

Comparison of CO₂ gasification of coal in isothermal and non-isothermal conditions

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Abstract. The thermogravimetric method allows to carry out measurements both in isothermal conditions for a given temperature and in non-isothermal conditions at a set heating rate. The aim of the work was to compare the process of gasification of the same coal in an atmosphere of CO₂ under isothermal and non-isothermal conditions. The measurements were carried out with the use of DynTHERM Thermogravimetric analyzer by Rubotherm. Char derived from Polish bituminous coal "Janina" was used as material for gasification. In case of the isothermal method the measurements were performed at three temperatures – 850 °C, 900 °C and 950 °C, while in case of the non-isothermal method for three heating rates, i.e. 3 K/min, 5 K/min and 10 K/min. Based on the results obtained, kinetics curves of conversion degree of the gasification process were developed and kinetic parameters of the gasification reaction i.e. reaction order, activation energy and pre-exponential factor were determined. The values of the kinetic parameters obtained from measurements performed in isothermal and non-isothermal conditions were compared.

1 Introduction

Gasification is an ecologically friendly and efficient method of coal conversion that allows production of chemicals or substitution of liquid fuels and natural gas, as well as high-efficiency electricity production [1]. In order to optimize the operation of gasification reactors enabling the appropriate fuel utilization, it is necessary to know in depth the phenomena taking place during this process. The assessment of fuel reactivity and proper determination of gasification kinetics are particularly important [2]. The use of thermogravimetric analysis (TGA) based on the measurement of the changes in sample mass during heating allows to evaluate the reactivity and kinetics of reaction for the materials tested [3]. The thermogravimetric method enables to carry out measurements both in isothermal conditions for a given temperature and in non-isothermal conditions at a set heating rate. The isothermal measurements are more common whereas the non-isothermal measurements are more relevance since are less cumbersome and yield more useful data with less experimentation [4]. In non-isothermal tests, the measured temperature differs from the temperature of the sample to a greater extent than in isothermal measurements, which in turn

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affects the designated kinetic parameters [5, 6]. Furthermore, the vast majority of the presented in literature research on gasification process are based on ex-situ method, i.e. previously prepared and cooled char is then used in the measurements. There are differences in the reactivity of chars that were prepared in an atmosphere of argon, cooled down and then gasified (ex-situ method), and chars that were formed in a CO₂ atmosphere and directly subjected to the gasification process (in-situ method) [7]. However, if the isothermal method is used, direct gasification is not possible.

The aim of this work was to compare the process of gasification of the char samples in an atmosphere of CO₂ under isothermal and non-isothermal conditions. The measurements were carried out with the use of DynTHERM Thermogravimetric analyzer by Rubotherm and char derived from Polish bituminous coal 'Janina' was used as material for gasification. In case of the isothermal method the measurements were performed at three temperatures – 850 °C, 900 °C and 950 °C, while in case of the non-isothermal method for three heating rates, i.e. 3 K/min, 5 K/min and 10 K/min. Based on the results obtained, kinetics curves of conversion degree of the gasification process were developed. With use of nth-order model kinetics parameters of the gasification reaction i.e. reaction order, activation energy and pre-exponential factor were determined as well as fitting of the measurement data to the model curves was assessed. The values of activation energy were also calculated based on isoconversional method. Finally, the values of the kinetic parameters obtained from measurements conducted in isothermal and non-isothermal conditions were compared.

2 Material and method

2.1 Material

Bituminous 'Janina' coal has been used for the study and results of proximate and ultimate analyses are provided in Table 1. Chars used for the measurements were prepared by heating the parent coal in an argon atmosphere up to 850 °C.

Table 1. Characteristics of 'Janina' coal.

Parameter	Value
Proximate analysis (wt%)	
Moisture - M ^{ad}	8.7
Ash - A ^{ad}	14.0
Volatile Matter - VM ^{daf}	46.1
Fixed Carbon - FC	41.7
Ultimate analysis (wt%)	
Carbon - C ^{daf}	77.8
Hydrogen - H ^{daf}	3.9
Sulfur - S ^{daf_t}	1.3
Nitrogen - N ^{daf}	1.1
Oxygen* - O ^{daf}	15.9

* - by difference

2.2 Equipment and examination methodology

In order to determine the kinetics of gasification chars derived from 'Janina' coal in CO₂ atmosphere, non-isothermal and isothermal measurements were conducted using the DynTHERM Thermogravimetric analyzer by Rubotherm. A fully automated instrument is a combination of two basic systems: i) system of the Magnetic Suspension Balance with

reactor, where basic measurements are taken, and ii) a gas and/or vapor dosing system, supplying gases to the reaction zone. Non-isothermal measurements were carried out through heating the char samples up to 1100 °C under 0.1 MPa with three heating rates, i.e. 3 K/min, 5 K/min and 10 K/min. Isothermal measurements were performed at three temperatures – 850 °C, 900 °C and 950 °C for 180 min. During the thermogravimetric measurements carbon dioxide of high purity (99.998%) was used. The char sample with a mass of 60 mg and particle size below 0.2 mm was gasified.

2.3 Methodology of kinetic analysis

Gasification reaction progress α (-) ranging from zero to one for both non-isothermal and isothermal measurements was determined based on equation:

$$\alpha = 1 - \frac{m}{m_0} \quad (1)$$

where m is current weight of the sample (mg) while m_0 is the initial weight of the char sample before gasification (mg).

The reaction order was determined by employing a rate law written as follows:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (2)$$

where t stands for time (min), n is the reaction order, and k is the reaction rate constant (1/min). The rate constant can be represented by the Arrhenius equation:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

where A , E_a , T and R are the pre-exponential factor (1/min), the apparent activation energy (J/mol), the reaction temperature (K), and molar gas constant (8.314 J/mol·K), respectively.

2.3.1 Non-isothermal method

In non-isothermal experiments, the temperature changes as well as the time, and connection between them is provided by heating rate β which remains constant throughout the experiment, and is the change in temperature with the time, dT/dt . Combining equation (2) and (3) and taking into account constant heating rate provides:

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) dT \quad (4)$$

The left-hand side of equation (4) may be integrated for various values of n , while the right-hand side cannot be integrated directly. The solution is to give an approximation as a series and then truncate it after a small number of terms. After that, the result for $n \neq 1$ is expressed as:

$$\ln \frac{1-(1-\alpha)^{1-n}}{(1-n)T^2} = \ln \frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a}\right) - \frac{E_a}{RT} \quad (5)$$

For most reaction $E_a \gg RT$ that is why the term $\ln \frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a}\right)$ in equation (5) can be considered to be constant. Therefore, these equations can be put in a linear form and the value

of n giving the best fit is identified by the correlation coefficient by means of linear regression [8]. Based on the equation (5) A and E_a can be determined from the intercept and the slope of a plot $\ln[\ln(1/(1-\alpha))]-2\ln T$ against $1/T$.

Activation energy can be also determined with the use of isoconversional method, through a series of measurements taken at different heating rates [9]. The integral isoconversional method is based on the equation:

$$\ln \frac{\beta}{T^2} = \frac{AT}{Eg(\alpha)} - \frac{E_a}{RT} \quad (6)$$

where $g(\alpha)$ is the best fitting model, identified by the correlation coefficient. Thus, E_a can be evaluated from the slope of a plot $\ln(\beta/T^2)$ against $1/T$, obtained from the curves at several heating rates.

2.3.2 Isothermal method

In isothermal experiments, the temperature is constant and reaction rate constant can be determinate on the basis on the n -order model and after integration of equation (2) is obtained [10]:

$$\frac{(1-\alpha)^{1-n}-1}{n-1} = kt \quad (7)$$

Activation energy and pre-exponential factor can be calculated from the slope of a plot $\ln(k)$ against $1/T$.

The activation energy for the gasification with CO_2 can be also determined according to the isoconversional method [11] from the equation:

$$\ln(t) = \ln \left[\frac{g(\alpha)}{A} \right] + \frac{E_a}{RT} \quad (8)$$

Even though $g(\alpha)$ in equation (7) is unknown, the activation energy E_a can be calculated from the slope of the $\ln(t)$ vs $1/T$ plots for α selected

3 Results and discussion

3.1 Non-isothermal conditions

The curves of progress of gasification process during heating with various heating rates (i.e. 3 K/min, 5 K/min and 10 K/min) are shown in Figure 1. As the heating rate increases, the curves move towards higher temperatures. The gasification reaction begins at temperatures of 660, 675 and 690 °C, and ends at 970, 1010 and 1060 °C for 3 K/min, 5 K/min and 10 K/min, respectively. Thus, the higher the rate of heating, the wider the temperature range in which the gasification process takes place.

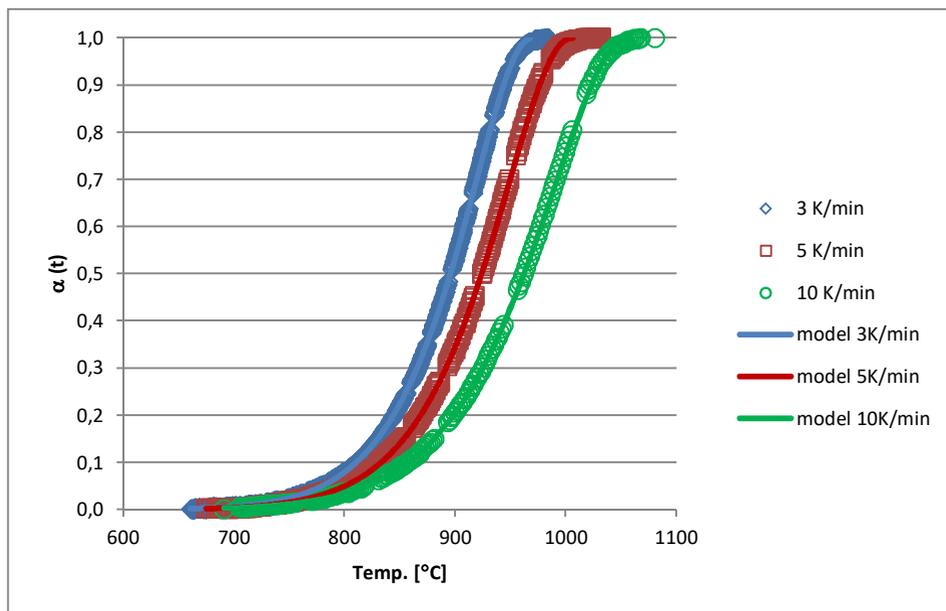


Fig. 1. Gasification reaction progress for various heating rates.

On the basis of the measured values of the conversion degree depending on temperature, the kinetic parameters and the reaction orders were determined (based on the equation (5)) and the obtained results along with the values of the coefficient of determination R^2 are presented in Table 2. The obtained values of the reaction order n were very similar for all analysed cases. As the heating rate increased, values of both activation energy and pre-exponential factor decreased, which is consistent with the literature reports [12, 13]. The obtained values of R^2 coefficient were very high. Moreover, the fitting of measurement data to model curves developed on the basis of these kinetic parameters was presented on Fig. 1. It can be seen that very good compatibility was obtained for the model used.

Table 2. Kinetic parameters of gasification for different heating rates.

Heating rate (K/min)	A (1/min)	E_a (kJ/mol)	n (-)	R^2 (-)
3	2.5E+07	199.0	0.57	0.9998
5	1.6E+07	194.8	0.59	0.9998
10	2.3E+06	175.7	0.59	0.9997

Next, the values of activation energy were determined using the isoconversional method (for conversion degrees from 0.1 to 0.9) based on the formula (6) and the results are presented in Table 3. Along with the increase in the conversion degree of the gasification reaction, the values of activation energy decreased. This phenomenon may result from the fact that in the analyzed gasification process diffusion and chemisorption play a role, as evidenced by the recorded reaction orders. Higher degrees of conversion are accompanied by a higher temperature, which promotes diffusion. According to [14] gasification can be divided into chemisorption stage and chemisorption neglected stage at higher temperatures, which affects the reduction of the activation energy. The obtained average value of E_a was 201.8 kJ/mol and is similar to the values obtained using the n-order model. Also in this case very high values of the R^2 coefficient were obtained. The values of activation energy determined with

both methods are similar to those obtained in many non-isothermal studies presented in the literature for similar coals (e.g. [15-17]).

Table 3. Activation energy calculated from isoconversional method for various conversion degrees in non-isothermal conditions.

Conversion degree (-)	E_a (kJ/mol)	R^2 (-)
0.1	238.9	0.9973
0.2	223.8	0.9956
0.3	213.1	0.9987
0.4	203.6	0.9986
0.5	196.6	0.9997
0.6	191.0	0.9998
0.7	187.3	1.0000
0.8	183.5	1.0000
0.9	178.7	1.0000

3.1 Isothermal conditions

Figure 2 shows the curves of conversion degree as a function of time for the analyzed temperatures of 850 °C, 900 °C and 950 °C. The increase in temperature has a significant effect on shortening the gasification process (150, 75 and 40 min. for 850 °C, 900 °C and 950 °C, respectively).

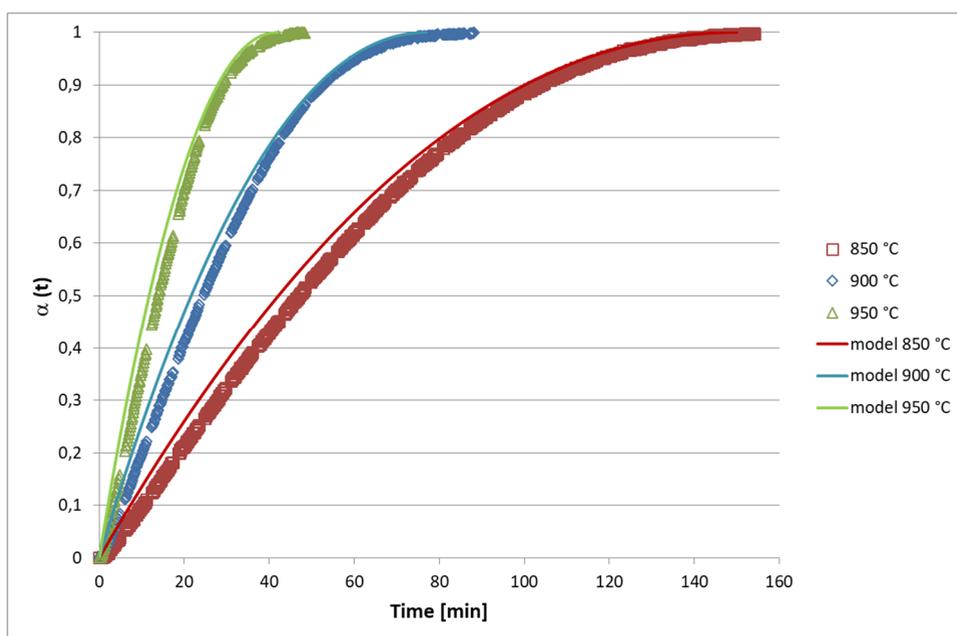


Fig. 2. Gasification reaction progress for various temperatures.

Based on the changes in the conversion degree over time for individual temperatures, the rate constants were calculated (using equation (7)) and the order of gasification reaction was determined. Then, the kinetic parameters A and E_a were calculated. The results obtained along with the values of coefficient of determination R^2 are presented in Table 4. Both the values of activation energy and pre-exponential factor differ from those obtained during non-isothermal studies and are lower. In turn, there is no significant difference in the obtained values of reaction order. The R^2 coefficients are characterized by very high values which slightly decrease with increasing temperature of the process.

The model curves developed on the basis of the obtained kinetic parameters are presented in Fig. 2. In order to assess their fitting to the measurements data. Good compatibility between the model and the measurement data was obtained, although slightly inferior compared to the non-isothermal method.

Table 4. Kinetic parameters of gasification for isothermal measurements.

Temperature (°C)	k (1/min)	R ² (-)	A (1/min)	E _a (kJ/mol)	n (-)
850	0.0140	0.9996	8.7E+04	146.0	0.53
900	0.0275	0.9991			
950	0.0504	0.9982			

As in the case of the non-isothermal process analysis, for the conversion degrees from 0.1 to 0.9 the values of activation energy were determined using the isoconversional method described by formula (8) and the results are summarized in Table 5. Unlike to the results from non-isothermal measurements, the values of activation energy grow as the conversion degree of the gasification reaction increase. This phenomenon may be due to the increase of mineral matter content in the char as the reaction proceeds [18, 19]. The obtained average value of E_a amounted to 138.1 kJ/mol and is slightly lower than this obtained by using the n-order model. Also in this case very high coefficients of determination R^2 were obtained. The values of activation energy determined with both methods also find confirmation in the results presented in the literature for similar coals using the isothermal method [20, 21].

Table 5. Activation energy calculated from isoconversional method for different conversion degrees in isothermal conditions.

Conversion degree (-)	E _a (kJ/mol)	R ² (-)
0.1	129.0	0.9993
0.2	130.8	0.9995
0.3	134.3	0.9997
0.4	136.8	0.9996
0.5	139.0	0.9999
0.6	140.3	0.9998
0.7	143.6	0.9998
0.8	144,2	0.9999
0.9	144.7	0.9999

3 Conclusions

The comparison of gasification of the same char samples in an atmosphere of CO₂ using thermogravimetric method under isothermal and non-isotonic conditions was performed. The values of activation energy determined using the n-order model for the non-isothermal method was in the range between 176-199 kJ/mol, while for isothermal measurements the value of E_a was lower and amounted to 146 kJ/mol. Also, the value of pre-exponential factor A was lower for isothermal measurements (8.7E+04 compared to 2.3E+06-2.5E+07). In turn, a similar reaction orders were obtained for both methods used in this work. In the case of using isoconversional method for conversion degrees from 0.1 to 0.9 the range of activation energy for non-isothermal measurements was from 179 to 239 kJ/mol and for isothermal measurements was lower and varied from 129 to 145 kJ/mol. In addition, for non-isothermal conditions, the activation energy decreased with the progress of the reaction, while in the case of isothermal conditions, the reverse relation was observed. For all analyzed cases, very high values of coefficient of determination R^2 (close to 1) were noted. Good compatibility between the model curves and the measurement data was also obtained, wherein slightly better fitting was obtained for the non-isothermal method.

This paper was prepared as a part of the Dean's grant of the Faculty of Energy and Fuels at the AGH University of Science and Technology, No. 15.11.210.449.

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