



Presentation of Experimental Biomass Gasification with Minimizing Gibbs Free Energy Mathematical Model

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1. Introduction

Thermochemical processing of biomass is the effective way of producing combustible gas (synthetic gas) The use of biomass by gasification has many advantages:

- using a wide range of biofuel and combustible waste types, even the wastes with the high moisture content,
- reduction in atmospheric pollution by using biofuels,
- the possibility of increasing the efficiency of equipment.

Today the technology of pyrolysis and gasification of need to be upgraded.

The synthesis of biogas is implement by various methods, for example, by the method of biochemical oxidation of raw materials, as presented in work (Kaosol & Sohgrathok 2013). This way makes it possible to get similar products (Malakahmad et al. 2013, Puah et al. 213), but these methods are not appropriate for all types of raw materials. Moreover it is difficult to predict the composition of the synthesized gas (Pavlenko & Koshlak 2019, Lavrov 1957).

Technological plants and systems for generating generator gas by biomass gasification currently need to be improved. There are methods to predict the composition of the generator gas and then its performance depending on the device parameters. The issue of processes are reflected in the works of many authors (Christus Jeya et al. 2014, Koroneos & Lykidou 2011) and others. Inthat papers, the experimental research of the gasification of solid fuels are shown, however the development of methods for predicting the composition of synthetic gas and determining the best parameters of the process has not been touched.

The method of predicting the composition of the gas is a big challenge for synthesis technologies, when it rise up the efficiency of the gas generator. To create a method for predicting the composition of the gas, we took as a basis the works of the authors (Zainal et al. 2001, Yang et al. 2006), where the energy characteristics of the resulting gases were evaluated. From our point of view it is highly important to know the composition and the influence of every component on the energy characteristics of the gas. It will allow to optimize the composition and predict the basic thermal characteristics. That was our main goal. In this article, we present the results of experimental research of multifactorial biomass gasification processes and the model of gasification based on the Gibbs free energy function.

2. Mathematical model and its solution

The main task of the research is to create a model of the biomass gasification process for predicting the composition of the synthetic gas and the parameters of the technology using a parameter – maximum thermodynamic efficiency. To do this, the following tasks must be done:

- investigate the whole processes of the gasification of biomass in installations with fluidized bed,
- go through a physico-chemical analysis of gasification processes,
- experimentally check the mathematical model.

The actual process of gasification depends on many parameters. Existing mathematical models of this process usually consider only some of them, so the modeling is not very accurate. The most of models are build on experimental data or hypotheses and correspond only with certain process.

In all existing approaches to mathematical modeling of the gas synthesis by gasification, the method for minimizing the free Gibbs energy should be considered. It does not need specification and chosen of specific gasification reactions (Jarungthammachote & Dutta 2008) and only takes into account the starting and end products of the process. This method is more suitable for viewing complex systems in which a large number of reactions occur. The method is based on the research of the equilibrium state of all those involved in the reactions of the gasification process.

The point of the method is the use of the thermodynamic potential of the system, the change of which goes to the minimum value under the condition of its equilibrium. The isobaric and isothermal potential (Gibbs energy) of a system of ideal gases is presented in the equation (1). Knowing the pressure in the gasification chamber is 1 ata, the properties of the gases approximate those of an ideal

gas, we write equation (2) in developed form. The issue of defining the composition of a synthetic gas with an equilibrium state of the system comes to the search for a composition that correlate to the minimum value of the function ($G_{tot} \rightarrow \min$) expressed by equation (3) under certain limiting conditions. The boundary conditions for this method of modeling the gasification process are the equations of the mass and energy balances of the elements of the system.

3. Basic simplifications of the mathematical model

The application of the thermodynamic equilibrium method require certain simplifications, the most important of which are presented:

- the time of passing of all gasification reactions is enough to get an equilibrium among all the gasification products,
- all gases involved in the gasification process have the properties of an ideal gas,
- the proportion of components of biomass which does not exceed 1%, and ash are not considered,
- the components of the synthesis gas produced are CO_2 , CO , H_2 , H_2O , CH_4 , C_2H_4 , C_6H_6 , N_2 .

1) Taking humidity into account. In most research on the gasification process, the authors do not take into account the humidity of the air supplied to the reactor, since their proportion will not be significant. However, the amount of moisture flowing in with the blowing air can reach 7% relative to 1 kg of fuel. This amount of moisture has a significant impact on the efficiency of the gasification process and should be considered in the mathematical model of the gasification process.

The w_{air} is determined by the dependence (total water mass per kg of dry fuel) and is presented in equation (4).

2) The presence of an unreacted carbon residue. In (X Li et al. 2001) it was experimentally proven that with increasing temperature in the reactor and the same parameters, the CO_2 concentration decreases in favor of CO . To produce 1 kmol of CO , you need twice as much oxygen as for the formation of 1 kmol of CO_2 with the same amount of carbon. Therefore, oxygen shows in the composition of other gas components (H_2O) or remains in the free form (O_2). However, gasification products contain practically no free oxygen in their composition under various gasification conditions, and the H_2O concentration decreases with increasing temperature in favor of H_2 . Therefore its sensible to talk about an increase in carbon conversion with increasing temperature. An increase in the rate of conversion of carbon also takes place with an increase in the amount of moisture entering the reactor (Skoulou et al. 2008, Miao et al. 2013, Pavlenko 2019).

The proposed model proposes to determine the amount of non-gasified carbon residue through empirical relationships obtained based on the results of the experimental studies carried out.

The obtained dependence is presented by equation (5).

This regression equation is obtained after statistical processing of experimental data. We assumed that the total carbon balance contains the main components CO, CO₂, CH₄, C₂H₄, C₆H₆ and unreacted carbon (C). It is obvious that the amounts of these components will depend on the factors mentioned above, the values of which have changed in the experiments within: $\alpha_{\text{bio}} = 0.05-0.5$; $T = 800-1000^{\circ}\text{C}$; $W = 5-50\%$.

- 3) Hydrocarbon yield based on empirical define. The emissions of such components as methane and other hydrocarbons (C_nH_m) cannot be well predicted using a stoichiometric model. Even if the relatively low yield of hydrocarbon compounds is not neglected, this has a considerable influence on the prediction of the yield of other components of the synthesis gas. Because of the fact that some of the hydrogen (H) and carbon (C) do not lead to the formation of molecules of the type (C_nH_m) but to the formation of other gas components, this cause an overestimation of the concentration of the combustible components of the synthesis gas in the stoichiometric model. It is proposed to determine the yield of some hydrocarbons based on empirical relationships that have been compiled from the results of experimental studies. The resulting dependence for the molar yield of CH₄ under the above experimental conditions is represented by equation (6).
- 4) Assuming non-adiabatic process conditions. Most of the work deals with the gasification process under adiabatic conditions (without heat loss or additional heat input). During real operating conditions, heat losses are unavoidable, and with a low input of the gas generator, heat losses can significantly reduce efficiency.

In the mathematical model, such components as heat losses in the gas generator are included in the energy balance equation, which offers the possibility of a more precise and comprehensive evaluation of the gasification process.

3.1. Equations of mass balances

The general mass balance equation for every jth element in the system containing M elements represents equation (8). The gasification process can be modeled without dividing it into stages and only considering the start and end products of the process that shows equation (7).

3.2. Equation of energy balance

The general equation of the energy balance for the gasification is equation (9) and its expanded form is equation (10) while the energy of the all elements of the system includes its energy of formation and the physical heat that is presented by equation (11).

The Lagrange multiplier use the Gibbs function and link all the conditions in equation (12).

The partial derivatives for each component of the synthetic gas equal zero and creates a system of equations (12) that solution makes it possible to determine the composition of the generator gas under certain conditions of gasification. Since the mole yield of CH_4 , C_2H_4 , and C_6H_6 is determined by empirical relationships, they will enter the system (13) as constant values for the chosen conditions of running the gasification process.

In the system of equations (13), in addition to the variables x_1, x_2, x_3, x_4 , the value of the free Gibbs energy (G_{fi}^0), the value of which depends on the temperature, is also taken into account. In this case, the temperature of the system can be determined from the general equation of the energy balance (10) and is a function of the final composition of the generator gas.

This task is solved by an iterative method.

Experimental investigations of the gasification process were driven in a fluid bed generator. Based on the results of experiment, the material and energy balances of the process were created for various gasification conditions, on the basis of which the efficiency of the gas generator and the quality of the thermochemical treatment of biomass could be fully assessed what Figures 1-4 shown. The lines marked with the letter "S" indicate the humidity of the biomass 14%, "S +" – humidity 35%.

The data obtained are presented on Figures 1-4. The lines shows calculated data, points are experimental.

$$\begin{aligned}
 G_{tot} &= \sum x_i \cdot \mu_i & (1) \\
 \mu_i &= G_{RT} P_i + \ln P_i & (2) \\
 G_{tot} &= \sum x_i \cdot (H_{fi}^0 - TS_i^0) + RT \sum x_i \ln \frac{x_i}{\sum x_i} & (3) \\
 w_{air} &= \frac{d_{air} \alpha_{bio} m_{bio} (M_{O_2} + 3,76 M_{N_2})}{M_{H_2O} 1000} & (4) \\
 \gamma &= 1 - \{0,63(0,589 \alpha_{bio} + 0,641)(0,0017 + 0,51)(0,0003W' + 0,963)\} & (5) \\
 CH_4 &= 0,0678(0,0722 - 0,0314 \alpha_{bio})(23,34 - 0,00977)(0,0003W' + 0,9626) & (6) \\
 CH_b O_c N_d + \alpha_{bio} m_{bio} (O_2 + 3,76 N_2) + w H_2 O + q V_{SG} + f \{V_{FG} + (\alpha_{sg} - 1) m_{sg} (O_2 + 3,76 N_2)\} = \\
 &= \gamma C + x_1 H_2 + x_2 CO + x_3 CO_2 + x_4 H_2 O + x_5 CH_4 + x_6 C_2 H_4 + x_7 C_6 H_6 + z N_2 & (7) \\
 \sum_{i=1}^N h_{ji} n_i^{out} + A_j^{out} &= \sum_{i=1}^N h_{ji} n_i^{in} + A_j^{in} & (8) \\
 \sum_{i=1}^n Q_i^{in} &= \sum_{i=1}^n Q_i^{out} & (9) \\
 H_{bio}^{in} &= w_{bio} H_{w_{bio}}^{in} + w_{air} H_{w_{air}}^{in} + w_{steam} H_{w_{steam}}^{in} + \alpha_{bio} m_{bio} (H_{O_2}^{in} + 3,76 H_{N_2}^{in}) + \\
 &+ q H_{SG}^{in} + f H_{FG}^{in} + Q_{ex} = \\
 &= \gamma H_C^{out} + x_1 H_{H_2}^{out} + x_2 H_{CO}^{out} + x_3 H_{CO_2}^{out} + x_4 H_{H_2O}^{out} + x_5 H_{CH_4}^{out} + \\
 &+ x_6 H_{C_2H_4}^{out} + x_7 H_{C_6H_6}^{out} + z H_{N_2}^{out} + Q'_{ach} + Q_{loss} & (10) \\
 H_i &= \Delta H_{fi}^0 + Q'_i & (11) \\
 L &= G_{tot} - \sum_{j=1}^M \lambda_j \left(\sum_{i=1}^N h_{ji} x_i^{out} + A_j^{out} - \sum_{i=1}^N h_{ji} x_i^{in} - A_j^{in} \right) & (12) \\
 \frac{\partial L}{\partial x_1} &= RT \cdot \ln \left(\frac{x_1}{\sum x_i + z} \right) + G_{fH_2}^0 + \lambda_H (2q - 2) = 0; \\
 \frac{\partial L}{\partial x_2} &= RT \cdot \ln \left(\frac{x_2}{\sum x_i + z} \right) + G_{fCO}^0 + \lambda_C (q - 1) + \lambda_O (q - 1) = 0; \\
 \frac{\partial L}{\partial x_3} &= RT \cdot \ln \left(\frac{x_3}{\sum x_i + z} \right) + G_{fCO_2}^0 + \lambda_C (q - 1) + \lambda_O (2q - 1) = 0; \\
 \frac{\partial L}{\partial x_4} &= RT \cdot \ln \left(\frac{x_4}{\sum x_i + z} \right) + G_{fH_2O}^0 + \lambda_H (2q - 1) + \lambda_O (q - 1) = 0; & (13) \\
 1 - \gamma + q(1 - \gamma) + f(1 - \gamma) &= x_2 + x_3 + x_5 + 2x_6 + 6x_7; \\
 (b + 2w)(1 + q + f) &= 2x_1 + 2x_4 + 4x_5 + 4x_6 + 6x_7; \\
 c + 2\alpha_{bio} m_{bio} + w + q(c + 2\alpha_{bio} m_{bio}) + f(c + 2\alpha_{bio} m_{bio} + w + 2\alpha_{sg} m_{sg}) &= \\
 &= x_2 + 2x_3 + x_4.
 \end{aligned}$$

where:

G_{tot} – the Gibbs energy of the system, kJ/kmol; μ_i – the chemical potential of the component of the system, kJ/kmol; x_i – the amount of substances in the component of the system, kmol.

P_i – the partial pressure of the i th component of the system, Pa; R – the universal gas constant, kJ/(kmol \cdot $^\circ$ C); T – the temperature of the system, K;

G_{fi}^0 – the standard free Gibbs energy of the formation of the component, kJ/kmol.

H_{fi}^0 – enthalpy of formation of the i -th component of the system, kJ/kmol;
 S_i^0 – entropy of the i -th component of the system, kJ/(kmol · K).
 d_{air} – moisture content of air, g/kg; α_{bio} – coefficient of excess air in the process of gasification; m_{bio} – the amount of oxygen for stoichiometric combustion of 1 km of biomass, kmol; M_i – molecular mass of the i -th component, kg/kmol.
 W' – the total mass of H_2O is given by 1kg of dry gasified fuel, kg (H_2O)/kg (dry biomass); γ – amount of carbon that remained in the ash residue, kmol.
 $x_1, x_2, x_3, x_4, x_5, x_6, x_7, z$ – predicted yield $H_2, CO, CO_2, H_2O, CH_4, C_2H_4, C_6H_6, N_2$, relatively, kmol; V_{SG} – total yield of volatile components in the gasification process, kmol; q – Synthesis gas recycling ratio in gas generator, units;
 m_{sg} – amount of oxygen for stoichiometric combustion of 1 kmole of generator gas, kmol; V_{FG} – amount of combustion products during stoichiometric combustion of 1 kmole of synthesis gas, kmol; w – total H_2O entering the gas generator, kmol; h_{ji} – the number of atoms of the j -th element in the i -th gas or liquid component of the system; n_i^{in}, n_i^{out} – the amount of substance of the i -th gas or liquid component at the entrance to the system and at the output from the system, kmol; A_j^{in}, A_j^{out} – the number of atoms of the j -th element in the solid form, per 1 kmol of biomass at the entrance to the system at the output of the system, respectively; Q_i^{in} – energy flow at the entrance to the gasification plant, W; Q_i^{out} – energy flow at the outlet from the gasification unit, W; H_{bio}^{in} – total energy of the dry part of the biomass, kJ; $H_{w_{bio}}^{in}$ – total energy of moisture of biomass, kJ; $H_{w_{air}}^{in}$ – the total energy of the water of the blown air supplied to the gas generator kJ; $H_{w_{steam}}^{in}$ – total energy of water vapor for gasification, kJ; $H_{O_2}^{in}, H_{N_2}^{in}$ – total energy O_2 and N_2 of air, kJ; H_{SG}^{in} – total energy of the recycled generator gas, kJ; H_{FG}^{in} – the total energy of the combustion products entering the gas generator, kJ; Q_{ex} – additional energy entering the gas generator from external sources, kJ; H_C^{out} – the total energy of the carbon residue, kJ; $H_{H_2}^{out}, H_{CO}^{out}, H_{CO_2}^{out}, H_{H_2O}^{out}, H_{CH_4}^{out}, H_{C_2H_4}^{out}, H_{C_6H_6}^{out}$ – total energy $H_2, CO, CO_2, H_2O, CH_4, C_2H_4, C_6H_6$ as gasification products, kJ; Q'_{ach} – loss of heat with ash, kJ; Q_{loss} – loss of heat to the environment (from the body of the gas generator), kJ
 ΔH_{fi}^0 – standard enthalpy of formation of 1 kmol of the i -th component, kJ/kmol. Standard enthalpy of substance formation; Q'_i – physical heat of 1 kmol of the i -th component of the system, kJ/kmol; L – the Lagrange function of the system; λ_j – the Lagrange multiplier at the j -th element.

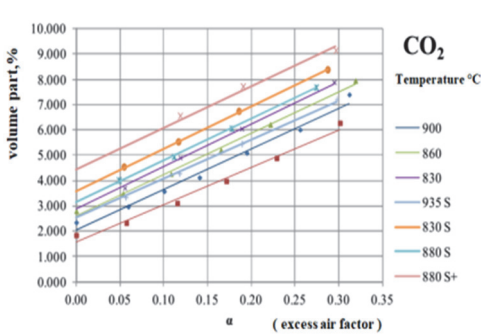


Fig. 1. Graphs for the CO₂ emission in the synthesized gas

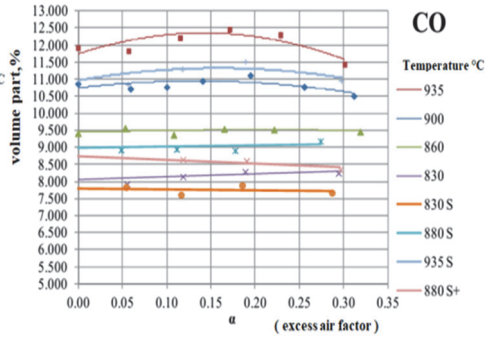


Fig. 2. Graphs for the CO emission in the synthesized gas

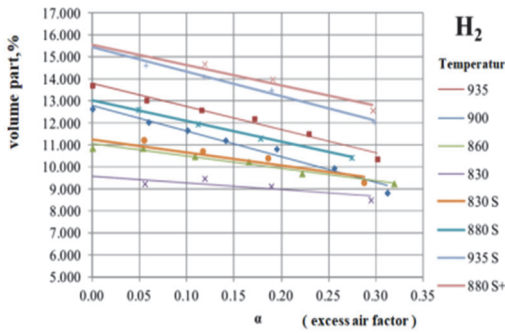


Fig. 3. Graphs for the H₂ emission in the synthesized gas

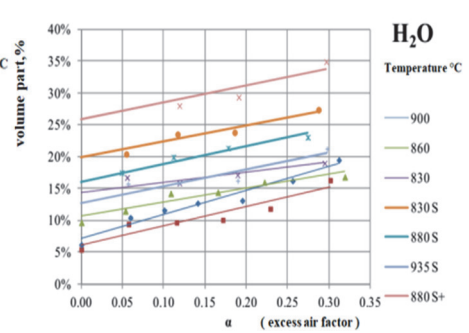


Fig. 4. Graphs for the H₂O emission in the synthesized gas

3.3. Checking the accuracy of the simulation

The accuracy of the mathematical model of the gasification process is checked using the experimental data. For this purpose, the correlation coefficients between the test and simulation results were determined under the same gasification conditions and the relative error of the data obtained. The starting data accepted for the modeling are identical to the conditions for carrying out experimental studies on biomass gasification. The results are shown in Figures 5-8.

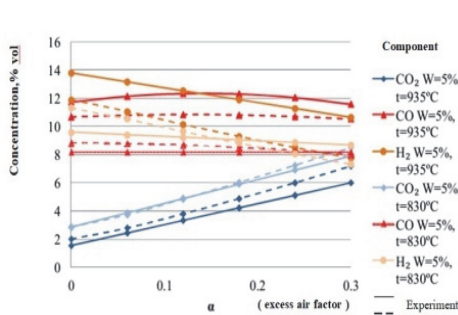


Fig. 5. Component output graph of synthesized gas with variable α and humidity $W = 5\%$

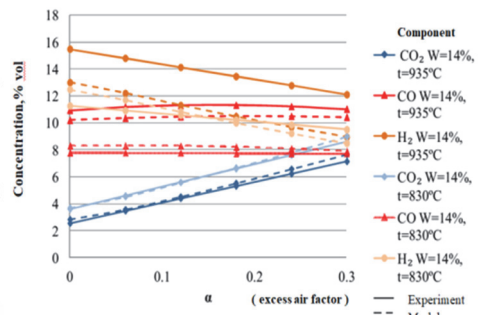


Fig. 6. Component output graph of synthesized gas with variable α and humidity $W = 14\%$

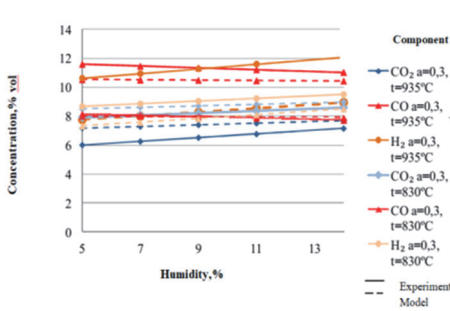


Fig. 7. Components output graph of synthesized gas at variable humidity

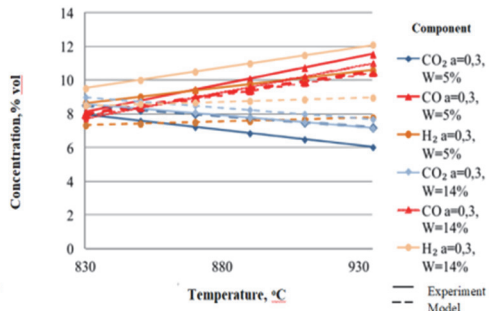


Fig. 8. Components output graph of synthesized gas at variable temperature

Analysis of the data obtained shows that the correlation coefficients between experimental data sets and arrays of simulation results are 0.99 and higher for the most of the experiments and only for few about 0.85...0.95. It is worth mentioning the high accuracy of the modeling for low temperatures process driven, the relative error in the modeling of the performance of the components of the generator gas is 5...10%. And a slightly higher error at high temperatures is 15...20%. An underestimation of the yield of the combustible components of the synthetic gas at high temperatures from the simulation results is characteristic. This accuracy is very high and enables an objective assessment of the impact of the parameters of the gasification process on the result.

Therefore, a new mathematical model of the gasification process of biomass was created, with the possibility to consider the thermodynamic efficiency of multifactorial influence (both separately and complex) on the energy properties

and the composition of the generated gas. Another important achievement of this study is the optimization of the biomass gasification process by determining the operating states of the gas generator.

4. Conclusions

A large scope of experimental single and multi-factor experimental research on biomass gasification under different conditions has been done. The compensation of the energy losses of the gas generator took into consideration the dynamics of exothermic reactions of the oxidation of biomass. This allowed to understand the effect of separate regime factors of the gas generator on the composition of the synthetic gas. Based on the minimization of the function of the isobaric isothermal potential (Gibbs energy), a mathematical model of the biomass gasification process was developed. It predicted the composition of the generator gas and the technological parameters of the gas generator. The model obtained provides high reliability of the predicted composition of the synthetic gas, the process temperature and the excess air factor in the reaction zone of the gas generator. The results obtained can be used in the creation of biomass gasification industrial plants.

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Abstract

The paper consists the results from the conducted experiment and the mathematical model of it. The presented process is biomass gasification and the modelling is based on complex parameter that is maximum thermodynamic efficiency and use the Gibbs free energy function and Lagrange multiplier. Referring to European Union strategy in terms of energy use it is highly recommended to increase the share of renewable energy in total energy production. The biomass is one of the most important sources of energy. Listed above methods of mathematical calculations let as define the composition of the gas produced and the efficiency that was reached. Also the precision of the model was evaluated. The effect of the work done is the possibility to use it to state the best condition for the process of biomass gasification technology.

Keywords:

gasification, pyrolysis, biomass, regenerative energy, synthetic gas, mathematical modeling, Gibbs energy

Prezentacja eksperymentalnego procesu zgazowania biomasy z modelem matematycznym minimalizacji energii swobodnej Gibbsa

Streszczenie

Artykuł przedstawia wyniki przeprowadzonego eksperymentu i jego model matematyczny. Przedstawiony proces dotyczy zgazowania biomasy, a modelowanie opiera się na złożonym parametrze, jakim jest maksymalna wydajność termodynamiczna, z wykorzystaniem funkcji energii swobodnej Gibbsa i mnożnika Lagrange'a. Nawiązując do strategii Unii Europejskiej w zakresie zużycia energii, zdecydowanie zaleca się zwiększenie udziału energii odnawialnej w całkowitej produkcji energii. Biomasa jest jednym z najważniejszych źródeł energii. Wymienione powyżej metody obliczeń matematycznych pozwalają określić skład wytwarzanego gazu i osiągniętą wydajność. Oceniono także precyzję modelu. Efektem wykonanych prac jest możliwość określenia najlepszych warunków prowadzenia procesu technologii zgazowania biomasy.

Słowa kluczowe:

gazyfikacja, piroliza, biomasa, energia odnawialna, gaz syntetyczny, modelowanie matematyczne, energia Gibbsa