Kinetics examination of pressurised steam gasification of beech wood

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Abstract. In Poland, among all renewable energy sources, share of biomass in electricity production is the largest. Great potential in biomass utilization involves use of gasification technology. The course of biomass gasification process in steam atmosphere is the subject of numerous scientific studies. The aim of this study was kinetics examination of pressurized beech wood waste gasification, that can be successfully used in industrial gasification. Measurements were carried out on a unique laboratory installation, that allows kinetics examination of solid fuels gasification with steam at wide range of pressures, via using thermovolumetric method. Formation rates of main gaseous products were determined, moreover, composition of post-reaction gas, as well as biomass conversion degree depending on the temperature were specified. Kinetic parameters of gasification were calculated and series of kinetic models were used to their designation ie Isoconvesional method, Integrated Core Model (ICM), Grain Model (GM) and Random Pore Model (RPM).

1 Introduction

In accordance with the requirements of the European Union, in 2020 the share of energy from renewable sources in gross final energy consumption is expected to reach 20% [1], and in Poland, according to a government document 'Energy Policy of Poland until 2030' at least 15% [2]. Over the past years the share of renewable sources in Poland is steadily increasing and in 2013 amounted to 8.7% [3], however it should be noted that this increase is insufficient. Among renewable energy sources the largest share in electricity production accounted for biomass [4].

Biomass for energy purposes can be used in many processes, ie combustion, co-combustion, gasification and pyrolysis, while the share of the first two technologies is dominant. It should be noted however, that using biomass for energy is associated with certain limitations, mainly due to the type of boilers used, properties of coal used [5], as well as the increased risk of chloride corrosion of steam superheater and fire hazard [6]. In addition, biomass requires adequate preparation to ensure the stable quality parameters [7].

The great potential in the use of biomass is linked with application of gasification technology. This applies particularly to low-power units, representing local source of clean energy, but also larger objects dedicated to the production of chemicals and liquid fuels. Currently, compared to other raw material the share of biomass in gasification process is small [8]. Biomass gasification plants, due to the high cost of obtaining a large amount of feedstock, are usually low-power units. According to the data compiled in the World Gasification Database [9], currently there are 35 biomass gasification plants working on an industrial scale, with a total capacity of 787 MW_{th}. In the vast majority the raw materials for gasification are wood and wood waste, much less, e.g. olive waste or rice husk. Biomass is subjected to gasification in order to generate electricity and heat, as well as to produce gaseous and liquid fuels. Technologies used include, among others: Envirotherm Circulating Fluidized Bed Gasification Process, Nexterra, Foster Wheeler Atmospheric Circulating Fluidized Bed Gasifier, Primenergy, Valmet, B&W Volund, ZeroPoint.

The course of the biomass gasification process in atmosphere of steam is the subject of numerous scientific studies. Research are carried out on the use of various types of biomass in the reactors of diverse construction, among others: pine chips in a fluidized bed [10] and fixed bed reactors [11]; bark of pine, Japanese oak [12] and pomace from olive oil production [13] in a fixed bed; oak, maritime pine and eucalyptus [14] as well as wood [15] and wood pellets [16], digestate from the production of ethanol [17], almond shell [18] in the fluidized bed reactors; waste from the processing of sugar cane in the cyclone reactor [19,20]; husks of sunflower, rapeseed, pine cones, cotton waste and pomace oil in thermogravimetric analyzer [21]; animal waste compost in a two-stage fluidized bed reactor [22]. During research influence of temperature, particle size, amount of steam and air fed to the reactor, as well as the type of biomass and catalysts used on the amount and the calorific value of the resulting gas are analyzed. Analyses of conversion degree, thermal efficiency and the amount of unreacted char are also made. Furthermore, the subjects of research are composition

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and properties of the ash and its influence on the biomass gasification process [19].

The key parameter for the gasification of biomass process is temperature, which determines the composition of the resulting gas [10,15,17,20,23] and its calorific value [14]. That is why the influence of temperature on the gasification process was investigated in this paper. Tests were carried out on a unique laboratory installation, which allows measurement of kinetics of solid fuels gasification process in steam atmosphere at wide range of pressures. Waste from the processing of beech wood, which can be successfully used on an industrial scale, were subjected to gasification process. For the tested biomass release rate of the main gas product, composition of resulting gas, as well as biomass conversion degree depending on the temperature were determined. Kinetic parameters of gasification process were also calculated and a series of kinetic models were used for their designation, ie isoconvesional method, Integrated Core Model (ICM), Grain Model (GM) and Random Pore Model (RPM).

2 Material and method

The subject of this study was woody biomass, which characteristics are shown in Table 1. Measurements were carried out at a pressure of 1.5 MPa and at temperatures of 700, 800 and 900 °C. Samples with a grain size of less than 0.2 mm. and a weight of 0.5 grams were used in the measurements. Flow rate of steam was 0.3 g/min, and the inert gas 1.5 l/min.

Table 1. Characteristic of woody biomass.

Parameter	**Symbol**	**Value, %**
Proximate analysis		
Moisture	M^a	6.12
Ash	A^a	0.2
Volatile matter	VM^{daf}	83.91
Ultimate analysis		
Carbon	C^{daf}	51.0
Hydrogen	H^{daf}	6.28
Sulfur	S^{daf}	0.01
Oxygen&Nitrogen*	$(O+N)^{daf}$	42.7

*calculated by difference

Measurement of the kinetics gasification process was carried out under isothermal conditions, using the installation which schematic diagram is shown in Figure 1. Installation and methodology used in this research has been successfully applied to examine coal and chars gasification process [24, 25]. The installation consists of several basic systems: a pressure reactor with a heating system (1-2) a system for feeding the reactor with the gasifying agent - steam (3-5), carrier gas - argon (6-7), and biomass, (8) system for collecting and purifying the resulting gas (9-11) and the gas analysis system (12-14). In the resulting gas the content of carbon monoxide and carbon dioxide is continuously controlled. For this purpose the analyzer operating on the principle of infrared radiation adsorption was used. In addition, the content of hydrogen and methane in the resulting gas was analyzed using gas chromatographs. The gas chromatograph used to analyze content of methane was equipped with a flame ionization detector (FID) and the chromatograph for the analysis of hydrogen content with thermal conductivity detector (TCD).

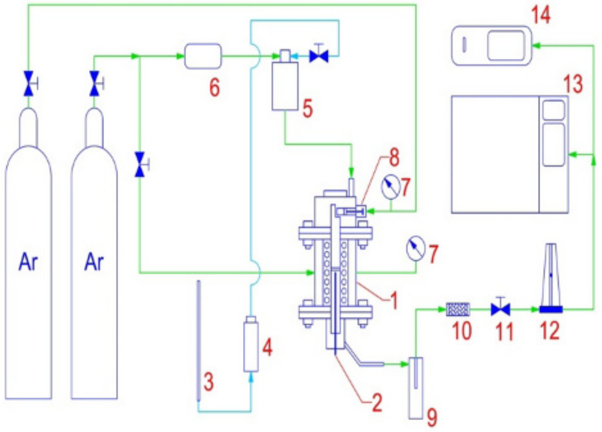

Figure 1. The laboratory equipment for kinetic examinations of biomass gasification process.
1 - reactor, 2 - thermocouple, 3 - water tank, 4 - water pump, 5 - steam generator, 6 - mass flowmeter, 7- pressure gauge, 8 – biomass feeder, 9 - cooler, 10 - filter, 11 - pressure regulator, 12- rotameter, 13 - gas chromatographs, 14 - CO, CO_2 IR analyser.

Based on the measurement of concentrations of carbon monoxide, methane and carbon dioxide in the resulting gas, the changes in formation rates of those gaseous products during gasification as a function of time were calculated, allowing determination of the gas composition and the conversion degree. The yield of each gasification product was calculated by determination of the area under the curve $dV/dt = f(t)$ and carbon conversion degree was evaluated based on the volume of a gaseous product containing this element:

$$\boldsymbol{X(t)} = \frac{(\boldsymbol{V_{co}(t)}+\boldsymbol{V_{CO2}(t)}+\boldsymbol{V_{CH4}(t)})\cdot \boldsymbol{M_C}}{\boldsymbol{V_{mol}}\cdot \boldsymbol{m}\cdot \boldsymbol{C^{daf}}} \cdot \mathbf{100}\ \% \qquad (1)$$

where:
$V_{CO}(t)$, $V_{CO2}(t)$, $V_{CH4}(t)$ - volume of released gas component at standard conditions as a function of time, dm^3/g
M_c- molar mass of carbon, g/mol
m – sample mass, g
C^{daf}- dry ash free carbon content, -
V_{mol} - volume of one mole of gas at temperature of 273 K and pressure of 101325 Pa, dm^3/mol

In next step curves of conversion rate determined for different temperatures were used to analyze the kinetics of biomass gasification process.

The effect of temperature and concentration of gaseous reactant on the gasification process rate can be expressed by the equation (2):

$$\frac{dX}{dt} = k(T)G(C)f(X) \qquad (2)$$

where:
k(T), and *G(C)* include the effect of temperature and the gas reactant concentration on the process rate, respectively and *f(X)* accounts for physical or chemical

changes occurring with the progress of the reaction. The apparent reaction rate constant *k(T)* and the concentration of the reagent *G(C)* are generally described in the form of an Arrhenius equation:

$$k(T)G(C) = k_0 e^{\frac{-E_a}{RT}} C^n \qquad (3)$$

where:
k_0 is pre-exponential factor, E_a is activation energy and n is an order of the reaction taking into account the concentration of the gas reactant.

In order to analyze the kinetics of the gasification process two approaches were used. Firstly, isoconversional method, which allows to determine the activation energy from the slope of *ln(t) = f(1/T),* was applied. Combining and transforming equations (2) and (3), provides:

$$\int_0^x \frac{dX}{f(X)} = \int_0^t C^n k_0 e^{\frac{-E_a}{RT}} dt \qquad (4)$$

which after integration and taking the logarithm gives:

$$\ln(t) = \ln\left(\frac{F(X)}{C^n k_0}\right) + \frac{E_a}{RT} \qquad (5)$$

The first term on the right hand side is a function of the reaction progress and the gaseous reactant concentration. If the concentration is constant and the time to reach a certain, founded conversion degree is a function of temperature, then equation (5) allows to determine the activation energy from the slope of *ln(t)=f(1/T),* even though *f(X)* in equation 2 is unknown. Then, in order to determine the activation energy and pre-exponential factor three models, describing heterogeneous gas-solid reaction, were used ie Integrated core model (ICM) Grain model (GM) and Random Pore Model (RPM).

The first of the models used was the ICM. Rate constant in this model is determined by the selection of the exponent n (representing the order of reaction) in equation (6), to obtain the best fit of experimental data to the model.

$$\frac{dX}{dt} = k_{ICM}(1 - X)^n \qquad (6)$$

GM model assumes that the surface of the reaction decreases non-linearly as the reaction proceeds, and RPM model assumes that the reaction surface changes as a result of two competing processes: the increase of the pore structure due to the gasification process and its destruction due to the coalescence of adjacent pores. The GM and RPM models are described by equations (7) and (8), respectively.

$$\frac{\mathrm{dX}}{\mathrm{dt}} = \mathrm{k_{GM}}(1 - \mathrm{X})^{\frac{2}{3}} \qquad (7)$$

$$\frac{\mathrm{dX}}{\mathrm{dt}} = \mathrm{k_{RPM}}(1 - \mathrm{X})\sqrt{1 - \Psi \cdot \ln(1 - \mathrm{X})} \qquad (8)$$

In RPM model Ψ parameter is associated with the pore structure of the test material and can be calculated from the equation:

$$\Psi = \frac{2}{2\ln(1 - X_{max}) + 1} \qquad (9)$$

where X_{max} is the conversion degree at maximum reaction rate. Due to the fact that in gasification process the greatest reaction rate are observed at the beginning, it can be assumed that $X_{max} = 0$ and then $\Psi = 2$.

3 Results and discussion

The achieved carbon conversion degree of tested biomass, calculated according to the equation (1), varies from about 80% at 700 °C to about 100% at a temperature of 900 °C (Figure 2). Simultaneously, time of gasification process is reduced. During the process unreacted char and tar, which was not analyzed, were also formed.

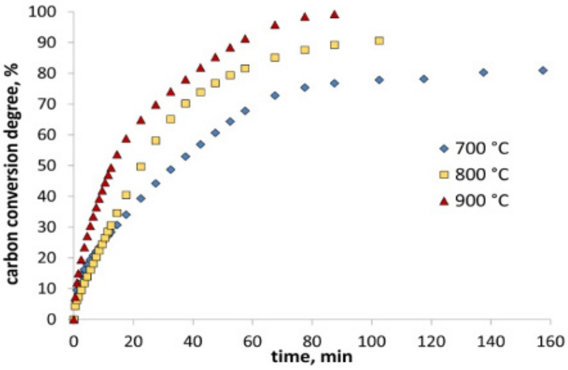

Figure 2. The curves of the carbon conversion degree.

With increasing temperature increases, however, the yield of carbon dioxide at the expense of the most important products ie hydrogen and carbon monoxide (Figure 3), which leads to reduction in calorific value of the fuel. The only component which yield does not change depending on the temperature is methane, that is formed in the first minutes of the process, during pyrolysis stage.

The kinetics analysis of the biomass gasification was started by determining the activation energy using isoconversional model (equation (5)). Calculations of activation energy were made for three conversion degrees, ie X = 0.3, 0.5, and 0.7. Fit of linearized isoconversional model to experimental data of biomass gasification process for conversion degrees 0.3, 0.5, 0.7 is shown in Figure 4, and activation energy, obtained on this basis, amounted to 43 kJ/mol.

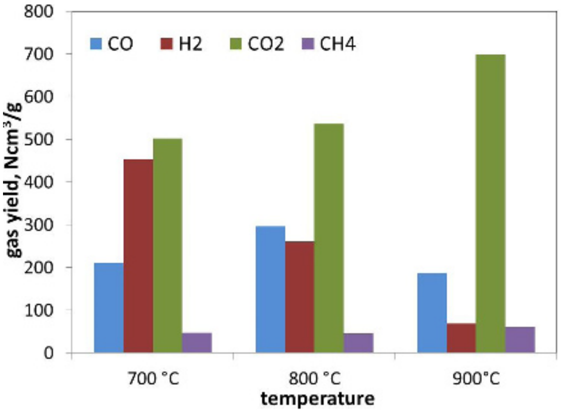

Figure 3. The effect of temperature on the resulting gas composition.

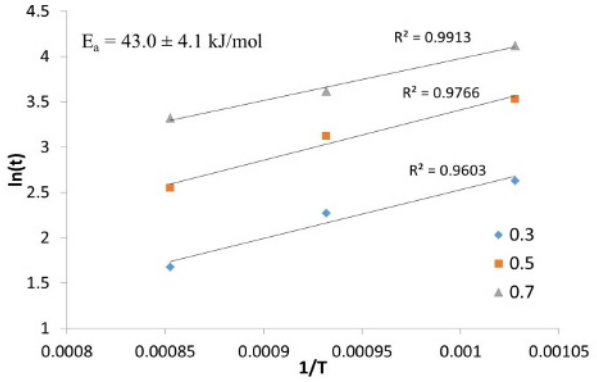

Figure 4. Fit of linearized isoconversional model to experimental data of biomass gasification process for conversion degrees 0.3, 0.5, 0.7.

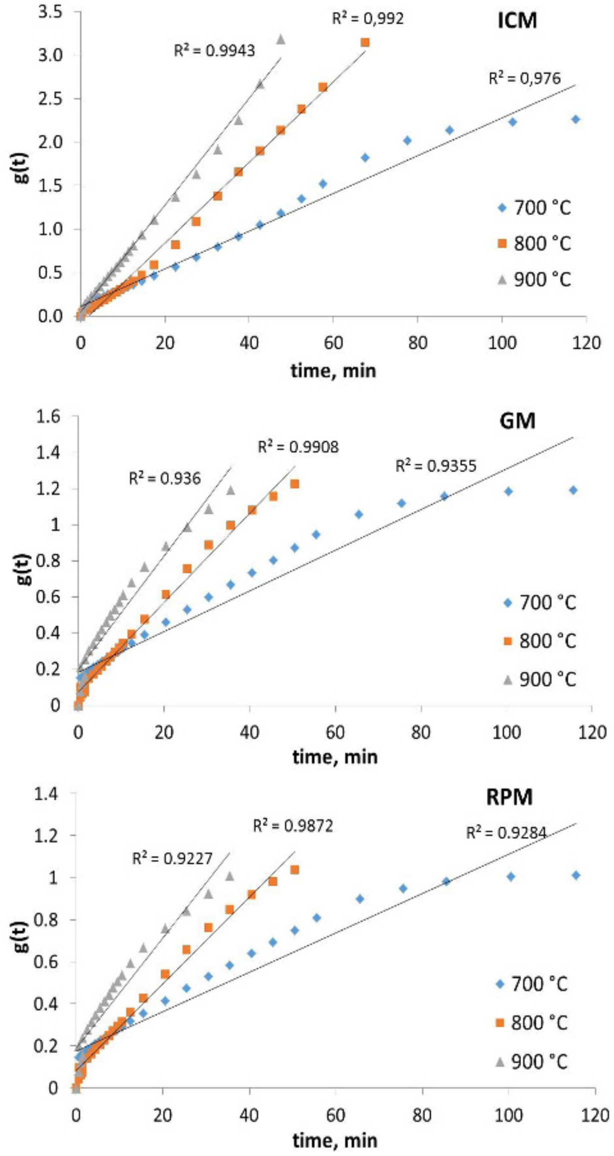

Figure 5. Fit of linearized kinetic equations to experimental data of biomass gasification process.

Due to the compensation effect of pre-exponential factor the knowledge of exclusively activation energy is not sufficient. That is why in the second approach typical models for this type of reaction (ICM, GM, RPM) were applied to determine both activation energy and pre-exponential factor. Fit of the linearized form of these equations to the experimental data are presented in Figure 5. The best fit, measured via coefficient of determination R^2, was obtained for the ICM model, while GM model and RPM did not give such good results. The kinetic parameters, calculated based on determined curves, are summarized in Table 2. The obtained values of the activation energy are similar to each other and amounted to 43.0 - 50 kJ/mol. The values of pre-exponential factor are comparable and were in the range between 7.59-02 and 1.86-01 1/s. The obtained values of activation energy are similar to the literature data, for example according to Haykiri-Acma et al [21] different types of biomass are characterized by diverse values of the activation energy, from 21.4 to 33.8 kJ / mol. When using the ICM model exponent n was also determined. The calculated value was 1.5 and does not correspond to any of the basic kinetic equations, and therefore it should not be considered as a reaction order (especially, that gasification process consist of several reactions) but only as a mathematical constant.

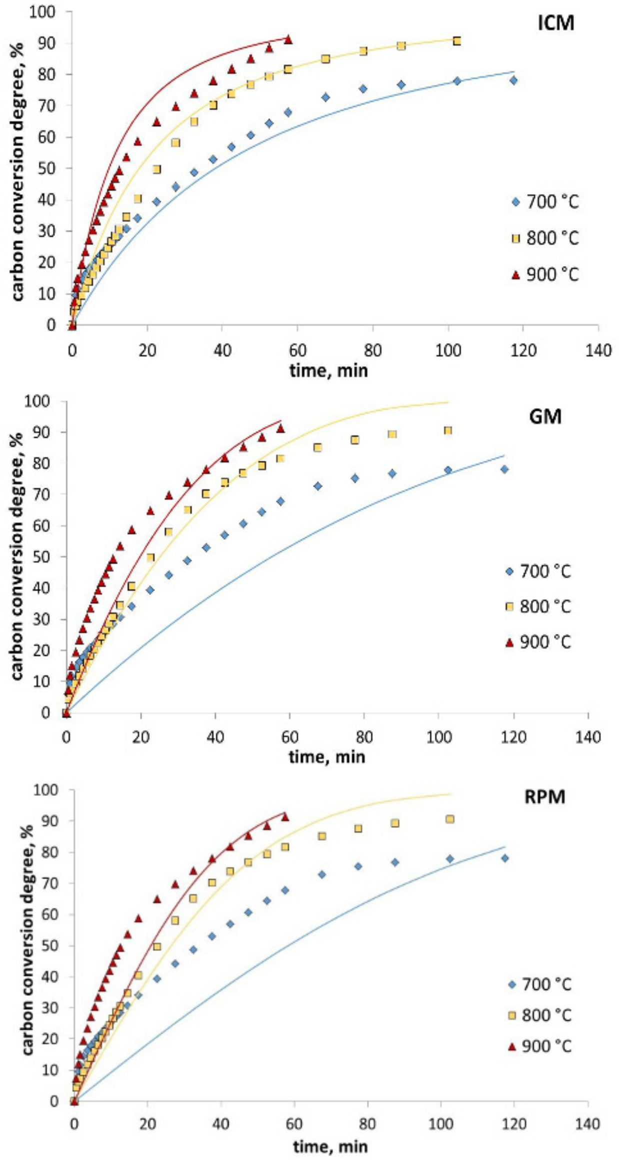

Figure 6. Comparison of the experimental data to model curves of conversion degree of the gasification process.

Table 2. Calculated values of kinetic parameters.

Model free	E_a , kJ/mol		
	43.0		
ICM	E_a , kJ/mol	k_0 , 1/s	
	50.0	1.86E-01	
GM	E_a , kJ/mol		
	49.4	9.03E-02	
RPM	E_a , kJ/mol	k_0 , 1/s	Ψ
	49.5	7.59E-02	2

The determined kinetic parameters allowed for modeling of conversion degree curves and comparison of models with experimental data (Figure 6). ICM model reflects very well the course of gasification process while GM and RPM models do not coincide satisfactorily with the experimental data, which suggests that they are not suitable to describe steam gasification of woody biomass process.

4 Conclusion

The process of steam gasification of waste wood industry for the production of synthesis gas seems to be a viable alternative to conventional combustion and co-combustion processes. The results obtained for beech wood confirmed the significant influence of temperature on the course and yields of the gasification process. With increasing temperature of gasification process the conversion degree and yield of carbon dioxide increases, while yield of hydrogen and carbon monoxide decreases. Activation energy determined for the steam gasification of beech wood was 43-50 kJ/mol, depending on the model used. The best fit of model calculations to experimental data was obtained for Integrated Core Model.

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