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Kinetic Study of Spiny Retamo (Ulex Eurioaeus L.) Waste Oxidative Pyrolysis

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The behavior of the pyrolysis and the kinetics of the spiny retamo (Ulex eurioaeus L.), problematic plant in the eastern slope in Bogotá Colombia, has been studied in a thermobalance, as a previous step for its valorization by pyrolysis in order to obtain fuels and chemical products. The kinetic model consists of a multicomponent mechanism that describes the formation of volatiles that involves three parallel and independent reaction networks that correspond to the decomposition of the three main pseudo-components of the biomass: hemicellulose, cellulose and lignin. Similarly, other products are considered as fixed coal and ashes produced. The thermogravimetric curves and the kinetic parameters have been compared with those obtained for other materials, and the chemical characteristics of the biomass have been determined. Although the samples are highly heterogeneous due to their composition, the degradation of these is similar to that of other lignocellulosic materials, which shows that their valorization pyrolysis is feasible.

1. Introduction

Biomass is considered one of the alternatives for promising fossil fuels for the production of biofuels, chemicals and energy. Vegetable biomass is a natural product that includes wood, agricultural residues, crop residues, algae, animal waste, organic fraction of municipal waste among others. Therefore, they have notable differences in their properties depending on their nature, the region and even the habitat in which they grow and develop (Ashter, 2018).

The spiny retamo (Ulex eurioaeus L.), is a shrub native to Europe that belongs to the family Fabaceae, characteristic for its long spines that can reach up to 5 cm in length and for its small yellow leaves, found in the tip of the shaped branches of individual or cluster. This species is classified as invasive in Colombia and in several countries of the world is a major concern in the Bogotá savanna, it generates alterations such as the loss of other species and the degradation of ecosystems. Being a species with great adaptive and colonizing capacities, the paramo ecosystems and high forest Andean are being affected by diversity, soils and the water resource (SiB, 2007).

This type of waste can be used as alternative raw material to fossil fuels due to the environmental problems caused during summer seasons. As a result, the interest in the development of biomass conversion routes to produce fuels and chemicals has increased, which are part of the broad concept of the biorefinery (Nizami et al., 2017). This concept includes several thermochemical and biological processes such as gasification, pyrolysis, combustion, hydrolysis, and fermentation (Williams et al., 2015). Within these routes of biomass conversion, pyrolysis has the best prospects of implementation at an industrial level because it is a conversion process where there is a thermal degradation that usually takes place in a temperature range between 300-600 ºC, producing a lot of products, including a solid known as char, a liquid known as bio-oil, and condensable and non-condensable gases (Aguado et al., 2000).

In order to improve the pyrolysis performance, a wide range of configurations of the reactors have been used, such as fluidized bed reactors, transport and circulating fluidized bed reactors, ablative reactors, auger reactors, vacuum reactors and conical spouted bed reactors (Amutio et al., 2012a). These types of configurations have been widely researched in laboratories but only few have been carried out on an industrial scale, leading this to one of the biggest challenges for the scaling of the pyrolysis processes is the energy supply, especially the energy required to heat the raw material and the fluidizing gas at the process temperature (Aguado et al., 2000;

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Erkiaga et al., 2014). This heat can only be partially supplied by gas fluidization due to certain limitations, such as a bypassing gas in the reactor and the low flexibility of the flow velocity and the gas inlet temperature (Amutio et al., 2013a). Amutio et al. (2012a) recommend the implementation of oxidative pyrolysis that involves the addition of a sufficiently low concentration of oxygen to allow the significant effects of a combustion reaction in the process, this being the step to adopt the process on industrial scale because the energy required is supplied in the pyrolysis process by the combustion of part of the pyrolytic products. This paper aims to provide information about the kinetics required for the large-scale auto thermal operation to be used in the development of a technology based on the conical spouted bed reactor.

2. Experimental

In this study, the spiny retamo have been studied by means of characterization of proximate and ultimate analysis in a Vario-Macro of Elementar and thermogravimetric analysis (TGA) Discovery 5500 of TA Instrument. The high heat value (HHV) has been measured in a Parr 6200 isoperibolic bomb calorimeter (Table 1). From these analyzes, it was possible to determine the ash content that is low, the fixed carbon and the volatile matter is high, which indicate that this biomass is suitable for a thermochemical valorization, either a pyrolysis or gasification, obtaining important products as a synthesis gas or active carbon (Table 1). Regarding the carbon and oxygen content, it is observed that it is high and very similar to that found by Balasundram et al. (2017) with rice husk, and a value very similar to hydrogen.

Table 1: Properties of the spiny retamo used in the study

Properties	Value
Ultimate analysis (% wt)	
Carbon	41,3
Hydrogen	6,26
Nitrogen	1,53
Oxygen	50,58
Proximate analysis (%wt)	
Moisture	3,68
Volatile matter	70,93
Fixed carbon	19,27
Ash	4,30
HHV (MJ kg^{-1})	19,43

The kinetic study has been carried out by thermogravimetry in a TGA 5500 thermobalance (Figure 1). The pyrolysis experiments have been conducted by subjecting the sample (approximately 10 mg) to a heating ramp of 15 °C min^{-1} from room temperature to 700 °C, using a nitrogen flow rate of 100 ml min^{-1}. The biomass particle size used in the runs is below 0.2 mm in order to avoid heat and mass transfer restrictions within the particle that would hinder the chemical process (Di Blasi, 2008; White et al., 2011).

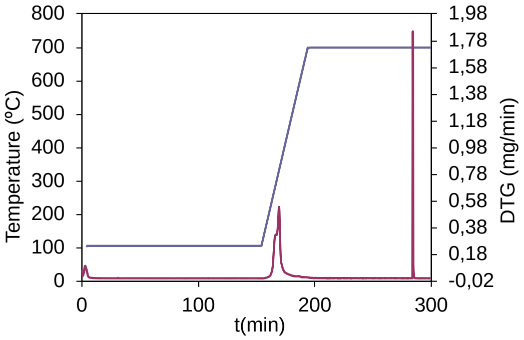

Figure 1: Derivate thermo-gravimetric (DTG) curve obtained in the test performed at 15 ºC/min.

2.1 Kinetic model

The kinetic model applied in this study consists of a multi-component mechanism that describes the formation of volatiles through the occurrence of three independent and parallel reactions, which correspond to the degradation of hemicellulose (HC), cellulose (C) and lignin (L). This study is based on the one proposed by

Amutio et al. (2012a) which considers that the oxidative pyrolysis process takes place in two stages: i) Pyrolysis and heterogeneous oxidation, and ii) char combustion. Accordingly, the influence of oxygen starts at the beginning of the pyrolysis process.

$$X = \sum_{i=1}^{n} X_i = X_{HC} + X_c + X_L \tag{1}$$

Biomass conversion, X, is defined as:

$$X = \frac{W_o - W}{W_o - W_\propto} \tag{2}$$

where W_o is the initial mass of the sample on a dry basis (at the end of the drying period), W_∞ the mass at the end of the pyrolysis step and W the mass at a given time. Similarly, the conversion of each constituent in the biomass is defined as:

$$X_i = \frac{W_{o,i} - W_i}{W_o - W_\propto} \tag{3}$$

Several studies (Lin et al., 2009; Mamleev et al., 2007) propose kinetic schemes for cellulose pyrolysis with a step for char formation. Nevertheless, Chen and Kuo (2011) reported that solid residue is hardly formed from the pyrolysis of individual hemicellulose and cellulose, but lignin pyrolysis is responsible for the formation of this material. In fact, it is well-known that the yield of char in the pyrolysis of biomass is directly related to the content of lignin (Mohan et al., 2006), or even the phenol compounds derived from lignin in the pyrolysis of biomass may undergo repolymerization reactions at temperatures above 100 ºC giving way to a solid residue or secondary char, also called pyrolytic lignin (Gayubo et al., 2010; Hosoya et al., 2007). Accordingly, the content of lignin may be calculated by summing the contribution of the deconvolution peak associated with lignin and the mass of char remaining at the end of the pyrolysis step (at the end of the isothermal period at 700 ºC. Thus, whereas the masses of hemicellulose and cellulose at the end of the pyrolysis step ($W_{\infty,HC}$ and $W_{\infty,C}$) are zero because these polymers are fully volatilized, the mass of lignin remaining in the particle ($W_{\infty,L}$) is the mass of the sample minus the ash content.

Many authors propose a first order kinetics for the degradation of the polymeric materials (Castro et al., 2012) whose overall kinetic equation is:

$$\frac{dX}{dt} = \sum_{i=1}^{n} \frac{dX_i}{dt} = \sum_{i=1}^{n} k_i \left(X_{i,\propto} - X_i\right) \tag{4}$$

where k_i is the kinetic constant corresponding to the degradation of each one of the three polymers. The kinetic constants are defined using the reparametrized Arrhenius equations, as follows:

$$k_i = k_{i,ref} exp\left[\frac{-E_i}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \tag{5}$$

where $k_{i,ref}$ is the kinetic constant at the reference temperature T_{ref} (500 ºC).

The kinetic parameters to be obtained by optimization are the kinetic constant at the reference temperature and the activation energy for each one of the three parallel reactions, and the content of two of the three polymers (the third one is obtained by subtraction). The error objective function (EOF) to be optimized is defined as the sum of the squared differences between the experimental DTG data and those calculated by the model:

$$EOF = \frac{\sum_{j=1}^{N}\left(\frac{dW_{j,exp}}{dt} - \frac{dW_{j,cal}}{dt}\right)^2}{N} \tag{6}$$

where N is the number of experimental data. The adjustment between the calculated results and the experimental values Xi is carried out by means of an algorithm written in Scilab (Figure 2). The optimization subroutine *fminsearch* (based on the Nelder-Mead algorithm) is used for minimizing the objective error function.

3. Results and discussion

The kinetic model applied in this study consists of a multi-component mechanism that describes the formation of volatiles through the occurrence of three independent and parallel reactions, which correspond to the degradation of hemicellulose (HC), cellulose (C) and lignin (L). This study is based on the one proposed by Amutio et al. (2012b) which considers that the oxidative pyrolysis process takes place in two stages: (i) Pyrolysis and heterogeneous oxidation; and (ii) char combustion. Accordingly, the influence of oxygen starts at the beginning of the pyrolysis process.

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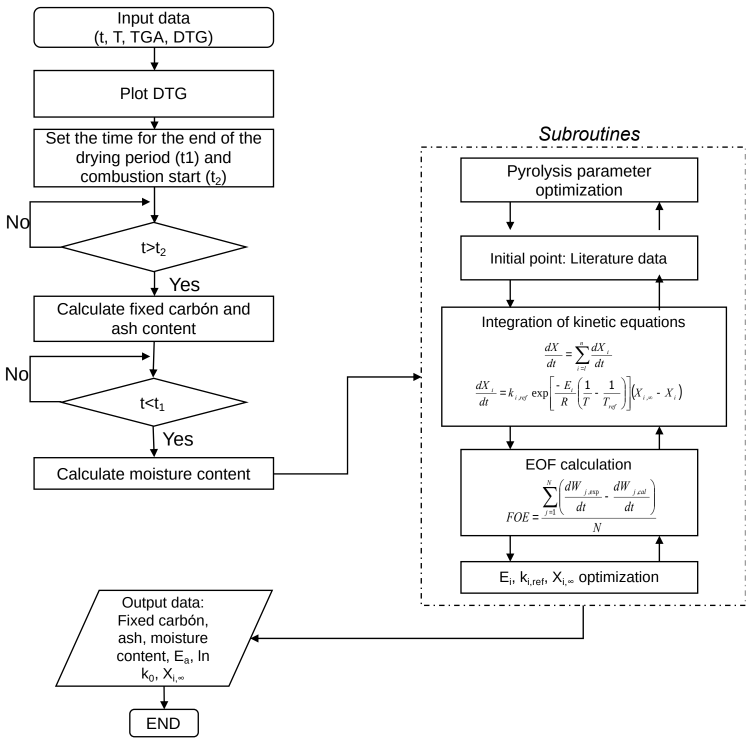

Figure 2: Flow charts of the algorithm designed for DTG deconvolution

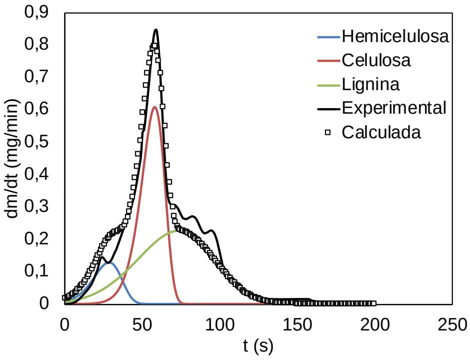

Figure 3: Adjustment by deconvolution of the three components of spiny retamo

In both cases, hemicellulose is the least thermally stable of the wood components due to the presence of acetyl groups (Bourgois et al., 1989). Lignin degradation starts at relatively low temperatures, proceeding over a wide range of temperatures (Nassar and MacKay, 1984). Furthermore, Sebio-Puñal et al. (2012) maintain that cellulose has higher thermal stability than hemicellulose and lignin due to its crystalline structure, but in this study, this is not always the case. Saldarriaga et al. (2015) found that in certain biomass types (*pinus insignis*, miscanthus or pellet) cellulose is the last polymer to begin its degradation, whereas in the remaining biomasses lignin begins its degradation at the same time or even later than cellulose. Once cellulose degradation has started, it is very fast and gives way to a characteristic sharp peak in the deconvoluted DTG curve.

Generally, with kinetic schemes of multiple stages is considered that the pyrolysis process is the sum of three independent reactions and parallel, without any interaction between them, corresponding to the degradation of hemicellulose, cellulose and lignin. In figure 3, shows the deconvolution of the biomass of the sawdust pine, where can see the main peak associated with cellulose, a left shoulder associated with the hemicellulose and a smaller peak at the right associated with the lignin. Also, it succeeded in developing a thermogravimetric method, which allows a better analysis of the raw material, since it was possible to optimize the heating ramp in order to perform an adequate degradation of the three components, with a step before drying, which allows the conditions described above are given properly.

In Table 2 it is observed that cellulose is generally the components with a high activation energy, with a value of 103.04 kJ mol^{-1} and the low activation energy corresponds to lignin. The kinetic parameters obtained are within the range of those published by other authors with other types of biomass, who also carried out the kinetic study considering three parallel reactions corresponding to hemicellulose, cellulose, and lignin. These results show that the spiny retamo can be valued by means of thermochemical treatments such as pyrolysis, because according to the initial characterization of the material (Table 1) and the kinetic parameters (Table 2), it is possible to obtain a char and a synthesis gas as primary product.

Table 2. Pyrolysis kinetic parameters values of frequency factor, k_0 and activation energy, E and pseudo-components contents.

Biomass	Kinetic parameters	Hemicellulose	Cellulose	Lignin
Bagasse	Log k_0 (s^{-1})	8.60	15.88	2.10
	E (kJ mol^{-1})	55.32	103.04	43.28
	Content (% wt)	7.60	30.17	36.33

Amutio et al. (2013b) argue that the most significant differences between kinetic results in the literature are mainly due to the methodological difference of data analysis used, rather than to the difference in the nature of the raw material. In general, the activation energy for different types of biomasses such as those presented in this study are within the similar ranges, as is the case of pinus insignus that has an activation energy for hemicellulose, cellulose and lignin of 117.4, 221.5 and 28.2 (Saldarriaga et al., 2015), 127, 252 y 33 kJ mol-1 for bagasse fiber (Sun et al., 2011), 90-170, 199-256 y 21-77 kJ mol-1 ranges for sugarcane bagasse (Zanchetta et al., 2018). Finally, the consideration of reaction orders leads to higher values of activation energy, mainly for lignin and hemicellulose in various types of biomass (Conesa and Domene, 2011; Manyà et al., 2003).

4. Conclusions

Currently Ulex eurioaeus L. species generates great problems for the population living in the city of Bogotá, because, in times of summer, it produces large fires affecting the endemic flora and fauna, likewise, it is an invasive species that affect and imbalances the ecosystem. Search alternatives such as biofuels from this type of species prevent environmental impacts caused by conventional fuels and is given a valorization to this type of species that turn out to be a problem for their handling. The study of thermal degradation and kinetics in a thermobalance provided useful information to assess the feasibility of the valorization of spiny retamo materials by pyrolysis.

The three parallel and independent reaction models considering the decomposition of the three main pseudo-components of biomass (hemicellulose, cellulose and lignin) adequately describe the degradation of the forest waste studied, confirming that this simple model is suitable for studying different types of lignocellulosic materials. The kinetic parameters indicate that the pyrolysis routes of the spiny retamo are similar to other lignocellulosic materials, which demonstrates the viability of their valorization by pyrolysis. In addition, the model allows to determine approximately the content of hemicellulose, cellulose and lignin of the raw materials, and specifically its high content of lignin. These characteristics will be reflected in the distribution of the pyrolysis product and its characteristics, which will be addressed in a future study.

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