



Studies of CO₂ gasification of the *Miscanthus giganteus* biomass over Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O promoter as catalysts

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Abstract

An assessment of the catalytic and non-catalytic gasification process of the *Miscanthus giganteus* (MG) biomass in an atmosphere of carbon dioxide was performed on the basis of thermogravimetric and thermovolumetric analyses. In the first step, the thermal behavior of biomass was determined by analyzing the mass loss during non-catalytic gasification with the use of TGA. The results of thermogravimetric analysis were used to assess the course of the biomass heating process in the atmosphere of CO₂ and to distinguish the individual phases of this process. Then, the thermovolumetric measurements of MG gasification were taken with the use of Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O promoter as catalysts. The obtained results allowed determining the process rate as well as composition of the resulting gas and yields of main gaseous products (CH₄, CO, H₂). The use of Ni/Al₂O₃-SiO₂ as catalyst resulted in the highest conversion rate of MG gasification into gaseous products with considerably increased contents of H₂ and CO. The second analyzed catalyst—Ni/Al₂O₃-SiO₂ with K₂O promoter—did not catalyze the gasification process. However, the use of both tested catalysts had a positive effect on reducing the methane content in the resulting gas. One can also suppose that it promotes the decomposition of the tar formed in the process.

Keywords Biomass · *Miscanthus giganteus* · Kinetics · CO₂ gasification · Catalyst

Introduction

With the expanding concerns about greenhouse gas emissions and climate change, non-renewable fossil fuels such as natural gas, petroleum and coal might no longer be considered as the only energy sources to meet our future energy needs. A diverse and versatile energy plan,

engaging both renewable and non-renewable energy sources, is undoubtedly required. In the long term, there is a particular need for global transition to 100% renewable energy and chemical feedstock to achieve efficient and sustainable growth [1–5]. Among the crucial aspects, the most important are: energy storage until consumption, efficiency in energy conversion technologies, carbon footprint, waste generation and impact of the quality of natural environment and human life [6, 7]. However, much attention has been paid to biomass conversion technologies into bioenergy. Consequently, nowadays a number of research studies are concentrated on investigating a proper technology for more efficient biomass production.

Miscanthus is one of the key biomass energy crops with relatively low maintenance and high energy density. It has a considerable role in the sustainable production of renewable fuels and chemicals via thermochemical conversion [8, 9]. The genus *Miscanthus* comprises around 17 species of perennial non-wood rhizomatous tall grasses native to subtropical and tropical regions originating from Asia; among them, *Miscanthus tinctorius*, *Miscanthus*

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sacchariflorus and *Miscanthus sinensis* are of primary interest for biomass production [10, 11]. In order to broaden the genetic base of *Miscanthus* and maximize the productivity and adaptive range of the crop, the sterile hybrid genotype *Miscanthus* × *giganteus* from *Miscanthus sacchariflorus* and *Miscanthus sinensis* has attracted profound attention and extensively used in Europe and recently in North America for productivity trials [12–14].

Thereby, comprehensive processes for biomass conversion, such as gasification and pyrolysis, combustion or fermentation can be used for bioenergy production and power generation. Among them, the thermochemical processes such as biomass gasification and pyrolysis have attracted the considerable attention from both industrial and academic researchers. The gasification process is considered as a self-sufficient autothermic technological process in terms of an energy balance. Moreover, it is characterized by flexibility, allows achieving high efficiency and enables optimal utilization of accessible biomass feedstock for power and heat generation as well as for fuels and chemical production [1, 15]. In the gasification process, a gas containing mainly hydrogen (H₂), carbon monoxide (CO) and methane (CH₄) is generated. This gas can be combusted or, as a synthesis gas, can be used for the production of liquid fuels, methanol or synthetic natural gas via catalytic methanation of carbon monoxide and carbon dioxide [16].

However, undesirable products such as unreacted char and tar are also produced during the gasification process [17–19]. Currently, numerous research projects connected with the use of catalysts to minimize the amount of these by-products are implemented. The especially challenging issue is the tar formation during pyrolysis stage of gasification [15, 20, 21]. However, tar can be eliminated through the catalytic cracking [22–24]. Catalysts with a noble metal (e.g., Ru, Pt and Rh) in their compositions have excellent properties in various reactions focused on an enhancement of gaseous yield and on tar cracking. However, these catalysts are expensive and highly susceptible to deactivation by poison such as sulfur and nitrogen oxides. Thereby, there is a need to develop affordable and efficient catalysts that are able to compete with catalysts containing costly metal elements. Taking into consideration the low cost and good activity, supported Ni catalyst is the proper alternative to noble metals [25, 26]. The nickel-based catalysts are generally applied to this purpose because they can effectively eliminate the tar by cracking and reforming processes as well as they enhance gaseous yields production in the steam gasification of solid biomass [27–29]. Nevertheless, the commercial Ni catalysts present a moderate-to-quick deactivation because of the build-up of surface carbon [24, 30]. Thus, some research investigations have been undertaken to improve the stability and activity of Ni

catalysts by using additional different supports or using metals [1, 31].

To assess the kinetics of the gasification process and the effect of catalysts' utilization, the thermogravimetric method is generally used. This is a rapid quantitative method for the examination of processes under isothermal or non-isothermal conditions and allows for the estimation of kinetic parameters for various decomposition reactions [32]. TGA of biomass samples has been extensively applied as a means of determining the characteristics of devolatilization and also of determining kinetic parameters [33, 34]. However, this method only provides information about the overall mass loss of the sample in relation to temperature and does not necessarily correspond to the complex chemical reactions in the thermal degradation of biomass. Moreover, in contrast to the thermovolumetric method, the TGA does not provide information about the gas generated in the process. Therefore, in order to comprehensively analyze the biomass gasification process, it is reasonable to use both the above-mentioned methods.

In this study, catalytic and non-catalytic gasification of *Miscanthus giganteus* biomass was analyzed by thermogravimetric and thermovolumetric methods. The proximate and ultimate analysis of *Miscanthus giganteus* samples as well as broad characteristic of catalysts used, i.e., Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O promoter, was presented. The results of TGA measurements were used to assess the course of the biomass heating process in the atmosphere of CO₂ and to distinguish the individual phases of this process. In turn, the thermovolumetric measurements allowed determining the rate of the process as well as composition of the resulting gas and yields of main gaseous products (CH₄, CO, H₂). Based on the performed measurements, the assessment of the use of the above-mentioned catalysts in the gasification process was made.

Materials and methods

Biomass samples of proximate and ultimate analysis

The experimental procedure for collecting the biomass based on the American Society for Testing and Materials (ASTM) was applied. The biomass samples were collected in the plastic bag from experimental field (at Mydlniki district of Krakow city), the Faculty of Energy and Mechanical Engineering, University of Agriculture in Krakow, Poland, which is usually amount of 15–20 kg, and investigated at the research laboratory under the Faculty of Energy and Mechanical Engineering, Krakow University of Agriculture, Poland. Before the experiments, the sample was shredded and sieved into particles in size

approximately 2 mm. The prepared sample was subjected to various analyses. (Each test was repeated at least 3 times in order to obtain a repeatable data.)

Ultimate analysis of biomass sample was performed by using Eltra CHS 580 elemental analyzer to determine carbon (C), hydrogen (H) and sulfur (S) contents as well as by using X-ray fluorescence (XRF) spectrometry for oxygen (O) content determination. Proximate analysis of biomass sample was performed according to European PN-EN/PN-ISO and ASTM standards for the determination of moisture [PN-EN 14774-3:2010; ASTM E-871], volatile matter [PN-EN 15148:2010.900], fixed carbon and ash [PN-EN 14775:2010], as well as for the determination of high heating value [PN-EN 14918:2010 and PN-ISO 1928].

Results of proximate and ultimate analyses are shown in Table 1. The *MG* is characterized by relatively high ash content, high heating value as well as high content of volatile matter, which allows easier ignition and gasification compared to coal.

Thermogravimetric analysis (TGA)

In order to (i) assess the course of the *MG* biomass heating process in the atmosphere of CO₂, (ii) distinguish individual phases of this process, such as evaporation, primary and secondary pyrolysis and gasification as well as (iii) assess the contribution of these phases to the whole process, the thermogravimetric measurements were taken. TGA non-isothermal measurements were taken 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 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 vapor dosing system, supplying gases to the reaction zone.

Table 1 Proximate and ultimate analysis of *MG* biomass

Ultimate analysis/mass%	Proximate analysis/mass%		
C ^a	52.1	Moisture—M ^a	9.7
H ^a	7.5	Volatile matter—VM ^{daf}	76.7
S ^a	0.04	Fixed carbon—FC ^a	10.4
O ^{*a}	35.9	Ash—A ^a	3.3
		High heating value—HHV (kJ/kg)	18,023

^aDry state

^{daf}Dry and ash-free state

*Chemical element obtained using X-ray fluorescence (XRF) spectrometry

After placed the biomass sample weighing 100 mg in a titanium container and transferred it to the reactor, the measurement has 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 mL min⁻¹. This stage lasted 30 min
- Stage II measurement: the temperature was ramped from ambient temperature to 950 °C with heating rate 3 K min⁻¹, through the system flowed 200 mL min⁻¹ of CO₂ supplied from the dosing system. At this stage evaporation of moisture, then, with increasing temperatures, pyrolysis and overlapping gasification processes occurred.

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

Catalysts Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O promoter

In the present study, two types of catalysts: Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O promoter, were used to assess their impact on resulting gas composition and yields of gaseous products from CO₂ gasification of *MG* biomass compared to non-catalytic gasification. Since Ni-supported catalysts are significantly active only at high temperatures (> 900 °C), the measurements were taken at higher temperature. Moreover, during biomass gasification process tar is formed; thus, catalysts were used to minimize this phenomenon. Catalysts Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O promoter (manufacturer: Pingxiang Hualian Chemical Ceramic Co., Ltd.) were provided by the Faculty of Chemistry of the Maria Curie-Skłodowska University in Lublin, Poland. Catalysts were ground and sieved to the particle size of 0.4–0.65 mm. The X-ray diffraction of catalysts was investigated by using X'Pert³ Powder PANalytical's newest X-ray diffractometer and determination of chemical compositions by using X-ray fluorescent (XRF) spectrometer. The surface characteristics of catalysts were evaluated by using JSM-5410 scanning microscope SEM.

Thermovolumetric analysis

The examinations were conducted with the application of unique laboratory equipment which enables examining the kinetics and product yields of biomass gasification with CO₂ (supplier: Air Liquide, Paris) under a high pressure. The equipment was accurately described in the works of Zubek et al. and Porada et al. [35–37], and its schematic diagram is shown in Fig. 1. The equipment is composed of

Fig. 1 Laboratory equipment for kinetic measurements of coal gasification: 1—reactor; 2—thermocouple; 3—sample feeder; 4—pre-heater; 5—mass flow meter; 6—CO₂ cylinders; 7—pressure gauge; 8—cooler; 9—filter; 10—pressure regulator; 11—rotameter; 12—gas chromatograph; 13—CO, CO₂ IR analyzer

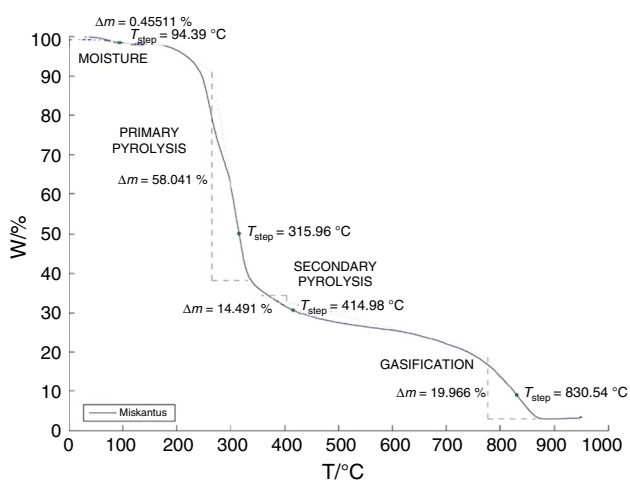
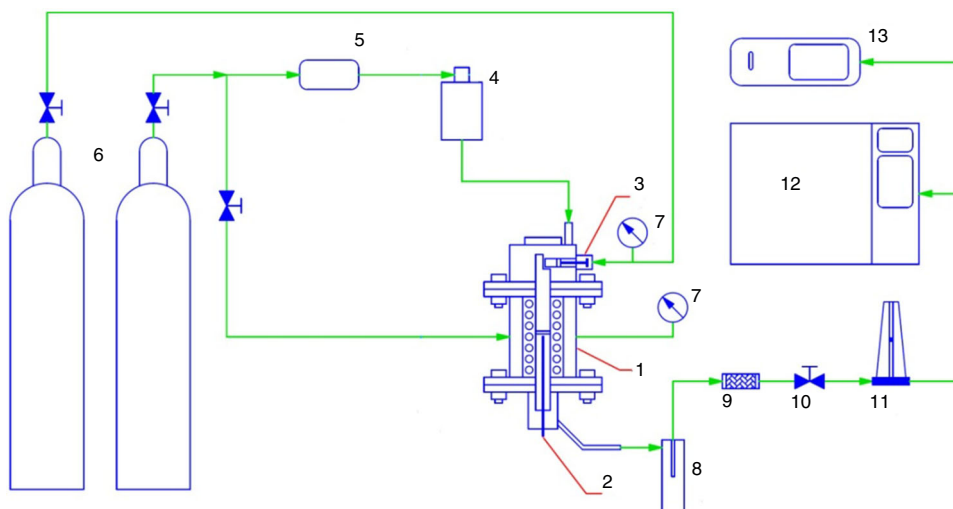


Fig. 2 TGA curves for *MG* biomass

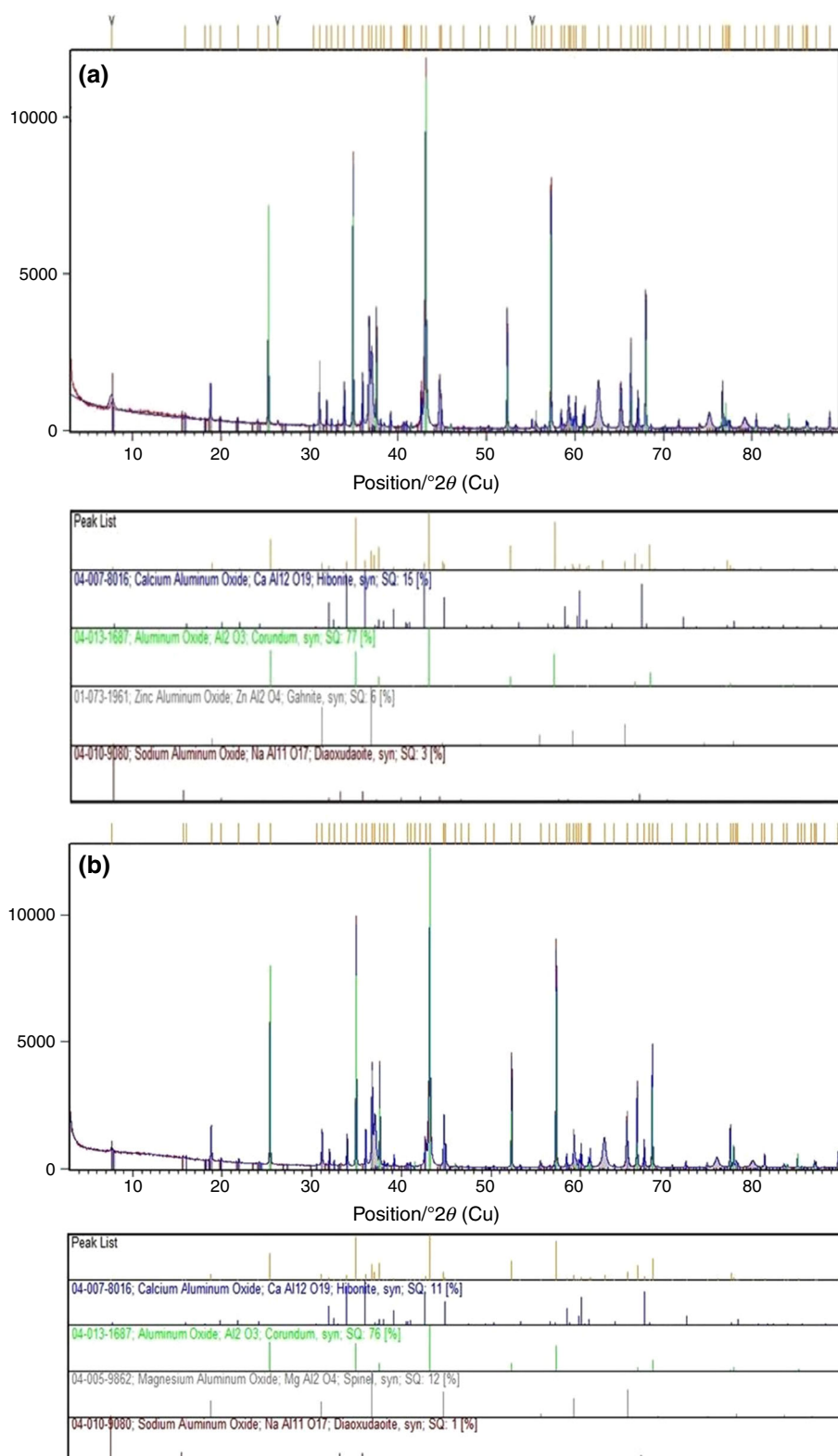
three basic systems, namely a high-pressure reactor with a heating system, system for feeding the reactor with CO₂ and biomass and a system for analysis and collection of the resulting gas. Inside the reactor there is a quartz retort with the diameter of 20 mm equipped with a grate. Upon stabilizing the parameters of the examinations, a sample of the biomass is introduced onto the grate. For this purpose, specially designed piston feeder is applied. The piston's movement is a result of opening the inlet valve on the pipe supplying the gas into the chamber of the feeder. The heating of the retort with a sample is conducted by means of an electric oven. The pressure casing of the quartz reactor is constituted of a heat-resistant steel blanket, the ends of which are closed with lids equipped with pipes supplying CO₂ and the pipes carrying away the resulting gas. Mineral wool fitted inside the casing forms the insulation of the oven. The temperature of the biomass sample is measured by a sensor of the thermocouple type K, which

Table 2 X-ray analysis of the Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O promoter as catalysts

Ni/Al ₂ O ₃ -SiO ₂		Ni/Al ₂ O ₃ -SiO ₂ with K ₂ O promoter	
Compound	ConcUnit/%	Compound	ConcUnit/%
Al	39.61	Al	41.55
O	37.99	O	39.74
Ni	17.12	Ni	14.11
Mg	2.706	Mg	3.206
Ca	1.228	Ca	0.9139
Cu	0.6833	Na	0.1792
Si	0.3049	Si	0.1722
Na	0.1952	Fe	0.09158
Fe	0.1005	K	0.05796
Zn	0.01125	Zn	0.00980
S	0.01030	Cl	0.008315
K	0.009257	Cr	0.007715
Cr	0.007188	Ga	0.004307
Cl	0.006442	Co	0.003580
Ga	0.005796	S	0.002508
Mn	0.004232	P	0.001511
P	0.001772	Cu	0.00104

served, simultaneously, for sending impulses to the controller-programmer maintaining the required temperature of the sample. The resulting gas flows through the condenser, where a water and tar condensate are separated and, subsequently, thoroughly dried and cleared on the filter. After decompression, in the resulting gas the contents of carbon monoxide and methane are determined in a continuous way by means of an analyzer based on the infrared radiation adsorption. Additionally, gas samples were taken in order to analyze them in respect of the content of

Fig. 3 XRD patterns of the Ni/Al₂O₃-SiO₂ (a) and Ni/Al₂O₃-SiO₂ with K₂O promoter (b) as catalysts



hydrogen via gas chromatograph equipped with a thermal conductivity detector (TCD).

A retort was positioned inside the reactor, and about 1 g of biomass (0.2 g catalysts with catalytic process, with

particle size 0.60 mm) of appropriate particle size was placed in the sample feeder. After closing with the lids, the reactor were compressed by CO₂ to the required pressure (1.0 MPa) and then the required flow of CO₂

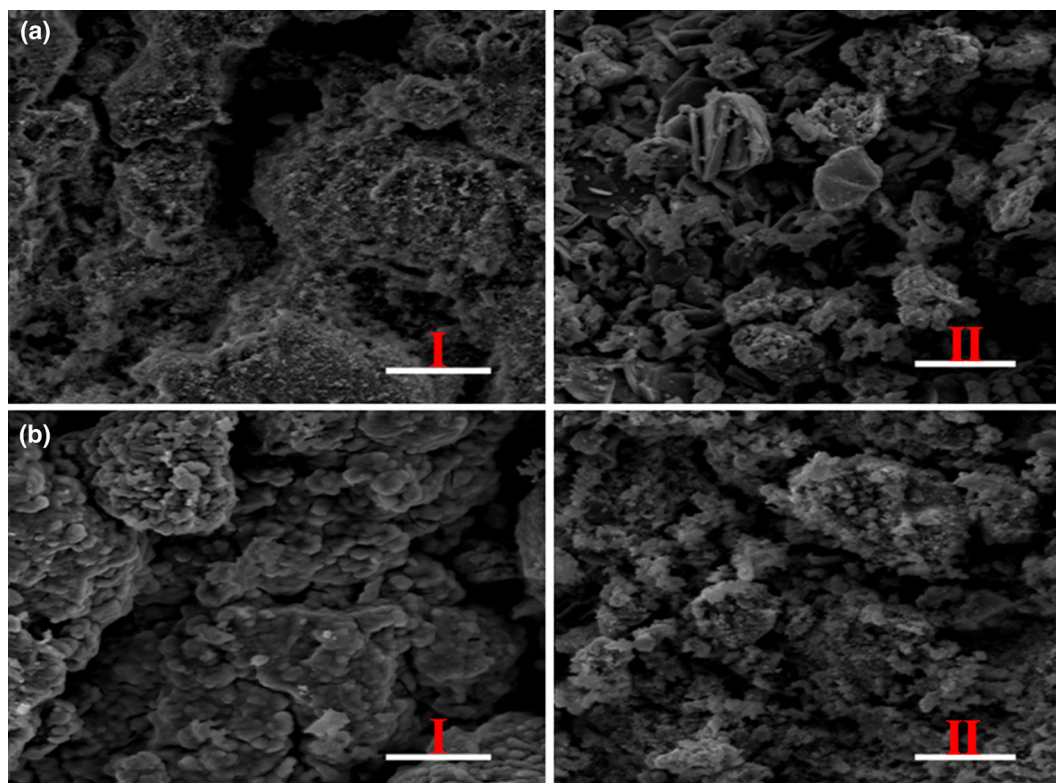


Fig. 4 High (I) and intermediate (II) magnification SEM surface image of Ni/Al₂O₃-SiO₂ (a) and Ni/Al₂O₃-SiO₂ with K₂O promoter (b) as catalysts

(2 dm³ min⁻¹) was adjusted. The heating of the reactor was activated after stabilizing the flow. After reaching the required examination parameters (the temperature of the reactor, pressure and the flow rate of CO₂), the valve supplying CO₂ to the sample feeder was opened for a second, which caused casting the biomass sample into the retort. The resulting gas flowed to the analyzer for the continuous determination of carbon monoxide and methane contents. In addition, samples were taken throughout the examination period and were then analyzed with respect to the hydrogen content. Generally, it took about 25 min for the gasification experiments to reach a stabilized state and to ensure the reliability of the obtained data. Each experiment was repeated several times, and the obtained results were in good agreement.

Based on the measurements of carbon monoxide, hydrogen and methane concentrations in the resulting gas, the formation rates were calculated for these products during the gasification of the examined samples. The obtained data enabled the calculation of the yields of the examined products.

Results and discussion

TGA results

Figure 2 shows the TGA curve of *MG* biomass during heating with constant heating rate. As can be seen, four stages may be distinguished: moisture evaporation, primary pyrolysis, secondary pyrolysis and gasification. Further analysis of the results does not include the moisture evaporation stage. Temperature range, in which conversion of the biomass proceeded, was between 200 and 870 °C.

Primarily, steep decline of curve which was associated with primary pyrolysis can be observed. At this stage, thermal decomposition occurred in temperature range of 200–400 °C which resulted in a loss of about 58% samples mass. The decline of curves showing the secondary pyrolysis stage was milder. Secondary pyrolysis started near 400 °C and took up to 730 °C. The mass loss of biomass sample in this stage was about 14.5%. In the last phase of the process, again steeper decline of curve can be observed, which illustrates the gasification stage. Gasification continued until only ashes remained in the crucible, and it was at temperatures close to 870 °C. During the gasification stage, the mass loss of sample was about 20%. As can be seen, the stage associated with the greatest mass

Table 3 Gasification of *MG* at 950 °C: concentration of gaseous product yields versus in respected time

Time/ min		Gas yield concentration/vol%										
		CH ₄	CO	H ₂		CH ₄	CO	H ₂		CH ₄	CO	H ₂
0	Non-catalytic gasification	0.0000	0.0000	0.0000	Catalytic	0.0000	0.0000	0.0000	Catalytic	0.0000	0.0000	0.0000
1		0.0540	0.1280	0.4434	gasification	0.0000	0.0000	0.7286	gasification with	0.0110	0.3430	0.4169
1.5		0.0970	2.3460	0.0943	with Ni/ Al ₂ O ₃ -SiO ₂	0.0150	2.4040	0.1734	Ni/Al ₂ O ₃ -SiO ₂	0.0290	2.6790	0.0761
2		0.0100	2.7540	0.0393	with K ₂ O	0.0000	3.0880	0.0648	promoter	0.0050	2.5300	0.0303
2.5		0.0000	2.5880	0.0245		0.0000	3.1710	0.0320		0.0000	2.3600	0.0149
3		0.0000	2.4930	0.0151		0.0000	2.9460	0.0175		0.0000	2.0860	0.0093
3.5		0.0000	2.2010	0.0091		0.0000	2.5220	0.0076		0.0000	1.7730	0.0046
4		0.0000	1.6860	0.0051		0.0000	1.5670	0.0033		0.0000	1.2060	0.0023
5		0.0000	0.8970	0.0023		0.0000	0.5160	0.0013		0.0000	0.5250	0.0009
6		0.0000	0.5450	0.0023		0.0000	0.3790	0.0013		0.0000	0.4000	0.0009
7		0.0000	0.3950	0.0009		0.0000	0.3410	0.0000		0.0000	0.3440	0.0000
8		0.0000	0.3570	0.0009		0.0000	0.2920	0.0000		0.0000	0.2960	0.0000
9		0.0000	0.3200	0.0009		0.0000	0.2550	0.0000		0.0000	0.2500	0.0000
10		0.0000	0.2840	0.0000		0.0000	0.2200	0.0000		0.0000	0.2140	0.0000
11		0.0000	0.2520	0.0000		0.0000	0.1870	0.0000		0.0000	0.1700	0.0000
12		0.0000	0.2230	0.0000		0.0000	0.1590	0.0000		0.0000	0.1380	0.0000
13		0.0000	0.1970	0.0000		0.0000	0.1340	0.0000		0.0000	0.1150	0.0000
14		0.0000	0.1730	0.0000		0.0000	0.1160	0.0000		0.0000	0.0940	0.0000
15		0.0000	0.1520	0.0000		0.0000	0.1010	0.0000		0.0000	0.0780	0.0000
17		0.0000	0.1150	0.0000		0.0000	0.0740	0.0000		0.0000	0.0470	0.0000
20		0.0000	0.0680	0.0000		0.0000	0.0530	0.0000		0.0000	0.0160	0.0000
25		0.0000	0.0240	0.0000		0.0000	0.0090	0.0000		0.0000	0.0000	0.0000

loss was the primary pyrolysis. Biomass feedstocks are characterized by a high content of volatile matter and low resistance to thermal decomposition, so the results obtained are in agreement with this statement.

Characterization of the Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O promoter as catalysts

The X-ray analysis and XRD patterns of the catalysts are listed in Table 2 and presented in Fig. 3, respectively. In Table 2, the elements are ranked from their highest content. When using the K₂O promoter, differences in the composition of the analyzed catalysts can be noted. (The potassium content in the catalyst with the promoter is clearly higher than in the case of a catalyst without a promoter.)

Figure 3a, b highlights similar diffraction peaks (1-blue, 2-green and 4-red) of calcium aluminum oxide (CaAl₁₂O₁₉)—hibonite (15%); aluminum oxide (Al₂O₃)—corundum (77%); sodium aluminum oxide (NaAl₁₁O₁₇)—diaoxudaoite (3%) for Ni/Al₂O₃-SiO₂ catalyst, and calcium aluminum oxide (CaAl₁₂O₁₉)—hibonite (11%); aluminum oxide (Al₂O₃)—corundum (76%); sodium aluminum oxide

(NaAl₁₁O₁₇)—diaoxudaoite (1%) for Ni/Al₂O₃-SiO₂ with K₂O promoter as catalyst. The only difference in X-ray diffraction peaks noted on third (gray) peak: zinc aluminum oxide (ZnAl₂O₄)—gahnite (6%) for Ni/Al₂O₃-SiO₂ catalyst, and magnesium aluminum oxide (MgAl₂O₄)—spine (12%) for Ni/Al₂O₃-SiO₂ with K₂O promoter as catalyst. Additionally, SiO₂ was also expected to detect, but perhaps because of its very low content (max 0.1 mass%) it was unable to be identified.

Scanning electron microscope (JEOL JSM—5410) was applied to investigate the surface area of catalysts; the images of the surface morphology are presented in Fig. 4. The surface image of the catalysts was detected at 1500 ×; bar: 14 microns.

During the experimental investigation of the catalysts' surface area analysis, it was recorded that the surface of both catalysts was highly compressed.

According to Maoyun et al. [38], catalyst deactivation is mostly controlled by coke deposition and sintering. As shown in Fig. 4, several large particles could be found on the SEM image of the Ni/Al₂O₃-SiO₂ with K₂O promoter as catalyst, whereas more non-uniform Ni particles were observed for the higher Ni content Ni/Al₂O₃-SiO₂ catalyst.

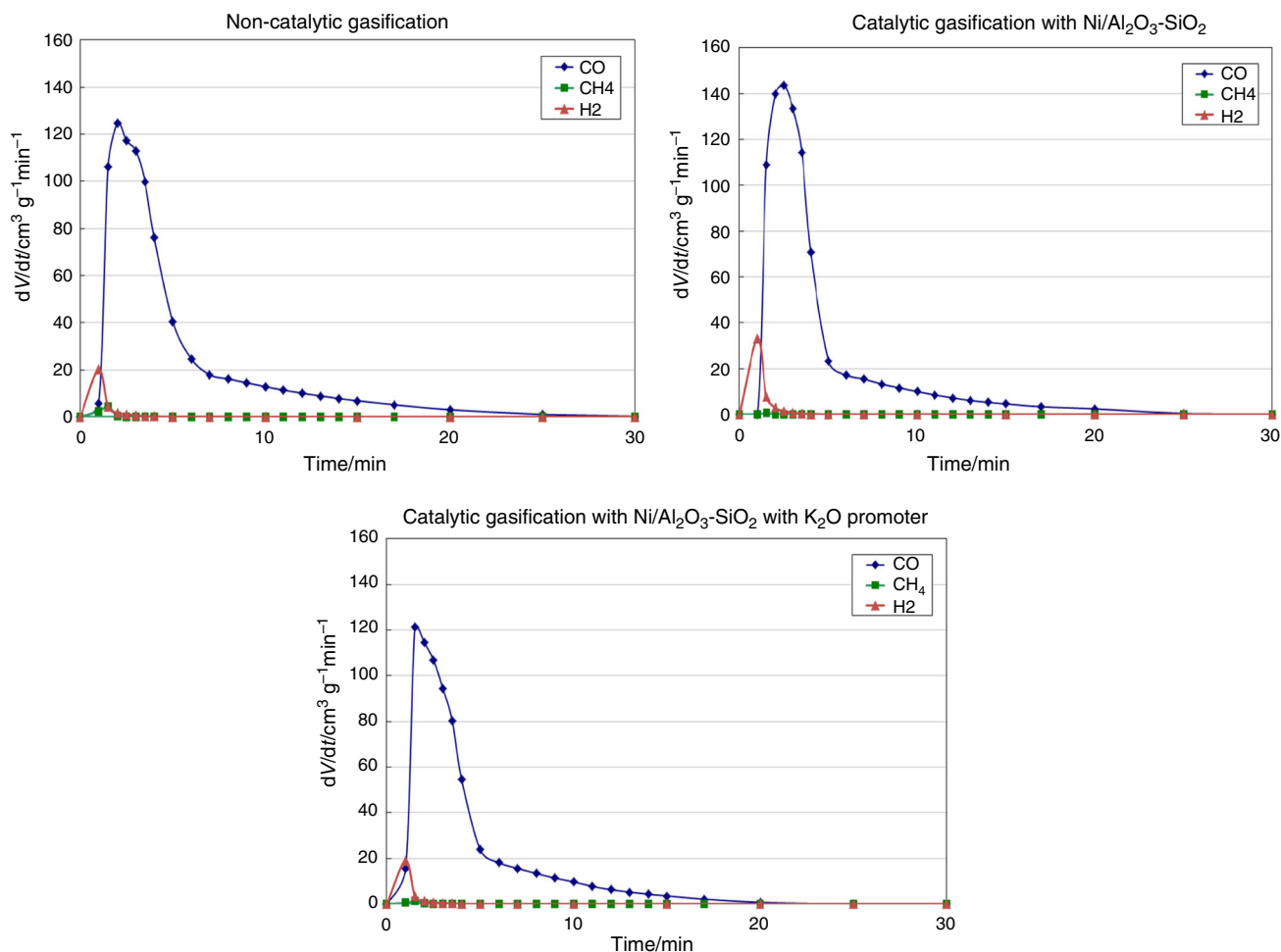


Fig. 5 Changes in the formation rate of the gaseous products during non-catalytic and catalytic gasification of *MG* at 950 °C

The Ni/Al₂O₃-SiO₂ catalyst is suggested to be more stable and efficient due to its well dispersion of Ni. Ni crystals could be observed for the both investigated catalysts. Additionally, different sizes of Ni crystals were also detected throughout the micrograph.

Wu and Williams [28] have reported a formation mechanism for coke deposited on Ni catalysts during gasification mechanism. They suggested that the fragmentation of a catalyst during the gasification process might be emerged from the reactions inside the catalyst where carbons are primarily formed and developed.

The Ni/Al₂O₃-SiO₂ catalyst is selected because of its agreeable results in synthesis gas steam-reforming reactions. No reports have been revealed on characterization of Al₂O₃- and SiO₂-supported catalysts for plant biomass and CO₂ conversion in the presence of O₂ and H₂O. Moreover, the application of core shell catalysts has not yet been researched for tri-reforming processes. Nevertheless, some authors like Walker et al. [39] tested the catalyst prepared by a deposition–precipitation method.

Catalytic and non-catalytic gasification by thermovolumetric method

Based on the measurements of concentrations of carbon monoxide, hydrogen and methane in the resulting gas (see Table 3), formation rates of these particular products during the gasification of the examined *MG* biomass samples were calculated.

When analyzing the concentrations of gaseous products from the process, one can observe the differences between gasification with and without catalysts. The higher concentrations of two main gaseous products, i.e., CO and H₂, were obtained during gasification with Ni/Al₂O₃-SiO₂, whereas in the other two analyzed cases the values of concentrations were similar. Significant differences were noted for methane, which basically was not created during the gasification with Ni/Al₂O₃-SiO₂, and during the measurements with the second catalyst—Ni/Al₂O₃-SiO₂ with K₂O, the concentration of methane was significantly lower in comparison with the non-catalytic gasification. These

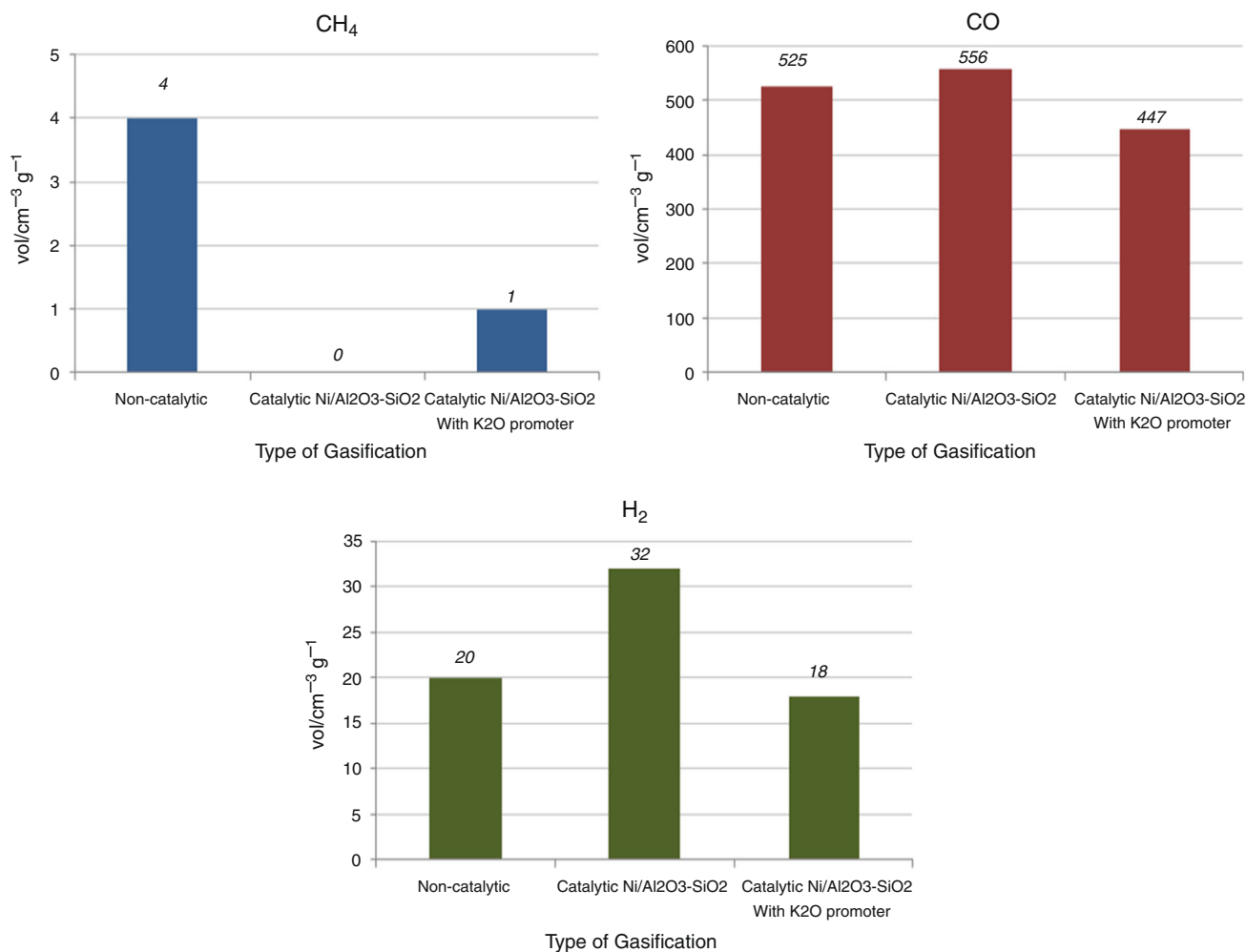


Fig. 6 Yields of CH₄, CO and H₂ [cm³ g⁻¹] from the catalytic and non-catalytic gasification of *MG* biomass at 950 °C

Table 4 Percentage share of gaseous products from non-catalytic and catalytic gasification of *MG*

Share/%	Type of gasification		
	Non-catalytic	Catalytic: Ni/Al ₂ O ₃ -SiO ₂	Catalytic: Ni/Al ₂ O ₃ -SiO ₂ with K ₂ O promoter
CH ₄	0.8	0	0.2
CO	95.6	94.6	95.9
H ₂	3.6	5.4	3.9

results prove that the utilization of the analyzed catalysts affects the decomposition of methane. One can also suppose that these catalysts cause decomposition of the hydrocarbons that form the tar.

Basically, the process of gasification is favored by the high temperature which amplifies the secondary hydro-cracking and shifts the reactions to conversion of hydrocarbons (C_nH_{2n}). This particular fact might be caused by the contribution of the reforming reactions which are favored and occurred at high temperature, hence becoming prevailing at temperatures higher than 800 °C [40–47]. The finite gas composition is a function of the common

reactions that at the same time come off by increasing the hydrogen and synthesis gas yields connected with the conversion of tar into synthesis gas. In addition, nickel-based catalysts have attracted the highest research interest among all non-noble metal catalysts, as it is broadly applied in industrial processes because of its inexpensive cost and great catalytic activity in conversion of hydrocarbons [48–52]. The hydro-cracking mechanism over Ni catalyst occurs via the process of absorbing the C_nH_{2n} species on a dual active site of the nickel catalyst followed by consistent α-scission of the C–C bonds. Herewith, the

resulting C^* species thereafter reacted with oxygen from dissociation absorbed steam to yield CO and H_2 [53–56].

Figure 5 shows the comparison of the kinetic curves of the formation of the main gasification products during the process without and with two analyzed catalysts: Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O promoter.

It can be observed that, despite differences in the formation rates of particular products, the character of their kinetic curves is similar. In all the cases, the primarily observed high reaction rate falls, and in the first phase the fall is very intense, while later on is much slower. A high formation rate of particular products in the primary phase of the process is caused by the pyrolysis stage. Thus, the curve shown in Fig. 2 confirmed that the most significant phase of the biomass gasification process was pyrolysis. The highest rates can be noted for the formation reaction of carbon monoxide since the predominant reaction during CO₂ gasification is Boudouard reaction [57–60]. In addition, from Fig. 5 it can be inferred that higher formation rates of carbon monoxide (CO) and hydrogen (H₂) were obtained during catalytic gasification with Ni/Al₂O₃-SiO₂ when comparing to non-catalytic as well as catalytic (with the second catalyst) gasification processes. This effect was observed during the pyrolysis stage, which is the most significant stage in the biomass gasification process. In turn, the use of Ni/Al₂O₃-SiO₂ with K₂O promoter negatively affected the formation rates of CO and H₂ in comparison with process without catalyst. Additionally, the use of both of the tested catalysts resulted in lower formation rates of the last analyzed gaseous component—methane. Hence, it can be concluded that Ni/Al₂O₃-SiO₂ effectively catalyzes formation reactions of main components of synthesis gas (CO and H₂) as well as decomposition of methane.

The yields of the gaseous product were determined based on the concentration of these gases during the gasification measurements. The received values per 1 g of biomass in dry and ash-free state and overall gaseous product yields [vol cm³] are presented in Fig. 6. An analysis of the presented data leads to the conclusion that the yields of carbon monoxide and hydrogen are the highest during the gasification processes in the presence of Ni/Al₂O₃-SiO₂ among all analyzed cases, whereas catalytic gasification with Ni/Al₂O₃-SiO₂ with K₂O promoter as catalyst resulted in lower yields of gaseous products than non-catalytic process. Moreover, the recorded yields of methane that was formed mainly at the initial stage of the process are much lower in case of catalytic gasification, especially in case of Ni/Al₂O₃-SiO₂. Thus, bio-gaseous product yields profiles affirmed that the properly selected catalysts activate depolymerization processes causing a strong decomposition (low solid yield) or a strong liquid phase cracking (low liquid yield), and hereof a higher gas

formation, since this gas was formed from liquid cracking [61, 62].

The results listed in Table 4, showing the percentage share of gaseous product from gasification processes, confirmed that the addition of catalysts affects the composition of the gas formed in the process. The presence of the catalysts resulted in a decrease in the percentage share of CH₄, while increasing the share of hydrogen in the resulting gas. This effect was particularly visible during gasification in the presence of Ni/Al₂O₃-SiO₂.

Thereby, according to overall analysis it can be inferred that the presence of Ni/Al₂O₃-SiO₂ catalyst caused acceleration of CO and H₂ formation reactions during gasification process of *MG* biomass, causing increased yields of so-called synthesis gas in the resulting gas. Moreover, this catalyst favors the decomposition of methane.

Conclusions

The analysis of catalytic and non-catalytic gasification of *MG* biomass for bio-gas was performed by thermogravimetric and thermovolumetric methods. The TGA measurements allowed to distinguish individual phase of the gasification (primary pyrolysis, secondary pyrolysis, gasification) as well as to determine their contribution to the whole process. The highest loss of sample mass was observed during pyrolysis stage (primary). In turn, the thermovolumetric analysis allowed determining the influence of two types of catalysts on the formation rates of CH₄, CO and H₂, their yields and composition of the resulting gas. A high temperature at 950 °C along with Ni/Al₂O₃-SiO₂ catalyst resulted in the highest conversion rate of *MG* biomass gasification into gaseous products with considerably increased content of H₂ (from 20 to 32 vol cm³ g⁻¹) and CO (from 525 to 556 vol cm³ g⁻¹) in comparison with non-catalytic process. The second analyzed catalyst—Ni/Al₂O₃-SiO₂ with K₂O promoter—did not catalyze the gasification process. However, the use of both analyzed catalysts had a positive effect on reducing the methane content in the obtained gas. One can also suppose that it favors the decomposition of the resulting tar. The obtained results indicated that there is a strong potential for producing renewable bio-gas (e.g., bio-synthesis gas) from plant biomass by a simple gasification process with inexpensive and abundant Ni/Al₂O₃-SiO₂ catalyst. Moreover, this research opens vast opportunities to convert plant biomass into useful and valuable bio-gas product.

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