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DRY TORREFACTION OF EUCALYPTUS SPP. SAWDUST USING CO2 AND N2

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Abstract. *The demand for world energy has increased considerably in recent years, about 85% of the world energy matrix is still from fossil fuels. The constant use of this type of fuel is very harmful to the environment, both for the extraction and for the emission of greenhouse gases. Biomass is nowadays the fourth most used energy source, Torrefaction is a process of pre-treatment of this biomass for energy generation, and it aims to reduce the problems of raw biomass, such as high moisture content, irregular geometry, low heating value, and high levels of volatile materials and alkaline components. The torrefaction process still has many challenges, one of which is the best trail gas used to create an inert atmosphere during torrefaction. In Brazil, the production of forest and industrial residues from wood is large, and this is an excellent opportunity to add value to these by-products. The CO2 and N2 gases were useful to create an inert atmosphere inside the torrefaction reactor. The N2 was more effective in maintaining a higher mass yield for torrefaction, with a low level of calorific value. CO2 causes a greater loss of volatile materials and a higher content of oil and fixed carbon.*

Keywords: *Dry torrefaction, sawdust, nitrogen, carbon dioxide, energy.*

1. INTRODUCTION

The demand for energy in the world is constantly increasing, almost 85% of this demand is met by burning fossil fuels such as coal, oil, and natural gas. The constant use of these fossil fuels has caused the emission of large quantities of Greenhouse Gases (GHG) to the atmosphere (Abbasi and Yozgatlilgil 2014; Saidur et al., 2011). Of the total GHG emitted, 3/4 correspond to carbon dioxide (CO2), which is the main anthropogenic emission responsible for global warming (Huaman and Jun 2014; Lin et al., 2011). According to the Intergovernmental Panel on Climate Change (IPCC, 2014) there is a significant correlation between the increase in GHGs and global warming.

To meet the high energy demand aimed at reducing GHG emissions, especially CO2, several alternatives were proposed, including the use of biomass. Biomass is the fourth source of energy in the world, its use through the combustion process for energy generation presents several challenges due to its irregular geometry, high moisture and volatile material content, low calorific value and high alkaline composition, in addition, its availability and operating problems (transport and storage) (Riaza et al., 2014; Saidur et al., 2011).

In this sense, dry torrefaction appears as a pre-treatment technology for biomass. Dry torrefaction is the thermal process where the biomass is heated between 200°C and 300°C in an inert atmosphere produced by the injection of a gas carrier (i.e. nitrogen, argon, helium). The result of dry torrefaction is a significant increase in heating value, a significant reduction in moisture content and an increase in apparent density (Bonassa et al., 2018; Da Silva et al., 2018; Proskurina et al., 2017; Chen et al., 2015). Thus, energy generation from torrefied biomass is relevant due to the better use of biomass.

Among the biomass that has potential for energy generation are agro-industrial and forestry residues. According to Oliveira et al., (2013), in Brazil residues derived from eucalyptus production have potential for energy generation. In 2010, the Brazilian production of legalized wood increased 8.26% compared to 2009, reaching a production of over 115 million m³, with most of the production concentrated in the South and Southeast. Waste derived from eucalyptus production in Brazil has an energy potential of approximately 140 PJ (1015 Joules), with the Southeast and South concentrating the largest amount 100.9 and 63.8 PJ respectively.

The literature presents a significant amount of works on the torrefaction of several biomass. Regarding the torrefaction of residues derived from eucalyptus production, several studies have shown that torrefaction has a positive effect on physical-chemical properties (Da Silva et al. 2017; Pinto et al., 2017; Pereira et al., 2016; Arteaga-Perez et al., 2015). Due to the cost related to nitrogen (N2), a drag gas commonly used in torrefaction to create an inert atmosphere, several studies have evaluated the possibility of using other gases. A gas that has the potential to be used as a carrier gas is CO2, a gas that can be obtained from energy generation using any carbon-based fuel; however, the literature presents few papers evaluating the effect of CO2 on biomass torrefaction (Li et al., 2018; Li et al., 2016b; Li et al., 2016a; Eseltine et al., 2013). Despite the works involving the torrefaction of eucalyptus production residues, there are still no studies comparing the effect of using N2 and CO2 in dry torrefaction.

2. MATERIALS AND METHODS

2.1 Eucalyptus spp.

Figure 1 shows the sawdust sample Eucalyptus spp used in the experimental tests, with samples between 250 - 500 µm sizes being separated. A mass of 20g was used for all experimental tests.

Figure 1: Eucalyptus spp sawdust.

2.2 Experimental setup of torrefaction

Figure 2 shows the experimental setup used for the test. The energy required for torrefaction is provided by a muffle oven. A gas flow rate (100ml/min) of N2 and CO2 was used to create an inert atmosphere inside the reactor and promote the output of the volatile material. A condenser with cold water was used to condense part of the volatile material. This study was considered torrefaction temperature between 200 and 300°C and the time was leave constant 30 min after attained the torrefaction temperature.

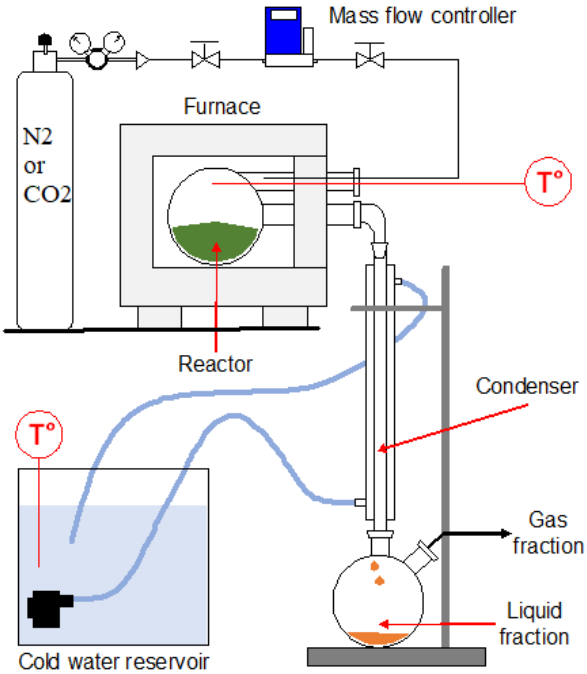

Figure 2. experimental setup of torrefaction.

2.3 Torrefaction performance

Mass (MY) and Energy (EY) yield parameters were used to evaluate the performance of torrefaction and calculated according to the Eqs. (1) and (2), all terms in dry basis:

$$MY = \frac{Weight\ of\ torrified\ biomass}{Weight\ of\ raw\ biomass} * 100 \tag{1}$$

$$EY = MY * \frac{HHV\ torrified\ biomass}{HHV\ raw\ biomass} \tag{2}$$

2.4 Characterization techniques

In this section is showed the techniques used for characterization. The compositional analysis was performed to determine the levels of hemicellulose, cellulose, and lignin, which are following the TAPPI standard. Proximate analysis was determined to determine moisture, ash, volatile matter, and fixed carbon, in order to understand the change in torrefied eucalyptus ssp. A Calorimeter IKA C500 was used to determine the High Heating Value (HHV) of torrefied eucalyptus spp. sawdust. All tests are performed in duplicate using a mass of (0.5 ± 0.05) g.

3. RESULTS AND DISCUSSION

3.1 Chemical characterization of Eucalyptus spp.

Table 1 shows the chemical composition of *Eucalyptus* spp. used in the study. The present study sought to use eucalyptus sawdust from small and medium-size sawmills in the Itapeva region, south of the state of São Paulo, as it is a region with large volume of forest and industrialization of wood. To use sawdust is a big challenge, as this type of company usually does not have quality control for the raw material, so the chemical analysis of eucalyptus to be used in the study is vitally important to try to predict what the thermal degradation will be like during the torrefaction process. According Nhuchhen (2014), the mass lost is higher in small particles, so, in this study the classification of particles was carried out and worked with particles between 250 – 500 µm, in order to achieve a standardization in the heat transfer inside the particles, having a lesser effect on the yield of the torrefied material.

It can be seen from the results on Table 1, eucalyptus has a high lignin content, typical hardwood indexes, which is better for energy, because its amorphous macromolecule is composed of aromatic compounds, with phenyl propane units, and because it is produced in the middle lamella and secondary wall during the maturation process, it incorporates into the last wall component, interpenetrating the fibrils, stiffening the cell wall. According to Pereira et al. (2016) torrefaction process changes the concentration of chemical constituents of wood, where hemicellulose and cellulose degradation occurs before lignin, although it starts first, its macromolecule undergoes a slower thermal degradation due to of its constitution.

Table 1: Chemical composition of *Eucalyptus* spp.

Parameter	% mass	Standard deviation
Holocellulose	63,55	-
Klason Lignin	27,66	1,14
Soluble lignin	4,78	0,89
Total lignin	32,44	-
Total extractives	2,97	0,60

3.2 Torrefaction results

Samples of torrefied eucalyptus spp. sawdust at different temperatures using CO2 and N2, had no visual qualitative difference. In higher torrefaction temperature the color of the eucalyptus spp. sawdust became darker with a more carbonized appearance, however, there is no qualitative differentiation in colors when the carrier gas is changed. Table 2 below shows the results obtained for proximate analysis, demonstrating the values for volatile materials, fixed carbon, and ash for torrefied eucalyptus spp. using CO2 and N2.

According to Caraschi et al. (2019), the content of volatile materials is one of the most important when dealing with biomass for energy generation, since the activation energy, that is, what gives ignition to the burning of the material depends on this concentration in the raw material. During the torrefaction process, part of the gas fraction and the liquid fraction of the material is removed, according to Cardona et al. (2019), who worked with a composite of leaves, bark and eucalyptus wood tailings, found values of 63.34 % (wet basis) for fresh biomass, using N2 as a carrier gas, a concentration that decreased as the torrefaction temperature increased, but at 300 ºC the value for volatile materials was 53.35 % higher than 37.13 % (dry basis) found when was used the CO2 as carrier gas, and closer to the 45.14% found when using N2,, that show us than the carrier gas influences yield, and, also that difference can be explained by the fact that the calculation base is different (wet versus dry basis) and the uniformity of the raw material, since only eucalyptus spp. sawdust separated in 250 mesh was used. Su et al., (2018) studied the bamboo torrefaction at 230ºC and 250ºC using N2 and CO2 respectively. The authors have noted that at 230ºC, when CO2 was used as gas carrier, the percentage of volatile material was lower than when N2 was used, as was the case in our study. In the analysis of fixed carbon, there was no significant difference for the temperature of 230ºC when using both gases, this difference appears only in 250ºC where there is a higher percentage of fixed carbon when using CO2, and again, the same happened with the sawdust of eucalyptus spp.

Ash content increased as torrefaction temperature increased along with fixed carbon content, however, there was a decrease in the concentration of volatile materials. The ashes come from mineral components in the wood, being undesirable in beneficiation and burning processes, as its components accelerate the wear of the cutting tools, as well as depreciate over time, causing erosion and rust in burning equipment, but their values are too low in the inner areas of the wood, most of which comes from the bark, Pereira et al (2016), who studied the torrefaction in eucalyptus spp. chips found values below those found in the present study, but with high variation among the results, due to the too low value of these compounds in wood. Araujo et al. (2018) worked with several eucalyptus species also found values below those found in the present study, however, all values increased after the torrefaction process.

Table 2: Proximate analysis of torrefied eucalyptus spp. sawdust.

Temperature (°C)	**Volatile material (%)**		**Fixed carbon (%)**		**Ash (%)**	
	CO2	N2	CO2	N2	CO2	N2
200	83.11	54.27	13.14	41.20	1.84	0.53
220	78.84	75.59	15.31	34.48	2.72	0.57
240	69.45	72.48	25.03	24.25	2.72	0.66
260	60.80	61.8	33.17	35.83	2.98	0.85
280	39.55	50.35	52.84	46.14	3.67	0.98
300	37.13	45.14	54.47	51.40	4.25	0.98

3.3 Correlation between mass yield and HHV

The mass yield of a process is important for the industry as it indicates the feasibility of performing a biomass pre-treatment or not. A large difference was observed between the analyzed extremes, with yields of 93.45 % and 35.55 % for the temperatures of 200 ºC and 300 ºC respectively for the torrefaction with CO2, when it was used N2, the mass yield was better, with the yields of 90.19% and 42.72% for the temperatures of 200ºC and 300ºC respectively, with a difference of 7.17% in the higher temperature for each carrier gas, this decreased in mass yield is explained by the degradation of the cellulose and hemicellulose chains during the torrefaction process. Of the wood constituents, hemicellulose is the first to have a complete thermal degradation, which starts at temperatures around 220 ºC and goes up to 315 ºC, the cellulose comes after, its chains begin to thermally decompose in the side groups, at temperatures for around 315 ºC going up to 400 ºC, and lastly, lignin, which begins to decompose before the other components, at 160 ºC, however, lignin is a macromolecule and has a high molar mass, making its thermal degradation more demanding, going to 900 ºC. However, the degradation of these constituents is not desired because they are the main constituents of wood that directly influence the HHV of the material and consequently the energy density (PINTO et al, 2017; PEREIRA et al, 2016; DA SILVA et al, 2018).

According to Arteaga Perez et al. (2015) studied species of eucalyptus globulus and pinus radiata, the difference between hardwoods and softwoods leads to different cell formations, directly affecting how each constituent will degrade during a torrefaction process, for the eucalyptus species studied by the authors, at 30 minutes, at 250 ºC the mass yield was 79.0 % and at 280 ºC was 56.0 %, higher than those found in the present study, which was 64.89 % at 240 ºC, 51.88 % at 260 ºC and 37.26% at 280 ºC, however, the average particle size used in the studies performed by Arteaga-Perez et al. (2015) was 2 to 4 mm, while the sawdust used in the present study averaged 0.058 mm. With smaller particles, the contact surface of the material is larger, being one of the possible causes of the material mass yield decrease. Li et al. (2015), studied the torrefaction of bamboo in CO2 atmosphere, reports that at temperatures up to 240ºC the mass loss is small, however, it grows after that temperature. Su et al. (2018) obtained similar results for roasting of bamboo particles in both atmospheres, where, as found in our study, the mass yield was higher when using N2 as carrier gas.

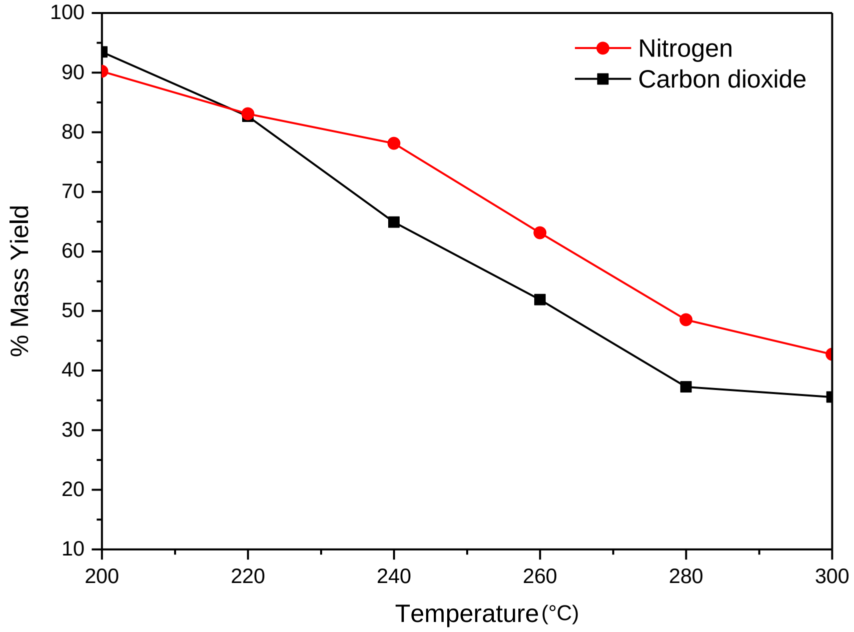

Figure 3: Mass Yield in torrefaction with CO2 and N2.

During torrefaction, the hygroscopic equilibrium moisture is evaporated, considerably increasing the HHV as less thermal energy is used. According to Pereira et al. (2016) hemicelluloses, which are the first constituents to be degraded, are the most hydrophilic compounds in wood constitution, so when subjected to temperatures above 200 °C, the torrefied biomass becomes more hydrophobic. As the torrefaction temperature increases, the HHV increases reaching a maximum of 27.7 MJ/kg at 280 °C, then declining to 26.74 MJ/kg at 300 °C when the carrier gas was CO2, when N2 was used, in this work was obtained a lower HHV, with the peak at a temperature of 300ºC, with 25.95 MJ/kg, and this shows how when it is used N2 as carrier gas, torrefied eucalyptus spp. gain in mass yield but may lose some of the HHV, however, it keeps increasing, which shows that the carrier gas causes a direct influence on the torrefaction. It is a degradation of lignin, causing a loss in HHV. Silveira et al. (2019) worked with *Eucalyptus grandis* macroparticles, reports linear growth with a positive correlation ($R^2 = 0.98$) between the decrease in mass yield and the increase in energy yield, a relationship also seen when compared the increase of HHV with the increase of the fixed carbon content of the material (while there is a decrease in the volatile material content). In the study by Su et al. (2018), where both inert atmospheres of CO2 and N2 were used, there was no significant difference in HHV.

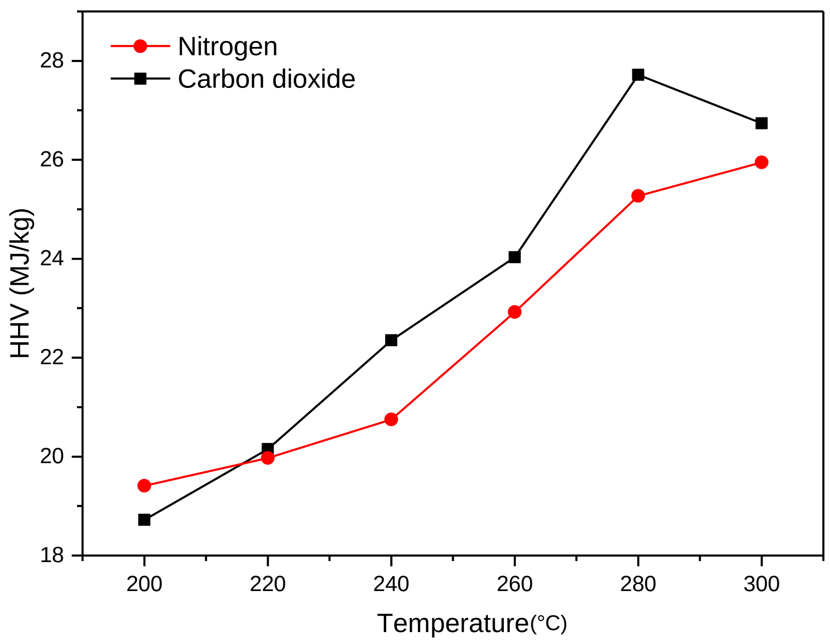

Figure 4: HHV in torrefaction with CO2 and N2.

4. CONCLUSIONS

The torrefaction of eucalyptus spp. sawdust increases HHV. Increasing the torrefaction temperature causes thermal degradation making the mass yield lower, however, using N2 as carrier gas there is a greater preservation of the components, causing a higher mass yield, with low loss of HHV. The fixed carbon content increases as the torrefaction temperature increases, being bigger with CO2 as well as the ash content, as there is less degradation using N2, there is consequently a higher content of volatile material. The fixed carbon content directly influences the HHV, so torrefaction proved to be consistent as a process of improvement of the raw material improving energy production, something also demonstrated in the HHV and mass yield. However, at temperatures above 280 ºC, there is a loss of material and HHV start to decrease, when CO2 are used as carrier gas, when N2 are used, there is no loss of mass yield or HHV reduce.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

Abbasi A., E., Yozgatlilgil, A. (2014). “A study on the effects of catalysts on pyrolysis and combustion characteristics of Turkish lignite in oxy-fuel conditions”. Fuel, v.115, p.841-849.

Arteaga-Perez, L. E.; Segura, C.; Bustamante-García, V.; Cápiro, O. G.; Jiménez, R. (2015) “Torrefaction of wood and bark from Eucalyptus globulus and Eucalyptus nitens: Focus on volatile evolution vs feasible temperatures”. Energy, v.93, p.1731-1741.

Bonassa, G.; Schneider, L.T.; Canever, V.B. Cremonez, P.A.; Frigo, E.P.; Dieter, J.; Teleken, J.G. (2018) “Scenarios and prospects of solid biofuel use in Brazil”. Renewable and Sustainable Energy Reviews, v.82, p. 2365-2378.

Chen, W. H.; Peng, J.; Bi, X. T. (2015) “A state-of-the-art review of biomass torrefaction, densification and applications”. Renewable and Sustainable Energy Reviews, v. 44, p. 847-866.

Da Silva C.M.S., Carneiro, A.C.O, Vital, B.R., Figueiró, C.G., Fialho, L.F., Magalhães M.A., Carvalho, A.G., Cândido, W.L. (2018). “Biomass torrefaction for energy purposes – Definitions and an overview of challenges and opportunities in Brazil”. Renewable and Sustainable Energy Reviews, v. 82, p. 2426-2432.

Da Silva, C. M. S.; Vital, B. R.; Carneiro, A. C. O.; Costa, E. V. S.; Magalhães, M. A.; Trugilho, P. F. (2017) “Structural and compositional changes in eucalyptus wood chips subjected to dry torrefaction” Industrial Crops & Products. v.109, p.598-602.

Eseltine D.; Thanapal S. S.; Annamalai, K.; Ranjan, D., (2013). “Torrefaction of woody biomass (Juniper and Mesquite) using inert and non-inert gases”. Fuel. v.113, p.379-388.

Huaman, R. N. E.; Jun, T. X. (2014) “Energy related CO2 emissions and the progress on CCS projects: A review”. Renewable and Sustainable Energy Reviews, v.31, p.368–385.

IPCC. Climate Change 2013 - The Physical Science Basis; Intergovernmental Panel on Climate Change, Ed.; Cambridge University Press: Cambridge, 2014.

Li M.F.; Chen, L. X; Li X., Chen, C. Z.; Lai, Y. C.; Xiao, X.; Wu, Y. Y., (2016b) “Evaluation of the structure and fuel properties of lignocellulosic through carbon dioxide atmosphere”. Energy Conversion and Management. v.119, p.463-472.

Li M.F.; Li X.; B. J.; Xu, J. K.; Yang S.; Sun, R. C., (2016a) “Influence of temperature on bamboo torrefaction under carbon dioxide atmosphere”. Industrial Crops and Products. v.76, p.149-157.

Li M.F.; Li X.; Bian. J.; Chen, C. Z; Yu, Y, T; Sun, R. C., (2015) “Effect of temperature ad holding time on bamboo torrefaction”. Biomass and Bioenergy. v.83, p.366-372.

Li, S. X.; Chen, C. Z.; Li, M. F.; Xiao X., (2018) “Torrefaction of corncob to produce charcoal under nitrogen and carbon dioxide atmospheres”. Bioresource Technology. v.249, v.348-353.

Lin, S., Kiga, T., Wang, Y., Nakayama, K. (2011) “Energy analysis of CaCO3 calcination with CO2 capture”. Energy Procedia, v.4, p.356-361.

Oliveira, J. L.; Da Silva, J. N.; Pereira, E. G.; Filho, D. O.; Carvalho, D. R. (2013) “Characterization and mapping of waste from coffee and eucalyptus production in Brazil for thermochemical conversion of energy via gasification”. Renewable and Sustainable Energy Reviews, v.21, p.52–58.

Pereira, M. P. C. F.; Costa, E. V. S.; Pereira, B. L. C.; Carvalho, A. M. M. L.; Carneiro, A. C. O.; Oliveira, A. C. (2016) “Torrefação de cavacos de eucalipto para fins energéticos”. Pesquisa Florestal Brasileira. 2016.

Pinto, F.; Gominho, J.; André, R. N.; Gonçalves, D.; Miranda, M.; Varela, F.; Neves, D.; Santos, J.; Lourenço, A.; Pereira, H. (2017) “Improvement of gasification performance of Eucalyptus globulus stumps with torrefaction and densification pre-treatments”. Fuel, v.206, p.289-299.

Proskurina, S.; Heinimo, J.; Schipfer, F.; Vakkilainen, E. (2017) “Biomass for industrial applications: The role of torrefaction”. Renewable Energy, v.111, p.265-274.

Riaza, J.; Khatami, R.; Levendis, Y. A.; Álvarez, L., Gil; M. V., Pevida, C., Rubiera, F., Pis, J. J. (2014) “Combustion of single biomass particle in air and in oxy-fuel conditions”. Biomass and Bioenergy. v64, p.162-174.

Saidur, R., Abdelaziz, E.A., Demirbas, A. Hossain, M.S., Mekhilef, S. (2011) A review on biomass as a fuel for boilers. Renewable and Sustainable Energy Reviews, v.15, p.2262–2289.

Su, Y., Zhang, S., Liu, L., Xu, D., & Xiong, Y. (2018). Investigation of representative components of flue gas used as torrefaction pretreatment atmosphere and its effects on fast pyrolysis behaviors. Bioresource Technology, 267, 584–590. doi:10.1016/j.biortech.2018.07.078

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