

# Kinetic Modeling for the Pyrolysis of Biomass Fuels derived from Oil Crops

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## Abstract

Three biomass fuels derived from oil crops, castor, jatropha and sunflower seeds were pyrolyzed by thermogravimetric analysis up to 900 °C. Jatropha residual cake presented the higher reactivity between the three. In order to describe the mass loss, an independent parallel reaction model was adopted and mathematically fitted, to determine kinetic constants. Activation energy values ranged from 30 to 197kJ/mol. This technique accurately predicted the devolatilization behavior of all samples tested.

## Introduction

Because of the future depletion of fossil fuels and the environmental hazards arising from their use, the introduction of heat and power generation from sustainable sources, such as biomass, has been made necessary. Biomass is a clean and renewable energy source, while being the third energy resource in the world after coal and oil [1]. Through thermochemical processes, like combustion, gasification and pyrolysis, biomass can be used for energy, chemicals and transport fuel production. The work undertaken within this study is focused on biomass fuels derived from residual cakes of plant seeds, after oil has been extracted. In particular, three kinds of fuels were examined: castor, jatropha and sunflower seeds. Not much work has been carried out in the field of pyrolysis kinetics regarding oil crops generally and these biomass fuels in particular. The purpose of this work is the presentation of the thermochemical properties and behavior of these biomass fuels during the pyrolysis process and also the determination of their kinetic parameters.

The study of pyrolysis kinetics provides necessary information regarding the engineering design of a pyrolyzer or a gasifier. In order to determine the role of different processes taking place in the pyrolyzer, in the final product yield and composition, non-isothermal thermogravimetric analysis (TGA) is employed as one of the best methods available for the study and understanding of the thermal behavior of biomass pyrolysis. This particular method has been extensively used by many researchers [2-4].

Biomass pyrolysis is a complex process, due to the large number and the diverse nature of the occurring reactions. In order to observe and understand the thermal degradation of biomass numerous models have been developed, which can be organized in the following categories: one step global reaction models, multi-reaction models and semi global models [5]. Also, isoconversional methods have been developed and employed [2]. These methods are model – free and are based on the assumption that reaction kinetics is not depended upon the heating rate. As a result, the conversion of the biomass material to products is

regarded as a one – step process [6]. In this work, the modeling of the pyrolysis kinetics will be performed using the independent parallel reaction (IPR) model, which employs reactions for the main constituents of biomass (cellulose, hemicellulose and lignin). The results obtained will be compared to the experimental ones, in order to determine the validity and performance of the model.

## Experimental

Pyrolysis tests were performed in a differential thermogravimetric analyzer TGA-6/DTG of Perkin Elmer (precision of temperature measurement  $\pm 2^\circ\text{C}$ , microbalance sensitivity  $< 5\mu\text{g}$ ), in the range 25-900°C. The flow rate of nitrogen was 45ml/min and the heating rate 10°C/min. Preliminary tests with different sample masses and sizes and gas flow rates were carried out, in order to check the influence of heat and mass transfer. Small masses (13-20mg) of each material, thinly distributed in the crucible and particle sizes of  $\sim 250\mu\text{m}$  were found proper to be used in the experiments.

## Kinetic Modeling

The different chemical compositions of components within the biomass material, make biomass pyrolysis a complex process. This process was described by the independent parallel first-order reactions model [7], each reaction corresponding to the decomposition of the biomass constituent components. The overall rate of conversion for N reactions can be expressed as:

$$\frac{d(m/m_0)}{dt} = -\sum c_i \cdot \frac{da_i}{dt} \quad i=1,2,3,\dots,N \quad (1)$$

$$\frac{da_i}{dt} = A_i \cdot \exp\left(\frac{-E_i}{R \cdot T}\right) \cdot (1 - a_i) \quad (2)$$

where:  $dm/dt$  is the total mass loss rate,  $m$  is the observed mass at time  $t$ ,  $m_0$  is the initial dry mass,  $A_i$  is the pre-exponential factor,  $i$  is the component index,  $E_i$  is the activation energy,  $a_i$  is the conversion ( $0 < a_i < 1$ ),  $T$  is the temperature,  $R$  is the universal gas constant and  $c_i$  is the fraction of volatiles produced by the  $i$ -th component.

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An algorithm in Matlab® code, developed at the Technical University of Crete, was used to obtain the optimal parameters ( $E_i, A_i, c_i$ ) that minimize, under constraints, the objective function:

$$O.F. = \sum_{j=1}^{j=Z} \left[ \left( \frac{dm}{dt} \right)^{exp}_j - \left( \frac{dm}{dt} \right)^{calc}_j \right]^2 \quad (3)$$

The deviation between the observed and the calculated curves, at the optimal set of parameters, was calculated as follows:

$$Dev(\%) = 100 \cdot \frac{\sqrt{O.F. \cdot (Z - N)}}{\max(-dm/dt)^{exp}} \quad (4)$$

where Z is the number of data points and N is the number of parameters employed in the model.

## Results and Discussion

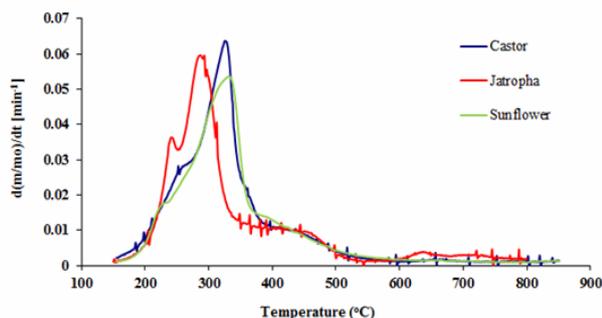
### Characterization of fuels

In Table 1 are presented the proximate and ultimate analysis results, as well as the calorific values of the biomass materials. All biofuels are characterized by high volatiles content, ranging from 78 – 84%, which makes them desirable for a good regulation of combustion or gasification processes. Sunflower presented the highest ash content value (10.6%). Also, the concentration of C and H was smaller for sunflower and jatropha, as was the concentration of O for castor. The high percentage of N in all samples indicates potential toxic  $NO_x$  emissions during combustion. However, the content of S is very low, which means that fewer emissions or corrosion will occur during their utilization for power production.

**Table 1.** Fuel analyses (% dry)

Sample	Castor	Jatropha	Sunflower
<b>Proximate analysis</b>			
Volatile matter	83.5	78.9	84.0
Fixed carbon	7.9	17.1	5.4
Ash	8.6	4.0	10.6
<b>Ultimate analysis</b>			
C	47.9	43.7	43.7
H	6.1	4.9	5.2
N	2.6	1.8	2.3
S	0.25	0.17	0.37
O	34.5	45.4	37.8
HHV (MJ/kg)	21.9	16.8	19.1

### Thermal decomposition characteristics



**Figure 1.** DTG curves for the pyrolysis of the fuels

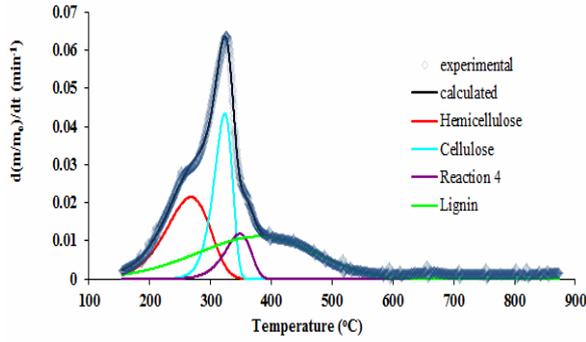
By examining Figure 1, it can be observed that the DTG curves of castor and sunflower present similar thermal behavior. Thermal decomposition started around 200°C, followed by the main weight loss in the temperature range of 200–400°C. The process was essentially completed up to 500°C.

In the case of jatropha, decomposition took place at lower temperatures compared with the other biomass materials. This behavior can be attributed to its high concentration in K, which as it has been observed in previous studies [7], affects the sensitivity of the reaction in a nitrogen environment, causing the initiation of thermal decomposition at lower temperatures. Taking into consideration that the reactivity of a fuel is proportional to its maximum reaction rate and inversely proportional to the temperature that corresponds to the peak [8], jatropha had the higher reactivity, followed by castor and sunflower.

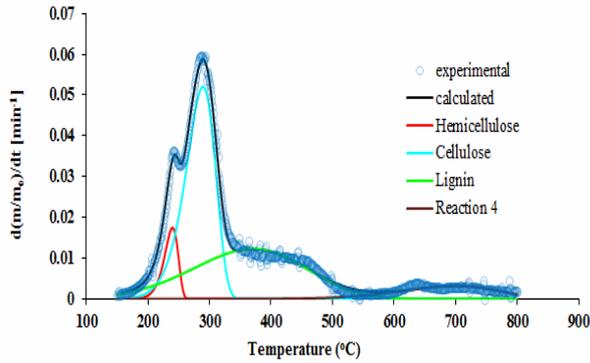
### Kinetics

In Figures 2 to 4, a comparison between the experimental and calculated DTG curves is presented for each biofuel. Regarding each biomass component, lignin proved to be the most stable one, as in all three samples tested it presented the greater decomposition temperature range. Hemicellulose is the least stable component and that is the reason why it decomposed “faster”. Finally, the cellulose reaction started last, as it was expected from the high values of its activation energy (Table 2). Even in the case of jatropha, where the activation energy of hemicellulose was higher, the cellulose reaction started last, but not with a great difference from the initial temperature of the hemicellulose reaction. Cellulose temperature range was characterized by the presence of the maximum reaction rate of the total reaction. Generally, the differences between the thermal behaviors of the three components are attributed to their different chemical structures. Hemicellulose is less thermally stable, due to its amorphous nature and cellulose presents this particular thermal behavior, because of its strong intra-molecular bonds. Lignin is a complex, heavily cross-linked polymer, which expresses heavier volatiles and subsequently is more thermally stable than the other two components [9,10]. The conclusions presented above regarding the thermal behavior of each component are in agreement with other relevant studies [3, 4, 7, 8, 11].

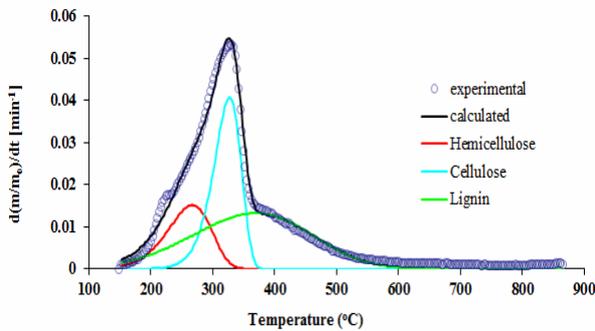
In order to determine the kinetic parameters of castor, a four independent reaction model was used. This was necessary, because of the shoulder which appears in the DTG curve in the temperature area between 340 – 380°C and is attributed to the thermal decomposition of cellulose. For jatropha, a four reaction model was also used. The reason behind this approach was the fact that the DTG curve presented fluctuations in the temperature area greater than 540°C, until the end of data. Thus, in order to obtain a better fit to the experimental data, an extra reaction was introduced, most probably attributed to the decomposition of lignin.



**Figure 2.** Kinetic modeling of castor pyrolysis



**Figure 3.** Kinetic modeling of jatropha pyrolysis



**Figure 4.** Kinetic modeling of sunflower pyrolysis

In reality, these fluctuations correspond to secondary reactions of biomass residues that contain carbon [12]. The model was proved successful in the determination of the kinetic parameters. The deviations between the calculated and the experimental values were less than 2.4% for every biomass fuel.

Kinetic parameters are illustrated in Table 2. For both castor and sunflower, the higher values of the kinetic constants appeared for the reaction of cellulose. Activation energy is the energy required for the initiation of each reaction. Subsequently, the greater its value is, the greater is the temperature in which each reaction starts. Cellulose demands more energy compared to the other components, due to its strong intra-molecular bonds, which prevent its decomposition in lower temperatures [9]. A high value for the pre-exponential factor indicates that more molecular collisions occur, which can lead to reaction. The number of the successful molecular collisions is given by the following relation:

$$k = Ae^{-E/RT} \quad (5)$$

Hence, it can be said that a great value of A indicates the occurrence of more reactions. Therefore, the high value of the pre-exponential factor for the reaction of cellulose corroborates the conclusion extracted from the study of the DTG curves, that for this particular reaction the highest values of the reaction rate occur. In the case of jatropha, the activation energy and the pre-exponential factor were higher for the reaction of hemicellulose, which leads to the conclusion that hemicellulose was more reactive than the other two components for this fuel. This statement is also supported by the shape of the DTG curve of jatropha in the area of hemicellulose decomposition, where a pronounced shoulder appeared [4, 8]. This phenomenon could further be attributed to high hemicellulose content in this jatropha sample, but the low value of the fraction of volatiles in both cases does not allow such a conclusion. In regards to the reaction of lignin, there were the lowest values of activation energy and pre-exponential factor presented. This fact could also be presumed by the DTG curves, as this reaction started at lower temperatures and its reaction

**Table 2.** Kinetic parameters of the biomass fuels

Sample	Hemicellulose			Cellulose			Lignin			4 <sup>th</sup> reaction			Dev. (%)
	E (kJ/mol)	A (1/min)	c	E (kJ/mol)	A (1/min)	c	E (kJ/mol)	A (1/min)	c	E (kJ/mol)	A (1/min)	c	
Castor	63.7	3.7E+05	0.196	195.7.6	8.9E+16	0.170	31.2	2.7E+01	0.268	148.0	1.2E+12	0.066	1.57
	70.8	5.6E+06	0.227	170.7	5.2E+14	0.240	33.7	2.8E+02	0.257	162.1	1.5E+13	0.049	1.3
Jatropha	196.8	9.9E+19	0.051	107.1	3.6E+09	0.321	32.4	4.0E+01	0.280	91.9	9.9E+03	0.066	1.59
	146.4	4.7E+14	0.106	135.5	2.3E+12	0.369	34.8	4.0E+02	0.239	99.3	1.3E+05	0.057	0.86
Sunflower	65.6	5.7E+05	0.145	135.3	2.3E+11	0.266	30.8	2.7E+01	0.317	-	-	-	2.34
	97.0	4.4E+09	0.094	108.2	2.3E+09	0.384	34.0	3.1E+02	0.262	-	-	-	1.94

rate was lower, compared to that of the other reactions. Lignin is the most thermally stable component, therefore it is more difficult to be decomposed. The conclusions made herein are also confirmed by previous studies [2, 4, 5, 8, 9].

About the fraction of volatiles, for castor the higher values corresponded to the lignin reaction and for jatropha to the reaction of cellulose. In the case of sunflower, the higher values of this kinetic constant appeared for the reaction of lignin. The values of this kinetic constant give a potentially useful picture of the lignocellulosic composition for each sample.

### Conclusions

Pyrolysis kinetics was successfully modeled using a three or four reaction independent parallel reaction model, with the calculated data being in good accordance with the experimental one. This technique accurately predicted the devolatilization behavior of all samples tested. Activation energy values ranged from 30 to 197kJ/mol. The greatest part of the mass loss occurred in the temperature range of 200 – 400°C. For jatropha, the main part of the materials decomposition took place at lower temperatures compared with the other biomass materials, probably due to its high potassium content. Also, this biofuel presented the higher reactivity between the crops examined and subsequently had the highest reaction rate.

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