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QUALITATIVE CHARACTERISTICS OF THE FUEL GAS OBTAINED AS A RESULT OF THE THERMOCHEMICAL PROCESSING OF PLANT BIOMASS BY THE PYROLYSIS METHOD

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Results of experimental investigations on determination of the output, composition, and combustion heat of the fuel gas obtained as a result of the pyrolysis of willow and alder sawdust, wood-waste pellets, peat, neutralized hydrolytic lignin, and plant-growing wastes (straw and flax boon) and the mechanisms of its formation under different pyrolysis conditions are presented.

Keywords: *pyrolysis, thermal decomposition, organic waste, energy carriers.*

Introduction. One of the most important problems challenging Belarusian power engineering is to decrease the proportion of imported resources in the fuel-energy balance and increase the share of local combustibles to as large as 25% of the total amount of the fuel used in stove and steam-water heating by 2012. To realize stable economic, technical, and social progress of society, it is necessary to use combustible wastes in thermal power generation. Among them are agricultural wastes consisting of plant remains and the wastes formed as a result of the processing of wood, polymeric, and other materials, the total yearly energy potential of which comprises 1.1–1.15 mln tons conditional fuel.

Formulation of the Problem. An analysis of the present state of the problem being considered and the modern tendencies for development of waste-processing methods [1–7] has shown that a promising and efficient way of reclamation of wastes that does not harm the environment is the thermochemical processing of them in the process of pyrolysis with formation of gaseous and high-calorific liquid and solid energy carriers.

The most important advantage of pyrolysis as a method of waste-processing is the possibility of obtaining not only fuel but also raw materials and other valuable products (technological carbon, charcoal, resins). As compared to the technologies of direct burning of combustible organic wastes, the pyrolysis of these wastes makes it possible to substantially decrease (by 2–5 times) the amount of flue gases and deleterious effluents to the atmosphere and calls for simpler systems for purification of the waste gases.

The output and quality of the pyrolysis products are determined by the composition of the materials processed, the conditions of their heating, the final heating temperature, and the pressure at which the heating process is realized. Of great importance are the type of equipment used, the method of heating, the time for which the volatile substances are found in the high-temperature zones, and other factors determining the uniformity of the temperature field, the depth of the "secondary" pyrolysis of the vapor and gases, and the formation of final products. The thermochemical transformation of the material processed is regulated by heating it slowly or rapidly to a definite temperature. Rapid pyrolysis, unlike slow pyrolysis, allows one to obtain decomposition products differing markedly in the output, composition, and properties. At present, rapid pyrolysis is considered a potentially promising method for thermochemical transformation of wood and other wastes, especially for the purpose of production of liquid fuels, chemical products, and gases; these materials are obtained depending on the temperature of the process: low-temperature rapid pyrolysis makes it possible to obtain a larger fraction of the liquid product, and gas is the main product of pyrolysis conducted at high temperatures [8, 9].

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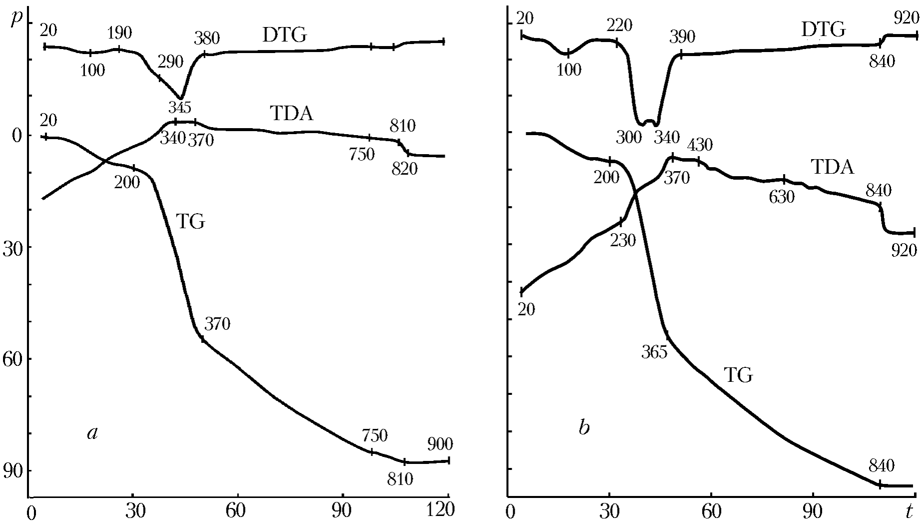

Fig. 1. Thermal analysis of straw (a) and flax boon (b). *p*, %; *t*, min.

In recent years, extensive investigations on the pyrolytic decomposition of plant biomass and other raw materials have been carried out in a number of countries. In these investigations, the technological parameters of the process were verified with the use of laboratory, demonstration, and pilot setups including different-design reactors (e.g., reactors with a circulating fluidized bed or a moving horizontal layer) for obtaining boiler fuel, biofuel, and pyrolysis gases [8–12].

The first investigations on the pyrolysis of plant biomass were devoted to solving the problem on the use of solid fuels [1]. However, since at that time the trend was to use more calorific fuels such as oil, gas, and coal, pyrolysis methods were not further developed. When the situation of the energy market changed, the use of local energy sources became a pressing problem.

In the CIS countries, the need for improvement of the equipment for burning of garbage gave rise to the development of the technology of pyrolysis that could be used not only for the reclamation of garbage, but also other wastes [13–17]. At present, the technologies of pyrolysis of plastic-material wastes are being intensively developed because from these materials not only solid fuels with a combustion heat of 18–20 MJ/kg, liquid fuels with a combustion heat of 40–41 MJ/kg, and gaseous fuels with a combustion heats of 12–16 MJ/kg, but also a number of variable raw materials can be obtained, which substantially improves the economic characteristics of the process. Among the indicated raw materials are carbonaceous material having a high adsorption capacity, pure hydrochloric acid, wax for impregnation of paper, board, and fabric, and other materials [13]. The heat and mass transfer in plant biomass and in plastic material, rubber, and sludge wastes and their decomposition in the process of pyrolysis in an superheated steam have been investigated and a technology for obtaining fuels as well as heat-insulating, filtering building materials and adsorbents, allowing one to substantially decrease or practically completely exclude the effluents of deleterious gaseous, liquid, and solid substances into the atmosphere has been developed [13]. An original technology of rapid pyrolysis of domestic garbage in the process of its intensive heating in a rotating furnace, on a moving conveyor, or in a tunnel kiln has been developed [14].

A promising direction for the Republic of Belarus is the use of gas-generating plants for production of heat energy, developed at the Institute of Problems of the Use of Natural Resources and Ecology of the National Academy of Science of Belarus; these plants can work on peat, wood wastes, mixtures of comminuted technical rubber products, and other solid fuels. [15–18].

The aim of the present work is to investigate the output, composition, and combustion heat of the fuel gas produced as a result of pyrolysis of willow and alder sawdust, wood-waste pellets, neutralized hydrolytic lignin, and plant-growing wastes (straw and flax boon) and the mechanism of its formation under different pyrolysis conditions.

Investigation Method. The investigations were carried out by the slow- and rapid-pyrolysis methods with the use of laboratory setups — pyrolysis reactors with a descending or stationary fuel layer and a horizontal pyrolysis reactor with a screw fuel feed. The composition of the pyrolysis gas was analyzed using a VTI-2 gas analyzer.

TABLE 1. Results of the Thermogravimetry Analysis of Plant-Growing Wastes in the Pyrolysis Regime

Material	Mass loss, % of dry substance; in the temperature range, ^{o}C				
	< 200	200—350	200—500	500—900	200—900
Straw	8.5	51.5	73.3	21.6	94.9
Flax boon	9.0	47.9	65.1	23.4	88.5

TABLE 2. Elemental Composition of Some Types of Vegetative Biomass [19–21]

Fuel	Content (rounded), % of combustible mass			
	C	H	S	O
Firewood	50	6	0.0	42
Peat	54—60	6	0.3	33
Hydrolysis lignin	59	5.8	0.3	32
Flax boon	51	6.1	0.1	42.8

The thermochemical transformations of the organic substance of straw and flax boon in the process of their pyrolysis under different conditions were simulated on an OD-103 derivatograph (Hungary) by the method of thermogravimetry (TG) analysis including, in the present work, a thermal differential analysis (TDA) and a differential thermogravimetry (DTG). In the TDA method, changes in the temperature of a sample are caused by physical transformations or chemical reactions arising in the sample as a result of a change in its enthalpy. These transformations lead to heat absorption or heat release, which is reflected by a TDA curve used for recording the mechanism of thermal reactions occurring in the sample. In addition to the TDA method, the DTG method allows one to follow the process of thermal decomposition of a sample with the use of a TG curve reflecting the information on the process (the change in the mass p of the sample) and its derivative — a TDG curve giving information on the rate of change in the mass of the sample depending on the time t. The derivatograms obtained are presented in Fig. 1.

Discussion of Results. As follows from the data of Fig. 1a (the DTG and TDA curves), the most intensive thermal decomposition of the organic substance of straw occurs with an exothermic effect in the temperature range 200–400^{o}C and leads to a 50% mass loss due to the release of volatile organic substances. The existence of the two maxima at 300 and 340^{o}C on the DTG curve is evidence of the decomposition of components of the straw carbohydrate complex — hemicelluloses, cellulose, and others. As the temperature of the sample increased further to 370^{o}C, the thermal decomposition of these substances slowed down and proceeded at a lower rate as long as the temperature became equal to 840^{o}C. The fixed residue having a low thermostability was transformed practically completely into volatile substances, and, at 840^{o}C, the organic substance of the straw was decomposed completely (the mass loss reached 95% due to the decomposition of the thermostable organomineral complexes with release of a fuel gas), which is clearly seen from the DTG, TDA, and TG curves.

These mechanisms are characteristic of the thermal decomposition of the organic substance of flax boon in the process of its pyrolysis (see Fig. 1b) with the only difference that, in the temperature range 200–500^{o}C, the thermal stability of this plant-growing waste is higher and its pyrolysis is completed at a temperature of 810^{o}C.

In Table 1, the dynamics of the loss in the mass of the straw and flax boon in the process of their thermogravimetry analysis is presented.

The composition of the organic mass of wood waste, peat, and flax boon consists of 50–60% carbon, 6% hydrogen, and 33–43% oxygen (Table 2); therefore, these materials can be used as raw materials for obtaining a synthesis gas that can be transformed into a liquid fuel in the process of catalysis by the Fischer–Tropsch method [22].

The fuel gas formed in the process of thermal decomposition of plant biomass at a temperature lower than 900^{o}C consists of carbonic acid gas, unsaturated compounds, carbon monoxide, hydrogen, and methane. The output, composition, and properties of this gas are determined by the composition, the fuel characteristics of the raw materials processed, and the technological parameters of the pyrolysis process.

As follows from the experimental data presented in Table 3, in the process of rapid pyrolysis of sawdust and lignin in a descending layer of a fuel, a gas with a high content of carbon oxide, methane, and hydrogen is formed, and the combustion heat of this gas is determined mainly by the indicated substances.

TABLE 3. Characteristic of the Gas Obtained under Different Conditions of Pyrolysis of a Plant Biomass at a Temperature of 800°C

Material	Composition of fuel gas, vol. %					Output of gas, % of dry substance	Lowest combustion heat, kcal/nm^3
	CO_2	C_nH_m	CO	H_2	CH_4		
Descending fuel layer, rate of heating is 400–500°C/min							
Willow sawdust	8.7	1.4	45.3	35.4	9.1	79	3268
Alder sawdust	8.3	3.1	45.7	28.2	14.5	72	3790
Alder sawdust with the use of a catalyst	10.2	1.4	45.2	29.6	13.6	85	3490
Lignin	11.0	0.7	36.6	39.1	12.5	65	3290
Moving fuel layer in an auger-type apparatus, rate of heating is 30–40°C/min							
Mixture of pine and fir sawdust	14.7	2.5	27.0	37.3	18.5	62	3635
Pellets of wood wastes	14.9	5.7	35.3	27.1	17.0	73	4000
Valley peat	17.2	6.6	25.8	37.9	12.5	72	3740
Rye straw	4.5	0	43.6	48.0	3.6	71	2865
Stationary fuel layer, rate of heating is 8–10°C/min							
Rye straw	24.6	1.5	23.7	31.5	18.8	70	3335
Flax boon	21.5	1.7	22.2	32.9	21.7	69	3610

The formation of hydrogen, the high content of which (28–39%) is characteristic of all the substances being investigated, in the process of rapid pyrolysis is mainly due to the secondary reactions — the interaction of the vapor-gas mixture with the coke. The differences in the content of carbon oxide between the gaseous products of the pyrolysis of wood wastes (neutralized hydrolytic lignin, willow and alder sawdust, wood-waste pellets) and peat are due to the higher content of oxygen in the elemental composition of the initial wood (42%) as compared to the peat (33%) (Table 2) as well as features of the structure and composition of the organic substance of the peat.

The combustion heat of the pyrolysis gas of all the plant biomass samples being investigated is provided at a level of 3300–4000 kcal/nm^3 not only by the hydrogen and carbon oxide contained in it, but also by methane formed in large amounts as a result of the thermal decomposition of the methoxyl groups (Table 3).

When the pyrolysis of a mixture of pine and fir sawdust was carried out in a screw-type apparatus, the output of the pyrolysis gas was somewhat lower than that of the other plant raw materials; however, its combustion heat was at the same level (3635 kcal/nm^3) due to the high content of methane and hydrogen in it. This is explained by features in the chemical composition of soft-wood sawdust, which is characterized by the presence of a large amount of gummy substances.

The pyrolysis of alder sawdust was carried out with the use of a catalyst through which the vapor-gas mixture was passed and subjected, thus providing an additional thermochemical treatment at the same temperature, which increased the output of the pyrolysis gas (to 85%) with no marked changes in its composition.

An investigation of the composition of the gas released as a result of the slow (8–10°C/min) pyrolysis of lignin and straw in a stationary fuel layer at different temperatures (Table 4) has shown that the content of individual components in the pyrolysis gas depends substantially on its temperature, which points to the fact that the organic substance of the materials being studied experiences several stages of transformation.

The transformation of organic compounds at a temperature lower than 500°C is caused by the primary decomposition reaction (the breaking of the intramolecular bonds between atoms C–C, C–H, C–O, and so on and the bonds between molecules) and, at a temperature of 500–900°C, by the secondary reactions of interaction and packing of the residual fragments of the initial molecules. Amplification of the vibrations in a molecule in the process of its heating leads to progressive detachment of groups that are unstable in energy at the moment [23]. The existence of definite bonds in this molecule is determined by the structure and composition of the initial substance. Moreover, each reaction proceeds at a definite rate; therefore, a change in the technological parameters of the process will also influence the thermal decomposition of the substance and introduce corrections for the composition and output of the final products.

TABLE 4. Characteristic of the Gas Obtained at Different Temperatures in the Process of Slow Pyrolysis (8–10°C/min) of Neutralized Hydrolytic Lignin and Straw

Temperature interval, °C	Gas composition, vol. %					Lowest combustion heat, kcal/nm^3
	CO_2	C_nH_m	CO	H_2	CH_4	
Neutralized hydrolytic lignin						
300—400	70.8	0.6	19.2	4.6	4.8	1190
400—500	56.4	0.5	21.7	5.9	15.5	2130
500—600	40.3	0.6	13.0	16.2	29.9	3770
600—700	17.8	0.5	15.2	50.2	16.3	3210
700—720	12.4	0.1	24.9	52.4	10.2	2990
700—800	10.7	0.6	41.5	42.6	4.6	2840
Straw						
300—400	54.9	0.4	38.5	4.2	1.9	1505
400—500	49.0	2.1	29.0	7.5	12.5	2424
500—600	40.3	2.2	26.0	8.4	23.2	3282
600—700	22.7	0.7	16.7	35.0	24.1	3625
700—800	12.5	0.6	42.5	28.6	15.8	2944

Thermal decomposition of a substance with detachment of the side chains of macromolecules where bonds are the least strong, including the reactions of dehydration decarboxylation and decarbonization of the oxygen-containing compounds of the organic substance of the initial material, begins at a temperature of higher than 150°C and is accompanied by the formation of low-molecular-weight gaseous and vaporlike products (H_2O) CO, CO_2, and others). Even at a temperature of 300–400°C, a maximum content of carbon dioxide is attained in the pyrolysis gas of lignin due to the decarbonization of the carboxylic acids under these conditions.

At temperatures lower than 400–500°C, carbon oxide is formed as a result of the decomposition of the carbonyl-containing compounds — the organic acids ($HCOOC \rightarrow CO + H_2O$); in this case, the content of carbon oxide is 21.7% in the pyrolysis gas of lignin and 38.5% in the pyrolysis gas of straw, and the carbon-oxide content regularly decreases with further increase in the temperature. At a temperature of 600°C and at higher temperatures a rigid semi-coke structure begins to form, the solid phase is subjected to further thermochemical transformations, organomineral complexes of the type of $Ca(RCOO)_2$ are decomposed, and secondary processes of interaction of the vapor-gas mixture formed with the solid phase proceed. Because of the reduction of CO_2 ($C + CO_2 \rightarrow 2CO$) formed at a high temperature as a result of the thermal dissociation of calcium and potassium carbonates ($CaCO_3 \rightarrow CaO + CO_2$), at 800°C the content of CO in the pyrolysis gas of the neutralized lignin increases to 41.5% and the CO content in the pyrolysis gas of the straw reaches 42.5%. The content of hydrogen increases gradually with increasing temperature and increases sharply after the major portion of the volatile compounds is removed (the hydrogen content is 50–52% in the composition of the lignin pyrolysis gas and 35% in the straw pyrolysis gas) due to the condensation of the aromatic compounds in the solid residue.

A characteristic of the thermal decomposition of both lignin and straw is a high content of methane in the pyrolysis gas at a temperature of 500–600°C, corresponding, under these conditions, to a maximum combustion heat. The high content of carbon oxide (38.5%) in the composition of the straw pyrolysis gas even at a relatively low temperature (300–400°C) has engaged our attention; in our opinion, this is due to the features of the chemical composition of the straw organic substance — the high content of carbonyl groups, the thermal decomposition of which is accompanied by the release of carbon oxide.

Conclusions. Our investigations of the mechanisms of gas formation in the process of slow pyrolysis of plant biomass wastes in a stationary layer have shown that the main amount of the combustion gas is formed at a temperature higher than 300°C, and the combustion heat reaches a maximum value at 600–700°C. In the process of thermal decomposition of straw and flax boon at a temperature of about 900°C, 90% of their organic substance can be transformed into volatile products (resin, water, gas). In the case where pyrolysis of these wastes is carried out in a moving layer at a temperature of 400°C and at higher temperatures, the content of the synthesis-gas components ($CO + H_2$) in the composition of the pyrolysis gas reaches 90%. The mechanisms of formation of the individual components (CO_2, CO, H_2, CH_4) in the composition of pyrolysis gas of different types of different types of plant biomasses are very different and are determined by their chemical composition.

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