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Chemical Engineering Research and Design

journal homepage: [www.elsevier.com/locate/cherd](http://www.elsevier.com/locate/cherd)

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# Thermogravimetric analysis and analytical pyrolysis of a variety of lignocellulosic sorghum

Wender S. Carvalho<sup>a</sup>, Tiago J. Oliveira<sup>a</sup>, Cássia R. Cardoso<sup>b</sup>,  
Carlos H. Ataíde<sup>a,\*</sup>

<sup>a</sup> Faculty of Chemical Engineering, Federal University of Uberlândia (UFU), Campus Santa Mônica, Bloco 1K, 38408-144 Uberlândia, MG, Brazil

<sup>b</sup> Department of Food Engineering, Federal University of Triângulo Mineiro (UFTM), 38025-180 Uberaba, MG, Brazil

## ARTICLE INFO

### Article history:

Received 11 March 2014

Received in revised form 10 October 2014

Accepted 18 November 2014

Available online 25 November 2014

### Keywords:

Biomass

Lignocellulosic sorghum

Kinetic parameters

Analytical pyrolysis

## ABSTRACT

Global economic growth and the deep concerns for human quality of life make it imperative to discover new technologies for generating renewable energy. Lignocellulosic biomass can be used as an alternative for energy production via thermochemical conversion processes such as pyrolysis. The constitution of each material causes it to display a particular characteristic when pyrolyzed, due to the proportion of its components. Hence, its characterization is very important to gain a better understanding of the pyrolysis process. This work involved the characterization and study of the thermal decomposition of a variety of lignocellulosic sorghum. Knowledge of the kinetics of pyrolysis was deepened by studying the decomposition of sorghum based on thermogravimetric analysis, using nitrogen as the purge gas at a flow rate of 30 mL/min. Analytical pyrolysis tests of this biomass were also performed in a temperature range normally employed in fast pyrolysis (823 and 923 K), using an inert helium atmosphere. The estimated values of activation energy ranged from 70.3 to 210 kJ mol<sup>-1</sup> and the pre-exponential factors showed results varying from 7.0 × 10<sup>4</sup> mol<sup>-2</sup> l<sup>2</sup> s<sup>-1</sup> to 5.0 × 10<sup>16</sup> s<sup>-1</sup>. The experimental derivative weight loss curves revealed the predominant presence of two major peaks at all the heating rates, the first corresponding mainly to hemicellulose decomposition and the second to cellulose decomposition. The change in temperature did not significantly influence the percentage area of the main detected components: 2-methyl-1,3-butadiene, acetic acid, limonene, and hexadecane, indicating a bio-oil of good quality (high amount of non-oxygenated compounds) compared with other types of sorghum.

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## 1. Introduction

Renewable resources derived from plant biomass are gaining increasing importance as alternatives for reducing our dependence on fossil fuels. Biorefineries will have an important role in fossil fuel reduction and help ensure the sustainability of the chemical sector. It is also likely to be the most effective use of biomass to replace the fossil fuel component in the grand energy sector (Brehmer et al., 2009). Sorghum has many uses or applications, according to its varieties. The most common types of sorghum are forage, grain, and sweet sorghum. Sweet sorghum,

which has high sugar content in the stalks, is used for the production of sugar and alcohol. EMBRAPA Milho e Sorgo (Maize and Sorghum Division) and several multinationals such as Monsanto and Ceres, for example, are developing varieties of lignocellulosic or fibrous sorghum in Brazil. This variety, which has larger stems that produce larger quantities of biomass, is being prepared for the future production of second generation ethanol. In the production of second generation ethanol, also called cellulosic ethanol, enzymes are used to extract the fuel directly from the cellulose of the plant's bagasse. Depending on market factors, lignocellulosic sorghum can also be used to generate electricity

\* Corresponding author. Tel.: +55 34 3230 9400; fax: +55 34 3239 4249.

E-mail address: [chataide@ufu.br](mailto:chataide@ufu.br) (C.H. Ataíde).

<http://dx.doi.org/10.1016/j.cherd.2014.11.010>

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### Nomenclature

$c_i$	mass fraction of pseudo-component $i$
$E_{a_i}$	Arrhenius activation energy for pseudo-component ( $\text{kJ mol}^{-1}$ )
$k_{0i}$	pre-exponential factor for pseudo-component $i$ (units dependent on the order of the reaction)
$k_i$	rate constant for pseudo-component $i$ (units dependent on the order of the reaction)
$m_0$	initial mass (mg)
$m_r$	residual mass (mg)
$m_t$	total mass (mg)
$n_i$	reaction order for pseudo-component $i$
R.T.	retention time (min)
$z$	number of pseudo-components

by burning in boilers, or to produce steam for heating processes in the food industry. Some researchers expect that the production of lignocellulosic sorghum will reach up to 60 tons of dry matter per hectare per year (de Oliveira, 2012). This productivity is about 2.5 times higher than that of sugarcane or corn.

A comparative evaluation of different types of biomass will allow for the choice of the one that offers the highest feedstock potential for the various existing thermal conversion technologies (Bridgwater, 2012). To this end, it is crucial to understand the thermal behavior and kinetic parameters of a biomass during its thermal conversion (Parthasarathy et al., 2013). The thermal analysis techniques, particularly thermogravimetric analysis (TG) and derivative thermogravimetric analysis (DTG), provide such information in a simple and fast way (White et al., 2011). Thermogravimetry measures the variations in weight of a given material as a function of temperature and time in a controlled atmosphere (Sait et al., 2012). Thermogravimetric measurements are highly accurate, provided temperature and other experimental conditions are well known and controlled (Várhegyi et al., 2009). Thermogravimetric measurements can be performed in three ways: by isothermal, semi-isothermal and non-isothermal methods. Dynamic thermogravimetric analysis (non-isothermal) offers an advantage over the other methods, because it is less difficult to maintain a constant heating rate than to keep an environment at a constant temperature, especially when exothermic reactions are involved. The literature reports that two methods are usually applied to describe the non-isothermal kinetics of the thermal degradation of lignocellulosic materials, which are essentially heterogeneous: the global reaction and independent parallel reactions. The global reaction methods are based on an isoconversional procedure and cannot provide a detailed description of mass loss data; however, they can estimate consistent kinetic parameters, which allows for a reasonable forecast of the final or global conversion of the pyrolysis process (Orfão et al., 1999). The other method, called independent parallel reactions, is based on the fact that the derivative weight loss curves often exhibit different peaks or shoulders. This characteristic indicates the occurrence of more than one type of reaction mechanism, and that the analyzed material consists of components having different reactivities. Therefore, the pyrolytic decomposition of heterogeneous materials, such as the lignocellulosic sorghum analyzed in this study, is best described considering the occurrence of independent parallel reactions, assuming the presence of pseudo-components.

It should be noted that kinetic parameters calculated by the Arrhenius equation can lead to slight errors in estimates. Since the kinetic theory of homogeneous reactions is adopted to describe typically heterogeneous reactions, it is plausible to assume that part of the inconsistency in the kinetic data of biomass obtained by the independent parallel reaction model can be attributed to the use of kinetic expressions that are adaptations of those used for homogeneous reactions and that do not incorporate dependent terms of the intrinsic nature of the solid state of the biomass.

Pyrolysis characteristics of various biomasses have been studied by many researchers in the past few decades and established significant information on the pyrolysis behavior and its kinetics (Mani et al., 2010). Several of these studies stand out and are described next. Mansaray and Ghaly (1999) determined the kinetic parameters of rice husks in the presence of oxygen and found a reaction order of 0.70–0.83 for hemicellulose and cellulose degradation, and of 0.20–0.29 for lignin degradation. Fisher et al. (2002) defined a single first-order reaction for cellulose decomposition. To determine the kinetic parameters of hemicellulose, a first order reaction in two consecutive steps was adopted. In a study of wood sawdust, Han and Kim (2009) used a reaction order of 0.65 for hemicellulose–cellulose degradation and of 0.24 for lignin degradation. Damartzis et al. (2011) used the procedure of independent parallel reactions to describe the thermal degradation of cardoon (*Cynara cardunculus*), employing a model with three first-order reactions. Amutio et al. (2013) studied the kinetics of forest shrub wastes from the Portuguese Central Inland Region, defined three parallel and independent reaction models considering the decomposition of the three main biomass pseudo-components (hemicellulose, cellulose and lignin) suitably describe the degradation of the forestry wastes studied, confirming that this simple model is adequate for studying different kinds of lignocellulosic materials.

Analytical pyrolysis is used extensively today, particularly the micropyrolysis gas chromatography–mass spectrometry technique (called Py-GC/MS). Products are characterized by means of the online separation analysis of vapors (Cardoso et al., 2011). This technique allows for the identification of the main compounds generated in pyrolytic reactions, as well as the study of the influence of variables such as temperature, size distribution of the sample, heating rates, and the use of catalysts in the composition and the concentration of products generated in the reactions (Lu et al., 2011). It is noteworthy that, in many cases, this technique has proved to be very useful due to its interpretability of data, operational flexibility and low cost. Another important advantage is that micropyrolysis uses small amounts of material and allows for the application of high heating rates to the sample. Gas chromatography coupled to mass spectrometry separates, identifies and quantifies the products generated. A proper understanding of the behavior of lignocellulosic materials under various pyrolysis operating conditions is essential to analyze the feasibility of using organic fuels or chemical products generated from various types of biomass.

To quantify compounds by the GC/MS technique requires calibration with standards. However, the chromatographic peak area of a given compound is considered to be linear with its quantity and the linear peak area percentage with its content (Lu et al., 2011). Therefore, the peak area percentages of identified compounds can be compared to observe changes in the content of pyrolysis vapors.

Piskorz et al. (1998) evaluate the yields of pyrolytic liquids from Italian sweet sorghum and sweet sorghum bagasse. The liquid product composition was similar to that obtained from fast pyrolysis of other grasses. The high sugar content (36%) of the sorghum resulted in high yields of carbon dioxide and liquid yields lower (52% at 798 K) than those from the bagasse at a lower temperature (63% at 723 K). A much higher conversion of the cellulose and hemicellulose to anhydrosugars, with a corresponding reduction in low molecular weight carbonyl compounds was obtained from deionized bagasse.

Cardoso et al. (2011) studied the fast and slow pyrolysis of tobacco and sweet sorghum residues. Compounds derived from holocellulose and lignin, as well as hydrocarbons and aromatic compounds, were identified as products. The predominant compounds in slow and fast pyrolysis of tobacco residue were found to be pyridine and 3-(1-methyl-2-pyrrolidinyl)-(S). In the pyrolysis of sweet sorghum bagasse, the main compounds identified were 2,3-dihydro-1-benzofuran and 2-methoxy-4-vinylphenol.

Lv and Wu (2012), who performed analytical pyrolysis of corncob and its main constituents (cellulose, hemicellulose and lignin), found that the decomposition of this biomass was a reflection of the scope of three main components. Hemicellulose contributed primarily to the formation of acids and ketones at around 573 K. Cellulose produced furans and small molecule aldehydes within a temperature range of

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