



ENERGY DENSIFIED BIOCHAR PRODUCTION FROM SLOW PYROLYSIS OF REED CANARY GRASS

Ahmad Rafizan Mohamad Daud

Faculty of Chemical Engineering, Universiti Teknologi MARA (UiTM), Shah Alam, Selangor, Malaysia

E-Mail: ahmad2057@salam.uitm.edu.my

ABSTRACT

Biochar is a carbon-rich solid product derived from slow pyrolysis of organic matter. The high energy content biochar is storable and easily transported for used as fuels. This study investigated the effect of process parameters on the yield of energy densified biochar from slow pyrolysis of a perennial reed canary grass. The grass was pyrolysed in a batch reactor at temperatures between 300-700 °C and 1 atm, with heating rate varied at 5, 10 and 20 °C/min. A steady nitrogen flow of 2.0ml/min was continuously purged into the reactor throughout the pyrolysis process. The biochar product was characterized by proximate and ultimate analysis followed by the determination of its heating value. The onset of the reed canary grass transformation into biochar was observed at temperature of 350 °C. The yield of the biochar decreased as the final pyrolysis temperature was raised while the yield of bio-oils and gases improved with pyrolysis temperature. The optimum reed canary grass pyrolysis was found to occur between 400-500 °C. The biochar produced composed mainly of carbon, oxygen and hydrogen elements. The heating value of the carbon rich biochar was determined at 27-28 MJ/kg comparable to those of low rank coal. The energy densified biochar produced from reed canary grass has the potential to be utilized as a substitute to conventional fuel.

Keywords: biomass, slow pyrolysis, biochar, renewable energy, reed canary grass.

INTRODUCTION

The interest in energy derived from biomass has been overwhelming in recent years. The surge in the consumption of biomass energy is attributed to the ever growing threat of greenhouse gases emission (CO₂, SO_x and NO_x), the depletion of fossil fuels reserves and the belief that biomass is a CO₂ neutral source of energy (McKendry^a, 2002), (McKendry^b, 2002), (Koçar and Civaş, 2013). Modern biomass used as fuel are mostly derived from forestry residues, agricultural residues and dedicated energy crops (Goldemberg and Coelho, 2003), (Lewandowski *et al.* 2003). Energy stored in the biomass can be converted into useful heat, power and chemical feedstock.

The energy in the biomass which is stored in the chemical bonds can be recovered through pyrolysis process- one of the many thermo-chemical conversion methods available (Demirbas, 2001). The biomass undergoes thermal degradation process in the absence of oxygen at temperature ranging from 300 °C to 750 °C to produce high energy content products in the form of carbonaceous biochar, pyrolysis oils and combustible gases. This process is largely influenced by heating rate and temperature. Slow pyrolysis in which the heating rate ranging from 5 K/min to 100 K/min favours the biochar generation, while the fast pyrolysis with heating rate of around 600-1000 K/min produced mostly bio-oils and gases products (Bridgewater and Peacocke, 2000), (Bridgewater, 2012). Therefore process parameters, such as feedstock materials, particle size, temperature and heating rate can be adjusted to maximize the targeted products. In this regard, the maximum yields of biochar can be achieved using low pyrolysis temperatures and low heating rates.

Perennial grasses such as miscanthus (*miscanthus* spp.), reed canary grass (*phalaris arundinacea*), giant reed (*arundo donax*) and switchgrass (*panicum virgatum*) have been identified as suitable energy crops (Lewandowski, 2003), (Lemus *et al.* 2002). Previous pyrolysis studies using perennial grasses for biochar production indicates that pyrolysis temperature, heating rate and residence time are important in determining the biochar chemical structure, physical properties and stability (Ronsse *et al.* 2013), (Mimmo *et al.* 2014). The biochar produced is storable, high in energy content, transportable and easy to handle during post treatment processes as well as at final consumption stage. These attributes make biochar an attractive green substitute to the conventional fuel.

This study intends to explore the effect of temperature and heating rate on the yield of biochar produced from slow pyrolysis of reed canary grass. The grass is pyrolysed in a tubular fixed bed reactor at various combinations of final pyrolysis temperature and heating rate.

MATERIALS AND METHOD

Feed Materials

Biomass species used in this study was a course perennial reed canary grass (*phalaris arundinacea*). The grass was chopped to small pieces (2-3cm length) and air dried in the laboratory which reduced the RCG moisture content to approximately 10.5%. The grass sample consisted of chopped stems, leaves and inflorescences.

Experimental Setup

The slow pyrolysis experimental rig employed consisted of a main fixed bed reactor, refractory lined



electric heater, gas ducting, two condensers arranged in series and a gas discharge hood. The full arrangement of the pyrolysis apparatus is shown in Figure-1 below. The heat supplied is controlled by a temperature controller connected to the electric heater. The reactor is fixed with thermocouples at three different points namely T1, T2 and T3 whereby T1 measurement was taken as the final pyrolysis temperature. One set of thermocouples was installed at the inlet and outlet of the first condenser designated as T4 and T5. All five thermocouples are connected to the data logger. A gas analyser takes gas input after the outlet duct of the second condenser and it was also connected to the data logger.

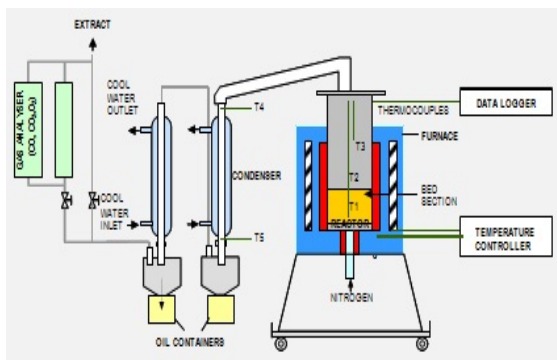


Figure-1. Slow pyrolysis experimental setup.

Slow Pyrolysis Experimental Procedure

Typically, 100 gms of grass was used for each runs. The grass sample was loaded onto the supporting wire mesh occupying approximately two third of the effective reactor volume. In the first set of experiment, the final pyrolysis temperature for each runs was set at 300 °C, 350 °C, 400 °C, 500 °C, 600 °C and 700 °C while heating rate was kept constant at 10 °C/min. The second set of experiment were conducted by varying the heating rate at 5, 10 and 20 °C/min at a fixed final pyrolysis temperature of 400 °C. Once the reactor reached the desired final pyrolysis temperature, the grass was held at that temperature for about an hour to allow it to be completely pyrolysed. The reactor was continuously purged with nitrogen gas at a fixed flow rate of 2 ml/min. The gases evolved were continuously condensed in the series condensers and pyrolysis oils were collected at the bottom of each condenser. Finally, the biochar was recovered after the experiment ended and characterized by proximate, ultimate and heating value determination. In addition, the gases evolution during slow pyrolysis of reed canary grass were recorded when the pyrolysis temperature was raised from 300 to 700 °C at 10 °C/min heating rate. Separate pyrolysis test was performed to specifically determine the compositions of the gases products which evolved from the pyrolysis process. The experiment for gas sampling analysis was held at 700 °C with 10 °C/min heating rate. Gases products were analysed using the gas analyzer and the gas chromatography (GC) unit.

RESULTS AND DISCUSSIONS

Effect of Temperature and Heating Rate on Product Yield

The mass yield results for reed canary grass pyrolysed at 10 °C/min heating rate is summarized in the Table 1 and illustrated in Figure-2. A high biochar yield of about 39.8% and 36.1% were recorded at low pyrolysis temperature of 300 °C and 350 °C respectively. Visual inspection conducted on the biochar samples produced under these conditions suggested that incomplete pyrolysis has occurred. The biochar appeared brownish when compared to biochar samples produced at 400 °C (Figure-3).

Table-1 also clearly shows that the reduction in the biochar yield were pronounced at temperatures below 400 °C indicating the released of water vapour, volatile matter and decompositions of hemicellulose and part of its cellulose and lignin content. Up to this stage, the biochar is thought to consist of mainly carbon and partially pyrolysed materials such as hydrocarbons of high molecular weight. As the pyrolysis temperature was increased, the biochar yield decreased while the liquid yield increased. The mass yield gained by the liquid fraction corresponded to the lost in the biochar mass yield. The drop in biochar mass yield is likely due to further decomposition of biomass cellulose and lignin components. According to Chen *et al.* (2003) above the pyrolysis temperature, almost all hemicellulose and cellulose are decomposed (Chen *et al.* 2003). Therefore, the remains in the form of biochar are mainly made up of lignin components. The normal biochar yield is in the range of 20% to 35% which corresponds to the percentage of lignin in most biomass species of around 20% to 40%. In this work, reed canary grass has been observed to be completely pyrolysed at temperatures of 400 °C and above. The biochar yield levelled off (circa. 32-28%) when the final pyrolysis temperature was raised between 400-700 °C. Generally higher pyrolysis temperature resulted in the pyrolysis of the high molecular weight components in the biochar through volatilization and thermal degradation processes.

Table-1. Products yield of RCG pyrolysed at 10 °C/min.

PYROLYSIS PARAMETERS			PRODUCT YIELD		
T1 °C	H.Rate °C/min	N ₂ ml/min	Char Wt. %	Liquid Wt. %	Gas+Loss Wt. %
300	10.0	2.0	39.88	25.81	34.31
350	10.0	2.0	36.14	23.31	40.55
400	10.0	2.0	32.02	29.05	38.93
500	10.0	2.0	28.47	29.03	42.50
600	10.0	2.0	30.39	31.59	38.02
700	10.0	2.0	28.01	31.96	40.03

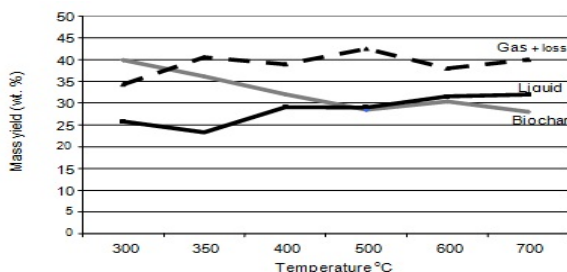


Figure-2. Products yield obtained at different pyrolysis temperatures (10 °C/min heating rate, sweep gas flow rate 2 ml/min).

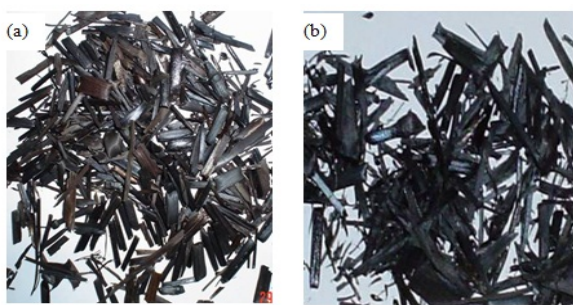


Figure-3. (a) Reed canary grass biochar pyrolysed at 300 °C and (b) biochar pyrolysed at 400 °C.

When pyrolysis temperature was increased from 300 to 700 °C, secondary reactions occurred. The semi pyrolysed high molecular weight hydrocarbons and the gases liberated at lower temperature undergo thermal degradation (Ravendrann *et al.* 1996) producing condensable thick black oils with strong smell. The condensation process took place in the two condenser arranged in series with cold water as cooling agent. The oil was a very complex mixture of water and various organic chemicals such as. The water content makes it detrimental for ignition while some other organic components are corrosive. The bio-oils were found to be composed of highly oxygenated compounds such as organic acids, esters, ethers, aldehydes, ketones, alcohols, furans and phenols with low nitrogen and sulphur content (Greenhalf *et al.* 2013). The presence of aliphatic and aromatic groups was also detected in the oil (Williams and Besler, 1996). In this work, the bio-oil produced was not characterized.

The non-condensable gases passed through the two condensers and released via the vent hood located just above the reactor. The gas+loses yield increased gradually with temperature from 34% to approximately 40% when the temperature was increased from 300 to 700 °C respectively. The figures presented in the Table-1 also includes loses that may occurred as the evolving gases travelled through the system to the exit point.

The effect of varying heating rate on product yield was further examined at 5 and 20 °C/min with pyrolysis temperature fixed at 400 °C as presented by Figure-4. It can be seen that the biochar yield was unaffected as heating rate was increased from 5

to 20 °C/min. Nevertheless, small movements in the yield of liquid and gas loss streams were observed where the liquid yield were slightly decreased while gas and loss streams were slightly increased with heating rate changed. Overall, the influence of heating rate on products yield was minimal.

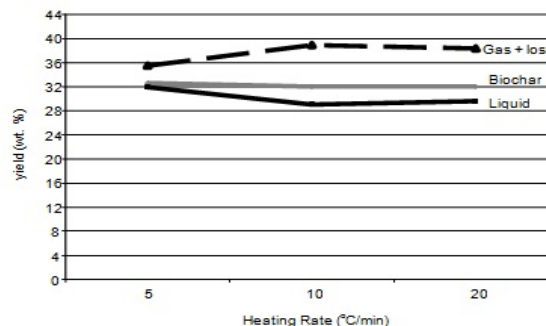


Figure-4. Mass yield at different heating rate for 400 °C final temperature.

Biochar Characterization –physicochemical Analysis

Biochar properties relates to pyrolysis process parameters of which it is produced. It provides critical information for process optimization and commercial viability of char production via slow pyrolysis process. The physicochemical properties of a reed canary grass biochar was accomplished through proximate and ultimate analyses. Moisture content, volatile matter content, ash content and fixed carbon content (proximate) were determined based on British Standard 1016 part 3 while the chemical compositions (ultimate) were determined based on the British Standard 1016 part 6.

The moisture content of the feed grass sample was determined at 10.5%. The reed canary grass biochar however showed a marked decrease in moisture content of under 3%. The ash and fixed carbon content increased with temperature while the volatile matter decreased as pyrolysis temperature was raised as illustrated in Figure-5. It is thought that the trend observed was related to the stages at which the reed canary grass was pyrolyzed. At temperature above 300 °C, vapours like CO, H₂, CH₄ and CO₂ were continuously given off. Also given off were water, acetic acid, methanol, acetone etc. (Williams and Besler, 1996). Tar starts to predominate as the temperature rises. This resulted in the drop of the volatile matter content of the char from 38% at 300 °C to just above 12% at 500 °C and an increased in the fixed carbon content from 48% to 68% respectively. Above 500 °C, the volatile matter, ash and fixed carbon content showed only little changes as pyrolysis temperature was further increased up to 700 °C. The transformation of raw reed canary grass to biochar was found to be completed at 500 °C. Biochar produced at this temperature contains some amount of tars. To drive off this tar, the carbonized material was subjected to higher pyrolysis temperature up to 700 °C. At this stage, the fixed carbon content of the biochar was approximately 73%. The ash content for the range studied increased from



approximately 11% at 300 °C to 15% at 350 °C and remained in the region of 15-18% there onwards. The ash content was rather high and may be attributed to foreign matters present in the raw reed canary grass.

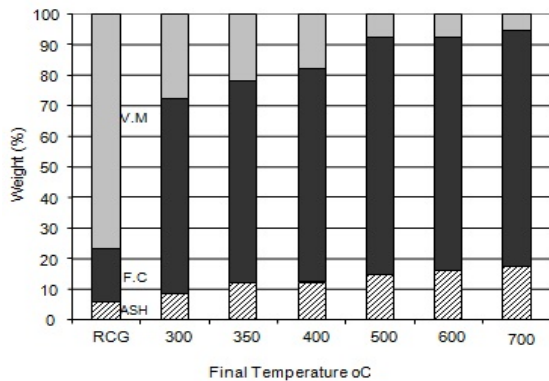


Figure-5. Reed canary grass biochar properties (ash, Volatile Matter-VM and Fixed Carbon-FC as wt.% basis).

Elemental compositional analysis indicated that the biochar mainly composed of carbon, hydrogen and oxygen elements. Figure-6 shows the trend of gradual enrichment of biochar with carbon and a loss in oxygen and hydrogen with temperature. The biochar was carbon rich, and depending upon the final pyrolysis temperature, the percentage gradually increased from 61% at 300 °C to slightly over 70% at 700 °C. Its carbon content improved with temperature while oxygen content depleted. The oxygen liberation rate was rather fast at pyrolysis temperatures below 500 °C but the rate slowed down beyond that temperature. The dropped in hydrogen is not significant if compared to the changes observed for both carbon and oxygen species. The decrease in the oxygen and hydrogen content can be associated with the loss of the volatile matter (Sharma *et al.* 2001), Jouiad *et al.* 2015).

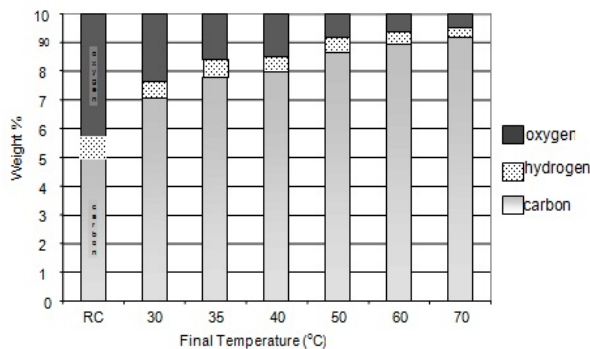


Figure-6. Elemental composition of reed canary grass derived biochar.

Heating value and energy yield

The calorific value of the raw grass sample was determined at 16.6 and 19.7 MJ/kg under 'as tested' dry

basis and dry ash-free basis respectively. The biochar produced by slow pyrolysis showed nearly 70% higher than the original heating value of the raw reed canary grass. It was however found that the calorific value of the biochar was not influenced by either pyrolysis temperature change or heating rate increment. Based on the 'as tested' dry basis results, the value obtained remained in the region of 25-28 MJ/kg for all pyrolysis parameters studied. With the elimination of ash from the char, the calorific value increased by nearly 30% of that 'as tested' dry basis to around 33MJ/kg. These values are comparable to that of lignite and coke. The heating value of reed canary grass biochar as compared to that of raw reed canary grass is presented in Figure-7.

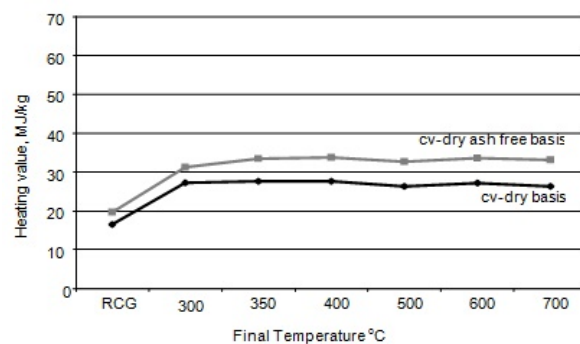


Figure-7. Heating value of RCG biochar obtained at pyrolysis temperature ranging from 300-700 °C.

Based on the char elemental compositions and heating value results, energy yield and carbon yield can be determined. The energy and carbon yield data is presented in Figure-8 together with the mass yield of biochar. It can be seen that both the energy and carbon yield were decreased with an increase in pyrolysis temperature. The energy yield was higher than carbon yield at pyrolysis temperature below 500 °C, while the carbon yield dominates at higher pyrolysis temperatures.

The Van Krevelen diagram was constructed to relate the hydrogen/carbon (H/C) ratio to that of oxygen/carbon (O/C) ratio. The point at upper right hand corner in the graph represents the unpyrolyzed reed canary grass sample. Both ratios for the biochars decreases with an increase in pyrolysis temperature. The H/C and O/C ratios were downed from 1.03 and 0.24 at 300 °C to ca. 0.40 and 0.04 at 700 °C respectively. The plots of these data gave linear relationship as per Figure-9. The linear relationship between the two ratios suggested that dehydration, decarboxylation and decarbonylation occurred during the pyrolysis of the reed canary grass (Beis *et al.* 2002). The dehydration process was predominant at lower temperature while decarboxylation and decarbonylation occurs mainly at higher temperature. As a result, the biochar became more carbonaceous at higher temperature.

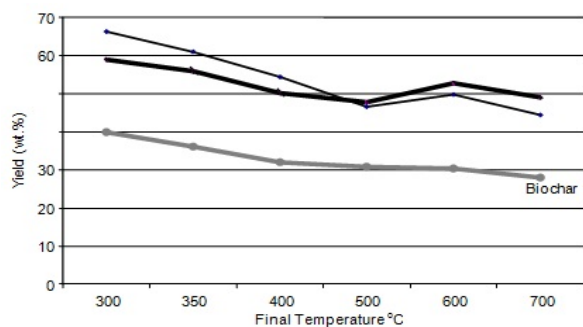


Figure-8. Biochar, energy and carbon yields obtained at pyrolysis temperature ranging from 300-700 °C.

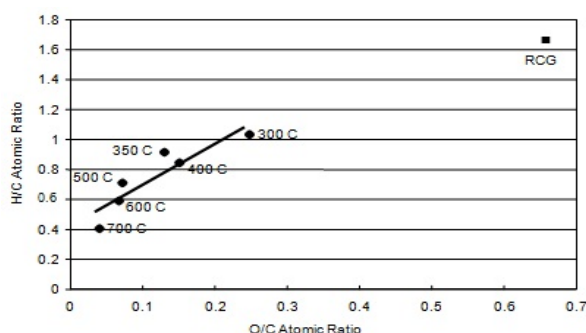


Figure-9. Relationship between H/C and O/C ratios of the biochar as represented by Van Krevelen diagram.

Gases Evolution

The composition of gases product which evolved from reed canary grass pyrolysis at final temperature of 700 °C with heating rate set at 10 °C/min was investigated. Six gas samples were taken for analysis at 300, 350, 400, 500, 600 and 650 °C. The data showed were obtained from Gas Chromatography (GC) analysis and combined with data taken from the gas analyzer unit for carbon monoxide (CO) and carbon dioxide (CO₂) species. Generally, the gas products mainly consist of H₂, CO, CO₂ and CH₄ with very low propane (C₃H₈) gas also presents. Two distinct gas evolution regions were observed. At temperature below 500 °C, CO and CO₂ were the main components liberated. As the temperature went higher up, H₂ displaced other gases as the major species evolved. Lower concentrations of CO, CO₂ and CH₄ were measured at high temperature.

The two stage products evolution from the slow pyrolysis process is related to the decompositions of cellulose, hemicellulose and lignin and has been shown by Shafizadeh (1982). Below 300 °C, cellulose decomposed thus produces mainly CO and CO₂. At higher temperature the decomposition of cellulose is by an alternative pathway where major gases evolved are CO, CO₂ and H₂. At 500 °C hemicellulose were decomposed to produce CO₂ and hydrocarbons like methane and propane. Above this temperature, second stage decomposition of cellulose and the hemicellulose residual occurred. Lignin decomposed throughout the temperature range investigated, producing CO and CO₂ at lower temperature

and at higher temperature releases the H₂ and CO. Figure-10 below shows the gas mole fraction of gases products evolved during the pyrolysis process of reed canary grass.

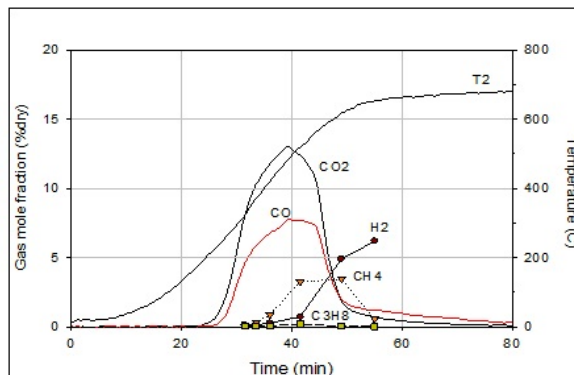


Figure-10. Gas mole fraction of gases products evolved during the pyrolysis process of reed canary grass (Temperature 700 °C and heating rate 10 °C/min).

CONCLUSIONS

This study revealed that reed canary grass biochar yield was highly influenced by the pyrolysis temperature while the effect of heating rate was less pronounced. The biochar yield decreases while the yields of bio-oils and gases were increased with pyrolysis temperature. The onset for pyrolysis transformation of raw reed canary grass to biochar was observed at temperature above 350 °C. The biochar produced became more carbonaceous in nature as the pyrolysis temperature was raised from 300-700 °C. Optimum biochar, energy and carbon yield were obtained at pyrolysis temperatures between 400-500 °C with heating rate fixed at 10 °C/min. The biochar which consisted of mainly carbon, hydrogen and oxygen exhibits high energy content comparable to those of low rank coal. The energy densified biochar has the potential to be used as a clean renewable fuel.

ACKNOWLEDGEMENTS

The author would like to express sincere gratitude to the Ministry of Education Malaysia and Universiti Teknologi MARA for the financial support provided through research funds 600-RMI/FRGS 5/3(25/2013). Special thanks to the Department of Chemical Engineering, The University of Sheffield for technical assistance throughout the project.

REFERENCES

- [1] McKendry P^a 2002. Energy from biomass (part 1): Overview of biomass. *Bioresource Technology*, Vol. 83, pp. 37-46.
- [2] McKendry P^b 2002. Energy from biomass (part 2): Conversion technologies. *Bioresource Technology*, Vol. 83, pp. 47-54.



- [3] Koçar G. and Civaş N. 2013. An overview of biofuels from energy crops: Current status and future prospects. *Renewable and Sustainable Energy Reviews*, Vol. 28, pp. 900–916.
- [4] Goldemberg J. and Coelho S. T. 2004. Renewable energy: traditional biomass vs. modern biomass. *Energy Policy*, Vol. 32, pp. 711-714.
- [5] Lewandowski I., Scurlock J. M., Lindvall E. and Christou M. 2003. The development and current status of perennial rhizomatous grasses as energy crops in the US and Europe. *Biomass and Bioenergy* Vol. 25, pp. 335 – 361.
- [6] Demirbaş A. 2001. Biomass resource facilities and biomass conversion processing for fuels and chemicals. *Energy Conversion and Management*, Vol. 42, pp. 1357-1378.
- [7] Bridgwater A. V. and Peacocke G. V. C. 2000. Fast pyrolysis process for biomass. *Renewable and Sustainable Energy Reviews*, Vol. 4, 1-73, Pergamon, Elsevier Science Ltd.
- [8] Bridgwater A. V. 2012. Review of fast pyrolysis of biomass and product upgrading. *Biomass and Bioenergy*, Vol. 38, pp. 68–94.
- [9] Lemus R., Brummer E. C., Moore K. J., Molstad N. E., Burras C. L. and Barker M. F. 2002. Biomass yield and quality of 20 switchgrass populations in Southern Iowa, USA. *Biomass and Bioenergy*, Vol. 23, pp. 433-442.
- [10] Ronsse F., Van Hecke S., Dickinson D. and Prins W. 2013. Production and characterization of slow pyrolysis biochar: influence of feedstock type and pyrolysis conditions. *Bioenergy*, Vol. 5, pp. 104–115.
- [11] Mimmo T., Panzacchi P., Baratieri M., Davies C. A., and Tonon G. 2014. Effect of pyrolysis temperature on miscanthus (*Miscanthus X giganteus*) biochar physical, chemical and functional properties. *Biomass and bioenergy*, Vol. 62, pp. 149-157.
- [12] Chen G., Andries J., Luo Z. and Spliethoff H. 2003. Biomass pyrolysis/gasification for product gas production: the overall investigation of parametric effects. *Energy Conversion and Management*, Vol. 44, pp. 1875-1884.
- [13] Raveendran K., Ganesh A. and Khilar K. C. 1996. Pyrolysis characteristics of biomass and biomass components. *Fuel*, Vol. 75, No. 8, pp. 987-998.
- [14] Greenhalf C. E., Nowakowski D. J., Harms A. B., Titiloye J. O. and Bridgwater A. V. 2013. A comparative study of straw, perennial grasses and hardwoods in terms of fast pyrolysis products. *Fuel*, Vol. 108, pp. 216–230.
- [15] Williams P. T. and Besler S. 1996. The influence of temperature and heating rate on the slow pyrolysis of biomass. *Renewable Energy*, Vol. 7, No. 3, pp. 232-250.
- [16] Sharma R. K., Wooten J. B., Baliga V. L. and Hajaligol M. R. 2001. Characterization of chars from biomass-derived materials: pectin chars. *Fuel*, Vol. 80, pp. 1825-1836.
- [17] Jouiad M., Al-Nofeli N., Khalifa N., Benyettou F., and Yousef L. F. 2015. Characteristics of slow pyrolysis biochars produced from rhodes grass and fronds of edible date palm. *Journal of Analytical and Applied Pyrolysis*, Vol. 111, pp. 183–190.
- [18] Beis S. H., Onay Ö. and Koçkar Ö. M. 2002. Fixed-bed pyrolysis of safflower seed: influence of pyrolysis parameters on product yields and compositions. *Renewable Energy*, Vol. 26, pp. 21-32.
- [19] Shafizadeh F. 1982. Introduction to pyrolysis of biomass. *Journal of Analytical and Applied Pyrolysis*, Vol. 3, No. 4, pp. 283-305.