KINETIC STUDY ON COMBUSTION OF COAL BLENDED WITH AGRO-INDUSTRIAL BIOMASS USING TGA

Natalia da Silva Ribeiro, nsribeiro2@gmail.com
Carlos Manuel Romero Luna, c_romeroluna@feg.unesp.br
Ivonete Ávila, iavila@feg.unesp.br
UNESP - Paulista State University, Engineering College of Guaratinguetá, Department of Energy, Av. Dr. Ariberto Pereira da Cunha, 333 - 12.516-410, Guaratinguetá-SP, Brazil.

Gretta Larisa Aurora Arce Ferrufino, gretta@lcp.inpe.br
National Institute For Space Research, Combustion and Propulsion Associated Laboratory, Presidente Dutra Highway, km 40, Cachoeira Paulista-SP, Brazil.

Abstract. *The combustion of fossil fuels such as coal, causing an increase in emissions of greenhouse gases (GHG) mainly carbon dioxide (CO2), which has direct link with global warming. Thus, increasing the use of renewable sources, such as biomass, for the production of energy is a solution to alleviate the crisis and negative impacts on the environment. The co-combustion of coal and biomass is shown as a short-term alternative to the problem of energy and environment and is considered as the most advantageous way of utilizing both resources. Brazil has large reserves of coal, as well as the availability of agro-industrial biomass, such as sugarcane bagasse and more recently inserting sorghum varieties. Biomass sorghum is one of the most promising crops for the production of energy and is an alternative to being used in the off-season of sugarcane. Their productivity is about 2.5 times higher than that of sugarcane. In this work, the kinetic combustion of blends between coal with sugarcane bagasse and biomass sorghum bagasse were studied and compared by TGA. The experiments were performed in a thermogravimetric analyzer SDTQ600, were used three heating rate (10°C/min, 15°C/min and 20°C/min) in an oxidizing atmosphere (synthetic air). Three biomass ratios were studied being 25, 50 and 75% respectively. Iso-conversional kinetic method (model-free kinetics) was applied for determining the activation energies (Ea). Results indicate that the blending ratio of 25% has the better combustion performance for both biomasses, with the average value of the activation energy equal to 123.57* kJ mol^{-1} *for sugarcane bagasse and 117.05* kJ mol^{-1} *for biomass sorghum bagasse.*

Keywords*: Co-combustion, Kinetic, Agro-industrial biomass, Sugarcane bagasse, Biomass sorghum.*

1. INTRODUCTION

The burning of fossil fuels in power generation causes an increase in emissions of greenhouse gases (GHG), mainly carbon dioxide (CO2), which has direct link with global warming (Specht, Redemann, and Lorenz 2016). In order to gradually reduce the damage caused by the combustion of fossil fuels, the demand for alternative fuels that reduce emissions of greenhouse gases tends to increase in the coming years. Thus, biomass has great potential to supply renewable energy demand, and subject of several studies (Al-Shemmeri et al. 2015; Behera et al. 2015; Kumar et al. 2015; Kwon et al. 2011; Perego and Bosetti 2011; Frau et al. 2014).

Biomass has some shortcomings, such as: seasonal availability, high moisture content, low heating value and low density. One way to overcome these shortcomings is to use the co-combustion technology of biomass and coal (López et al. 2016). Brazil has various sources of biomass, among which the following may be noted: bagasse and straw from sugar cane and newly inserting the high biomass sorghum (lignocellulosic sorghum). Lignocellulosic sorghum has a greater amount of fibrous matter and your productivity is about 2.5 times higher than sugar cane or corn. The variety of sorghum developed in Brazil is an alternative used in the off-season of sugarcane (Farrow, Sun, and Snape 2015). The literature presents several works related to the co-combustion of coal and biomass mixtures. However, no literature reference on the mixture of coal and sorghum bagasse.

Co-combustion is one of the most advantageous techniques for using biomass residues and reducing the use of fossil fuels, among the main advantages, we can highlight the low cost, increased participation of biomass for electricity generation and reduce CO2 emissions (Tabet and Gökalp 2015).

The biomass and coal have different physical and chemical properties that provide different thermal behavior during co-firing (Park et al. 2010). The proportion of each raw material used in the mix and the process temperature directly affects the performance of products (Morita, Pécora, and Ramirez-Behainne 2013).

Thermogravimetric analysis (TGA) is used to investigate the thermal decomposition characteristics of materials. Thermogravimetric analysis (TGA) is a widely used technique for determining the kinetic parameters of the combustion of solid fuels such as biomass and coal. The kinetic parameters provide information about the thermal decomposition process, structure and composition of materials (Garcia-Maraver et al. 2015).

The determination of the kinetic parameters of biomass and biomass-coal blends is critical to the development of technological processes and modeling ovens on an industrial scale (Mortari et al. 2010). Several studies in the literature

focus on the determination of kinetic parameters, such as activation energy and the constant of reaction in fuels combustion processes. Model-free methods (iso-conversional methods) enable determination of kinetic parameters without knowledge of the reaction mechanism (Álvarez et al. 2016). In iso-conversional methods, for a constant extent of conversion, α, reaction rate depends only to temperature and reaction kinetics does not related with heating rate (Ceylan and Topçu 2014).

The aim of this study is to investigate the thermal behavior of coal blends with sugar cane bagasse and sorghum biomass combustion atmosphere (20% O2 – 80% CO2). The activation energy of the thermal decomposition process and ignition temperature of these fuels were determined using thermogravimetric techniques. Iso-conversional kinetic method (model-Free Kinetics) was used for activation energy determination (Ea) of the combustion process.

2. MATERIALS AND METHODS

2.1 Samples

In this study, samples of Brazilian bituminous coal (CE4500), sugarcane bagasse (SB) Biomass sorghum (BS) were used. Table 1 shows the chemical composition of the samples.

Table 1. Chemical composition of materials

	Coal CE 4500	Sugarcane bagasse	Biomass sorghum
Proximate analysis/mass %			
Moisture	1.1	4.4	6.16
Volatile matter	22.8	83.9	77.84
Fixed carbon	24.3	7.7	18.18
Ash	51.8	4	3.98
Ultimate analysis/mass %			
Carbon	49.2	45.1	41.91
Hydrogen	3.41	4.9	6.24
Nitrogen	1.16	0.3	0.32
Sulfur	1.63	n.d.	0.92
Oxygen *	7.4	38.6	50.61
High Heating Value (MJ/Kg)	18.81	17.33	17.72

(Carvalho et al. 2015; Cruz and Crnkovic 2016; Kazanc et al. 2011)
n.d. Not detected; * Calculated by difference

2.2 Thermogravimetric analysis

The study of the thermal decomposition behavior of the materials was performed with non-isothermal tests in a thermogravimetric analyzer TG/DTA/DSC - TA Instruments - SCTTGA-DSCQ600. Blends were then prepared with 25, 50 e 75 weight percentages of biomass. Particle size of 63 μm was used for all materials in order to ensure homogeneity of the mixture. Approximately 5 mg of sample was used for all experiments. The tests were carried out in conventional combustion atmosphere with 20% O_2 - 80% N_2. The programming equipment was fitted with a heating rate of 10°C/min, 15°C/min and 20°C/min from room temperature to 800 ° C. The flow rate of carrier gas used was 100 mL min^{-1}.

2.3 Kinetic Method

The model used to calculate the activation energy as a function of the conversion extent of a chemical reaction was the Model Free Kinetics. Model free kinetics was presented by (Vyazovkin and Wight 1997; Sergey Vyazovkin and Wight 1999). The model free kinetics is based on iso-conversional techniques to calculate the activation energy (Eα) according to the degree of conversion (α) of the chemical reaction (Cruz and Crnkovic 2016).

The kinetics of heterogeneous reactions in solids is usually described in terms of a single step kinetic correlation. Equation 1 shows the general equation of kinetic analysis, this equation allows to calculate the activation energy (Eα) for a conversion (α) (VYAZOVKIN; WIGHT, 1997).

$$\frac{d\alpha}{dt} = k\,(T) f(\alpha) \quad (1)$$

Under non-isothermal conditions, the temperature varies with a constant heating rate (β=dT/dt), according to Eq. (2).

$$\frac{d\alpha}{dt} * \frac{dt}{dT} = \frac{1}{\beta}\, K(T)\, f(\alpha) \quad (2)$$

The rate constant (K) is expressed according to Arrhenius (Eq. 3). A is a pre-exponential factor and R (8.314 J K^{-1} mol^{-1}) universal gas constant.

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (3)$$

Equations 1, 2 and 3 may be generalized and shown as equation 4:

$$\frac{d\alpha}{dt} = \frac{1}{\beta}\left[A exp\left(-\frac{E}{RT}\right)\right] f(\alpha) \quad (4)$$

From Equation 4, obtains

$$\frac{1}{f(\alpha)} d\alpha = \frac{A}{\beta} exp\left(-\frac{E}{RT}\right) dT \quad (5)$$

Equation 6 represents the integration of equation 5 from zero to α in function of T:

$$\int_0^{\alpha} \frac{1}{f(\alpha)} d\alpha = g(\alpha) = \frac{A}{\beta} exp\left(-\frac{E}{RT}\right) dT \quad (6)$$

Provided that E/2RT>>1, the integral of temperature can be approximated as equation 7:

$$\int_{T0}^{T} e^{-E/RT} dT \;\approx\; \frac{R}{E} T^2 e^{-E/RT} \quad (7)$$

Substituting Equation 7 into Equation 6, and applying the natural logarithm operator, one has:

$$\ln \frac{\beta}{T_{\alpha}^2} = \ln\left[\frac{RA}{E_{\alpha} g(\alpha)}\right] - \frac{E_{\alpha}}{R}\,\frac{1}{T_{\alpha}} \quad (8)$$

This method allows you to isolate the g (α) function of the linear coefficient. However, in complex processes determine this function is difficult, because it is assumed incorrectly, can lead to errors in determination of kinetic parameters. To apply the Model-Free Kinetics method it is necessary to obtain at least three different heating rates (β) and respective conversion curves evaluated from the TGA curves measured (Vyazovkin and Wight, 1999). For each value of α, $\ln\left(\frac{\beta}{T_{\alpha}^2}\right)$ is plotted against $\frac{1}{T_{\alpha}}$ for a line whose slope is –Eα/R, which provides the activation energy values.

3. RESULTS AND DISCUSSION

3.1 Thermal behavior of pure materials

The DTG curve of coal and biomasses in the combustion atmosphere (O_2/N_2) are illustrated in Figure 1. The DTG curves of biomasses showed two overlapping peaks producing a single peak, with a shoulder on the left side of the DTG. This shoulder corresponds to decomposition of the hemicellulose, which has low thermal stability and its decomposition occurs at lower temperatures. The peak with the shoulder hemicellulose corresponds to decomposition of cellulose, which is the main component of the cell wall of biomass (Kazanc et al. 2011; Vamvuka et al. 2003). The thermal decomposition hemicellulose and cellulose of SB occurs between 228-350 ° C, and the maximum rate of decomposition of cellulose occurs at 331 ° C. The decomposition of hemicellulose and cellulose of the BS has a behavior similar to SB and occurs between 180-340 ° C. The maximum rate of decomposition of BS cellulose occurs at 304 ° C. Lignin is a component of stiffening cell wall of biomass and decomposes gradually over a wide temperature range. Lignin has a complex structure more thermally stable than cellulose and hemicellulose and total breakdown of the structure occurs at higher temperatures (Zhou et al. 2015). The thermal decomposition of SB lignin occurs between 390-465 ° C and the maximum rate of decomposition occurs at 442 ° C. The decomposition of BS lignin is more intense than SB, occurs between 420-440 ° C and the maximum rate of degradation occurs at 431 ° C. The thermal decomposition of coal occurs between 370-583 ° C, and the maximum rate of decomposition occurs at 498 ° C.

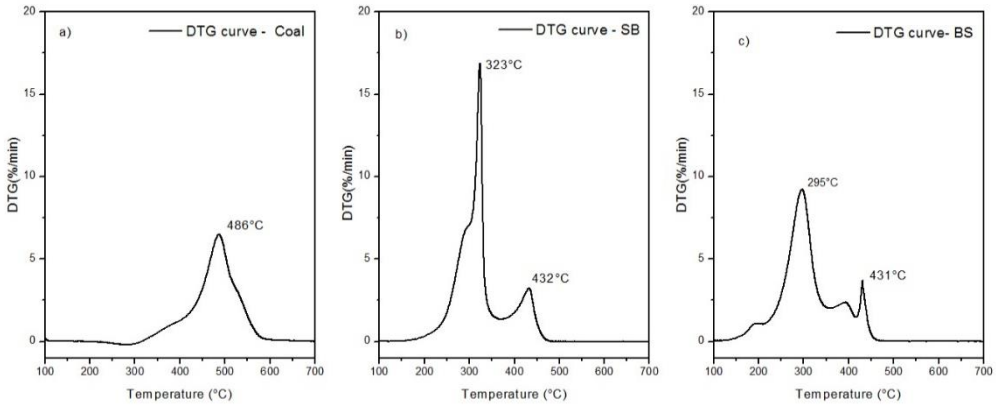

Figure 1. Combustion DTG profiles of coal, SB and BS with heating rate of 10°C/min

Table 2 shows the combustion parameters such as ignition (Ti) and burnout (Tb) temperature, maximum rate of weight loss (DTG_{max}/%min) for pure materials.

Table 2 Combustion parameters for pure materials

	Ti / °C	Tb / °C	DTGmax/% min	Tmax/°C
Coal	370	583	9.13	498
Sugarcane bagasse (SB)	228	465	24.12	331
Biomass sorghum (BS)	180	440	22.73	431

3.2 Co-combustion of blends

The DTG curves of blends combustion atmosphere are illustrated in figure 2. The SB DTG curves have two mass loss events in all biomass ratios. The BS DTG curves show two mass loss events in the proportion of 25% biomass and three events in the proportions of 50 to 75%. In proportion of 25% of BS, degradation of cellulose and residual lignin overlaps the peak of coal degradation, and only two events are observed. The reduction of ignition and burnout temperature is proportional to the increased proportion of biomass in the mixture.

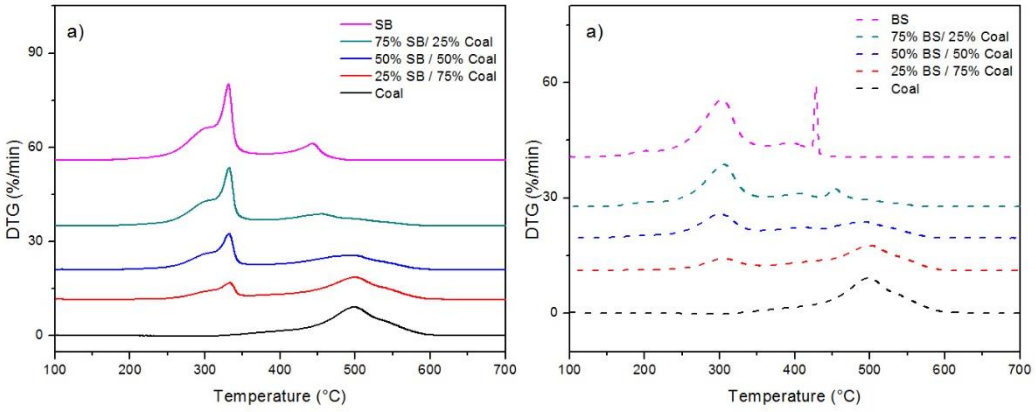

Figure 2. (a) DTG profiles of Sugarcane bagasse blends at 10°C min; (b) DTG profiles of Biomass sorghum blends at 10°C min

4. ACTIVATION ENERGY DETERMINATION

Model Free Kinetics was applied to determine the activation energy (Eα) based on the degree of conversion (α) of thermal degradation of materials. The activation energy curves versus the degree of conversion of the mixtures are presented in Figure 3. The activation energy values were obtained for a single event, between the ignition temperature and burnout temperature. For both biomasses, the lower activation energy metering is found in the proportion of 25% biomass in mixture with coal, 123.57 kJ mol^{-1} for sugarcane bagasse and 117.05 kJ mol^{-1} for biomass sorghum. These activation energy values are lower than the value found for pure coal (163.33 kJ mol^{-1}). This shows that the presence of biomass facilitates the volatilization process, reducing the activation energy of the reaction.

Up to 50% biomass in the mixture, the activation energy values are similar, 168.4 kJ mol^{-1} and 168.3 kJ mol^{-1} for 50% and 75% of SB and BS, respectively. For coal, blends with BS activation energy values are 144.6 kJ mol^{-1} for 50% and 148.51 kJ mol^{-1} for 75% of BS. In proportions above 50% biomass in the mixture, the coal presence does not significantly affect the combustion. Thus the activation energy values are similar (Gil et al. 2010).

The behavior found for both mixtures is consistent with the reported in the literature. The mixtures activation energy has a tendency to increase with the increase of the proportion of biomass in the mixture (Buratti et al. 2015). The co-combustion of coal and biomass presents significant improvements in coal combustion and reduces the activation energy to the proportion of 40% biomass in the mix (Kocabas-Atakli, Okyay-Oner, and Yurum 2015). The curve versus activation energy conversion (α) indicates that the activation energy of both mixtures decreases with increasing degree of conversion ratios of 25 and 50%. This behavior is consistent with the one presented by (Leroy et al. 2010; Aboyade et al. 2011)

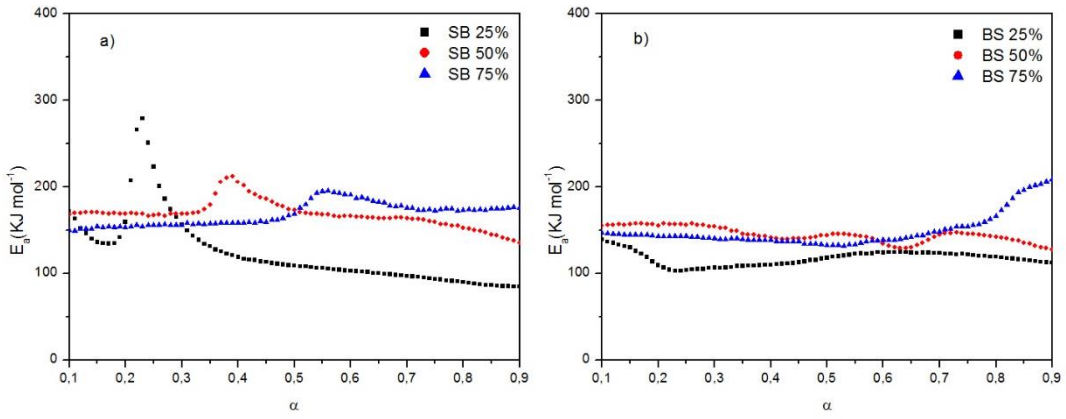

Figure 3. (a) Activation energy versus conversion for coal and SB blends; (b) Activation energy versus conversion for coal and BS blends.

The values of Eα (KJ mol-^{1}) of mixtures with both the biomasses are presented in Tab. 3. These activation energies corresponding conversions between 0.1 and 0.9.

Table 3. Activation energy for conversions 0,1 - 0,9

Blend	α - 0,1 KJ mol^{-1}	α - 0,2 KJ mol^{-1}	α - 0,3 KJ mol^{-1}	α - 0,4 KJ mol^{-1}	α - 0,5 KJ mol^{-1}	α - 0,6 KJ mol^{-1}	α - 0,7 KJ mol^{-1}	α - 0,8 KJ mol^{-1}	α - 0,9 KJ mol^{-1}
25% - SB	172.2	159.51	156.04	118.87	109.09	102.87	96.74	89.62	84.82
50% - SB	168.18	169.1	169.24	205.64	173.36	166.04	163.89	152.61	135.69
75% - SB	150	153.73	155.97	158.36	168.9	190.79	175.41	173.44	175.36
25% - BS	139.25	109.43	106.72	109.8	117.99	123.87	123.54	119.17	112.21
50% - BS	155.58	155.37	154.02	141.44	143.89	134.71	144.66	142.49	127.56
75% - BS	147.25	143.26	140.15	138.53	132.61	138.59	148.1	166.24	208.67

5. CONCLUSIONS

This study investigated the thermal decomposition of coal and biomass blends. Model-Free Kinetics was applied to determine the activation energy as a function of conversion (Eα) of the decomposition process in combustion atmosphere. The presence of biomass improves the performance of coal combustion and reduces the activation energy. Both mixtures in a proportion of 25% show a sharp inflection between 20% and 30% conversion. This fact is possibly related to the burning of bagasse components. The values obtained showed that, for pure biomass, sorghum has lower activation energy than sugar cane bagasse. For the mixtures, the lower activation energy is found in the proportion of 25% biomass, this is the optimal condition. The results of Eα are directly related to the conditions and types of fuel.

6. REFERENCES

Aboyade, A. O; Hugo, T. J; Carrier, M ; E. L. Meyer, R. Stahl, J. H. Knoetze, and J. F. Gorgens. Non-isothermal kinetic analysis of the devolatilization of corn cobs and sugar cane bagasse in an inert atmosphere. Thermochimica Acta, v. 517, n. 1-2, p. 81–89, 2011.

Al-shemmeri, T. T.; Yedla, R.; Wardle, D. Thermal Characteristics of Various Biomass Fuels in a Small Scale Biomass Combustor. Applied Thermal Engineering, abr. 2015.

Álvarez, A. et al. Determination of kinetic parameters for biomass combustion. Bioresource technology, p. 36–43, 2016.

Behera, B; Rahut D. B; Jeetendra A, and Ali A. Household collection and use of biomass energy sources in South Asia. Energy, abr. 2015.

Buratti, C; M. Barbanera; P. Bartocci, and F. Fantozzi. Thermogravimetric analysis of the behavior of sub-bituminous coal and cellulosic ethanol residue during co-combustion. Bioresource technology, v. 186, p. 154–62, jun. 2015.

Carvalho, W. S; T. J. Oliveira, C. R. Cardoso, and C. H. Ataíde. Thermogravimetric analysis and analytical pyrolysis of a variety of lignocellulosic sorghum. Chemical Engineering Research and Design, v. 95, p. 337–345, mar. 2015.

Ceylan, S.; Topçu, Y. Pyrolysis kinetics of hazelnut husk using thermogravimetric analysis. Bioresource technology, v. 156, p. 182–188, 2014.

Cruz, G.; Crnkovic, P. M. Investigation into the kinetic behavior of biomass combustion under N_2/O_2 and CO_2/O_2 atmospheres. Journal of Thermal Analysis and Calorimetry, v. 123, n. 2, p. 1003–1011, 2016.

Farrow, T. S.; Sun, C.; Snape, C. E. Impact of CO_2 on biomass pyrolysis, nitrogen partitioning, and char combustion in a drop tube furnace. Journal of Analytical and Applied Pyrolysis, v. 113, p. 323–331, maio 2015.

Frau, C. et al. Characterization of several kinds of coal and biomass for pyrolysis and gasification. Fuel, v. 152, p. 138–145, out. 2014.

Garcia-maraver, A. J. A. Perez-Jimenez, F; Serrano-Bernardo, and M. Zamorano. Determination and comparison of combustion kinetics parameters of agricultural biomass from olive trees. Renewable Energy, v. 83, p. 897–904, 2015.

Gil, M. V; D. Casal; C. Pevida;, J. J. Pis, and F. Rubiera. Thermal behaviour and kinetics of coal/biomass blends during co-combustion. Bioresource technology, v. 101, n. 14, p. 5601–8, jul. 2010.

Kazanc, F; R. Khatami, P. M. Crnkovic, and Y. A. Levendis. Emissions of NOx and SO_2 from Coals of Various Ranks, Bagasse, and Coal-Bagasse Blends Burning in O_2 / N_2 and O_2 / CO_2 Environments. Energy & Fuels, v. 25, n. 7, p. 2850–2861, jun. 2011.

Kocabas-atakli, Z.; Okyay-oner, F.; Yurum, Y. Combustion characteristics of Turkish hazelnut shell biomass, lignite coal, and their respective blends via thermogravimetric analysis. Journal of Thermal Analysis and Calorimetry, v. 119, n. 3, p. 1723–1729, 2015.

Kumar, A; N. Kumar; P. Baredar, and A. Shukla. A review on biomass energy resources, potential, conversion and policy in India. Renewable and Sustainable Energy Reviews, v. 45, p. 530–539, maio 2015.

Kwon, K. C. et al. Catalytic deoxygenation of liquid biomass for hydrocarbon fuels. Renewable Energy, v. 36, n. 3, p. 907–915, mar. 2011.

Leroy, V; D. Cancellieri, E. Leoni, and J. L. Rossi. Kinetic study of forest fuels by TGA: Model-free kinetic approach for the prediction of phenomena. Thermochimica Acta, v. 497, n. 1-2, p. 1–6, 2010.

López, R; C. Fernández, O. Martínez, and M. E. Sánchez. Techno-economic analysis of a 15MW corn-rape oxy-combustion power plant. Fuel Processing Technology, v. 142, p. 296–304, fev. 2016.

Morita, E.; Pécora, A. A. B.; Ramirez-behainne, J. J. Co-pyrolysis of pinus sawdust and coal in fixed bed bench scale reactor. 22nd International Congress of Mechanical Engineering (COBEM 2013). Anais. Ribeirão Preto: 2013

Mortari, D. A; C. Fernández, O. Martínez, and M. E. Sánchez. Study of Thermal Decomposition and Ignition Temperature of Bagasse , Coal and Their Blends. Thermal Engineering, v. 9, p. 81–88, dez. 2010.

Park, D. K; S. D. Kim; S. H. Lee, and J. G. Lee. Co-pyrolysis characteristics of sawdust and coal blend in TGA and a fixed bed reactor. Bioresource technology, v. 101, n. 15, p. 6151–6, ago. 2010.

Perego, C.; Bosetti, A. Biomass to fuels: The role of zeolite and mesoporous materials. Microporous and Mesoporous Materials, v. 144, n. 1-3, p. 28–39, out. 2011.

Specht, E.; Redemann, T.; Lorenz, N. Simplified mathematical model for calculating global warming through anthropogenic CO_2. International Journal of Thermal Sciences, v. 102, p. 1–8, abr. 2016.

Tabet, F.; Gökalp, I. Review on CFD based models for co-firing coal and biomass. Renewable and Sustainable Energy Reviews, v. 51, p. 1101–1114, nov. 2015.

Vamvuka, D; E. Kakaras, E. Kastanaki, and P. Grammelis. Pyrolysis characteristics and kinetics of biomass residuals mixtures with lignite. Fuel, v. 82, n. 15-17, p. 1949–1960, 2003.

Vyazovkin, S.; WIGHT, C. A. Kinetics in solids. Annual review of physical chemistry, v. 48, p. 125–149, 1997.

Vyazovkin, S.; WIGHT, C. A. Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data. Thermochimica Acta, v. 340-341, p. 53–68, dez. 1999.

Zhou, C; G. Liu, T. Fang, and P. K. S. Lam. Investigation on thermal and trace element characteristics during co-combustion biomass with coal gangue. Bioresource technology, v. 175, p. 454–462, 8 Nov. 2015.