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CORN STOVER THERMAL DECOMPOSITION IN PYROLYTIC AND OXIDANT ATMOSPHERE

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ABSTRACT

The pyrolysis and combustion of corn stover were studied by dynamic thermogravimetry and derivative thermogravimetry (TG-DTG) at heating rates of 5, 10, 20 and 50 K min⁻¹ at atmospheric pressure. For the simulation of pyrolysis and combustion processes a kinetic model based on the distribution of activation energies was used, with three pools of reactants (three pseudocomponents) because of the complexity of the biomass samples of agricultural origin. The experimental thermogravimetric data of pyrolysis and combustion processes were simultaneously fitted to determine a single set of kinetic parameters able to describe both processes at the different heating rates. The model proposed achieves a good correlation between the experimental and calculated curves, with an error of less than 4 % for fitting four heating rates simultaneously. The experimental results and kinetic parameters may provide useful data for the design of thermo decomposition processing system using corn stover as feedstock. On the other hand, analysis of the main compounds in the evolved gas is given by means of a microcromatograph.

Keywords

Corn Stover, Biomass, Pyrolysis, Combustion, Kinetic parameters, biogas

Introduction

Biomass has major interest as a renewable energy source in the context of climate change, mitigation and energy security. Energy from biomass is based in short rotation forestry and energy crops that can contribute to the energy needs of the modern society [1]. Several species have been investigated for the thermo chemical conversion processes; and their kinetic parameters and decomposition characteristics have been determined using thermogravimetric analysis [2,3]. In the literature there is also study about the influence and interaction between the main characteristics of biomasses that allow to be used as raw material for energetic applications [4].

Corn (maize) is an important food for many people in the world. It is also a good source of industrial products such as starch [5], vitamin [6], fiber [7], oil [8] and ethanol [9]. The global corn production increased from 599.35-867.52 million tonnes (44.74% increase) during the period of 2001-2011 (United States Department of Agriculture, 2011), which is much higher than the increase in the world population of 12.34% during the same period.

The residue that is left on the soil surface after corn grain has been harvested is corn stover. It consists of cob, leaves and stalk fractions [10]. These fractions are important residues of corn processing and consumption. For every 1 kg of dry corn grains produced, about 0.15 kg of cobs, 0.22 kg of leaves and 0.50 kg of stalks are produced [11,12]. This results in the production of about 130.13, 190.85 and 433.76 million tons of cobs, leaves and stalks in 2011, respectively. Currently, these residues have a number of limited applications including: (a) use of corn cobs as building material and activated carbon [13,14], (b) use of corn leaves as a feedstock for fermentable sugars and supplemental fiber source for paper pulp [15] and (c) use of corn stalks as livestock feed and biofertilizer [16,17].

However, these materials can be used as an energy source in thermochemical conversion processes such as gasification, pyrolysis and combustion [18,19] for energy production and other high-value chemical co-products. Despite being very promising resources, the characterization is the first fundamental step when dealing with wastes in order to understand the conversion behavior and efficiently use these materials as fuels. The properties of a given biomass material such as corn stover greatly influence the design and operation of thermochemical conversion systems [5].

During the thermal decomposition of materials in the presence of oxygen, three different behaviors can be distinguished [20,21]: *pyrolysis + combustion of the residue formed* (i.e., during the combustion process there is a first step of pyrolysis, followed by the reaction of oxygen with the residue of pyrolysis), *oxidative pyrolysis* (in this case, the combustion takes place in parallel to pyrolysis; combustion is faster and takes place at lower temperatures; oxygen reacts with the solid that is being decomposed before reaching the flame formation), and *combustion delayed respect to the pyrolysis* (the presence of oxygen produces partial oxygenation of solid material, causing the apparent delay in the decomposition of the solid).

Although commercial thermogravimetric systems have a high precision, the sample temperature is not directly measured or controlled. In the presence of oxygen, given the high exothermicity of the combustion reactions, a thermal runaway may occur with the temperature inside the sample becoming considerably higher than that foreseen by the assigned program and the sample being oxidized at high reaction rate. As the highest reaction rate in an experiment is

roughly proportional to the sample mass and the heating rate in the kinetic regime, in addition to being obviously dependent on the reactivity of the given sample and on the oxygen partial pressure [22], the sample mass should be adequately reduced until no difference is seen in the normalized weight loss curves. In this way it is also guaranteed that spatial temperature gradients are negligible and oxygen diffusion is not the limiting process. Unfortunately, numerous thermogravimetric measurements reported in literature about biomass combustion show the occurrence of thermal runaway, with the consequent formulation of erroneous reaction mechanisms. A significant number of studies are available where, in addition to the determination of the weight loss characteristics, the examination of the data has led to mechanisms of different complexity with kinetic parameters, in particular the activation energies, dependent on the conversion level and/or the heating rate such. In other cases, only a single heating rate is considered. These models although based on experimental data apparently not impugned by heat and mass transfer effects, are not truly valid over widely variable conditions. Indeed, only kinetic models capable of explaining the shift in the thermogravimetric curves with the heating rate, without changing the kinetic parameters, can be considered potentially correct [23].

Biomass decomposition studies are usually based on the kinetic model of three independent parallel reactions, associated with the main pseudo-components (hemicelluloses, cellulose and lignin). The proportions of these constituents and the presence the ions inorganic can vary the decomposition characteristics from one species to another, even within the same species [2,24,25]. Another influencing factor is the heating rate at which the experiments are carried out [26]. Despite the numerous weight loss measurements available in the literature, a systematic classification of biomass fuels, based on thermogravimetric analysis, and general mechanisms to interpret such measurements are not available.

The aim of this study was to develop a kinetic model for the thermal decomposition of corn stover both in the absence and in the presence of oxygen, by simultaneous fitting of thermogravimetric curves obtained at different heating rates. It was used a distribution of activation energy model (DAEM) for this study. Also a study of the composition of the gas evolved is presented.

Materials and methods

The material employed in this study was corn stover that was collected from the province of Zaragoza (Spain). The sample was crushed to a particle size between 75 to 125 μm . The proximate and ultimate analyses as well as their heating values which were carried out according to standard methods are given in Table 1. The ultimate analysis was performed using a LECO CHNS (LECO Instruments, TruSpec CHNS) analyzer and the proximate analysis of the material was made using a Hobersal mod 12-PR/400 furnace (Table 1). The calorific value was determined with a calorimeter bomb (IKA, C2000).

[Table 1]

Corn stover samples were subjected to thermogravimetric analysis using a DTG-60H Shimadzu instrument. The samples were spread on a alumina sample holder of ϕ 6 mm. The analyses were made using an inert atmosphere of N_2 , and an oxidative atmosphere of air. The flow rate of air and N_2 are 50 mL min^{-1} . The experiments started with a 60 min purging

period at room temperature and a heating rates of 5, 10, 20 and 50 K min⁻¹, up to a final temperature of 1150 °C. The sample mass used in all runs was ca. 10 mg.

Thermogravimetric experiments were carried out with a thermogravimetric analyzer (TG) coupled to a microGC (Varian Inc, CP-4900) for the analysis of TGA evolved gases. The microGC was equipped with a molecular sieve (10mx0,32mm) and a Poraplot Q column (10mx0,15mm), with separate injectors and TCD detectors. Thirteen gases were monitored: H₂, O₂, N₂, CH₄, CO, CO₂, C₂H₆, C₄H₄, C₃H₈, C₃H₆, C₃H₄. Pure helium was used as purge gas. The injection time on both columns are 100 ms. The temperatures of injector and detector were maintained at 110 °C. The oven temperatures were kept 105 °C. The column pressure is 50 psi for the Molsieve column, and 30 psi for the Poraplot Q column.

Kinetic model and optimization method

A DAEM has been selected and used in the present work for analyzing the decomposition of corn stover due to the good results obtained by other authors with similar materials [27,28]. This model assumes different parallel reactions with a Gaussian activation energy distribution. According to the model, the sample is composed by the sum of *M* pseudocomponents, where *M* is usually between 2 and 4. Here, a pseudocomponent is the totality of those decomposing species that can be described by the same reaction kinetic parameters in the given model. The number of reacting species is obviously much higher than *M* in a complicated mixture of plant materials. The reactivity differences are described by different activation energy values. On a molecular level, each species in pseudocomponent *j* is assumed to undergo a first-order decay. The corresponding rate constant (*k*) and mean lifetime (*τ*) are supposed to depend on the temperature by an Arrhenius relationship:

$$k(T) = \tau^{-1} = A_j e^{-E/RT} \quad (1)$$

Let $\alpha_j(t, E)$ be the solution of the corresponding first-order kinetic equation at a given *E* and *T*(*t*) with conditions $\alpha_j(0, E) = 0$ and $\alpha_j(\infty, E) = 1$:

$$d\alpha_j(t, E)/dt = A_j e^{-E/RT} [1 - \alpha_j(t, E)] \quad (2)$$

we will denote *D_j*(*E*) to the density function of the species differing by *E* within a given pseudocomponent. *D_j*(*E*) is approximated by a Gaussian distribution with a mean *E_{0,j}* and width parameter σ_j :

$$D_j(E) = \frac{1}{\sigma_j \sqrt{2\pi}} \exp \left(-\frac{1}{2} \left(\frac{E - E_{0,j}}{\sigma_j} \right)^2 \right) \quad (3)$$

The overall reacted fraction of the *j*th pseudocomponent, $\alpha_j(t)$ is obtained by integration:

$$\alpha_j(t) = \int_0^\infty D_j(E) \alpha_j(t, E) dE \quad (4)$$

The normalized sample mass, *m*, and its derivative are the linear combinations of $\alpha_j(t)$ and $d\alpha_j/dt$, respectively:

$$-dm/dt = \sum_{j=1}^M c_j d\alpha_j / dt \quad \text{and} \quad m(t) = 1 - \sum_{j=1}^M c_j \alpha_j(t) \quad (5)$$

where a factor C_j is introduced that equals the amount of volatiles formed by a unit mass of pseudocomponent.

The unknown model parameters were evaluated from series of experiments by minimizing the sum S_N of the differences between the observed data and their counterparts calculated from the given model:

$$S_N = \sum_{k=1}^N \sum_{i=1}^{N_k} \frac{\left[\left(\frac{dm}{dt} \right)_k^{obs}(t_i) - \left(\frac{dm}{dt} \right)_k^{calc}(t_i) \right]^2}{N_k h_k^2} \quad (6)$$

Where N is the number of runs evaluated simultaneously, a subscript k indicates the different experiments, t_i denotes the time values in which the discrete experimental values were taken, N_k is the number of t_i points in a given experiment, and h_k denotes the heights of the evaluated curves that strongly depend on the experimental conditions. The division by h_k^2 serves the purpose of normalization. The quality of the fit was characterized by the following quantity:

$$fit_N (\%) = 100 S_N^{0.5} \quad (7)$$

The points represented, which have been those used for the kinetic analysis, have been selected according to techniques recommended by Caballero et al. [29] so that:

- The derivative of the points is calculated accurately and correctly.
- The points are equally spaced on a representation derivative of weight versus temperature.
- The fitting is simultaneous, with no variation of the kinetic constants, for at least three different heating rates.

Besides this, we use numerical techniques for solving differential equations and optimization methods prior definition of a proper objective function [27,29], as has been already commented.

For the decomposition of corn stover, a good result has been obtained by using $M=3$ (three pseudocomponents) both in pyrolytic and in oxidant atmospheres. The software used for optimization has been Matlab®, and the programs were developed by the authors. Matlab® function 'fmincon' is used for optimization of the parameters, that allows to using linear and nonlinear constraints (such as the sum of coefficients c_j is unity), as well as bounds for the values of the optimized variables. The parameters to be optimized, considering three pseudocomponents, will be: three values of A_j , three values of $E_{0,j}$, three values of σ_j and two values of c_j , because the sum of all three c_j must be unity (11 parameters in total).

Results and discussion

Kinetic model

Figures 1 and 2 present the thermal decomposition of corn stover in pyrolytic and oxidant atmosphere, respectively, at the four heating rates used. Note that in the presence of air (combustion runs) the high exothermic process leads to a great increase of the temperature that the control system of the thermobalance attempts to compensate, which is why even temperature decreases in some zones. Of course, for the kinetic analysis of such runs, the temperature read by the thermocouple is used in the mathematical calculations, and not the programmed temperature.

The results of the kinetic modeling are also in Figures 1 and 2, but will be discussed later. In the Figures it can be seen both the effect of heating rate for the same process and the comparison of mass loss for different processes, pyrolysis and combustion.

The decomposition in oxygen atmosphere (combustion) is type oxidative pyrolysis (as described before), as can be seen in Figures 1-2, i.e., the combustion takes place in parallel to pyrolysis but is faster, in such a way that the decomposition is not of the type pyrolysis + combustion of the residue formed that is found in other materials [20,21].

[Figures 1 and 2]

Table 2 shows the values of the optimized parameters, together with the fit % for each process (considering all four heating rates). Combustion runs have been fitted with two sets of kinetic constants, by maintaining or not the activation energies found in pyrolysis. Table 2 shows all results. Table 2 also shows the values of the same parameters obtained by Cai et al. [30] for corn stover pyrolysis and Trinic et al. [31] for a similar material (corn cob) for comparison. The first conclusion is that both processes can be satisfactorily fitted using DAEM with three pseudocomponents, even the uncommon behavior of combustion curves when decreasing temperature. Furthermore the decomposition in oxidative atmosphere can be almost explained by only two pseudocomponents (c_3 is very small in combustion) but this is not true in the pyrolytic process.

Comparing with values found in literature for corn pyrolysis [28,30,31], the values are similar but some differences should be remarked: in the present study broader distribution of activation energies are found in general (i.e., higher values of σ_i); slight differences could be explained by variances in the materials used.

Comparing two sets of parameters for combustion process (Table 2) we can see that, obviously the fit% is better when we allow to vary the activation energies, but not significant differences are found. Only small changes in parameters is produced; for example, activation energies slightly change in combustion. Significant differences are found in the decomposition of the third pseudocomponent, but they should be ignored because its contribution to the total weight loss is nil.

[Table 2]

We can discuss also the behavior of each pseudocomponent; Figures 3 and 4 shows the evolution of the weight loss for each pseudocomponent in the pyrolysis and combustion, respectively, where we can appreciate the differences. On the one hand, in the combustion process the decomposition of the first pseudocomponent is much narrower than in pyrolysis, and it is also accelerated (higher value of preexponential factor), but the major change is in the behavior of pseudocomponent 2 (F2) that is much more broader than in pyrolysis, in such a way that the decomposition order of F1 and F2 seems to change.

[Figures 3 and 4]

Gas evolution with temperature

The gases evolved from pyrolytic (inert atmosphere) runs were analyzed as described before. Figure 5 presents the results for runs performed at three heating rates from 5 to 20 K min⁻¹, in terms of %wt min⁻¹ produced. For calculation of this amount, analysis of a small portion of the gas and measure of the flowrate is needed, in such a way that the following is calculated:

$$\% \text{ wt./min} = \frac{(\text{gr compound/mL}) * (\text{flowrate, mL/min})}{(\text{gr corn stover})} * 100$$

where (gr compound/mL) is the amount detected in the microcromatograph. Runs at 50 K min⁻¹ gave poor results because of the swiftness of the process, and the data corresponding to this heating rate is not shown.

In the graphs shown in Figure 5, the values of $\text{wt.\% min}^{-1}$ in the case of the higher heating rate (20 K min^{-1}) are higher than those found at the lower heating rate (5 K min^{-1}), because decomposition rate is obviously higher at the high heating rate.

[Figure 5]

As the behavior at the different heating rates is similar, in Figure 6 all gases evolved at the lower heating rate is shown for comparison. Four different processes can be distinguished at all the heating rates studied:

- The first one is centered at approx. 610 K ($\approx 340^\circ\text{C}$) and the evolution of *methylacetylene*, CO_2 and CO is observed.
- A second peak close to the first one is produced at ca. 740 K ($\approx 470^\circ\text{C}$) with production of hydrogen, ethane, ethylene, propane, propene, *methylacetylene* and CO_2 . Also some methane and a slight increase in CO could be found.
- A third process is found at ca. 1000 K ($\approx 730^\circ\text{C}$) with CO_2 evolution.
- At higher temperatures a new evolution of CO , propane and H_2 is present.

From these data we can observe that the evolution of CO is initially associated to the CO_2 production, i.e., the production of CO is basically an oxidation, but at higher temperatures an important production of CO with H_2 is observed, indicating that gasification of residue is being produced.

[Figure 6]

If one compares the gas evolution (Figure 6) with the pseudocomponent fractions included in the kinetic model presented before (Figure 3), it is remarkable that the decomposition of fractions F1 and F2 are the responsible for the evolution of the main gases, in the processes produced between ca. 550 and 700 K . Furthermore, when pseudocomponent F3 is decomposing (at approx. 1000 K), the main gas production is CO_2 . Later decomposition of the solid residue from the pyrolysis is the responsible for the further and last production of CO and H_2 at the final stages.

Conclusions

A kinetic model for the pyrolysis and combustion of corn stover has been obtained. Both processes can be satisfactorily fitted using DAEM with three pseudocomponents. One set of parameters in each case can explain all the experiments at the different heating rates used (5 , 10 , 20 and 50 K min^{-1}). Furthermore, combustion runs have been fitted with another set of kinetic constants by maintaining the activation energies found in pyrolysis.

On the other hand, the evolution of the main compounds in the pyrolysis runs was investigated by means of a microcromatograph. The results showed variations of the gas composition in function to the temperature. The main gases released were CO_2 , CO , CH_4 and H_2 .

The release of CO can be attributed to the biopolymer pyrolysis at low temperature and to the tar cracking at high temperatures. The emission of hydrocarbons happens on a larger range of temperature and is due to the pyrolysis of the three biopolymers. Finally, H_2 is mainly emitted at higher temperature and comes mainly from the tar cracking.

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Figures

Figure 1. Corn stover pyrolysis at different heating rates. Experimental and calculated values.

Figure 2. Corn stover combustion at different heating rates. Experimental and calculated values.

Figure 3. Evolution of the weight loss of each pseudocomponent during the pyrolysis of corn stover at different heating rates.

Figure 4. Evolution of the weight loss of each pseudocomponent during the combustion of corn stover at different heating rates.

Figure 5. Analysis by microchromatograph of the evolved gases during the pyrolytic decomposition at three different heating rates. X-axis represents Temperature in K, and Y-axis is the evolved gas in (% wt. min⁻¹).

Figure 6. Analysis by microcromatograph of the evolved gases during the pyrolytic decomposition at 10 K min⁻¹.

Tables

Table 1. Proximate and ultimate analyses and Heating Value of the corn stover

	Method	Dry basis	Wet basis
Moisture content	UNE-EN 14774-1:2009	--	4,47
Proximate analysis			
Volatiles (%)	UNE-EN 15148:2009	79,10	75,55
Ash (%)	UNE EN-14775:2009 (550 °C)	8,10	7,75
Fixed Carbon (%)	Calculated	12,80	12,23
Ultimate analysis			
C (%)	UNE-EN 15104:2011	44,60	24,85
H (%)		6,00	8,27
N (%)		0,73	0,40
S (%)	UNE-EN 15289:2011	0,10	0,06
Cl (%)	UNE-EN 15289:2011	0,50	0,28
O (%)	Calculated	48,07	66,14
HHV, kcal/kg	UNE-EN 14918:200	4.340	4.020
LHV, kcal/kg	Calculated	2.420	1.980

Table 2. Values of the optimised parameters and fit %. Last two columns presents values found in literature for similar materials.

	Corn stover pyrolysis	Corn stover combustion *	Corn Stover combustion**	Corn cob pyrolysis [28,31]	Corn stover pyrolysis [30]
$\log(A_1, s^{-1})$	11,34	12,42	12,49	14,45	13,00
$E_{0,1}$ (kJ/mol)	156,13	*	156,89	177,0	179,60
σ_1 (kJ/mol)	3,42	2,02	2,05	4,3	5,88
$\log(A_2, s^{-1})$	9,52	7,60	7,21	13,87	13,94
$E_{0,2}$ (kJ/mol)	124,42	*	119,13	185,0	207,38
σ_2 (kJ/mol)	2,01	13,44	12,12	1,9	1,17
$\log(A_3, s^{-1})$	11,09	12,46	10,73	12,98	16,00
$E_{0,3}$ (kJ/mol)	187,27	*	185,90	194,0	239,34
σ_3 (kJ/mol)	36,43	21,72	37,15	34,6	31,41
c_1	0,488	0,545	0,5452	0,24	0,163
c_2	0,262	0,454	0,4272	0,37	0,253
c_3 (by difference)	0,249	0,001	0,0276	0,17	0,164
fit %	2,01	2,20	1,50	---	---

* The fitting is done maintaining the same values of activation energies than in pyrolysis.

** The fitting is done with all parameters allowing to vary.

Highlights

- The decomposition of corn stover is studied in a thermobalance.
- A kinetic model is proposed for the overall decomposition at different heating rates.
- Comparison of pyrolysis and combustion is provided.
- GC analysis of the gas evolved is given at different heating rates.