

KINETIC STUDY OF THE PYROLYSIS AND GASIFICATION OF ROSA MULTIFLORA AND MISCANTHUS GIGANTEUS BIOMASSES VIA THERMOGRAVIMETRIC ANALYSIS

by

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The thermal behaviour of the Rosa multiflora (3 groups: control, irradiated 3 × 3 seconds, and 3 × 9 seconds by low power laser of wavelength 672 nm) and Miscanthus giganteus (3 groups: R, V, and Z) biomass by thermogravimetric analysis (TGA) was studied at heating rate 3 K per minute from ambient temperature to 950 °C. The TGA tests were performed in high purity CO₂ (99.998%) with a flow rate 200 mL per minute and 100 mg of sample, milled and sieved to a particle size below 250 μm. In contrast to the majority of the conducted examinations, which are carried out with the use of chars, the measurements were conducted for raw biomass. The kinetics parameters of the biomass conversion process were determined from the experimental data by integral methods (Murray and White; Senum and Yang). The methods used have allowed distinguishing and analysing the different stages of the process, i. e. the primary and secondary pyrolysis as well as gasification. Both methods gave comparable results. The activation energy determined using more accurate Senum and Yang method ranged from 85-88 kJ/mol (primary pyrolysis), from 29-32 kJ/mol (secondary pyrolysis), and from 173-190 kJ/mol (gasification) for Rosa multiflora biomass and from 86-111 kJ/mol (primary pyrolysis), from 22-25 kJ/mol (secondary pyrolysis), and from 181-217 kJ/mol (gasification) for Miscanthus giganteus. The pre-exponential factor was in the range of 5.95 · 10⁶ to 13.05 · 10⁶ min⁻¹ (primary pyrolysis), 2.25-4.22 min⁻¹ (secondary pyrolysis), and 13.96 · 10⁶ to 1.18 · 10⁸ min⁻¹ (gasification) for Rosa multiflora biomass and 6.94 · 10⁶ to 1.79 · 10⁹ min⁻¹ (primary pyrolysis), 0.88-1.62 min⁻¹ (secondary pyrolysis), and 131.54 · 10⁶ to 1.92 · 10⁹ min⁻¹ (gasification) for Miscanthus giganteus biomass.

Key words: TGA, kinetics, biomass, pyrolysis, gasification, laser biotechnology

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Introduction

There is a worldwide drive for decreasing reliance on fossil fuels, the burning of which contributes significant amount of carbon emissions leading to the impact of global warming. Also, there is a shift from non-RES to bio-energy due to continuous depletion of fossil fuels. Furthermore, since bio-fuels are derived from biomass, they essentially decrease emissions of harmful gases such as NO_x [1, 2] and SO_x . Examples of generally used biomass include plant matter such as forest residues (dead trees, branches, and tree stumps), yard clippings, various fast growing and energy efficient plants, woodchips and municipal solid waste [3-5]. The benefit of using biomass arises due to its renewable nature which comes from the ability to utilize the emitted CO_2 for growing next generation of biomass through photosynthesis cycle. Consequently, in recent years, the use of biomass-derived fuels has been steadily increasing, and they currently contribute around 13% of the world's energy supply [6]. In addition, biomass is currently a promising renewable energy and potentially neutral in relation to global warming. Plant materials can be applied with biochemical or thermochemical conversion processes focused on the production of fuel gases, chemicals, bio-oils, synthesis gas, bio-methane, and energy [7, 8]. The sources of biomass can be divided in two domains. The first based on the use of the organic fraction of municipal wastes and the residual material from forestry to agriculture, such as wood, straw, *etc.* The second domain is the growing of energy crops, meaning the cultivation of plants such as whole cereal plants, willows, *Miscanthus giganteus*, *Rosa multiflora* and fodder grasses specifically to generate electricity, or produce bio-fuels and bio-gases.

Kinetics of reactions

Thermal analysis techniques such as TGA have been broadly used because they provide rapid quantitative methods for the examination of processes under isothermal or non-isothermal conditions and allow for the estimation of effective kinetic parameters for various decomposition reactions [9]. Moreover, 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 method only provides information about the overall weight loss of the sample in relation to temperature and does not necessarily correspond to the complex chemical reactions in the thermal degradation of biomass. Nevertheless, the data provide useful comparisons of reaction parameters such as temperature and heating rate. The TGA of biomass samples has been extensively applied as a means of determining the characteristics of devolatilisation and also to determine kinetic parameters [10, 11].

The chemistry of biomass is complicated but the major components which can be isolated by analytical methods are cellulose, hemicelluloses, lignin, and extraneous compounds. Shafizadeh and McGinnis [10] used TGA to determine the thermal degradation of cottonwood and its components and concluded that the thermal behaviour of the major components of the biomass could be extrapolated to the original material. As well as, few authors have applied different reaction kinetic models for the description of the decomposition of plant species. Mass losses or mass loss rates are commonly described by models assuming biomass as the sum of its constituents or sum of pseudo-components [12-14].

Kinetic parameters can be calculated using two different experimental TGA methods. In the isothermal method, decomposition measurements are performed at constant temperature [13-15]. The alternative is the dynamic or non-isothermal method which is usually preferred as the full temperature range is considered. The sensitivity and error can be improved if the measurements are performed using different linear heating rates and the kinetic parameters can be calculated using isoconversional methods [15-18]. Different analytical and mathematical

approximations can be applied to calculate the kinetic parameters by the temperature integral [19]. The approximations developed by Murray and White, Senum and Yang, Friedman, Ozawa-Flynn-Wall (OFW), Kissinger-Akahira-Sunose (KAS) and Vyazovkin are among the most commonly used [19-23].

In the present study, TGA experiments with biomass (*Miscanthus giganteus* and *Rosa multiflora*) were performed using DynTHERM TGA under non-isothermal conditions.

Plant biomass increment via laser biotechnology

Bio-energy production from biomass sources has been attracting world-wide research in renewable energy field to comprehensively understand bio-energy development, considering energy crisis in majority of the developing and developed countries. Among various alternative sources of energy, biomass has drawn enormous attention as feedstock for clean energy production. Nowadays, a lot of research studies are focused on investigation a proper technology for more efficient biomass production.

Application of environmentally friendly laser biotechnology could be applied for more efficient increase of biomass for bio-energy production by using different clean- or bio-technologies. Moreover, this innovative bio-technology is also very effective for reclamation and an efficient biomass production in deteriorated areas as contribution to sustainable development of different regions and countries [24].

Research conducted by Dobrowolski *et al.* on industrial plants cultivated on post-industrial areas showed that increase in iron content (in comparison with control group) and the lower level of lead (0.95 ppm of dry weight in the control group, 0.50 ppm of dry weight in the experimental group) and copper concentration (4.05 ppm of dry weight in the control group, 3.65 ppm of dry weight in the experimental group) was accompanied by higher dry biomass of the potato tuber, flax, willow, Pennsylvanian malvae, *Miscanthus* and some other species of plants.

Proper time of exposure to selected wavelength and high energy density of coherent light is able to stimulate adaptation to suboptimal environmental conditions, the growth rate of plants and efficiency of reclamation of deteriorated areas, the biomass production as well as bioremediation of selected toxic metals from contaminated soil and waste water treatment in hydro-botanic plants [25, 26].

According to Dobrowolski and Zielinska-Loek [27] laser photostimulation of inoculums of selected fungi could also be a supporting factor of stimulation of moulds living in mycorrhiza and adaptation of the infected roots of seedlings to contaminated soil. Proper photostimulation of inoculums of selected moulds and bacteria could also accelerate biodegradation of some organic pollutants of water and soil.

Referring to laser stimulation of different species of plants for better adaptation to the contamination of soil with petrochemical pollutants: Dobrowolski *et al.* [28] carried a research study on the application of laser bio-technology for the enhancement of the biodegradation of hydrocarbons as a result of using an adequate algorithm of photostimulation of inoculums of fungi selected from soil contaminated by petrol pollutants for a long time. The increase of the biomass production on energy plantations as a result of laser photostimulation of plants cultivated in suboptimal environmental conditions (*e. g.* on contaminated soil) as well as application of similar method for increase of biomass production in hydro-botanic wastewater treatment plants, promotion low carbon energy production and sustainable development could be recommended for large-scale application [7, 25-27]. Thus, application of environmentally-friendly

laser biotechnology could contribute to a better bioremediation of contaminated land and water and at the same time to the development of biomass production as a source of renewable bio-energy and creative contribution to biologically-based green economy.

Further application of clean thermo technologies (e. g. pyrolysis or gasification) could be an efficient mechanism to convert a biomass produced in the result of laser photostimulation to bio-energies like bio-gas, bio-fuel, bio-oil, bio-char, syngas, methane, and etc.

Materials and methods

Preparation of samples

This research methodology consists of sampling selection method, sorting procedure and laboratory analysis of three groups (*R*, *V*, and *Z*) of *Miscanthus giganteus* and three groups (control and two stimulated by low power medical laser) of the *Rosa multiflora* biomass after 6 years field experiments accommodated at experimental energy plantations of the University of Agriculture in Krakow, Poland, was undertaken.

Application of laser biotechnology

Laser irradiation of *Rosa multiflora*'s cuttings was made in 2009 at the Department of Environmental Biotechnology and Ecology, AGH University of Science and Technology. An apparatus Medical Laser (D 68-1) emitted red light with a wavelength of 672 nm and power of 20 mW on *Rosa multiflora*'s cuttings, by the application of two exposure times intermittent: 3×3 seconds and 3×9 seconds. Exposed cuttings along with control group (non-irradiated) were planted in spring of 2009, the spacing of 70×70 cm in leached brown soil.

Biomass samples, proximate, and ultimate analysis

The procedure was applied for collecting the biomass based on the American society for testing and materials (ASTM). Samples of biomass weighing 10 or 15 kilos were collected into plastic bags from experimental field (at Mydliniki distric of Krakow city) then were separated as shown in fig. 1 and investigated at the research laboratory of Faculty of Energy and Mechanical Engineering, University of Agriculture in Krakow, Poland and investigated at the research laboratory under the Faculty of Energy and Mechanical Engineering. Prior to the ex-



Figure 1. Samples of *RM* (control, laser irradiated 3×3 seconds and 3×9 seconds) and *MG* (*R*, *V* and *Z*)

perimental process, the biomass of *Rosa multiflora* (*RM*) and *Miscanthus giganteus* (*MG*) were shredded and sieved into particles in size of approximately 2 mm. Further prepared samples were referred to various elemental and analytical analyses.

Proximate analysis

Proximate analysis consist of moisture content determination and then, for dry biomass, determination of volatile matter, ash content, fixed carbon and calorific (energetic) value.

- Moisture content

The percent moisture of the woody biomass samples was determined by drying the sample in an oven at 105 °C for 3-4 hours until a constant weight is reached. The procedure for determination of moisture content has been done following European Standard PN-EN 14774-3:2010 and ASTM standards E 871.

– Volatile matter

The volatile matter content was determined by thermal decomposition of 1 g of the sample during heating without oxygen in the muffle furnace at a temperature of 900 ± 10 °C for precisely seven minutes, following Furnace Thermocouple Thermojunction Method – European Standard PN-EN 15148:2010.900.

– Ash and fixed carbon content

Ash content of woody biomass is non-combustible residue that remains after burning up biomass. Woody biomass samples by weight of minimum 1 g were burned in an oven at 500 ± 10 °C for at least 60 min, then residue was weighted, following European Standard PN-EN 14775:2010.

Fixed carbon is defined as carbon which is found in the material which left after completion of volatile matter test. Fixed carbon is calculated by removing the content of volatile matter, moisture and ash from the original mass of the biomass sample.

– Calorific value

In this research project, amount of calorific value was obtained by using a bomb calorimeter (Model: KL-12 Mn), following European Standard PN-EN 14918:2010 and PN-ISO 1928.

Ultimate analysis

Ultimate analysis was used to determine the content of C, H, and S in biomass sample by using Eltra CHS 580 Elemental Analyzer.

In the CHS-580 the sample is burnt in an oxygen atmosphere at temperatures up to 1550 °C. The combustion gasses (CO_2 , H_2O , SO_2) coming from the furnace first pass through a dust filter and then into the heated H_2O infrared cell. After the water vapour is chemically absorbed, the dried CO_2 and SO_2 gas is detected in the additional infrared cells.

Thermogravimetric analysis

Thermogravimetric non-isothermal measurements were made according to the ASTM E1641-07 method using a DynTHERM TGA by Rubotherm, which enables examining the kinetics of gasification with CO_2 under a high pressure. A fully automatic instrument is a combination of two basic systems: system of the magnetic suspension balance and a gas and/or vapour dosing system, supplying gases to the reaction zone.

After placement the biomass sample weighing 100 mg in a titanium container and transfer it to the reactor, the measurement started, which can be distinguished.

- Stage I – stabilization: stabilizing the initial conditions, *i. e.* the pressure at 0.1 MPa, the flow of carbon dioxide 200 mLmin^{-1} . This stage lasted 30 minutes.
- Stage II – measurement: the temperature was ramped from ambient temperature to 950 °C with heating rate 3 Kmin^{-1} , through the system flowed 200 mLmin^{-1} of CO_2 supplied from the dosing system. At this stage evaporation of moisture, then, with increasing temperatures, pyrolysis and overlapping gasification processes occurred.

All TGA tests were performed in high purity carbon CO_2 (99.998%). The loss in weight during the measurement was recorded continuously, and the results were presented as a function of temperature.

Kinetic parameters estimation

Both kinetics parameters: activation energy and pre-exponential factor of decomposition process were determined simultaneous from the TGA data by integral methods developed

by Murray and White [23], and Senum and Yang [29]. The kinetic parameters for each stage: primary pyrolysis, secondary pyrolysis, and gasification were determined separately and not, as is usually found in the literature, for the entire process.

Experiments with pre-determined heating rate

Kinetics of thermal decomposition of plant biomass using TGA is usually described by a first order kinetic reaction equation which can be expressed:

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

where

$$\alpha = 1 - \frac{m}{m_0} \quad (2)$$

where α [-] stands for degree of conversion ranging from zero to one, m [mg] – the current weight of the sample, m_0 [mg] – the original weight of the sample, t [min] – stands for time, and k [min⁻¹] – the reaction rate constant. The reaction rate constant depends on the temperature according to the Arrhenius equation:

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

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

Combining eqs. (2) and (3) provides:

$$\frac{d\alpha}{dt} = A(1-\alpha)\exp\left(-\frac{E}{RT}\right) \quad (4)$$

In non-isothermal experiments, the sample is heated with a predetermined rate $B = dT/dt$ which remains constant throughout the experiment. The derivative $d\alpha/dt$ is then expressed:

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT} \frac{dT}{dt} = B \frac{d\alpha}{dT} \quad (5)$$

and eq. (4) takes the form:

$$\frac{d\alpha}{dT} = \frac{A}{B}(1-\alpha)\exp\left(-\frac{E}{RT}\right) \quad (6)$$

The variation of the progress variable α with temperature is obtained upon integration of eq. (6). Introducing a new variable $x = E/RT$ provides:

$$-\ln(1-\alpha) = \frac{AE}{BR} p(x) \quad (7)$$

Integral methods

Murray and White, Senum and Yang

While obtaining the kinetic parameters from experimental data, the $p(x)$ integral is not calculated directly. Instead, some approximations are used like this developed by Murray and White [23]:

$$p(x) \cong \frac{\exp(-x)}{x^2} \quad (8)$$

Inserting the approximation into eq. (7) and after taking the logarithm one obtains:

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right] = \ln \left(\frac{AR}{E\beta} \right) - \frac{E}{RT} \quad (9)$$

Hence, when the heating rate β is given, A and E can be determined from the intercept and the slope of a plot $\ln[-\ln(1-\alpha)/T^2]$ against $1/T$.

Senum and Yang [29] derived another approximation:

$$p(x) \cong \frac{\exp(-x)}{x^2} \frac{x^3 + 18x^2 + 86x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (10)$$

After inserting this approximation into eq. (10), where $x = E/RT$, a non-linear regression is required to obtain kinetics parameters.

This method uses the non-linear regression proposed by Senum and Yang [29], which makes it more accurate over a wider range of TGA data and circumvents the inaccuracies related to the analytical approximation of the temperature integral.

Results and discussion

Results from proximate analysis

Proximate analysis involves determination of moisture content, volatile matter, ash content, fixed carbon, and calorific value. Comparative results from proximate analysis 3-groups of *RM* biomass (control, laser irradiated 3×3 seconds and 3×9 seconds) and three groups of *MG* (*R*, *V*, and *Z*) are shown in tab. 1.

Table 1. Proximate analysis of *RM* and *MG* biomasses

Parameter	Group of <i>RM</i> biomass			Group of <i>MG</i> biomass		
	Control (non-irradiated)	Laser irradiated 3×3 seconds	Laser irradiated 3×9 seconds	<i>R</i>	<i>V</i>	<i>Z</i>
Moisture – M^a [%]	18.3	19.4	18.6	8.8	9.7	8.9
Volatile matter – V^{daf} [%]	76.4	76.1	76.7	79.9	80.0	80.1
Fixed carbon – FC [%]	5.9	5.5	5.4	10.7	10.4	10.04
Ash – A^a [%]	2.4	2.4	2.2	3.9	2.9	2.2
Calorific value [MJkg ⁻¹]	17.6	18.3	17.7	16.9	18.0	17.2

The results of all analyses included in the proximate analysis demonstrate very similar properties of all samples within a single species. The difference in the moisture content of *RM* samples is a little over 1% and is in the range between 18.3% and 19.4%. The *MG* biomass is characterized by much lower moisture content, between 8.8% and 9.7%. It is directly affected by chemical and physical properties of material which enable it to absorb the exiting water in the environment. Content of fixed carbon shows the opposite trend – for *RM* biomass oscillates at 5% while for *MG* this value is about two times higher. The difference between the samples of biomass of different species, but not so significant, can also be seen in the ash content. All groups of *RM* have a similar level of ash, between 2.2% and 2.4%, while most groups of *MG* (*V* and *R*) have slightly higher ash content. All tested samples are characterized by almost identical values of one of the most important parameters of the proximate analysis - content of volatile matter. The share of volatile matter in all three groups of *RM* is at 76%, while for all groups of *MG* is slightly higher and is located in the vicinity of 80%. Both parameters volatile matter and ash content have influence on the gasification/pyrolysis characteristics [5]. Woody biomass is eas-

ier to ignite and to gasify than coal apparently due its volatile matter although the pyrolysis is expected to be more rapid and difficult to control.

Calorific value of the fuel is affected by volatile matter content, which reflects the degree of metamorphism, ash and moisture content. As the calorimetric measurements were performed on dry samples, and other parameters affecting this parameter are comparable for all samples, the obtained calorific value results are very similar. The calorific value for *Rosa* stands at between 17.6 and 18.3 MJ/kg. Samples of *Miscanthus* reached very similar values, from among which the highest calorific value indicated group *V* – 18.0 and the lowest group *R* – 16.9 MJ/kg. Similar values can be found in the literature describing biomass for energy purposes, and therefore can be inferred that *RM* and *MG* biomass can be an effective energy source.

Results from ultimate analysis

Ultimate analysis demonstrates determination of chemical characteristics of *RM* and *MG* biomasses sample. The results of ultimate analysis are summarised in tab. 2. As can be seen, results obtained for each groups of *RM* and *MG* are very similar. Samples of *RM* are characterized by a slightly higher carbon content and lower hydrogen and oxygen content compared to the *MG* samples.

Table 2. Ultimate analysis of *RM* and *MG* biomasses

Chemical elements	Groups of <i>RM</i> biomass			Groups of <i>MG</i> biomass		
	Control (non-irradiated)	Laser irradiated 3 × 3 seconds	Laser irradiated 3 × 9 seconds	<i>R</i>	<i>V</i>	<i>Z</i>
C ^{daf} (%)	53.53	53.11	53.16	52.70	52.06	52.38
H ^{daf} (%)	7.19	7.22	7.37	7.74	7.48	7.47
S ^{daf} (%)	0.04	0.04	0.03	0.04	0.04	0.03
O [*] (%)	29.31	29.63	29.88	35.15	35.91	35.13

*Chemical element obtained using X-ray fluorescence spectrometry

Results from TGA

Figures 2 and 3 show the TGA curves of *RM* and *MG* at heating rate 3 K per minute. As can be seen in the figures showing weight loss of samples at a temperature, four stages may be distinguished: moisture evaporation, primary pyrolysis, secondary pyrolysis, and gasification (analysis of the results does not include the moisture evaporation step). On the curves the temperatures of conversion peak in each stage were marked, tagged based on the derivative weight as a function of temperature. Temperature range, in which conversion of the biomass from *RM* and *MG* groups proceeded was between 200 °C and 850 °C and general character of all curves is similar.

Curves showing weight loss of three groups of *RM* biomass were almost identical. Initially, steep decline of curves which was associated with primary pyrolysis can be observed. At this stage thermal decomposition occurred which resulted in a loss of about 53% samples weight in each case. Conversion peaks in this stage occurred in very similar temperatures for each *RM* biomass, between 313 °C and 317 °C. The decline of curves showing the secondary pyrolysis step was milder. This pyrolysis started near 348 °C and took up to 650 or 660 °C, depending on samples: irradiated had a slightly higher temperature of the end of secondary pyrolysis (660 °C) and a higher temperature at which the conversion peak occurred, between 413 °C and 416 °C. In the case of control samples, secondary pyrolysis completed at a temperature of 650 °C and a peak appeared at a temperature of 388 °C. An average weight loss of *RM* biomass

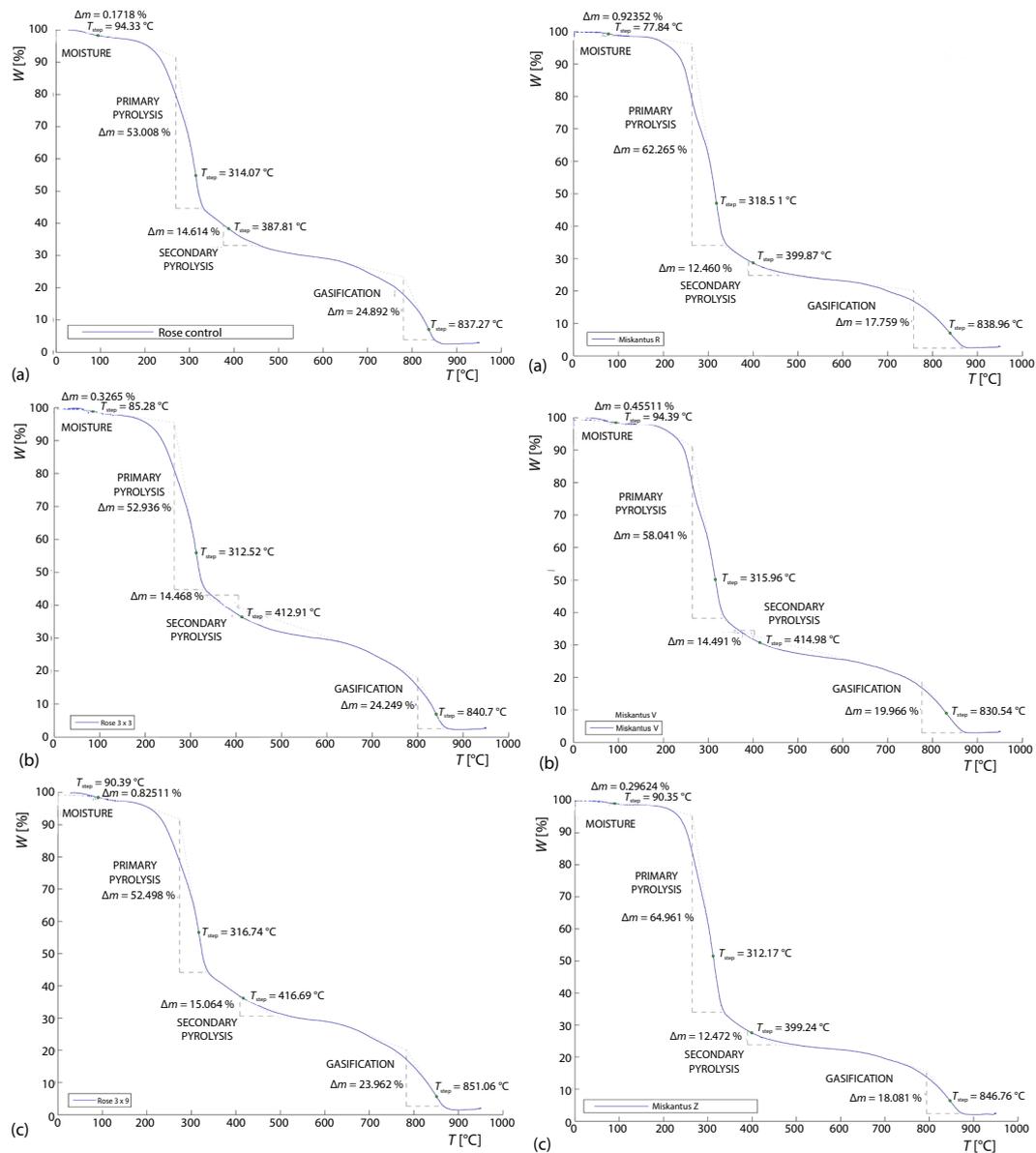


Figure 2. The TGA curves for *RM*; (a) control, (b) laser irradiated 3 × 3 seconds, and (c) 3 × 9 seconds

Figure 3. The TGA curves for *MG* (groups: *R*, *V*, and *Z*)

was 15%. In the last step, again steeper decline of curves can be observed, which illustrated the gasification stage. Gasification continued until only ashes remain in the crucible, in all cases it has been in temperatures close to 865 °C, and the temperatures of conversion peak were in the range 837-851 °C. During gasification weight loss of samples fluctuated around 24%. The differences in the TGA curves for the *RM* samples are negligible and it can be said that the conversion by the action of temperature and carbon dioxide is carried out in the same way.

Slightly bigger differences occurred both between different groups of *MG* as well as between the two studied species. They were connected, however, with loss of sample mass in the individual stages, and not with the temperature ranges in which these stages appeared. As the temperature ranges were very similar for all tested samples, regardless of species, the temperatures of conversion peaks were also similar and for *MG* biomass were within the ranges: for primary pyrolysis between 312-319 °C, for secondary pyrolysis 399-414 °C and for gasification 831-847 °C. Differences appeared in percentage weight loss of the sample. While loss during primary pyrolysis of *RM* samples was equal and amounted to 53%, for *R* and *Z* groups of *MG* was much greater, approximately 63-65%, whereas for the *V* group was 58%. In the second step, secondary pyrolysis, weight loss of *MG* biomass was in most cases smaller compared to *RM*. The weight loss of *Z* and *R* group, as their course was almost identical, was the same and amounted to 12%. Slightly greater mass loss was characterised by sample *V* – 14% and this value was such as for *RM* samples. In the last gasification stage, samples *R* and *Z* were characterized by loss of weight of the order of 18% and the sample *V* slightly higher, of the order of 20%. As can be seen, the stage associated with the greatest weight loss was the primary pyrolysis. Biomass feedstocks are characterized by a high content of volatile matter

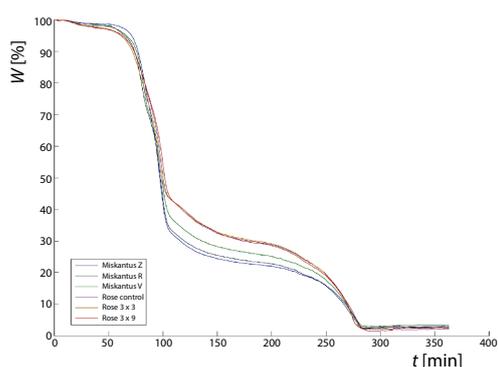


Figure 4. Changes in mass of analysed samples (for color image see journal web site)

and low resistance to thermal decomposition so the results obtained are in agreement with this statement. The *MG* biomass to a greater extent were converted at lower temperatures, resulting in increased weight loss during primary pyrolysis, while the lower during secondary pyrolysis and gasification processes, compared to *RM* biomass. However, since the ultimate and proximate analysis demonstrated very similar characteristics of all the samples, the overall loss of weight was almost identical in each case, fig. 4.

Table 3 shows comparison of TGA characteristic for biomass which is the subject of this research.

Table 3. The TGA characteristics for *RM* and *MG*

Feedstock	Decomposition range [°C]	Peak degradation temperature [°C]		
		Primary pyrolysis	Secondary pyrolysis	Gasification
<i>RM</i> (control)	200-850	314	388	837
<i>RM</i> (laser irradiated 3 × 3 seconds)	200-850	313	413	841
<i>RM</i> (laser irradiated 3 × 9 seconds)	200-850	317	417	851
<i>MG</i> (<i>R</i>)	250-850	319	400	839
<i>MG</i> (<i>V</i>)	250-850	316	415	831
<i>MG</i> (<i>Z</i>)	250-850	312	399	847

Determination of the activation energy and the pre-exponential factor

For each stage *i. e.* primary pyrolysis, secondary pyrolysis and CO₂ gasification the kinetic parameters were calculated using both methods Murray and White [23] and Senum and Yang [29]. This is a sensible approach, because usually only energy activation is determined, the pre-exponential factor is overlooked. Erroneous to assume that knowing only the activation energy is possible to describe kinetics of the process, since both these parameters affect the course of the process. A plot $\ln[-\ln(1 - \alpha)]/T^2$ against $1/T$, which is shown in fig. 5 (figure for *V* group of *MG*), allowed to determine kinetics parameters by Murray and White method. For Senum and Yang method, non-linear regression was used, and results for both integral methods are summarized in tab. 4. Results for Murray and White and Senum and Yang methods were very similar. Comparing the results of the kinetic parameters determined by both methods can be noticed that in the case of primary pyrolysis and gasification differences were negligible and the results were

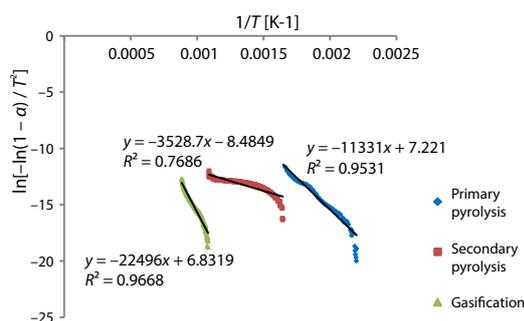


Figure 5. The slope of a plot $\ln[-\ln(1 - \alpha)]/T^2$ against $1/T$ (for color image see journal web site)

Table 4. Kinetic parameters determined by integral methods

Feedstock	E_a [kJmol ⁻¹]		Pre-exponential factor, A [min ⁻¹]		Reference
	¹ M and W	² S and Y	¹ M and W	² S and Y	Present work
<i>RM</i> (control)	^a 89 ^b 40 ^c 189	^a 88 ^b 32 ^c 187	^a 13.04 · 10 ⁶ ^b 12.79 ^c 83.16 · 10 ⁶	^a 13.05 · 10 ⁶ ^b 4.22 ^c 83.16 · 10 ⁶	
<i>RM</i> (laser irradiated 3 × 3 seconds)	^a 80 ^b 40 ^c 192	^a 87 ^b 29 ^c 190	^a 1.79 · 10 ⁶ ^b 11.53 ^c 1.18 · 10 ⁸	^a 9.39 · 10 ⁶ ^b 2.25 ^c 1.18 · 10 ⁸	
<i>RM</i> (laser irradiated 3 × 9 seconds)	^a 86 ^b 42 ^c 175	^a 85 ^b 31 ^c 173	^a 5.94 · 10 ⁶ ^b 16.82 ^c 13.96 · 10 ⁶	^a 5.95 · 10 ⁶ ^b 3.34 ^c 13.96 · 10 ⁶	
<i>MG</i> (<i>R</i>)	^a 86 ^b 27 ^c 218	^a 86 ^b 25 ^c 217	^a 6.94 · 10 ⁶ ^b 1.14 ^c 1.92 · 10 ⁹	^a 6.94 · 10 ⁶ ^b 1.01 ^c 1.92 · 10 ⁹	
<i>MiG</i> (<i>V</i>)	^a 94 ^b 29 ^c 188	^a 94 ^b 22 ^c 187	^a 46.49 · 10 ⁶ ^b 2.21 ^c 66.33 · 10 ⁶	^a 46.49 · 10 ⁶ ^b 0.88 ^c 66.33 · 10 ⁶	
<i>MG</i> (<i>Z</i>)	^a 112 ^b 31 ^c 183	^a 111 ^b 25 ^c 181	^a 1,79 · 10 ⁹ ^b 3,32 ^c 31,54 · 10 ⁶	^a 1,79 · 10 ⁹ ^b 1,62 ^c 31,54 · 10 ⁶	
Two parallel reactions					
Wood biomass	^a 183.3 / ^b 107.5		^a 10 ¹³ / ^b 4.28 10 ⁶		see [43]

Results obtained using ¹Murray and White; ²Senum and Yang methods
^aprimary pyrolysis; ^bsecondary pyrolysis; ^cgasification

often even identical. Minor differences can be observed in the case of secondary pyrolysis stage, for which the values determined using the Senum and Yang method in every case were lower than the values determined by the method of Murray and White. As the literature reports indicate, the Senum and Yang method, due to the ratio of two polynomials is termed more rational [30]. Because of that, it is more prudent to analyse the results identified by this method. Activation energy determined using Senum and Yang method for all groups of *RM* ranged from 85-88 kJ/mol (primary pyrolysis), from 29-32 kJ/mol (secondary pyrolysis), and from 173-190 kJ/mol (gasification), and for all groups of *MG* activation energy were 86-111 kJ/mol (primary pyrolysis), 22-25 kJ/mol (secondary pyrolysis), and 181-217 kJ/mol (gasification). Simultaneously with the activation energy pre-exponential factor was determined. Values varied from $5.95 \cdot 10^6$ to $13.05 \cdot 10^6$ L per min (primary pyrolysis), 2.25 to 4.22 L per min (secondary pyrolysis), and $13.96 \cdot 10^6$ to $1.18 \cdot 10^8$ (gasification) for *RM* biomass, and $6.94 \cdot 10^6$ to $1.79 \cdot 10^9$ L per min (primary pyrolysis), 0.88 to 1.62 (secondary pyrolysis), and $31.54 \cdot 10^6$ to $1.92 \cdot 10^9$ L per min for *MG* biomass. It is difficult to compare these results because the biomass gasification with CO_2 , despite many advantages, is not a popular issue. However, among the different methods of energy production from biomass, gasification is considered as the most suitable option as it is a simple and economically viable process to produce thermal energy or decentralized electricity generation [31]. In the literature of some studies on biomass gasification using air as gasifying agent [32], oxygen [33] or steam [34, 35] can be found. The CO_2 is not a popular gasifying agent because the reaction of CO_2 with carbon (the Boudouard reaction) is highly endothermic and hence highly energy intensive [36]. However, use of this gas can play a major role in CO_2 recycle thus reducing CO_2 pollution [37, 38]. Moreover, unlike steam no energy is required for vaporization, a wide range of H_2/CO ratio in syngas can be achieved to suit different applications as well as use of CO_2 results in a reactive char producing more volatiles resulting in efficient gasification [36, 39]. There are some reports about use of CO_2 as gasifying agent, but in case of gasification of char from biomass [40], not the raw feedstock. Although gasification of char derived from coal or biomass is widely considered and well-known issue, it is not entirely practical. Preparation of the char *i. e.* devolatilization of the raw material and cooling the char prior its utilization in the gasification process significantly affect the morphology of char, and thus the whole gasification process [41, 42]. It is important to know the gasification process of raw feedstock which may simulate course of process in gasification plants. Research conducted and presented in this article represents a new and practical approach to biomass gasification and determined kinetic parameters can be considered as a simplified base for simulation of pyrolysis and gasification of *RM* and *MG* biomasses.

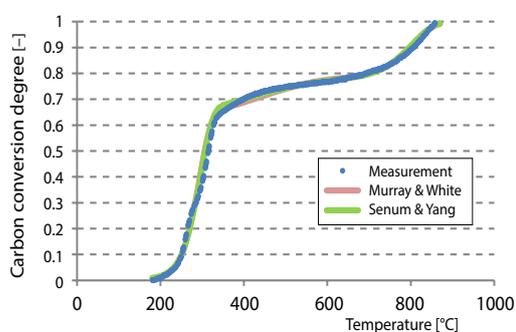


Figure 6. Fit of models to the experimental data
(for color image see journal web site)

Taking into account the contribution of individual stages in the whole process, fig. 6 shows fit of first order reaction model with approximation proposed by Murray and White and Senum and Yang methods to experimental data. The resulting curves almost coincided with the experimental curve, especially at the stage of the gasification and primary pyrolysis. This was also confirmed by coefficients of determination, R^2 , calculated on the basis of the slope of a plot $\ln[-\ln(1 - \alpha)]/T^2$ against $1/T$, which for primary pyrolysis and gasification stage reached

value of above 9 and for secondary pyrolysis was always lower, in the range between 7-8 for all samples. The weakest fit obtained for secondary pyrolysis can still be considered sufficient. Very good entire fit allows drawing conclusion that the proposed models are correct and kinetic parameters received on their basis are reliable.

Conclusion

Using TGA, non-isothermal gasification process of two species of biomass, *RM* and *MG*, in the atmosphere of CO₂ was investigated. In contrast to the majority of examinations, which are carried out with the use of chars, these measurements were conducted for raw feedstock. In the process three main stages such as primary pyrolysis, secondary pyrolysis and gasification were distinguished. The first step was accompanied by the highest loss in mass of the samples, more than half, related to the violent separation of volatiles. In further stages – overlapping secondary pyrolysis and gasification, weight loss of samples was much smaller. On the basis of obtained experimental data and using first order reaction model combined with two integral methods Murray and White and Senum and Yang both kinetic parameters. The activation energy and the pre-exponential factor for each stage of the process were determined. This enabled a more precise approach to kinetics of gasification issue, because unlike most of the conducted research, the equally important as the activation energy pre-exponential factor was highlighted. Moreover, each individual stage were precisely analysed which in turn made it possible to describe the whole process. Determined values show that there is negligible difference in the kinetic parameters of pyrolysis and gasification determined by both methods, however, the method Senum and Yang is considered to be more accurate. A good fit of chosen models to experimental data suggests that determined kinetic parameters are reliable. Thus, gasification of biomass in the atmosphere of CO₂, although so far it is not a popular topic, it has the potential to become an alternative to other methods of converting biomass into energy, especially if it is possible to accelerate the growth of biomass which are characterized by properties typical for energy crops like all studied in this research groups of *RM* and *MG* biomass.

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