MECHANICAL AND THERMAL PRE-TREATMENT OF BIOMASS FOR THE THERMOCHEMICAL CONVERSION

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This paper presents investigations on some residual biomass kinds and analysis mechanical and thermal pre-treatment approaches to improve thermochemical conversion process. Four different biomass samples were dried, mechanical grinding and sieving to decrease the moisture content and particle size to increase conversion efficiency. Samples had an initial moisture content of >10%, after drying all samples have a similar humidity (≈5%). A grinding time of 5-10 minutes has proven to be sufficient to obtain a high fraction of particle size less than 1mm, more effective for thermochemical conversion. This pre-treatment has improved the yield, the smaller particles lead to a higher gas fraction.

Keywords: residual biomass; drying; mechanical pre-treatment; grinding; sieving;

1. Introduction

Our society and economy is strongly dependent on energy from fossil fuels. Most (84%) of the energy in the world comes from fossil fuels and this demand will increase because the world energy consumption is expected to increase at 53% by 2035[1] (EIA, 2012). As prices increase, unconventional fossil resources such as tar sand oil, shale gas, arctic and deep water oil, may become economically viable to extract and use, but they are a limited resource and present risks to environment and people health [2,3,4]. The finite reserves, excessive consumption, and established contribution to the greenhouse effect of the fossil fuels is an important reason for the development of renewable technologies as sustainable and long-term solutions. These technologies are relied on biomass, wind, solar, water or geothermal raw resources as their primary energy source. From all these renewable resources, the biomass is the only resource that can produce power, liquid fuels, and chemicals, thus making it a very attractive option for all countries with abundant and various biomass resources [5,6,7]. Biomass

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can be converted to intermediate compounds that can be used to produce power, liquid and gas fuels, and chemicals through thermochemical (pyrolysis, gasification or combustion) ways. The biomass can be converted to energy (thermal energy by combustion process, into thermal energy and a flammable gas mixture known as syngas by gasification process and into mostly bio-oil, an energy rich liquid, as well as an amount of syngas,solid biochar and tar during pyrolysis process[6, 8, 9,10]. The presence of inorganics in biomass is harmful, to the processes, for example, during thermochemical conversion include fouling of surfaces ,equipment corrosion, catalysts deactivation, material bed agglomeration in reactors [7,8,11]. This paper aims to present a methodology for thermal and mechanical pre-treatment of biomass and to show how these treatments improve the biomass conversion process to use it as renewable energy source. Also, this paper is focused on the main thermochemical conversion processes (pyrolysis, gasification, and combustion) with the aim to elucidate the fate of inorganics from biomass during these processes and presents the way by which the pre-treatment and post-treatment methods could control these inorganic elements.

2. Pre-treatments for thermochemical conversion of biomass

An alternative and promising form of bio-energy production is by biomass thermochemical conversion. The thermochemical conversion includes processes such as pyrolysis, gasification and combustion which can be used to produce heat, electricity or liquid and gaseous precursors for transformed them into liquid or gaseous fuels or valuable chemical feedstocks, as is presented in Fig. 1.

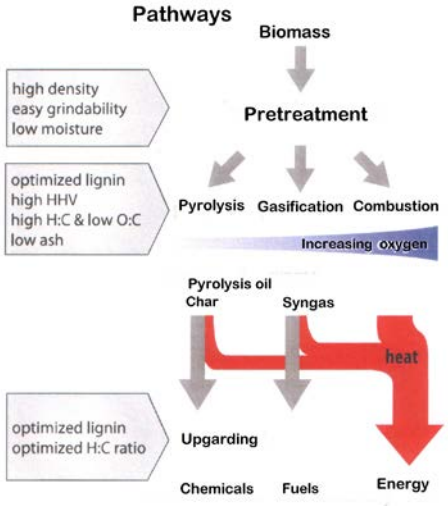


Fig.1. The diagram including the steps involved in biomass processing platform used for thermochemical energy production

The pre-treatment is very important and the first step in biomass processing pathway. It is also the key process to change the undesirable characteristics of biomass material in order to increase its conversion efficiency and reduce the cost [12,13,14].In the context of the biomass thermochemical conversion platform, the pretreatment is traditionally used to ensure and facilitate the material storage and handling, but and to increase the conversion process efficiency.

However, in last years, the pre-treatment methods are beginning to be used for the improving of specific biomass characteristics [13,14, 15,16]. In this context, the biomass pre-treatment techniques are grouped in the following categories: (i) mechanical (e.g.,cutting, crushing, grinding and mechanical sieving); (ii) thermal pre-treatment(e.g., torrefaction, steam/liquid hot water pre-treatment, ultrasound/microwave irradiation); (iii) chemical (e.g., treatment with bases,acids, or ionic liquids); and (iv) biological pre-treatment (e.g., enzymatic, or microbial).

3. **Methodology**

Four types of local residual biomass consisting of rapeseed oil cake, walnuts, nuts and apricots shells, with different in fibre content were used in this study (Fig. 2).

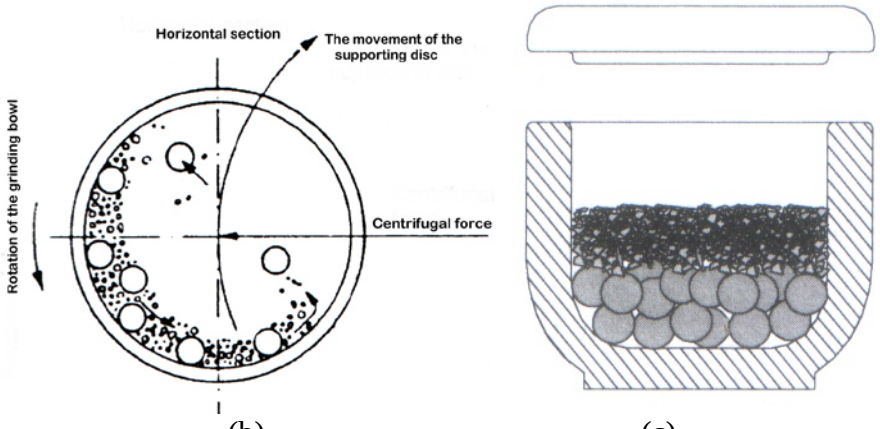
Fig.2. Residual biomass samples: (1)-rapeseed oil cake (raw-left and grinding- right); (2)-walnuts shells (raw-left and grinding-right);(3)-nuts shells(raw-left and grinding-right); (4)-apricot stones(raw-left and grinding-right);

Mechanical biomass pre-treatment includes all of the methods that employ mechanical energy to assure the modifications in the biomass properties and refer to pressing(for example for oil extracting from seeds, or biomass palletization) cutting, crushing and grinding to reduce particle dimensions and sieving to fractionate biomass material based on particle sizes.

In this work we study mechanical pre-treatment of residual biomass (such as rapeseed oil cake, walnut, apricot, plum and nuts shells. The goal of pretreatment is to make the biomass accessible for thermochemical conversion.

Each kind of residual biomass (Fig. 2) was ground to different fractions using the "pulverisette 6"planetary mono-mill (Fig. 3a) according to ASTM 7084-04.

(a)



(b) (c)

Fig.3. (a)- overview of a planetary mono-mill; (b)- developing of the centrifugal force; (c)- the level of bowl filling.

Before grinding the sample were dried at 85^{O}C for three hours to avoid the agglomeration and the sticking of the particles to the mill bowl. The four samples were divided into portions with approximately the same volume (≈ 300cm^3).

A drying temperature of 85° C and not 100 ° C was chosen to reduce the removal of organic compounds having evaporation temperatures above this temperature, compounds which by conversion result in the generation of more combustible gases.

First, it was placed the grinding balls in the empty bowl and then was filled the material to be ground on top of the balls. The bowl must be fill only 2/3 of the bowl volume with grinding material and grinding balls and 1/3 of the bowl volume is left free as space to develop centrifugal force (Fig. 3c).

Grinding time was established in the range 2 to 10 mins, rotation speed of 300 rpm. Balls to biomass sample mass ratio corresponded to 10:1. After the grinding material was sieved into more fractions of various particle size as : (1) up to 0.5mm ; (2) 0.5–1,0 mm; (3) 1.0–2.0 mm; and (4) >2.0mm . For this operation it was used CISA
sieving system (Fig. 4).

(a) (b) (c)

Fig.4. (a)-the CISA sieving system used in all experimental texts; (b)-sieving screens; (c)-sieving mechanism

After sieving, the mass retained on each sieve was collected and weighted. After each operation , the sieves were cleaned for dust removal. For all four fraction the density by volume was determined.

Operating time during all tests made with the sieve shaker was established on five mins and an amplitude on 1.5mm. As all milling operations were performed using the same procedure during sample preparation, the results were comparable and these were used to identify thes divergence as well as the relations induced during thermochemical conversion by particle size (as shown in our research [16].

The raw residual biomass samples were characterized by using proximate and ultimate analysis. The moisture, volatile compounds,fixed carbon and ash amount were established according to ASTM standards: D 2016 74; D3174 89 and D1102 84, respectively.

The ultimate analysis was achieved to determine the amount of carbon (C), hydrogen (H), nitrogen (N), and oxygen (O), using a Carlo Erba 1106 analyzer, according to ASTM D 5373.The composition was determined according to ASTM D 3176. The extractives and lignocellulosic content of each biomass material was determined using TAPPI test methods [15].

4. Results and discussion

The yield of products obtained from biomass by thermochemical conversion varies according to the technology used, the operating parameters, the composition, particles size, kind of biomass used, etc. In this context it is necessary to know all these characteristics.

Table 1, 2 , 3 and Table 4 show the proximate, ultimate and component analyses of all biomass samples that were analyzed in this research. As can be seen, all samples have a moisture content of> 10%, which requires a drying of the samples before being subjected to the conversion process. Also, the lignin content is> of, what is reflected in the ash content determined.

Table 1

Proximate, ultimate and component analyses of rapeseed oil cakes

Proximate analysis (raw wt%)		Ultimate analysis (dry wt%)		Component analysis (dry wt%)	
Moisture	10.62	C	45.91	Extractives[b]	19.42
Volatile matter	67.71	H	6.19	Cellulose	28.56
Fixed carbon	15.40	N	6.89	Hemicellulose	41.50
Ash	6.27	S	0.88	Lignin	4.89
		O[a]	40.13		
Density(bulk)(g/cm^3)	0.0485	H/C molar ratio	1.62		
		O/C molar ratio	0.65		

[a]Calculated from the difference; [b]Toluene/alcohol (2/1, v/v);

Table 2.

Proximate, ultimate and component analyses of walnuts shells

Proximate analysis (raw wt%)		Ultimate analysis (dry wt%)		Component analysis (dry wt%)	
Moisture	11.59	C	47.67	Extractives[b]	14.40
Volatile matter	65.31	H	5.67	Cellulose	32.58
Fixed carbon	14.80	N	0.34	Hemicellulose	40.38
Ash	7.30	S	0.73	Lignin	6.25
		O[a]	45.59		
Density(bulk)(g/cm^3)	0.0361	H/C molar ratio	1.42		
		O/C molar ratio	0.72		

[a]Calculated from difference; [b]Toluene/alcohol (2/1, v/v);

Table 3.

Proximate, ultimate and component analyses of nuts shells

Proximate analysis (raw wt%)		Ultimate analysis (dry wt%)		Component analysis (dry wt%)	
Moisture	10.59	C	47.24	Extractives[b]	13.84
Volatile matter	64.31	H	5.12	Cellulose	30.48
Fixed carbon	19.78	N	0.28	Hemicellulose	39.44
Ash	5.32	S	0.43	Lignin	6.05
		O[a]	46.93		
Density(bulk)(g/cm^3)	0.0286	H/C molar ratio	1.30		
		O/C molar ratio	0.74		

[a]Calculated from difference; [b]Toluene/alcohol (2/1, v/v);

Table 4

Proximate, ultimate and component analyses of apricot shells

Proximate analysis (raw wt%)		Ultimate analysis (dry wt%)		Component analysis (dry wt%)	
Moisture	10.48	C	48.16	Extractives[b]	12.64
Volatile matter	63.73	H	5.37	Cellulose	31.28
Fixed carbon	19.58	N	0.84	Hemicellulose	40.27
Ash	6.21	S	0.42	Lignin	6.86
		O[a]	45.21		
Density(bulk)(g/cm^3)	0.0462	H/C molar ratio	1.33		
		O/C molar ratio	0.7		

[a]Calculated from difference; [b]Toluene/alcohol (2/1, v/v);

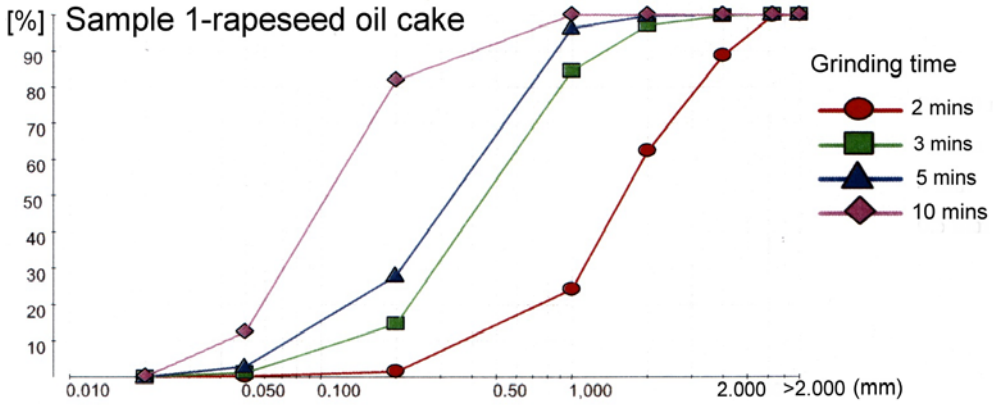
During the grinding process, the material to be ground is crushed and torn apart by grinding balls in grinding bowl. The centrifugal forces created by the rotation of the grinding bowl around their own axis and the rotating supporting disc are applied to the grinding bowl charge of material and grinding balls.

Since the directions of rotation of grinding bowls and supporting disc are opposed, the centrifugal forces are alternately synchronized and opposite. Thus, friction results from the grinding ball and the material being ground alternately

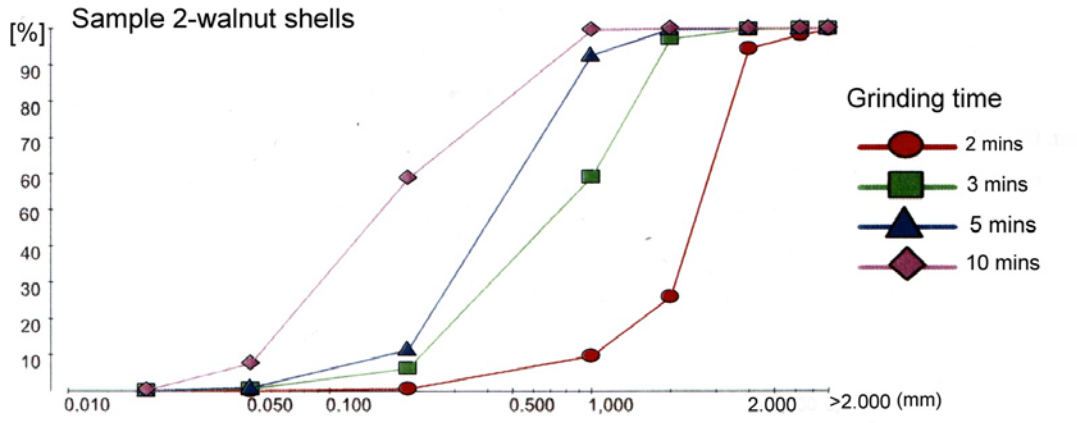
rolling on the inner wall of the bowl, and impact results when they are lifted and thrown across the bowl to strike the opposite wall (Fig. 3b).

The impact energy of the grinding ball in the normal direction attains values up to 40 times higher than gravitational acceleration. Loss-free comminution is guaranteed by a hermetic seal between grinding bowls and lid - even if suspensions are being ground.

Sieving results of grinding materials (1)-rapeseed oil cake; (2)-walnuts shells;(3)-nuts shells and (4)-apricot stones are presented in Fig. 5 (a, b) and Fig.6 (a,b). In every fraction it is clear that various kind of biomass acts differently in grinding process, although it was performed in the same conditions.

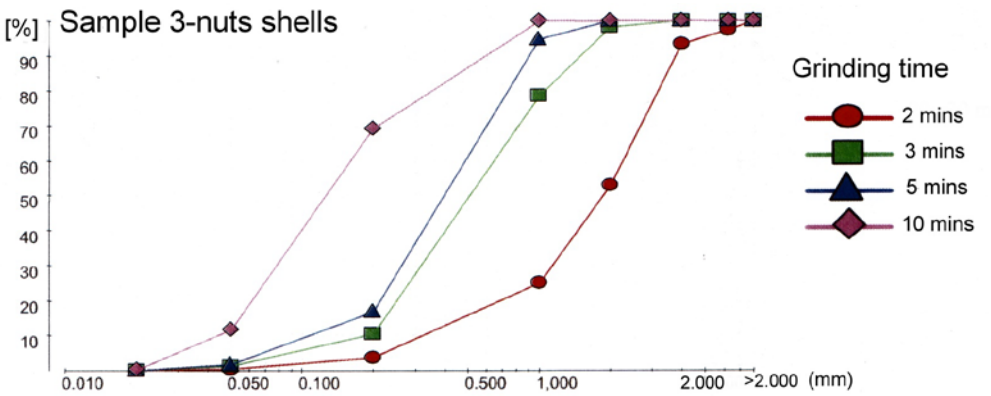


(a)

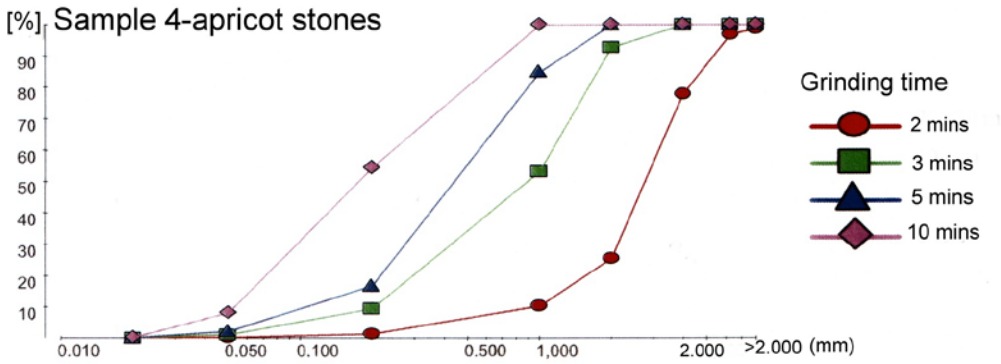


(b)

Fig. 5.The distribution of the particle size in each grinding fraction related to grinding time. (a):Sample 1-rapeseed oil cake; (b):Sample 2-walnut shells;



(c)



(d)

Fig. 6. The distribution of the particle size in each grinding fraction related to grinding time. (a): Sample 3-nuts shells; (b): Sample 4-apricot stones .

All four residual biomass samples were dried the same way, having after drying step a similar humidity (≈5%) during the grinding process.

In all four grinding fractions, materials from sample 2 and sample 4 appeared to have particles with bigger dimensions than those of materials from sample 1 and sample 3. Also, the size of the particles is correlated with the grinding time, for a longer grinding time for all the samples, smaller particle sizes were obtained. A grinding time in the range of 5-10 minutes seems to be sufficient to obtain a high fraction of particle size less than 1mm, effective for thermo-chemical processing.

The pyrolysis tests carried out in accordance with the procedure described in reference [16] were performed to determine the gas yield obtained for each particle fraction collected after grinding the sample consisting of rapeseed oil cake. The results are consistent with data presented in other studies [17-22]. The average values of gas yield and particle sizes are shown in Fig. 7.

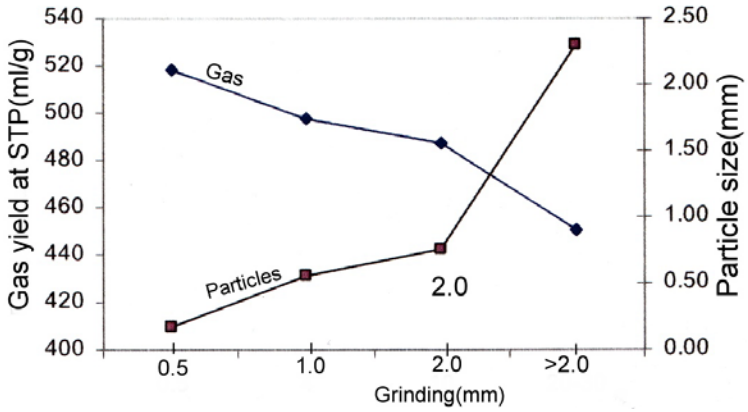


Fig. 7. Gas yield and the value of particle size related to grinding fraction

It illustrates that the grinding treatment has effects on mean particle size and gas yield. It can see that the smaller value of the particle size leads to a higher gas yield.

5. Conclusions

From the experimental tests, the following conclusions are drawn:

(i)To improve the efficiency of the biomass conversion process into energy, fuels and valuable chemical compounds, this requires a pre-heat and mechanical pre-treatment;(ii)By a drying process the initial moisture content from biomass is decreased and this improved the grinding, sieving as well as the conversion process;(iii)By mechanical grinding and sieving pre-treatment the biomass particle size was reduce under 2 mm, a suitable particle size for an conversion process. A grinding time in the range of 5-10 minutes has proven to be sufficient to obtain a high fraction of particle size less than 1 mm, much more effective for thermo-chemical processing; (iv) The grinding and sieving pre-treatment has effects on the product yield, the smaller value of the particle size leads to a higher gas yield.

Acknowledgment

The authors gratefully acknowledge the financial support from the Ministry of Research and Innovation from Romania, National Plan of Research & Development in Energy and Environmental field. Project no. PN 18 12 03 01/2018

R E F E R E N C E S

[1] *EIA.* Most states have Renewable Portfolio Standards. Available on line at: http://www.eia.gov/ todayinenergy/detail.cfm?id=4850 (Accessed November3,2012) , 2012.

[2] *Kelly, E.N.,Schindler,D.W.,Hodson,P.V.,Short,J.W.,Radmanovich,R.,and Nielsen,C.C.,* Oil sands development contributes elements toxic at low concentrations to the Athabascariver an ditstributaries.Proc.Natl.Acad.Sci.U.S.A.107,2010,pp16178–16183. doi:10.1073/pnas. 1008754107

[3] *Osborn, S.G.,Vengosh,A.,Warner,N. R., and Jackson,R.B.* Methane contamination of drinking water accompanying gas-wel ldrilling and hydraulic fracturing. Proc.Natl.Acad. Sci.U.S.A. 108,2011,pp. 8172–8176.doi: 10.1073/pnas.1100682108

[4] *Frohlich,C.* Two-yearsurvey comparingearthquakeactivity and injection-welllocationsin the BarnettShale,Texas. Proc. Natl.Acad.Sci.U.S.A. 109, 2012, pp.13934–13938. doi:10.1073/pnas. 1207728109

[5] *Maniatis, K., Millich, E.,* Energy from biomass and waste: the contribution of utility scale biomass gasification lants. Biomass and Bioenergy 15 (3), 1998,pp.195– 200.

[6] *Stevens, C.; Brown, R. C.* Thermochemical Processing of Biomass:Conversion into Fuels, Chemicals and Power; John Wiley & Sons:Chichester, U.K., 2011.

[7] *Woolcock, P., Brown,J.,* Review of cleaning technologies for biomass -derived syngas, Biomass and Bioenergy, 52,2013,pp.54-58;

[8] *Abdoulmoumine, N.; Adhikari, S.; Kulkarni, A.; Chattanathan, S.,* A Review on Biomass Gasification Syngas Cleanup. Applied Energy,155,2015, pp.294-307. https://doi.org/10.1016/j.apenergy.2015.05.095

[9] *Leijenhorst, E. J.; Wolters, W.; van de Beld, L.; Prins, W. Staged*, Biomass Gasification by Autothermal Catalytic Reforming of Fast Pyrolysis Vapors. Energ Fuel.;29(11), 2015, pp.7395-7407

[10] *Doshi, V.; Vuthaluru, H. B.; Korbee, R.; Kiel, J. H. A.*, Development of a modeling approach to predict ash formation during co-firing of coal and biomass. Fuel Process. Technol. 90, 2009, pp.1148–1156.

[11] *Keown, D. M.; Hayashi, J.-i.; Li, C.-Z.,* Effects of volatile–char interactions on the volatilisation of alkali and alkaline earth metallic species during the pyrolysis of biomass, Fuel, 87, 2008, pp. 1187-1194.

[12] *Pandey, A.; Negi, S.; Binod, P.; Larroche, C.* Pretreatment of Biomass: Processes and Technologies; Elsevier: Amsterdam, 2014.

[13]*Carpenter, D.; Westover, T. L.; Czernik, S.; Jablonski, W.,* Biomass feedstocks for renewable fuel production: a review of the impacts of feedstock and pretreatment on the yield and product distribution of fast pyrolysis bio-oils and vapors ,Green Chem. 16,2014,pp. 384− 406.

[14] *Zhang,H. Meng,X., Liu,C.,Wang,Y.,Xiao,R.,* Selective low-temperature pyrolysis of microcrystalline cellulose to produce levoglucosan and levoglucosenone in a fixed bed reactor, Fuel Processing Technology 167,2017, pp.484–490

[15] *Sluiter,A., Hames,B., Ruiz R.,Scarlata,C.,Sluiter,J.,* Templeton, D., Crocker, D., Determination of structural carbohydrates and lignin in biomass, Laboratory Analytical Procedure, (2008).

[16] *David,E., Armeanu, A., Sandru,C., Niculescu,V.,* 2018**,** Obtaining of Fuel Gas from Catalytic Conversion of Residual Biomass, Progress of Cryogenics and Isotopes Separation Vol. 21(1), 2018,pp.83-96;

[17] *Kinoshita T., Ohki T., Yamagata Y.,* Woody biomass supply potential for thermal power plant, Japan. Appl Energy, 87, 2010, pp.2923–2927.

[18] *Mani S., Tabil G.L., Sokhansanj S.,* Grinding performance and physical properties of wheat and barley straws, corn stover and switchgrass, Biomass Bioenergy,27, 2004,pp.339–352.

[19] *Baum M.M., Street P.J.,* Predicting the combustion behaviour of coal particles. Combust Sci Technol,3, 1971, pp.231–243.

[20] *Savat P., Ryckmans Y., Verhoest C.*, Sustainable use of biomass in power plants in Europe. VGB Power Tech., 4, 2012,pp.48–50.
[21] *Silva, R.V., Ueki, M,M,, Spinelli, D., Bose Filho, W.W., Tarpani, J.R.* Thermal, Mechanical, and Hygroscopic Behavior of Sisal Fiber/Polyurethane Resin-based Composites. J. Reinf. Plast Compos. 29, 2010, pp. 1399-1417.
[22] *d'Almeida, J.R.M.,Aquino, R.C.M.P., Monteiro, S.N.*, Tensile mechanical properties, morphological aspects and chemical characterization of piassava (Attalea funifera) fibers. Compos. Part A. 37,2006, pp. 1473–1479.