Chemistry for Sustainable Development **15** (2007) 691–697

Comparison of Heat Treatment Processes for Barzas Sapromixite and Brown Coal in Various Gas Media

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(Received June 17, 2007; revised October 24, 2007)

Abstract

Thermal conversions of sapromixite from Barzas deposit in an inert medium, hydrogen medium, and that of synthesis gas have been studied in a flow-through reactor under atmospheric pressure and in an autoclave under a pressure of up to 7 MPa. A higher conversion level of brown coal as compared with sapromixite is determined by a low metamorphic degree of brown coal and by its high content of highly reactive oxygen-bearing fragments. However, the yield of resins from sapromixite in a temperature range of 450–850 °C is 3-4 times higher when compared to the yield from brown coal. It has been found that an increased yield of resins under variations in heat treatment conditions is caused for the most part by a decrease in the formation of gases and water. The yield of semicoke has no any significant changes. The process flow diagram has been suggested that explains the observed effects. It has been demonstrated that unlike heat treatment in an autoclave, when employing a flow-through reactor and atmospheric pressure, the composition of the gas medium has no tangible effect on the conversion level of combustible. Meanwhile, the liquid yield at a temperature of devolatilization of coal, 650 °C, in a current of hydrogen and synthesis gas is at least 1.5 times higher by comparison to the yield in devolatilization of coal in an inert medium. A procedure of devolatilization of sapromixite has been suggested that affords an enhanced liquid yield as compared with the conventional process by way of using the products of gasification of a fixed residue of the process as the gas heat carrier.

INTRODUCTION

Devolatilization of coal, i.e. its heating to 500–550 °C with no air access, requires the least expenses (calculated per one ton of the raw material) when compared to alternative technologies of high-level processing of solid combustible minerals [1, 2]. Main products of devolatilization of coal are combustible gas, resin, and semicoke. The basic purpose of coal devolatilization processes in the technologies that were developed in the 19th century was generation of fuel gas that was in use for urban lighting. Later, the emphasis shifted towards generation of liquid products. To take an example, the procedure of devolatilization of coal has been used to process ~30 million tons of coal in Germany in 1944, 2 million tons of resin has been produced, from which 1.3 million tons of petrol has been received by hydrogenation [3]. As of now, different ways of devolatilization of coal are now being applied on the industrial scale to yield mostly solid products from humic coals [4–10].

One of the differences of sapropelite coals from humic consists in a higher (by the factor of 3–5) yield of primary resin from devolatilization of coal [11–14]. Sapropelites constitute transformation products of a biomass of inferior plants from salty water bodies. The biomass contains more hydrogen and less oxygen, than does the initial vegetative material from which humic coals were formed. By virtue of the fact that the initial vegetative material is practically free of any aromatic compounds, the proportion of carbon in sapropelite coals that is bonded within aromatic structures is significantly less, than it is in humic coals that are analogous in their metamorphism stage. The structure of aliphatic compounds that is the main component of organic matter of sapropelite coals contains long methylene (up to C_{33}) chains in great quantity. Carbon chains in the macromolecules are connected among themselves by heteroatomic bonds that are dominated by simple ethereous bonds [15–17]. Polynaphthen prevails in the organic mass of sapropelites. This component is a source of naphthenic and paraffin hydrocarbons that are formed during the devolatilization of coal [18, 19].

In this relation, sapropelite coals are more promising than humic coals to yield liquid organic products by the procedure of devolatilization of coal. The assessment of resources of sapropelite coals as raw material to manufacture synthetic liquid fuels (SLF) has been performed in the first half of past century. In the territory of Siberia, Budagovskoye deposit of sapropelites (Irkutsk Region) and Barzas deposit of sapromixite (Kemerovo Region) with the confirmed reserves of sapropelites of 20–30 million ton each have been recognized to hold promise. Explorations that are more recent have demonstrated that the number of deposits with reserves of sapropelite coals may be substantially greater [12, 20].

Today, several variations of the process of devolatilization of coal for mineral fuels have been developed [1, 3, 4, 6, 7]; however, all of them are of power consuming nature (the appropriate amount of heat comprises 1200–1500 kJ/kg of raw material). Meanwhile, approximately one-half of the applied heat is consumed to compensate endothermic effects of pyrolysis, and the remaining heat is expended to dry, to heat the fuel, and as heat losses. Devices of devolatilization of coal are subdivided into furnaces with external and internal heating [1, 3, 4, 21]. In the furnaces with external heating, the heat from combustion zone enters into coal devolatilization zone through the wall of the reaction chamber. In furnaces with internal heating, a preheated gaseous or solid heat transfer medium is introduced in the coal devolatilization zone. Development of the variants of the technology of coal devolatilization with the internal heat input that depend on the application of solid heat transfer media (ceramic particles, coke, ashes, metal balls [1–4, 22, 23]) is in progress. In this case, it becomes possible to ensure an intensive heat exchange and to produce steam-gas mixtures that are not diluted with flue gases.

The purpose of this work is a comparative study of the effect of a gaseous medium that is applied as the heat transfer medium on the liquid yield of devolatilization of sapromixite and brown coal.

EXPERIMENTAL

The sample of sapromixite coal has been taken from Barzas deposit (bed sample). For comparison, we used humic coal from the Borodino deposit of Kansk-Achinsk field. The samples of coals were kept in a tight tare (in the nitrogen atmosphere) at ambient temperature from the moment of sampling up to its application in the experiment. Coals were grinded in a disintegrator 8255 Nossen (Germany) before the application. Particle size distribution: >3 mm – 0.4–0.9 %, 1–3 mm – 47–57 %, 0.25–1 mm – 23–32 %, <0.25 mm – 18–21 %. Composition of the initial coals is given in Table 1. The process of devolatilization of coal was conducted in a set-up (the reactor capacity of 150 mL, the height of the coal layer of ~8 cm) that has been made from stainless steel and that was equipped with a system of programmed heating at a rate from 2 to 100 °C/min, the heating rate in this work was 10 °C/min. Heating was performed from the room temperature to reach a preassigned temperature that was varied during the experiments. The sample exposition at a given temperature measured 30 min in all cases. Besides the main reactor, the set-up included coolers and collection containers for liquid and gaseous products. Heat treatment of samples was performed in the current of preheated argon (the model of

TABLE 1

Characteristics and composition of coals, %

Parameter	Barzas sapromixite	Borodino coal
Water content W^r	17.3	31.3
Percentage of ash A^d	26.5	7.1
Volatile-matter content V^{daf}	51.3	46.8
Carbon C^{daf}	77.9	71.2
Hydrogen H^{daf}	7.5	4.8
Nitrogen N^{daf}	1.5	0.8
Sulphur S^{daf}	0.6	0.2
Oxygen O^{daf} (from the difference)	12.5	23.0

the conventional process of devolatilization of coal with the gas heat transfer medium), in the current of hydrogen (hydropyrolysis under atmospheric pressure), and in the current of synthesis gas that was produced by steam-oxygen gasification of a fixed residue from devolatilization of sapromixite. Experiments were conducted with the flow rate of the gas heat transfer medium (24±2) L/h that ensures the maximum yield of resins at the given set-up. The coal devolatilization procedure is described in more detail in the work [19].

Gasification occurred in a reactor that is analogous to the reactor of devolatilization of coal at the oxygen : steam ratio that was equal to 1 : 3, and at the temperature (780±10) °C. The produced synthesis gas was collected in a gas collector and then applied in coal devolatilization experiments. Composition of synthesis gas (vol. %): H_2 66.5, CO 32.4, CH_4 1.1.

Investigation of thermal decomposition of sapromixite at an elevated pressure of argon and hydrogen was conducted in a rotating autoclave with the capacity of 0.25 L by the procedure that is described in [24]. 10 g of coal that had been dried at 100 °C to reach the water content of <1 mass %, with the particle size of <0.1 mm was loaded into an autoclave. Before the beginning of the experiment, the autoclave was blown through with argon for deaerating. An initial pressure of argon in the tests on thermal dissolving of coals in argon measured 0.3 MPa, the preassigned initial pressure of hydrogen in hydropyrolysis was 3.0 MPa. The respective operating pressure in the autoclave at the process temperature of 430 °C was 1.0 and 7.0 MPa. The heated autoclave was held at a process temperature over the course of 1 h.

Composition of the produced gas was determined with the use of a LKHM-80 chromatograph. Separation of ingredients was conducted serially with columns (the length of 3 m) that were filled with molecular sieves NaX and with absorbent carbon AG-3, at the temperature of columns of 50 °C. The detector was a katharometer, the temperature of the detector was 50 °C; the carrier gas was helium.

Composition of initial coal, resin, and semicoke was determined by the procedures [22, 25].

RESULTS AND DISCUSSION

Dispersion, standard deviation, and confidence interval that characterize the accuracy of the experiment have been determined in the first stage of the experiments. The received statistical characteristics are given in Table 2. By virtue of the fact that experiments with all gases were conducted with identical coal batches

TABLE 2

Statistical treatment of experimental results for devolatilization of Barzas sapromixite with the gas heat transfer medium (argon, 570 °C, exposition for 1 h)

Experiment No.	Yield, mass %			
	Semicoke	Resin	Water	Gas
1	56.9	12.9	3.9	26.3
2	57.1	13.3	5.2	24.4
3	56.3	13.1	4.8	25.8
4	57.1	12.7	3.3	26.9
5	55.9	13.4	3.9	26.8
6	55.6	14.1	3.3	27.0
7	56.8	13.2	3.6	26.4
8	56.3	14.3	4.5	24.9
9	56.4	13.0	3.4	27.2
10	56.8	13.5	3.7	26.0
Average (M_y)	56.4	13.4	4.1	26.0
Dispersion (s^2)	0.2910	0.2102	0.3933	0.7657
Confidence interval for the probability of 0.95 (±)	0.4	0.4	0.5	0.6

(of sapromixite and brown coal), with the same equipment and during an identical time interval, the statistical characteristics that are given in Table 2 can be applied for all gas heat transfer media.

Figure 1 shows the plot of conversion level *versus* the temperature of devolatilization of brown coal in an inert medium and that of sapromixite in the medium of inert gas, hydrogen, and synthesis gas. Conversion level was calculated as the loss of organic mass of the sample. It is evident that the type of gas heat carrier has no considerable effect on the character of change and conversion level of sapromixite. Experimental data on thermodecomposition of sapromixite can be well described by a general expression as a second order polynom (see Fig. 1) at the approximation reliability $R^2 = 0.96$. The maximum conversion level at heat treatment in a current of gas heat carrier is as great as 59.5 % at 850 °C.

A higher conversion level of brown coal as compared with sapromixite is caused by its high content of highly reactive oxygen-bearing fragments.

It is worth noting also that conversion level for fuel under conditions of a standard determination procedure of volatile matter content (a crucible with a ground-in cover, 850 °C, the exposition of 7 min) for sapromixite is lower by an average of 7 % than that in a flow-through reactor at the same temperature. This difference ranges up to 13 % for brown coal. It appears that it is caused by the secondary pyrolysis of volatile matter in the crucible and by the formation of an additional quantity of a solid product whereas volatile matter in the flow-through reactor is quickly lift out of the body of the pyrolysis sample with the gas heat transfer medium.

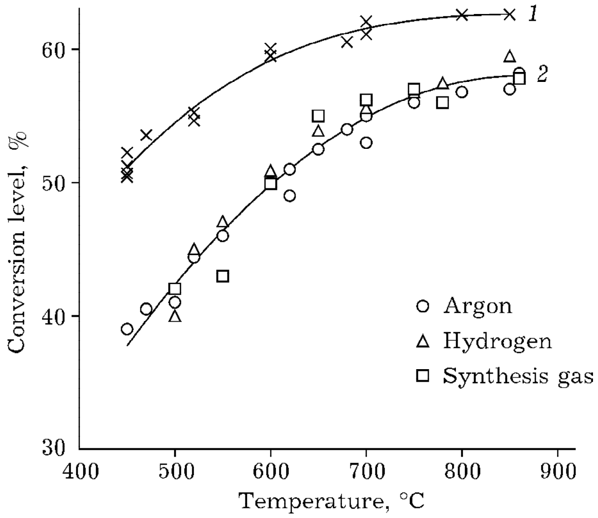

Fig. 1. Plot of conversion level of brown coal in the medium of argon *(1)* and Barzas sapromixite in various gas media *(2)* *vs.* the process temperature.

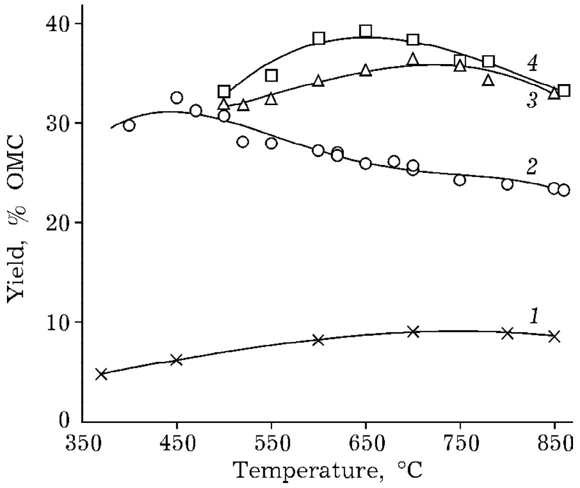

Fig. 2. Plot of yield of resins *vs.* the treatment temperature of brown coal and Barzas sapromixite in various gas media: *1* – brown coal in the medium of argon, *2–4* – sapromixite in the medium of argon (*2*), hydrogen (*3*), and synthesis gas (*4*).

Shown in Fig. 2 is an effect of composition of gaseous atmosphere on the yield of resins with coal devolatilization process. The maximum yield of resins in an inert medium (32.5 % per organic mass of coal) is evidenced at a temperature of ~450 °C. In a current of hydrogen, the maximum yield of resins comprises 36.4 % at a temperature of 700 °C; in a current of synthesis gas, 39.2 % at 650 °C. Composition of gas media exerts an essential influence not only on the yield, but also on the dynamics of the formation of resins. The maximum yield of resins in the medium of hydrogen and synthesis gas shifts in the region of high temperatures. At 650 °C, the yield of resins that have been produced in a current of synthesis gas and hydrogen is approximately 1.5 times higher when compared to the yield of resins that have been produced in a current of argon. The yield of resins from brown coal throughout the temperature range is 3–4 times lower as compared with the yield of resins from sapromixite. The decrease of this magnitude at high temperatures with reference to the maximum is less considerable for brown coal, than for sapromixite (4.5 and ~15 rel. %, respectively).

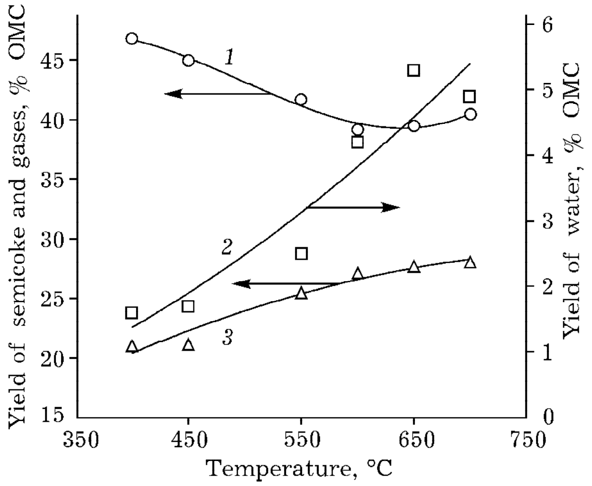

Fig. 3. Plot of yield of semicoke (*1*), pyrogenous water (*2*), and gases (*3*) during devolatilization of Barzas sapromixite in the medium of argon.

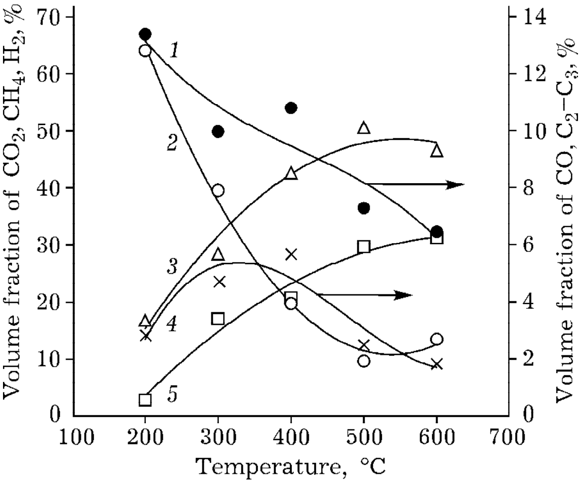

Fig. 4. Composition of gaseous products of pyrolysis of Barzas sapromixite at various temperatures. The heating rate 10 °C/min, the flow rate of argon of 24 L/h, duration of sampling for one sample 0.5–1.0 min, water from the sample was removed by cooling down to ambient temperature: *1* – CO, *2* – CO_2, *3* – CH_4, *4* – C_2–C_3, *5* – H_2.

Curves of dependence of variation in the yield of main products in thermodecomposition of sapromixite on the temperature are kindred for all gas media. Figure 3 presents typical dependences that have been received in an inert medium. It is evident that an increase of the process temperature above a certain value leads to a decreased yield of resins with an appropriate growth of the yield of pyrogenous water and gas. It is significant that composition of the gas medium in these conditions has no considerable effect on the yield of semicoke that amounted to (39±0.5) mass % at 650 °C for all gas heat carriers that have been used.

Correlation of these results with data in Fig. 1 allows an inference that the gain in the yield of liquid organic products under heat treatment in the medium of hydrogen and synthesis gas is caused by secondary reactions that occur with volatile matter of coal in the gas phase. The additional quantity of water and gases arises apparently by destruction of resins, which is indirectly supported by an increase in the content of methane and hydrogen in the pyrolysis gases with an increase of the process temperature (Fig. 4). It may be suggested on the basis of the data acquired that the main products of the secondary pyrolysis of resins from Barzas sapromixite are water and gaseous products, and the proportion of semicoke that has arisen again is insignificant.

Being thermally decomposed under autoclave conditions in the medium of argon, sapromixite exhibited the maximum conversion level of its organic mass into benzene-extractable products at 430 °C. A rise in the process temperature, similarly to devolatilization of coal in a flow-through set-up, was followed by a decrease of liquid yield and by an increase in the formation of a solid non-extractable residue. It appears that this is related to the fact that an intensification of secondary reactions of conversion to yield semicoke for the liquid products that have already arisen occurs with an increase of temperature.

TABLE 3

Conversion level and yield of sapromixite pyrolisis products in an autoclave at 430 °C, mass %

Conditions of the process	Conversion level	Liquid yield with b.p.	
		<180 °C	>180 °C
Pyrolysis in argon (*P* = 1.0 MPa)	62	3.5	45.9
Pyrolysis in hydrogen (*P* = 7.0 MPa)	69	9.0	39.0

Table 3 gives results of experiments on heat treatment of sapromixite in an autoclave. Conversion level of sapromixite in the medium of hydrogen at the pressure of 7.0 MPa is higher by comparison to the conversion in argon medium. Coincidentally with this, an increase in the yield of volatile fraction takes place and the yield of the products that boil off at the temperatures higher than 180 °C drops. In-depth study of liquid products of thermodecomposition of sapromixite has demonstrated [26, 27] that with the availability of hydrogen in the system, hydrogenation of the formed liquid components proceeds even without application of catalysts.

The gain in the yield of resins (of final liquid products) with the use of hydrogen and synthesis gas is indicative of an essential effect of the medium of devolatilization of coal on conversion processes for primary liquid products. A minor change of the yield of semicoke in various media in a flow-through reactor is caused apparently by structural features of organic mass of Barzas sapromixite. Meanwhile, the observed gain in the yield of liquid organic products in reducing gases is related to the decreased yield of pyrolysis gases, *i.e.* hydrogen and synthesis gas will hinder the decomposition of primary liquid products. In particular, the decrease of the yield of carbon monoxides (see Fig. 4, curves *1* and *5*) in gaseous products of the devolatilization of coal that is observed with an increase of the process temperature may be determined by polyreactions.

It is common knowledge that thermal degradation of coal runs through a radical mechanism [1, 28]. Organic matter of Barzas sapromixite is typified mostly by non-aromatic structure and availability of a sufficiently long (more than 30 carbon atoms) hydrocarbon chains. An assumption can be made that primary products that have been formed from it undergo further conversion according to a radical mechanism of destruction of polyolefin hydrocarbons [29]. Starting from this concept, the gain in the yield of resins in the medium of hydrogen and synthesis gas is attributable to the gas phase interaction of hydrogen and synthesis gas with radical fragments that arise from coal and primary liquid products. The resulting of this interaction is that their saturation and loss of the activity occurs. These gases play a part of inhibitors for free-radical reactions of destruction of liquid products, which involves a gain in the yield of the last-mentioned and a shift of the maximum of their formation towards the region of high temperatures.

Semicokes of Barzas sapromixite are distinguished throughout the studied interval of temperatures for their low mechanical strength and they manifest practically no any sorption activity. Meanwhile, they preserve fairly high combustion heat (from 16.9 to 18.5 MJ/kg), which enables their use as powdered fuel or the raw material to yield synthesis gas. By virtue of the fact that devolatilization of coal in the medium of synthesis gas ensures the maximum yield of resins, a new process of devolatilization of Barzas sapromixite has been developed on this basis that is distinguished for its higher liquid yield from analogous processes [30]. Its essence consists in the fact that the gas heat carrier that heats up coal at the stage of devolatilization contains hydrogen and carbon monoxide that is generated, in its turn, through gasification of semicoke by air and steam mixture.

CONCLUSION

It has been demonstrated that unlike processes of heat treatment of Barzas sapromixite in an autoclave, the composition of gaseous atmosphere with a flow-through reactor and atmospheric pressure has no tangible effect on the conversion level of combustible. Meanwhile, the yield of organic liquid products in a current of hydrogen and synthesis gas at a temperature of devolatilization of coal, 650 °C that is most often used in conventional technologies is at least 1.5 times higher by comparison to the traditional process.

A higher conversion level of brown coal as compared with sapromixite is determined by a lower metamorphic degree of brown coal and by its high content of highly reactive oxygen-bearing fragments. Meanwhile, the yield of resins from sapromixite in a temperature range of 450–850 °C is 3-4 times higher when compared to the yield of resins from brown coal.

It has been found that an increased yield of resins under variations in heat treatment conditions occurs preferentially due to a decrease in the formation of gases and water. Meanwhile, the yield of semicoke has no any significant changes.

A procedure of devolatilization of sapromixite has been suggested that affords an enhanced liquid yield as compared with the conventional process by way of using the products of gasification of a fixed residue of the process as the gas heat carrier.

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