

Effect of Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O Promoter Catalysts on H₂, CO and CH₄ Concentration by CO₂ Gasification of *Rosa Multiflora* Biomass

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Abstract — The thermal behaviour of the *Rosa mutiflora* biomass by thermogravimetric analysis was studied at heating rate 3 K min⁻¹ from ambient temperature to 950°C. TGA tests were performed in high purity carbon dioxide (99.998%) with a flow rate 200 ml/min and 100 mg of sample, milled and sieved to a particle size below 250 μm. Moreover, yields of gasification products such as hydrogen (H₂), carbon monoxide (CO) and methane (CH₄) were determined based on the thermovolumetric measurements of catalytic (Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O promoter catalysts) and non-catalytic gasification of the *Rosa mutiflora* biomass. Additionally, carbon conversion degrees are presented. Calculations were made of the kinetic parameters of carbon monoxide and hydrogen formation reaction in the catalytic and non-catalytic CO₂ gasification processes. A high temperature of 950°C along with Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O promoter catalysts resulted in a higher conversion of *Rosa mutiflora* biomass into gaseous yield production with greatly increasing of H₂ and CO contents. Consequently, H₂ and CO are the key factors to produce renewable energy and bio-gases (synthesis gas). The parameters obtained during the experimental examinations enable a tentative assessment of plant biomasses for the process of large-scale gasification in industrial sectors.

INTRODUCTION

The world is about to face a crisis which threatens the existence of civilization. This is an energy crisis which will grow up when there are not enough energy sources to manage with the demand of world as the demand for energy increases. Energy crisis can be defined as a great strait in supply of energy sources in an economy. It is very hard to say that the solution of

this crisis, which will leave the world in a big economic and social crisis, will not be solved by the technology. World population is expected to double by the middle of the 21st century [1], and economic development will almost certainly continue to grow. Global demand for energy services is expected to amplify by as much as an order of magnitude by 2050, while primary-energy demands are expected to increase by 1.5–3 times [2,3]. Simultaneously, concern will likely

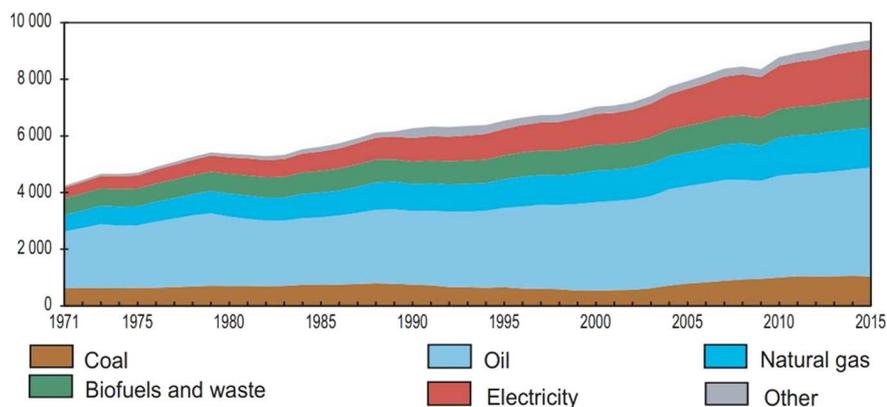


Figure 1

World total final consumption by fuel (millions ton of oil equivalent) [5].

increase regarding energy-related environmental concerns such as acid precipitation, stratospheric ozone depletion and global climate change. The need for energy in the world increases 1.6% in average annually. If the countries continue with their present politics, the need for energy will be half as much in 2030 as it is today [4]. That is, the continuous development in global consumption of energy is an unavoidable problem. This situation alerts many countries around the world face the problem of energy independence and energy security. Another expanding concerns are 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. Currently, fossil fuels such as oil, coal, electricity and natural gas represent the prime energy sources in the world [5] as shown in Figure 1. However, it is anticipated that these sources of energy will be depleted within the next 40–50 years [6]. The decreasing fossil fuel resources cause both insufficiency in providing demand and increase in prices and it triggers the structural change in energy production and resources. In this context, 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 [7].

Among the crucial aspects the most important are: energy storage until consumption, efficiency in energy conversion technologies, carbon foot print, wastes generated and impact to the quality of natural environment and human life [8, 9]. However, much attention has been paid to biomass conversion technologies into bio-energy. Consequently, nowadays number of research studies are concentrated on investigation a proper technology for more efficient biomass production.

Biomass is one of the earliest sources of energy particularly in rural areas where it is frequently the only accessible and affordable source of alternative energy.

Biomass is made up of carbohydrates [10] and it is a renewable energy source with immense specific properties. In comparison with other renewable technologies such as wind or solar, biomass has several problems connected with energy storage; in a sense, biomass is stored energy. Moreover, biomass is a multilateral fuel that can produce products like biogas, liquid biofuels and electricity, etc. Occasionally biomass is classified as combustible materials that can be used as an energy source. Biomass is undoubtedly renewable energy source because its supplies are incessant. We can always cultivate crops and trees, rapid growing plants, as well as waste will always exist. Especially, energy crops will play more important role in mid and long term perspective.

Thereby, comprehensive thermochemical processes for biomass conversion, such as gasification and pyrolysis, combustion, fermentation, can be used for bio-energy production and power generation. Among these processes, biomass gasification and pyrolysis technologies have attracted the considerable attention from both industrial and academic researchers due to its high conversion efficiency [7, 11]. However, the gasification process is considered as a self-sufficient autothermic technological process in terms of an energy balance. The heat capacity and energy recovery of biomass gasification are more than the pyrolysis and combustion processes which are imputed towards the optimal utilization of accessible biomass feedstock for power and heat generation whereas both hydrogen and carbon contribute to the heating/or calorific value to a considerable extent. In addition, biomass gasification is a process to convert biomass feedstock into combustible gaseous products such as hydrogen (H_2), synthesis gas ($H_2 + CO$), carbon monoxide (CO) and methane (CH_4) [12]. The synthesis gas produced from form gasification is easy to convert to synthetic natural gas via catalytic methanation of carbon monoxide and carbon dioxide [13]. The hydrogen rich gas production cost from

gasification process is dependent on the process parameters and gasifier design [14] that were utilized. The biomass gasification process for syngas (synthesis gas) and hydrogen production seems to be among the most economically affordable processes [15] after supercritical water partial oxidative gasification [16, 17]. Thereby, a hydrogen rich gas production from biomass (e.g. plant, wood, waste, sewage, etc.) gasification has a great potential to be further developed as an alternative to the present syngas or hydrogen production process. Moreover, gasification of biomass is considered to be the most universal technique for conversion of a distinguish of biomass feedstocks, such as plant biomass (e.g. *Rosa multiflora*, *miscanthus giganteus*, *eucalyptus*, etc.), industrial waste, food waste, kitchen waste, wood waste, etc. can be converted to bio-energy for useful replacement of products derived from petrochemical technological processes [8, 18, 19]. However, undesirable products, such as char and tar are also produced during gasification and pyrolysis processes. Currently, there are numerous research projects have been implementing connected with catalyst activity for an additional gaseous yields extraction from tar cracking and char yield reduction from gasification and pyrolysis processes. Nickel based catalyst is extensively applied in chemical industries and is verified as one of the most effective transition metal catalysts [20, 21] in biomass gasification for cracking and reforming of tar [22] as well as for enhancement of gaseous yields production.

In this study, we report the catalytic conversion of plant biomass (*Rosa multiflora*) into bio-gaseous yields (H_2 , CO and CH_4) from CO_2 gasification using $Ni/Al_2O_3-SiO_2$ and $Ni/Al_2O_3-SiO_2$ with K_2O promoter catalysts, under the reaction conditions temperature of $950\text{ }^\circ\text{C}$ and pressure of 10 bar.

1 MATERIALS AND METHODS

1.1 Biomass Sample. Proximate and Ultimate Analysis

Applied experimental procedure for collecting the biomass based on the *American Society for Testing and Materials (ASTM)*, and European PN-EN standards. The biomass sampling was collected in the plastic bag from the 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 Production and Power Engineering, Krakow University of Agriculture, Poland. Afterwards, the biomass of *Rosa multiflora* (further designated as RM) was weighted by using a weight balance and data was recorded. Prior to the experiments, the sample was shredded and sieved into particles in size approximately 2 mm using an automated

siever (model: LPzE-2e). Further prepared sample was referred to various elemental and analytical analyses (each test was repeated 3 times in order to obtain a precise data).

Ultimate analyses were used to determine the CHS and O content in biomass sample by using Eltra CHS 580 elemental analyzer. Such experimental analysis presents the weight percent (wt%) of carbon (C), hydrogen (H) and sulphur (S) in the biomass sample simultaneously, and the weight percent of oxygen is determined by difference via X-ray fluorescence (XRF) spectrometry.

Proximate analysis was investigated according to European PN-EN/PN-ISO and ASTM standards for determination of moisture (PN-EN 14774-3:2010; ASTM E-871) [8, 23, 24], volatile matter (PN-EN 15148:2010.900) [8, 11, 24–26], fixed carbon and ash (PN-EN14775:2010), as well as determination of gross calorific value/high heating value (PN-EN 14918:2010 and PN-ISO 1928) [8, 24] in biomass sample.

1.2 Thermogravimetric Analysis (TGA)

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 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 ml/min. This stage lasted 30 min.

Stage II: measurement: the temperature was ramped from ambient temperature to $950\text{ }^\circ\text{C}$ with heating rate 3 K/min, through the system flowed 200 ml/min of CO_2 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 weight during the measurement was recorded continuously, and the results were presented as a function of temperature.

1.3 Catalysts $Ni/Al_2O_3-SiO_2$ and $Ni/Al_2O_3-SiO_2$ with K_2O Promoter

The tar formed during gasification is one of the challenging issues, catalytic gasification for tar reduction has been promising [11, 27, 28]. Since a few decades, the use of

catalyst in biomass gasification had attracted much attention. During the gasification process, catalytic cracking was the most efficient method to eliminate the tar formation in the gas mixture [29–31]. The nickel supported catalysts have been generally applied, because it could effectively eliminate tar and enhance hydrogen production in the steam gasification of solid biomass [24, 32, 33]. Nevertheless, the commercial Ni catalysts present a moderate to quick deactivation because of the build-up of surface carbon [31, 34]. Thus, some research investigations [7, 35] have been undertaken to improve the stability and activity of Ni catalysts by using additional different supports or using metals.

In this study, two types of catalysts Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O as promoter were used for gas analysis and productivity from CO₂ gasification of RM biomass. However, Ni supported catalysts are significantly active only at high temperatures (>900 °C). Furthermore, during biomass gasification process tar was formed, catalysts were used to eliminate tar. Catalysts Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O as promoter were collected from the Faculty of Chemistry of the Maria Curie-Skłodowska University in Lublin, Poland. Catalysts were ground and sieved the particle with a size of 0.4–0.65 mm. The Ni/Al₂O₃-SiO₂ with K₂O as promoter and Ni/Al₂O₃-SiO₂ were used as catalysts in order to make a comparison for efficient synthesis gas (or hydrogen rich gas) production from gasification process. The X-ray diffraction (XRD) 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, X-ray patterns of the catalysts were listed in Table 1 and Figures 2 and 3 respectively. The surface characteristics of catalysts were evaluated by using JSM-5410 Scanning Microscope and SEM image of the catalysts are displayed in Figures 4 and 5.

1.4 Calculation Formation Rate and Carbon Conversion Degree

Based on the measurements of carbon monoxide, hydrogen, methane and carbon dioxide concentrations in the resulting gas, the formation rates were calculated for these products during the gasification of the examined samples. The obtained data enabled calculation of the yields of the examined products and formal kinetic parameters of the reaction of CO and H₂ formation.

The formation rate of a given product can be expressed by the equation:

$$\frac{dV}{dt} = k \cdot (V_{\infty} - V), \quad (1)$$

TABLE 1

X-ray analysis of the Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O promoter catalysts.

Ni/Al ₂ O ₃ -SiO ₂		Ni/Al ₂ O ₃ -SiO ₂ with K ₂ O promoter	
Compound	Conc. unit, %	Compound	Conc. unit, %
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

where k , constant reaction rate [1/min]; V_{∞} maximal volume of gas product [cm³]; V , volume of released gas component at time t [cm³]; t , time [min].

After the separation of variables and integration, one can obtain:

$$\ln \frac{V_{\infty}}{V_{\infty} - V} = k \cdot t. \quad (2)$$

The graph $\ln \frac{V_{\infty}}{V_{\infty} - V}$ as a function of t should be a straight line with a slope equal to k , *i.e.* the constant reaction rate of formation of a given product gas.

While determining the constant reaction rates of formation of the examined products for different temperatures of gasification, formal values of activation energy and pre-exponential factor can be calculated by means of the Arrhenius equation.

The carbon conversion degree can be estimated on the basis of the formula:

$$X = \frac{(V_{CO} + V_{CO_2} + V_{CH_4}) \cdot M_c}{V_{mol} \cdot m \cdot C^{daf}} \cdot 100\%, \quad (3)$$

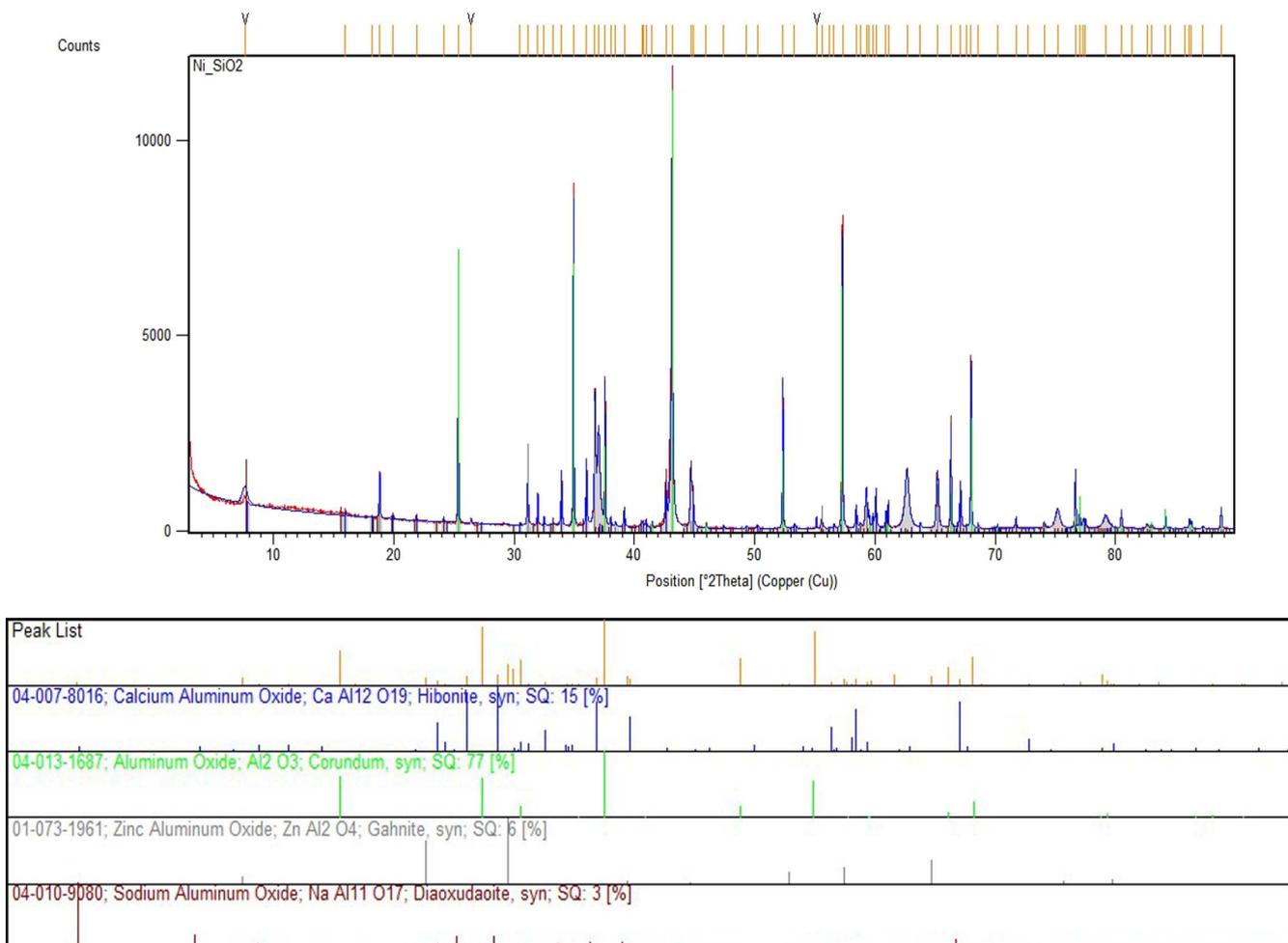


Figure 2

XRD patterns of the Ni/Al₂O₃-SiO₂ catalyst.

where V_{CO} , V_{CO_2} , V_{CH_4} , volume of released gas component [dm³/g]; M_c , molar mass of carbon [g/mol]; m , sample mass [g]; C^{daf} , dry ash free carbon content [-]; V_{mol} , volume of one mole of gas at temperature of 273 K and pressure of 101325 Pa [dm³/mol].

1.5 Gasification Apparatus and Procedure (Thermovolumetry 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 under a high pressure for a particle size (2 mm) distribution of plant biomass samples. The equipment was accurately described in the works of Porada et al (2016) and Zubek et al (2017) [36, 37] and its schematic diagram is shown in Figure 4. The equipment is composed of three basic systems, namely: a high pressure reactor with a heating system, feeding the reactor with CO₂ system and plant biomass as well as a system for analysis and collection of the resulting

gas. Inside the reactor there is a retort with the diameter of 20 mm equipped with a grate made of sintered quartz. Upon completion stabilizing the parameters of the examinations, a sample of the examined biomass is introduced onto the grate. For this purpose, specially designed piston sample 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 selected 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 plant biomass sample was measured by a sensor of the thermocouple type K, which served, simultaneously, for sending impulses to the controller-programmer maintaining the required temperature of the sample. The resulting gas flows to the condenser, where a water and tar condensate is separated and, subsequently, thoroughly dried and cleared on the filter.

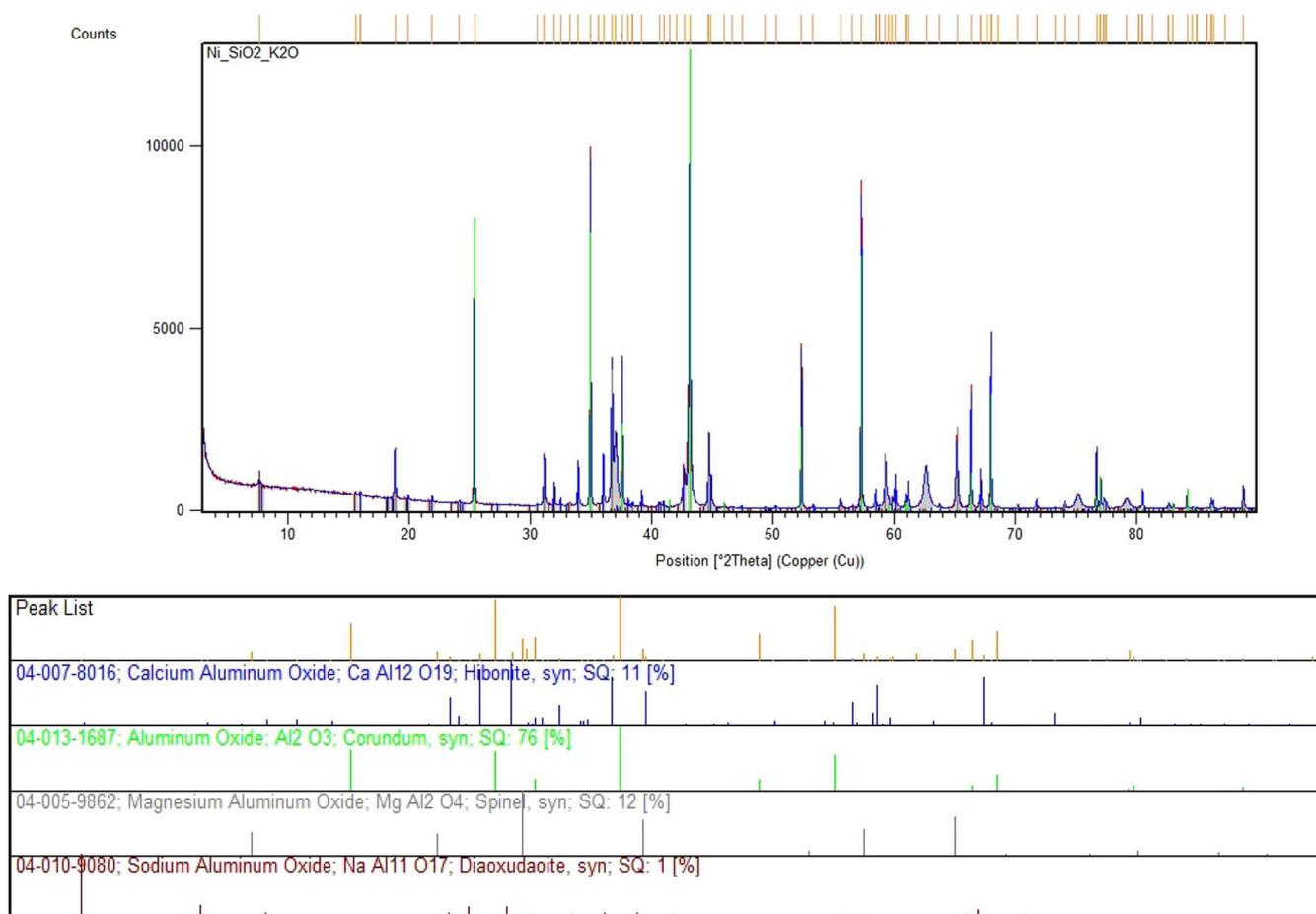


Figure 3

XRD patterns of the Ni/Al₂O₃-SiO₂ with K₂O as promoter catalyst.

After decompression, in the resulting gas, the contents of carbon monoxide (CO) and carbon dioxide (CO₂) 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 later in respect of the content of hydrogen via gas chromatograph equipped with a Thermal Conductivity Detector (TCD).

A reaction retort was positioned inside the reactor and about 1 g of biomass (0.2 g catalysts with catalytic process, with grain size 0.60 mm) of appropriate grain size was placed in the sample feeder. After closing with the lids, the reactor and the sample feeder were compressed by CO₂ to the required pressure (10 bar) and then the required flow of CO₂ (2 dm³/min) was adjusted. The heating of the reactor was activated after stabilizing the flow. After reaching the required examination parameters (the temperature of the reactor – 950 °C, 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 reactor. The resulting gas flowed to the analyzer for the continuous determination of carbon monoxide and carbon dioxide contents. In addition, its samples were taken

throughout the examination period. The samples were then analyzed in respect of the content of hydrogen and gaseous hydrocarbons. Generally, it took 20 min for the gasification experiment to reach a stabilized state and to ensure the reliability of test data. Each experiment was repeated several times, and the obtained results were in good agreement.

2 RESULTS AND DISCUSSIONS

2.1 Proximate and Ultimate Analysis

Proximate analysis embraces determination of moisture content, volatile matter, ash content, fixed carbon and also gross calorific value of composite sample. The analysis was conducted following to European PN-EN/PN-ISO and ASTM standard methods, and ultimate analysis displays determination of chemical characteristics of selected biomass sample. Results from proximate and ultimate analysis were shown in Table 2.

The table shows moisture content (14.66 wt%) and fixed carbon (10.56 wt%). The moisture content is measured and determined with the amount of water lost from selected

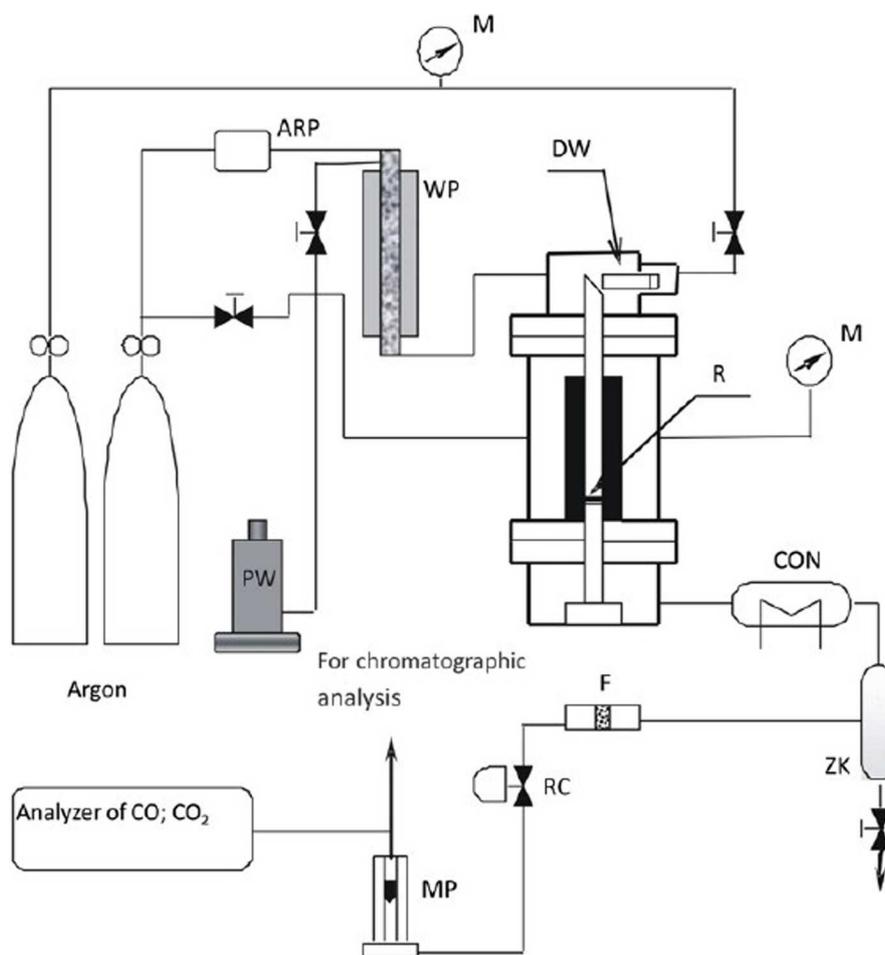


Figure 4

Schematic diagram of the lab-scale biomass gasifier: R - reactor; WP - steam generator; PW - water pump; CON - condenser; ZK - tar separator; MP - rotameter; DW - coal feeder; ARP - mass flowmeter; M - pressure gauge; F - gas filter; and RC - backpressure regulator.

TABLE 2
Proximate and ultimate analysis of RM biomass.

Ultimate analysis, wt%		Proximate analysis, wt%	
C	53.11	Moisture	14.66
H	7.22	Volatile matter	71.67
S	0.04	Fixed carbon	10.56
N	N/A	Ash	3.11
O*	29.63	Gross calorific value, HHV (MJ/kg)	18.593

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

materials upon drying to a constant weight. It is directly affected by physical and chemical properties of material which enable it to absorb the outlet water in the environment [11]. Fixed carbon is the carbon remaining on surface as charcoal. Additionally, Table 2 highlights processed RM biomass has

volatile matter content (71.67 wt%) and ash content (3.11 wt %); both parameters have direct influence on the gasification characteristics. The plant's biomass is easier to ignite and to gasify than coal apparently due its volatile matter. The calorific value (heating value) of biomass was obtained to be 18.593 MJ/kg based on the bomb calorimeter test. The results of ultimate analysis which were investigated by Eltra CHS 580 Elemental Analyzer and XRF spectrometry are also shown in Table 2.

2.2 TGA Results

Figure 5 shows the TGA curves of RM biomass at heating rate 3 K/min. As can be seen from the figure, it shows the weight loss of sample at a temperature, 4 stages may be distinguished: moisture evaporation, primary pyrolysis, secondary pyrolysis and gasification (analysis of the results does not include the moisture evaporation step). The temperatures of conversion peak in each stage were marked

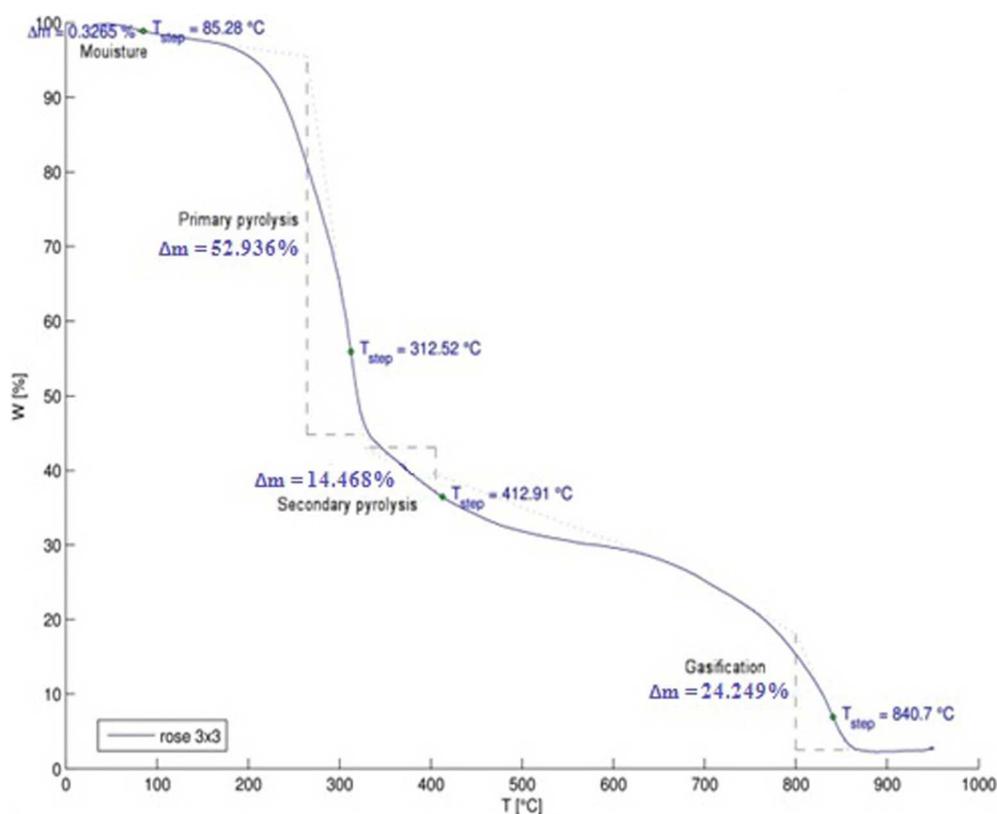


Figure 5

TGA curves for RM biomass.

on the curves, tagged based on the weight as a function of temperature. Temperature range, in which conversion of the biomass proceeded, was between 200 °C and 950 °C.

Initially, steep decline of curve 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. Conversion peaks in this stage occurred in temperatures between 313 and 317 °C. The decline of curves showing the secondary pyrolysis step was milder. This pyrolysis started near 348 °C and took up to 660 °C and a higher temperature at which the conversion peak occurred was 416 °C. An average weight loss of biomass was 15%. In the last step, again steeper decline of curve can be observed, which illustrates the gasification stage. Gasification continued until only ashes remain in the crucible and it has been in temperatures close to 865 °C, and the temperature of conversion peak was 841 °C. During the gasification, the weight loss of samples fluctuated around 24%.

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.

Thermal analysis techniques such as thermogravimetric analysis (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 [38]. 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. TGA of biomass samples has been extensively applied as a means of determining the characteristics of devolatilisation and also to determine kinetic parameters [39, 40].

2.3 Characterization of the Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O Promoter Catalysts

Figures 2 and 3 provided 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) –

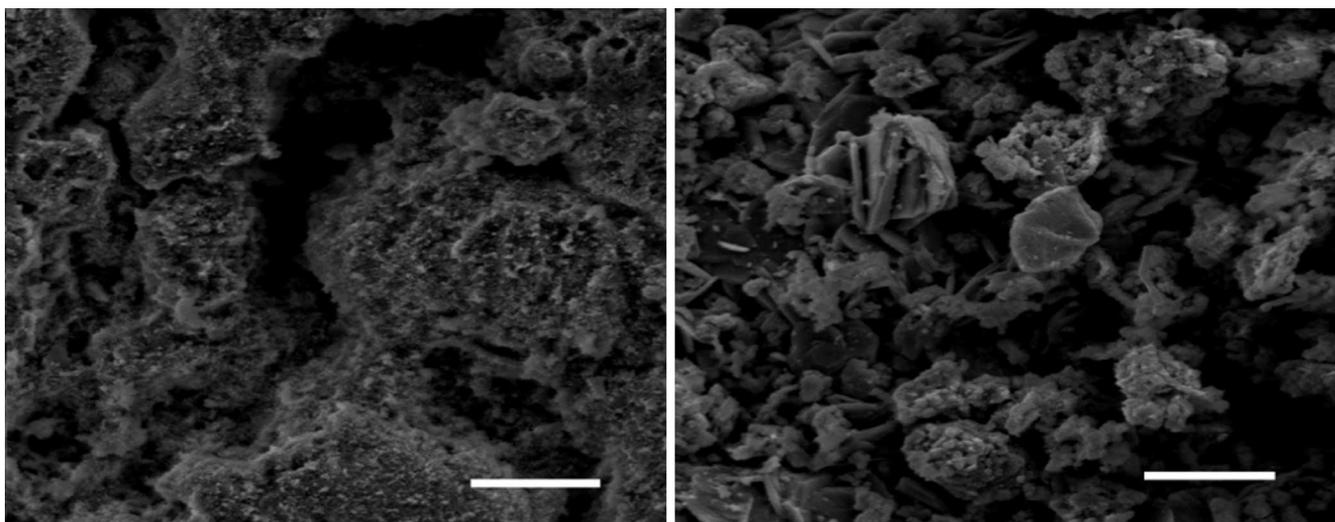


Figure 6

High (left) and intermediate (right) magnification SEM surface image of catalyst Ni/Al₂O₃-SiO₂.

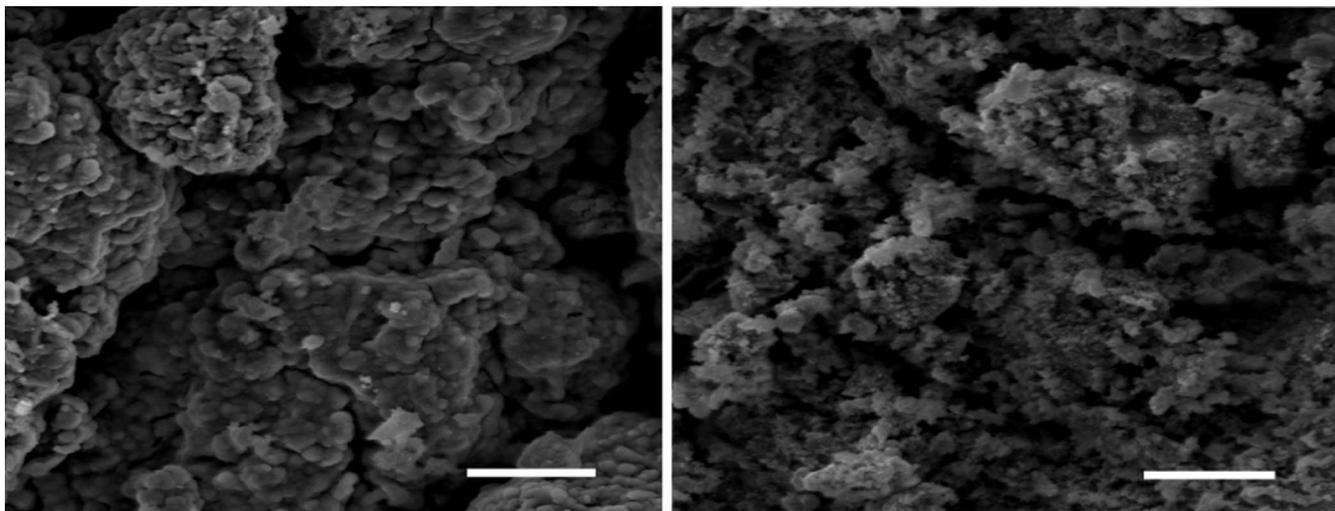


Figure 7

High (left) and intermediate (right) magnification SEM surface image of catalyst Ni/Al₂O₃-SiO₂ with K₂O promoter.

corundum (76%); sodium aluminum oxide (NaAl₁₁O₁₇) – diaoxudaoite (1%) for Ni/Al₂O₃-SiO₂ with K₂O as promoter catalyst. The only difference in X-ray diffraction peaks noted on third (grey) 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 as promoter catalyst. Additionally, SiO₂ was also expected to detect, but perhaps because of its very low content (max 0.1 wt%) 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 Figures 6 and 7. 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. (2010) [23] catalyst deactivation is mostly controlled by coke deposition and sintering. As shown in Figures 6 and 7, several large particles could be found on the SEM image of the Ni/Al₂O₃-SiO₂ with K₂O promoter catalyst, whereas more non uniform Ni particles were observed for the higher Ni content Ni/Al₂O₃-SiO₂ catalyst. The Ni/Al₂O₃-SiO₂ catalyst is suggested to be more stable and efficient due to its well dispersion of Ni. As shown in Figures 6 and 7, Ni crystals could be observed for the both investigated catalysts. Additionally, different sizes of Ni crystals were also detected throughout the micrograph.

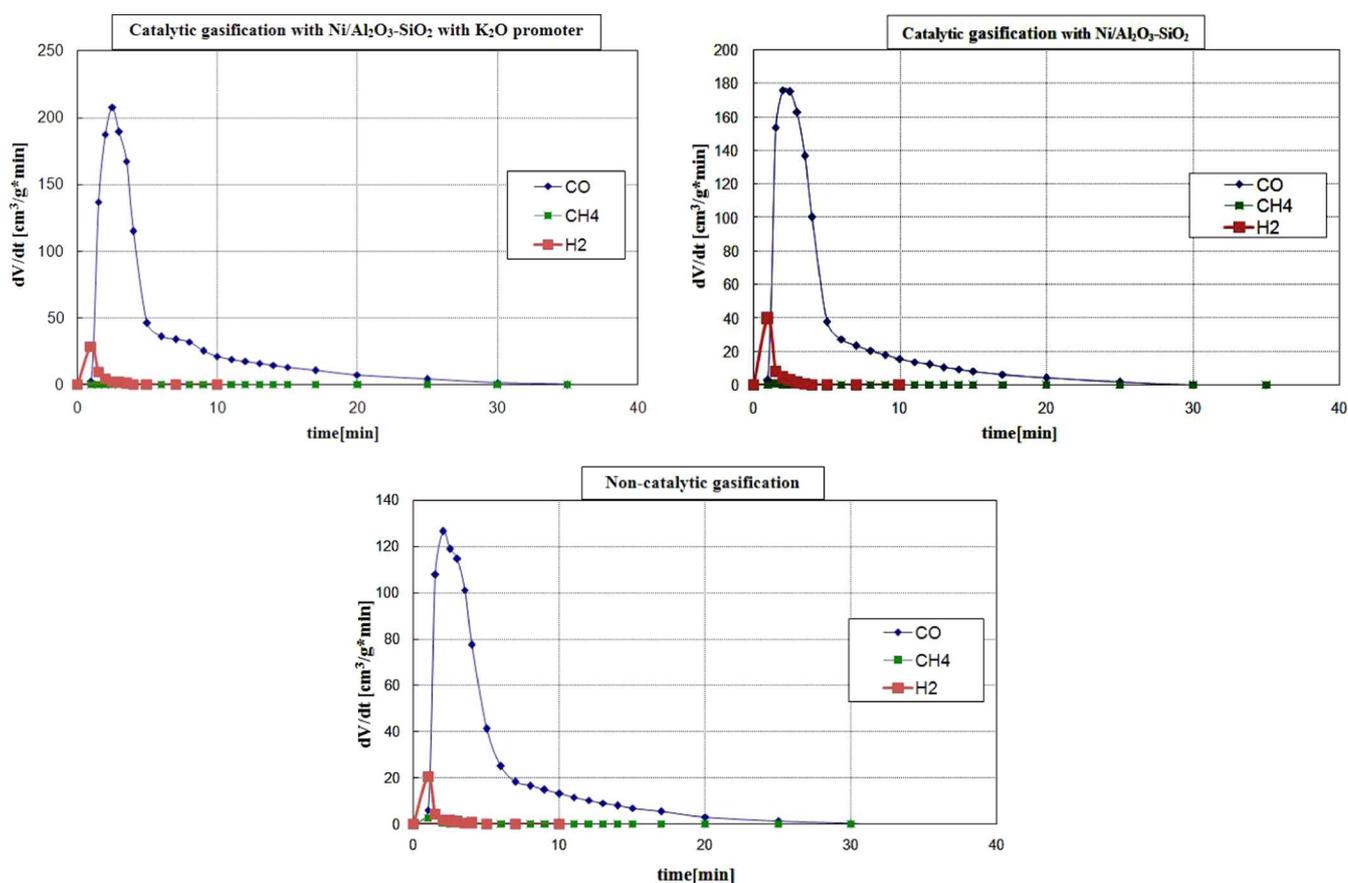


Figure 8

Variations in formation rate of the tested gases during non-catalytic and catalytic gasification of RM at temperature of 950 °C and pressure of 10 bar.

Wu and Williams (2010) [32] 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.* (2012) [41] tested catalyst prepared by a deposition-precipitation method.

2.4 Catalytic and Non-catalytic Activity

Based on obtained results it was summarized that the gasification products were principally affected by the gasification parameters such as temperature, time, pressure,

flow rate, catalysts and size of sample. Temperature and the presence of catalysts were among the most considerable parameters which influenced the product gas yields from the gasification process. The efficiency of catalyst is strongly influenced on synthesis gas (H₂ + CO) formation during the gasification process.

The plant biomass gasification experiments at the reactor temperature of 950 °C with Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O promoter catalysts, and CO₂ (gasifying agent) gasification without catalyst were carried out to study the influence of the catalysts on gaseous (CH₄, CO and H₂) product yields at respected time from gasification process were presented in Table 3.

The CO₂ yield was not recorded because it was used as a gasifying agent and when pure CO₂ used, the conversion degree was smaller than in case of technical CO₂. This could result due to the oxygen in the technical CO₂, which leads to the oxidation of C to CO.

Based on the measurements of concentrations of carbon monoxide, hydrogen and methane in the resulting gas, formation rates were calculated for particular products during the gasification of the examined biomass samples.

TABLE 3
Gasification of RM at 950 °C: concentration of gaseous product yields versus in respected time.

Time, min	Gas yields concentration, vol%								
	Non-catalytic gasification			Catalytic gasification with Ni/Al ₂ O ₃ -SiO ₂			Catalytic gasification with Ni/Al ₂ O ₃ -SiO ₂ with K ₂ O promoter		
	CH ₄	CO	H ₂	CH ₄	CO	H ₂	CH ₄	CO	H ₂
0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
1	0.1110	0.2260	0.2009	0.0000	0.0590	0.7698	0.0000	0.0380	0.5569
1.5	0.0360	3.2850	0.0507	0.0180	2.9900	0.1933	0.0000	2.6670	0.1834
2	0.0100	3.6000	0.0274	0.0040	3.4270	0.0871	0.0000	3.6540	0.0857
2.5	0.0000	3.6350	0.0154	0.0000	3.4100	0.0492	0.0000	4.0460	0.0449
3	0.0000	2.7850	0.0058	0.0000	3.1670	0.0216	0.0000	3.6880	0.0263
3.5	0.0000	1.2730	0.0022	0.0000	2.6630	0.0111	0.0000	3.2650	0.0127
4	0.0000	0.3900	0.0010	0.0000	1.9520	0.0045	0.0000	2.2380	0.0083
5	0.0000	0.2490	0.0000	0.0000	0.7320	0.0022	0.0000	0.9000	0.0028
6	0.0000	0.1920	0.0000	0.0000	0.5370	0.0022	0.0000	0.7040	0.0026
7	0.0000	0.1610	0.0000	0.0000	0.4570	0.0013	0.0000	0.6620	0.0017
8	0.0000	0.1420	0.0000	0.0000	0.3980	0.0013	0.0000	0.6250	0.0015
9	0.0000	0.1220	0.0000	0.0000	0.3510	0.0013	0.0000	0.4900	0.0008
10	0.0000	0.1010	0.0000	0.0000	0.3080	0.0000	0.0000	0.4150	0.0000
11	0.0000	0.0780	0.0000	0.0000	0.2710	0.0000	0.0000	0.3680	0.0000
12	0.0000	0.0630	0.0000	0.0000	0.2380	0.0000	0.0000	0.3460	0.0000
13	0.0000	0.0520	0.0000	0.0000	0.2050	0.0000	0.0000	0.3190	0.0000
14	0.0000	0.0400	0.0000	0.0000	0.1800	0.0000	0.0000	0.2850	0.0000
15	0.0000	0.0310	0.0000	0.0000	0.1590	0.0000	0.0000	0.2560	0.0000
17	0.0000	0.0160	0.0000	0.0000	0.1220	0.0000	0.0000	0.2090	0.0000
20	0.0000	0.0000	0.0000	0.0000	0.0800	0.0000	0.0000	0.1500	0.0000

The selected examples of the variations in the formation rates of particular products during gasification under the pressure of 10 bar and the temperature of 950 °C for the RM are shown in Figure 8. It can be observed that, despite the differences in the formation rates of particular products, the character of their kinetic curves is similar. In all cases it was observed that the primarily high reaction rate falls, and in the first phase the fall is very big, while later on it is much slower. The highest rates can be noted for the formation reaction of carbon monoxide (CO). Immensely high evolution rates of particular products in the primary phase of the process are result of the pyrolysis [42]. In addition, from the analysis of the figure it can be inferred that the higher evolution rate of carbon monoxide (CO) and hydrogen (H₂) is recorded during catalytic gasification with

Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O promoter catalysts comparing to non-catalytic gasification process. Catalytic activity of Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O promoter catalysts was substantially affected in higher evolution rate of carbon monoxide (CO) and hydrogen (H₂) than non-catalytic process (see Fig. 8 and Tab. 3). Regarding to hydrogen yield formation, Ni/Al₂O₃-SiO₂ catalyst displayed a slight better results than the Ni/Al₂O₃-SiO₂ with K₂O promoter catalyst and non-catalytic reaction processes. Based on the obtained results it can be concluded that these additives catalyzed the formation reaction of gaseous products and the concentration of gases were increased, comparing to non-catalytic gasification. However, impact of both catalysts on formation rate of methane (CH₄) was inefficient comparing to non-catalytic gasification. Hence, it can be concluded that Ni/

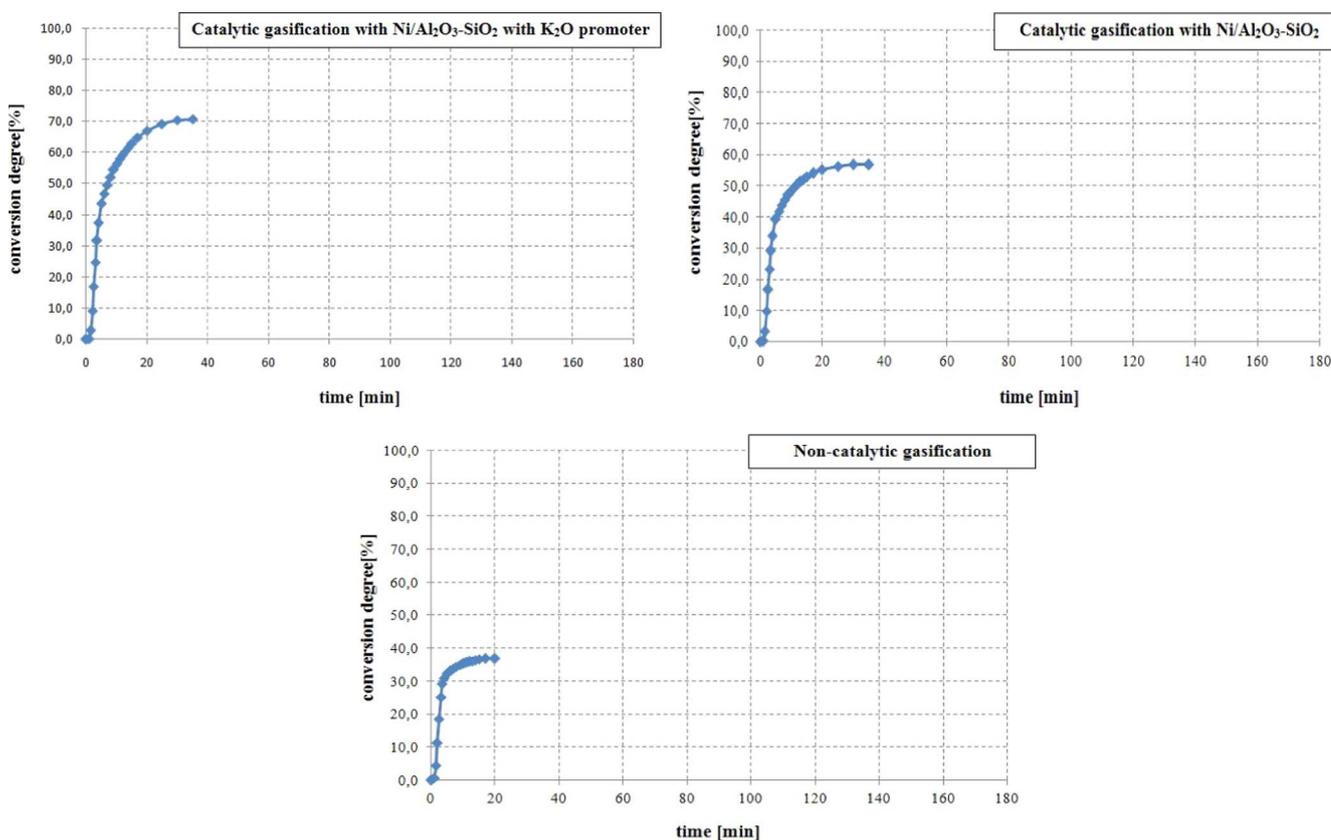


Figure 9

Variations in carbon conversion degree during non-catalytic and catalytic gasification of RM at temperature of 950 °C

Al₂O₃-SiO₂ along with Ni/Al₂O₃-SiO₂ with K₂O promoter catalysts are active in evolution rate increment of CO and H₂, so called synthesis gas (H₂ + CO).

Generally, 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 because of the contribution of the reforming reactions which are favored and occurred at high temperature, hence becoming prevailing at temperatures which are higher than 800 °C [43–50]. The finite gas composition is a function of the common reactions that at the same time come off by increasing the 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 [51, 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 H₂ [53–56].

The next stage involved the elaboration of the curves of carbon conversion degree. Figure 9 shows the conversion degree for the RM at 950 °C temperature from the catalytic and non-catalytic gasification process. From the analysis of the presented curves, it can be observed that temperature has a significant impact on the conversion degree. A comparative analysis of the examined biomass samples demonstrates that the higher reactivity for the RM biomass was during catalytic gasification. These changes in conversion degree and reactivity might be because of alkali index and the O/C ratio.

The calculation of the product gas yields was enabled via the kinetic curves formation reactions of the examined gases extracted during the gasification measurements. The received values per 1 g of biomass in dry and ash-free state and overall gaseous products yields [vol. cm³] are presented in Figure 10 and Table 4 respectively. An analysis of the presented data leads to the conclusion that with the temperature, in most cases, the yields of carbon monoxide and hydrogen increased in the process of catalytic gasification of the examined RM biomass. As well as, higher hydrogen (H₂) yield concentration is observed especially from the catalytic gasification using Ni/Al₂O₃-SiO₂ catalyst than non-catalytic and catalytic Ni/Al₂O₃-SiO₂ with K₂O promoter catalyst. Thus, bio-gaseous product yields profile affirmed that the catalysts might activate

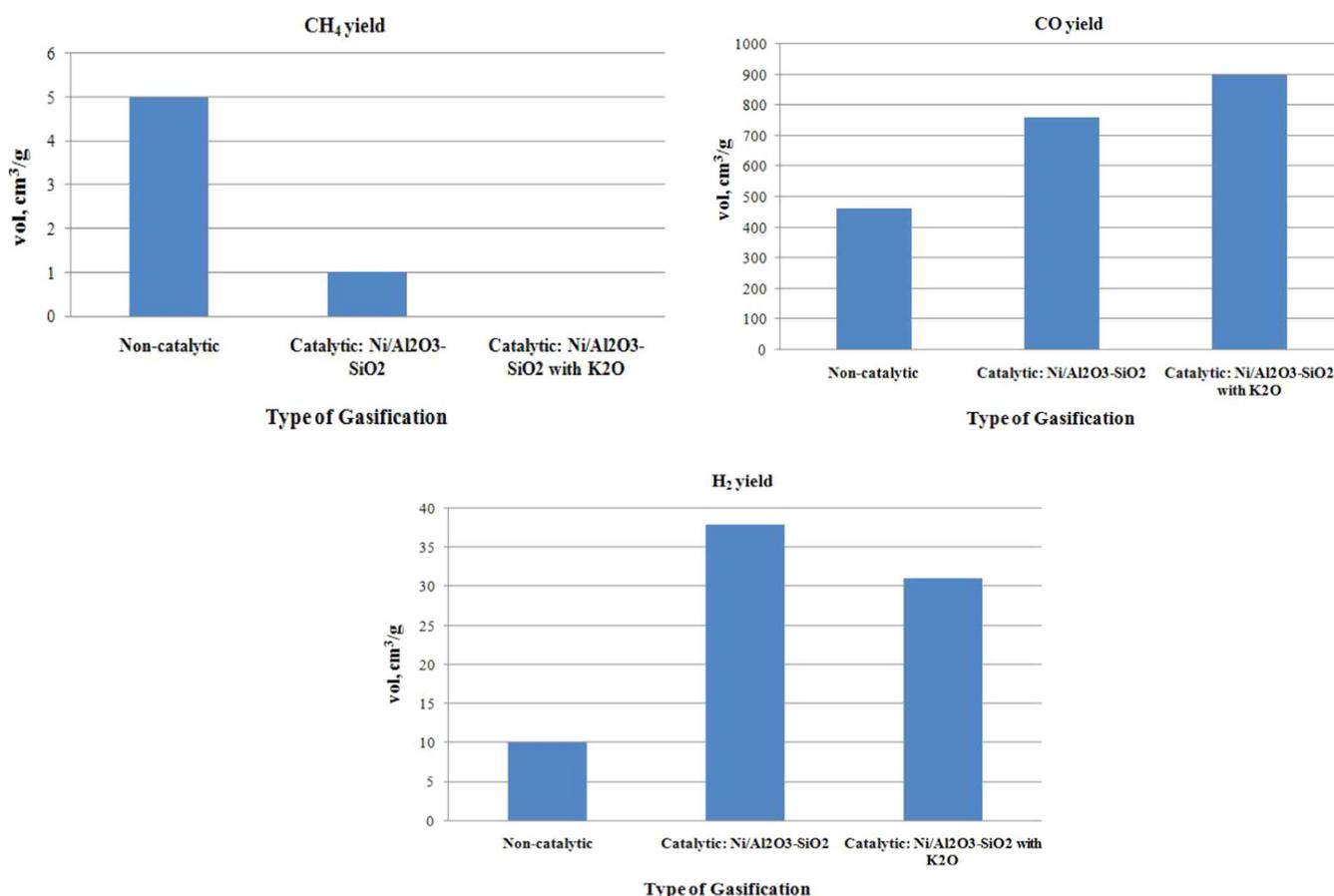


Figure 10

Comparison yields of CH₄, CO and H₂ (cm³/g) in the catalytic and non-catalytic gasification processes of examined RM biomass at 950 °C and pressure of 10 bar.

TABLE 4

Overall gaseous product yields from non-catalytic and catalytic Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O promoter gasification of RM at 950 °C reactor temperature.

Gas yields, [vol. cm ³]	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	5	1	0
CO	464	760	900
H ₂	10	38	31

depolymerization processes to 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 [57, 58]. The recorded yields for methane are much smaller and it is formed mainly at the initial stage of the process during non-catalytic CO₂ gasification process.

Thereby, according to overall analysis it can be inferred that the Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O as promoter catalysts along with the high temperature significantly enhanced synthesis gas ration (H₂ + CO) and concentration. However, the catalysts were not efficient in methane

formation, but the catalysts played a significant role in enhancing the quantity and quality in extraction of syngas yield.

CONCLUSION

The catalytic and non-catalytic gasification of RM biomass for bio-gas (CH₄, CO and H₂) analysis was performed in a lab scale reactor. Factors such as gasification temperature, time, pressure, particle size and flow rate were tested which demonstrate a significant effect on the production of gaseous

yields. A high temperature 950 °C along with Ni/Al₂O₃-SiO₂ and Ni/Al₂O₃-SiO₂ with K₂O promoter catalysts resulted in a higher conversion of RM biomass into bio-gas production with considerable amount of H₂ (31 and 38 vol, cm³/g) and CO (760 and 900 vol, cm³/g). Both of the catalysts were not efficient in methane formation, but Ni/Al₂O₃-SiO₂ catalyst especially enhanced H₂ yield from the gasification process of RM.

The results indicate 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 and Ni/Al₂O₃-SiO₂ with K₂O promoter catalysts. Moreover, this research opens vast opportunities and mechanisms to convert plant biomass into useful and valuable bio-gas product.

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