

The Influence of Laser Biotechnology on Energetic Value and Chemical Parameters of *Rose Multiflora* Biomass and Role of Catalysts for bio-energy production from Biomass: Case Study in Krakow-Poland

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Abstract A study of energy recovery from three groups (control, laser stimulated (3times/3sec) and laser stimulated 3times/9sec) of *Rose multiflora* biomass after 5 years field experiments was undertaken. The energy content of *Rose multiflora* biomass control group is 17.574 MJ/kg, laser stimulated (3times/3sec) group is 18.255 MJ/kg and laser stimulated (3times/9sec) group is 17.698 MJ/kg. The elemental composition of the samples was investigated using Eltra CHS 580 analyzer and it shows that the *Rose multiflora* biomass of control group contains 53.53% of carbon, 7.19% of hydrogen and 0.04% of sulfur; laser stimulated (3times/3sec) group of *Rose multiflora* biomass contains 53.11% of carbon, 7.22% of hydrogen and 0.04% of sulfur; and laser stimulated (3times/9sec) group of *Rose multiflora* biomass contains 53.16% of carbon, 7.37% of hydrogen and 0.03% of sulfur. The energy flow (exothermic and endothermic) and thermal degradation analysis were carried out using calorimeter (model: KL-12Mn) and European PN-EN and ASTM standards respectively. It has been observed that *Rose multiflora* biomass is more reactive to combustion as compared to municipal solid waste (MSW). Moreover, pyrolysis and gasification can be used to convert *Rose multiflora* biomass to liquid or gaseous fuel. This paper also presents analysis of chemical properties, surface area analysis and concentration of Ni/SiO₂ and Ni/SiO₂ with K₂O as promoter for catalytic cracking of tar and enhancing bio-yield production from technologies such as pyrolysis and gasification of biomass.

Keywords: laser biotechnology, rose multiflora, biomass, catalyst, pyrolysis, gasification, energy

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1. Introduction

One of the most promising alternatives to meet the increasing demands of the human population for energy sources is the production of bio-energy from biomass of plants. Wide scale studies strongly support development of production of different sources of bioenergy and biofuel [1-7].

Several green and eco-friendly technologies are already developed and applied world-wide to produce renewable energy. Most of them use the sun energy directly or via

energy carriers as the main energy source. In any green energy technology, there are several key aspects. Among them the most important are: efficiency in energy conversion, energy storage until consumption, carbon foot print, wastes generated and environmental impact [8]. However, much attention has been paid to biomass conversion technologies into bio-energy. Accordingly, nowadays a lot of research studies are focused on investigation a proper technology for more efficient biomass production.

With 92 percent of its energy still coming from coal and ambitious European Union targets to reach, Poland is on the lookout for renewable energy opportunities. That

translates to opportunities for biomass production with the target for bio-energy extraction. Biomass energy has been recognized as a most promising and most important renewable energy source in near future for Polish conditions. The total technical potential for biomass resource has been calculated at 755 PJ. Largest resources relate to the agricultural residues, forestry residues and forestry fuel wood. Energy crops will play more important role in mid and long term perspective. Among energy crops tested in the country conditions are: short rotation coppice of willow (e.g. *Salix viminalis*), perennial grasses like *Miscanthus s. giganteus*, *Miscanthus s. sacchariflorus*, *artichoke*, *Rosa multiflora* and *Sida hermaphrodita* [9].

Biomass is one of the earliest sources of energy particularly in rural areas where it is frequently the only affordable and accessible source of energy. Biomass is made up of carbohydrates [10]. Biomass is a renewable energy source with very specific properties. Compared to other renewable technologies such as wind or solar, biomass has few problems with energy storage; in a sense, biomass is stored energy. In addition, biomass is a versatile fuel that can produce biogas, liquid fuels and electricity. Sometimes biomass is classified as combustible materials that can be applied as an energy source. Biomass is a renewable energy source because its supplies are interminable. We can always grow trees and crops, fast growing plants, and waste will always exist.

1.1. Catalytic Activity

Thermo-chemical processes for biomass conversion, such as combustion, gasification and pyrolysis, can be used for power generation and bio-energy production. Among these processes, biomass gasification and pyrolysis have attracted the most attention from both industrial and academic researchers due to its high conversion efficiency [11]. Biomass gasification is a process to convert biomass feedstock into combustible gaseous products such as hydrogen, syngas, carbon monoxide and methane. If main products from gasification of biomass are combustible gaseous products, pyrolysis of biomass is also a process to convert biomass not only into gaseous products but also into bio-oil or bio-fuel [12]. However, undesirable products like tar and char are also produced during gasification and pyrolysis [8,11,12]. Currently, there are many research projects have been undertaken related to catalyst activity for tar cracking and char yield reduction from gasification and pyrolysis processes.

Different types of catalysts such as zeolites [12,13], calcined dolomite [12], calcined rocks [14], iron ores [15], alkali metals [16], Ni-based catalysts [17,18], and noble metals [19,20] have been studied for their efficiency on tar removal in biomass gasification and pyrolysis. From the point of catalytic reactivity and economic reasons, Ni-based catalysts are considered the most promising for a tar removal and synthetic gas reforming [21]. Nickel catalysts are usually supported by metal oxides such as Al_2O_3 , SiO_2 , MgO or natural materials such as dolomite, olivine, activated charcoal, bio-char [12,22,23] etc. In addition, Ni-based catalysts promote the reduction in the reforming temperature, and tar increase in the hydrogen content of the syngas produced. The influence of the preparation method over the catalysts properties has been previously

reported in the literature [24,25], as well as different oxide supports such as SiO_2 [24,26] and Al_2O_3 [27, 28] have been tested for their usefulness for on tar reduction and catalyst properties.

Moreover, Ni/ SiO_2 catalysts have been studied for ethanol and methanol reforming [24, 29], and for tar reforming [30] giving an effective performance. SiO_2 was selected as the support because it produces a higher sintering resistance and higher metallic surface area compared with other oxide supports [31]. Different promoters such as Al, Ce, and Mg have been added to different Ni-based catalysts in order to enhance their catalytic activity and selectivity, to increase the steam adsorption, and to reduce the carbon deposition over the catalyst surfaces [32,33,34,35].

In this study, two types of catalysts NiO/ SiO_2 and NiO/ SiO_2 with K_2O as promoter have been analytically investigated.

1.2. Laser Biotechnology as Mechanism for Efficient Production of Biomass

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, effective reclamation and an efficient biomass production in deteriorated areas as contribution to sustainable development of different areas [36]. Wide-scale application of laser biotechnology could contribute to decrease a concentration of green-house gases and primary prevention of climatic change and also to progress in re-naturalization of regions abundant with rivers, increase of water retention and prevention against flood incidents [37]. Laser biotechnology is an efficient mechanism for increase of biomass production in deteriorated areas due to empirically selected algorithms.

Long term study results showed that laser stimulation caused on plant biomass increment and greater uptake of trace and biogenic elements from contaminated water and soil. Application of laser stimulation of different species of plants, soil bacteria and fungi in environmental biotechnology was introduced by Dobrowolski in 1978. Additionally, this laser technology enables the optimization of bioremediation processes, such as removal of pollutants from sewage and soil reclamation as well as increase of biomass production by plants cultivated in polluted soils [38,39].

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) could contribute to promotion of low carbon energy production and sustainable development in different regions and countries [39]. Thus, application of eco-friendly laser biotechnology could contribute both to better bioremediation of contaminated land and water as well as for the development of biomass production as a source of renewable bio-energy.

Other real perspective to increase bio-energy production may be connected with proper management of biodegradable waste [40]. Better application of organic

wastes for large scale energy production could be also connected with proposals submitted by president of the International Consortium of Clean Energy (Prof. Grob). Results of series of experimental studies initiated and coordinated by Dobrowolski may be starting point for innovative international project focused on research-developing studies for optimization of the application of Laser Biotechnology (as Polish priority on world scale) for more efficient biodegradation of petrochemical pollutants and reclamation of contaminated areas with a linkage to biomass and bio-energy production.

2. Materials and Methods

This research methodology consists of sampling selection method, sorting procedure and laboratory analysis to identify proximate and ultimate analysis of three groups (control, laser stimulated (3times/3sec) and laser stimulated 3times/9sec) of the *Rosa multiflora* biomass after 5 years field experiments accommodated at experimental site of the University of Agriculture in Krakow, Poland was undertaken. Generally, there are two formal types of sampling and analysis methods based on ASTM and European PN-EN standards.

Accordingly, research methodology will help for management categories in order to improve energy extraction routes from biomass of roses.

2.1. Method for Biomass Characterization

2.1.1. 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 in Krakow in cooperation with prof. J. W. Dobrowolski.

An apparatus Medical Laser (D 68-1) emitted red light with a wavelength of 672 nm and λ power of 20 mW on *Rosa multiflora* cuttings, by the application of two exposure times intermittent a) 3times x 3 seconds, and b) 3times x 9 seconds. Exposed seedlings along with control group (non-irradiated) were planted in spring of 2009, the spacing of 70 x 70 cm. in leached brown soil.

2.1.2. Biomass Sampling

The procedure was applied for collecting the biomass based on the American Society for Testing and Materials (ASTM), the biomass sampling was pick up in the plastic bag from Experimental Field (str. Mydliniki), the Faculty of Energy and Mechanical Engineering, University of Agriculture in Krakow, Poland which is usually an amount of 15 or 20 kg and investigated at the research laboratory under the Faculty of Energy and Mechanical Engineering, University of Agriculture in Krakow, Poland. Next, the biomass of roses was separated according to the selected classification: 1) control group; 2) laser stimulated group – 3x3 (times/sec) and 3) laser stimulated group – 3x9 (times/sec). Each group was weighted by using a weight balance and data was recorded. Further prepared samples were referred to various elemental and analytical analyses (each test was repeated 3 times in order to obtain a precise data).

2.2. Proximate Analysis of Biomass Sample

Proximate analysis consist of moisture content, volatile matter, ash content, fixed carbon and determination of calorific (energetic) value. Moisture content, volatile matter, ash content and fixed carbon determined by put the selected sample to different range of the temperature, between 100°C to 950°C. The laboratory methods for measuring the proximate analysis of biomass samples in this research project were carried out based on ASTM and European PN-EN standards. These standards determine the condition of lab analysis such moisture, volatile matter, ash and fixed carbon.

2.2.1. Moisture Content

The percent moisture of the woody biomass samples was determined by weighting of the samples into dish and drying the samples in an oven at 105°C for 3-4 hours after which it was cooled and then reweighted to constant weight. The procedure for determination of moisture content has been done following European Standard PN-EN 14774-3:2010 and ASTM standards E 871. The similar methodology for determination of moisture content has been used by Maoyun, et al [41]. The percent moisture content was calculated as a percentage loss in weight before and after drying [42,43].

$$\begin{aligned} \text{Moisture content} \\ = [(\text{Wet Weight} - \text{Dry Weight}) / \text{Wet weight}] \times 100 (\%) \end{aligned} \quad (1)$$

2.2.2. Volatile Matter Content

The volatile matter content was determined by the method of ignition of the sample at 900°C, following Furnace Thermocouple Thermojunction Method – European Standard PN-EN 15148:2010. The samples of woody biomass material used in the moisture content determination were prepared in duplicate and 10-14g of biomass placed in a crucible. The crucible with its content was placed in the muffle furnace at a temperature of (900±10)°C, and heated for precisely seven minutes, timed with a stop watch. The similar experiments for moisture content determination have been done by a few scholars such as Tursunov et al (2015) [8], Amin and Yang (2012) [42] and Edema et al (2012) [43]. After combustion, the crucible was then removed from the furnace and cooled. After cooling the crucible with its sample content were weighted accurately and volatile matter calculated as:

$$\begin{aligned} \% \text{ volatile matter} \\ = \text{loss in weight} \times 100 / \text{weight of sample} \quad (2) \\ - \{ \% \text{ moisture} \} \end{aligned}$$

2.2.3. Ash and Fixed Carbon Content

Ash content of woody biomass is the non combustible residue left after biomass is burnt up, which is represents the natural substances after carbon, oxygen, sulfur and water.

Analysis include of woody biomass samples were taken in duplicate of >0.1 g/cm² each and ignited to heat up to (500±10)°C for at least 60 min, following European Standard PN-EN 14775:2010. The dish was removed from the muffle furnace. The dish was allowed to cool down

before the residue was weighted. The ash content of the sample was calculated as:

$$\% \text{ ash} = \text{weight of sample} \times 100 / \text{weight of the sample} \quad (3)$$

Fixed carbon defined by carbon found in the material which is left after completion of volatile test. Fixed carbon is determined by removing the mass of volatile from the original mass of the biomass sample:

$$\begin{aligned} & \text{Fixed Carbon (Wt\% wet basis)} \\ & = 100 - \left(\begin{array}{l} \text{Wt\% moisture content} + \text{Wt\% Ash} \\ + \text{Wt\% volatile matter} \end{array} \right) \quad (4) \end{aligned}$$

2.2.4. Calorific (Energetic) Value

Determination of the heating value (energetic value) of woody biomass samples can be investigated either experimentally or by using mathematical models. Experimental determination by using a bomb calorimeter utilize a sample size of 1 g or either 2 g which is inadequate to account for the vast variance in biomass composition, thus requiring bigger sample size [8]. Furthermore, the experimental method is tedious and also requires technical skills in handling the equipment and the combustion by products as well. As for the mathematical models, they were created to avoid over reliance on lengthy experimental technique. In this research project, amount of heating value (calorific value) was determined by using a bomb calorimeter (Model: KL-12 Mn), following European Standard PN-EN 14918:2010 and PN-ISO 1928.

The measurement consists in complete combustion of sample in pressurized oxygen atmosphere. The sample is placed in a special calorimetric bomb immersed in water. In this way the measurement of water temperature increase is carried out. The heat of combustion is calculated automatically and displayed on computer's monitor. The measuring accuracy of temperature increase is 0,001°. The control unit of the calorimeter is PC computer. All measuring and check functions are completely automatized. Apart from the heat of combustion, also the calorific value is calculated.

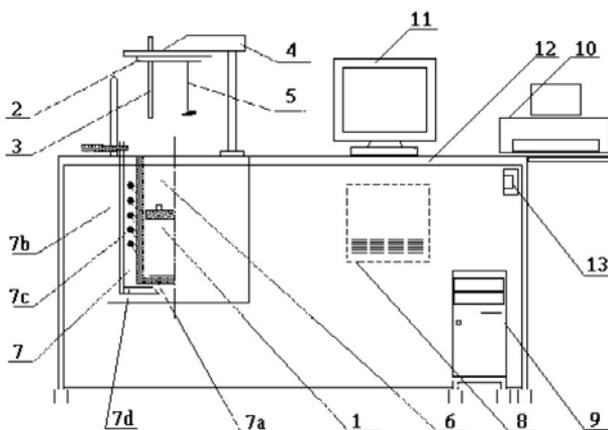


Figure 1. Diagram of calorimeter KL-12 Mn: 1-bomb calorimeter; 2-calorimeter cover; 3-temperature sensor; 4-cover holder with mechanical mixer drive; 5-mechanical mixer; 6-calorimetric vessel; 7-calorimeter jacket: a) internal wall, b) external wall, c) coil, d) manual mixer; 8-calorimeter control unit; 9-computer; 10-printer; 11-monitor; 12-calorimeter table; 13-power strip

The combustion heat is automatically calculated by the following formula:

$$Q_s = K (T_3 - T_2 - k) \quad (5)$$

where:

Q_s - heat of combustion, [kJ/kg] or [MJ/kg]

K - fixed calorimeter, [kJ/kg]

T_2, T_3 - temperature characteristic balance, [K]

k - correction for heat exchange calorimeter area,

$$k = 0.5[0.2(T_2 - T_1) + 0.2(T_4 - T_3)] + 0.2(n-1)(T_4 - T_3) \quad (6)$$

where:

n - the number of minutes in the cycle

T_1, T_4 - temperature characteristic balance, [K]

The calorific value is determined from the following equation:

$$Q_w = Q_s - \frac{r}{100} + (8.94H^a - W^a) \quad (7)$$

where:

Q_w - calorific value, [kJ/kg] or [MJ/kg]

W^a - moisture content in the test sample, [%]

H^a - hydrogen content in the test sample, [%]

r - heat of water vaporization, $r = 2454$ kJ/kg.

2.3. Ultimate and Trace Elemental Analysis

Ultimate analysis was used to determine the CHS content in biomass sample by using Eltra CHS 580 Elemental Analyzer. Such analysis presents the weight percent of carbon, hydrogen, and sulphur in the sample simultaneously.

After weighing the sample in a ceramic boat, the weight is transferred from the interfaced balance to the PC. If required, sample weights can also be entered manually. Then the ceramic boat is introduced into the furnace for combustion. The average analysis time is 60 to 180 seconds. The detector signals and instrument parameters are displayed during analysis. Evaluation of the signals and display of the results are done automatically; the data can be transferred to a laboratory information management system (LIMS).

In the CHS-580 the sample is burnt in an oxygen atmosphere at temperatures up to 1,550 °C. The furnace temperature can be freely selected in steps of 1 °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 vapor is chemically absorbed, the dried CO_2 and SO_2 gas is detected in the additional infrared cells. Depending on the configuration, it is possible to combine up to three infrared cells with different sensitivities.

Trace elemental analysis of *Rose multiflora* biomass sample was investigated using JSM-5410 Scanning Microscope with an optional EDS (energy dispersive X-ray spectrometer).

2.4. Catalysts

Catalysts Ni/SiO_2 and Ni/SiO_2 with K_2O as promoter were collected from the Chemical Faculty of the Maria Curie-Skłodowska University in Lublin, Poland.

The Ni/SiO_2 with K_2O as promoter and Ni/SiO_2 were used as catalysts in this study in order to make a comparison for efficient syngas (or hydrogen rich gas)

production as well for tar reduction in gasification/pyrolysis processes. The X-ray diffraction of catalysts was evaluated by using JSM-5410 Scanning Microscope with an optional EDS (energy dispersive X-ray spectrometer).

2.4.1. Surface Area Analysis

The surface area analysis of Ni/SiO₂ and Ni/SiO₂ with K₂O as promoter catalysts by using Scanning Electron Microscope (JSM—5410, courtesy of JEOL, USA). Schematic diagram of scanning electron microscope is shown in Figure 2.

The JSM-5410LV Scanning Elctrone Microscope can be used for observation of the entire Area of large sized specimens up to 5-inch in diameter by rotating them. The whole series of operation including vacuum evacuation, image observation, focusing, and photographing have been automated. Moreover, provision of digitally processed still image allows very easy observation of images even in a bright room, making the JSM-5410 outstanding in operability.

Figure 2 shows a column structure of a conventional SEM. The electron gun, which is on the top of the column, produces the electrons and accelerates them to an energy level of 0.1–30 kV. The diameter of electron beam produced by hairpin tungsten gun is too large to form a high-resolution image. So, electromagnetic lenses and apertures are used to focus and define the electron beam and to form a small focused electron spot on the specimen. This process demagnifies the size of the electron source (~50 μm for a tungsten filament) down to the final required spot size (1–100 nm). A high-vacuum environment, which allows electron travel without scattering by the air, is needed. The specimen stage, electron beam scanning coils, signal detection, and processing system provide real-time observation and image recording of the specimen surface.

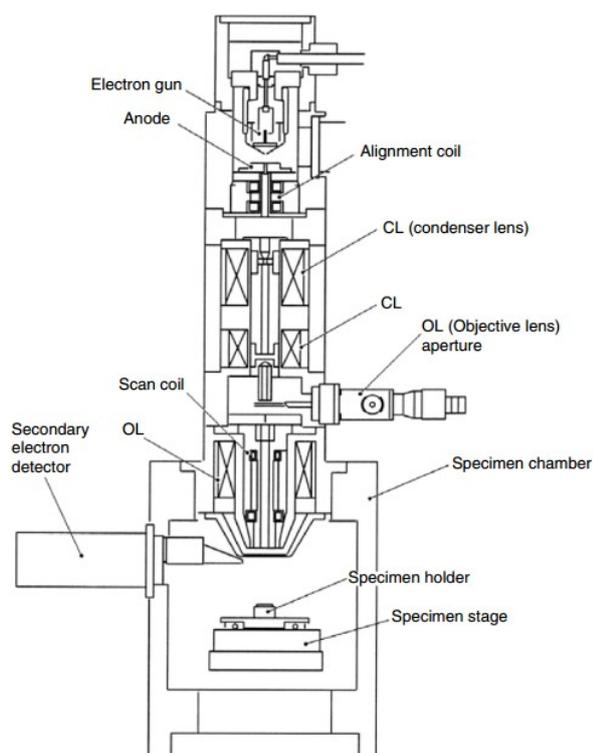


Figure 2. Schematic diagram of a scanning electron microscope (JSM—5410, courtesy of JEOL, USA)

3. Results and Discussions

3.1. Results from Proximate Analysis

Proximate analysis involves determination of moisture content, volatile matter, ash content, fixed carbon and also calorific value. The analysis was according to ASTM and European PN-EN standards. Comparative Results from proximate analysis 3-groups of *Rose multiflora* biomass (control, laser stimulated 3times/3sec and laser stimulated 3times/9sec) are shown in Table 1 and Figure 3 respectively. Additionally, Figure 4 highlights the comparison on calorific (energetic) value of three groups of the *Rose multiflora* biomass.

Table 1 and Figure 3 illustrate that the proximate and of *Rose multiflora* biomass used in this research. They show lower moisture content (18.27 wt %) in control group of *Rose multiflora* biomass than laser irradiated group 3times/3sec (19.35 wt %) and laser irradiated 3times/9sec (18.58 wt %), and fixed carbon content shows the opposite tendency with greater wt % in control group (5.98 wt %) than laser irradiated group 3times/3sec (5.51 wt %) and laser irradiated group 3times/9sec (5.37 wt %). The moisture content is measure with the amount of water lost from materials upon drying to a constant weight. It is directly affected by chemical and physical properties of material which enable it to absorb the exiting water in the environment. Fixed carbon is the carbon remaining on surface as charcoal.

Table 1. Proximate analysis of *Rose multiflora* biomass

Parameters	Group of Rose Multiflora Biomass		
	Control (non-irradiated)	Laser irradiated 3times/3sec	Laser irradiated 3times/9sec
Moisture (wt %)	18.27	19.35	18.58
Volatile (wt %)	73.05	72.48	73.59
Fixed carbon (wt %)	5.98	5.51	5.37
Ash (wt %)	2.7	2.66	2.46
Calorific value (Mj/kg)	17.574	18.255	17.698

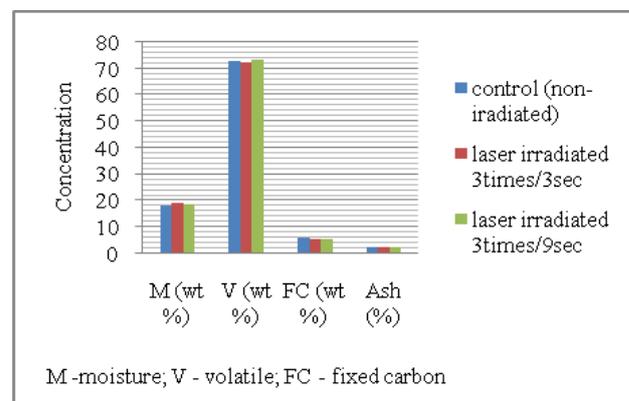


Figure 3. Results comparison from proximate analysis of *Rose multiflora* biomass

Table 1 and Figure 3 show processed biomass has volatile matter content in control group (73.05 wt %), in laser irradiated 3times/3sec (72.48 wt %) and laser irradiated 3times/9sec (73.59 wt %). Ash content in control group (2.7 wt %), in laser irradiated 3times/3sec

group (2.66 wt %) and in laser irradiated 3times/9sec group (2.46 wt %); both parameters volatile matter and ash content have influence on the gasification/pyrolysis characteristics [8]. Woody biomass is easier 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.

In addition, Table 1 and Figure 4 highlight the comparative analysis of calorific (energetic) value in each group of *Rose multiflora* biomass. It can be noted that laser irradiated 3times/3sec group has highest calorific (energetic) value (18.255 MJ/kg) comparing to laser irradiated 3times/9sec (17.698 MJ/kg) and control group (17.574 MJ/kg), the results were obtained based on the bomb calorimeter test. Thus, it can be concluded that application of proper algorithm of coherent light of the laser biotechnology has an efficient and positive impact on increase of energy value in *Rose multiflora* plant.

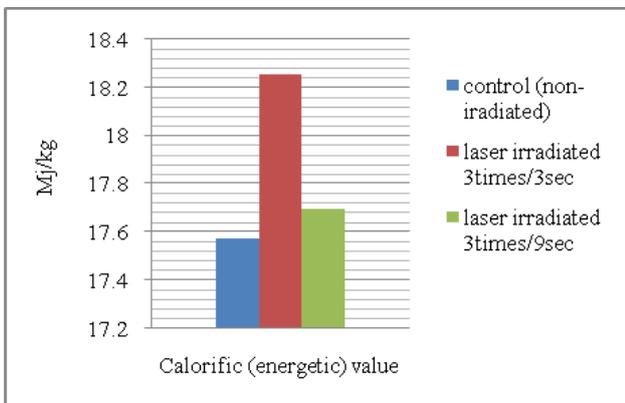


Figure 4. comparison on calorific (energetic) value of three groups of the *Rose multiflora* biomass

3.2. Results from Ultimate and Trace Elemental Analysis

Ultimate analysis demonstrates determination of chemical characteristics of *Rose multiflora* biomass sample. The results of ultimate analysis that was investigated by Eltra CHS 580 elemental analyzer is shown in Table 2.

Table 2. Ultimate analysis of *Rose multiflora* biomass

Chemical Elements	Group of Rose Multiflora Biomass		
	Control (non-irradiated)	Laser irradiated 3times/3sec	Laser irradiated 3times/9sec
C (carbon)	53.53 (wt%)	53.11 (wt%)	53.16 (wt%)
H (hydrogen)	7.19 (wt%)	7.22 (wt%)	7.37 (wt%)
S (sulfur)	0.04 (wt%)	0.04 (wt%)	0.03 (wt%)

The quantitative element content and X-ray patterns of the *Rose multiflora* biomass are listed in Table 3 and Figure 5 respectively.

Thus, Table 3 and Figure 5 indicate that Mg, Ca, P, S, Cl and K were the main components in all groups of *Rose multiflora* biomass. The apparatus Scanning Electron Microscope with an optional EDS (energy dispersive X-ray spectrometer) could also detect the elements O and C, but it hasn't technical possibility to identify a concentration of these elements, due to this fact O and C chemical elements are not included in Table 3.

Table 3. Quantitative element content calculated on the basis of gelatin biological patterns

spectrum	Rose multiflora - control (non-irradiated)						Organic matrix
	Chemical elements						
	Mg	P	S	Cl	K	Ca	
1	0.08	0.08	bld	bld	0.72	0.86	98.26
2	bld	0.06	0.10	bld	0.81	1.36	97.68
3	bld	bld	bld	bld	0.48	0.17	99.35
4	bld	0.06	bld	bld	0.44	0.40	99.09
5	bld	bld	bld	bld	0.38	bld	99.62
Rose multiflora – laser irradiated 3times/3sec							
1	bld	0.08	bld	bld	0.48	0.46	98.98
2	bld	0.08	bld	bld	0.45	0.27	99.20
3	bld	0.07	bld	bld	0.60	0.26	99.06
4	bld	0.07	bld	bld	0.53	0.23	99.18
5	bld	0.08	bld	bld	0.53	0.25	99.13
Rose multiflora – laser irradiated 3times/9sec							
1	0.10	0.11	bld	bld	0.80	0.25	98.74
2	bld	0.07	bld	bld	0.38	0.81	98.75
3	bld	0.07	bld	0.26	0.41	0.40	98.86
4	bld	0.09	bld	0.31	0.66	0.47	98.47
5	bld	0.10	0.25	0.15	1.04	2.37	96.10

bld – below the level of detection.

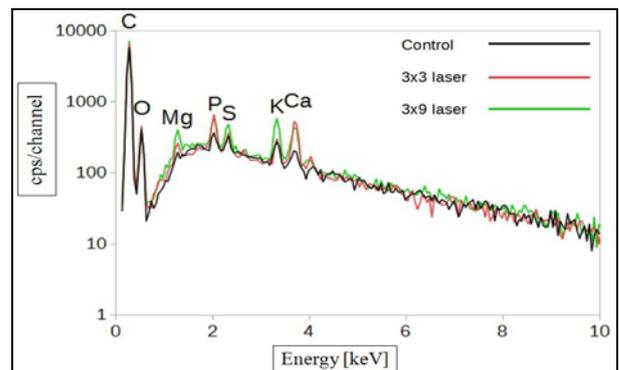


Figure 5. X-ray Patterns of *Rose multiflora* biomass

3.3. Results of X-ray Patterns and Surface Area of Catalysts

The surface characteristics and X-ray patterns of the fresh catalysts are listed in Table 4 and Figure 6-Figure 8 respectively.

Table 4. Surface characteristics Ni/SiO₂ and Ni/SiO₂ with K₂O as promoter catalysts

Chemical Elements	Catalyst	
	Ni/SiO ₂	Ni/SiO ₂ with K ₂ O as promoter
Mg (magnesium)	1.74 (wt %)	3.69 (wt %)
Al (aluminum)	19.07 (wt %)	31 (wt %)
Ca (calcium)	0.96 (wt %)	0.99 (wt %)
Ni (nickel)	48.26 (wt %)	30.28 (wt %)

Figure 6 and Table 4 indicate that Ni, Mg, Al and Ca were the main components in both type of Ni/SiO₂ and Ni/SiO₂ with K₂O as promoter catalysts.

Scanning Electron Microscope (JSM—5410) was used to analyze the surface area of catalysts; the images of the

surface morphology are presented in Figure 7 and Figure 8. The surface image of catalysts was detected at 1500x; bar: 14 microns.

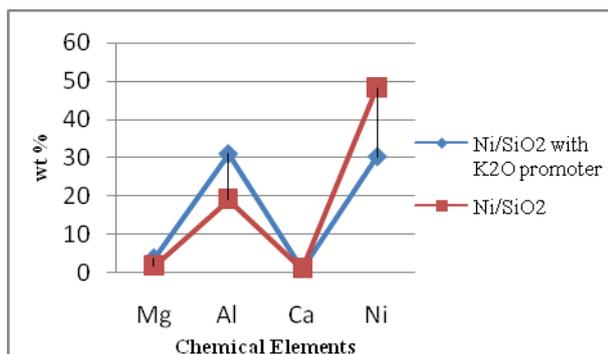


Figure 6. X-ray Patterns of Ni/SiO₂ and Ni/SiO₂ with K₂O as promoter catalysts

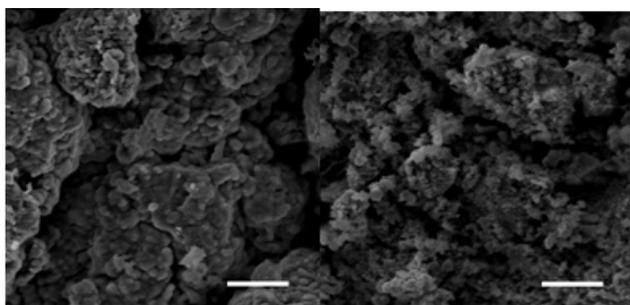


Figure 7. High (left) and intermediate (right) magnification SEM surface image of catalyst Ni/SiO₂, K₂O as promoter (NiO min. 17wt%; SiO₂ max. 0.1wt%)

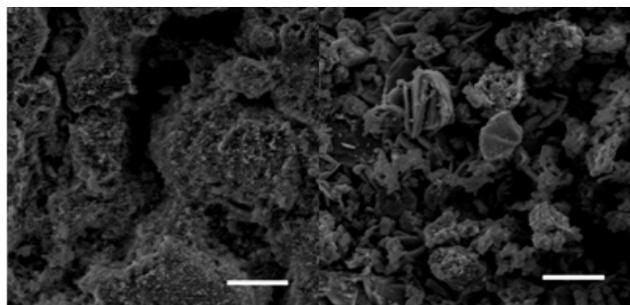


Figure 8. High (left) and intermediate (right) magnification SEM surface image of catalyst Ni/SiO₂ (NiO min. 10.5wt%; SiO₂ max. 0.1 wt %)

During the experimental study of the catalysts surface area analysis it was noted that the surface of both catalysts was highly compressed.

It is known that catalyst deactivation is mostly controlled by coke deposition and sintering [44]. From the SEM analysis, sintering seemed to be a problem for the investigated catalysts especially those prepared by wet impregnation. As shown in Figure 7 and Figure 8, several large particles could be found on the SEM image of the Ni/SiO₂ with K₂O as promoter catalyst, while more non uniform Ni particles were observed for the higher Ni content Ni/SiO₂ catalyst. The Ni/SiO₂ catalyst is suggested to be more stable due to its good dispersion of Ni. As shown in Figure 7 and Figure 8, Ni crystals could be observed for all the investigated catalysts. Different sizes of Ni crystals were also found throughout the micrograph (Figure 7-Figure 8).

A formation mechanism for coke deposited on Ni catalysts during gasification has been reported by Wu and

Williams [45]. They suggested that the fragmentation of a catalyst during the gasification process might be originated from reactions inside the catalyst where carbons are initially formed and developed.

The Ni/SiO₂ catalyst is selected due to its satisfactory results in methane and syngas steam reforming reactions [46]. No reports have been revealed on characterization of SiO₂ supported catalyst for methane and CO₂ conversion in the presence of O₂ and H₂O. Moreover, the application of core shell catalysts has not yet been studied for tri-reforming processes. However, some authors [46] tested catalyst prepared by a deposition-precipitation method.

4. Conclusions and Recommendations

This paper presented the study of three groups (control, laser stimulated (3times/3sec) and laser stimulated (3times/9sec)) of *Rose multiflora* biomass characterization of Krakow city of Poland. The proximate and ultimate analysis of the 3-groups of *Rose multiflora* biomass was precisely studied. The ultimate analysis showed that average amount of sulfur was small (0.03-0.04 wt %) in all groups of biomass which is link to low SO₂ release during the pyrolysis or gasification process.

The energy content of *Rose multiflora* biomass control group is 17.574 MJ/kg, laser stimulated (3times/3sec) group is 18.255 MJ/kg and laser stimulated (3times/9sec) group is 17.698 MJ/kg. Hence, energy content of laser stimulated group 3times/3sec is higher than other groups of *Rose multiflora* biomass, this was about 60-70 % of energy contained in coal Therefore, biomass from plants has a good potential to be used as a fuel or synthetic gas.

Moreover, Ni/SiO₂ and Ni/SiO₂ with K₂O as promoter catalysts have been widely studied. It is suggested, that Ni based catalysts have an efficiency to eliminate tar from reactors and enhance bio-yields (e.g. bio-gas) production from pyrolysis or gasification processes.

There are also real perspectives for wide-scale application of laser biotechnology for more intensive biomass production in areas out of use or contaminated areas by toxic metals, or by petrochemicals.

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