Effect of Temperature and Heating Rate on the Char Yield in Sorghum and Straw Slow Pyrolysis

ALEXANDRU FILIPOVICI[1], DUMITRU TUCU[1], ANDRZEJ BIALOWIEC[3], PRZEMYSLAW BUKOWSKI[3], GEORGE CATALIN CRISAN[1], SEPTIMIU LICA[2], JAKUB PULKA[3], ARKADIUSZ DYJAKON[3], MARCIN DEBOWSKI[3]

[1] Politechnica University of Timisoara, Mechanical Engineering Faculty, Department for Mechanical Machines, Equipment and Transportation, 300222, Timisoara, Romania

[2] Politechnica University of Timisoara, Electronics and Telecommunications Faculty, Applied Electronics Department, 2 Victoriei Sq., 300006, Timisoara, Romania

[3] Wroclaw University of Environmental and Life Sciences, Faculty of Life Sciences and Technology, Institute of Agricultural Engineering, Wroclaw, Poland

Different approach to valorise the sweet sorghum using pyrolysis process to obtain valuable resources for energy production: bio-char, bio-oil and syngas are presented in the paper. In this study the influence of process parameters of slow pyrolysis on sorghum and straw were analysed. Temperatures used in the process varied from 400 to 800°C and heating rate parameter varied from 10°C . min^{-1} to 65°C . min^{-1}. The experiments were conducted using a lab scale slow pyrolysis reactor with electric heaters, equipped with a thermo balance analyzer to collect data of pyrolysis process. The achieved product yield can vary significantly according to the slow pyrolysis parameters. The temperature influenced more on the bio-char yield compared to the heating rate parameter. The highest bio-char yield (over 35% weight,) was obtained at 400°C and heating rate of 10°C . min^{-1}.

Keywords: Slow pyrolysis, bio-char, sorghum, thermal decomposition

Nowadays, may be observed a big concern on research, development and implementation of new suitable solutions to cover the increased energy demand, fossil fuel depletion or to avoid climate changes [1, 2]. Attention is also focused on high unexploited potential of biomass feedstock and residues (forestry and agriculture). Biomass feedstock include also sweet sorghum, an attractive fast grooving plant, with good adaptability to different climate conditions and soil, lower water and nutrient requirements and high productivity. These characteristics offer a great potential to generate bio-fuel [3-5].

Sweet sorghum has a short growth period, of 120-150 days, producing around 20-30 Mg . ha^{-1} of green biomass [3, 6].

Because of high moisture content (70–80%), sweet sorghum must be properly harvested and stabilized to avoid the fast deterioration that starts immediately after harvesting if ambient temperatures are above 15 °C [7-9]. After harvesting, different parts of the plant, such as stalks and leaves, are often used for burning.

Direct combustion of biomass has the advantage of its heating value, but also comes with a pack of disadvantages, like high moisture content and low density of material that leads to additional costs of drying, storage, transportation or palletizing [10].

An interesting option for the combustion of sorghum and straw is their conversion trough out the pyrolysis process into acceptable alternative bio-fuels.

Pyrolysis is a thermal decomposition process of solid vegetal material (sweet sorghum and straw in this case), performed in inert conditions, in the presence of a carrier gas, obtaining three phases: solid (bio-char), liquid (bio-oil, as condensable vapours) and gas (syngas).

If the purpose of biomass pyrolysis is to maximize the yield of liquid products, a low temperature, a high heating rate and a short gas residence time is required. To obtain a high gas yield, the pyrolysis process has to be carried out under conditions of high temperature, low heating rate and long gas residence time. For a high yield of char production, a low temperature, a low heating rate process and a longer residence time should be applied.

To use sorghum and straw as an alternative carbon source for producing bio-fuels, the studies on the effects of pyrolysis process conditions are required, in order to maximize the yields of the most economically valuable products.

In addition to the energetic value and use for energy production, bio-char from biomass can be applied to soil as fertilizer, to improve the soil properties [11].

The main objective of this study was to investigate the effects of thermal treatment conditions of sorghum and straw in pyrolysis, focusing on qualitative and quantitative characterization of bio-char yield, in presence of carbon dioxide stream.

Experimental part

Materials

The agricultural waste from a sorghum plantation and straw were used as the feedstock in this study:

- sweet sorghum, 3 years age, grinded at 1 mm, particle medium diameter;
- straw grinded at 2-3 mm, particle medium diameter.

The materials were initially dried in oven, 24 h at 105°C, in order to avoid the heating process efficiency drop during pyrolysis caused by water vaporization [12, 13].

Pyrolysis Equipment

Several slow pyrolysis experiments were carried out in an electrically heated fixed bed reactor. The PID (Proportional Integral Derivative), controller using the thermocouples installed in the reactor, enabled to precisely set the required heating rate and the final temperature of the process.

In order to determine the mass losses during the slow pyrolysis, the biomass sample is placed in a special cuvette, located on the analytical balance. The process parameters,

* email: tucusalix@gmail.com

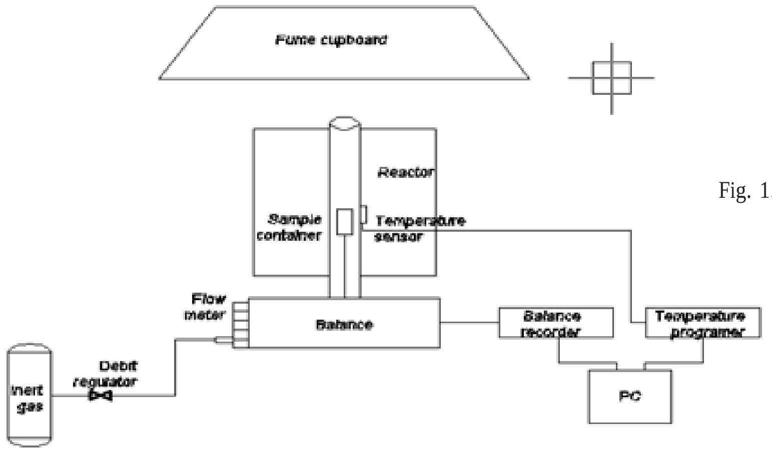

Fig. 1. The construction of the experimental stand for pyrolysis

as well as mass change, are registered by a computer. Based on collected data, specific diagrams were drawn.

The inert atmosphere inside of the reactor is assured by CO_2 under atmospheric pressure. The schematic diagram of the experimental stand is depicted in figure 1.

Experimental procedure

Experimental investigation consisted in two sets of experiments, to determine temperature effect, heating rate effect and study the thermal decomposition, as follows:

- to determine temperature effect, the reactor and the biomass sample (1.2 g), were externally heated at four levels of temperatures (400, 500, 600, and 800°C), with a 10°C’Šmin^{-1} heating rate; Once the temperature inside the reactor reached the set value, the sample of the material was maintained in the given conditions until no weight lost appeared;

- to determine the heating rate effect, the reactor with the 1.2 g biomass sample was externally heated, four times, with different heating rates (10°C . min^{-1}, 20°C . min^{-1} , 40 °C . min^{-1}, 65 °C. min^{-1}) at 800 °C each run. Once the temperature inside the reactor reached the set value, the sample of the material was maintained in the same conditions until no weight lost appeared. Vegetal material mass, *m*, and bed centre temperature, *t*, were continuously recorded as a function of heating time. For each experiment, 80 mL . min^{-1} CO_2 gas flow rate was maintained.

The bio-char yield during pyrolysis process was calculated according to following equation:

$$X_{char} = \frac{m_2}{m_1} \cdot 100\% \qquad (1)$$

where:

X_{char} – biochar yield, % mass.

m_1 – initial mass of the raw (dry) material before pyrolysis, g.

m_2 – final mass of the biochar after pyrolysis, g.

Results and discussions

Temperature and heating rate effect

In figures 2 and 3 are revealed diagrams concerning the effects of temperature and heating rate on the char yield of sorghum.

From the evolution of vegetal materials during the process we can observe the main stages of the pyrolysis process. At temperatures lower than 180°C, mass lost occurs from drying stage, with release of the H_2O contained in the raw material.

Between 180 and 280°C we can observe mass lost, due to depolymerisation and torrefraction specific reactions, resulting compounds such as CO, CO_2, acetic acid or extractives.

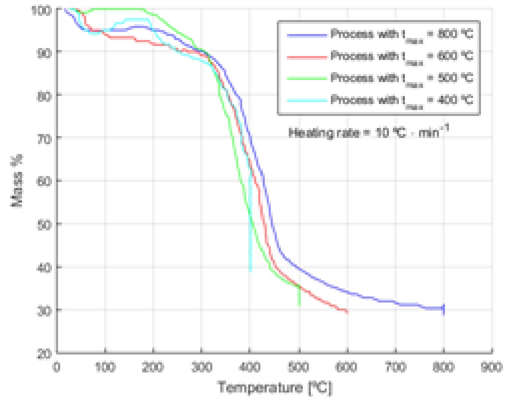

Fig. 2. Evolution in time of sample sorghum mass during pyrolysis at different temperatures

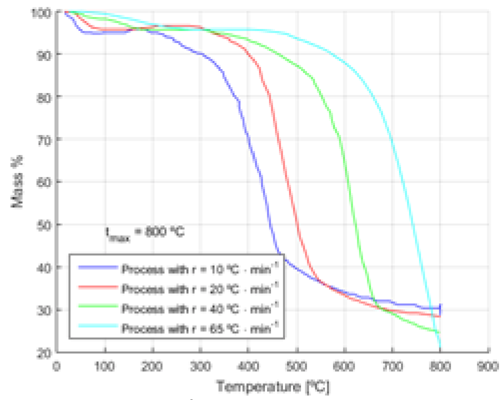

Fig. 3. Evolution in time of sorghum mass sample during pyrolysis on different heating rates

Between 280-500°C, there are endothermic reactions, specific for devolatilization with organic components, tars, CO, CO_2. In this range of temperatures, the highest char yield can be obtained with lower energy consumption.

Increasing temperature of the process from 500 to 700°C, the volatile components are decomposed, leading subsequently to gas yield increase.

At temperatures higher than 700°C, previous studies developed on biomass pyrolysis have shown that the increased temperature decreases the char yield, primarily due to gasification reactions, that occurs at higher temperatures [14].

Heating rate has an important influence on the process. At low temperature and higher heating rate, less water was lost by evaporation, leading to higher gasification reaction with lower char yield.

Variation curves, proved the influence of the two process parameters on the char yield, showing that maximum char production is obtained at lower temperatures and heating rates.

Process modelling

For quantitative characterization of pyrolysis char yield, experimental data plotted in figures 4 and 5, were employed

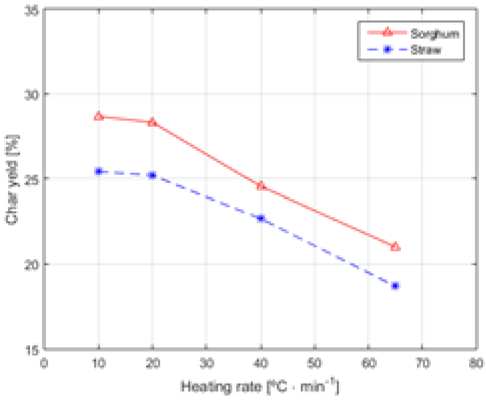

Fig. 4. Experimental data at different heating rates

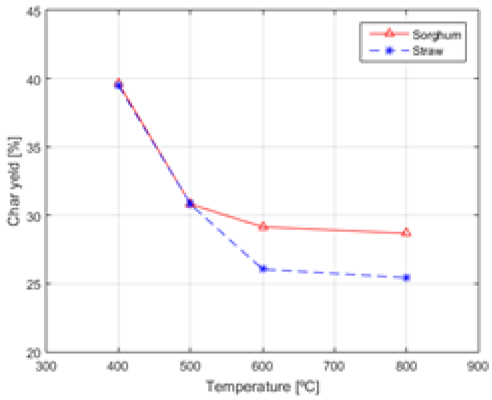

Fig. 5. Experimental lata at different final process temperature

in a mathematical model using a multiple regression analysis.

The multiple linear regression was used to establish the dependences between the char yield, final process temperature and heating rate, by fitting a multiple linear equation to collected data [15].

Formally, the model for multiple linear regression was:

$$X_{char} = p_1 + p_2 \cdot X_t + p_3 \cdot X_r \quad (2)$$

where:

X_{char} – biochar yield, % mass.

X_t – final process temperature, °C.

X_r – heating rate, °C . min^{-1}.

p_1, p_2, p_3 – estimated parameters of the population regression line.

The model is expressed as: Data = Fit + Residual, where the *Fit* term represents the expression: $p_1 + p_2 \cdot X_t + p_3 \cdot X_r$

The *Residual* term represents the deviations of the observed values X_{char}.

In table 1 are presented the results from the analysis of variance (ANOVA), to determine the significance of regression analysis for sorghum and straw.

In table 2 is presented overall regression accuracy for tested material.

Characteristic values of coefficients were determined to obtain the mathematical model witch predicts the char yield, as a variable of temperature and heating rate:

Sorghum:

$$X_{char} = 45.1552 + (-0.0201) \cdot X_t + (-0.1183) \cdot X_r \quad (3)$$

Straw:

$$X_{char} = 47.9579 + (-0.0281) \cdot X_t + (-0.0922) \cdot X_r \quad (4)$$

As we compare the probability level of the parameters heating rate and temperature, we can observe that pyrolysis temperature has a much more significant impact on the bio-char yield, compared to the heating rate parameter, due to the pyrolysis process reactions.

This state is accurate due the fact that in our experiments, the standard deviation and significance level of regression have a quite small value.

In table 3 is presented the reliability of the regression's X_{char} – intercept and parameters of the char yield regression line for sorghum and straw.

Table 1
ANOVA STATISTICS

Material		df	SS	MS	F	Significance F
Sorghum	Regression	2	166.474	83.237	9.660	0.029425976
	Residual	4	34.467	8.617		
	Total	6	200.944			
Straw	Regression	2	224.3767	112.1884	11.2849	0.022664389
	Residual	4	39.7659	9.9415		
	Total	6	264.1426			

Table 2
REGRESSION STATISTICS PARAMETERS

	Sorghum	Straw
Multiple R	0.9102	0.9217
R Square	0.8285	0.8495
Adjusted R Square	0.7427	0.7742
Standard Error	2.9356	3.1531

Table 3
STATISTICS COEFFICIENTS

Material		Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Sorghum	Intercept	45.1552	5.1039	8.8472	0.0009	30.9846	59.326
	Temperature	-0.0201	0.0085	-2.3659	0.0772	-0.0436	0.0035
	Heating rate	-0.1183	0.0677	-1.747	0.1556	-0.3063	0.0697
Straw	Intercept	47.9579	5.4820	8.7483	0.0009	32.7375	63.1783
	Temperature	-0.0281	0.0091	-3.0856	0.0367	-0.0534	-0.0028
	Heating rate	-0.0922	0.0727	-1.2683	0.2735	-0.2942	0.1097

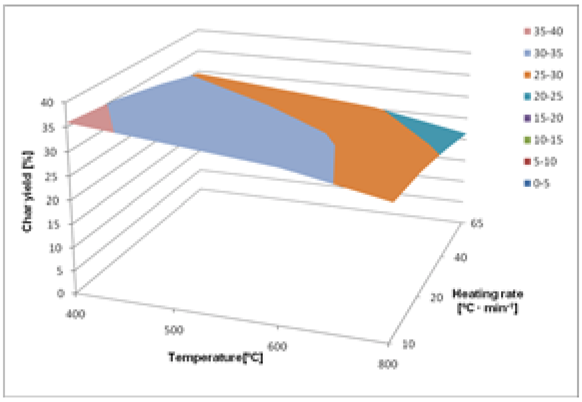

Fig. 6. 3D Mathematical model representation of sorghum pyrolysis char yield

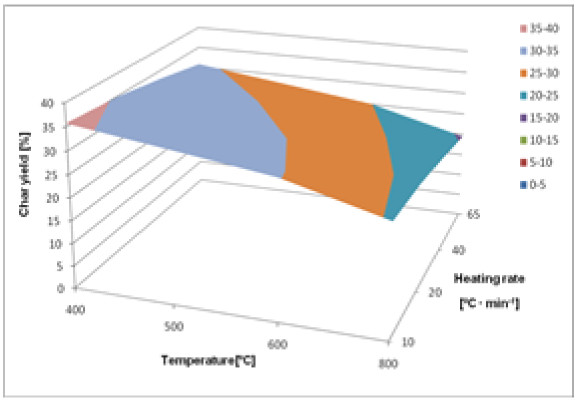

Fig. 7. 3D Mathematical model representation of straw pyrolysis char yield

Fitting model

Using the mathematical model described above, data matrix was determined, to express the process factor dependence, illustrated in figures 6 and 7. For both materials, the maximum altitude on z axis (char yield), is obtained for the following set of parameters: 10°C . min^{-1} heating rate and 400°C temperature.

In order to observe the similarity of biomass materials, correlation between two sets of data in similar experiment, for sorghum and straw has been calculated. Population Pearson correlation coefficient between X_{straw} and $X_{sorghum}$, has been determined using the following formula:

$$R_{XstrawXsorghum} = \frac{n \cdot \sum X_{straw,i} \cdot X_{sorghum,i} - \sum X_{straw,i} \cdot \sum X_{sorghum,i}}{\sqrt{n \cdot \sum X_{straw,i}^{2} - \left(\sum X_{straw,i}\right)^{2}} \cdot \sqrt{n \cdot \sum X_{sorghum,i}^{2} - \left(\sum X_{sorghum,i}\right)^{2}}} \quad (5)$$

The correlation in the experiment with constant heating rate and different final temperatures was 97.96%. In the second experiment, with different heating rate and constant final temperature, the correlation was 99.13%.

The global correlation between experiments was 98.46%, implying that similar phenomena during pyrolysis are conducted for both biomasses. Sorghum and straw could be used in the same pyrolysis equipment, under the same process conditions for maximal char yield production.

Conclusions

Product yields, obtained during the thermal transformation, depend on different factors that influence their composition and properties. The most important factors are: raw material properties, pyrolysis equipment type, process parameters (heating rate and temperature), residence time, carrier gas type and flow.

A series of experiments were conducted in order to study the behaviour of sorghum and straw during the pyrolysis process. Considering the process factors: final temperature and heating rate, a mathematical model was determined, using multiple regression analysis.

Using the obtained mathematical models, we may predict the char yield, under any given temperature and heating rate parameters, leading to optimization of pyrolysis process in fixed bed reactors.

In order to compare sorghum characteristics with a common type of biomass, correlation between two sets of data from similar experiment, for sorghum and straw, has been calculated.

Comparing the values from mathematical model, similar behaviour of the pyrolysis effect on the char production, can be observed for both vegetal materials. Maximum char yield is 39.46 % for sorghum and 39.66 % for straw.

Similar results were presented by Yan Q. et al., where pyrolysis char of pine had a maximum value of 35.5 % at 450°C [16]. A higher char yield was obtained on the Bamboo, where at 400 °C pyrolysis temperature, 45 % of char was produced [17].

The mathematical model can predict product yield under conditions of temperature and heating rate and can facilitate the design, optimization and operation of fixed bed reactors.

Pyrolysis biochar could become an efficient product for energy production and soil improver, with an important contribution on reduction of green gas effect [18].

Acknowledgements:This work was partially supported by the strategic grant POSDRU/159/1.5/S/137070 (2014) of the Ministry of National Education, Romania, co-financed by the European Social Fund – Investing in People, within the Sectoral Operational Programme Human Resources Development 2007-2013 and cross-border grant Partnership for promoting green energy in the rural area of the Romanian-Serbian cross-border region – GEROS, MIS ETC code:1414.

Nomenclature

df – degree of freedom (ANOVA)
F – F-test statistic coefficient (ANOVA)
m_1 – initial mass of dry material, placed intro reactor, g
m_2 – final mass of the obtained char (after pyrolysis), g
MS – mean of squares (ANOVA)
p_1 – parameter estimation for the intercept (regression)
p_2 – parameter estimation for the temperature influence (regression), 1 . $^oC^{-1}$
p_3 – parameter estimation for the heating rate influence (regression), min.$^oC^{-1}$
R – statistical correlation coefficient
SS – sum of squares (ANOVA)
X_{char} – mass percentage of biochar yield from initial biomass material, %
$X_{shorgum}$ – biochar yield from shorgum, %
X_{straw} – biochar yield from straw, %
X_r – heating rate used during pyrolysis process, .^{o}C. min^{-1}
X_t – final temperature of pyrolysis process, .^{o}C

References

1.TUCU, D., GOLIMBA, A-G., SLAVICI, T., **38th** I. Symp. on Agr. Eng. Opatija, 2010, p. 455-462.
2.TUCU, D., HOLLERBACH, W., **39th** I. Symp. on Agr. Eng. Opatija, 2011, p. 171-178.
3.MAO, Y., LI, J., LI, S., CHANG, S., ZHAO, G., Fuel, **144**, 2015, p. 90-95.
4.GNANSOUNOU, E., DAURIAT, A., WYMAN, C. E., Biores. Techn., **96**, 2005, p. 985-1002.
5.LI, S., LI, G., ZHANG, L., ZHOU, Z., HAN, B., HOU, W., App. Energy, **102**, 2013, p. 260-265.
6.WU, X. R., STAGGENBORG, S., PROPHETER, J. L., ROONEY, W. L., YU, J. M., WANG, D. H., Ind. Crops and Prod., **31**, 2010, p. 164-170.
7.ZEGADA-LIZARAZU, W., MONTI, A., Bioenerg. Res., **8**, 2014, p. 450-458.
8.WU, X., STAGGENBORG, S., PROPHETER, J. L., ROONEY, W. L., YU, J., WANG, D., Ind. Crop Prod., **31**, no. 1, 2010, p. 164–170.
9.BLUDAU, D. A, **5th** E. C. Conf. biomass for energy and ind., Policy, Environment, Prod. and Harvest. (Lisbon, Portugal), 1, 1990, p. 1260–1266.
10.HONUS, S., BUKOWSKI, P., **4th** I. C. on Frontiers of Manuf. and Design Sci., App. Mech. and Mat., 496-500, 2014, p:947-952.
11.WICNIEWSKI, D., GOLASZEWSKI, J., BIALOWIEC, A., Arch. of Environmental Protection, **41**, no. 3, 2015, p. 70–75.
12.KHOR, K. H., ZAINAL, A. Z. A., LIM, K. O., J. of Oil Palm Research, **21**, 2009, p. 577-587.
13.NOOR, N. M., SHARIFF, A., ABDULLAH, N., Iranica J. of Energy & Environment (Spec. Issue on Environmental Tech.), **3**, 2012, p. 60-65.
14.ENCIANAR, J. M., GONZALEZ, J. F., GONZALEZ, J., Energy Fuels, **23**, no. 9, 2000, p. 4605-4611.
15.PREACHER, K. J., CURRAN, P. J., BAUER, D. J., J. of Edu. and Behavioral Stat., **31**, no. 4, 2006, pp. 437-448, doi: 10.3102/10769986031004437.
16.YAN, Q., TOGHIANI, H., YU, F., CAI, Z., ZHANG, J., Forest Prod. J., **61**, no. 5, 2011, p. 367-371
17.HERNANDEZ-MENA, L. E., PÉCORAA, A. A. B, BERALDO, L. A., Chem. Eng. Trans., **37**, 2014, p. 115-120.
18.PARVULESCU, O. C., DOBRE, T., CEATRA, L., IAVORSHI, G., MIREA, R., Rev. Chim. (Bucharest), **62**, no. 1, 2011, p. 89

Manuscript received: 15.12.2016