



CO-FIRING STUDY OF SUGAR CANE BAGASSE AND COAL APPLYING THERMOGRAVIMETRIC ANALYSIS AND KINETIC

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Abstract. *The use of biomass as energy source to replace or reduce the use of fossil fuels has recently attracted increasing attention owing to energy crisis problems. The co-processing of coal and biomass is of great interest especially considering that these mixtures can reduce greenhouse gas emissions, sulfur dioxide and nitrogen oxides. The combustion characteristics of sugar cane bagasse and coals, as well as the co-firing (25% bagasse and 75% coal) have been examined through thermogravimetry (TG). The TG results have indicated that the thermal degradation processes of the pure materials are characterized by three visually distinguishable stages for biomass – moisture release (1st stage), combustion of volatile matter (VM), cellulose, hemicelluloses and lignin (2nd stage), and combustion of char and lignin (3rd stage); and two stages for coals - moisture release (1st stage) and combustion of VM and char (2nd stage). TG curves for the bagasse/coal blend are very close to the parent materials suggesting that the interaction between bagasse and coals are slight. In addition, the kinetic study indicates that for pure materials, activation energy is, in average 121 ± 36 and 107 ± 20 kJmol^{-1} for bagasse and coals respectively and for the blend 110 ± 35 kJmol^{-1} , which also confirm that there is no synergism effect between bagasse and coal, i.e., it seems that the volatiles released during bagasse devolatilization may not react with coal.*

Keywords: *co-firing, sugar cane bagasse, thermogravimetry, kinetic.*

1. INTRODUCTION

The use of biomass as energy source to replace or reduce the use of fossil fuels has shown an increasing interest in the energy industry worldwide. Furthermore, the application of this fuel can be an efficient process to reduce the CO₂ emissions to the atmosphere (Shen *et al.*, 2009).

Due to concerns regarding climate change, the use of alternative energy sources to replace fossil fuels is gaining increasing importance.

The co-processing between biomass and coals generates great interest especially considering that these mixtures can reduce greenhouse gas emissions, including sulfur oxides (SO₂) and nitrogen oxides (NO_x) mainly (Kazanc *et al.*, 2012). Brazil is the largest producer of sugar cane and, consequently, the largest producer of sugar cane bagasse ($1,6 \times 10^{11}$ kg of biomass per year - Final Report BEN 2011).

The co-firing of sugar cane bagasse and coals is advantageous because it is easy to apply and demands low cost since the existing plants for burning coal requires only a few modifications to adapt the use of blends (Riaza *et al.*, 2012). Co-processing methods provide great potential to produce electricity and economic advantages (Nimmo *et al.*, 2010).

The knowledge of the biomass characteristics and their blends with other fuels, including coals, besides the combustion kinetics of these materials are essential in the design and operation of conversion systems and modeling of combustion in furnaces in industrial scale (Munir *et al.*, 2009). According to Shen *et al.* 2009, the knowledge of biomass decomposition – either pure or mixed with coals – during a thermochemical conversion - is important to the development of an efficient technological process (Shen *et al.*, 2009). Most studies on the kinetics decomposition of biomass is focused on pyrolysis in an inert atmosphere. However, recently more attention has been directed to biomass decomposition in oxidative environments, but is still lacking information on this topic (Shen *et al.*, 2009; Safi *et al.*, 2004; Yorulmaz and Atimtay, 2009).

To our knowledge, there are few studies focusing on the synergistic interactions and impacts of biomass in co-processing with coals. The high thermochemical reactivity of some biomass and the high content of volatile material suggest that possibly occur synergistic effects when mixed with coals (Fermoso *et al.*, 2010; Edreis *et al.*, 2013).

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This study aims to investigate the thermal behavior of two different bituminous coals and a biomass (sugar cane bagasse) by using thermogravimetric analysis (TGA) and "Model Free Kinetics" model, and evaluate the interaction of these materials (biomass and coals) for applications in co-generation processes.

2. METHODOLOGY

2.1 Samples

Two coals and a biomass have been studied. Both are classified as bituminous coals, one is from Criciúma-SC (South region of Brazil) called CE4500 and the other from the Pennsylvania (United States of America), called PSOC1451. The biomass studied is sugarcane bagasse, which is from the central region of São Paulo State (Brazil).

Prior to thermogravimetric experiments, the samples were crushed and sieved to compose the average grain size range of 89.5 μm i.e, the fraction chosen for this work was that obtained from the sieves 105 and 74 μm . The bagasse before be triturated was washed in water and dried in oven at 80° C for 24 hours.

Table 1 shows the chemical characteristics of the materials.

Table 1: Chemical composition of coals and sugar cane bagasse.

rank and fuel source	PSOC 1451** Bituminous coal, (USA)	CE 4500*** Bituminous coal (Brazil)	Bagasse** Sugar cane bagasse (Brazil)
Proximate Analysis			
moisture (%)	2.5	1.2	4.4
volatile matter (%)	33.6	23.1	83.9
fixed carbon (%)	50.6	24.5	7.7
ash (%)	13.3	51.2	4.0
Ultimate Analysis			
Carbon (%)	71.9	49.4	44.3
hydrogen (%)	4.7	3.7	5.7
oxygen (%)*	6.9	7.9	45.5
nitrogen (%)	1.4	1.06	0.2
sulfur (%)	1.4	2.35	0.07
ash (%)	13.7	35.59	4.2

* by difference.

** by Kazanc *et al.*, 2011.

*** by Ávila, 2008.

The samples for this study were in both forms: pure and blended. The blends are composed by of 75% coal and 25% bagasse. For the blend with the Brazilian Coal, the blend is named as CE4500/Bag and for the blend with USA Coal, is named as PSOC/Bag.

2.2 Thermogravimetric experiments

Thermogravimetric experiments (TG) and derivative thermogravimetry (DTG) were performed in a Shimadzu TGA-51 analyzer using sample mass of 7.0 \pm 0.5 mg and an alumina crucible. The atmosphere used was synthetic air, under a flow rate of 100 mL min⁻¹. The temperature program was set from room temperature up to 650 °C for pure bagasse; for pure coals and the blends the temperature ranged between room temperature and 750 °C

2.3 Kinetic study

Five heating rate: 10, 15, 20 25 e 30 °C min⁻¹ were applied. The model used in the calculations was the "Model Free Kinetics", based on Arrhenius Equation.

The "Model-free kinetics" applies isoconversional techniques to obtain the activation energy (E_α) as a function of conversion (α) of the chemical reaction [$E=f(\alpha)$] (Vyazovkin and Dollimore, 2006; Vyazovkin and Wight, 1999).

The calculation of the activation energy by "Model-free kinetics" is made according to Eq. 1:

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

where E_a [kJ/mol] is the activation energy related to each conversion value (α), β is the heating rate [K/min], T_α temperature [K] related to each α value and $g(\alpha)$ the integral form of the inverse function $f(\alpha)$, that is the model reaction.

2.4 Synergy study

The effect of synergistic interactions was evaluated by comparing the experimental and theoretical TG / DTG curves.

Theoretical DTG curves were constructed based on the weighted average from pure samples (75% coal + 25% bagasse) of experimental DTG curves according to Eq. 2:

$$\frac{dm}{dt}(\text{mixture}) = 0.75 \left(\frac{dm}{dt} \right)_{\text{coal}} + 0.25 \left(\frac{dm}{dt} \right)_{\text{bagasse}} \quad (2)$$

where m is the mass obtained from TG curve.

3. RESULTS AND DISCUSSION

3.1 Thermogravimetric results

The TG and DTG curves of sugar cane bagasse, coals and the blends (25% bagasse/75% coal) are shown in the Fig. 1 and 2. Figure 1 show the results obtained for the CE 4500 coal and the Fig. 2 shows the results obtained for the PSOC 1451 coal.

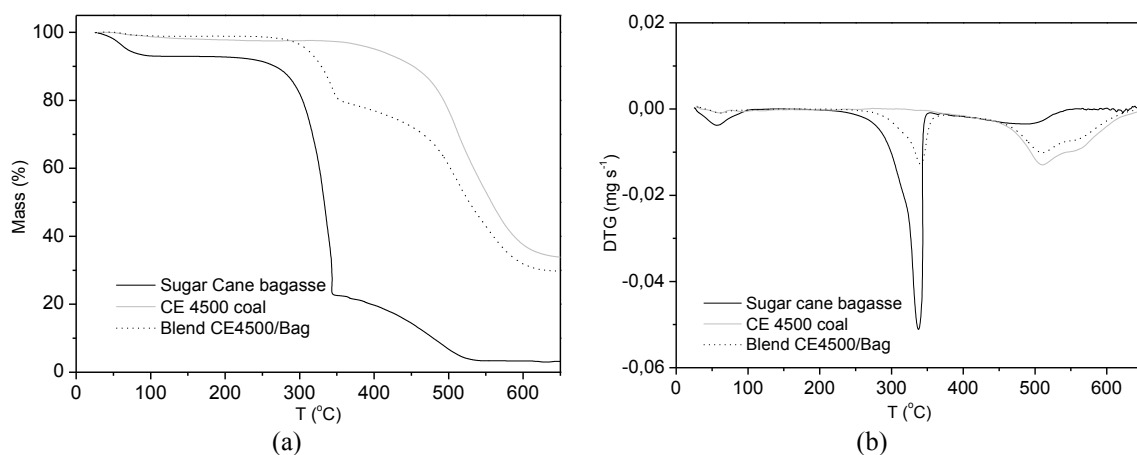


Figure 1. TG (a) and DTG (b) curves of the sugar cane bagasse, CE 4500 and the blend (25% bagasse/75% CE 4500), in synthetic air atmosphere (100 mL min^{-1}) at $20 \text{ }^\circ\text{C min}^{-1}$.

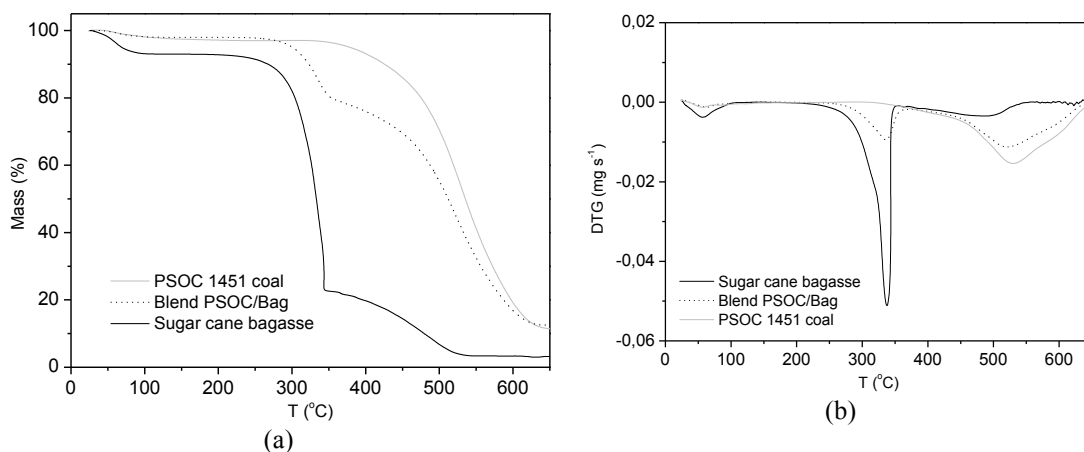


Figure 2. TG (a) and DTG (b) curves of the sugar cane bagasse, PSOC 1451 and the blend (25% bagasse/75% PSOC 1451), in synthetic air atmosphere (100 mL min^{-1}) at $20 \text{ }^\circ\text{C min}^{-1}$.

In the case of pure bagasse, after the weight loss related to moisture - which occurs between 30 and 100 °C, there are two main events of mass loss that are characteristic of lignocellulosic materials (Quensanga and Picard, 1988; Aiman and Stubington, 1993; Byrne and Nagle, 1996; Yang *et al.*, 2007; Guimarães *et al.*, 2009). In the first mass loss event from 180 °C, there is the hemicellulose and lignin decomposition (Souza *et al.*, 2006). The second step - which start at 343 °C, is related to the decomposition of cellulose, hemicellulose and lignin. In this step, the decomposition of lignin begins to dominate the rate of mass loss, and the remaining lignin continues to decompose above 400 °C. According to Yang *et al.*, 2007, the hemicellulose mass loss takes place between 220 and 315 °C, the cellulose, between 315 to 400 °C and the lignin between 160 and 900 °C (Yang *et al.*, 2007).

In the literature there are several studies reporting on the combustion of biomass in synthetic air atmosphere (Nimmo *et al.*, 2010; Fang *et al.*, 2013; Wang *et al.*, 2012; Ramajo-Escalera *et al.*, 2006; Khatami *et al.*, 2012). These studies have reported that the TG curves for many biomasses have shown three characteristic events of mass loss.

The TG and DTG curves obtained for the pure coals exhibit the occurrence of at least two distinct events of mass loss, and the beginning of the thermal degradation process starts at 367 °C. According Crelling *et al.* 1992 these events are identified as primary and secondary combustion.

Comparing the combustion process behavior of the coal and the biomass, it is observed in DTG curves (Figure 1 and 2 (b)) that the maximum reaction rates of bagasse sample is found in the second stage of mass loss. (between 200 and 350 °C, approximately) due to the high content of volatile material and the high ability to release heat at low temperature, while the maximum reaction rates of coals occurs in the third stage, related to the fixed carbon combustion (above 367 °C). This effect is due to the high ignition temperature of coal which causes higher rates of reaction are mainly concentrated in the later stage (char combustion) (Fang *et al.*, 2013; Wang *et al.*, 2012; Ramajo-Escalera *et al.*, 2006; Khatami *et al.*, 2012; Crelling *et al.* 1992).

For the blends, it is interesting to note that between 200 and 600°C there is also two main events of decomposition. The first one starts around 246°C, which is close to the initial decomposition of the pure bagasse. The second event also occurs close to the pure bagasse, however, from 480°C the peak to the DTG shifts to a higher temperature when compared with pure bagasse, which may be influenced by the ignition of the coal

3.2 Kinetic study

The E_a versus α curves for pure bagasse, pure coals and blends are presented in Fig. 3 and 4. The profile of E_a versus α curves show the complexity of the combustion process, mainly for the pure bagasse and for the blends. For both coals the range of E_a shows a stable behavior, which can be confirmed through the standard deviation (around 20 kJ mol⁻¹)

On the other hand, for the pure bagasse the standard deviation is the highest (83.916 kJ mol⁻¹), which suggest that this material presents a more complex combustion behavior.

The Fig. 3 shows the E_a versus α curve of the bagasse, CE 4500 coal and the blend (bagasse/coal).

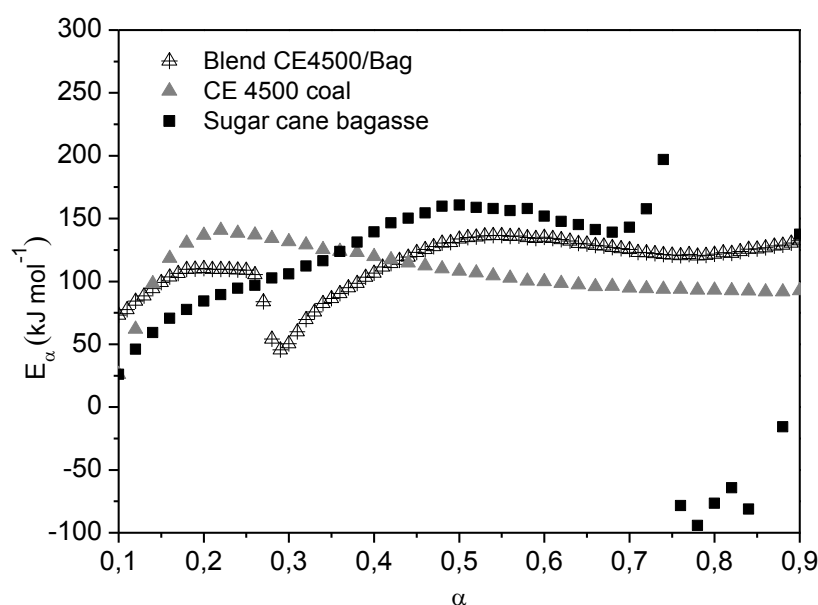


Figure 3. The E_a versus α curve of CE 4500, sugar cane bagasse and blend (25% bagasse/75% CE4500), under synthetic air atmosphere.

The Figure 4 shows the E_α versus α curve of the bagasse, PSOC 1451 coal and the blend (bagasse/coal).

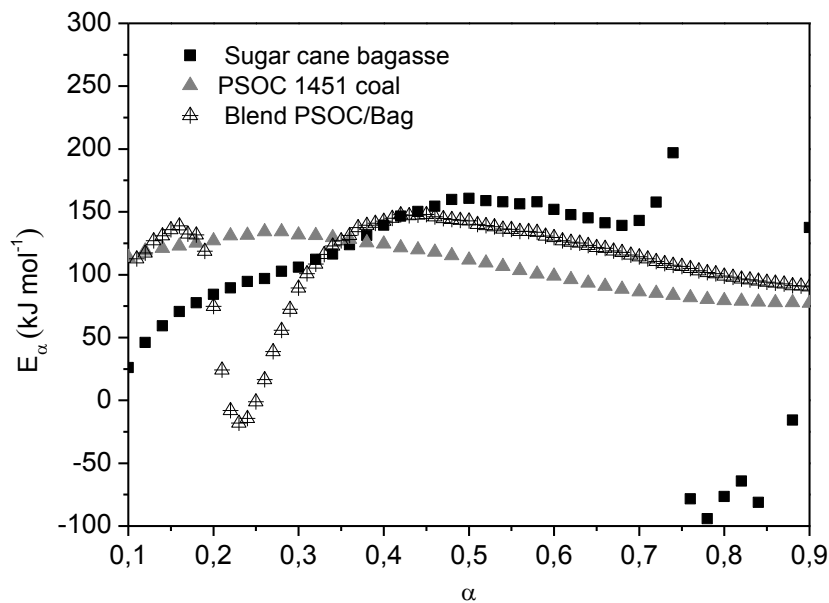


Figure 4. E_α versus α curve of PSOC 1451, sugar cane bagasse and of the blend (25% bagasse/75% PSOC), under synthetic air atmosphere.

Through E_α versus α curves (Fig. 3 and 4) it can be observed that the thermal decomposition of the blend occurs in two separate steps. Possibly the first one is related to the burning of the constituents from bagasse and after 30% of conversion, coal starts burning. Despite presenting a profile change of the curve, the value of activation energy was not much higher than the values obtained for the pure materials (Tab. 2).

Table 2: E_α average and standard deviation values related to the decomposition of CE 4500, PSOC 1451, sugar cane bagasse, blend CE4500/Bag and blend PSOC/Bag.

Materials	Average (kJ mol ⁻¹)	Standard deviation (kJ mol ⁻¹)
Sugar cane bagasse	121.59	36.42
CE 4500	107.129	20.532
PSOC 1451	107.199	19.881
Blend CE 4500/Bag	113.331	22.078
Blend PSOC/Bag	109.411	38.242

Comparing Fig. 3 and 4, we note that the behavior for both coals is similar. It is noteworthy that the two pure coals showed almost the same average value of activation energy.

As regards the blends, the behavior was also similar, i.e. the values were 113 and 109 kJ mol⁻¹, for CE 4500 and PSOC 1451 respectively. The blends with both coals show a sharp inflection near 25% of conversion.

The results of the E_α values for the pure materials 107 ± 19 and 91 ± 83 kJ mol⁻¹ for the bagasse and coal, respectively, and to the mixture 109 ± 38 kJ mol⁻¹ confirms that there is no synergistic effect between bagasse and coal. Possibly the volatiles released during the bagasse devolatilization not interfere in the coal burning.

3.3 Synergistic effect

The effects of synergism may occur due to the high amount of volatile material present in sugarcane bagasse and due to its high reactivity. When the blend of bagasse and coal is fed into a reactor or other system thermal, biomass thermal decomposition occurs rapidly. The volatile material released possibly favors the advance of the thermal decomposition of coal (Crelling *et al.* 1992). Figure 5 compares the TG and DTG curves theoretical and experimental obtained for the blend of bagasse and coal PSOC 1451.

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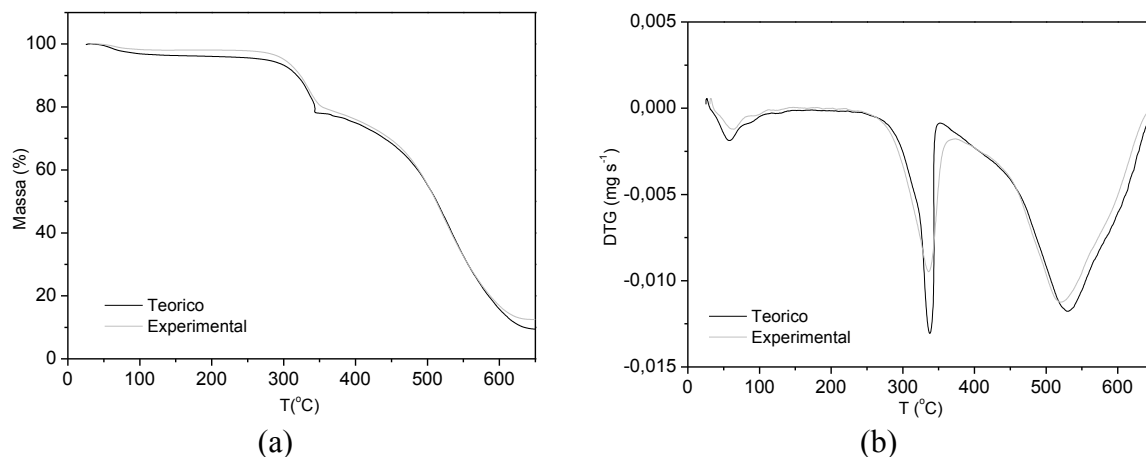


Figure 5: TG (a) e DTG (b) theoretical and experimental curves of the blend with sugar cane bagasse and coal PSOC 1451, under air atmosphere and heating rate of 20 °C min⁻¹.

As can be seen in Fig. 5, in the case of coal blend PSOC 1451 and bagasse under air atmosphere is not observed interaction between the components. The mass loss events are identical, as well as the shape of the curves. Although the experimental DTG curve (Fig. 5 b) exhibits a reaction rate lower than expected in the first peak (330 °C), the curves, both as TG DTG, theoretical and experimental are very close, indicating that in this case there is no occurrence synergism.

Although the DTG experimental curve (Fig. 5 b) shows a lower rate reaction than expected in the first peak (330 °C), the curves, both TG and DTG, theoretical and experimental are very close, indicating that in this case there is no occurrence synergism. This result also is obtained for the blend of bagasse coal and CE 4500, as shown in Figure 6.

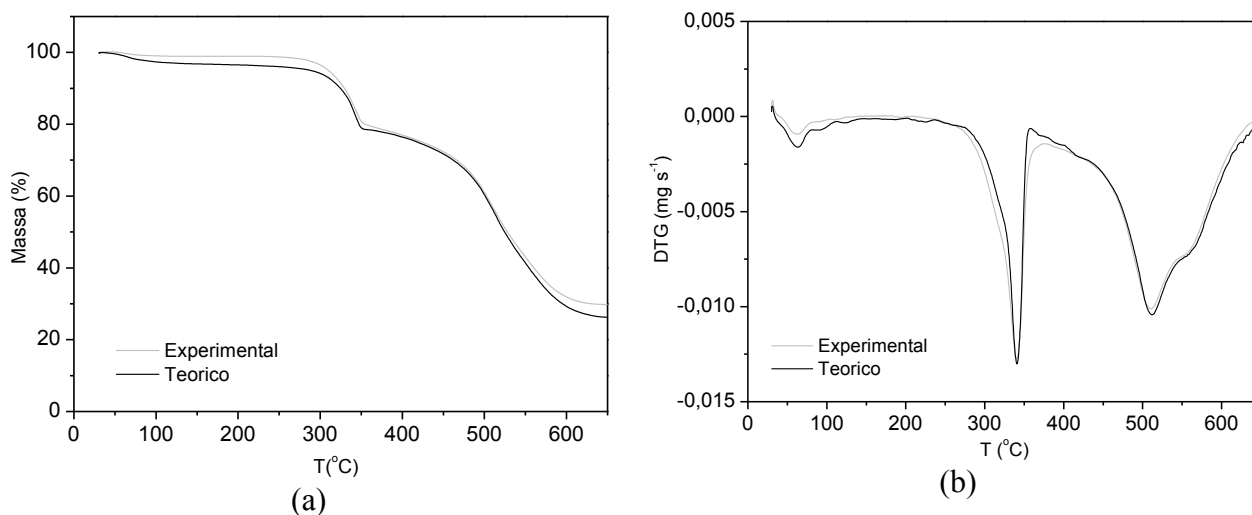


Figure 6. TG (a) e DTG (b) theoretical and experimental curves of the blend with sugar cane bagasse and CE 4500, under air atmosphere and heating rate of 20 °C min⁻¹.

For the case of the blend with coal CE 4500 there is no difference between the theoretical and experimental curves. Even in relation to reaction rates.

In this study, considering synthetic air atmosphere and heating rate of 20 °C min⁻¹, was not detected synergistic effects or any interaction between the bagasse and coal during thermal decomposition of the blends.

4. CONCLUSION

Due to the great interest in reducing CO₂ emissions and other pollutants, and also the search for alternative renewable energy sources to reduce the use of fossil fuels, this paper shows a study on the co-processing of sugar cane bagasse and coals, using thermogravimetry.

In thermal degradation of pure materials, through the TG and DTG curves are observed three events of mass loss. The curves obtained for the blends are very close to those obtained for the pure materials and individual. The events are summed.

$E\alpha$ values obtained for the blends are not much higher than the values obtained for the pure material, indicating no negative interference on the use of mixtures.

As regards the study of synergistic effects, it is concluded that under synthetic air atmosphere, volatile material released from the bagasse does not influence the onset of thermal decomposition of coal. This result is strengthened with the comparison of TG and DTG of theoretical and experimental blends and also the $E\alpha$ values.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

- Aiman, S; Stubington, J.F. Biomass and Bioener. 1993, 5 (2), 113.
- Ávila, I. (2008). 296f. Tese (Doutorado) – Universidade de São Paulo, Escola de Engenharia de São Carlos, São Carlos, 2008.
- Byrne, C.E.; Nagle, D.C. Carbon. 1996, 35 (2), 259.
- Crelling, J.C. Hippo, E.J., Woerner, B.A. West, D.P. Jr. Fuel. 1992, 71, 151.
- Edreis, E. M. A.; Luo, G.; Li, A.; Chao, C.; Hu, H.; Zhang, S.; Gui, B.; Xiao, L.; Xu, K.; Zhang, P.; Yao, H.. Bioresource Technology (2013), doi: <http://dx.doi.org/10.1016/j.biortech.2013.02.112>
- Fang, X.; Jia, L.; Yin, L. Biomass and Bioener. 2013, 48, 43.
- Fermoso, J.; Gil, M.; Pevida, C.; Pis, J.; Rubiera, F.. Chemical Engineering Journal. 2010, 161, 276.
- Final Report BEN 2011 - https://ben.epe.gov.br/downloads/Relatorio_Final_BEN_2011.pdf
- Guimarães, J.I.; Frollini, E.; Silva, C.G.; Wypych, F.; Satyanarayana, K.G. Ind. Crop. Prod. 2009, 30, 407.
- Kazanc, F.; Khatami, R.; Crnkovic, P. M.; Levendis, Y. Energy & Fuels. 2011, 25, 2850.
- Khatami, R.; Stivers, C.; Joshi, K.; Levendis, Y. A.; Sarofim, A. F. Combust Flame. 2012, 159, 1253.
- Munir, S.; Daood, S.S.; Nimmo, W.; Cunliffe, A.M. Gibbs, B.M. Bioresources Technol. 2009, 100, 1413.
- Nimmo, W.; Daood, S.S.; Gibbs, B.M.. Fuel. 2010.
- Quensanga, A.; Picard, C. Thermochim. Acta. 1988, 125, 89.
- Ramajo-Escalera, B.; Espina, A.; García, J. R.; Sosa-Arno, J. H.; Nebra, S. A. Thermochim. Acta. 2006, 448, 111.
- Riaza, J.; Gil, M.V.; Álvarez, L.; Pevida, C; Pis, J.J.; Rubiera, F. Energy. 2012, 41, 429.
- Safi, M.J.; Mishra, I.M.; Prasad, B. Thermochim. Acta. 2004, 42, 155.
- Shen, D.K.; Gu, S.; Luo, K.H., Bridgwater, A.V.; Fang, M. X. Fuel. 2009, 88, 1024.
- Shen, D.K.; Gu, S.; Luo, K.H., Bridgwater, A.V.; Fang, M. X. Fuel. 2009, 88, 1024.
- Souza, E.; Rambo., C.R.; Montedo, O.R.K.; Hotza, D.; Oliveira, A.P.N. Exacta. 2006, 4 (2), 289.
- Vyazovkin, S.; Dollimore, D. (2006). Journal of Chemical Information and Computer Sciences, vol. 36, p.42-45.
- Vyazovkin, S.; Wight, C.A. (1999). Thermochim Acta. 1999, 340, 53.
- Wang, Q.; Zhao, W.; Liu, H.; Jia, C.; Xu, H. Energy Procedia. 2012, 17, 869.
- Yang, H.; Yan, R.; Chen, H.; Lee, D. H.; Zheng, C. Fuel. 2007, 86, 1781.
- Yorulmaz, S. Y.; Atimtay, A.T. Fuel Process. Technol. 2009, 90, 939.