



BIONATURE 2014

The Fifth International Conference on Bioenvironment, Biodiversity and
Renewable Energies

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BIONATURE 2014 Editors

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BIONATURE 2014

Foreword

The Fifth International Conference on Bioenvironment, Biodiversity and Renewable Energies (BIONATURE 2014), held between April 20 - 24, 2014 in Chamonix, France, covered these two main areas: environment and renewable and sustainable energies.

Environmental change awareness is a key state of spirit and legislation for preventing, protecting, and ultimately saving the planet biodiversity. Technical and practical methods for applying bio-agriculture for the public's health and safety are primary targets. The goal is the use of ecological economic stimuli in tandem with social and governmental actions preventing deforestation, pollution, and global warming. To cope with the climate and landscape changes advanced technical inventory of tools and statistics on lessons learned are needed to derive appropriate measure and plan accordingly.

Replacing the classical energy with alternative renewable energy (green energy), such as bioenergy, eolian energy, or solar energy is an ecological and economic trend that suggests important socio-economic advantages: using native renewable resources, increasing of self-sufficiency rate of energy and promoting use of clean energy, and that way, polluting emissions to the air will be reduced. Bioenergy is renewable energy derived from biological sources, to be used for heat, electricity, or vehicle fuel. Biofuel derived from plant materials is among the most rapidly growing renewable energy technologies. In several countries corn-based ethanol is currently the largest source of biofuel as a gasoline substitute or additive. Recent energy legislation mandates further growth of both corn-based and advanced biofuels from other sources. Growing biofuel demand has implications for U.S. and world agriculture. Eolian energy is currently used throughout the world on a large scale. In the past decade, its evolution shows its acceptance as a source of generation, with expressive growth trends in the energy matrices in the countries where this source is used Eolian energy is renewable and has very low environmental impact. To generate it, there are no gas emissions, no effluent refuse, and no other natural resources, such as water, are consumed. Photovoltaic technology makes use of the energy in the sun, and it has little impact on the environment. Photovoltaics can be used in a wide range of products, from small consumer items to large commercial solar electric systems. The event brought together the challenging technical and regulation aspects for supporting and producing renewable energy with less or no impact on the ecosystems. There are several technical integration barriers and steps for social adoption and governmental legislation to favor and encourage this kind of energy.

We take here the opportunity to warmly thank all the members of the BIONATURE 2014 Technical Program Committee, as well as the numerous reviewers. The creation of such a high quality conference program would not have been possible without their involvement. We also kindly thank all the authors who dedicated much of their time and efforts to contribute to BIONATURE 2014. We truly believe that, thanks to all these efforts, the final conference program consisted of top quality contributions.

Also, this event could not have been a reality without the support of many individuals, organizations, and sponsors. We are grateful to the members of the BIONATURE 2014

organizing committee for their help in handling the logistics and for their work to make this professional meeting a success.

We hope that BIONATURE 2014 was a successful international forum for the exchange of ideas and results between academia and industry and for the promotion of progress in the fields of bioenvironment and renewable energies.

We are convinced that the participants found the event useful and communications very open. We also hope the attendees enjoyed the charm of Chamonix, France.

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Biomass Pyrolysis Kinetics Researching

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Abstract— The biomass pyrolysis technology (carried out at moderate temperatures up to 1000°C) allows improving of energy efficiency and workability of biomass utilization. The pyrolysis process controlling (with desired composition of products) is possible by changing the process parameters (temperature, pressure, heating rate, the biomass hold up time in pyrolysis reactor). Availability of kinetic equations linking technological parameters and vent of the pyrolysis products with biomass hold up time at preset temperature range is the necessary condition for pyrolysis process controlling. Obtaining of the pyrolysis kinetic parameters based on experimental data of the thermogravimetric analysis was the purpose of this study. Then, kinetic constants were obtained for various types of plant biomass, such as wood, corn straw, rice husk, and chicken litter, namely, the order of the pyrolysis process, the activation energy and pre-exponential factor. Obtained constants allow the reactor characteristics calculating for fixed products of pyrolysis process receiving.

Keywords - biomass conversion; kinetic parameters; pellets; pyrolysis.

I. INTRODUCTION

Biomass thermochemical conversion in the power-producing purposes is subdivided into two technologies: gasification and pyrolysis. Gasification purpose is reception of gaseous fuel with the maximal degree of energy conversion (0,70-0,75) to the combustion heat of received fuel. The gasifier maximal temperature exceeds 1000 °C. Carbon of ash content is gasified to the limit by gasifying agents. However, gas thermotechnical characteristics do not satisfy to the modern power technologies with high intensity of heat and mass exchange: combustion heat does not exceed 10,5-10,9 MJ/nm³, adiabatic combustion temperature is about 1400-1500 °C. The chemical compound of many kinds of biomass (crop residues, abilities to live, sewage sludge, etc.) limits the maximal temperature of conversion due to the formation of low-melting eutectics.

The biomass pyrolysis technology (carried out at moderate temperatures up to 1000°C) allows to improve energy efficiency and workability of biomass utilization. In the pyrolysis process decomposition of organic compounds of the initial biomass is carried out with forming of non-condensable gases (CO, CO₂, H₂, CH₄, etc.), the solid residue, and vapors. The vapors are condensated under cooling in a mixture of high-molecular liquids (bio-oil) with a high energy density [1][2]. The pyrolysis process controlling (with desired composition of products) is possible by changing the process parameters (temperature, pressure, heating rate, the gas environment composition, the biomass hold up time in pyrolysis reactor). Availability of

kinetic equations linking technological parameters and vent of the pyrolysis products with biomass hold up time at preset temperature range is the necessary condition for pyrolysis process controlling. Obtaining of the pyrolysis kinetic parameters based on experimental data of the thermogravimetric analysis was the purpose of this study. The authors studied many types of biomass, not only well-known, i.e., wood, but also those data which is under-explored: crop wastes and chicken litter [3].

This paper contains theoretical calculation of kinetic parameters, using experimental data, and experimental method description and obtained data. In conclusion, there is a discussion of legality of using this method to determine the kinetic parameters for different types of biomass.

II. THEORETICAL FOUNDATIONS

The physical-chemical basis of our method is [4]:

Biomass pyrolysis process is a simultaneous occurrence of many reactions. However, total reaction can be schematically represented by a single-component model as:

Initial sample => Volatile compounds + solid residue

Reaction rate can be written as a standard kinetic equation:

$$-\frac{dc}{d\tau} = kc^n. \quad (1)$$

c – sample current mass, n – the order of the reaction, k – rate constant of the total-reaction;

$$c = 1 - \frac{V_{Tf}}{V_k}$$

V_{Tf} – volatile matter loss at the temperature T_f , V_k – volatile matter loss at the end of the pyrolysis process.

We can finally get the formula for the rate constant using the Arrhenius equation:

$$-\frac{dc}{dT} = c^n \frac{Z}{\beta} e^{-\frac{E}{RT}} \quad (2)$$

β and Z – heating rate and pre-exponential factor, E – activation energy.

In (2), there are three unknowns: the activation energy E , pre-exponential factor Z , and the reaction order n .

Obtaining of a system of three equations is required to find these unknowns. The inflection point is the characteristic point of the kinetic curve. Exactly for this point required three equations could be found.

The first equation is obtained by applying (2) for the inflection point. The maximum of decomposition rate with certainty is obtained from the experimental derivative thermogravimetric analysis (DTG) curve:

$$\left(\frac{dc}{dT}\right)_{T=T_f} = W_{\max} = -Z \frac{e^{-\frac{E}{RT_f}} c_f^n}{\beta} \quad (3.1)$$

The second one could be found by equating the second derivative at this point to zero:

$$-\frac{Z}{\beta} e^{\frac{-E}{RT_f}} * C_f^{n-1} \left(\frac{dc}{dT}\right)_{T=T_f} - \frac{Z}{\beta} e^{\frac{-E}{RT_f}} * C_f^n \frac{E}{RT_f^2} = 0$$

Solving this equation for E may be received:

$$E = -nRT_f^2 \frac{W_{max}}{C_f} \quad (3.2)$$

The third equation is obtained by integrating the basic equation (2): the left part in the range from 1 to C_f, the right one in the range from T₀ to T_f:

$$\int_1^{C_f} \frac{dc}{c^n} = -\frac{Z}{\beta} \int_{T_0}^{T_f} \frac{e^{\frac{-E}{RT}}}{T^2} dT = -\frac{ZE}{\beta R} \left(\frac{e^{-X}}{X} - \int_X^{\infty} \frac{e^{-u}}{u} du \right) = -\frac{ZE}{\beta R X^2} \left(X - X^2 e^X \int_X^{\infty} \frac{e^{-u}}{u} du \right),$$

$$X = \frac{E}{RT_f}$$

Expression for $\frac{e^{-X}}{X^2}$ can be obtained by dividing both sides of (3.2) at RT and T and substituting as substituting the value $\frac{dc}{dT}$ from (3.1):

$$\frac{E}{RT} * \frac{RX}{E} = -\frac{n}{c_f} \left(-\frac{Z}{\beta} e^{\frac{-E}{RT_f}} * C_f^n \right)$$

Or

$$\frac{X^2 R}{E} = \frac{nZe^{-X} C_f^{n-1}}{\beta}$$

As a result, we obtain:

$$\frac{e^{-X}}{X^2} = \frac{R\beta}{EnZ C_f^{n-1}}$$

$$\int_1^{C_f} \frac{dc}{c^n} = -\frac{1}{nc_f^{n-1}} (X - X^2 e^X \int_X^{\infty} \frac{e^{-u}}{u} du)$$

For n ≠ 1:

$$\frac{n}{n-1} (1 - c_f^{n-1}) = X - X^2 e^X \int_X^{\infty} \frac{e^{-u}}{u} du$$

Transforming, we obtain:

$$nc_f^{n-1} = 1 + (n-1) \left[1 - X + X^2 e^X \int_X^{\infty} \frac{e^{-u}}{u} du \right]$$

Denoting the expression in parentheses as P(X):

$$nC_f^{n-1} = 1 + (n-1)P(X) \quad (3.3)$$

The system of (3.1), (3.2), and (3.3) the subscript f refers to the parameter values at the inflection point.

$$P(X) = 1 - X + X^2 e^X \int_X^{\infty} \frac{e^{-u}}{u} du, \quad (4)$$

$$X = \frac{E}{RT_f}$$

Definite integral in (4) cannot be expressed in terms of elementary functions. It is the exponential integral function whose values are given in the special mathematical tables.

In this paper, for (4), we obtained the regression equation with a correlation coefficient of 0.996 for the entire relevant range of values of the pyrolysis process X:

$$P(X) = 1,132X^{-0,858} - 6,968 \times 10^{-4} \quad (5)$$

Solving (3.1-3.3) and (4) with using of TGA data kinetic parameters n, E и Z can be obtained as follows:

1) Determine the coordinates of the inflection point on the experimental curve and the following parameters for this

point: share decomposed substance, decomposition rate and temperature.

2) Solve system (3).

$$\begin{cases} \left(\frac{dc}{dT}\right)_{T=T_f} = W_{max} = -Z \frac{e^{\frac{-E}{RT_f}} * C_f^n}{\beta} \\ E = -nRT_f^2 \frac{W_{max}}{C_f} \\ nC_f^{n-1} = 1 + (n-1)P(X) \end{cases} \quad (3)$$

3) Plot the calculated curve of thermal decomposition of biomass samples according to the equation:

$$V_T = V_K(1 - C_T), \quad (6)$$

$$C_T = \exp\left(\frac{1}{1-n} \ln\left(1 - \frac{ZE(1-n)(1-P(X))}{\beta R e^{X X^2}}\right)\right).$$

A solution of (3) together with (5) and (6) was obtained by using MathCad 14.

III. EXPERIMENTAL STUDIES

Thermogravimetric data were obtained on a modern thermoanalyzer SDT Q600 firm "TA Instruments" (USA). It is a high-precision instrument with a wide range of opportunities. Thermogravimetric analysis (TGA) and DTG curves can be received with different heating rates in an artificially created gas atmosphere during pyrolysis process at the different final temperatures, etc. The pyrolysis process parameters for all kinds of biomass have a decisive influence on the kinetic regularities of this process.

At the studies first stage, namely, a thermal analysis of all types of biomass was carried out in a nitrogen atmosphere with a heating rate of 10 K/min. TGA and DTG measurements were performed simultaneously. The DTG curve could precisely determine undecomposed biomass content, rate of decomposition and temperature at the inflection point. All these values correspond to the maximum on the DTG curve. This method allows receiving the correct input data for solving the system of equations (3).

Sample weight was measured by comparing the mass microbalance empty cup and cup with sample.

Low sample weight (less than 100 mg) and size suggest pyrolysis proceeding in the kinetic mode without internal and external diffusion limitations.

Sample weight was measured by comparing the mass microbalance empty cup and cup with sample. Table I shows sample weight data.

TABLE I. SAMPLE WEIGHTS

Type of biomass	Weight, mg
Wood	30.47
Rice husk	55.8
Corn straw	62.3
Chicken litter	69.39

A typical recording of the thermal degradation of biomass is shown in Fig.1. According to graph, we can find initial data at the inflection point for determining kinetic parameters (in this case, for wood):

- Temperature, T_f = 639 K;
- Undecomposed biomass content, C_{per} = 0.466;

- Rate of decomposition, $W_{max} = -0.0104$ 1/K

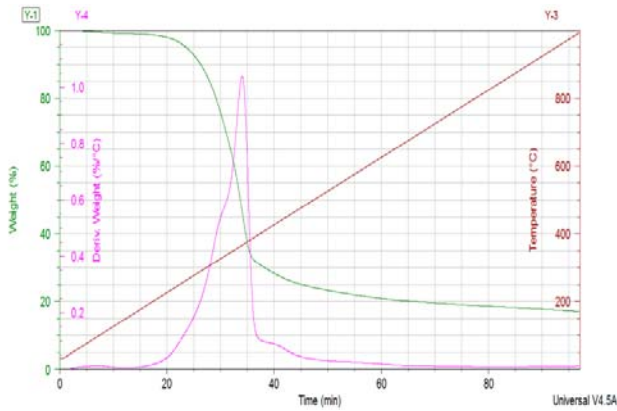


Figure 1. The characteristic curve of the biomass pyrolysis process

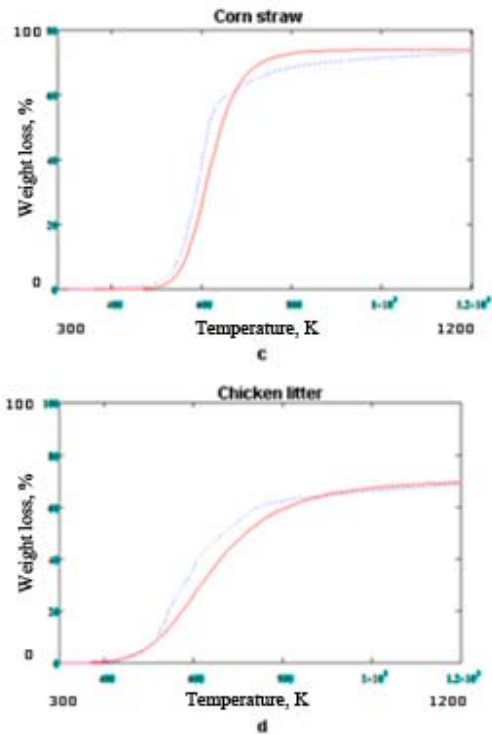
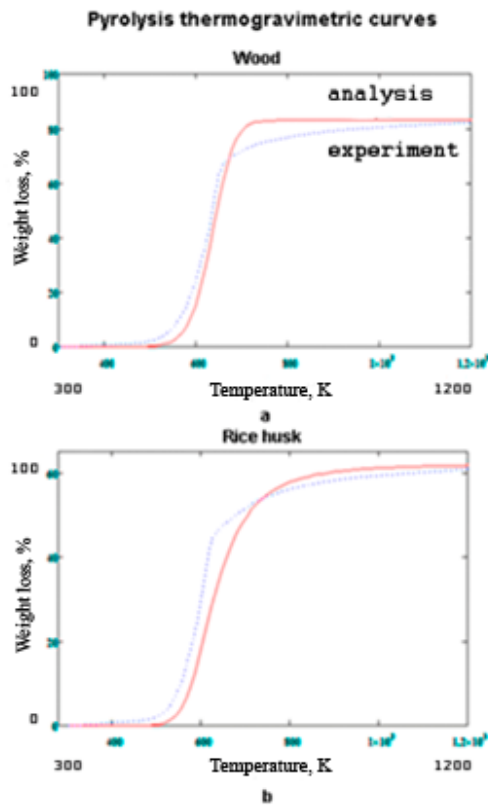


Figure 2. Pyrolysis thermogravimetric curves

Various kinds of biomass pyrolysis curves (analysis and experimental) are shown in the graphs in Fig.2: a – wood pellets; b – rice-husk pellets; c – corn-straw pellets; d – chicken litter pellets.

The results of different kinds of biomass pyrolysis exploration are shown in Table II.

TABLE II. INITIAL AND CALCULATED DATA FOR EACH BIOMASS SORT

Kind of biomass	Initial data (in the inflection point)		
	Decomposition rate, W_{max} , 1/K	Temperature, T_f , K	Undecomposed biomass content, C_f
Wood	-0.0104	639	0.466
Corn straw	-0.008	609	0.571
Rice husk	-0.00698	609	0.651
Chicken litter	-0.0042	604	0.624
Kind of biomass	Kinetic parameters		
	Order of the process, n	Pre-exponential factor, Z , s	Activation energy, E , kJ/moll
Wood	1,371	$1.55 \cdot 10^6$	103.94
Corn straw	2.268	$1.25 \cdot 10^6$	98.16
Rice husk	3.526	$5.29 \cdot 10^7$	116.59
Chicken litter	2.23	2.87	34.47

Kind of biomass	The maximum discrepancy between experiment and calculation, %
Wood	3.6
Corn straw	2.4
Rice husk	7
Chicken litter	7

Based on these results, we can conclude that the pyrolysis process is a sum of the parallel-serial reactions (because the order of the process is not an integer number).

IV. DISCUSSION

The obtained data indicate the correctness of using this method to determine the kinetic parameters for different types of biomass. The largest discrepancy between calculated and experimental curve is 7%, which can be considered as acceptable. The obtained data can be used for pyrolysis reactor characteristics calculations. Explored phytogenic kinds of biomass (wood, corn straw, rice husk, chicken litter) have only one inflection point at TGA curve and one extreme at DTG curve. The main components of these biomass types are lignin, cellulose and hemicellulose which determine the thermal decomposition kinetics of the thermochemical degradation. The complex nature of the thermal decomposition and differed kinetic parameters of chicken litter due to its structure: biomass, which contains the minimum amount of lignin and cellulose (chicken manure) and phytogenic biomass (litter). On the DTA curve there are several clear-cut inflection points, in which the rate of decomposition passes through an extreme.

V. CONCLUSION AND FUTURE WORK

Based on the proposed method, the following kinetic constants were obtained: the order of the pyrolysis process, the activation energy and pre-exponential factor - for various

types of plant biomass: wood, corn straw, rice husk, chicken litter.

Obtained constants allow calculating the reactor characteristics for fixed products of pyrolysis process receiving.

Waste made of biomass utilization is of considerable interest from both an ecological and power-engineering point of view.

Some further research directions:

- the kinetics constants for different heating rates determination;
- the pyrolysis kinetics in various gas atmospheres exploration;
- study the effect of internal thermal effects (exothermic) on the kinetics of pyrolysis.

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Thermotechnical Characteristics of Granulated Fuel Made of Chicken Litter: Researching and Ways of its Upgrading

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Abstract— Experimental data on the effect of heat treatment (torrefaction) on thermotechnical properties of chicken litter pellets are presented. Initial raw material was heated in a nitrogen atmosphere with the rate of 10°C/min up to the torrefaction temperature T_t and then was held at this temperature during some time. Process of heat treatment lasted 60 minutes. Experiments were carried out at three temperatures $T_t = 230, 250$ и 270°C . To investigate the properties of the initial and torrefied materials the thermogravimetric analysis and differential scanning calorimetry were used. As a result, the data on the influence of torrefaction on devolatilization, ash content and combustion value of the granulated chicken litter were obtained. In addition hygroscopic properties of initial and torrefied material was measured. Listed thermotechnical characteristics were compared with similar characteristics of granular fuel made of wood. As a result of executed investigations it was shown that the torrefied granulated chicken litter can be used as a solid fuel for autonomous heating systems.

Keywords - biomass; solid fuel; torrefaction; pyrolysis

I. INTRODUCTION

Agricultural waste, both vegetable and animal origin, are renewable hydrocarbon resources and relate to one of the most promising and environmentally friendly substitute of fossil fuel. Usage of agricultural waste for energy purposes would solve not only the problem of their utilization, but also significantly increases the power availability of agricultural industry by domestic resources. In addition, utilization of agricultural waste will contribute to solving a number of environmental problems associated with agricultural production. Last circumstance is primarily concerned with waste of livestock and poultry breeding.

Average chicken farm produces up to 300 tons of litter (consisted of manure and wood sawdust) per day. Simple storage of chicken litter leads to pollution of ground, water and air. The composition of the chicken manure is as following: water - 50-70%, organic matter - about 25%, nitrogen - 0.7-1.9%, phosphoric acid - 1.5-2.0%, potassium oxide - 0.8-1.0%, lime - 2.4%, magnesium - 0.8%, sulfur - 0.5%. Chicken manure contains valuable microelements such as copper, manganese, zinc, cobalt, boron, as well as active ingredients. Fresh chicken manure, usually, contains hazardous pathogenic bacteria, as well as in large amounts contains nitrogen, phosphorus, and sulfur. Content of nitrogen and phosphorus in chicken manure is 4-5 times more than in cattle manure [1]. The upper layer of the ground, on which litter is stored, contains about 4950 kg/ha of mineral nitrogen (including 2500 kg/ha of the nitrate),

which is in 17 times higher in comparison with uncontaminated soil.

There are two ways of chicken litter utilization: to use it as fertilizer and as raw stock for fuel production.

Biogas and bio-fertilizer are two products of technology of the chicken litter processing, based on anaerobic fermentation. Such kind of technologies are widespread. If satisfied all specific process parameters such as optimal fermentation temperature, continuous mixing of raw materials, and well-timed loading and unloading of the raw material in reactor it is possible to produce up to 6 m³ biogas from 1 m³ of reactor. Biogas, produced a result of action of bacteria, consists of methane (60-70%), carbon dioxide (30-40%), hydrogen sulfide (0-3%) and hydrogen impurities, nitrogen oxides and ammonia. Calorific value of biogas reaches 25 MJ per cubic meter that is equivalent to combustion of 0.6 liters of gasoline, 0.85 liters of spirit, 1.7 kg of wood or use 1.4 kWh of electricity.

Besides energy generation, the bioconversion process allows to solve another problem. Fermented chicken litter, when used in agriculture as fertilizer, helps increasing crop yield a 10-15% compared with the unfermented chicken litter. This is explained by the fact that during the anaerobic treatment, the mineralization and nitrogen fixation occur [1].

Chicken litter can also be used as a solid fuel. Production of solid fuel from chicken litter requires preliminary pelletization. Chicken litter pellets can be used as an intermediate product for further processing, or directly as a solid fuel. In the first case gasification of chicken litter pellets can be proposed for the production of gaseous fuel. This technology allows to convert chicken litter pellets into gaseous fuel with combustion value about 5000 kJ/m³ [2]. Composition of gaseous fuel, received by this technology is shown in Table I.

TABLE I. COMPOSITION OF GASEOUS FUEL, PRODUCED FROM CHICKEN LITTER PELLETS

Gas component	Volume content, %
CO	15-22
H ₂	16-22
CH ₄	1.0-2.5
CO ₂	11-15
N ₂	45-48

The main drawback of this technology is the high content of nitrogen and carbon dioxide in the produced gas mixture that lead to decrease of its combustion value.

As a solid fuel chicken litter pellets can be used for burning in the pellet boilers. It is also possible to use them for co-firing with straw, wood chips or coal. The main disadvantage of chicken litter pellets is its low heating value. So we encounter the need to raise the combustion heat of chicken litter pellets. One way of solving this problem is thermal treatment of pellets in neutral gas environment. This process is well known as a torrefaction and is widely used for processing different types of vegetable biomass into solid fuel [3][4]. In course of torrefaction not only the moisture removal from an initial raw material, i.e., its drying, occurs but also partial thermal decomposition of an organic constituent of biomass takes place. As a result a solid hydrophobic product is formed. In addition its specific combustion value surpasses a similar value for initial raw material [4].

The present paper is devoted to investigation of influence of the torrefaction conditions on such properties of chicken litter pellets as devolatilization, specific combustion value and hygroscopicity.

II. EXPERIMENTAL CONDITIONS

Thermal processing (torrefaction) of pellets consisted in their heating in the inert gas environment (nitrogen) to the torrefaction temperature $T_t = 230, 250$ and 270°C at the rate of $10^\circ\text{C}/\text{min}$ and holding at this temperature during some time. Total time of the process of heat treatment was equal to 60 min. In Fig.1, one can see the temperature profile during torrefaction.

When heating the mass change of pellets takes place as a result of devolatilization. For measurements of the quantitative characteristics associated with mass loss of raw materials during heating the thermogravimetric (TGA) analysis was carried out. For this purpose, the thermogravimetric analyzer SDT Q600 was used. The SDT Q600 was capable also to perform the differential scanning calorimetry (DSC) and it was used during investigations of the influence of torrefaction on the combustion value of granulated biomass fuel.

As raw materials there were used chicken litter pellets. Moisture content of the pellets was equal to 4.6%, ash content in terms of the dry basis – 13.7%, the yield of volatile matter in terms of the dry basis – 73.5%. Results of ultimate analysis in terms of the dry ash free basis were as follows: carbon – 48%, hydrogen – 6.4%, nitrogen – 5.9%.

III. RESULTS AND DISCUSSION

A. Heating in neutral gas environment (nitrogen)

As mentioned above, in the process of torrefaction the release of volatile matter, caused by thermal decomposition of the organic constituents of raw material, takes place. In Fig. 1, the TG curves describing mass losses of samples during torrefaction at different torrefaction temperatures are presented. Ibid the TG curve describing the mass loss when

heated up to 800°C is shown. After the sample temperature reaches the value of T_t the rate of mass losses decreases because of reduction of sample mass. As it appears from Fig. 1, mass losses account for 27, 34 and 37 % at torrefaction temperature 230, 250 and 270°C , correspondingly. From a comparison of curves, shown in Fig. 1, follows that these losses are noticeably less than total content of volatile matter in the initial sample.

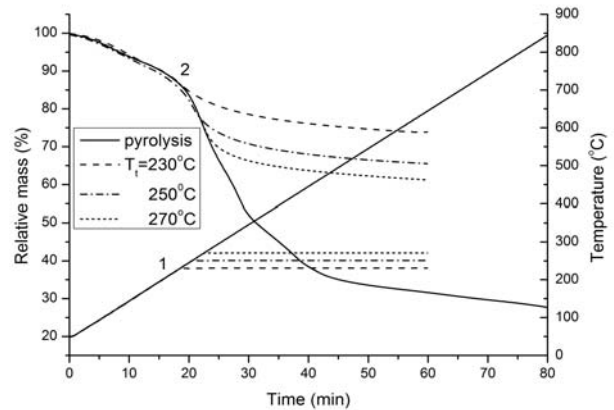


Figure 1. Change of temperature (1) and relative mass (2) of chicken litter pellets during pyrolysis and torrefaction at different temperatures T_t .

Since wood sawdust is a part of chicken litter it is natural to compare the yield of volatile matter from them and from chicken litter pellets. As mentioned above, content of volatile matter in the chicken litter pellets is 73.5% (in terms of the dry basis). A similar parameter for sawdust is 82%. Fig. 2 presents data on the rate of mass loss as function of temperature (so-called DTG curves) for wood sawdust and chicken litter pellets.

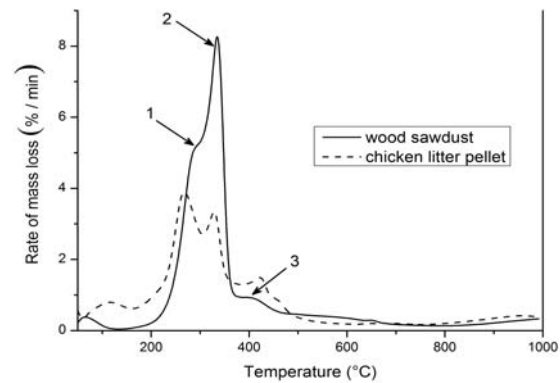


Figure 2. Rate of mass loss of wood sawdust and chicken litter pellets during heating in nitrogen at the rate of $10^\circ\text{C}/\text{min}$.

The DTG curve, corresponding to wood sawdust, has three representative knees (are marked by arrows) associated with thermal decomposition of hemicellulose (1), cellulose (2) and lignin (3). On the DTG curve, corresponding to the chicken litter pellets, the beginning of devolatilization is shifted to lower temperatures. The representative knees, associated with thermal decomposition

of hemicellulose, cellulose and lignin, are persisted, although their amplitudes are varied considerably.

Noticeable qualitative and quantitative differences are observed for the DSC curves that describe the heat flow required to maintain a given heating rate of wood sawdust and chicken litter pellets (see Fig. 3). The first endothermic effect for chicken litter pellets is observed in the temperature range 120-270°C. For sawdust the maximum of the first endothermic effect, associated with the decomposition of cellulose (see Fig. 2), falls on temperature of about 360°C. In the temperature range 390-480°C exothermic effect, caused by decomposition of lignin, results in change of sign of heat flow in the case of sawdust. At temperatures above 650°C, DSC curves for wood sawdust and chicken litter pellets coincide practically.

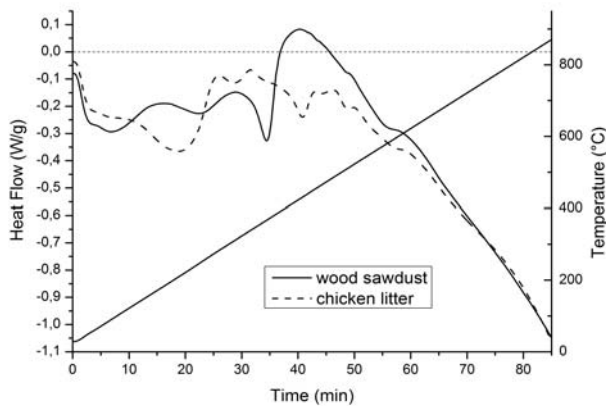


Figure 3. DSC curve of wood sawdust and chicken litter pellets in nitrogen at the heating rate of 10°C/min.

B. Heating in oxidizing gas environment (air)

DTG curves, measured in oxidizing gas environment and in particular in air, differ considerably from similar curves, measured in a neutral gas environment. This difference is primarily due to the fact that heterogeneous oxidation reactions go in air. In Fig. 4, DTG curves measured in air for initial and torrefied chicken litter pellets are shown.

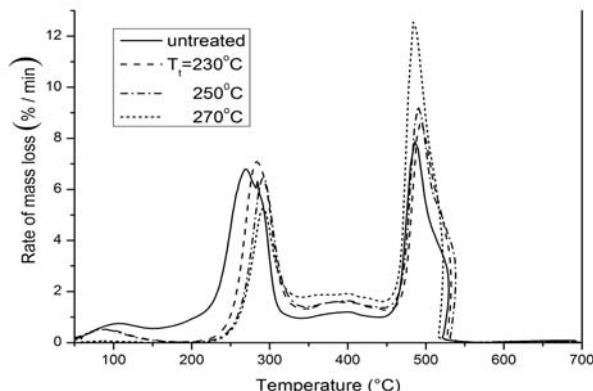


Figure 4. Rate of mass loss of untreated and torrefied chicken litter pellets during heating in air at the rate of 10°C/min.

On the DTG curve measured in nitrogen, the basic mass loss is observed only in the temperature range 200-450°C and is connected with devolatilization (see Fig. 2). On the DTG curve, measured in air, in the temperature range 450-530°C there is observed the second peak of mass loss that is associated with the oxidation of char residue. Shift of first maximum towards higher temperatures for the DTG curves corresponding to the samples, processed at higher torrefaction temperatures (see Fig. 4), is explained by decreasing content of least thermostable organic component, namely hemicellulose, in their composition.

DTG curves, shown in Fig. 4, correlate well with the DSC curves describing the heat generation caused by oxidation reactions proceeding during heating pellets in the air (see Fig. 5).

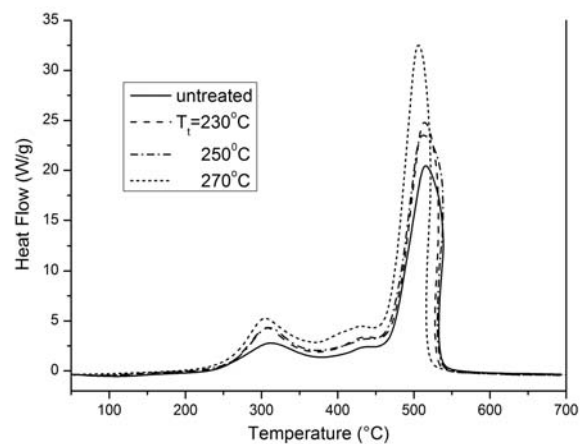


Figure 5. DSC curve of untreated and torrefied chicken litter pellets in air at the heating rate of 10°C/min.

The first maximum in the DTG curves shown in Fig. 5 is associated with the oxidation of the volatile matter, the second – with oxidation of the char residue. As seen from Fig. 5, an increase of torrefaction temperature leads to an increase in the amplitude of both peaks. This behavior is explained by the fact that with increasing T_t the combustion value of volatile matter (the first peak) and the relative fraction of the char residue (the second peak) are increasing also. As a result the combustion value of torrefied pellets exceeds the combustion value of initial pellets and increases with increasing the torrefaction temperature.

C. Thermotechnical characteristics of torrefied chicken litter pellets

Table II presents the main characteristics of the initial chicken litter pellets and the pellets torrefied at different temperatures, which are important if we discuss the usage them as a solid fuel. From the presented data it follows that an increase of torrefaction temperature results in appreciable increase of specific combustion value. Unfortunately, at the same time the ash content, that in chicken litter pellets is several times greater than in peat and especially in wood pellets, increases also. Decrease of the volatile content in torrefied pellets (see Table II) leads to decrease of soot

content in combustion products and decrease of smoke emission.

TABLE II. THERMOTECNICAL CHARACTERISTICS OF UNTREATED AND TORRIIFIED CHICKEN LITTER PELLETS

Characteristics	Untreated pellet	Pellet torrefied at		
		230°C	250°C	270°C
Relative combustion value	1	1.32	1.41	1.65
Ash content (dry basis), %	13.7	16.6	18.6	20.8
Content of volatile matter (dry basis), %	73.5	63	58.7	56.6

Other important characteristic of any solid fuel is its hydrophobic properties. To determine the effect of torrefaction on these properties the corresponding measurements were carried out. During measurement a test sample was placed into a desiccator, in which 100% humidity at a temperature of 26°C is maintained. Periodically measurements of mass of test sample were carried out. Results of experiments are presented in Fig. 6.

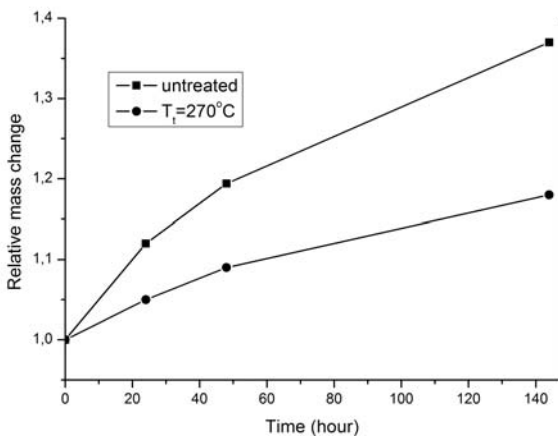


Figure 6. Relative mass change of initial and torrefied (at temperature 270°C) pellets as a result of water vapour uptake.

The presented data show that the initial sample absorbs water vapor from the air considerably faster than the sample torrefied at temperature of 270°C. It is necessary to note that untreated chicken litter pellets swelled and fell apart after

140 hours presence in a desiccator with the abovementioned conditions. At the same time, pellets torrefied at temperature of 270°C, conserved their shape and hardness. Such a behavior simplifies storage and transportation of torrefied pellets.

From these data one can see that the torrefaction allows to improve essentially the hydrophobic property of granulated biomass fuel. The limit moisture content of pellets torrefied at $T_t = 270^\circ\text{C}$ is practically half in comparison with untreated pellets. It is necessary to note, that untreated wood pellets swelled and fell apart when in contact with water. The torrefied wood pellets kept the form in the similar conditions.

IV. CONCLUSION

Experimental investigations of influence of thermal treatment (torrefaction) on the properties of chicken litter pellets were fulfilled. Measurements were carried out by methods of the thermogravimetric analysis and the differential scanning calorimetry in neutral and oxidizing gas environment (nitrogen and air, respectively). As a result of performed experimental investigations it is shown that thermal processing of chicken litter pellets allows to improve its consumer properties, namely, to increase the specific combustion value and to improve hydrophobic properties. Thus torrefied chicken litter pellets can be recommended for using as a solid fuel.

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Development Of Technology For Biomass Processing Into Heat and Power

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Abstract — Results of experimental investigations in the field of bioconversion are presented. The technology is connected with pyrolytic conversion of biomass into synthesis gas which can be used as a gas fuel for power unit on the base of gas-diesel engine. It is shown that as a result of biomass pyrolysis and the subsequent cracking of emanating products by their filtration through charcoal at the temperature 1000°C it is possible to receive 1.4m³ of gas with heating value about 11.7 MJ/m³ per one kg of original raw material.

Keywords - biomass conversion; pyrolysis; syngas.

I. INTRODUCTION

Developing the technologies for conversion of different kinds of biomass into gas fuel and pure carbon materials is rather an actual problem both from the point of view of natural resources conservation, and from the point of view of creating autonomous plants to produce both electricity and heat operating on local kinds of fuel. Very attractive natural raw material is wood and peat. Wood and peat fall under category of renewable hydrocarbon resources. About 70% of the territory of the Russia is covered with forests, which makes up about 23% of world reserves [1]. The development of efficient methods of processing the waste of the lumbering and wood-working industry is a very urgent problem from the standpoint of environmental protection, because the decay of wood waste is accompanied by emission of carbon dioxide, phenol compounds and other harmful substances while the thermal effect of attendant chemical reactions is not utilization. In regard to peat reserves in Russia, which account for about 42% of those around the world, they are equivalent to about 70 billion tons of standard coal that exceeds the total oil and gas resources [2]. Growth of peat reserves only in Russia is estimated at 260 -280 million tons per year but only few percent of that quantity is extracted and used now [3]. From the 1960's the use of peat began to rapidly decrease as more natural gas was produced and consumed. The amount of peat consumed in 1990 had dropped by more than a factor of 8 as compared with that in 1965 and its fraction in the country's energy balance had decreased by a factor of 22 for the same period of time [2]. Utilization of raw or partially processed wood and peat for needs of power engineering is represented rather inconvenient and demands essential investments as it leads to radical reconstruction of the whole technological chain of electricity production. An alternative way to use the abovementioned hydrocarbon resources for power purposes links to developing a technology for processing them into high-calorific gas mixtures.

Gasification and pyrolysis are the most popular methods that developed for producing gas fuel from biomass. Both of them have some advantages and disadvantages. Air gasification is the easiest method to convert biomass into gas. However, the resulting gas contains up to 60% carbon dioxide and nitrogen and its calorific value is generally around 4 - 5 MJ/m³ which is too low. Overall efficiency of gasification gas power plant is limited to 20%. The gasification products also contain undesirable substances, such as tars and dust which are need to be removed [4]. To increase a calorific value of the gasification products oxygen or water steam gasification can be used. The gas produced by oxygen and steam gasification contains no nitrogen and small amount of carbon dioxide. The maximum gas yield reaches 1.3 m³ per kg of raw material and its calorific value is about 11 MJ/m³ [5]. Steam gasification is the widespread process because of its simplicity. The main disadvantage of the process is concerned with necessity of steam generation which reduces overall effectiveness of power plant. Use of oxygen for the purpose of gasification demands an air separation unit in technological chain that leads to rise in price of end product.

During pyrolysis of solid hydrocarbon raw material, heating is carried out without air access, and, therefore nitrogen is absent in the end products. Products of biomass pyrolysis are non-condensable pyrolysis gas, char and liquid fraction consisting of tar and pyrolytic liquor. Calorific value of gas produced in the process of biomass pyrolysis is considerably higher than calorific value of gas produced in the air gasification process. Composition of pyrolysis products depends both on biomass properties and on a number of technological parameters, such as heating rate, final temperature, characteristic time of residence in reaction zone and so on. Insignificant degree of processing of initial raw materials into pyrolysis gas is main disadvantage of this technology. Significant increase the gas yield can be achieved by high-temperature conversion of liquid fraction. For this purpose the catalytic [6] and non-catalytic [7][8] methods can be used. In the present paper the scheme similar to the scheme offered in [6] for processing of wood sawdust is considered. Experimental feasibility of the technology based on such scheme was partially presented in [9]. Synthesis gas consisted from carbon oxide and hydrogen and char are the end products of this technology.

Char is a brittle porous material with carbon content about 90%. It would be possible to use it in various industrial applications, for example metallurgy, if its stress-strain property is not too low. The other technology which is

presented in this paper allows to produce a hard carbon composite material with carbon content up to 98% from char. Composite is formed as a result of deposition of pyrocarbon on the surface of char in the process of heterogeneous pyrolysis of gaseous hydrocarbons which are blown through reaction volume filled by char [10]. The gaseous mixture at the exit of reactor contains hydrogen which concentration may be easily varied by change in operating parameters and may reach 90% (volume) and more. As the gaseous hydrocarbons in this technology natural gas, low-pressure gas field, oil gas and hydrocarbon waste gases of different industrial enterprises may be used.

Comparison of behavior of different biomass types during their processing by means of two abovementioned technologies, experimental research of the influence of different factors (temperature, heating rate, residence time) on the composition and volume of the producible gaseous mixtures, the quantitative characteristics of the heterogeneous pyrolysis of saturated hydrocarbons in the process of their filtration through the porous carbonic medium were the purposes of this paper.

The second section describes experimental reactor and conditions of experiments. The third section describes weight loss of different materials during pyrolysis and pyrolysis gas volume and composition measurement. The fourth section describes results of experiments with pyrolysis liquid and gaseous products cracking and obtaining synthesis gas. The fifth section describes an experimental power plant based on the technology of two-stage thermal conversion of biomass into synthesis gas, which is used as fuel for gas-diesel power generator.

II. EXPERIMENTAL CONDITIONS

All the experiments were carried out at the setup similar to one used in [9][10] and schematically presented in Figure 1. It consisted of a high-temperature reactor A, a gas supply system and a gas expense controller G at the entrance of reactor, and a system of extraction and analysis of gas at the exit of reactor including condenser B, eudiometer C and chromatograph. The samples of the gas for chromatography were taken out in the point D. The reactor was a stainless steel tube with an inside diameter of about 37 mm, which was placed within two-section furnace with independent heaters for each section. Each section was 300 mm length. The heaters allowed varying the temperature inside the reactor from 100 to 1200°C. Such construction of the furnace made possible to use the reactor in one and two chamber regimes.

In the first case, the top chamber of reactor was not heated up and was empty. During experiments the behavior of different raw materials situated in bottom chamber at the stage of pyrolysis, activation and also the process of pyrocarbon deposition from gaseous hydrocarbons on the surface of char were investigated. The gas supply system made it possible to carry out experiments in different gas media and monitor the volumetric gas flow through the reactor. The pressure in reactor was equal to 10^5 Pa.

The two chamber regime was used for investigation of pyrolysis of different raw materials, composition and yield of

gas produced in process of its thermal conversion. Raw material 1 (see Figure 1) was placed into the bottom chamber. Char 2 obtained by pyrolysis of the same raw material was placed in the top chamber. The depth of char bed was equal to 50 mm. Before experiments the top chamber was heated up to temperature T_2 that was held further at the constant level. After that the temperature of the bottom chamber was raised at the rate 10°C/min. Thus, gases and vapour formed during pyrolysis of initial raw material passed through the porous carbon bed with the fixed temperature T_2 (further this mode is designated as «pyrolysis with cracking»).

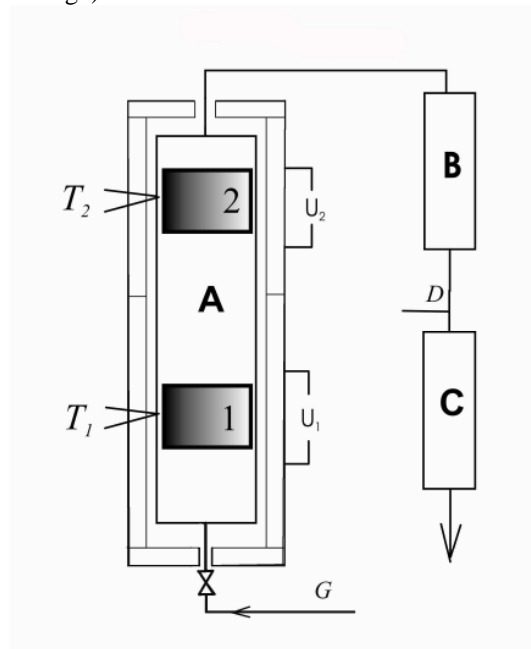


Figure 1. Experimental installation scheme

As a result of homogeneous and heterogeneous chemical reactions in the high-temperature zone a decomposition of pyrolysis gases and vapour took place. Conversion degree depended both on the temperature T_2 and on the residence time in a high-temperature zone. The output gas mixture passed through the condenser B. Non-condensable gas came into the eudiometer C. Comparison of the composition and the output of the gases formed at presence and absence of the char in the top chamber of the reactor gave an opportunity to compare efficiency of conversion of initial raw material into combustible gas under different operation conditions. Wood and peat pellets were used as initial raw material. Humidity of the samples was 6% and 10% for wood and peat respectively.

III. PYROLYSIS OF WOOD AND PEAT PELLETS

The different raw materials pyrolysis experiments were carried out in one chamber regime of reactor. During the experiments raw material was heated in oxygen-free medium from room temperature to 1000°C. The fulfilled experimental investigations showed similar behavior of peat and wood pellets during their thermal processing. The change in the

temperature of samples and the corresponding change in their mass are presented in Figure 2. The data shown in Figure 2 correspond to a heating rate of approximately 10°C/min. It can be seen that the loss of mass occurs mainly in the temperature interval from 200 to 600°C and ranges from 65 (for peat pellets) to 75% (for wood pellets) of the initial mass. The change in the mass with a further increase in the temperature is insignificant and is equal to around 5% of the initial mass in the temperature interval from 600 to 1000°C. The obtained char is a brittle porous material containing around 80 and 90% of carbon for peat and wood pellets, respectively. This difference mainly depends on the difference of ash level of the initial raw materials. Changing the heating rate from 2 to 35°C/min resulted in the mass of char decreasing by no more than 10% and the specific volume of open pores increasing by around 20%. The specific volume of open pores for char from wood and peat pellets is equal to 0.5 and 0.28 cm³/g, respectively.

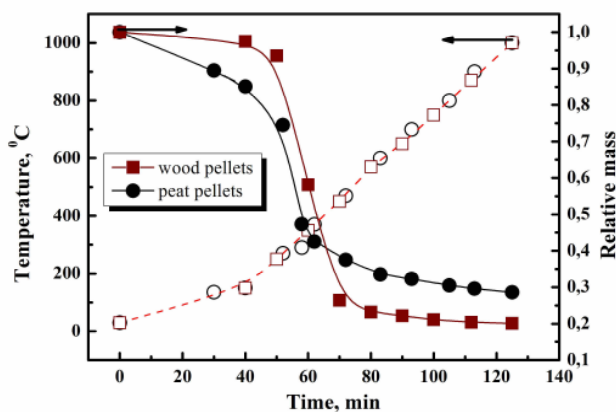


Figure 2. Temperature change and relative mass loss of wood and peat pellets in the pyrolysis process

The chromatographic analysis of composition of the gases evolved during pyrolysis of wood and peat pellets was fulfilled in the temperature range 250 – 1000°C at the heating rate 10°C/min. Gas yield and its composition for wood and peat pellets are very similar. Major gas components are H₂, CO, CO₂ and C_nH_m. Note that methane constituted the main part in the hydrocarbon mixture C_nH_m. At temperature above 500°C the carbon dioxide content substantially decreased whereas the content of combustible gases (methane, hydrogen and carbon monoxide) increased that led to increase of the calorific value of the product gas mixture. The overall gas yield was equal to 0.29 m³ per kg of initial raw material. The lower calorific value of product gas was equal to Q_L = 9,6 MJ/m³. Extraction of the gas evolved in the temperature range 500 – 1000°C leads to the appreciable increase of the calorific value of product gas up to 13 MJ/m³ but the gas yield decreases to 0.18 m³ per kg of initial raw material.

IV. PYROLYSIS AND CRACKING

Increasing the conversion degree of raw material into a combustible gas can be achieved as a result of high-temperature thermal processing of gases and vapors emanating in process of pyrolysis. For this purpose two chamber regime of reactor was used. The data on gas volume (per kg of peat pellets) obtained in the process of heating of the bottom chamber of the reactor at different temperatures T₂ are shown in Figure 3. In the same Figure, the similar data received in «pyrolysis» mode are also shown. As follows from the presented data the volume of the gas produced in mode «pyrolysis with cracking» was much more than the volume of the gas produced in «pyrolysis» mode. This difference increased essentially with increasing the top chamber temperature T₂. Simultaneously, reduction of quantity of the liquid fraction collected in the condenser B was observed. For the temperature T₂ = 1000°C there was no liquid fraction in the condenser that was evidence of full tar and pyrolygneous liquor conversion into gas. Chemical interaction of pyrolygneous liquor with char was confirmed by char mass loss in the top chamber of the reactor which increased with growth of temperature T₂.

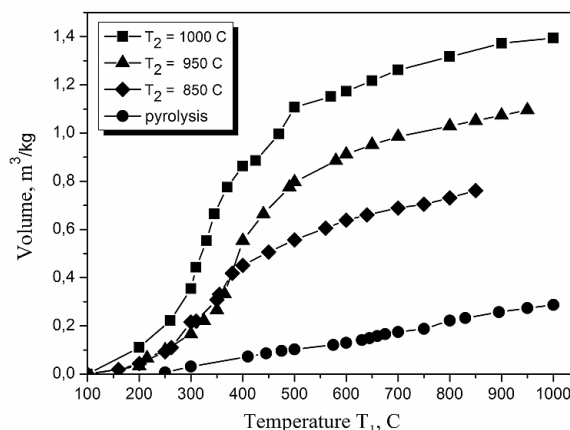


Figure 3. Gas yield per one kg of raw material during thermal processing of peat pellets for different regimes

The mass of char formed in the bottom chamber did not depend on the temperature in the top chamber and was about 30% for peat pellets and 20% for wood pellets. It is followed from Figure 3 that in mode «pyrolysis with cracking» main volume of gas was generated in the temperature range 250 – 500°C that corresponded to the temperature range of condensable fraction formation during pyrolysis.

Figure 4 shows the results of chromatography of the gas composition during heating of the bottom chamber at two temperatures of the top chamber T₂. One can see that carbon dioxide and methane content in output gas decreased with the rise of temperature T₂. For temperature T₂ = 1000°C the content of carbon dioxide and methane didn't exceed one percent. Thus, the temperature increase in the top chamber leads to raise the rate of disoxidation of CO₂ and heterogeneous pyrolysis of methane. It should be noticed that

for the top chamber temperature $T_2 = 1000^\circ\text{C}$ the gas composition practically does not depend on the bottom chamber temperature at its changing in the range 250 – 500 $^\circ\text{C}$, i.e., in the area of main gas release (see Figure 3).

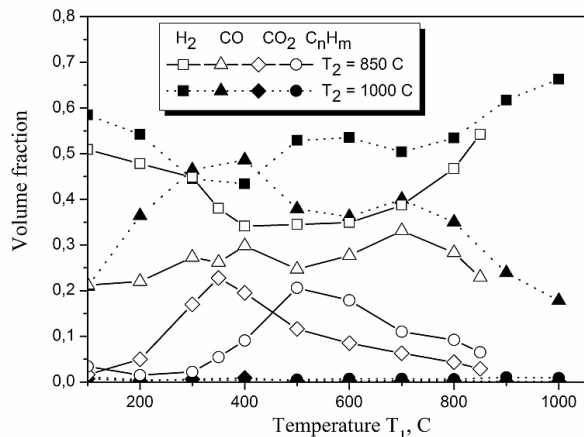


Figure 4. Composition of output gas in mode «pyrolysis with cracking»

Calorific values of the gas mixtures obtained by thermal processing of wood and peat pellets were calculated on the base of experimental data similar to presented in Figure 4. In Table I and Table II data on content of combustible components in the gas mixtures obtained by thermal processing of peat and wood pellets for «pyrolysis with cracking» mode and its high and low calorific values are presented. Similar data for gas mixture obtained in «pyrolysis» mode are shown in the same Tables.

TABLE I. COMPOSITION AND CALORIFIC VALUE OF GAS MIXTURES OBTAINED FROM PEAT PELLETS

T_2, C	Volume fractions of combustible components			Calorific value, MJ/m^3	
	H_2	CO	C_nH_m	Q_H	Q_L
850	0,40	0,27	0,08	11,7	10,6
950	0,43	0,40	0,02	11,3	10,4
1000	0,49	0,41	0,01	11,7	10,6
Pyrolysis	0,23	0,19	0,13	10,4	9,6

TABLE II. COMPOSITION AND CALORIFIC VALUES OF GAS MIXTURES OBTAINED FROM WOOD PELLETS

T_2, C	Volume fractions of combustible components			Calorific value, MJ/m^3	
	H_2	CO	C_nH_m	Q_H	Q_L
850	0,39	0,28	0,10	12,5	11,5
950	0,47	0,41	0,01	11,5	10,6
1000	0,46	0,46	0,00	11,7	10,9
Pyrolysis	0,28	0,26	0,16	13,4	12,2

The data comparison shows that calorific value of gas mixture obtained in «pyrolysis with cracking» mode practically does not depend on the top chamber temperature T_2 and differs about 10% from calorific value of gas mixture obtained in «pyrolysis» mode. For peat pellets it is more in «pyrolysis with cracking» mode and for wood pellets it is more in «pyrolysis» mode. The gas composition is much more sensitive to the temperature T_2 . As stated above the temperature T_2 increase leads to CO_2 and CH_4 content decrease. For the temperature $T_2 = 1000^\circ\text{C}$ the product gas mixture consists of CO and H_2 in practically equal parts.

If calorific value of the gas mixture obtained in «pyrolysis with cracking» mode slightly differs from calorific value of the gas mixture obtained in «pyrolysis» mode, the gas volumes are essentially different (see Figure 3). That means the «pyrolysis with cracking» mode allows increasing the conversion degree of the initial raw material into gas phase.

V. PILOT POWER PLANT

On the base of experimental data mentioned above, there was designed an experimental power plant of electric power up to 50 kW shown at Figure 5.

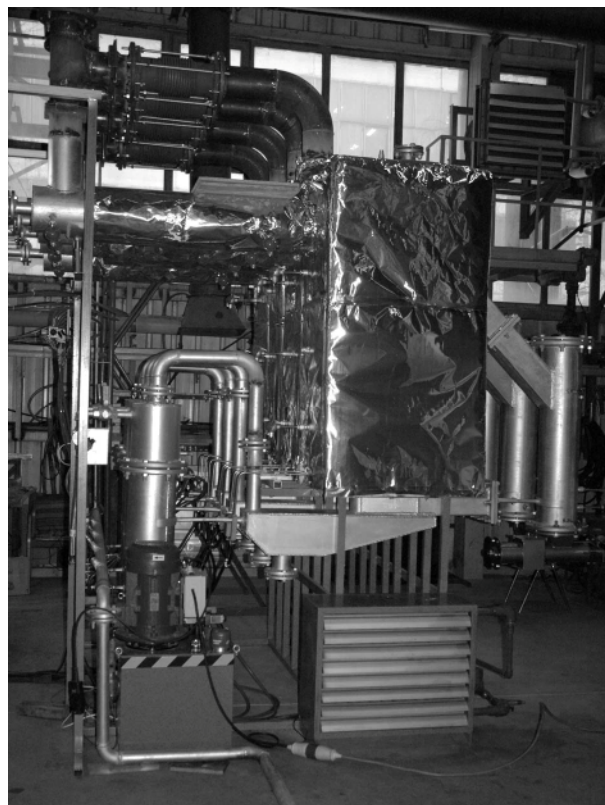


Figure 5. Pilot power plant (biomass processing unit).

The power station consists of biomass processing unit, control and measurement system, and a gas-diesel engine with an electric generator.

VI. CONCLUSIONS AND FUTURE WORK

As a result of the pyrolysis and the subsequent cracking of emanating volatile products over a char at the temperature 1000°C it is possible to increase the conversion degree of initial raw materials and to receive about 1.4 m³ of gas with calorific value approximately 11.7 MJ/m³ from one kilogram of wood or peat pellets.

Experimental investigations have shown that wood and peat pellets can be used in the technology for integrated processing of raw hydrocarbon materials for obtaining carbon material and synthesis gas.

Future work will include energy balance determination for the technology and series of pilot power plant tests.

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