http://dx.doi.org/10.21577/0103-5053.20170071

J. Braz. Chem. Soc., Vol. 28, No. 11, 2202-2210, 2017.
Printed in Brazil - ©2017 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

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Article

Investigation on Prospective Energy Power from Corncob Husk Biomass and its Biochars by Kinetic Parameters and Isoconversional Models

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The biofuel properties of biomass play an important role in achieving their utilization on agro-systems and industries. In this context the biomass waste of maize, corncob husk, and its biochars were taken into account to be investigated by thermogravimetric analysis, thermodynamic parameters for non-isothermal analyses using the Ozawa-Flynn-Wall kinetic isoconversional model in order to comprehend its possible fuels features. It was also investigated the compounds generated after pyrolysis and their relation with oxidation reactions for the safe-handling and storage. It was found that corncob husk biochar produced at 300 °C shows the best qualities as a solid biofuel, since it requires less energy input through pyrolysis to be produced. Finally, analysing the compounds generated and remained on the biochar's surface, by Fourier transform infrared spectroscopy (FTIR) analysis, biochars produced at low temperatures present one of the lowest features prone to oxidation reactions.

Keywords: corncob husk biomass, biochar, Ozawa-Flynn-Wall, kinetic parameters, auto-ignition

Introduction

The advance of bioenergy technology in the last decade has received attention due to its important influence on global warming and anthropogenic carbon dioxide emission. As biomass is able to capture atmosphere carbon in its biological structures while it grows, it is currently defined as a carbon-neutral fuel.[1] Because of that, the exploration of biofuel properties of biomass plays an important role in sustainable agro-systems and agro-industries. Nevertheless the use of biomass not only has the potential usage as solid biofuels, but also has the potential use as carbon based byproducts obtained from biomass pyrolysis: biochar. Biochar is a carbon rich solid material produced by thermal decomposition of organic matter, generally biomass wastes.[2] Biochar is also known as a multifunctional material in agro-systems which is employed primarily as a soil conditioner for immobilizing metals, improvement of drought resistance, recovery and fertilization of the soil.[3] Both biomass and biochar can be used to design and fulfill a lifecycle favoring a competitive agricultural based world economy, inside farms and overall agro and energy based industries. However, the energy content of biochar is also a safety matter, since the physical and chemisorption of oxygen during its storage can lead and induce to self-ignition at room or lower temperatures.[4]

It is known that maize is a promising crop (both final product and wastes). The USA corn production, just for grains production was estimated on 386.75 mmt (million metric tons), while China and Brazil reach the numbers 21683.50 mmt (estimated production).[5] The final processing wastes of maize crops, as fuel form, are not widely known in the literature. Also, the literature does not discuss the thermal behavior of corncob husk, which is needed information for determining the energetic power as biomass and as biochar. In this context, the objective of this study was to quantitatively classify the thermal conversion features of corncob husk (CH) biomass into biochar by means of ignition and burnout characteristics obtained through thermogravimetric analysis (TGA), as well as its thermodynamic parameters for non-isothermal analyses using the Ozawa-Flynn-Wall (OFW) kinetic isoconversional model. It was also investigated, by Fourier transform infrared spectrometry (FTIR), the volatile compounds which remain on the biochar surface in the presence of oxygen and nitrogen after its pyrolysis process

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in order to investigate the carbonized biomass stabilization during storage to achieve the safe-handling of biochar made of CH biomass. The resulting data may be used to enhance the understanding of these agricultural residues behavior as biofuels, since kinetic models are important to optimally design a pyrolysis system and, subsequently, provide a useful base for further application in local recovery of energy (e.g. farms), as well as its storage security under air and nitrogen atmospheres.

Experimental

Biomass and biochar preparation

The corncob husk residues used as biomass and for the biochar production were separated and stored into a wooden bay for prior natural drying for 7 days (Figure 1). After this period the biomass was collected and washed in tap water to remove dust and then dried in an oven with mechanical air circulation for 48 h at 80 °C. Subsequently, the dried samples were ground in a Willey mill (MA048) with a fixed rotation of 1730 rpm, followed by sieving (Solotest Sieve, 35 mesh).

In order to attain a better investigation of CH as a carbonized biomass, biochars were produced in a muffle furnace at nine different temperature regimes: 250, 300, 400, 450, 500, 550, 600, 700 and 800 °C, designated, respectively, as BC250, BC300, BC400, BC450, BC500, BC550, BC600, BC700 and BC800. The thermal processing condition selected was a slow pyrolysis cycle with an increase of 5 °C min^{-1}.[6] The slow pyrolysis regime was selected as a standard procedure for this work in order to prioritize char production since it is known that the slow pyrolysis typically produces 35% char compared to 10% yield for the fast pyrolysis.[7-9] The retention time of the samples produced by slow pyrolysis on targeted temperature was 120 min. The samples were then naturally cooled at room temperature for 12 h (overnight). Subsequently, the samples were stored in labeled polypropylene bottles at room temperature until their use.

Thermogravimetric analysis

The CH biomass and its biochars samples were analyzed by thermogravimetric (TG) methods in order to determine the main parameters which may influence the thermal conversion and stabilization behavior under oxygen and nitrogen atmospheres. The combustion characteristics of corncob husk were determined on a simultaneous DSC-TG equipment, TA Instruments, model SDT Q600, nitrogen (99.99% pure) and air (pure), gas at a 100 mL min^{-1} flow rate, at dynamic atmosphere and on alumina pans. The TG and DTG (derivative thermogravimetric) analyses for the biomass were performed at three different heating rates (5, 7.5 and 10 °C), from 25 to 800 °C, for each sample. The sample weight, for each experiment, was maintained at around 2.25 ± 0.02 mg.

Kinetic study

The one-step global model assumes that biomass degradation processes results in a single reaction:[10]

$$\text{Biomass} \xrightarrow{k} \text{Water} + (\text{Volatiles} + \text{Gases})_1 + (\text{Biochar})_1 \quad (1)$$

where k is defined as the rate constant of reaction whose temperature dependence is expressed by the Arrhenius equation:

$$k = Ae^{\left(-E\alpha/RT\right)} \quad (2)$$

where Eα is the apparent activation energy (kJ mol^{-1}); T is the absolute temperature (K); R is the universal gas constant (8.31 J K^{-1} mol^{-1}); A is the pre-exponential factor (s^{-1}).

The rate of transformation from solid-state to volatile product is described by the following expression:[11,12]

$$\frac{d_\alpha}{d_t} = k(T)f(\alpha) \quad (3)$$

where α is the conversion degree of the process; k(T) is the time of process; f(α) is the rate constant and the reaction model.

Figure 1. (a) Fresh corncob husk (CH) residues used as biomass and for the biochar production; (b) CH biomass separated and stored into a wooden bay for prior natural drying for 7 days; (c) ground CH biomass.

Conversion (α) represents the normalized form of weight loss data of decomposed sample and is defined as follows:[13]

$$\alpha = \frac{m_i - m_\alpha}{m_i - m_f} \tag{4}$$

where m_i is the initial mass of the sample; m_α is the actual mass; m_f is the mass after combustion.

Combining equations 2 and 3 gives the fundamental expression of analytical methods to calculate kinetic parameters, on the basis of TG results, as follows:

$$\frac{d_\alpha}{d_t} = A \times f(\alpha) \times e^{\left(-E\alpha/_{RT}\right)} \tag{5}$$

The expression of the function f(α) and its derivative f(α) are used for describing solid-state first order reaction:

$$f(\alpha) = (1-\alpha)^n \tag{6}$$

where n is the reaction order.

Substituting expression 6 into equation 5 gives the expression of reaction rate in the form:

$$\frac{d_\alpha}{d_t} = A \times (1-\alpha)^n \times e^{\left(-E\alpha/_{RT}\right)} \tag{7}$$

For non-isothermal TG/DTG experiments at linear heating rate ($\beta = {}^{d_T}\!/_{d_t}$), equation 7 can be written as:

$$\frac{d_\alpha}{d_t} = \frac{A}{\beta} \times (1-\alpha)^n \times e^{\left(-E\alpha/_{RT}\right)} \tag{8}$$

Equation 8 states the part of the biomass consumed at a precise period of time. Here, the activation energies were acquired from non-isothermal TG/DTG. The procedures used to determine kinetic parameters were non-isothermal and isoconversional Ozawa-Flynn-Wall (OFW) methods and, therefore, performed assessments at different heating rates were necessary.

The Ozawa-Flynn-Wall method

Non-isothermal thermogravimetric studies are a widely held method to investigate the kinetics and thermodynamics behavior of biomass. An isoconversional integral technique is a precise method for the estimation of the activation energy values without having information about the kinetic model of the reaction pathways. Therefore, the OFW kinetics isoconversional method was applied:[14]

$$\ln(\beta) = C\alpha - \frac{E\alpha}{RT} \tag{9}$$

where β is the heating rate; Eα is the apparent activation energy; Cα is the function of the conversion degree α; R is the universal gas constant 8.31 J K^{-1} mol^{-1}; T is the absolute temperature (K).

Three different values of heating rate (β) were applied. In this work, the pre-exponential factor (A) and enthalpy (ΔH) (thermodynamic parameters; equations 10 and 11) were calculated using the OFW isoconversional method at an intermediate value of beta (i.e. 7.5 °C min^{-1}).

$$A = \beta E\alpha \exp\left(\frac{\frac{E\alpha}{RTm}}{RTm^2}\right) \tag{10}$$

$$\Delta H = E\alpha - RT \tag{11}$$

where Tm is the DTG peak temperature.

Ignition and burnout temperatures

The ignition temperatures (IT) of the biomass were determined from TG by two different methods: intersection method (IM) and deviation method (DM), for the three different heating rates 5, 7.5 and 10 °C. The burnout temperatures (BOT) of the biomass were determined from the single peak of DTG curve, more specifically, the second peak. Both IT and BOT were calculated in order to investigate the effect caused by different heating rate values in these variables. These temperatures were calculated as indicated by Lu and Chen[15] and the summary calculations can be seen in the Supplementary Information data.

Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra for biochars samples were made using the pellet technique by mixing 0.1 mg of dried biochar with 0.99 mg of pre-dried and pulverized spectroscopic-grade KBr (Merck) and collected by a FTIR spectrometer Jasco 410™ operating in the spectral range from 4000 to 400 cm^{-1}.

Results and Discussion

Thermogravimetric analysis of biomass in air and nitrogen

Figure 2a shows the thermal analysis for corncob husk biomass. For this sample it was verified that there was a small variation of mass with the increase of heating rate: 82, 89 and 92% for air atmosphere. For N_2 atmosphere the mass variation was more significant when the heating rate was increased: 67, 76 and 87%, for an initial temperature of breakdown at 120 °C, ending in 600 °C.

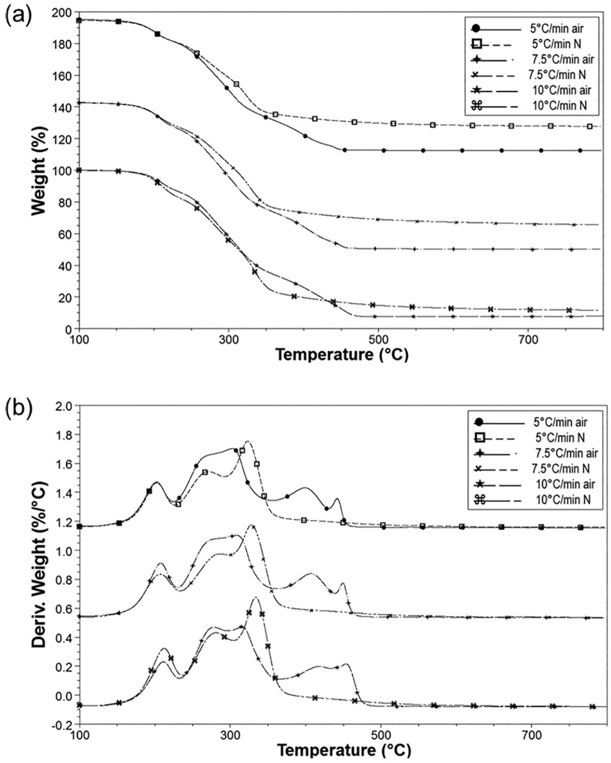

Figure 2. Distributions of (a) TG and (b) DTG of corncob husk. All curves compare the analysis in air and N_2 atmospheres at the heating rates of 5; 7.5 and 10 °C min^{-1}.

In the DTG curve (Figure 2b) for CH biomass, three steps of degradation were verified, which the first happened quickly, in a single stage. The second and third reactions are characterized as overlapping reactions. In the first region of thermal decomposition (dehydration for pyrolysis; < 250 °C), the first few changes that occur in biomass are related to the loss of water and a mild cellulose depolymerization[16] and, therefore, the mass decreased only slightly. The release of water molecules (moisture) is highlighted by the first peak in the DTG curve. The second reaction is caused by the degradation of lignocellulose (ca. 300 °C) and it is a route which shows a formation process of free radicals that are started by homolytic breakdown of chemical bonds. Free radicals that drive the process are initially formed by thermal action between structural inorganic impurities and the oxygen present in the biomass. An additional source of free radicals that can exist at the same time is due to the low atmospheric oxygen levels which may be present in the early stages of pyrolysis.[16] At this stage, carboxyl and carbonyl groups are formed and subsequently cleaved to produce carbon dioxide and carbon monoxide.[17] Between 250 and 350 °C the complete depolymerization of cellulose occurs, resulting in a great loss of mass because of volatilization and the creation of arrays of amorphous carbon. In this region of temperature (ca. 330 °C) the first formation signs of aromatic carbons still occur and it can be one of the reasons for the overlapping of this step reaction. However, up to 350 °C, polyaromatic graphene sheets begin to grow at the expense of the array of amorphous carbon. In addition, the intensity of the main peak changed only from 0.54 to 0.55% min^{-1} under atmospheric air, but under the N_2 atmosphere it increased from 0.59 to 0.89% min^{-1}.

In view of the temperature of the two main DTG peaks it is possible to identify the combustion efficiency of corncob husk: 308 and 328 °C for air and N_2, respectively. Additionally, the CH biomass DTG analysis data also show that the corncob husk biomass is composed by a complex matrix because there are overlapping reactions sequels, which can be related to the intricacy of this biomass.

Kinetic study

The isoconversional method is the assessment of the dependency of the real $E\alpha$ needed on the conversion or temperature evolvement. The usage of this dependency for assembly kinetic calculations becomes necessary in order to explore the mechanisms involved in thermal breakdown.[14] In other words, in isoconversional kinetic analysis, the biomass degree of conversion (α) is expected to be constant, and also the ratio of reaction depends totally on the temperature of reaction (T).[18] In this context, Figure 3 represents the curves of conversion degree *vs.* temperature at different heating rates, 5, 7.5 and 10 °C min^{-1} for corncob husks (a) in air atmosphere and (b) in N_2 atmosphere. One predominant stage can be seen in the progression of the systems and, thus, CH thermal degradation is described as a homogeneous process. Commonly, as the heating rate slows, the temperature at which conversion occurs is lower.[19]

Corncob husk is an herbaceous biomass material. Therefore, the first stage of conversion, the portion between the temperatures 80 and 200 °C can be linked with thermal degradation of cellulose. Information from TG and DTG curves in the breakdown range of $0.1 < \alpha < 0.9$ were used to determine the kinetic parameters of the process in all subsequent calculations. Figure 4 represents ln β *versus* α (1/T) by means of TG curves present in Figure 2.

The value of the $E\alpha$ declines with the intensification of the conversion processes. Thus, the activation energy of the CH biomass for the extreme alpha values of 25 and 95% are 2.79 and 67.17 kJ mol^{-1}, respectively, for air atmosphere; and 7.63 and 71.69 kJ mol^{-1} for N_2 atmosphere, respectively. The difference between the activation energies is due to responses of the solid-state samples, which are not

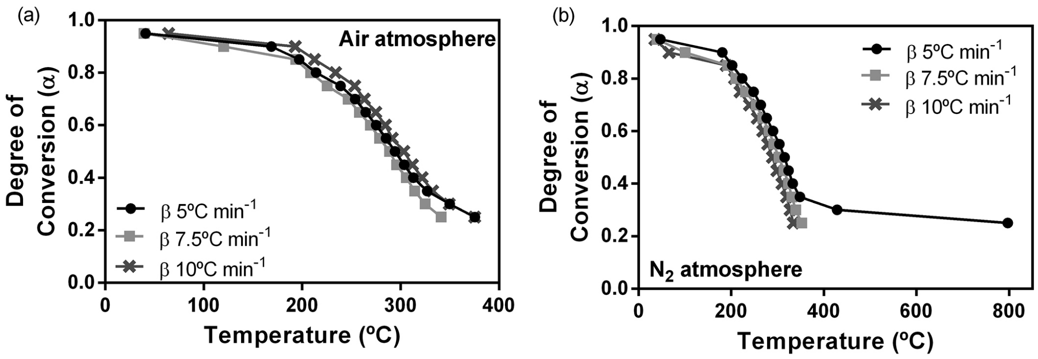

Figure 3. Curves of conversion degree *vs.* temperature at different heating rates and different atmospheres (a) for CH at air atmosphere; (b) for CH at N_2 atmosphere. One predominant stage can be seen in the progression, thereby illustrating a homogeneous process.

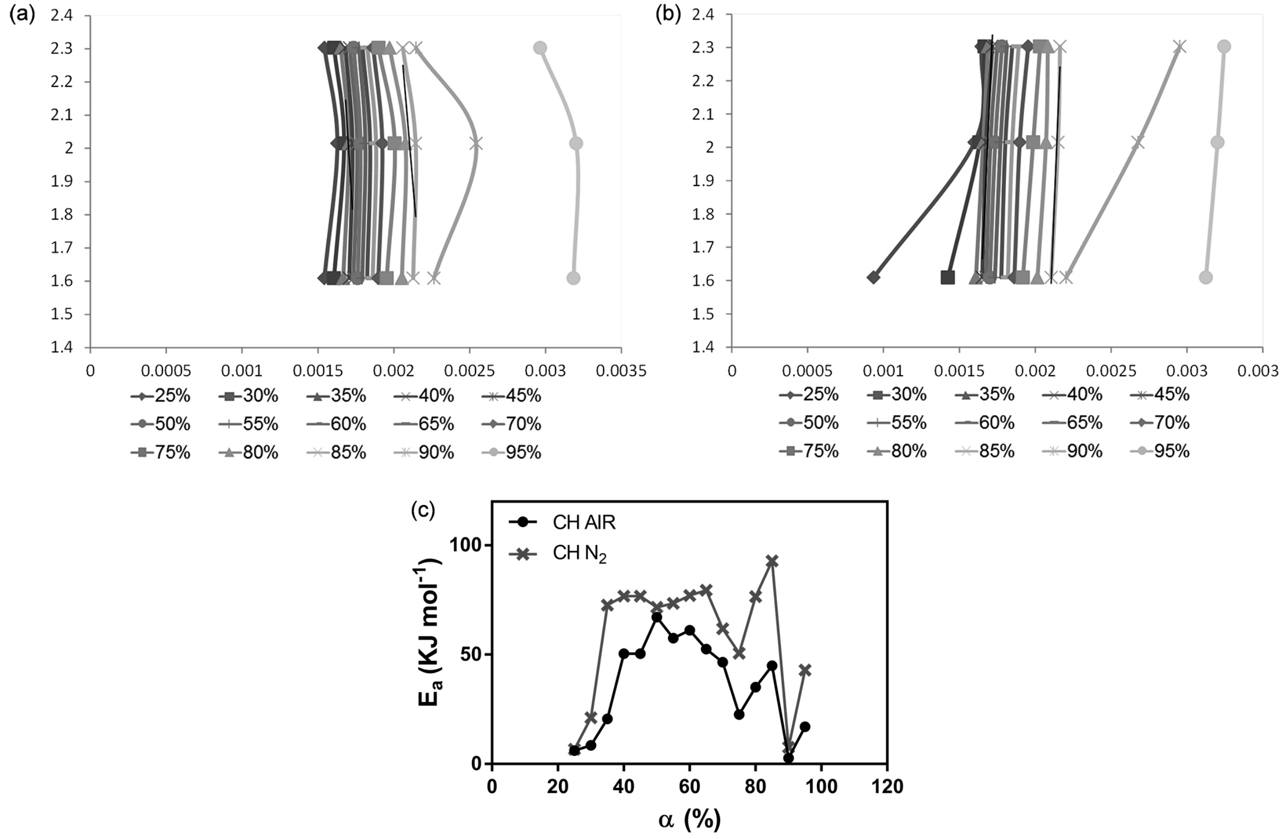

Figure 4. The Ozawa-Flynn-Wall isoconversion method applied to the thermal processing TG data of (a) CH at air atmosphere; (b) CH at N_2 atmosphere in open pans within 25-95% of conversion and (c) changes of activation energy during biomass breakdown process for both atmospheres studied. The apparent activation energy varies with increasing conversion rates and indicated volatiles degradation approximately at an α 50-85% and is directly related with the reactivity of the CH biomass.

decomposed in a simple one-step mechanism. In contrast, this decomposition occurs and follows a complex multi-step reaction[20] because of the biomass complexity, mainly at lower conversion stages. For that reason it is commonly accepted that values of the activation energy on the range of 60-120 kJ mol^{-1} are reasonably low and indicates that the higher values of activation energy is required to decompose biomass with greater lignin amounts.[21] For lignocellulosic biomass the activation energy can vary from 80 to 200 kJ mol^{-1} for hemicellulose, 195-286 kJ mol^{-1} for cellulose and 18-65 kJ mol^{-1} for lignin.

The first activation energy value observed was small due to cleavage of weak chemical bonds and the removal of biomass' volatile constituents and also because at the start of the thermal breakdown all the strong bonds of the biomass were not cleaved.[22] Figure 4c represents the values of Eα during the heating process at both studied atmospheres. If the variance between Eα values is minor, smaller is the energy used at thermal conversion process of this biomass.[23] It is also important to highlight that the chemical stability of a material is directly proportional to the value of activation energy.[13] Since the pre-exponential factors are directly related to the biomass structures,[23] Table 1 shows the kinetic parameters at the point of maximum conversion for corncob husk for the three heating rates analyzed.

The values of first order pre-exponential factors for CH biomass ranged from 10^{-2} to 10^{5} s^{-1} and 10^{0} to 10^{9} s^{-1}, for air and N_2 atmospheres, respectively. The low pre-exponential factors ($< 10^{9}$ s^{-1}) may indicate a surface feedback of corncob husk biomass, as well as a tight complex, and difficulty to breakdown.[24] The lower values of A and Eα found in CH biomass indicate a quicker and easier degradation effect of this biomass, at the respective degrees of conversion, when compared with biomass of non-lignocellulosic origin.[25]

Ignition and burnout temperatures

Ignition temperature (IT) is defined as the smallest temperature at which a fuel ignites spontaneously in an environment deprived of an external source of ignition.[26] The IT is greatly associated with safety in storage and delivery when coal or char is employed as a fuel in industry. On the other hand, the burnout temperature (BOT) of a fuel is an indicator of its reaction degree.[27] Therefore, the higher the BOT value, the smaller amount of the combustible components left in the fuel; i.e., the BOT states the temperature at which the fuel is virtually fully consumed.

Figure 5a shows the ignition and burnout temperatures obtained from IM and DM CH biomass. The IT of corncob husk calculated by IM ranged from 218 to 223 °C for air atmosphere and from 235 to 240 °C for N_2 atmosphere. The IT did not increase notably with the heating rate. Using the DM method, the IT ranged from 112 to 220 °C. The difference of IT values measured by IM and DM is consistent with the fact that the IM method is based on cellulose reaction, while DM is based on lignin hemicellulose, which is more reactive than cellulose and lignin.[28,29] Once biomass was ignited, the procedure initiates with the combustion of hemicellulose and volatile matter. In this context, the BOT of corncob husk biomass was between 341 and 352 °C for air atmosphere and, for N_2 atmosphere, between 354 and 365 °C. When biomass was ignited, the combustion of volatile matter ruled the chemical reactions. The primary step of biomass combustion is related to the homogeneous reaction. When the chemical reactions shift to burnout, char combustion takes over, and this secondary step reaction dynamics is consequence of a heterogeneous reaction.[15] Therefore, the heating rate has more impact on changing BOT than on IT.

In Table 2, the equations of the regression lines and their coefficients of determination (R^2 values) for the profiles of the IT and BOT are given. The values calculated for corncob husk, for both IM and DM methods, are characterized by

Table 1. Kinetic parameters of corncob straw biomass in air and N_2 atmosphere

α / %	CH air atmosphere			CH N_2 atmosphere		
	Eα / (kJ mol^{-1})	ΔH	A / s^{-1}	Eα / (kJ mol^{-1})	ΔH	A / s^{-1}
25	6.134	6.13×10^{3}	3.04×10^{-2}	6.782	6.78×10^{3}	3.61×10^{-2}
30	8.562	8.56×10^{3}	7.55×10^{-2}	21.132	2.11×10^{4}	2.02×10^{0}
35	20.607	2.06×10^{4}	2.29×10^{0}	72.651	7.26×10^{4}	3.46×10^{5}
40	50.487	5.05×10^{4}	3.06×10^{3}	76.782	7.68×10^{4}	6.47×10^{5}
45	50.487	5.05×10^{4}	3.82×10^{3}	76.782	7.68×10^{4}	8.70×10^{5}
50	67.163	6.72×10^{4}	2.12×10^{5}	71.687	7.17×10^{4}	3.89×10^{5}
55	57.528	5.75×10^{4}	2.99×10^{4}	73.447	7.34×10^{4}	8.16×10^{5}
60	61.166	6.12×10^{4}	9.11×10^{4}	77.066	7.71×10^{4}	2.58×10^{6}
65	52.596	5.26×10^{4}	1.57×10^{4}	79.476	7.95×10^{4}	7.24×10^{6}
70	46.555	4.66×10^{4}	4.65×10^{3}	61.870	6.19×10^{4}	1.72×10^{5}
75	22.622	2.26×10^{4}	1.21×10^{1}	50.650	5.06×10^{4}	2.03×10^{4}
80	35.168	3.52×10^{4}	5.61×10^{2}	76.520	7.65×10^{4}	3.53×10^{7}
85	44.952	4.49×10^{4}	1.26×10^{4}	92.814	9.28×10^{4}	6.48×10^{9}
90	2.790	2.79×10^{3}	2.38×10^{-2}	7.628	7.63×10^{3}	3.59×10^{-1}
95	17.034	1.70×10^{4}	6.95×10^{1}	42.966	4.30×10^{4}	3.82×10^{6}

CH: corncob husk; α: conversion; Eα: apparent activation energy; ΔH: enthalpy; A: pre-exponential factor.

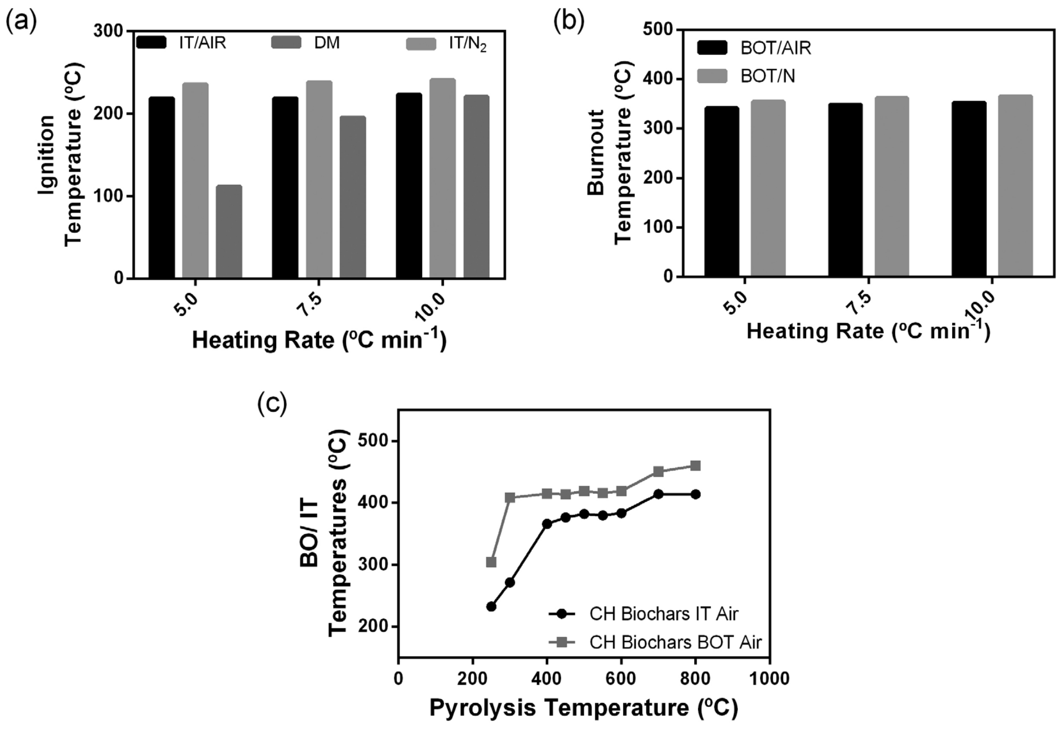

Figure 5. Ignition (IT) and burnout temperatures (BOT) of corncob husk by TG analysis: (a) IT calculated by intersection and deviation method; (b) BOT calculated by intersection method; (c) BOT and IT for CH biochars calculated by intersection method.

Table 2. Regression lines and coefficients of CH biomass ignition and burnout temperatures

Method	Regression line		R^2	
	Air	N_2	Air	N_2
Ignition temperature				
IM	y = 6.068x + 343.7	y = 2.190x + 344.3	0.9933	0.9683
DM	y = −21.72x + 338.9		0.9108	
Burnout temperature				
IM	y = 6.068x + 343.7	y = 2.190x + 344.3	0.9933	0.9683

IM: intersection method; DM: deviation method; R^2: coefficient of determination.

a linear relationship (R^2) and also, they show identical behavior.

The analysis of IT and BOT were also made on nine different biochars produced from corncob straw. By means of ignition temperatures, BC250 and BC300 show the best values for biofuels application. Low ignition temperatures of 271.73 and 323.34 °C indicate that BC250 requires lower energy input to start the material ignition. BC400 to BC600 fairly maintains the stability values for IT, ranging from 367 to 383 °C. Burnout temperatures indicate that BC300 is the most suitable material for biofuel application, because this temperature is the lowest pyrolysis temperature with the higher BOT value and lower IT value. In other words, BC300 requires less energy during pyrolysis to be produced; finally, its combustible components remaining in the fuel are almost completely consumed during the burn. These results suggest that the presence of amorphous carbon, as shown in TG/DTG analysis is an indicator for worthy carbon based biofuels.

Compounds generated and remained on the biochar's surface - safe-handling and storage

The FTIR spectra point out the signature of compounds generated during the pyrolysis process. As shown in Figure 6, the main components were CO_2, CO, CH_4, CH_3OH, phenols and C=O (carbonyl groups). The organic oxygen in the samples is evolved during the pyrolysis according to the level of hemicelluloses and lignin breakdown. The main wave numbers considered on the FTIR peaks of the biochars for air and nitrogen atmospheres were: CO_2: 2358 cm^{-1}; CO: 2181 cm^{-1}; CH_4: 3022 cm^{-1}; CH_3OH: 1046 cm^{-1}; phenols: 1100 cm^{-1}; and C=O: 1740 cm^{-1}.

By the analysis of the generated absorbance is observed how much energy was absorbed in a specific wavelength region. Overall is noted that the pyrolysis atmosphere is an important parameter, because peak intensities are greater under air atmosphere and demonstrate the more oxidized status of the sample, thus leading to more potential safety and storage risks. All samples showed non-linear relationship with pyrolysis temperature. Particularly, the sample BC550 presents the lowest levels of each evolved pyrolytic product investigated on the structure of this biochar, even under inert atmosphere. Subsequently, BC450 appeared to be more sensitive to oxidation reactions because it is known that physical adsorption of oxygen is followed by chemical adsorption.[30] The BC450 seems to not be suited for safe handling and storage in uncontrolled environments, whether for use in fuels or agriculture, because its intrinsically oxidized nature made this material more prone to auto-ignition, based on the evolved pyrolytic products in its chemical structure.

However, when the results of IT and BOT temperatures, as well as TG and kinetics parameters, are combined with the results shown on Figure 6, they converge to a possible suggestion about the BC300: BC300 required less energy during pyrolysis to be produced, less external energy input to start ignition and its combustible components left in the fuel are almost completely consumed in the burn. This material also presents one of the lowest sensibility features prone to oxidation reaction, especially under nitrogen atmosphere. Finally, BC250, BC300 and BC550 appeared to be the more inert materials to handle and store.

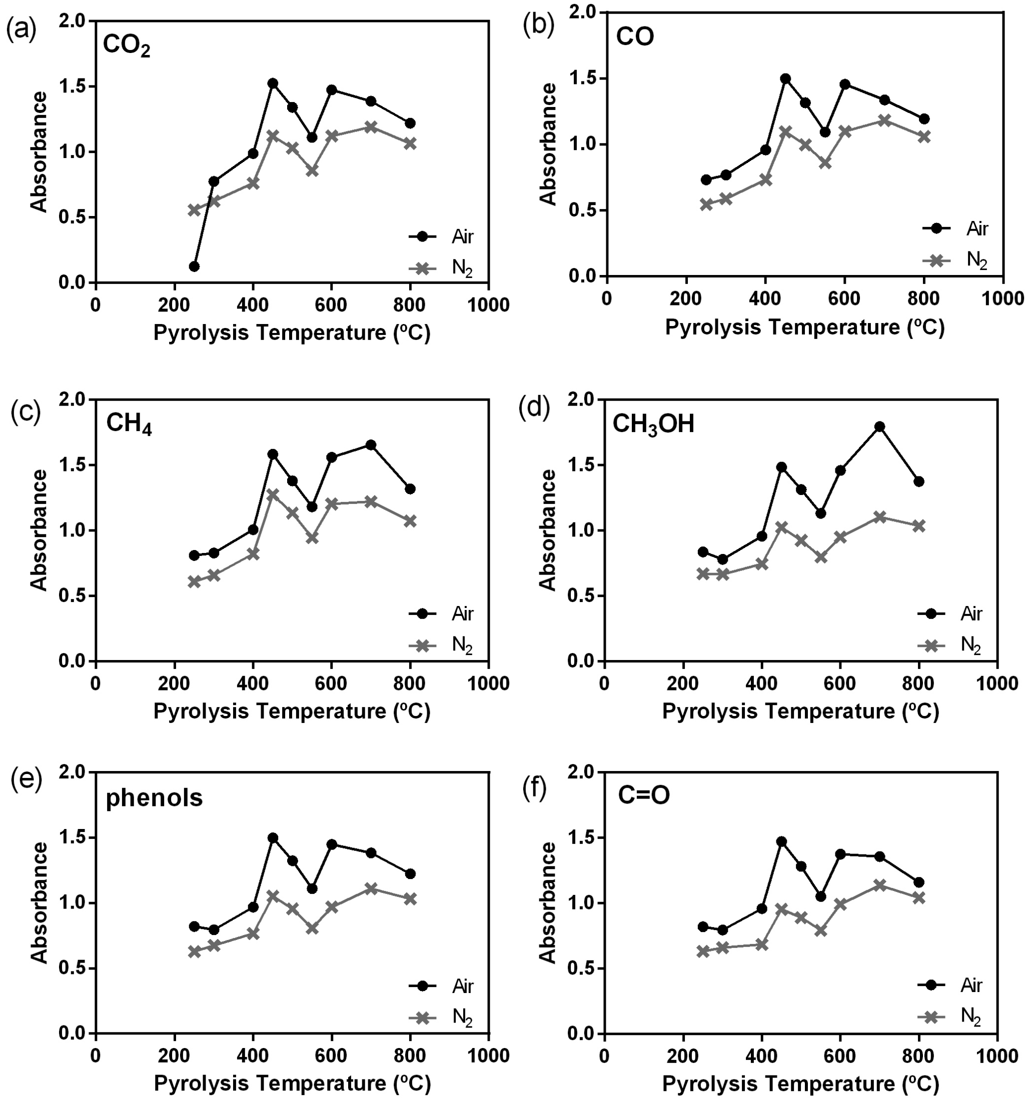

Figure 6. FTIR based profiles of the biochars created through pyrolysis of CH biomass with the main components (a) CO_2; (b) CO; (c) CH_4; (d) CH_3OH; (e) phenols; (f) C=O.

Conclusions

Observing the ignition temperatures for CH biomass is concluded that corncob husk biomass is a loose complex, and therefore, the decomposition of this biomass does not require a lot of energy input. Through the ignition and burnout temperatures, BC300 shows the best qualities as a biofuel, because compared to the other temperatures its production required less energy during pyrolysis. The formation of crystalline sheets of carbon as suggested by the TG analysis seems to be an important feature for pore development on biochar, directly influencing the propensity of the material to be indicated as fuel.

Regarding material safety in biofuel use, BC250, BC300 and BC550 appeared to be the more inert materials to handle and store, since their propensity for oxidation reactions appeared to be the lowest. In contrast, BC450 appeared to be more prone to oxidation reactions, forming carbon-oxygen complexes and oxygenated carbon-species given the evolved pyrolytic products identified in its chemical structure, which leads this particular material to be more prone to self-heating and auto-ignition, not being safe for storage and handling.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

The authors would like to thank the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP), Proc. 2013/08373-0, 2013/24168-8 and 2016/08215-4; CNPq for the scholarship and financial support; and Prof Nilson Cruz of Laboratory of Technological Plasmas (LaPTec, UNESP, Sorocaba) for granting the FTIR equipment for the biochar analysis.

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Submitted: February 14, 2017
Published online: April 17, 2017