KINETICS OF PYROLYSIS AND GASIFICATION USING THERMOGRAVIMETRIC AND THERMOVOLUMETRIC ANALYSES

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Abstract

The carbon dioxide gasification process of Miscanthus giganteus biomass was examined using two methods. First an isothermal thermovolumetric method was applied. The measurement was conducted at 950°C and pressure of 0.1 MPa. Based on the continuous analysis of different kinds of gases formed during the gasification process, the thermovolumetric method allowed the determination of yields and composition of the resulting gas as well as the rate constant of CO formation. Then a non-isothermal thermogravimetric method was applied, during which the loss of weight of a sample as a function of temperature was recorded. In the course of the measurement, the temperature was raised from ambient to 950°C and the pressure was 0.1 MPa. As a result, a change in the carbon conversion degree was obtained. Moreover, TGA methods allow distinguishing various stages of the gasification process such as primary pyrolysis, secondary pyrolysis and gasification, and determining kinetic parameters for each stage. The presented methods differs from each other as they are based either on the analysis of changes in the resulting product or on the analysis of changes in the supplied feedstock, but both can be successfully used to the effective examination of kinetics of the gasification process. In addition, an important advantage of both methods is the possibility to carry out the gasification process for different solid fuels as coal, biomass, or solid waste in the atmosphere of a variety of gasification agents.

Key words: Pyrolysis, gasification, kinetics, TGA, thermovolumetrics

1 INTRODUCTION

Gasification is a clean and effective method for converting fossil fuels to a gas which has a very broad range of applications in syntheses of chemicals, substitutes of petroleum and natural gas as well as in power generation [22], [25], [26]. It enables not only the diverse utilization of produced syngas, but also allows for a reduction of the negative impact of fuel utilization on the environment [5]. Various solid fuels such as coal, biomass, or even solid waste may be gasified [6], [7], [10] by a variety of gasification agents like air, oxygen, steam, carbon dioxide, or mixtures thereof [3], [6], [11], [16], [24]. The gasification process, therefore, gives wide possibilities of practical use. However, in any case, in order to develop and optimise the operation of gasification reactors, it is necessary to acquire thorough knowledge of the kinetics of the process. An analysis of the course of gasification reveals that it is a complex process which involves fuel pyrolysis with the formation of char and volatile products of pyrolysis, as well as gasification of the resulting char. The pyrolysis is a relatively short stage, nevertheless plays an important role in the whole process, because has a direct impact on the kinetics of char gasification. The pyrolysis affects the properties of char and particularly its reactivity [4], [17]. During devolatilization, the porosity changes from about 20 to even over 80%, and, to a large extent, also the pore surface area increases, which directly affects the growth of the reactivity of char [8]. Furthermore, the conditions, under which the pyrolysis is carried out, like temperature, pressure, character of atmosphere [1], [12], [19], [21] affect the char reactivity, and therefore the whole process. That is why, in spite of the fact that the gasification of char is the slowest stage, limiting the course of the entire process, the pyrolysis stage should not be underestimated. However, the complexity of gasification process requires constant examinations and analyses to understand it comprehensively [23]. The impacts of particular factors on the gasification process, and especially the carbon conversion degree as well as the yields of gaseous products of the process are assessed most frequently with the aid of thermovolumetric and thermogravimetric methods. In the vast majority of cases, the examinations of gasification kinetics are conducted for chars, thus gasification of raw feedstock still remains a valid problem. The preparation of char, i.e. devolatilization of the raw material and cooling the char prior its utilization in a gasification process significantly affect the morphology of char, and thus the whole gasification

process [13]. It is important to know the gasification process of raw feedstock which may simulate the course of the process in gasification plants.

Knowledge about the kinetics of the process is very important because it is the basis for the design of reactors which enable the practical use of biomass in the gasification process. Therefore, the aim of the study was to analyse a gasification process of solid fuel, using two methods, thermovolumetric and thermogravimetric ones, characterized by a different approach. The use of these methods has allowed a more detailed insight into the kinetics of a complex gasification process of raw feedstock, and not, as is often found in the literature, a char gasification process. This original approach is certainly more complicated because it takes into account a pyrolysis process; however it reflects a process which occurs in industrial gasification reactors.

The comparison of both methods was shown based on the gasification of Miscanthus giganteus. The material was gasified in the carbon dioxide atmosphere at pressure of 0.1 MPa. During the examinations, two stages of pyrolysis could be distinguished and a CO2 gasification stage, according to the Boudouard reaction (1):

$$C + CO_2 \rightarrow 2\,CO \tag{1}$$

Based on the results of thermovolumetric measurements, the formation rates and yields of CO, H2, and CH4 were calculated. The constant rate of CO formation was calculated as well. The thermogravimetric method enabled the calculation of kinetics parameters for each stage of the process: primary pyrolysis, secondary pyrolysis, and CO2 gasification.

2 METHODS OF GASIFICATION PROCESS EXAMINATION

Thermal analysis techniques such as thermogravimetric and thermovolumetric analyses have been broadly used in gasification experiments, because they provide rapid data for the examination of processes under isothermal or non-isothermal conditions and allow for the estimation of effective kinetic parameters for the fuel conversion process [15], [18]. The thermogravimetric analysis (TGA) is an analytical technique which records the loss of weight of a sample as the temperature is raised at a uniform rate. The TGA data provides useful comparisons of reaction parameters such as temperature and heating rate. On the other hand, the thermovolumetric method is based on the continuous analysis of different kinds of gases, which are formed during the gasification process. This approach gives practical information on the composition of the gas from gasification, thus enabling the determination of its further use.

2.1 Thermovolumetric method

The examination of CO_2 biomass gasification was conducted on unique laboratory equipment which enables performing measurements under isothermal conditions for solid fuel samples. The diagram of the experimental equipment is shown in Figure 1, and a thorough a description of its operation was presented in previous works [13], [14].

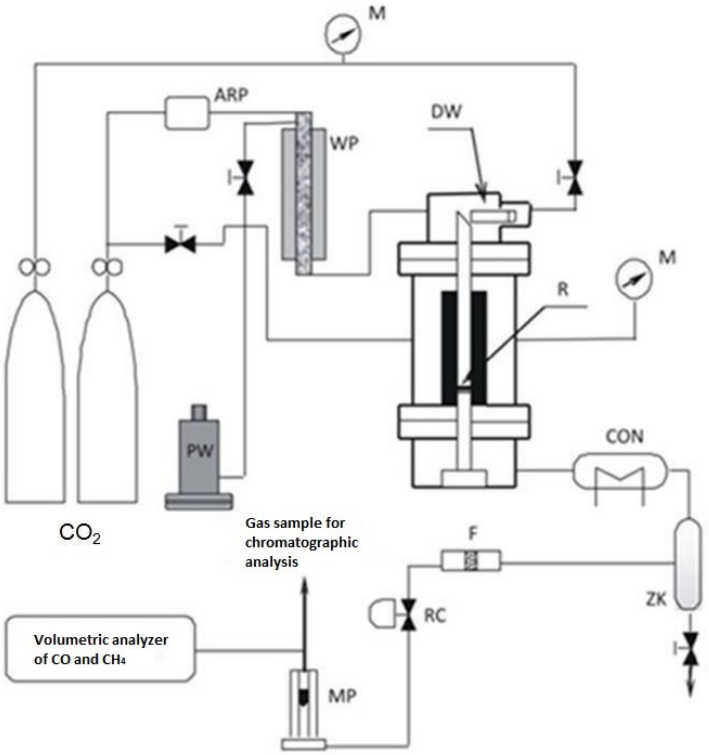

Figure 1: Laboratory equipment for kinetic measurements of coal gasification: R - reactor; CON – condenser; WP - gas pre-heater; ZK - tar separator; MP - rotameter; DW - coal feeder; ARP - mass flowmeter; M - pressure gauge; F – gas filter; RC - backpressure regulator

The equipment was adapted for purposes of the gasification process with CO_2. It was composed of three basic systems, namely: a pressure reactor with a heating system, a CO_2 and solid fuel feeding system, and a system for collecting and analysing the resulting gas. The contents of carbon monoxide and methane in the resulting gas were determined continuously with the use of an analyser based on the principle of infrared radiation absorption. In addition, the gas samples were collected and analysed in respect of hydrogen content with the use of a gas chromatograph Clarus 580 GC – Arnel equipped with a thermal conductivity detector (TCD). The basic parameters of the chromatograph are shown in Table 1.

Table 1: Basic parameters of gas chromatograph Clarus 580 GC – Arnel

Parameter	Value
Temperature of oven (°C)	60
Flow of carrier gas – argon (cm^3/min)	40
Flow of carrier gas – helium (cm^3/min)	30
Temperature of TCD detector (°C)	200
Voltage on TCD detector (mA)	+120
Flow of reference gas to TCD detector (cm^3/min)	49

A sample of biomass with a weight of 0.5 g and a grain size below 0.5 mm was placed in the sample feeder of the reactor. After closing, the reactor was filled with CO_2 up to 0.1 MPa and then the flow of output gas was adjusted. After setting the CO_2 flow to a level of 2 dm^3/min, the reactor was heated up to the 950 °C. Next, after reaching the required parameters (temperature, pressure, and flow rate), the sample was placed in the reactor by opening the valve supplying the sample feeder with compressed argon for several seconds. The resulting gas was continuously analysed in respect of carbon monoxide and methane contents, and its samples were taken throughout the examination period in order to analyse the hydrogen content later on.

Based on the measurement of concentrations of the main components of the resulting gas (CO, H_2, and CH_4), the formation rates of gaseous products were calculated. Assuming the first order reaction, the formation rate of the gaseous product can be expressed by the integrated equation (2):

$$ln\frac{V_\infty}{V_\infty - V} = k \cdot t \tag{2}$$

where:
k - constant reaction rate [1/min],
V_∞ - maximal volume of gas product [cm^3],
V - volume of released gas component at time t [cm^3],
t - time [min].

2.2 Thermogravimetric method

The thermogravimetric non-isothermal measurements were made according to the ASTM E1641-07 method using a DynTHERM Thermogravimetric Analyzer by Rubotherm, which enables examining the kinetics of gasification with carbon dioxide under high pressure. The fully automatic instrument is a combination of two basic systems: Magnetic Suspension/ Balance System and a gas and/or vapour dosing system, supplying gases to the reaction zone.

After placing the biomass sample weighing 100 mg with a grain size below 0.5 mm in a titanium container and transferring it to the reactor, the two-stage measurement started:

Stage I - stabilization: stabilizing the initial conditions, i.e., the pressure at 0.1 MPa, the flow rate of carbon dioxide at 200 ml/min. This stage lasted 30 min.

Stage II - measurement: the temperature was ramped from ambient temperature to 950 ^oC with a heating rate of 3 K/min; through the system, 200 ml/min of CO_2 flowed supplied from the dosing system. The final temperature of the process was designed to ensure the total conversion degree of the tested biomass, and the slow heating rate provided individual reactions enough time to reach their completion, or equilibrium, and avoid their overlapping with the adjacent higher temperature reaction. At this stage, the evaporation of moisture, then, with increasing temperatures, the pyrolysis and overlapping gasification processes took place.

The TGA test was performed in high purity carbon dioxide (99.998%). The loss in weight during the measurement was recorded continuously, and the results were presented as a function of temperature.

Both kinetics parameters: activation energy and pre-exponential factor of decomposition process were determined simultaneously from the TGA data by using the first order kinetic reaction equation, assuming a constant predetermined heating rate, expressed by the equation (3):

$$\frac{d\alpha}{dT} = \frac{A}{B}(1-\alpha)exp\left(-\frac{E}{RT}\right) \tag{3}$$

After integration, the equation (3) takes the form as follows (4):

$$-ln(1-\alpha) = \frac{AE}{BR}p(\chi) \tag{4}$$

The calculation for the non-isothermal process also requires to introduce some approximations like these developed by Murray and White [20] according to (5), or Senum and Yang [20] according to (6):

$$p(x) \cong \frac{exp(-x)}{x^2} \tag{5}$$

$$p(x) \cong \frac{exp(-x)}{x^2}\frac{x^3 + 18x^2 + 86x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{6}$$

Hence, the activation energy and the pre-exponential factor may be determined from the intercept and the slope of a plot ln[-ln(1-α)/T2] against 1/T in the Murray and White method, or using a non-linear regression in the case of the Senum and Yang method. This approach allows to determine the kinetic parameters for each stage separately: primary pyrolysis, secondary pyrolysis, and gasification, and not, as is usually found in the literature, for the entire process.

3 RESULTS

3.1 Tested sample

In contrast to the majority of conducted examinations of gasification, which are carried out with the use of chars, the measurements were conducted for the pre-dried energy crop – Miscanthus giganteus biomass. The proximate and ultimate analyses of this biomass are summarized in Table 2.

Table 2: Proximate and ultimate analyses of Miscanthus giganteus

Parameter	Miscanthus giganteus
Proximate analysis	
Moisture - M^a (%)	3.7
Volatile matter - V^{daf} (%)	80.0
Fixed carbon (%)	10.4
Ash - A^a (%)	2.9
Calorific value (MJ/kg)	18
Ultimate analysis	
C^{daf} (%)	52.1
H^{daf} (%)	7.5
S^{daf} (%)	0.04

The results of the proximate analysis show that the content of volatile matter is dominant. The low ash content, which is typical for biomass, as well as the low moisture content, resulting from the pre-drying, contributed to a relatively high calorific value equal to 18 MJ/kg. The contents of the elements included in the ultimate analysis are similar to the average contents of these elements in solid biofuels [9].

3.2 Thermovolumetric method

The isothermal thermovolumetric method was used for the examination of Miscanthus giganteus gasification process. Thanks to such an approach, the conditions of measurements better reflect the process of gasification occurring in commercial reactors. The conducted measurements allowed for the determination of resulting gas composition as well as the calculation of carbon conversion degree. The changes in the formation rates of particular gaseous products during the gasification of the examined biomass under specified conditions (a) as well as yields of particular gases (b) are shown in Figure 2.

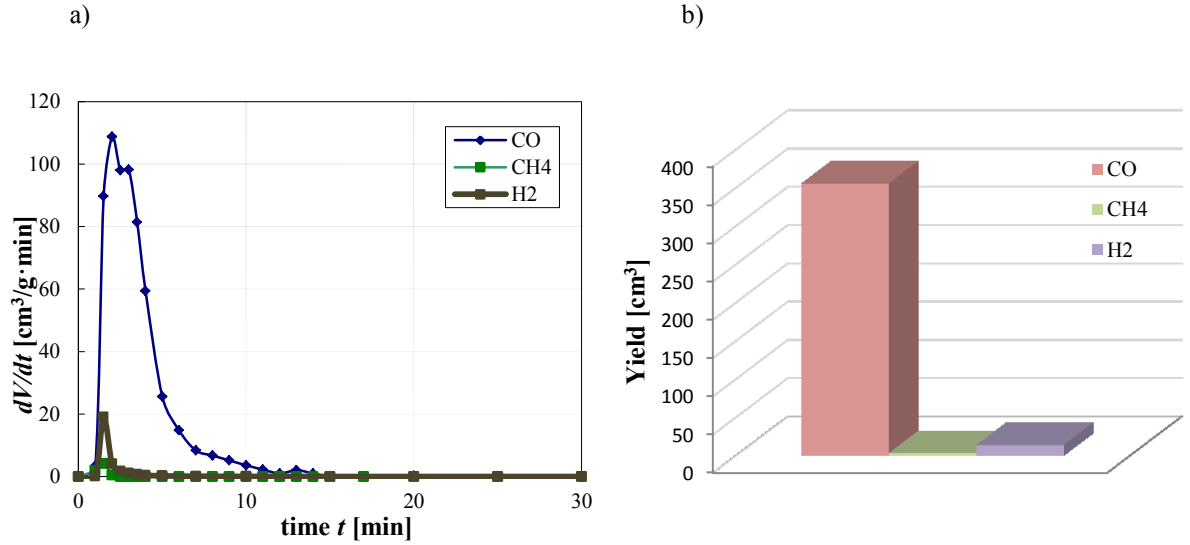

Figure 2: Kinetics of gasification process; a) changes in formation rate of gaseous products; b) yields of gaseous products

It can be seen that the highest formation rate is achieved for carbon monoxide. The formation rates of hydrogen and methane are much lower, wherein, the formation of methane is barely noticeable. At the initial

stage of the gasification process, a dynamic increase in the reaction rates of particular products can be observed, which is associated with the pyrolysis process. The formation of hydrogen and methane is completed at this stage, and in the main phase of the gasification process, only the carbon monoxide formation can be observed as a result of the Boudouard reaction (1). The yield of carbon monoxide is the highest, and it is the main component formed in the process. The constant rate of CO formation, calculated based on the results, was equal to 0.25 1/min.

3.3 Thermogravimetric method

The TGA of biomass samples has been extensively applied as a means of determining the characteristics of conversion and also to determine kinetic parameters [2]. Figure 3 shows the loss of sample weight as a function of temperature during heating in the atmosphere of CO_2. Three main stages may be distinguished: primary pyrolysis, secondary pyrolysis, and CO_2 gasification. The steep decline of the curve, which can be observed between 200°C and 350° C is associated with the primary pyrolysis. The biggest weight loss, about 58%, occurred at this stage. Then, the secondary pyrolysis started and lasted up to reaching a temperature of 650°C. In this step, the weight loss was much smaller and achieved a little over 14%. Finally, in the last step, again a steeper decline of the curve can be observed, which illustrated the CO_2 gasification stage. The gasification continued until only ash remained in the crucible that means at temperature close to 865°C, and the weight loss was about 20%.

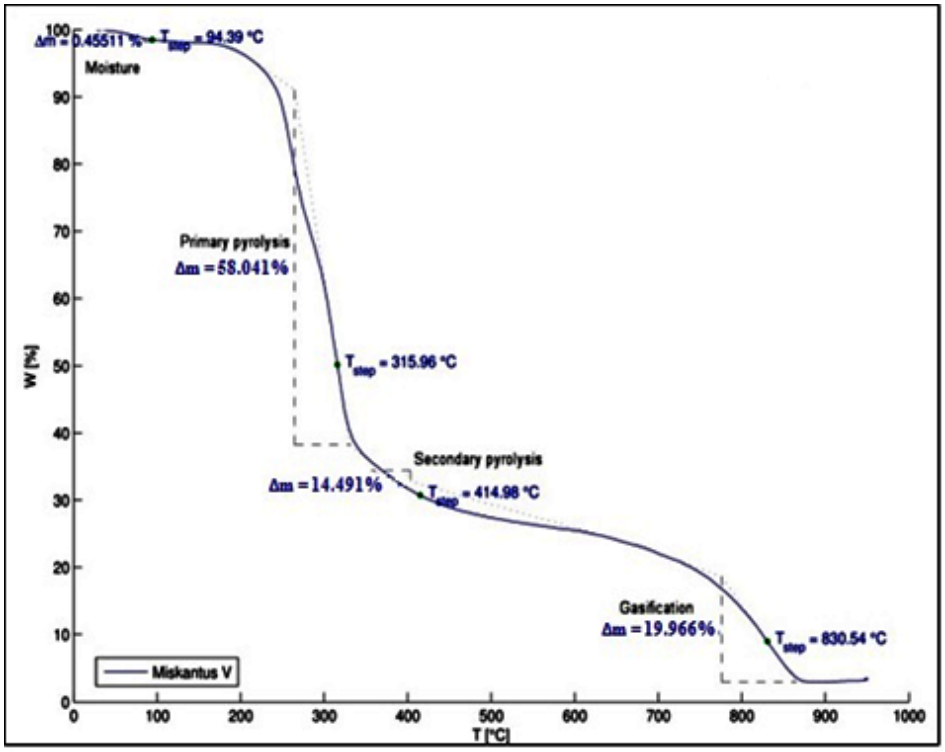

Figure 3: TGA curve for Miscanthus giganteus

For each stage, the kinetics parameters, i.e. the activation energy E_a and the pre-exponential factor A were determined using the first order kinetic reaction model with approximations by Murray and White, and Senum and Yang [20]. The obtained results are summarized in Table 3. Comparing the results of the kinetic parameters determined by both methods, it can be noticed that in each stage differences were negligible, and the results were often even identical.

Table 3: Kinetic parameters determined by integral methods for Miscanthus giganteus

Stage	Primary pyrolysis		Secondary pyrolysis		Gasification	
Kinetics parameter	E_a (kJ/mol)	A (min^{-1})	E_a (kJ/mol)	A (min^{-1})	E_a (kJ/mol)	A (min^{-1})
Murray and White	94	46.49E+06	29	2.21	188	66.33E+06
Senum and Yang	94	46.49E+06	22	0.88	187	66.33E+06

Taking into account the contribution of individual stages to the whole process, Figure 4 shows the fit of the first order reaction model with the approximations proposed by Murray and White, and Senum and Yang [20] to the experimental data. The resulting curves almost coincided with the experimental curve, especially at the stage of the gasification and primary pyrolysis. The weakest fit obtained for the secondary pyrolysis can still be considered sufficient. The very good entire fit allows us to draw such conclusions that the proposed models are correct and kinetic parameters received on their basis are reliable.

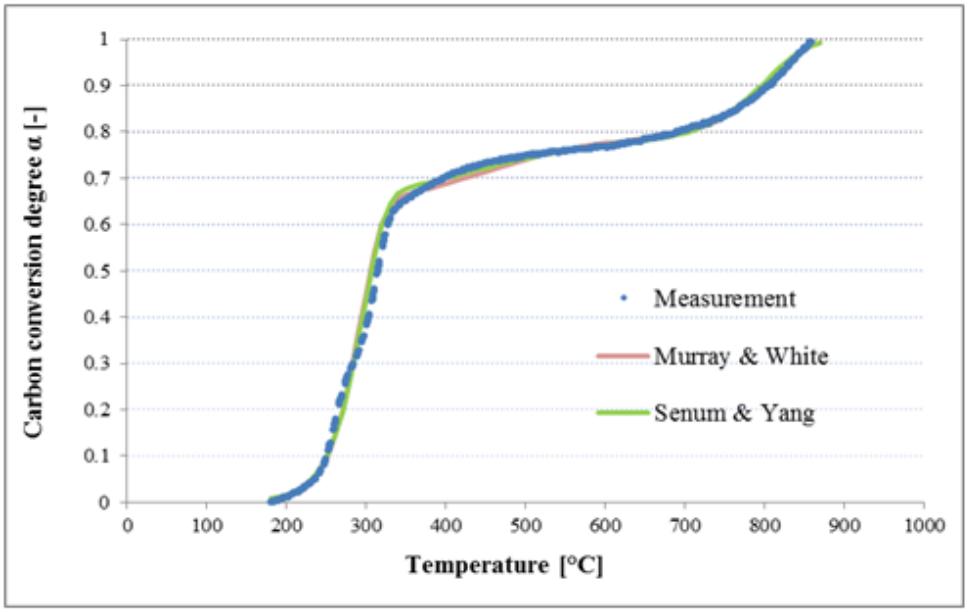

Figure 4: Fit of models to experimental data

CONCLUSIONS

The kinetics of iso- and non-isothermal gasification of raw Miscanthus giganteus biomass in the carbon dioxide atmosphere was examined by using thermovolumetric and thermogravimetric methods. This original approach that took into account a pyrolysis stage allowed for the analysis of kinetics of the raw material gasification process. The information obtained in this way is relevant from the viewpoint of the design of gasifiers, whereby the biomass gasification has the potential to become a practical solution in terms of energy generation. Results from the thermovolumetric method gave quantitative and qualitative information regarding the resulting gas during the whole process. The results showed that the CO_2 gasification stage is largely determined by the formation rate of carbon monoxide. However, the TGA analysis enabled to distinguish shares of particular stages during the CO_2 gasification of biomass, and the largest weight loss occurred during the pyrolysis (primary and secondary). This approach made possible to determine both kinetics parameters: activation energy and pre-exponential factor for each stage, i.e. primary pyrolysis, secondary pyrolysis, and gasification. The kinetic parameters determined by means of the methods of Murray and White, and Senum and Yang were almost identical and may be considered as reliable. As can be seen, the thermovolumetric and thermogravimetric methods give different kinds of information; nevertheless, both of these methods are useful and appropriate for the analysis of the whole gasification process. These methods can be used for a variety of solid fuels as coal, biomass or solid waste in the atmosphere of a variety of gasification agents.

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