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Biomass Pyrolysis and Gasification Comprehensive Modeling for Effective Power Generation at Combined Cycle Power Plant

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Abstract

Thermogravimetric experiments were carried out for a few types of wood with determination of the kinetic parameters characterizing the pyrolysis process. In the present work the various kinetic models used for this purpose are suggested. Analyzing software tool for calculation of thermal conversion products and reactor balance is developed. The optimal temperature range for biomass pyrolysis is identified using this tool. The influence of steam and air flow rates on the gasification products is represented. The impact of operating parameters on the synthesis gas composition was evaluated. Comparison of the computational model and the results obtained during experimental studies on the existing gasifier were carried out. The combined cycle power plant involving the biomass gasification process has been numerically simulated in the Aspen Plus. Calculations of the optimal operating parameters of different thermal process components and of the entire combined cycle power plant system were performed.

1. Introduction

The most common method of using organic raw materials (e.g. biomass) for power generation consists of two stages: the preprocessing of a source material into pellets, which leads to a considerable increase of the energy content of raw material and decreases expenditures for its transportation even at small distances, and the combustion of the granulated raw material in boilers. Nevertheless, the combustion of solid raw materials seems not to be an optimum method of its use, mostly if we are dealing with up to 10 MW power generating units. The preliminary conversion of solid fuel into a gaseous or liquid state followed by its use in power generating units based on gas turbines or internal gas engines seems most reasonable. In this context, the production of synthesis gas (a mixture of hydrogen and carbon monoxide) by the pyrolysis of biomass is widely used. It is well known that this gas can be obtained from almost any product of organic origin, including many species of wood, peat, sunflower seed husk, and straw. In this case, the use of peat requires material expenditures for its production, whereas the use of wood waste and agricultural wastes for power supply purposes at manufacturing enterprises leads to an increase in the profitability of an enterprise due to a decrease in expenditures for both waste utilization and the purchase of energy resources.

2. Experimental

Process of the thermal decomposition of different kind of biomass has been investigated in the thermoanalyzer NETZSCH STA 449 C Jupiter, which registered thermogravimetric (TG) dependences. Accuracy of the mass measurements was equal to 1%, the temperature measurements – 0.5 °C. Declared accuracies are confirmed by the thermoanalyzer specifications and allow one to get highly precision results in subsequent calculations. Mass limit of a sample was equal to 200 mg. In experiments samples with mass up to 50 mg were used. Heating of samples were carried out in argon flow from room temperature up to 1000 °C with

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heating rate of 10 °C/min. Argon volumetric velocity through the heating chamber was equal to 150 cm^3/min. Characteristic time of the heating chamber gas exchange did not exceed 20 sec. The samples were placed into a platinum crucible. The experimental TG curves for different materials under study had similar form. Sample mass changing during heating may be divided into several characteristic ranges. The range corresponding to the temperature interval from room up to 150 °C is characterized by small mass changing (about 2–10%), which is caused by loss of physical water. Up to the temperature of 200 °C the mass stabilization is observed. During the temperature rise the mass loss connected with intensive volatile outlet, was observed. At the temperature over 400 °C the process of thermal decomposition slows down and at the temperature of 600 °C it practically finished.

2.1. Kinetics models of biomass pyrolysis

It is used various kinetic models differing the number of independent parallel or independent consecutive (typical for separate temperature intervals) chemical reactions responsible for volatile outlet for description of the biomass pyrolysis. The models, in which the process of decomposition is represented as a sequence of independent reactions, were not considered in this paper because they are not universal for different materials simulation [1].

Kinetic schemes, modeling the thermal decomposition by a set of independent parallel reactions, considering that each reaction included in the scheme describes the decomposition of individual component entered into composition of initial raw material are widely used. The rate constants are represented in Arrhenius form. In this case the change of the relative mass of each component caused by thermal decomposition may be presented as:

$$\frac{dX_j}{dt} = -k_{oj} \cdot \exp\left(-\frac{E_j}{RT(t)}\right) \cdot X_j^n \qquad (1)$$

where $X_j = \frac{m_j(t)}{M_0}$; t – time; $m_j(t)$ – mass of j-th component; M_0 – the total mass of volatile, i.e. initial mass of dry sample minus nonvolatile carbon residue formed as a result of heating; T – temperature (K); E_j – activation energy (kJ/mole); n_j – reaction order; k_{oj} – preexponential factor (s^{-1}). In the initial moment the condition, $\sum_j X_j(t=0) = 1$, is satisfied.

Maximum value of j is equal to the number of the independent parallel chemical channels of thermal decomposition of initial raw material or to the number of components entered into its composition. Kinetic parameters (k_{0j}, E_j, n_j) are determined by minimization of the error functional:

$$F = \sum_{i=1}^{N} (X_{ej} - \sum_{j=1} X_{ji})^2 \longrightarrow \min \qquad (2)$$

The error functional (deviation of the experimental curve from the calculated one) was minimized using the DSFD optimization algorithm. The DSFD (Direct Search of Feasible Direction) [2], in fact, includes 3 different methods that complement each other:

1) direct search method of rotating coordinates of the starting point;

2) secondary method of search of possible directions in the region close to the optimum;

3) the method of penalty functions to the inequality constraints and optimized variables.

A calculation program was developed in the C++ Builder software tool. It makes possible to select the kinetic parameters of pyrolysis process in such a way that the error of experimental curve description according to the least squares method does not exceed 0.5%. An analysis of the results shows that the values of all corresponding kinetic parameters for cellulose are quite close to each other: the deviation from the average values is less than 10% (Table 1). For lignin and hemicellulose, the deviation of kinetic parameter values is somewhat larger, which can be explained by different chemical structures of these polymers. The fourth component is characterized by the most essential quantitative deviation of data and can be used in the model like correlation component. Thus, the temperature corresponding to the peak yield of this component is 250 °C for pine and 400 °C for oak. Thus it is not always possible to exactly identify the fourth component as water or another biomass component different from those mentioned above. The obtained kinetic parameters are universal ones for each type of wood and are almost independent of the experimental conditions. Besides, the performed investigations have demonstrated that the thermal conversion of natural polymers (hemicellulose, cellulose, and lignin) is similar for different kinds of biomass.

In the simplest single-channel scheme (j = 1) the process of decomposition is described with a single overall reaction, which is responsible for the thermal decomposition of raw material throughout the temperature range 200–1000 °C (Fig. 1).

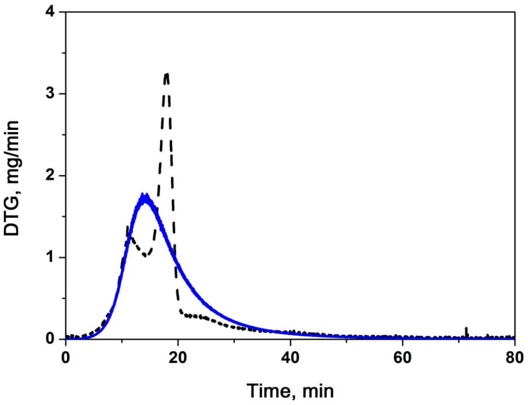

Fig. 1. DTG curves for oak: dotted lines are experimental, continuous are calculated by single-channel scheme.

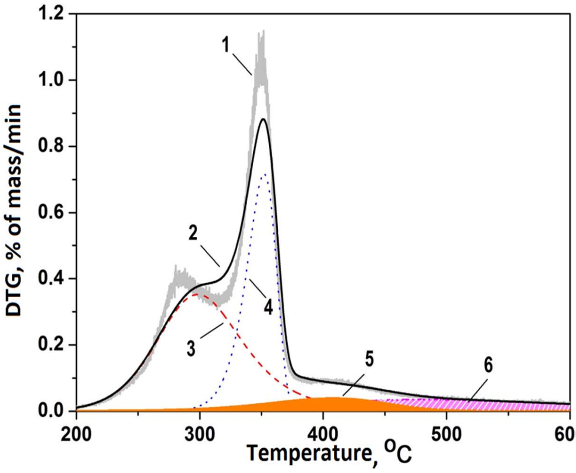

Fig. 2. DTG curves for oak: 1 – experimental and 2 – calculated, 3 – hemicellulose, 4 – cellulose, 5 – lignin, 6 – fourth component.

Three (j = 3) and four (j = 4) channel-models are most commonly used in relation to biomass [3–5]. Background for this is the fact that the basic components of biomass are hemicellulose, cellulose and lignin. In addition, on the differential thermogravimetric (DTG) curves, measured in the temperature range 200–1000 °C, one can observe three peaks of the mass loss rate. Inclusion in calculation the fourth channel makes it possible to improve the accuracy of the description of the experimental TG and DTG curves (Fig. 2).

The values of kinetic parameters, calculated on the basis of four-channel model (1), as well as the calculated values of mass fractions of hemicellulose, cellulose and lignin are shown in Table 1.

Table 1
Kinetic parameters and mass fractions, calculated using four-channel model

Component	Kinetic parameters	Oak	Pine	Birch
Hemicellulose	ln k0	14.99	16.56	17.19
	E (kJ·mol^{-1})	109.6	122.9	119.9
	n	2.04	2.21	1.26
	X, %	32.84	41.43	29.96
Cellulose	ln k0	45.26	49.08	44.62
	E (kJ·mol^{-1})	273.0	299.6	273.8
	n	1.001	1.001	1.001
	X, %	22.38	29.64	37.30
Lignin	ln k0	0.001	0.001	0.001
	E (kJ·mol^{-1})	58.85	69.25	63.23
	n	2.487	2.864	4.044
	X, %	11.14	11.69	11.86

2.2. Thermal conversion products analysis

The thermal decomposition kinetics of coal coke was considered in detail in [6, 7]. The proposed model may be used to investigate the pyrolysis and gasification of other solid fuels. In the present work, we use an analogous computational model to assess the composition and thermal conversion products of biomass. On the basis of chemical thermodynamics, we may calculate the equilibrium composition of coal pyrolytic products if we know the temperature, pressure, and elementary composition of the initial material. The results are in good agreement with experimental data. Accordingly, this method permits rapid computer simulation of the process and determination of the condition for maximum yield of decomposition products. To investigate the equilibrium composition in the pyrolysis of biomass with fixed temperature and pressure, we consider conversion model:

$$[Biomass]\xrightarrow{T,P,\alpha(O_2),\alpha(H_2O)}[C,CO,H_2,CO_2,N_2,O_2,SO_2,CH_4,H_2O,etc]$$

The number of moles of simple materials (basic components), which is specified as the initial information, is determined on the basis of the sample's elementary composition. In optimization, the target function is the differential of the Gibbs energy, which is equal to zero in the equilibrium state:

$$\Delta G_{reaction}=\sum_{i=1}^{M}n_i\cdot(\Delta G_i^0+R\cdot T\cdot\ln P)+R\cdot T\cdot\sum_{i=1}^{M}n_i\cdot\ln n_i-R\cdot T\cdot n\cdot\ln n\rightarrow\min$$

with the additional conditions:

$$\sum_{i=1}^{M}a_{ji}\cdot n_i=b_j\qquad(j=1,2,\ldots,m)\qquad\sum_{i=1}^{M}n_i-n=0$$

Here is the Gibbs energy ΔG, J/kg; n_i is the number of moles of component i; n is the total number of moles in the system; P is the absolute pressure, Pa; a_{ji} are the stoichiometric coefficients for the formation of the components from atoms; m is the number of types of atoms; b_j is the number of moles of atoms of type i in the system.

Except the gas composition, it's determined the heat of combustion of the mixture and its volume. If the number of moles of carbon in the coke residue is known, we may calculate its content as a proportion of the initial mass.

The developed method is used for solving the equation system for estimating the equilibrium composition of a multicomponent system. The Gibbs energy differential, which is equal to zero at equilibrium, was used as the target function in solving the optimization problem. The developed method was registered as the Fuel Thermal Conversion (FTC) computer program, using to analyze the effect of the power installation's operating conditions by varying the temperature, pressure, and steam – air flow rate in a thermal conversion chamber.

The FTC software is applied to study the thermal conversion of various types of local solid fuels, including wood, peat, and coal. According to calculations for the wood sample, the fractions of hydrogen and carbon monoxide increase with the decrease of methane content in the gas phase during heating. It leads to a smaller calorific value of the pyrolysis products. On the other hand, a growth of temperature leads to a larger total amount of the gas phase per mass of the initial sample and simultaneously to a smaller fraction of water vapor and carbon dioxide in the mixture, and to a smaller amount of fixed carbon residue. As a result, a higher pyrolysis gas calorific value per mass of initial wood at 1 atm is obtained. The peak of this curve is reached in the temperature range 825–875 °C (Fig. 3).

The pyrolysis process was calculated taking into account the yield of aromatic compounds, because the condensed phase of it can block the pyrolyzer's working cavities with liquid fractions of heavy hydrocarbons, thus leading to emergency shutdown of the entire equipment set. During wood pyrolysis, $C_{24}H_{12}$ (coronen) and C_6H_6 (benzene) have the largest contribution in the formation of aromatic compounds; the fractions of the other components, including benzo(a)pyrene, are significantly smaller. It has been found that the fraction of aromatic hydrocarbons at temperatures of 880–910 °C does not exceed 0.5 vol.% and 9 wt.%. As the temperature increases to 1000 °C, their concentration drops to the minimal values. Thus, the increase of temperature can be considered as a positive factor that helps to decrease the yield of aromatic compounds.

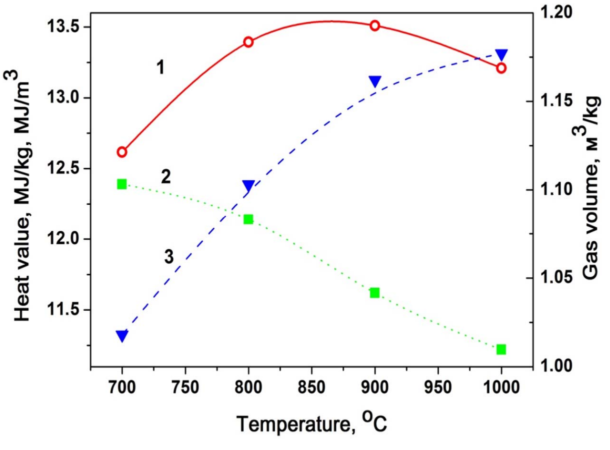

Fig. 3. Heat of combustion and volume of gaseous products in pyrolysis: (1) – chemical energy of the gaseous products per mass of the initial sample; (2) – heat of combustion of the gaseous products; (3) – volume of gaseous products per mass of the initial sample.

The chemical thermodynamic approach used in the simulation of pyrolysis may also be used to calculate the equilibrium composition of the gasification products of the biomass, for specified temperature, pressure, and elementary composition of the initial material. In Figs. 4 and 5, it's shown the composition of the synthesis gas (syngas) as a function of the air and steam flow rates in the gasification reactor. As we see in Fig. 4, variation in the air flow rate significantly affects the composition of the gaseous products. The content of H_2, CO, and CH_4 declines by 2.5, 3.3, and 5.5 vol.%, respectively. The H_2O content increases by 8%. It is observed the significant decrease in the mixture's heat of combustion (26%) with increase in the air supply to the chamber by almost 150%. Small variation in steam flow rate on gasification has little influence of the composition of the pyrolytic gas according to Fig. 5. However, increase in the steam content during thermal conversion of the biomass reduces the heat of combustion of the syngas.

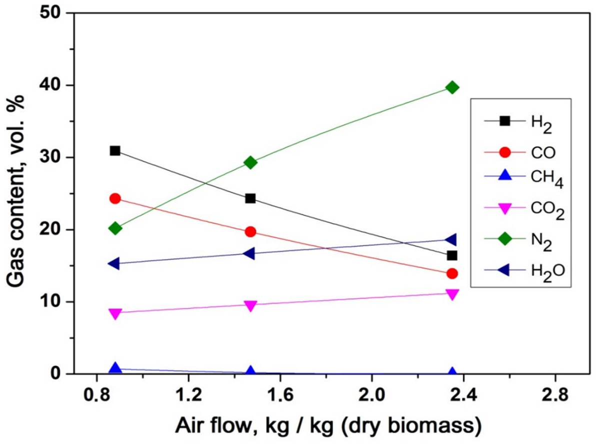

Fig. 4. Dependence of the composition of the syngas on the air consumption in gasification.

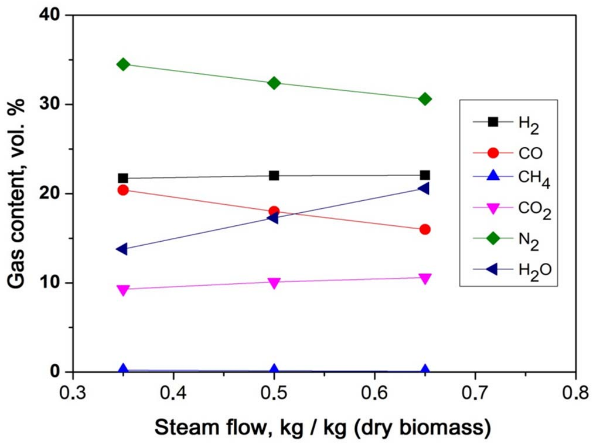

Fig. 5. Dependence of the composition of the syngas on the steam consumption in gasification.

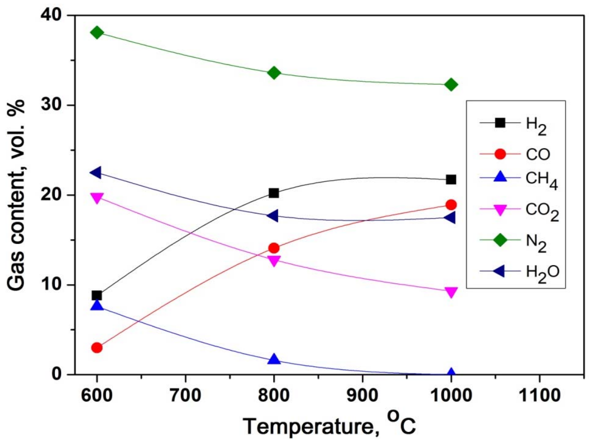

Fig. 6. Dependence of the syngas composition on the temperature in gasification.

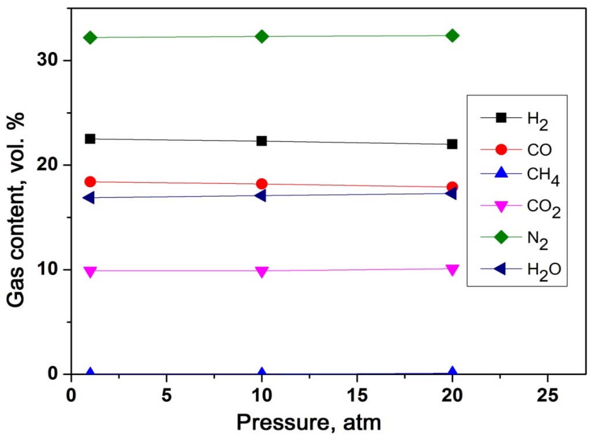

Fig. 7. Dependence of the syngas composition on the pressure in gasification.

In Figs. 6 and 7, it is shown the calculated dependence of the gaseous products composition on the temperature and pressure in the reactor chamber. From Fig. 6, we note the strict influence of temperature on the gasification products: the proportion of H_2 and CO increases rapidly with increase of the temperature. The methane content in the syngas declines, but the overall volume of gas produced increases as well as its heat of combustion. Note that, with increase in temperature in the gasification chamber from 650 to 950 °C, the chemical energy of the syngas increases by almost 150%.

As follows from Fig. 7, the pressure in the reactor has significantly less influence than the temperature. During the increase in pressure, there is a rise in the content of the ballast components: nitrogen, carbon dioxide, and water vapor. The proportion of methane also increases. However, the yield of hydro-gen and carbon monoxide and the heat of combustion of the mixture decline, as well as the total volume of gaseous products. Nevertheless increasing the rated pressure in the reactor leads to reducing its overall size and hence reducing the overall equipment costs.

The developed calculation software can be applied for modeling the pyrolysis and gasification processes of any solid organic fuel at the specified operating parameters in a continuous conversion reactor. The calculation results were compared with the experimental data obtained on a solid fuel gasification test bench (Table 2).

The calculated composition, yield, and chemical energy of the gas correspond to the maximum characteristics of the product from the reaction proceeding for infinitely long period of time. The gas parameters (yield and chemical energy) obtained on the test bench are close to the calculated ones. Calculated and experimental syngas volumes differ in 10% range, thus the calculated data is always quantitatively more than other. It means that calculation shows the theoretically possible maximum of product yield, while in experiment it's quite difficult to access 100% conversion of initial raw. Discrepancies can be explained by the errors existing in the experimental investigations, i.e., due to the fact that in practice it is not possible to achieve the same ideal gas parameters as in calculations.

2.3. CCPP modeling with biomass gasification

Computer modeling of the combined cycle power plant (CCPP) based on the biomass gasification process was carried out using the Aspen Plus software developed by Aspen Tech Inc. It is possible to construct and run the blocks for calculating the solid organic fuel gasification or pyrolysis processes (Fig. 8). The main advantage of such modeling is that all stages of the power generating system can be analyzed, starting from calculation of continuous chemical gasification processes up to estimation of the electricity generation efficiency [8, 9]. The gasification block considers a block for computing the biomass decomposition process and a Gibbs reactor, in which the procedure of calculation of the equilibrium gas composition is directly performed. The temperatures (°C) is determined for each substance flow in Fig. 8.

Steady state simulation model for gasification has been developed using Aspen Plus. The model can be used as a predictive tool for optimization of the gasifier performance CCPP operating parameters. Developed gasifier model consists of 3 main elements: block for conversion of fuel ultimate analysis data into conventional components (DECOMP); block for steam/air gasification process using Gibbs equilibrium (GASIFIER); block for separation volatiles and char after thermal conversion (SEPSG). Temperature levels in °C for each flow are indicated at stream lines [10].

The optimal operating parameters for various components of the thermal process arrangement and for the entire CCPP system were calculated using the above mentioned software. Figure 9 shows the results of varying the air/fuel ratio for studying its influence on the flue gas temperature at the turbine inlet and on the useful gas turbine electric power output. Decreasing the air flow rate supplied

Table 2

Calculated and experimental data for gasification of solid fuel

Parameter	Wood		Rubber		Plastic	
	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated
Syngas temperature, °C	850		950		950	
Reactor pressure, kPa	102		102		102	
Air/fuel ratio	0.5		0.5		0.5	
Syngas volume, m^3/kg	3.27	3.53	4.55	5.05	4.53	5.01
Syngas composition, %:						
CH_4	5.78×10^{-4}	0.0	1.59×10^{-4}	0.0	1.41×10^{-4}	0.0
CO	14.97	16.01	20.99	20.92	16.13	16.12
H_2	12.34	11.25	10.31	10.02	13.47	13.04
CO_2	11.22	10.26	5.72	5.69	6.56	6.53
H_2O	10.08	10.71	4.11	4.04	7.99	7.83
N_2	51.39	51.77	58.89	59.33	55.85	56.48
Gas chemical energy per mass of raw material, kJ/kg	10531	11419	17127	18806	15804	17241

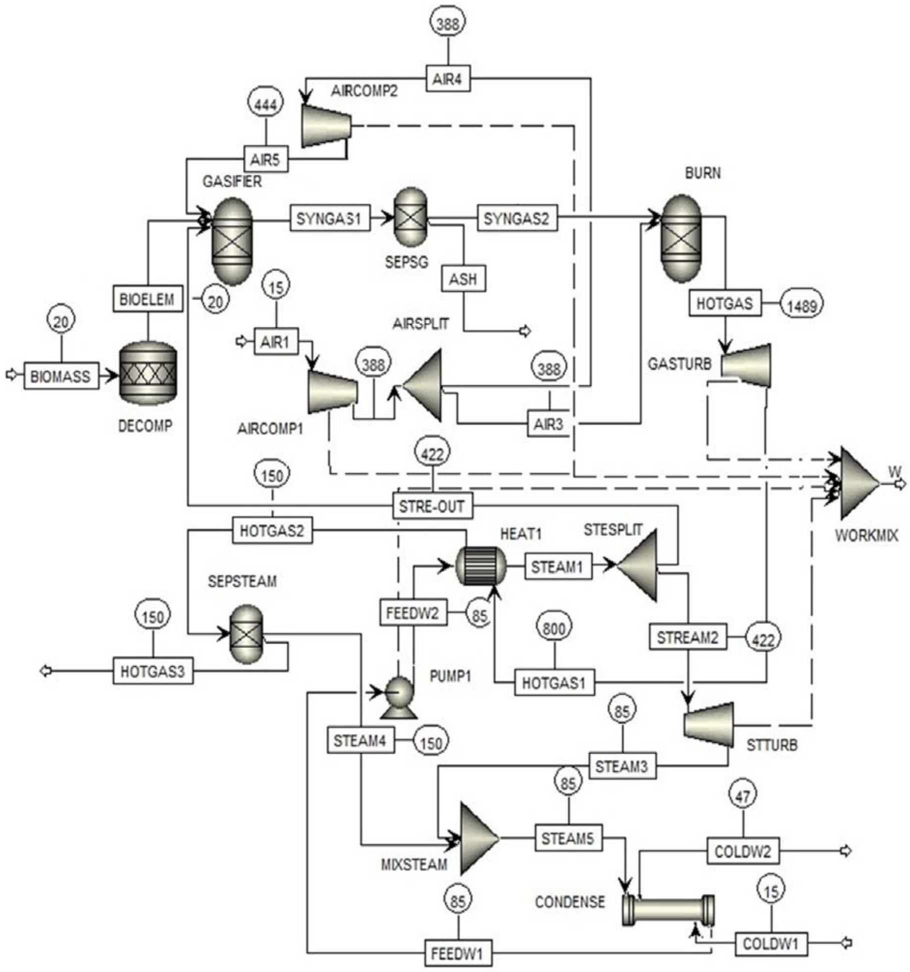

Fig. 8. Aspen Plus simulation model of biomass gasifier.

to the combustion chamber entails a growth of the flue gas temperature and of the electric power output at the same consumption of initial fuel. However, modern gas turbines have the upper temperature limit (1500 °C) determined by the operational parameters and characteristics of the metal used for making the rotor blades.

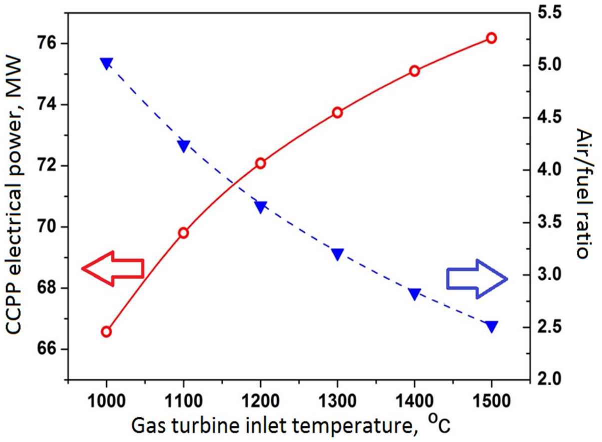

Fig. 9. Variation of gas turbine parameters using Aspen Plus.

3. Results and discussion

It is obvious from Fig. 1, that the single-channel model can be used only for qualitative description of TG curves. Its usage for estimation of the thermal decomposition rate will lead to significant errors. Four-channel model describes the experimental DTG curves quite well (see Fig. 2). From the dependences shown in Fig. 2, it follows that a disintegration of the hemicellulose and cellulose occurs in a narrower temperature range in comparison with lignin. The maximum of decomposition rate for these components correspond to the temperatures below 400 °C. Decomposition of lignin is observed in the temperature range 300–750 °C. The decomposition rate of lignin is in 5–8 times less than that of hemicellulose and cellulose. Kinetic parameters of decomposition of cellulose, calculated from TG curves measured for different materials, are quite close to each other. So the activation energy difference is within 15%. The largest spread of values is observed for the kinetic parameters corresponding to lignin. It is conditioned by notable difference in chemical composition of lignin in different kinds of biomass. The content of components (hemicellulose, cellulose and lignin) in samples from the different organic raw materials, defined along with kinetic parameters, correlates well with results of the chemical analysis known from the literature.

Developed FTC software can be used for to analyzing the effect of the power installation's operating conditions by varying the temperature, pressure, and steam–air flow rate in a pyrolysis or gasification reactor. Thus Temperature interval 825–875 °C can be used as recommended for wood pyrolysis in terms of maximum syngas chemical energy, volume and decrease of yield of aromatic compounds.

Aspen Plus functionally allows varying and optimizing a wide range of CCPP parameters, including air flow for gasifier and gas turbine; initial fuel mass flow; operating parameters of gasifier and turbine cycles (pressure, temperature); energy consumption of auxiliary equipment and etc. The total efficiency of CCPP can be reached up to 65% on the base of using of integrated optimization tool.

4. Conclusion

On the basis of the experimental thermogravimetric curves the kinetic parameters (reaction order, activation energy, and preexponential factor) of thermal decomposition of various types of biomass have been calculated. It is shown that four-channel model, in which the process of thermal decomposition is considered as the disintegration of the different components (hemicellulose, cellulose and lignin), describes quite well the experimental TG and DTG curves. Usage of the four-channel model allows along with the kinetic parameters to calculate the mass fractions of hemicellulose, cellulose and lignin in the investigated materials.

The synthesis gas and char prepared from different types of biomass can be used in small scale power engineering for the combined production of electrical and thermal energy for the needs of the power supply of settlements and small cities. Comparative analysis of steam – gas cycles based on the pyrolysis and gasification of biomass permits the following conclusions [11].

1. Cycles with biomass pyrolysis are economically expedient with electrical loads of 1–10 MW, on account of the relatively low initial capital expenditure.
2. Cycles with biomass gasification becomes affordable at power above 10 MW. That is due to the reduction in relative costs for drying and preparation of the initial fuel relative to pyrolysis, as well as the possibility of reducing the size of the continuous gasification reactor with increase of the pressure.
3. The electrical efficiency of the steam – gas cycle with biomass gasification is more than 40% when the power is 50 MW, as against 30–35% for the cycle with pyrolysis at analogous loads. The fuel efficiency for maximum district heating loads is 18.5% in the system with biomass pyrolysis and 20–22% in the system with biomass gasification. In that case, the total electrical and thermal efficiency is 50% in the case of pyrolysis and >60% for gasification. The proposed cogeneration system based on a steam – gas cycle with biomass gasification may be widely used in regions of Russia with a decentralized power supply system, thanks to its high fuel efficiency (60%, including 40% for electrical energy and 20% for heat), wide power range (5–50 MW), and low environmental impact and also to the availability of the fuel, which is readily regenerated. The results may be used to develop cogeneration systems with different solid fuels, including coal and lignite, peat, shale, biomass, and domestic and industrial waste.

References

[1]. P. Kalita, G. Mohan, G.P. Kumar and P. Mahanta, *J. Renew. Sustain. Ener.* 1 (2009) 1–12. DOI: 10.1063/1.3126936.

[2]. M. Pappas, J. Moradi. Proceedings of the American society of mechanical engineers: Ser. V. Design and engineering technology 4 (1975) 158–165.

[3]. A.G. Barneto, J.A. Carmona, J.M. Alfonso and J.C. Ferrer, *Ind. Eng. Chem.* 48 (2009) 7430–7436. DOI: 10.1021/ie900453w

[4]. A.V. Fedyukhin, I.L. Maikov, V.A. Sinelshchikov. Book of Abstracts of International Conference on Interaction of Intense Energy Fluxes with Matter. Nalchik. Russia (2011) 114–115.

[5]. A.M. Gyul'maliev, I.A. Sultanguzin, A.V. Fedyukhin, *Solid Fuel Chem.* 46 (2012) 164–167. DOI: 10.3103/S0361521912030056.

[6]. Yu.V. Konovalova, V.N. Trifanov, A.M. Gyul'maliev, S.G. Gagarin, I.A. Sultanguzin, *Solid Fuel Chem.* 38 (2004) 13–16.

[7]. A.M. Gyul'maliev, I.A. Sultanguzin, A.V. Fedyukhin, T.A. Stepanova, *Solid Fuel Chem.* 48 (2014) 164–169. DOI: 10.3103/S0361521914030057.

[8]. Th. Damartzis, S. Michailos, A. Zabaniotou, *Fuel Process. Technol.* 95 (2012) 37–44. DOI: 10.1016/j.fuproc.2011.11.010.

[9]. J. François, L. Abdelouahed, G. Mauviel, M. Feidt, C. Rogaume, O. Mirgaux, F. Patisson, A. Dufour, *Chem. Eng. Trans.* 29 (2012) 769–774. DOI: 10.3303/CET1229129.

[10]. I.A. Sultanguzin, A.V. Fedyukhin, S.Yu. Kurzanov, A.M. Gyulmaliev, T.A. Stepanova, V.A. Tumanovsky, D.P. Titov, *Thermal Engineering* 62 (2015) 359–364. DOI: 10.1134/S0040601515050110.

[11]. A.V. Fedyukhin, I.A. Sultanguzin, T.A. Stepanova, E.V. Voloshenko, S.Yu. Kurzanov, M.V. Isaev, *Coke and Chemistry* 56 (2013) 302–306. DOI: 10.3103/S1068364X13080024.