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Kinetic and energy study of thermal degradation of biomass materials under oxidative atmosphere using TGA, DTA and DSC

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***Abstract*—The purpose of this work is to gain knowledge on thermal behavior of biomass decomposition under oxidative atmosphere in order to evaluate their usefulness for energy and to develop technically and economically feasible systems for the conversion of this biomass to energy.**

Almond shells, nut shells, acorn shells and acorn cups are an attractive source of biomass energy since they are renewable and abundantly available, they can provide a continuous supply of solid, liquid and gaseous fuels trough thermochemical conversion. GA, DTA and DSC were used under air sweeping to record oxidative reactions in dynamic conditions .Two dominating and exothermic reaction zones were observed for all varieties of biomass samples. The mass loss in the first reaction zone was significantly higher than this in the second reaction zone. The kinetic parameters (activation energy, pre-exponential factor) were determined for the two reaction zones. The activation energies were in the range of 68-92 kJ.mol^{-1} and 128 -137 kJ.mol^{-1} for the first and the second reaction zones, respectively. The heat released by the biomass sample was in the range of 871-1350 kJ.kg^{-1}.In order to classify the biomass fuels, we use the ignition temperature, the ignition index and the heat released by the sample; almond shells have the best characteristics (lowest ignition temperature and the higher enthalpy value).

Keywords-TGA;DTA;DSC;biomass,renewable energy,kinetic parameters,enthalpy value, ignitability.

I. INTRODUCTION

The control of energy consumption is one of the major challenges of our century in the context of sustainable development. The economic growth and the growth of the population will be translated inevitably by an increase of the energy needs accompanied with an intensive use.

With regard to the predictable exhaustion of the fossil resources and the environmental problems engendered by their consumption, the use of alternative energy sources is essential to continue to fulfill our global energy needs while preserving the environment. Among the various renewable forms of energy, we find the biomass with her various types. In terms of energy applications, “biomass” refers to the material derived directly from plants, but, strictly speaking, animal-derived materials also fall within its broad definition [1].Various mechanical, biological and thermo-chemical conversion technologies have been developed to produce different types of energy from biomass.

The thermal degradation characteristics of lignocellulose materials are strongly influenced by their chemical composition (cellulose, hemicelluloses and lignin contents) [2, 3].Several studies have been undertaken to investigate the thermal behavior of lignocellulosic biomass [4, 5, 6, 7]

Almond shells, nut shells, acorn shells and acorn cups as a renewable source of energy can provide a continuous supply of solid, liquid and gaseous fuels trough thermochemical conversion. However a proper understanding of the thermal degradation plays an important role in the development of technically and economically feasible systems for this conversion. The aim of this work is to study the thermal degradation behavior of almond shells, nut shells, acorn shells and acorn cups under oxidizing environment. We adapted the DSC in order to measure the heat flow released by the biomass sample undergoing thermal decomposition, we used TGA to measure the mass loss in order to estimate the kinetic parameters of this degradation and we employed DTA to characterize the physico-chemical thermicity reactions samples.

II. EXPERIMENTAL PROCEDURE

A. *Samples Preparation*

Almonds, acorns and walnuts were collected for the study, they were obtained from Morocco. After shelling these fruit, we milled and sieved the shells to pass through a 500µm mesh. In order to characterize our sample before the thermal analysis, we measured their moisture content by using the standard NF-ISO, 1994 and determined their appropriate composition by following the protocol detailed in the article of Shiguang Li [8].Tables I and II show the results of the moister content and the constitutional analysis respectively.

B. Thermogravimetric Analysis (TGA) Coupled with Differential Thermal Analysis (DTA)

TGA and DTA experiment of our samples is performed using an apparatus of the type Shimadzu TA-60 under an oxidative atmosphere, the samples have a particle size<500 µm in order to obtain homogeneous samples. To ensure the uniformity of the sample temperature, a small size is recommended by Ghaly and Ergudenler [9], Mansaray and Ghaly [6] found that a sample with sizes in the range of 10-20 mg gives a good reproducibility (coefficient of variation =1,1%).Therefore sample weighing 12 mg were used throughout the study, the samples were heated from the ambient temperature to 900°C at an increment rate of 20°C/min.

C. Calorimetric Analysis (DSC).

We adapted the differential scanning calorimeter in order to measure the heat flow released during the combustion of our samples. The combustion experiments were performed using Shimadzu's DSC-60.The experiments are carried out with a powder sample having a weigh of 2 mg and a particle size < 500 µm in order to uniform the sample and to obtain satisfactory measurement results, using an aluminum crucible with a lid. The DSC runs were conducted under air atmosphere at a rate of 100 ml.min^{-1} in the temperature range of 86 -500°C at a heating rate of 20°C.min^{-1}.

III. RESULTS AND DISCUSSION

A. TGA and DTA Results

The dynamic thermal analyses (DTA, TGA and DTG) results obtained for the four biomass samples are shown in *"Fig. 1".*

TABLE I. MOISTURE CONTENT

Biomass samples	Almond shells	Nut shells	Acorn pericarp	Acorn cups
moisture content	11,66%	13%	9,16%	4%

TABLE II. RESULTS OF THE CONSTITUTIONAL ANALYSIS

Biomass samples	Almond shells	Nut shells	Acorn cups	Acorn shells
Extractible (%)	12,66	13,33	12,94	14,99
Hemicelluloses (%)	38,42	42,46	44,33	56,51
Cellulose (%)	19,23	0,45	16,5	2, 34
Lignin (%)	29,69	43,76	24,53	26,16

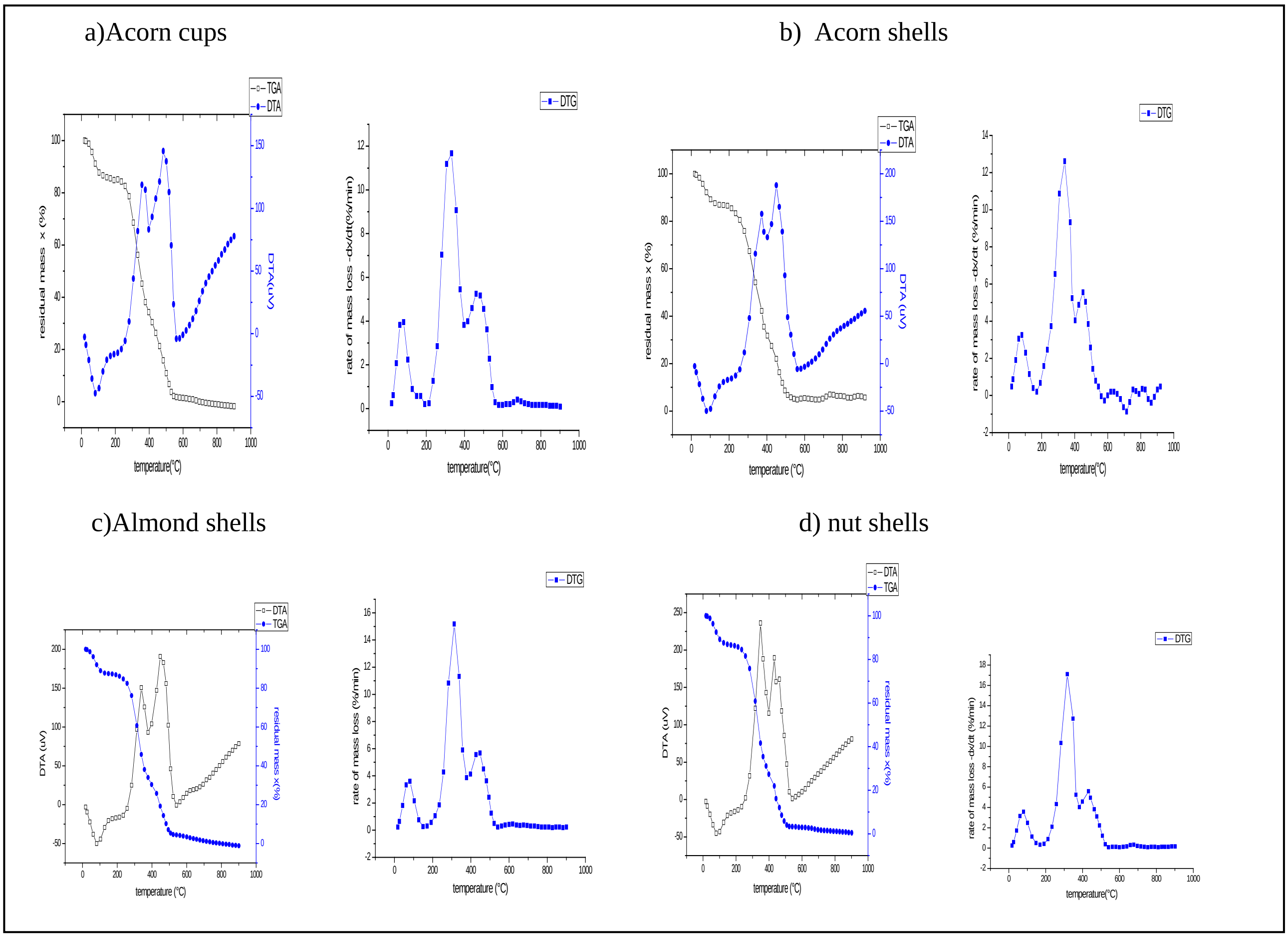

Fig.1.TGA,DTG and DTA curves of biomass samples

We notice that the thermal degradation of these samples under oxidizing atmosphere passes by three principles stages:

- Phase of drying during which the humidity is evacuated T < 200°C, endothermic phenomenon,

- Phase of oxidation of volatile matters in the range of 169 - 403°C, exothermic reaction,

- Phase of oxidation of the carbon residue in the range of 377 - 561°C, exothermic reaction,

The significant data of the thermal degradation of our samples, namely the temperature of the beginning and the end of reaction, the mass loss are grouped in the table III and IV.

TABLE III . MAIN CHARACTERISTIC OF THE FIRST DEGRADATION

Biomass samples	**Phase of devolatilization**			
Acorn cups	**Range of temperature (°C)**	**mass loss (%)**	**Tmax (°C)**	**Vmax (%min-1)**
	214,11-397,26	65,74	332 ,45	11,67
Acorn shells	169,87- 402,6	68,27	339,39	12,60
Almond shells	171-377,35	53,21	312,86	15,17
Nut shells	190,97-382,21	55,12	316,69	17,1

TABLE IV . MAIN CHARACTERISTIC OF THE SECOND DEGRADATION

Biomass samples	**Phase of oxidation**			
Acorn cups	Range of temperature (°C)	masse loss (%)	Tmax (°C)	Vmax (%min-1)
	397,26-560,34	32,54	460,93	5,25
Acorn shells	402,6– 560,9	26,88	449,98	5,55
Almond shells	377,35-541,1	29,59	447,71	5,67
Nut shells	382,21-541,28	27,81	432,04	5,58

The first exothermic phenomenon engenders an average mass loss of 60,58 % for all samples, the second causes a loss of 29,2 %.The first thermal process is due to the degradation of extractibles, cellulose and hemicelluloses, the second is engendered by the degradation of the hemicelluloses and the lignine [10] .

In order to classify the fuels we chose to use the initial ignition temperature Ti which is defined according to W.Cuiping and al [11] and the ignition index Di.TableV presents the results:

TABLE V THE IGNITION CHARACHTERISTICS

Samples	**Ti**	**Di**
Almond shells	283,22	83,1
Nut shells	284,208	93,5
Acorn cups	287,948	58,64
Acorn shells	298,136	61

Almond and nut shells exhibit the best ignition performance (lowest ignition temperature and the higher ignition index) in comparison with the other samples.

B. *Kinetic Parameters*

Although, thermogravimetric analysis is one of the major thermal analysis techniques used to study the kinetics of thermal decomposition reactions of carbonaceous materials under non isothermal conditions [4, 6, 7, 12, 13, 14], there is no generally accepted method for determining kinetic parameters from thermogravimetric data. The kinetics of the decomposition reactions are largely described by first-order Arrhenius law.

The kinetic of the reaction in all studies is described as:

$$\frac{d\alpha}{dt} = f(\alpha)k(T) \qquad (1)$$

Where

$$\alpha = \frac{m_0 - m}{m_0 - m_f} \quad f(\alpha) = (1-\alpha)^n \quad K(T) = A\exp(\frac{-E}{RT})$$

Liu [13] found that the first order equation gives the best fits to the experimental data .

Based on the above theory, we take:

$$f(\alpha) = 1 - \alpha$$

And we have: $\beta = \frac{dT}{dt}$ so the eq. (1) became:

$$\frac{d\alpha}{f(\alpha)} = \frac{K(T)}{\beta} dT \qquad (2)$$

Integrating the eq.2, we obtain:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T0}^{T} \exp(\frac{-E}{RT}) dT$$

Solving the integral is difficult, there has no exact solution and it’s done only by numerical solution or by analytical approximation. Using the approximation proposed by Coats and Redfern [15], we obtain:

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (3)$$

The term $\frac{2RT}{E}$ is much less than unity for the thermal decomposition of polymer materials [13], so it can be neglected, the eq.3 may be written under the linear form:

$$y = Ax + B$$

Where:

$$y = \ln\left[\frac{g(\alpha)}{T^2}\right],\ x = \frac{1}{T},\ A = -\frac{E}{R},\ B = \ln\left(\frac{AR}{\beta E}\right)$$

Constants A and B are estimated by linear regression of the TGA data. Because of the two-step nature of thermal decomposition reactions, it was necessary to determine and use different kinetic parameters to describe the thermal degradation over the entire temperature range with higher accuracy. The kinetic parameters results (pre-exponential factor, activation energy) and the correlation coefficient R^2, for each sample for the first and the second reaction zones are reported in table VI.

TABLE VI . KINETIC PARAMETERS OF THE THERMAL DEGRADATION OF DIFFERENT SAMPLES OF BIOMASS

Sample	Temperature range (°C)	Activation energy (kJ.mol^{-1})	Frequency factor (s^{-1})	R^2
Almond shells	171-377,35	81	9,9x104	0,98
	377,35-541,1	130	15,4x106	0,94
Nut shells	190,97-382,21	88	4x105	0,98
	382,21-541,28	130	18x106	0,94
Acorn cups	169,87- 402,6	92	6,9x105	0,97
	402,6– 560,9	128	5x106	0,92
Acorn shells	169,87- 402,6	68,5	5x103	0,96
	402,6– 560,9	137	33x106	0,91

The results of the kinetic parameters of the first reaction zone had a 96- 98 % confidence range. The activation energies determined in the first reaction were in the range of 68-92 kJ.mol-1(depending on the biomass sample).The second reaction zone had a 91 and 94 % confidence range. The activation energies of the second stage reaction arrive to about the same value (128-137 kJ.mol^{-1}). The higher kinetic parameters obtained in the second reaction zone is due to the fact that the big part of the sample is degraded at the level of the first process (mass loss of 60, 58 %) and that the reactivity of the sample decreases (the reaction of combustion of carbon at the second stage is slow in comparison with the devolatilization at the first stage).

C. DSC Results

"Fig. 2", shows the experimental DSC thermograms for all samples.

As in the TGA and DTA curves ,the DSC curve presents three phenomena, an endothermic one due to the loss of water present in the sample and two exothermic reaction regions ,first region is due to the combustion of light volatile matters, the second region represents the combustion of fixed carbon.

The same results are given by other authors [5, 16]. Table VI present the heat liberated during the combustion of biomass samples in the range 86-500°C that is based on the area under DSC curve. We determined it by executing the [Analysis]-[Heat] command, selecting the temperature range and clicking the [Analyze] button. All the enthalpy values are expressed in kilojoules per Kilogram. The value of ΔH is in the range:[871-1350 kJ.kg^{-1}].DSC studies are useful in order to classify the fuel according to their evolved energy when subjected to an external heat flow. Our results show that the almond shells and acorn cups are the more energetic fuels flowed by nut shells and that the acorn shells are the less energetic.

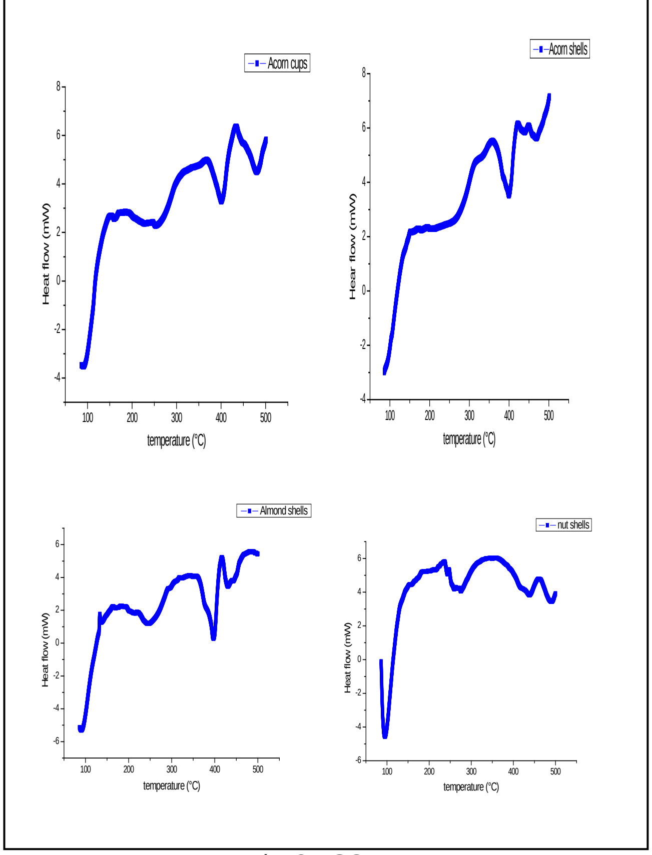

Fig. 2.DSC curves

TABLE VI. HEAT LIBERATED DURING THE COMBUSTION

Sample	Enthalpy values (kJ.kg^{-1})
Almond shells	1 350
Nut shells	1260
Acorn cups	1330
Acorn shells	871

IV. CONCLUSION

Reactions of thermal degradation show multi-step characteristics. We showed that thermal analysis and calorimetric investigations are useful tools in order to get information on the kinetic parameters, ignitability and the energy released during the combustion of lingo-cellulosic biomass. Our results shows that the thermal degradation of almond, nut, acorn shells and acorn cups under oxidizing atmosphere exhibit three main phenomenon :an endothermic one corresponding to the evaporation of the water contained in the sample and two exothermic phenomenon ,the first is due to the oxidation of volatile matters ,the second to the oxidation of the carbon residue . We also found that the kinetic parameters (activation energy, pre-exponential factor) of the first exothermic phenomenon are lower than those of the second one. Our results show that the almond shells and acorn cups are the more energetic fuels flowed by nut shells and acorn shells and that almond and nut shells exhibit the best ignition performance (lowest ignition temperature and the higher ignition index) in comparison with the other samples.

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