WNIOSEK O PORTFOLIO:

Opracowanie koncepcji zwiększenia ekektywności przetwarzania biomasy

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Integrated Biomass System and Technology: Application of Eco-Friendly Laser BioTechnology for More Efficient Increase of Biomass for BioEnergy Production via Alternative Clean Technologies

1. Background and Literature Review

1.1 Perspectives of Wide-Scale Application of Laser Bio-Technology for Enhancement of Biomass Production under Suboptimal Conditions (including areas out of use)

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 [but not instead of food production] . Wide scale studies strongly support development of production of different sources of bioenergy and biofuel (Junginger et al, 2006; Larson 2006; Obenberger et al, 2006; Bain 2007; Bauen et al, 2009; Grausonou et al, 2009; Fischedick et al, 2011; Chum et al, 2014; Zwickel et al, 2014).

According to UE Poland has to develop energy production from renewable sources. Introduction on wide scale new more efficient methods of biomass and bioenergy production may be especially promising and the most ecologically friendly method for facing these requirements. There are massive areas which are out of use in Poland, thus application of already tested laser photo stimulation of seeds or seedlings of plants before their cultivation; could significantly increase biomass production under suboptimal conditions. Introduction of this biotechnology could support reclamation of deteriorated areas. (Dobrowolski and Rozanowski 1998; Dobrowolski 2000, 2001; Dobrowolski and Zielinska-Loek 2002; Dobrowolski et al, 2004, 2012; Jakubik and Sliwka 2009).

Empirically selected algorithm of plants stimulation with coherent light [of high energy density] is able to significantly enhance biomass production. Such kind of reclamation is reasonable from economic point of view. Low power lasers are recommended for short time irradiation of selected species of plants, accordingly cost connected with biostimulation is comparatively lower than economic value of biomass produced in the result of stimulation (Dobrowolski 2000).

The proposed method is immensely useful for taking into consideration of European Union recommendation for increase biomass-to-energy applications by 20 % until 2020.

Biomass is the main source of energy in majority developing countries, therefore, our proposal of dissemination laser bio-technology for enhancement of biomass production might be useful especially in these developing countries (e.g. in rural areas).

This eco-innovation could be also very useful for better adaptation of their agriculture and food production to climatic change (including adaptation during the most sensitive periods, namely at germination of seeds and early development of plants). Proper algorithm of photo-stimulation of seeds, seedlings and cuttings of selected local plants could increase the resistance to a longer dry periods and water deficiency, salinity and higher concentration of different pollutants.

Laser bio-technology would be also useful for more efficient protection of biodiversity in ecological hotspots (e.g. Brazil, Madagascar, Nepal, etc.). Photo stimulation with coherent light of high energy density of seedlings of fast growing trees could massively increase wood production in areas after reclamation as well as in energy plantations. Over exploitation of primary forest could be eliminated in the result of wood production enhancement.

Introduction of this bio-technology with reforestation of some rural areas would be very useful for stimulation growth of some species of trees and wood production.

This way innovative technology would be very useful to construct wooden houses instead of constructed housed made with papyrus e.g.in the main center of food production near the biggest lake in Madagascar.. In the result of construction of houses made of wood reduce risk of contamination of indoor environment with toxinogenic fungi. Thus, we could contribute to primary prevention of health hazard connected with pathogenic moulds and mycotoxins. Contamination of living houses by some toxinogenic fungi e.g. Aspergillus flavus and Penicillum meleagrinum according to discovery of Polish scientists Aleksandrowicz and Smyk are associated not only with higher risk of dermatosis but also increase rate of incidence of some neoplastic diseases among people and breeding animals (Vohora and Dobrowolski 1990).

At the same time, phytocenosis of papyrus as valuable ecosystem of would be protected. This could contribute to protection of biodiversity by prevention of extinction of endemic animals in very limited areas like above-mentioned association of plants.

Application of laser bio-technology could reduce very common in developing countries waterborne diseases by more efficient treatment of wastewater, as well as new method for increase biomass production (of algae and water plants) in hydrobotanic plants

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 low carbon energy production and sustainable development in different regions and countries.

The authors would like to start with special projects focused on dissemination Polish laser biotechnology supported by improved pyrolisis both in European countries as well as in interested in such ecoinnovation developing countries e.g. Brazil, Madagascar, Nepal. Interested in such cooperation are both well known experts and creative representative of university youth involved in long-term training in this field by one of the authors (J.W.D.).

Thus, application of eco-friendly laser biotechnology could contribute both to better bioremediation of contaminated land and water as well as for development of biomass production as a source of renewable bio-energy.

Promotion on large scale laser biotechnology contributing for enhancement of fixation carbon dioxide by stimulated plants maybe a subject of evaluation of multidisciplinary team of experts (including plant physiology and GIS and infrared spectral analysis). Approximately evaluated extra assimilation of carbon dioxide may be very useful for official request of Polish government to EU authority for permission for respectively bigger emission of this air pollutant. Positive reply could stimulate activity of some sectors of Polish economy e.g. production of building materials. This could also contribute for significant increase of biomass production in Poland following European Union recommendation.

Result of the recent unpublished experimental studies on the influence of laser light on different species of plants open new perspective of biomass production in areas out of use.

In supplementation of introduced by Dobrowolski et al. new application of laser photostimulation of inoculum of Trichophyton mentagofites var.granulosum for much more efficient biodegradation of petrochemical pollutants including PAH there were carried out the recent experiments on very successful application of empirically selected algorithms of laser irradiation of whole biocenosis from the area of the oldest oil well for much more efficient reclamation of area contaminated by hydrocarbons (Dobrowolski and Pastuszak, 2014).

Application of proper algorithm of coherent light [of high energy density could] in relation to seeds of crees Cardamine parviflora and summer lupine Lupinus hartwegi caltivated on soil petrochemically polluted significantly increase biomass production. Especially promising for the future study is enhancement of growth rate of lupine as symbiothic plant with nitrogen fixating bacteria very important for stimulation reclamation of deteriorated area and sustainability of biomass production (Dobrowolski and Kaminska 2014).

The resent results indicate also perspective of more efficient reclamation of area contaminated by very high amount of toxic trace metals like Pb and Cd in result of irradiation of seeds of sunflower Helianthus (Dobrowolski and Kaleta, 2014) and great pumpkin Cucurbita maxima (Dobrowolski and Lisowska 2014) by empirically selected algorithm of laser light.

New perspective of significant increase of biomass production as source of biofuel are open in result of increase of laser photostimulation of seeds of Sorghum vulgar variety Sucrosorgo 506 resistance to low temperature during critical period of germination. This is climatic limiting factor in Central Europen countries for introduction this cereal for wide scale cultivation (Dobrowolski and Kozik 2011).

Other real perspective of increase bioenergy production may be connected with proper management of biodegradable waste (Horsek and Hrebicek 2014). 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 laboratory and experimental studies initiated and coordinated by Dobrowolski may be starting point for innovative international project focused on research-developing studies for optimization application Laser Biotechnology (as Polish priority on world scale) for more efficient biodegradation petrochemical pollutants and reclamation of contaminated areas including linkage to biomass and bioenergy production.

1.2. State of the Art in Application of Pyrolysis and other Technologies for an Efficient Production of Bio-Energy

Long term research experiences emphasize that pyrolysis is one of the alternative methods for municipal solid waste treatment, and this method offers more benefits. During the pyrolysis process, organic matter thermally decomposes in an environment that is devoid of any oxygen. A heat source is required for the pyrolysis process, yet no heat source is needed for gasification, inasmuch as this process is self sustaining thermally. When both gasification and pyrolysis processes occur at the same time, the gasification combustion reactions is able to provide the heat source needed for the pyrolysis process to execute the reactions. In this process no heat source outside of the gasification process is needed for pyrolysis. Thus, pyrolysis is the thermal decomposition of biomass occurring in the absence of oxygen. It is the fundamental chemical reaction that is the precursor of both the combustion and gasification processes and occurs naturally in the first two seconds. The products of biomass pyrolysis include biochar, bio-oil and gases including methane, hydrogen, carbon monoxide, and carbon dioxide.

Depending on the thermal environment and the final temperature, pyrolysis will yield mainly biochar at low temperatures, less than 450 ^{0}C, when the heating rate is quite slow, and mainly gases at high temperatures, greater than 800 ^{0}C, with rapid heating rates. At an intermediate temperature and under relatively high heating rates, the main product is bio-oil.

Pyrolysis can be performed at relatively small scale and at remote locations which enhance energy density of the biomass resource and reduce transport and handling costs. Heat transfer is a critical area in pyrolysis as the pyrolysis process is endothermic and sufficient heat transfer surface has to be provided to meet process heat needs. Pyrolysis offers a flexible and attractive way of converting solid biomass into an easily stored and transported liquid, which can be successfully used for the production of heat, power and chemicals (Tursunov et al, 2011; Tursunov, 2014 a, b.).

The recent review of biomass processing technologies, including pyrolysis is the subject of monographic book (Streznov and Evans 2015). Current trades of bio-energy production from biomass are supporting factor of our proposals for wide-scale application of improved pyrolysis to produce bio-energy from the biomass sources.

Based on above mentioned information we can infer that Application of eco-friendly Laser Bio-Technology is an immensely efficient mechanism for more effective production of biomass in deteriorated areas and it is an intelligent biomass supplier for bio-energy production via alternative clean technologies such as pyrolysis (e.g. gasification).

As well as, integration of innovative laser biostimmulation as a method of enhancement of biomass production in areas out of use with more efficient conversion of biomass into bio-energy by improved pyrolitic technology towards to sustainable development of many rural areas.

Proposed concept would be useful both for improvement environmental quality (more efficient treatment of wastewater, reclamation of deteriorated areas, increase of biomass production in energy plantations etc.) and at the same time contribute to increase biomass and bio-energy production. Extra biomass would be a source of energy for improvement life quality of inhibitors of rural areas by energy supply for cooling or heating system as well as hot water supplementation and bio-gas etc.

Poland has to pay penalty to EU in the result of renewable energy sources deficiency. At the same time Poland has vast areas out of use.

Wide scale application recommended by team “Eco-friendly Laser Bio-technology and efficient Pyrolytic method” could significantly contribute to solution of this problem. In the way reasonable from cost-benefit balance.

1.3 Recommendations for the Future

Our experiences would be also very useful for transfer of “Know-How” to some European countries and especially to many developing countries for both protection of bio-diversity and improvement of life quality of inhibitors of rural areas.

Training of young experts interested in introduction of this eco-innovation to their home countries seems to be the best way for contribution of common action following UNESCO program “Man and Biosphere” and Decade of Education on Sustainable Development as well as recommended by EU in October 2014 Biologically-based Green Economy as the top priority at university education in EU countries.

President of the International Clean Energy Consortium prof. G. Grob [who contributed with key note lecture at 14th International Conference on Sustainable Development and Ecoinnovation at AGH-UST in Krakow in 2012]; declared that he would like to develop cooperation in this field with interested Polish experts and their coworkers.

Real new perspective of very significantly increase of bioenergy production from common wood wastes and different sources of biomass produced by plants are connected with new result of basic studies carried out in leading on international scale team of experts in Japan (Nakazawa et al, 2013). The basic limiting factor of management these common in Poland and all over the world organic wastes is degradation of cellulose as significant component of each cell of plants. Therefore, practically very important fact is that this multidisciplinary team increased up to 6 times cellulose degradation activity [compare to hydrolyze cellulose by cellulases from cellulotic fungi and bacteria]. They applied biomimetic method and constructed innovative Nanocellulosomes from the biotinylated biocatalitic domain Carbohydrate-Binding Models [CBMs] of endoglucanase and processive endoglucanase on nanoparticles. The result of application of synthetic organelles was really important synergistic enhancement of cellulose degradation activity by CBMs clustered on selected nanoparticles [ibidem]. Leader of this team of Japanese expert found laser biotechnology as real perspective of father improvement of this new on international scale synthetic Nanocellulosomes and informed prof.Jan W. Dobrowolski that is open for cooperation. This ecoinnovation may be a key factor for increase efficiency of use of biomass and organic wastes for bioenergy production.Therefore introduction of relative to this perspective Joint Polish-Japanese Pilot Project is recommended.

This may be also contribution to increase fixation of CO_2 by large scale application of laser stimulation of cultivated plants. Therefore, this activity is complementary to activity focused on low carbon energy production coordinated (in Poland) by AGH University of Science and Technology.

2. Progress of Research Project

2.1 Materials and Methods for Proximate Analysis of Biomass

This research methodology consists of sampling selection method, sorting procedure and laboratory analysis to identify proximate analysis of biomass of the roses accommodated at Field Experiment (str. Mydlniki), the Faculty of Energy and Mechanical Enginering, University Agriculture in Krakow, Poland. Generally, there are two formal types of sampling and analysis methods based on ASTM D 5231-5292 and European Standard PN-EN.

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

2.2 Method of Biomass Characterization

2.2.1 Sampling of Biomass (Roses)

The procedure was applied for collecting the biomass based on the American Society for Testing and Materials (ASTM), the sampling was pick up of 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 group – 3x3 (times/sec) and 3) laser group – 3x9 (times/sec). Each group was weighted by using a weight balance and data was recorded.

Fig.1. Experimental Field – Biomass of Roses

Irradiation multiflorum rose cuttings were made in 2009 in the Department of Environmental Biotechnology and Ecology, University of Science and Technology in Krakow in cooperation with prof. J. W. Dobrowolski.

An apparatus Medical Laser D 68-1 emits red light with a wavelength of 672 nm and λ power of 20 mW. The use of two exposure times intermittent a) 3 x 3 seconds, and b) 3 x 9 seconds. Exposed seedlings were planted in spring of 2009, the spacing of 70 x 70 cm. leached brown soil.

Fig.2. Medical and Blue Diode Laser

In addition, biomass of the roses' stalks and leaves were separated in order to identify and to compare energetic value of each of them. As well as, other sort of proximate analysis has been applied individually both for stalks and leaves.

2.3 Proximate Analysis of Biomass Sample

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

2.3.1 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 2-3 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. The similar methodology for determination of moisture content has been used by Maoyun, et al. The percent moisture content was calculated as a percentage loss in weight before and after drying (ASTM 1998; Amin and Yang 2012, Edema et al, 2012).

% Moisture content = [(Wet Weight - Dry Weight)/Wet weight]x100% (1)

Fig.3. Lab Furnace used for determination of moisture content in the materials

2.3.2 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 4 minutes, timed with a stop watch. The similar experiments for moisture content determination have been done by a few scholars such as Amin and Yang (2012) and Edema et al. 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:

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

Fig. 4. Muffle Furnace used for determination of volatile matter, ash and fixed carbon content

2.3.3 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/cm^2 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:

% ash = weight of sample × 100 / weight of the sample
(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:

Fixed Carbon (Wt% wet basis) =100-(Wt% moisture content + Wt% Ash + Wt% volatile matter)   (4)

2.3.4 Calorific 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 (Reilly et al, 1982; Vessilind et al, 1981). 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.

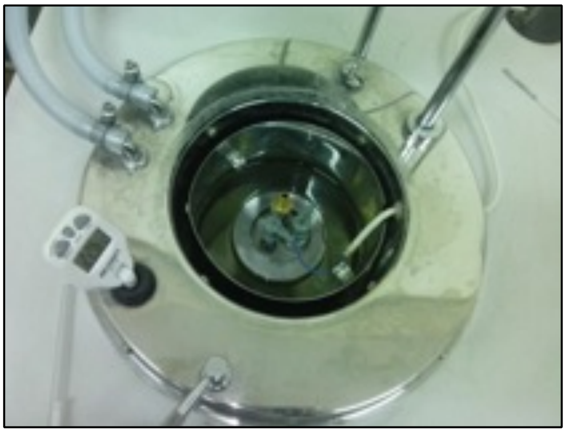


Fig. 5. Bomb Calorimeter used for determination calorific value (heating/energetic value) in the materials

2.4 Sample Preparation for Ultimate and Trace Elemental Analysis

Prepared woody biomass (roses) samples after proximate analysis have been prepared for ultimate and trace elemental analysis. Dry biomass sample was shredded into small particle size approximately 0.5 – 1 mm initially using mini shredder and after laboratory mill to shred the samples into smaller particles. Shredded biomass samples were then pressed by using manual presser in order to turn the samples into pill form (weight of sample pills – 0.4g). Following experiment has been investigated under requirement of the Laboratory for Trace Elemental Testing Materials, Jagelonian University, Krakow, Poland.

Fig. 6. Mini Shredder (right), Laboratory Mill (left) and Manual Presser used for shredding and pressing the of samples

Fig. 7. Prepared Sample for Ultimate and Trace Elemental Analysis

2.5 Results and Discussions

2.5.1Results from Proximate Analysis of Woody Biomass Samples of the Roses

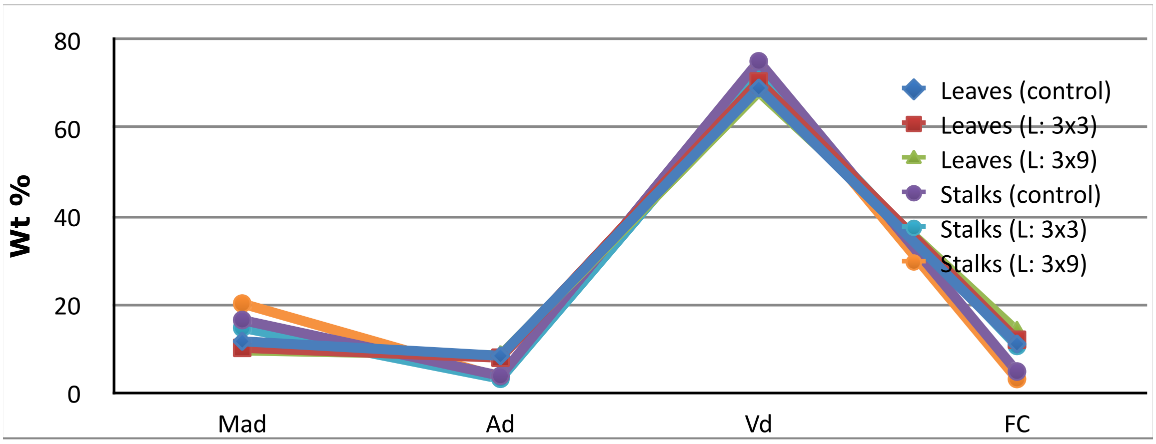
Proximate analysis involves determination of moisture content, volatile matter, ash content, fixed carbon and also calorific value (heating/energetic value) of composite sample. The analysis was according to ASTM and European Standards PN-EN methods. Results from proximate analysis were shown in Table 1.

Table 1. shows the proximate analysis of the biomass of roses (stalks and leaves) [3 groups: control, laser group 3x3 (t/sec) and 3x9 (t/sec)] used in this research. The table shows moisture content of leaves control (11.69 %), laser irradiated leaves group 3x3 (t/sec) (10.12 %) and laser irradiated leaves group 3x9 (t/sec) (9.52 %); stalks control (16.42 %), laser irradiated stalks group 3x3 (t/sec) (14.66 %) and laser irradiated stalks group 3x9 (t/sec) (20.15 %). 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. shows processed woody biomass of the samples: leaves control has volatile matter content (69 %), laser irradiated leaves group 3x3 (t/sec) (70.05 %) and laser irradiated leaves group 3x9 (t/sec) (68.12 %); stalks control (75.06 %), laser irradiated stalks group 3x3 (t/sec) (71.67 %) and laser irradiated stalks group 3x9 (t/sec) (73.36 %). Ash content: leaves control (8.31 %), laser irradiated leaves group 3x3 (t/sec) (7.88 %) and laser irradiated leaves group 3x9 (t/sec) (8.42 %); stalks control (3.77 %), laser irradiated stalks group 3x3 (t/sec) (3.11 %) and laser irradiated stalks group 3x9 (t/sec) (3.43); both parameters have influence on the pyrolysis and gasification characteristics (burning biomass technologies). Biomass of wood 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. The calorific value (heating/energetic value) of biomass of roses were obtained to be: leaves control (15.792 $MJ \cdot kg^{-1}$), laser irradiated leaves group 3x3 (t/sec) (16.425 $MJ \cdot kg^{-1}$) and laser irradiated leaves group 3x9 (t/sec) (16.015 $MJ \cdot kg^{-1}$); stalks control (16.923 $MJ \cdot kg^{-1}$), laser irradiated stalks group 3x3 (t/sec) (17.675 $MJ \cdot kg^{-1}$) and laser irradiated stalks group 3x9 (t/sec) (17.364 $MJ \cdot kg^{-1}$) based on the bomb calorimeter test.

Table 1: Proximate Analysis of Woody Biomass of the Roses

Parameters	Type of biomass						
	Measurement	Leaves control	Leaves 3x3 (t/sec)	Leaves 3x9 (t/sec)	Stalks control	Stalks 3x3 (t/sec)	Stalks 3x9 (t/sec)
M		11,69	10,12	9,52	16,42	14,66	20,15
A_d	I	8,45	7,53	8,48	3,20	3,43	3,54
	II	8,16	8,23	8,35	4,34	2,79	3,32
	Average	8,31	7,88	8,42	3,77	3,11	3,43
V_d	I	68,86	70,34	66,48	75,16	69,13	72,56
	II	69,14	69,75	69,75	74,95	74,22	74,15
	Average	69,00	70,05	68,12	75,06	71,67	73,36
FC [%]	Average	11	11,95	13,94	4,75	10,56	3,06
Q_i	I	15,801	16,938	16,021	16,939	17,845	17,434
	II	15,783	15,912	16,010	16,906	17,505	17,294
	Average	15,792	16,425	16,015	16,923	17,675	17,364
Q_s	I	16,717	16,034	16,932	17,844	18,764	18,353
	II	16,698	16,824	16,921	17,824	18,421	18,213
	Average	16,708	16,429	16,927	17,834	18,593	18,283

Mad - moisture content ; Ad - ash content; Vd - volatile content ; Qi - the calorific value; Qs - heat of combustion; FC – fixed carbon

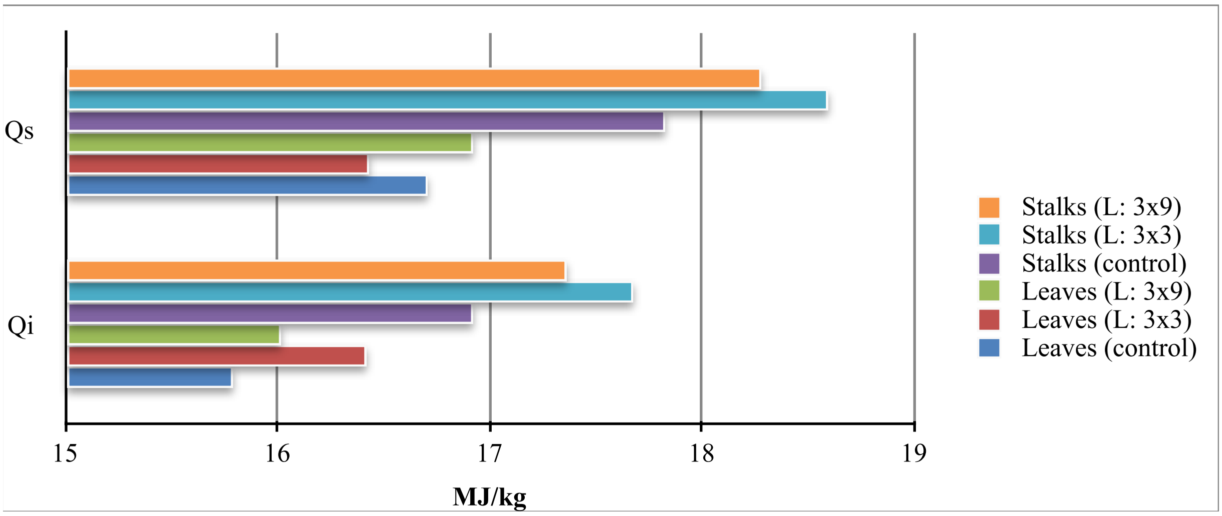


Mad - moisture content ; Ad - ash content; Vd - volatile content ; FC – fixed carbon

Fig.8. Comparative proximate analysis of biomass sample – leaves and stalks of Rose

Fig.8. illustrates the comparative results from proximate analysis of biomass sample – leaves and stalks of Roses (3 groups). Regarding to biomass leaves of roses, moisture

content in control group has shown 11.69 % which is slightly higher than other groups of leaves irradiated by laser. Ash content in leaves with 8.42 % in laser irradiated group 3x9 (t/sec) has shown similar results with ash content of 8.31 % in control group, while ash content of laser irradiated group 3x3 (t/sec) indicates a lower percentage 7.88 % comparing to control and laser irradiated 3x9 (t/sec) groups. The comparatively higher volatile matter content (70.05 %) was indicated in laser irradiated group 3x3 (t/sec) and comparatively higher fixed carbon content (13.94) in laser irradiated group 3x9 (t/sec). Regarding to biomass stalks of roses, moisture content in laser irradiated group has shown 20.15 % which is higher than other two groups, control (16.42 %) and laser irradiated 3x3 (t/sec) (14.66 %). The results from ash content in stalks of each group have shown a similar tendency. The comparatively higher volatile content (75.06 %) was indicated in control group and higher concentration of fixed carbon content with 10.56 % was indicated in laser irradiated group 3x3 (t/sec). Hence it can be inferred, that application of laser bio-technology has influence on some particular proximate characteristics of the samples comparing to control group.



Qi - the calorific value; Qs - heat of combustion;

Fig. 9. Comparative analysis of energetic value and combustion heat of the biomass sample – leaves and stalks of Rose

Fig.8. illustrates the comparative results of energetic value and combustion heat of the biomass sample – leaves and stalks of Roses (3 groups) obtained based on the bomb calorimeter test. Regarding to biomass leaves of roses, it can be seen that laser irradiated 3x3 (t/sec) and 3x9 (t/sec) indicate higher concentration of calorific value (heating/energetic value) – 16.425 MJ·kg^{-1} and 16.015 MJ·kg^{-1} than control group. Insignificant difference in concentration of the heat of combustion (16.927 MJ·kg^{-1}) is indicated in laser irradiated group 3x9 (t/sec). Regarding to biomass stalks of roses, it can be seen that laser irradiated 3x3 (t/sec) and 3x9 (t/sec) indicate higher concentration of calorific value (heating/energetic value) – 17.675 MJ·kg^{-1} and 17.364 MJ·kg^{-1} than control group (16.923 MJ·kg^{-1}). Concentration of the heat of combustion is indicated a similar tendency as calorific (heating/energetic value) in biomass samples of stalks. Higher concentration of combustion heat in

laser irradiated group 3x3 (t/sec) – 18.593 MJ·kg^{-1} and 3x9 (t/sec) – 18.283 MJ·kg^{-1}. Hence it can be concluded, that eco-friendly application of laser bio-technology is an essential technology (mechanism) for enhancement of energetic value in biomass plantations.

2.5.1 Results from Ultimate and Trace Elemental Analysis of Biomass Samples of the Roses

The results from ultimate and trace elemental analysis of woody biomass samples of the roses (each group) are going to be obtained and investigated by the beginning of next month (February 2015). These analyses will be carried out at chemical research laboratory of Jagellonian University; research laboratory of the Faculty of Ceramics, AGH University of Science and Technology; and research laboratory of University of Agriculture in Krakow.

2.6 Next Milestones of Research Project

2.6.1 Modification of Biomass Technology and Combustion Parameters (Process for Biomass Pyrolysis)

Since pyrolysis is endothermic, various methods to provide heat to the reacting biomass particles have been proposed: partial combustion of the biomass products through air injection. This results in poor-quality products. Direct heat transfer with a hot gas, the ideal one being product gas that is reheated and recycled. The problem is to provide enough heat with reasonable gas flow-rates. Indirect heat transfer with exchange surfaces (wall, tubes). It is difficult to achieve good heat transfer on both sides of the heat exchange surface (Elliott et al., 1991).

Direct heat transfer with circulating solids: Solids transfer heat between a burner and a pyrolysis reactor. This is an effective but complex technology. For flash pyrolysis, the biomass must be ground into fine particles and the insulating char layer that forms at the surface of the reacting particles must be continuously removed. The following technologies have been proposed for biomass pyrolysis. Fixed beds used for the traditional production of charcoal. Poor, slow heat transfer result in very low liquid yields (Bridgwater and Evans, 1993).

Augers: This technology is adapted from a Lurgi process for coal gasification. Hot sand and biomass particles are fed at one end of a screw. The screw mixes the sand and biomass and conveys them along. It provides a good control of the biomass residence time. It does not dilute the pyrolysis products with a carrier or fluidizing gas. However, sand must be reheated in a separate vessel, and mechanical reliability is a concern. There is no large-scale commercial implementation (Diebold, 1997).

Ablative processes: Biomass particles are moved at high speed against a hot metal surface. Ablation of any char forming at the particles surface maintains a high rate of heat transfer. This can be achieved by using a metal surface spinning at high speed within a bed of biomass particles, which may present mechanical reliability problems but prevents any dilution of the products. As an alternative, the particles may be suspended in a carrier gas and introduced at high speed through a cyclone whose wall is heated; the products are diluted with the carrier gas. A problem shared with all ablative processes is that scale-up is made difficult; since the ratio of the wall surface to the reactor volume decreases as the reactor size is increased. There is no large-scale commercial implementation (Elliott et al., 1991). Rotating cone: Pre-heated hot sand and biomass particles are introduced into a rotating cone. Due to the rotation of the cone, the mixture of sand and biomass is transported across the cone surface by centrifugal force. Like other shallow transported-bed reactors relatively fine particles are required to obtain a good liquid yield. There is no largescale commercial implementation.

Fluidized beds: Biomass particles are introduced into a bed of hot sand fluidized by a gas, which is usually a recirculated product gas. High heat transfer rates from fluidized sand result in rapid heating of biomass particles. There is some ablation by attrition with the sand particles, but it is not as effective as in the ablative processes. Heat is usually provided by heat exchanger tubes through which hot combustion gas flows. There is some dilution of the products, which makes it more difficult to condense and then remove the bio-oil mist from the gas exiting the condensers. This process has been scaled up by companies such as Dynamotive and Agri-Therm. The main challenges are in improving the quality and consistency of the bio-oil (Antonelli, 1989).

Circulating fluidized beds: Biomass particles are introduced into a circulating fluidized bed of hot sand. Gas, sand, and biomass particles move together, with the transport gas usually being a recirculated product gas, although it may also be a combustion gas. High heat transfer rates from sand ensure rapid heating of biomass particles and ablation stronger than with regular fluidized beds. A fast separator separates the product gases and vapors from the sand and char particles. The sand particles are reheated in fluidized burner vessel and recycled to the reactor. Although this process can be easily scaled up, it is rather complex and the products are much diluted, which greatly complicates the recovery of the liquid products (Maoyun et al., 2006).

The most significant parameters are temperature and heating rate. Under fixed bed conditions, with biomass as fuel, the bio-oil yield is exhibiting a peak value (55-75%) at moderate temperatures (400-550°C) and high heating rates (Encinar et al., 2000; Gonzalez et al., 2004; Onay et al., 2001; Acikgoz et al., 2004; Schroder, 2004). Char formation is minimised by high heating rates and high temperature (Williams et al., 1996; Gonzalez et al., 2003), while the carbon content in the charcoal and its heating value (based on the carbon content) are increasing with increasing temperature and slow heating rate (Encinar et al., 2000). The optimal conditions for char production will have to take into account the conflicting effect of temperature in order to produce a satisfying amount of charcoal with acceptable properties. The yields of each and every gas species of the pyrolysis gas-phase mixture are magnified by increasing temperature and high heating rates (Zabaniotou et al., 1994; Encinar et al., 1996; Williams et al., 1996; Barbooti, 1998; Schroder, 2004; Becidan et al., 2007), except carbon dioxide which is often reported to reach a plateau at high temperatures (800-900°C) (Encinar et al., 1996; Becidan et al., 2007).

According to above mentioned information and literature background, ongoing project is going to involve modified biomass technology such as pyrolysis. Critical parameters such as: temperature, heating rate as well as holding time, particle size, flow rate, reactor specification etc. are very important in pyrolysis technology.

2.6.2 Catalytic Bio-energy Production from Biomass

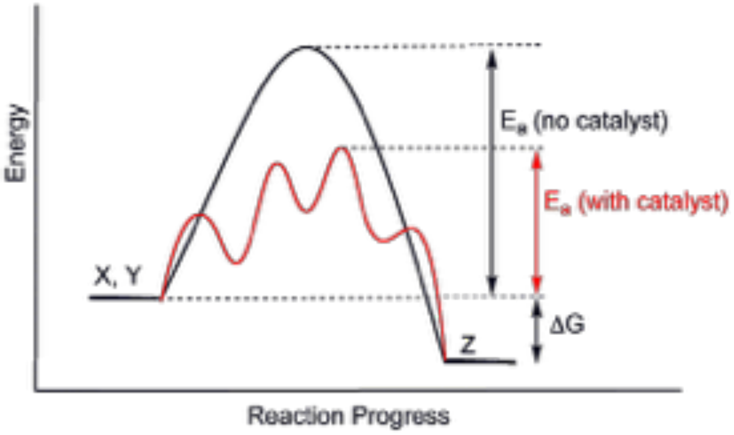


Fig. 10. Energy diagram the effect of catalyst in a hypothetical exothermic chemical reaction X+Z to give Z. (Robertson, 1970)

Generic potential energy diagram showing the effect of catalyst in a hypothetical exothermic chemical reaction X + Y to give Z. the presence of the catalyst opens a different reaction pathway (shown in red) with lower activation energy. The final result and the overall thermodynamic are the same.

Catalysts work by providing an (alternative) mechanism involving a different transition state and lower activation energy. Consequently, more molecular collisions have the energy needed to reach the transition state. Hence, catalysts can enable reactions that would otherwise be blocked or slowed by a kinetic barrier. The catalyst may increase reaction rate or selectivity, or enable the reaction at lower temperatures. This effect can be illustrated with a Boltzmann distribution and energy profile diagram.

In the catalyzed elementary reaction, catalysts do not change the extent of a reaction: they have no effect on the chemical equilibrium of a reaction because the rate of both the forward and the reverse reaction are both affected (see also thermodynamics). The fact that a catalyst does not change the equilibrium is a consequence of the second law of thermodynamics. Suppose there was such a catalyst that shifted equilibrium. Introducing the catalyst to the system would result in reaction to move to the new equilibrium, producing energy. Production of energy is a necessary result since reactions are spontaneous if and only if Gibbs free energy is produced, and if there is no energy barrier, there is no need for a catalyst. Then, removing the catalyst would also result in reaction, producing energy; i.e. the addition and its reverse process, removal, would both produce energy. Thus, a catalyst that could change the equilibrium would be a perpetual motion machine, a contradiction to the laws of thermodynamics (Robertson, 1970).

If a catalyst does change the equilibrium, then it must be consumed as the reaction proceeds, and thus it is also a reactant. Illustrative is the base-catalysed hydrolysis of esters, where the produced carboxylic acid immediately reacts with the base catalyst and thus the reaction equilibrium is shifted towards hydrolysis.

The SI derived unit for measuring the catalytic activity of a catalyst is the katal, which are moles per second. The productivity of a catalyst can be described by the turn over number (or TON) and the catalytic activity by the turn over frequency (TOF), which is the TON per time unit. The biochemical equivalent is the enzyme unit. For more information on the efficiency of enzymatic catalysis, see the article on Enzymes.

The catalyst stabilizes the transition state more than it stabilizes the starting material. It decreases the kinetic barrier by decreasing the difference in energy between starting material and transition state (Robertson, 1970).

Significant efforts have been put in to developing a cost effective method to eliminate tar in gasification/pyrolysis. Among all the proposed solutions, the use of catalysts in gasification/pyrolysis in-situ is the most promising approach. Catalyst used in biomass gasification can be categorized into three types; they are natural mineral catalyst, alkali metal catalyst and transition metal catalyst. Dolomite and olivine are two of the most commonly used natural mineral catalysts in biomass gasification.

In this project, our team is willing to use two different catalysts (dolomite and Ni-based catalysts) with needed supporters. For example, Orio et al. (1996) investigated four different dolomites (from Norte, Chilches, Malaga and Sevilla) for oxygen/steam pyrolysis and gasification of wood in a downstream catalytic reactor. The main chemical difference between the various samples has been the Fe2O3 content: the Malaga and Sevilla dolomites had low levels of Fe2O3 compared to the dolomites from Norte and Chilches. These samples were tested as catalysts at varying steam carbon ratios and temperatures ranging from 805 to 875 °C. Tar conversion was of the order of 95% for the Norte dolomite and the lowest conversion of 77% was found for the Sevilla dolomite. The gas yields were increased by the catalyst for all of the dolomites. The order of activity was: Norte-Chilches-Malaga-Sevilla. Interestingly, the surface areas of the Chilches and Norte dolomites were lower than those of the Malaga and Sevilla materials. The higher activity of the Norte and Chilches dolomites may be accounted for by their higher Fe2O3 contents and also by their larger pore diameters. The increase in gas yield was 10–20 vol.%, resulting in an increase of 15% in the “lower heating value” (LHV) of the gas. The hydrogen content of the gas increased by 4 vol.%, while the content of CO, CO2 and CH4 was relatively unchanged (Orio et al, 1996).

Vassilatos et al. (1992) researched calcined Glanshammar and Sala dolomites and accordingly, studied the effects of temperature, catalyst contact time and steam/carbon ratio. With the calcined dolomite increasing the temperature, it gave increased gas yields as with the results published by (Orio et al., 1996) and by (Delgado et al., 1997). The effect on the gas composition was also similar to that described by (Orio et al, 1996), this being an increase in the CO and CO2 content. The tar content decreased with increased catalyst loading, for both the Glanshammar and Sala dolomite (Vassilatos et al., 1992).

In a separate publication, Alden et al. (1996) reported an investigation of Glanshammar dolomite for the dry reforming of tars from a MSW gasifier. With calcined dolomite at 800 °C they found a 70% reduction of the tar content and a further 10–15% reduction at 900 °C. Tar yields were further decreased when the pressure was increased to 10 bar. Nevertheless, increasing the pressure also had the effect of raising the partial pressure of CO2, leading to carbonisation of the catalyst. At higher pressure, the function of the catalyst seemed to be more influenced by the partial pressure of the gaseous component as well as by the temperature. The increased pressure has the effect of increasing the residence time in the catalyst bed and hence of achieving a higher tar conversion (Alden et al., 1996).

Some experimental studies (Alden et al., 1996; Lammers, 1996) show the catalytic reforming of naphthalene over dolomite. The former group reported that the degree of conversion of naphthalene when passed over calcined dolomite at 800 °C varied with the composition of the carrier gas. A conversion of 96% was achieved using a carrier gas composition of 15% CO2 (balance N2), while only 79% conversion was achieved with 18% H2O in the gas. The resulting product gas compositions are shown in Table 2.

Table 2: The product composition (vol. %) when converting naphthalene over calcined dolomite at 800 °C (Alden et al, 1996; Lammers, 1996).

Carrier gas	**Gas Yields (vol %)**				**Dolomite**
	H2	**CO**	**CO**	**CH**	
86%N	1.6	2.8	16	0.67	**No**
86%N	2.9	15	4.6	0.13	**Yes**
82%N	11	4.3	1.9	0.22	**Yes**

Research experimental results by (Williams and Horne, 1994) who pyrolyzed biomass in the form of wood in a fluidized bed and upgraded vapors with catalysts in a fixed bed downstream. Furthermore, the details of the materials balance calculation at different reactor temperatures over the range of 750–900 °C were presented in Table 3. The overall material balance had a closure of 94.40%.

Table 3: Product yields and recovery from catalytic pyrolysis of MSW at different reactor temperature (Williams and Horne, 1994).

Temperature (	**Production yield**			**Recovery %)**
	Gas (wt %)	**Oil (wt %)**	**Char (wt %)**	
750	43.42	34.55	18.53	96.50
800	64.84	16.06	16.53	97.43
850	75.63	7.71	15.42	98.76
900	78.87	5.13	14.92	98.92
900	44.07	37.98	15.86	97.91

a Recovery (wt %) = Gas (wt %) + Oil (wt %) + Char (wt %).

According to (Tursunov, 2014b; Tursunov et al, 2011) temperature and the presence of catalysts are among the most important parameters that influenced the product yield from this process. Studies had also found that maximum pyrolytic oil can be obtained in the temperature range of 400 and 550°C. Due to the secondary reactions, the pyrolytic oil yield decreased parallel with gas amount increasing as temperature operated over 500°C.

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Experimental studies by (Tursunov, 2014b) indicates that MSW pyrolysis experiments at the reactor temperature of 750 °C with zeolite and calcined dolomite were carried out to study the influence of the catalysts on product yields, the product yields (gas, oil and char) from pyrolysis process which is presented in Table 4 and Fig. 11 respectively. As illustrated in Table 4 and Fig. 11, there was a remarkable increase in gas yield from 24.98 wt% with zeolite to 56.67 wt% with calcined dolomite. The oil yield decreased significantly from 36.35 wt% with zeolite to 10.88 wt% with calcined dolomite. It was because that the low oil yield resulted from oxygen removal to water, CO_2 and CO, from coke formation on the catalysts and from a significant increase in gas yield due to catalysis (Tsai et al, 2007). The char yield resulted 38.66 wt% with zeolite and 32.44 wt% with calcined dolomite. Furthermore, the details of the materials balance calculation at different reactor temperatures over the range of 200–750 °C were presented in Table 4. The overall material balance had a closure of ~ 99.99%.

Table 2.2 Product yields and recovery from catalytic pyrolysis of MSW at different reactor temperature (Williams and Horne, 1994).

Temperature (	**Production yield**			**Recovery %)**
	Gas (wt %)	**Oil (wt %)**	**Char (wt %)**	
750	43.42	34.55	18.53	96.50
800	64.84	16.06	16.53	97.43
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900	44.07	37.98	15.86	97.91

[a] Recovery (wt %) = Gas (wt %) + Oil (wt %) + Char (wt %).

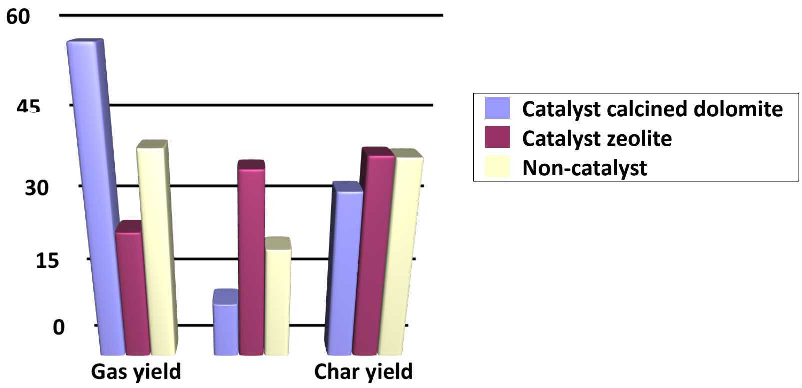

Fig. 11. Comparison of the overall gas, char and oil yield components of catalytic (calcined dolomite; zeolite) and non-catalytic pyrolysis (Tursunov, 2014b)

Thus, pyrolysis product yields profile confirmed that the catalysts promote depolymerization processes to yield a strong decomposition (low solid yield) or a strong liquid phase cracking (low liquid yield), and hence a higher hydrogen formation, since this gas was formed from liquid cracking.

A large number of studies have been conducted and reported in the literature using commercial nickel based catalysts in biomass gasification to promote steam-reforming, water–gas shift reactions and to eliminate tar. These studies can be categorized into two groups. The first group focuses on using nickel catalyst as the primary catalyst in the gasifiers and the second group concentrates on using it as the secondary catalyst in post gasification or post pyrolysis reactor.

There are several benefits of using nickel catalyst as the primary catalyst. First, nickel is one of the most effective transition metals for tar cracking and reforming. In addition to reducing the tar content, nickel catalyst improves the quality of the gaseous product in biomass gasification or pyrolysis. Second, it is economically attractive. Because both gasification and gas clean-up processes occur in-situ, no downstream reactor or extra heating is required, which results in lower plant capital and operating cost

2.6.3 Application of Computer Software for Controlling Internal Combustion Process

<u>Pocket Gas Analyzer and Theory of Operation</u>

The gas analyzer uses the Nondispersive Infrared Sensor (NDIR) measurement method. This method measures HC, CO and CO2 using fixed, non – scanning infrared light frequencies to characterize the gas concentrations. The concentration of a gas volume is a function of the quantity of gas molecules in the sample. The absorption of infrared light increases with the number of gas molecules in the light path. As the concentration of infrared-absorbing gas increases, the transmission of infrared light decreases. A basic automotive NDIR measurement system includes the following elements (PGA, 2007):

(i) Infrared source: An infrared light source produces a wide range of light at frequencies covering the infrared band extending into the visible spectrum. The infrared source is positioned on one side of a sample cell with an infrared detector on the other.

(ii) Sample Cell: The conditioned vehicle exhaust gas to be measured is transported through the sample cell that allows infrared light to pass through the sample.

(iii) Infrared Filters: An optical band pass filter is used to select a specific band of infrared light. The filter wavelength is based on the gas to be measured. Separate infrared filters are used in the measurement of HC, CO, and CO2 gas concentrations.

(iv) Infrared Detector: infrared light not absorbed by the sample gas is transmitted to infrared detectors. The detectors produce an output voltage that is proportional to the measured light.

(v) NOx and O2 are measured using a chemical cell that produces an output voltage that is proportional to the gas at the sample cell.

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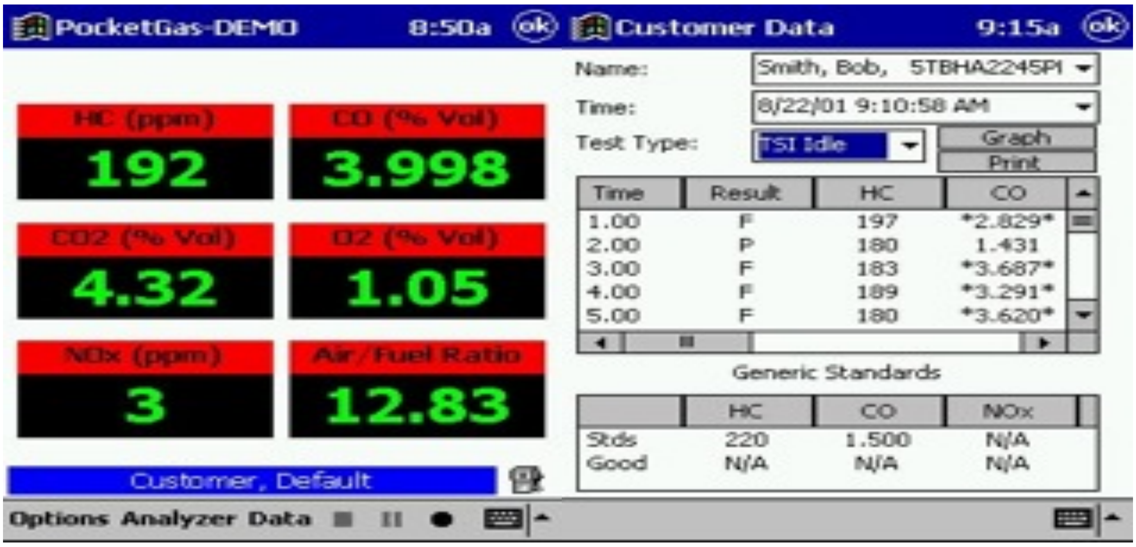

HC (ppm): 192
CO (% Vol): 3.998
CO2 (% Vol): 4.32
O2 (% Vol): 1.05
NOx (ppm): 3
Air/Fuel Ratio: 12.83
Customer, Default

Name: Smith, Bob, 5TBHA2245PI
Time: 8/22/01 9:10:58 AM
Test Type: TSI Idle

Time	Result	HC	CO
1.00	F	197	*2.829*
2.00	P	180	1.431
3.00	F	183	*3.687*
4.00	F	189	*3.291*
5.00	F	180	*3.620*

Generic Standards

	HC	CO	NOx
Stds	220	1.500	N/A
Good	N/A	N/A	N/A

Fig. 12. Pocket Gas analyzer and customer data

Fig. 13. Appearance and Naming of Gas Analyzer Pocket Gas.

It is very critically important to mention that Pocket PC of Gas Analyzer is significant factor to determine gas (HC, CO and CO2) in respected time and temperature during pyrolysis or combustion processes. The obtained results from Pocket PC can be easily copied into notebook and the range of gas yields could be investigated in different temperatures and times.

Catalyst Pilot Plant System Software

Catalyst Pilot Plant System software is smart software which can be applied catatest fixed-bed reactors. This software allows operating, setting all parameters (temperature, heating rate, holding time) and controlling a combustion reactor via computer. Below Fig. 14. Illustrates basic appearance of pilot plant system software on computer screen.

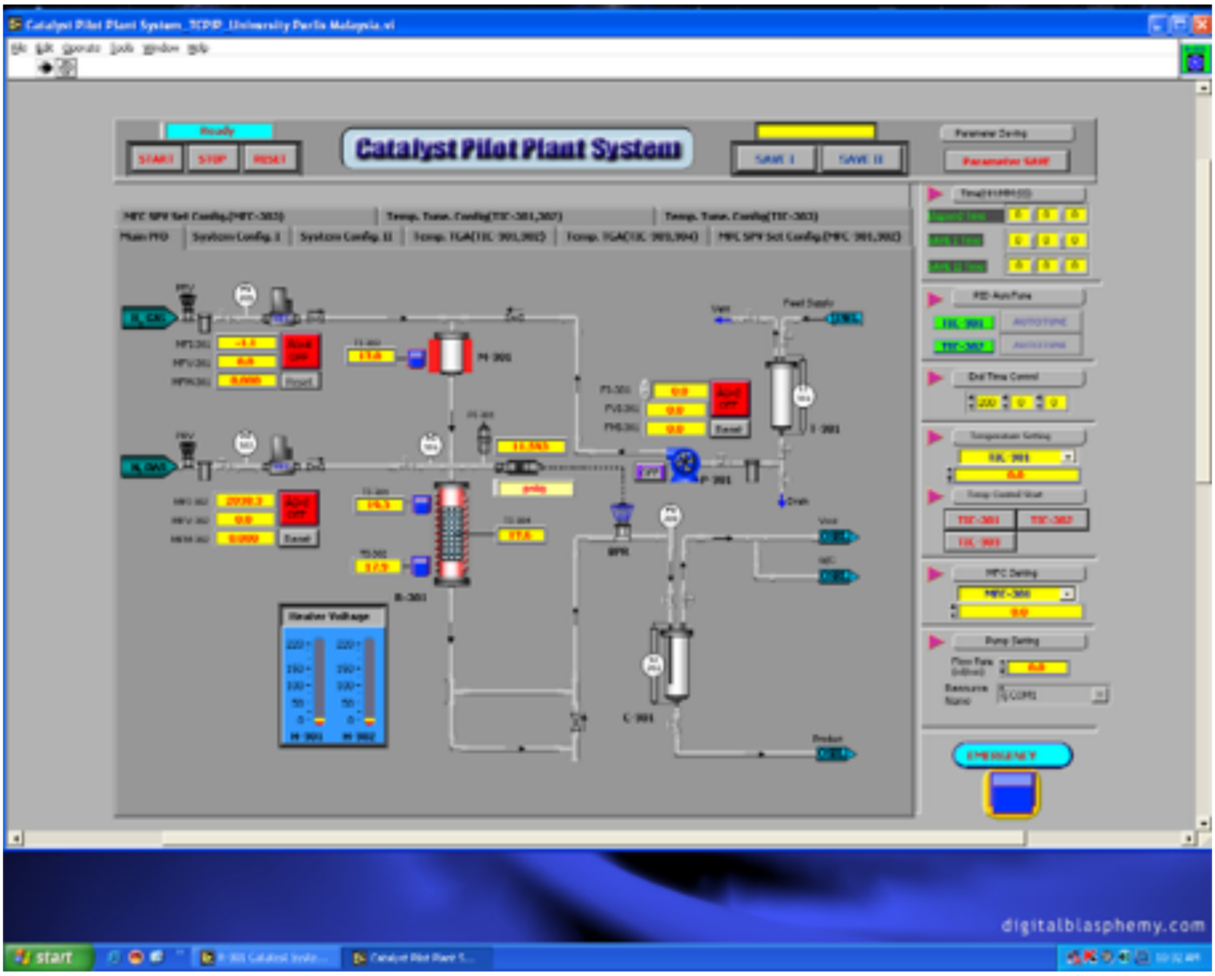

Fig.14. Catalyst Pilot Plant System Software

In this research project our team is willing to apply above mentioned computer software in order to enhance certainty and efficiency of combustion process. In addition, these software technologies assure the safety and accuracy during the reaction.

3. Conclusion and Future Work

This report has presented original finding related to different group of biomass of roses' characterization obtained from the experimental field of Krakow University of Agriculture, Krakow, Poland. The proximate analysis of biomass of the roses show that, application of laser biotechnology has significant impact on enhancing energetic value in plantations by using proper selected algorithms. Energy content of biomass leaves and stalks in laser irradiated groups 3x3 (t/sec) and 3x9 (t/sec) determined by bomb calorimeter are about 17.675 MJ·kg^{-1} (leaves of laser irradiated group) and 18.593 MJ·kg^{-1} (stalks of laser irradiated group), this is about 56 % of energy containing in coal. Wood Biomass has a good potential to be used as a fuel.

Dolomite is a suitable catalyst for the removal of hydrocarbons, which are evolved in the pyrolysis (gasification) of biomass. Dolomites increase gas yields at the expense of liquid products. With suitable ratios of biomass feed to oxidant, almost 100% elimination of tars can be achieved. The dolomite catalyst deactivates due to carbon deposition and attrition; however, dolomite is cheap and easily replaced. The catalyst is most active if calcined and placed downstream of the gasifier in a fluidised-bed at temperatures above 800 °C. The reforming reaction of tars over dolomite occurs at a higher rate with carbon dioxide than steam. Dolomite activity can be directly related to the pore size and distribution. A higher activity is also observed when iron oxide is present in significant amounts. Nevertheless, there is another type of catalyst (Ni based catalyst) which is active for reforming the methane present in the product gas and hence they are suitable catalysts if syngas is required. The main function of both catalysts dolomite and nickel is to act as a guard bed for the removal of heavy hydrocarbons prior to the reforming of the lighter hydrocarbons to produce a product gas of syngas quality.

Pyrolysis and gasification modified technologies is suggested to apply for optimization its efficiency limiting as much as possible the emissions and minimizing the maintenance requirements. Furthermore, a versatile combustion system which could be fed with different biomass fuels, from agricultural residues has to be attained. With all those resources the boiler should present the efficiency and zero emissions expected results. Most important parameters such as temperature and heating rate will be profoundly studied and most accurate temperature and heating rate for biomass combustion technologies will be announced. In addition, IT and ICT (based on computer software) technologies opens new opportunities for bio-energy production from biomass sources than typical manual way of production bio-energy. Major advantages of this technology enable the burning process of biomass by high accuracy, certainty and safety, as well as it accelerate the process of combustion thus saving extra time.

There are real perspectives of supplementation of plants by laser-stimulation for biomass production in areas out of use including reclamation places of deposition of wastes. Linkage between more efficient management of the natural environment with progress in production of bioenergy from renewable sources could contribute to development of sustainable labor market.

Future work and milestones include more profound research on modification of biomass technology and combustion parameters which are immensely essential in bio-energy production from biomass, research on newly developed catalytic bio-energy production from biomass of plants, comprehensive investigation the possible use of the organic fractions of woody biomass as an energy resource through a process of most effective and up to date combustion technology controlled by computer software programs (e.g. direct combustion, gasification, pyrolysis, hydrolysis etc) in a lab-scale reactors with newly discovered catalysts as well as bio-yield production efficiency from different group of biomass of plants generated by application of laser biotechnology.

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