 25$ %)	48	700	0.21	5.4	353.4

*The yield of fuel gas was calculated as a sum of total physical heat of the products passing out of the upper part of the reactor and the low heat value of combustible components (gas, tar, dust-like carbonized fuel).

** Data on oxygen consumption in the experiment modelling the known Winkler's process.

gas (103 nm^3/h) corresponds to the minimal productivity with respect to fuel gas (284 MJ/h). Therefore, optimization of the process implies the choice of parameters providing the maximal intensification of one of the two its separate stages (carbonization or gasification) depending on the demand for fuel gas or synthesis gas.

OBTAINING LIQUID PRODUCTS THROUGH HYDROGENATION AND THERMAL TRANSFORMATION OF BROWN COAL

Two groups of technologies for obtaining liquid fuel from coal are known. One of them includes the processes of direct destructive hydrogenation of coal with hydrogen under increased pressure and temperature in the presence of catalysts (hydrogenation processes), heating in the inert atmosphere (pyrolysis processes) and thermal dissolution of coal by extraction [26]. However, the resulting coal liquids in their initial form are poorly suitable for use as motor and boiler fuel, so additional application of catalytic processes is necessary for their hydro-processing in order to decrease the concentration of sulphur and other undesirable admixtures in liquid fuel.

Another direction in obtaining synthetic fuel is based on vapour oxygen gasification of coal into synthesis gas; motor and boiler fuel can be obtained by its catalytic processing.

With respect to such index as coal consumption for the production of 1 t of liquid product, and the energy efficiency of the process, the technologies of direct liquation of coal have advantages. However, the technologies of obtaining liquid fuel through gasification have already passed industrial mastering and allow one to obtain high-quality motor fuel immediately. In addition, they are safer from the viewpoint of ecology and less sensitive to the variations of the composition of initial raw material in comparison with the technologies of direct destructive hydrogenation of coal.

By present, more than 30 technological schemes of direct destructive hydrogenation of coal have been developed. They were tested with the demo installations with different productivities but all of them lag behind in their efficiency against the technologies of the production of similar products from oil. This is connected with the fact that thermochemical transformations of the organic matter of coal into low molecular weight organic compounds proceed with not very high selectivity and under more rigid conditions than those involved in oil processing [27].

In order to improve coal hydrogenation processes, the approaches are developed on the basis of the use of preliminary activation of coal, the application of cheap iron ore catalysts in combination with hydrogen-donating solvents or with organic raw material with increased hydrogen content (oil, lignin, synthetic polymers) [28–32].

Below we will consider the recent results on intensification of thermal transformations of brown coal from the KAB into liquid products, their composition and possible areas of application.

Activity of dispersed iron ore catalysts in thermal liquation of brown coal

The majority of coal hydrogenation technologies include several stages (Fig. 4). The selection of optimal parameters at each of them allows one to optimize hydrogen consumption and the composition of results liquid products. As a rule, iron-containing catalyst is used at the first stages of coal liquation. The requirements to these catalysts are determined by the features of the technological scheme of the process. A general condition is the necessity to introduce catalytically active components into the coal-oil mass in the highly dispersed form.

It was established previously that mechanical activation of the materials of ore origin containing iron minerals as the major phase causes a substantial increase in their catalytic activity towards coal hydrogenation. However, with an increase in the duration of treatment, we observe the formation of relatively large aggregations of small particles. In order to inhibit particle association process, mechanochemical activation of iron ore samples differing from each other in the composition of the major crystal phase (haematite and pyrrhotite) in water was carried out.

It was discovered that the treatment in activator mill AGO-2 results in a substantial increase in the specific surface of iron ore materials (up to 47–85 m^2/g) and a decrease in par-

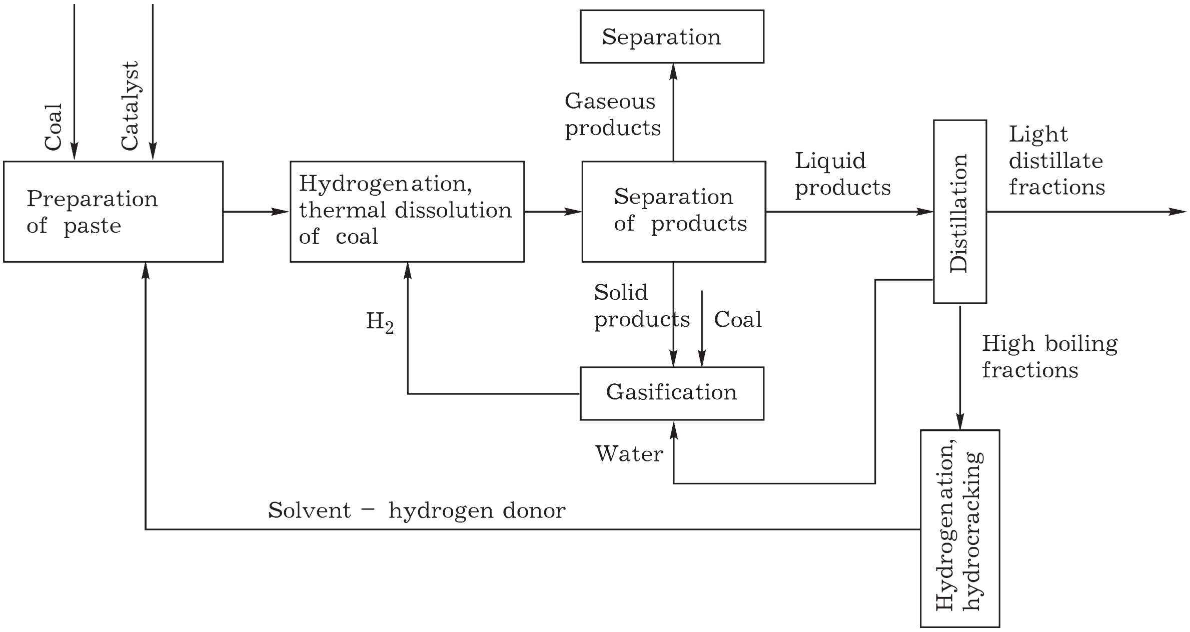

Fig. 4. Schematic diagram of the thermal transformation of coal into liquid hydrocarbon products.

ticle size. The maximal specific surface was obtained for the sample containing haematite. The diffraction patterns of the treated samples indicate a decrease in their crystallinity and changes of their chemical composition.

According to the results of scanning electron microscopy, about a half of the particles in activated samples have a size below 100 nm. The particles are present as associates with complicated structure. The size and structure of particle associates are determined by the duration of mechanical treatment and the nature of iron-containing sample.

The effect of the time and intensity of treatment of iron ore catalysts and the methods of their introduction into the raw material on the catalytic properties for hydrogenation in tetraline and hydropyrolysis of brown Kansk-Achinsk coal was studied.

A correlation between the chemical composition, specific surface, method of introduction of iron ore catalysts into the raw material and the activity of the catalysts in the processes under investigation was discovered experimentally. It was demonstrated that dispersed iron-containing catalysts added as a powder to brown coal during hydropyrolysis cause an increase in the degree of transformation of the organic matter of coal (OMC) by 16–20 rel. % (Table 4).

During hydrogenation of coal, the addition of iron-containing catalysts dispersed preliminarily in tetraline with the help of ultrasound causes a substantial increase in the degree of OMC conversion (up to 85–89 %). Coal conversion increased mainly due to an increase in the yield of petrolenes. Pyrrhotite exhibits higher catalytic activity than haematite.

During coal hydrogenation, tetraline gets dehydrated and transforms into naphthalene by 59–71 %. Calculations show that the consumption of hydrogen from tetraline by coal in the presence of catalysts was 2.0–2.3 % per OMC, gaseous hydrogen 2.3–2.5 % per OMC.

We tested both individual substances (isopropyl alcohol, toluene, tetraline, naphthalene etc.) and technical paste-forming agents (high-boiling fractions of oil and products of coal hydrogenation) as past-formers. The established trend was an increase in the catalytic activity with an increase in the number of aromatic rings and the degree of condensation of polycyclic aromatic compounds in a statistical mean solvent molecule. The catalytic action of iron-containing ore samples is reduced to hydrogenation of polycyclic aromatic compounds or liquid products of coal decomposition with the formation of partially hydrogenated derivatives possessing the ability to donate hydrogen. The

TABLE 4

Effect of catalysts on the parameters of hydropyrolysis and hydrogenation of brown coal in tetraline environment at 430 °C, mass %

Catalysts	Degree of OMC conversion	Yield			Tetraline/naphthalene ratio
		Gases	Asphaltenes	Petrolenes	
		*Hydropyrolysis of coal**			
Absent	50	18.4	1.6	30.0	–
Hematite	58	19.6	2.1	36.3	–
Pyrrhotite	60	21.3	2.4	36.3	–
Supported	50	17.4	1.8	30.8	–
		Hydrogenation in tetraline environment			
Absent	57	14.8	1.4	40.8	0.56
Hematite (3.3 mass %)**	85	21.4	9.3	54.3	0.38
Pyrrhotite (3.1 mass %)**	89	16.9	11.1	61.0	0.41
Supported (3.0 mass %)**	52	15.6	2.8	33.6	0.69

*Hydrogen pressure in autoclave before experiment: 6.0 MPa.

**Iron content per coal mass.

latter compounds donate hydrogen during thermal destruction of coal.

It was established that the high degrees of OMC conversion and the high yield of distillate products are achieved during hydrogenation of brown coal not only in the case of the combination of optimal methods of activation of iron ore catalysts and their introduction into the raw material but also due to the use of paste-forming agent with the maximal hydrogen donating ability.

Joint thermal destructive hydrogenation of brown coal and polyolefins in the presence of iron ore catalysts

It was shown previously [33, 34] that the joint thermal transformations of fossil coal with synthetic polymers can be used to enhance the yield and the quality of the resulting liquid products. Such polymers as polyethylene, polypropylene, polystyrene with the high H/C ratio are able to act as the sources of hydrogen in these processes.

It was shown that synergic effects are observed in the joint thermal transformations of brown coal and synthetic polymers; these effects point to the chemical interaction of the products of transformations of mixture components. In particular, during joint pyrolysis in the atmosphere of hydrogen, the degree of coal conversion increases substantially with an increase in the mass concentration of polyolefin in the reaction mixture (from 52 mass % in the absence of polymer additives to 85 mass % for the mass concentration of polyolefin in the initial raw material 80 %).

The use of ore-originated iron-containing catalysts activated mechanochemically causes an increase in the degree of conversion of the mixture of coal and synthetic polymers under joint hydropyrolysis by 10–13 mass %, while the yield of liquid products increased by 9.4–13.3 mass %.

We studied the composition of liquid products of the joint thermal transformation of brown coal from the Berezovka deposit in KAB with synthetic polymers under autoclave conditions under hydrogen pressure in the presence of dispersed iron ore catalysts.

In these experiments, the fraction of liquid products boiling out below 180 °C (fraction I) was distilled from the autoclave under vacuum; the sampled substances were condensed in a trap cooled with liquid nitrogen. Then the autoclave content was extracted with benzene. The extract purified from the solvent was fractionated by vacuum distillation into products boiling within temperature range 180–350 °C (fraction II) and the residue from distillation with the boiling onset temperature of 350 °C (fraction III).

The concentrations of individual hydrocarbons in the low-boiling fraction were determined by means of gas chromatography-mass spectrometry. The fraction of liquid products boiling within the range 180–350 °C was examined by means of high-efficiency thin layer chromatography, IR and NMR spectroscopy.

It was established that thermal destruction of the mixtures of coal with synthetic polymers is characterized by increased (in comparison with hydrogenation of coal alone) yield of distillate fractions I and II (Table 5). The use of dispersed iron-containing catalysts in these processes causes further increase in the yield of these fractions by a factor of 1.2–1.6. The highest yield of fractions I (36.6 mass %) and II (32.4 mass %) was obtained after hydropyrolysis of the coal/polypropylene mixture in the presence of the catalyst containing pyrrhotite.

The light fraction of liquid products of hydropyrolysis (b.p. <180 °C) contains mainly paraffins C_2–C_{12} (70–75 mass %). The chemical structure of these compounds is determined by the type of the used synthetic polymer. Mainly linear hydrocarbons are formed in hydropyrolysis of coal/polyethylene mixture, while the products of the decomposition of coal/polypropylene mixture are characterized by increased concentration of structural isomers.

The concentration of aromatic hydrocarbons in fraction I increases with an increase in coal content of the initial mixture and reaches 23 mass % for the components ratio in coal/synthetic polymer mixture equal to 80/20. Aromatic compounds are represented mainly by alkyl derivatives of benzene and phenols. The use of catalysts for hydropyrolysis of coal/synthetic polymer mixtures causes a substantial decrease in the concentration of olefin hydrocarbons in this fraction.

According to the data of gas chromatography – mass spectrometry, fraction II has complicated composition, which does not allow us to identify some of the compounds with satisfactory reliability. We established that this fraction of liquid products formed in the joint transformations of coal and polyolefins contains a number of alkyl aromatic and oxygen-containing compounds that are absent from the products of individual decomposition of the components of the mixture. For detailed analysis, fraction II was preliminarily separated into the groups of substances by means of liquid column chromatography.

The compounds extractable with hexane are mainly represented by paraffins and olefins C_{12}–C_{26}. The concentration of these compounds in fraction II increases from 70 to 88 mass % with a decrease in the mass concentration of coal in the mixture under pyrolysis from 80 to 20 %.

In the aromatic part of products, we established the presence of alkyl derivatives of benzene, phenols, and alkyl derivatives of naphthalene and anthracene. The use of catalysts in hydropyrolysis of the mixtures of coal with synthetic polymers is accompanied by a decrease in

TABLE 5

Yield of the fractions of liquid products in the process of thermal transformation of coal/polymer mixture (1 : 1) in the atmosphere of hydrogen (working pressure 8 MPa), mass %

Catalysts	Fraction I (<180 °C)	Fraction II (180–350 °C)	Fraction III (>350 °C)
		Coal/polyethylene mixture	
Absent	9.7	13.2	39.8
Pyrrhotite	16.3	18.4	41.3
Hematite	15.2	17.9	37.0
		Coal/polypropylene mixture	
Absent	24.8	25.7	7.6
Pyrrhotite	36.6	32.4	1.9
Hematite	34.3	30.2	3.5
		Coal	
Absent	5.6	7.5	14.3
Hematite	7.2	11.4	19.4

the intensity of peaks in the regions of polycyclic and heterocyclic compounds in the high performance thin layer chromatograms and an increase in peak intensities in the region of monocyclic compounds. These data agree with the results obtained by means of ^{13}C NMR.

So, hydropyrolysis of the mixtures of coal with synthetic polymers is characterized by increased yield of distillate fractions that can be considered on the basis of their composition as valuable raw material for the production of motor fuel. The use of fine iron ore catalysts in the joint hydropyrolysis causes a sharp decrease in the content of olefins and polycyclic aromatic hydrocarbons in the distillate products.

Modification of the properties of polymer bitumen binders obtained by thermal dissolution of brown coal in black oil

To improve the characteristics of oil bitumen, modifying additives are used. These additives are synthetic thermoplastic polymers and elastomers, as well as the wastes from their production. Under the typical conditions of asphalt production, the dissolution of the majority of synthetic polymer materials in oil bitumen is impeded. Because of this, bitumen modification with synthetic elastomers is preceded by preliminary dissolution of the polymer in organic solvents (usually originating from oil), then the modifying agent is added to the binder. However, this method cannot be used in the case when modifying agents are polymer materials with limited or poor solubility in oil products. These materials include the wastes from the production of oil-resistant kinds of caoutchouc, worked out rubber scrap, including auto tires manufactured on that basis; efficient methods of utilization have not yet been developed for these materials.

We demonstrated previously that high-quality binders for road construction can be obtained by thermal dissolution of brown coal and a number of synthetic polymer materials (polyethylene, polypropylene, wastes from rubber products of different kinds) in the residues of oil distillation at 350–380 °C [35–38]. High-boiling residue containing up to 25 mass % products of polymer thermodestruction corresponded to the requirements of the State Standard (GOST) to oil road bitumen and had the optimal ratio of oil, tar and pyrobitumen. The product can be used as a binder for road construction without separating the non-dissolved part of coal and mineral components from it, which simplifies the technology of its preparation. This method allows one to modify binders using a broad range of polymer materials including those insoluble in oil bitumen at moderate temperatures.

Development and production of modifying agents suitable for transportation over large distances and able to mix well with oil bitumen at 120–180 °C directly during the preparation of asphalt are of substantial practical interest. For this purpose, investigation of the solubility of oil-resistant caoutchouc in the liquid products of coal thermal transformation was performed. These products differ from the products of oil origin by increased concentration of aromatic hydrocarbons.

It was established that the optimal concentration of the polymer in solution (modifying agent for bitumen) is 25–30 mass %. In this case, the dissolution proceeds rapidly (for less than 1 h), while the resulting modifying agent is well mixed with oil bitumen during heating. Bitumen samples modified with caoutchouc-containing components are characterized by increased concentration of pyrobitumen and tar. Pyrobitumen provides the hardness of bitumen and high softening temperature, while tar provides malleability and elasticity. Experimental tests showed that the modifying agents obtained by the dissolution of oil-resistant caoutchouc and wastes of its production (coagulum) in the products of semicarbonization of coal and thermal dissolution of brown coal decrease the brittle temperature of bitumen and increase extensibility, especially at 0 °C (Fig. 5). Due to this, it is possible to obtain asphalt concrete stable against the formation of cracks during winter.

It was shown that fine-grained rubble asphalt/concrete mixtures prepared using the modified binder of optimal composition are characterized by a substantial increase in the compression strength at 20 and 50 °C, as well as by the higher water resistance coefficient for short-term (1 day) and long-term (14 and 30 days) saturation with water in comparison with the mixtures based on initial bitumen.

Asphalt concrete with the optimal content of modifying agents based on oil-resistant ca-

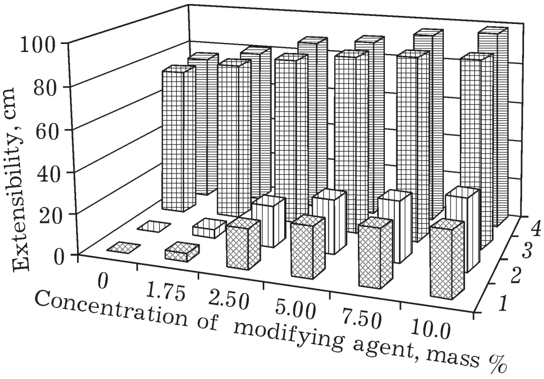

Fig. 5. Dependence of extensibility of composite binder on the concentration of modifying agent at 0 (*1*, *2*) and 25 °C (*3*, *4*): *1*, *3* – bitumen + modifying agent 1 (30 mass % coagulum + 70 mass % coal char tar); *2*, *4* – bitumen + modifying agent 2 (30 mass % caoutchouc + 70 mass % high boiling products of thermal dissolution of brown coal in oil black).

outchouc in the composite binder (2.5–5.0 mass %) exceeds the requirements of GOST 9128–97 and can be used for making the upper layers of road paving.

CONCLUSION

Russian Federation lags behind industrially developed countries in the area of technologies for obtaining synthetic fuel from coal. However, it is Russia where the necessity to develop the industry of synthetic fuel from coal becomes increasingly urgent due to a number of reasons, such as an increase in the cost of oil mining, difficulties of transportation of cheap coal from Siberia to the central regions of the country, ecological limitations for large-scale combustion of coal near mining sites with subsequent transmission of electric power over large distances.

The most suitable coal basis for the development of industrial plants engaged in fine processing of coal is the Kansk-Achinsk brown coal basin. Brown coal from the KAB has the lowest prime cost in RF but it is a low-quality energy raw material and is poorly suitable for long-range transportation. However, the high reactivity of brown coal provides the reasonability of using it for fine processing.

The most promising directions of fine processing of Kansk-Achinsk coal is to obtain refines solid fuel and synthesis gas. The brown coal char is transportable and ecologically safer fuel; it is used as carbon reducing agents in ferrous and nonferrous metallurgy, cheap carbon sorbents, and raw material for the production of synthesis gas.

Methanol or dimethyl ether obtained from synthesis gas is necessary for petroleum chemical industry and for the production of motor fuel. Synthesis gas can be processed at the site or transported through pipelines to the neighbouring regions from the Krasnoyarsk Territory.

An optimal version seems to be the development of a technology of SASOL type which is based on coal gasification and the treatment of the resulting synthesis gas to obtain motor fuel and chemical products. This technology has passed long-term industrial tests in the Republic of South Africa (the first plant was put into operation in 1955, today the plants of total capacity about 4.5 mln t of liquid products per year are functioning) [39].

A promising direction of processing the KAB coal is also its thermodissolution with the formation of coal oil. A plant manufacturing liquid fuel by means of coal hydrogenation has been built in China recently [40].

As a result of investigations performed at the ICCT, SB RAS, in the area of development of the technologies aimed at obtaining synthetic fuel from brown coal of the Kansk-Achinsk basin, more efficient processes than the conventional ones have been proposed: autothermal pyrolysis and gasification of brown coal in reactors with the fluidized bed of catalytically active slag, production of liquid fuel and binders for road construction by means of thermal dissolution of coal and its mixtures with carbon-containing wastes in the presence of activated iron ore catalysts [25, 41–45].

It is reasonable to involve the new generation of the developed processes of obtaining synthetic fuel from brown coal for the creation of industrial technologies of fine processing of KAB coal.

REFERENCES

1 Fedorov N. A., *Chem. Sust. Dev.*, 4, 4 (1996) 459.
2 Sevastyanov V. N., Butkin V. D., Kuznetsov B. N., Protsaylo M. Ya., Belyakova G. Ya., Pchelintsev O. S.,

Nozdrina N. I., Velikiy P. P., Isaev A. S., Protopopov V. V., Kochetkov A. V., Belyakov G. P., KATEK: Poisk Vedet Nauka, Krasnoyarsk, 1984.

3 Whitehurst D. D., Mitchell T. O., Farcasiu M., Coal Liquefaction, Acad. Press, NY, 1980.

4 Schilling H.-D., Bonn B., Kraub U., Kohlenvergasung, Verlag Gluckauf GmbH, Essen, 1981.

5 Kuznetsov B. N., Kataliz Khimicheskikh Prevrashcheniy Uglya i Biomassy, Nauka, Novosibirsk, 1990.

6 Kuznetsov B. N., *Izv. RAN. Ser. Khim.*, 5 (1994) 792.

7 Kuznetsov B. N., *Khim. Ust Razv.*, 9, 4 (2001) 443.

8 Kuznetsov B. N., *Int. J. Hydr. Energy*, 34 (2009) 7057.

9 Kuznetsov B. N., *Kinetika i Kataliz*, 50, 6 (2009) 886.

10 Kuznetsov B. N., *Kataliz v Prom.*, 3 (2009) 69.

11 Panov V. I., Povysheniye Elektroenergetiki za Schet Energotekhnologicheskikh Skhem Toplivoispolzovaniya, VINITI, Moscow, 1975.

12 Smirnova T. S., Kirsanov V. I., Markina T. I., Zyryanov V. M., Sinteticheskiye Topliva iz Ugley, Moscow, 1984, p. 110.

13 Fomin A. P., Enik G. I., Kler D. V., Zaytseva G. N., *Khim. Tv. Topl.*, 6 (1992) 98.

14 Shchipko M. L., Kuznetsov B. N., *Chem. Sust. Dev.*, 5, 2 (1997) 209.

15 Shchipko M. L., Kuznetsov B. N., *Fuel*, 74 (1995) 751.

16 Shchipko M. L., Kuznetsov B. N., *Fuel*, 77 (1998) 527.

17 Veprikova E. V., Rudkovskiy, Shchipko M. L., Kuznetsov B. N., *Khim. Khim. Tekhnol.*, 48, 8 (2005) 70.

18 Shchipko M. L., Kuznetsov B. N., Volova T. G., Rudkovskiy A. V., *Khim. Tv. Topl.*, 5 (2003) 58.

19 Shabanov V. F., Kuznetsov B. N., Shchipko M. L., Volova T. G., Pavlov V. F., Fundamentalnye Osnovy Kompleksnoy Pererabotki Ugley Kateka dlya Polucheniya Energii, Izd-vo SO RAN, Novosibirsk, 2005.

20 Fan Xiaoxu, Lu Qinggang, Na Yongjie, Liu Qi, *J. Therm. Sci.*, 16, 3 (2007) 277.

21 Sanz A., Corella J., *Fuel Proc. Technol.,* 87 (2006) 47.

22 Shchipko M. L., Kuznetsov B. N., VII Vseros. Konf. “Goreniye Tverdogo Topliva” (Proceedings), Novosibirsk, 2009, vol. 3, pp. 76–82.

23 Aznar M. P., Caballero M. A., Corella J., Molina G., Toledo J. M., *Energy and Fuels*, 20, 3 (2006) 1305.

24 Herguido J., Corella J., Gonzalez-Saiz J., *Ind. Eng. Chem. Res.*, 31 (1992) 1274.

25 RU Pat. No. 2333929, 2008.

26 Kuznetsov B. N., Sharypov V. I., *Kataliz v Prom.*, 5 (2007) 51.

27 Yu. Falbe (Ed.), Khimicheskiye Veshchestva iz Uglya, Khimiya, Moscow, 1980.

28 Sharypov V. I., Baryshnikov S. V., Chumakov V. G., Beregovtsova N. G., Moiseeva G. A., Kuznetsov B. N., *Khim. Tv. Topl.*, 6 (1995) 39.

29 Sharypov V. I., Baryshnikov S. V., Beregovtsova N. G., Skvortsova G. P., Pavlenko N. I., Kuznetsov B. N., *Khim. Tv. Topl.*, 3 (1996) 134.

30 Sharypov V. I, Kuznetsov B. N, Beregovtsova N. G., Reshetnikov O. L., Baryshnikov S. V., *Fuel*, 1 (1996) 39.

31 Kuznetsov B. N., Sharypov V. I., Baryshnikov S. V., Beregovtsova N. G., *Khim. Ust Razv.*, 7, 6 (1999) 687.

32 Sharypov V. I., Kuznetsov B. N., Baryshnikov S. V., Beregovtsova N. G., Selyutin G.E., Chumakov V. G., Kamianov V. F., *Fuel*, 6 (1999) 663.

33 Sharypov V. I., Kuznetsov B. N., Golovin A. V., Sidelnikov V. N., Doroginskaya A. N., Beregovtsova N. G., Baryshnikov S. V., *Khim. Ust Razv.*, 5, 2 (1997) 201.

34 Sharypov V. I., Beregovtsova N. G., Kuznetsov B. N., Cebolla V. L., Collura S., Finqueneisel G., Zimmy T., Weber J. V., *J. Anal. Appl. Pyrol.*, 78 (2007) 257.

35 Sharypov V. I., Beregovtsova N. G., Kuznetsov B. N., Baryshnikov S. V., IX Mezhdunar. Nauch.-Prakt. Konf. “Khimiya – XXI vek: Novye Tekhnologii, Novye Produkty” (Proceedings), Kemerovo, 2006, pp. 239–242.

36 Kuznetsov B. N., Sharypov V. I., Beregovtsova N. G., Baryshnikov S. V., 5 Mezhdunar. Kongr. po Upravleniyu Otkhodami i Prirodookhrannym Tekhnologiyam “WasteTech-2007” (Proceedings), Moscow, 2007, pp. 168–169.

37 Sharypov V. I., Baryshnikov S. V., Kiselev V. P., Beregovtsova N. G., Bugaenko M. B., Kuznetsov B. N., IX Mezhdunar. Nauch.-Prakt. Konf. “Khimiya – XXI vek: Novye Tekhnologii, Novye Produkty” (Proceedings), Kemerovo, 2008, pp. 224–226.

38 Sharypov V. I., Kiselev V. P., Beregovtsova N. G., Baryshnikov S. V., Kuznetsov B. N., III Mezhdunar. Nauch.-Prakt. Konf. “Prioritety i Osobennosti Razvitiya Baikalskogo Regiona” (Proceedings), Ulan Ude, 2008, pp. 328–331.

39 Nierop P., Erasmus H. B., Zyl J. W., Book of Proc. “2000 Gasification Technologies Council”, San Francisco, USA, 2000.

40 Jerald J. F., Qingyun S., Richard A. B., Yuzhuo Z., Xiangkun R., Book of Proc. “Twenty-First Annual Int. Pittsburg Coal Conf.”, Osaka, Japan, 2004.

41 RU Pat. No. 2333930, 2008.

42 RU Pat. No. 2330053, 2008.

43 RU Pat. No. 2131904, 1999.

44 RU Pat. No. 2159791, 1999.

45 RU Pat. No. 2103317, 1998.