

## Development of Complex Technologies for Biomass Processing

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**Abstract**—There are presented two technologies of biomass processing. One technology is concerned with manufacture of hydrogen and pure carbon materials. It based on the process of heterogeneous pyrolysis of gaseous hydrocarbons during filtration through porous medium. As a porous material it is suggested to apply a charcoal formed as a result of thermal processing of biomass (wood, peat and agricultural waste). The advantages of this technology are the waste-less character of biomass processing and wide range of the end products. Another technology is a technology of conversion of biomass into synthesis gas. The experimental data on quantity and composition of the gaseous products formed in the process of thermal treatment of wood and peat are presented. It is shown that as a result of peat and wood pyrolysis and the subsequent cracking of emanating products at temperature 1000 °C it is possible to produce about 1.4 m<sup>3</sup> of gas with calorific value 11.7 MJ/m<sup>3</sup> from one kg of original raw material.

**Keywords**- biomass, pyrolysis, pyrocarbon, syngas, hydrogen

### I. INTRODUCTION

Today utilization of biomass for power engineering in most cases is more expensive, than use of traditional fossil fuels. As a result a biomass can be competitive in the market of power resources only under the condition of state budgetary support. Under the global financial and economic crisis a budgetary support becomes problematic.

In present conditions, any scientific and technical activity in the field of energy supply should be based on two basic principles:

- full-scale mutually beneficial international cooperation;
- attractiveness of developing technologies to investors both from the economic and ecological points of view.

The first principle will provide for integration of experimental possibilities and intellectual efforts of specialists from different countries. Such integration will be the guarantor of the common successes. Practical realization of the second principle can be successful only at complex processing of a biomass with production of a wide range of the commodity output which are in popular demand in the market, namely: gaseous and liquid fuels, including hydrogen, and also carbon materials with predetermined properties – active carbon, coke, pyrocarbon.

The role of Russia in the development of the international cooperation should be considerable as there is concentrated about 42 % of peat and about 23 % of wood world reserves in Russia. Use of peat and wood waste does not demand

preliminary expenses for biomass growing, soil recultivation and other nonproduction expenses. The level of scientific and technical workings in Russia gives opportunity to hope for development of economically justified technologies of biomass utilization for power engineering. Application of biomass complex processing technologies which are developing today in Russia will allow to satisfy the requirements of Russian and partially international markets in ecologically clean fuels. Now Russia one of the main supplier of the fossil fuels on the foreign market and in the future it can make the essential contribution to formation of biofuel market and can become one of the major biofuel exporter.

Technologies of complex thermal biomass processing developed in Joint Institute for High Temperatures of Russian Academy of Sciences (JIHT) are stated below. Both technologies are based on pyrolysis of such raw materials as wood and peat and agricultural waste. Distinction between these technologies consists in the end products which can be obtained. One technology is the technology of complex processing of biomass with production of technical hydrogen and pure carbon materials [1, 2] and another is the wasteless technology of biomass processing with production of high-calorific gas fuel [3].

The main features of technologies under consideration, characteristics of end products and results of experimental investigations substantiating these technologies are presented and discussed.

### II. PRODUCTION OF CARBON COMPOSITE AND TECHNICAL HYDROGEN

At the first stage of the technology for production of pure carbon materials and technical hydrogen a raw material (peat, wood or agricultural waste) are heated approximately to a temperature of 600 °C in a gas medium free of oxygen. As a result there is produced a charcoal which is a brittle porous material with the carbon content exceeding 90%. At the second stage a gaseous hydrocarbon is blown through the charcoal bed heated up to the temperature about 1000 °C. For these purpose natural gas, oil gas and waste burning gases of petrochemical manufactures can be used. Passing through the porous carbon structure formed at the first stage, gaseous hydrocarbons decompose into hydrogen and carbon which stuffs the porous carbon matrix and transforms it to a solid composite with carbon content up to 98 %. Carbon materials with such properties are in popular demand in the market.

Produced hydrogen may be used as a pure gas fuel for energy purpose. The both stages of the technology can be carried out in one device.

All methods of hydrogen production for power engineering existing now are not repaying and some financial support is need for its realization. The scheme stated above, when hydrogen production fulfilled simultaneously with the production of pure carbon materials, is paying back, as the price of produced carbon materials covers all expenses for manufacture of hydrogen and its subsequent power use.

The photo of pyrocarbon samples received with the help of the developed technology is presented in Figure 1.

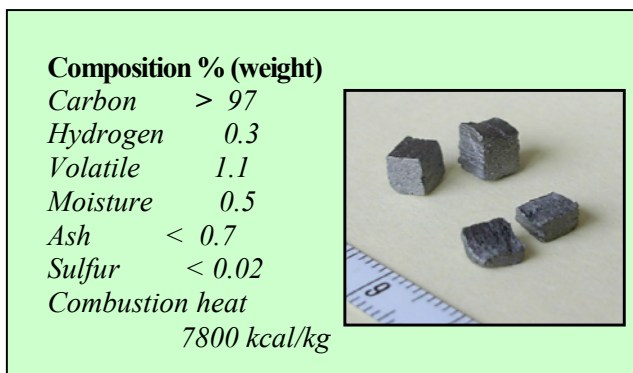


Figure 1. Samples of the carbon composite and their composition.

The results of porosity measurements give the opportunity to imagine a character of structure modification of a sample in process of the heterogeneous pyrolysis of gas hydrocarbons and its final internal structure. Figure 2 shows the time evolution of the volume fraction of open and closed pores of a charcoal sample [4]. One can see that the volume fraction of open pores decreases and the volume fraction of closed pores increases in process of the methane pyrolysis. After 100 minutes the volume fraction of closed pores is practically constant. This fact indicates that after 100 minutes pyrolysis is in progress practically only on outer surface of

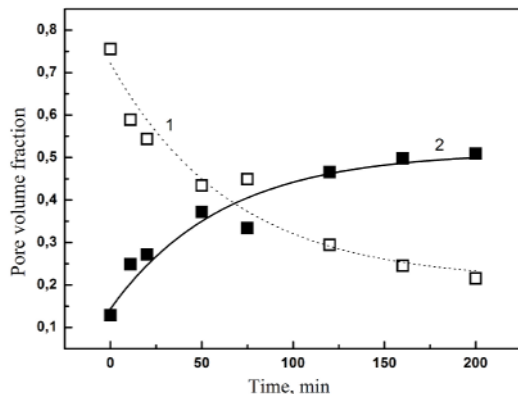


Figure 2. Change of open (1) and closed (2) pore volume fraction of wood char sample in process of methane pyrolysis.

the sample while internal pores become closed for methane diffusion though their volume fraction is about 50%.

The hydrogen content in gaseous products at the exit of reaction volume depends on the operation conditions and may reach 80 – 90 volume percents. The rest is not decomposed gaseous hydrocarbons.

### III. PRODUCTION OF SYNGAS

The second technology of bioconversion is the technology of wasteless production of synthesis gas. Present day technologies of solid hydrocarbon raw materials conversion into gas can be divided on two basic groups: gasification and pyrolysis. During gasification the thermal decomposition of initial raw materials occurs in the oxidizing gas environment and the product gas contains combustion products of raw materials. At air gasification the product gas is also substantially diluted by nitrogen. As a result the combustion heat of gas mixtures produced at gasification usually does not exceed 6 MJ/m<sup>3</sup> usually. Use of such low-calorific gas in the modern power units is ineffectively. Essential improvement of characteristics of power gas produced with the help of existing processes of biomass gasification cannot be received.

During pyrolysis the heating of initial raw materials occurs without oxidizer access. Pyrolysis products are char, noncondensable gases CO<sub>2</sub>, CO, H<sub>2</sub>, CH<sub>4</sub>, C<sub>n</sub>H<sub>m</sub>, N<sub>2</sub> and volatiles. In cooling the volatiles form liquid fraction which consists of tar and pyrolyneous liquor. While pyrolysis makes it possible to produce gas mixtures with a calorific value up to 20 MJ/m<sup>3</sup>, the main demerits of the given method is the presence of the considerable carbon dioxide fraction (up to 30 % volume) in pyrolysis gases and rather low gas yield, which reaches 0.3-0.4 m<sup>3</sup> per kg of initial raw materials at best. As a result the efficiency of energy conversion, determined as the ratio of the product gas thermal value to thermal value of initial raw materials, does not exceed 0.3. Thus, the main objective of technological advancement is an increase of conversion degree of initial raw materials into gas together with conservation of enough high specific combustion heat of product gas mixtures.

The technology of biomass (peat, wood and agricultural waste) thermal processing with production of high calorific power gas developed in the JIHT is based on high-temperature processing of the pyrolysis gases and volatiles. The method is similar to the one suggested in [5] for processing of wood sawdust and used in [3] for processing of wood waste and peat. It consists in filtration of volatiles and gases, forming by pyrolysis of initial raw materials, through the porous carbon bed kept at a fixed temperature  $T_f$  (further this regime is referred to as «pyrolysis with cracking»). As the carbon material (filter) the char obtained as a result of initial raw material carbonization was used. Due to the developed surface of the carbon filter there is a fast heating of volatiles and gases to the temperature  $T_f$ . As a result of homogeneous and heterogeneous chemical reactions in the high-temperature zone an intensive decomposition of pyrolysis gases and volatiles takes place. The conversion degree depends both on the temperature  $T_f$  and the interaction time of volatile products with heated

carbon surface. As follows from the data presented in Figure 3 the increase in the char filter temperature  $T_f$  leads to essential increase in the yield of gaseous products ( $T_c$  – current temperature of processed raw material, heating rate –  $10\text{ }^\circ\text{C}/\text{min}$ ).

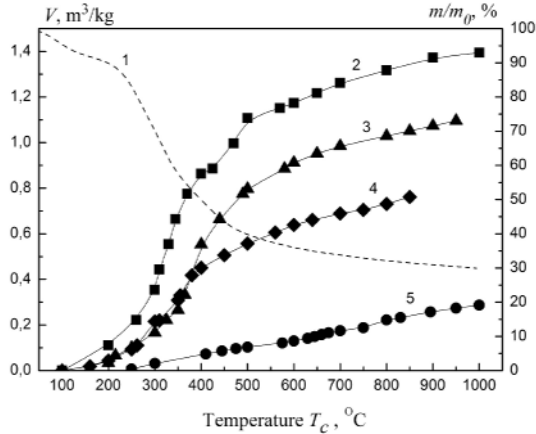


Figure 3. Change in relative mass of raw material (1) and volume gas yield per one kg of raw material (2-5) in heating of peat pellets: regime «pyrolysis with cracking» at  $T_f = 1000\text{ }^\circ\text{C}$  – 2,  $950\text{ }^\circ\text{C}$  – 3,  $850\text{ }^\circ\text{C}$  – 4; regime «pyrolysis» – 5.

Simultaneously with the growth of gas yield the reduction of quantity of the liquid fraction in the end products is observed. For the temperature  $T_f = 1000\text{ }^\circ\text{C}$  there is no liquid fraction that is evidence of full tar and pyrolygneous liquor conversion into gas. Thus during the filtration through the char filter decomposition of the volatiles, forming in process of thermal destruction of raw material and condensing as a tar, takes place. In addition interaction of pyrolytic water with char leads to generation of hydrogen and carbon monoxide.

Change of operating parameters results in change of product gas composition. From results of chromatographic analysis it is follows that carbon dioxide and methane content in the product gas decreases with the rise of the char filter temperature  $T_f$ . Composition, specific combustion heat and volume of gas mixture produced from peat and wood are presented in Table I and II. For temperature  $T_f = 1000\text{ }^\circ\text{C}$  the content of carbon dioxide and methane does not exceed one percent. An increase of the char filter temperature leads to raise the rate of disoxidation of  $\text{CO}_2$  and the rate of heterogeneous pyrolysis of methane and other paraffin hydrocarbons. As a result at  $T_f = 1000\text{ }^\circ\text{C}$  the product gas mixture consists of  $\text{CO}$  and  $\text{H}_2$  in practically equal parts.

From comparison of the Tables I and II data one can see that the specific combustion heat of gas mixtures produced at different operating conditions are rather close to each other. One of the main advantages of the «pyrolysis with cracking» regime is a considerable increase of the volume gas yield and, as a consequence, a rise in the degree of conversion of biomass into gas.

TABLE I. COMPOSITION, SPECIFIC COMBUSTION HEAT AND VOLUME OF PRODUCT GAS PRODUCED FROM ONE KG PEAT PELLETS

$T_f, \text{ }^\circ\text{C}$	Volume, $\text{m}^3/\text{kg}$	Volume fractions of combustible components			Combustion heat, $\text{MJ}/\text{m}^3$	
		$\text{H}_2$	$\text{CO}$	$\text{C}_n\text{H}_m$	$Q_H$	$Q_L$
850	0.76	0.40	0.27	0.08	11.7	10.6
950	1.1	0.43	0.40	0.02	11.3	10.4
1000	1.39	0.49	0.41	0.01	11.7	10.6
Pyrolysis	0.29	0.23	0.19	0.13	10.4	9.6

TABLE II. COMPOSITION, SPECIFIC COMBUSTION HEAT AND VOLUME OF PRODUCT GAS PRODUCED FROM ONE KG WOOD PELLETS

$T_f, \text{ }^\circ\text{C}$	Volume, $\text{m}^3/\text{kg}$	Volume fractions of combustible components			Combustion heat, $\text{MJ}/\text{m}^3$	
		$\text{H}_2$	$\text{CO}$	$\text{C}_n\text{H}_m$	$Q_H$	$Q_L$
850	0.83	0.39	0.28	0.10	12.5	11.5
950	1.24	0.47	0.41	0.01	11.5	10.6
1000	1.39	0.46	0.46	0.00	11.7	10.9
Pyrolysis	0.26	0.28	0.26	0.16	13.2	12.1

Change of the gas calorific value at reactor output in process of raw material heating (rate –  $10\text{ }^\circ\text{C}/\text{min}$ ) is presented in Figure 4. As one can see from Figure 4, in the «pyrolysis» regime the calorific value of output gas at temperature of processed raw material above  $550\text{ }^\circ\text{C}$  is higher than the calorific value of output gas in the «pyrolysis with cracking» regime. However the calorific value of output gas in the «pyrolysis» regime is strongly changes in process of raw material heating.

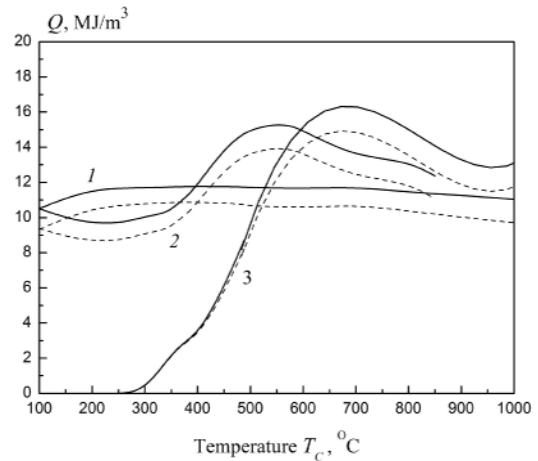


Figure 4. High (solid line) and low (dash line) calorific values of output pyrolysis gas vs. temperature of raw material (peat pellets) in different regimes of thermal processing: «pyrolysis with cracking» at  $T_f = 1000\text{ }^\circ\text{C}$  – 1,  $850\text{ }^\circ\text{C}$  – 2; «pyrolysis» – 3.

As appears from comparison of the dependences presented in Figure 4, in the «pyrolysis with cracking» regime an increase of the temperature  $T_f$  depresses a temperature influence on the calorific value of output gas.

As mentioned above at  $T_f = 1000$  °C the output gas is a mixture of CO and H<sub>2</sub>. Relation between volume fractions of this components in temperature range  $T_c = 250 - 500$  °C (that is in the range of main gas release) does not change practically. As consequence the calorific value of output gas does not depend on the temperature of processed raw material. This circumstance is rather important from the point of view of the subsequent usage of product gas mixtures, for example, as a fuel for power plant on the base of internal combustion engine.

The ratio of thermal value of gas obtained by thermal processing of one kg of the raw material to calorific value of one kg of the utilized raw material is about 0.7 – 0.8. Significant advantage of suggested technology is the absence of liquid fraction in the end products. Such gas mixture can be used as a gas fuel for power unit on the base of gas piston engine. Burning of the gaseous fuel produced from biomass raw materials by developed technology can be carried out without reconstruction of the existing gas-fired power equipment while the direct use of wood waste or peat (for example, peat or wood pellets) requires considerable structural modifications of the existing power installations meant for electricity generation.

#### IV. CONCLUSION

1. The technology of manufacture of carbon materials and hydrogen based on the process of heterogeneous pyrolysis of gaseous hydrocarbons during filtration through porous structure formed as a result of thermal decomposition of biomass are presented. The carbon material produced by the developed technology may be used as a high calorific solid fuel and as a raw material for various industries, for example, metallurgy. The gaseous mixture at the exit of reaction volume contains hydrogen which concentration may be easily varied by change in operating parameters and may reach 90 volume percents. Natural gas of low-pressure gas fields, oil gas and waste hydrocarbon gases of petrochemical manufacture can be used as gaseous raw material for this technology.

2. It is shown that the mixed technology of thermal processing of different kinds of biomass, involving the stage of pyrolysis and the subsequent cracking of volatile products by their filtration through charcoal, it is possible to increase the efficiency of energy conversion of biomass into gas by several times. At the charcoal temperature 1000 °C and given residence time it is possible to produce about 1.4 m<sup>3</sup> of gas with specific combustion heat about 11.7 MJ/m<sup>3</sup> per one kg of original raw material. The produced gas mixture consists generally of carbon oxide and hydrogen.

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