Kinetic Study of Lignocellulosic Biomasses Pyrolysis Using Thermogravimetric Analysis

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Abstract

In this work, a kinetic analysis was performed to investigate the energy potential of abundant agricultural residues: date residues, olive stones, and spent coffee grounds. The TGA experiments were carried out from room temperature to 700°C under an inert atmosphere at different heating rates of 5, 10, 15 and 20°C.min^{-1}. Friedman's method seems to be the most appropriate because it contains no mathematical approximation that reduces the systematic error. The average activation energies obtained with the Friedman model are 159, 168, 201, and 170 kJ.mol^{-1} for date stems, date seeds, olive stone, and spent coffee grounds, respectively.

Keywords; agricultural residues, pyrolysis, TGA, model-free, activation energy

Introduction

Biomass is a promising renewable energy source whose development and utilization can solve environmental pollution and fossil energy shortage problems. Biomass generally includes wood, agricultural crops, food, yard, animal manure and human sewage [1]. Tunisia, like other developing countries, needs to classify and to use all its available biomass resources in the background of national sustainable development strategies by taking into consideration environmental issues.

Among the abundant biomass sources in Tunisia, agricultural residues such as date residues, olive stones, and spent coffee grounds can be considered as an original renewable source of energy [2]. Currently, Tunisia produced around 250,000 tons of dates in 2016 [3]. Date seeds are considered as wastes and are discarded or merged into animal feed. Likewise, date stems have no economic value. Moreover, Tunisia is in the top third olive oil-producing country by 190,000 tons of olive. Therefore olive stones thrown by Office National de l'Huile industry are present in large quantities [4]. Another residue that also caught our attention is the spent coffee grounds. Indeed, coffee is the second most-consumed product in the world. Hence, a massive amount of this residue is generated [5]. Tunisian coffee consumption is around 595 cups consumed on average per person in 2017 [6]. Thus, the annual generation is around 50,000 tons of coffee residues. In the absence of recovery ways, this significant quantity of waste turns out to be a great threat to the environment. It causes damage to the ground and the surrounding zones in which they are dumped. Biomass could be valorized into energy or valuable products through different conversion processes such as combustion, liquefaction, pyrolysis, and gasification [7]. Among these processes, pyrolysis is considered as an attractive alternative to using biomass for generating valuable products. Pyrolysis is a thermal decomposition of an organic compound by a significant increase in the temperature. The process is carried out under an inert atmosphere, with various range of residence time for the solid biomass (from a few minutes to several hours). Pyrolysis process produces solids residues (char), condensable liquids (tar), and non-condensing gases. Operating conditions such as temperature, heating rate, particle size, and residence time, influence significantly the composition as well as the proportions of pyrolysis products. The pyrolysis of biomass takes place in several types of reactors: fluidized bed reactors, rotating cone and auger/screw reactor [9].

The kinetic study is a crucial step to set up these devices, establish the operating conditions, design, optimize the process and finally to scale-up to an industrial process. The significant results of a kinetic investigation are the activation energy and the pre-exponential factor. Thermogravimetric Analysis (TGA) is widely used for the kinetic study of biomass thermal degradation. As were mentioned by Cai et al. [10], from 2000 until nowadays, 1350 papers are published in scientific journals dealing with the biomass pyrolysis kinetic study using TGA. It confirms that TGA is an accurate method to obtain experimental data for the kinetic study of biomass degradation.

Two types of kinetic parameters determination methods can be applied for non-isothermal experiments: the fitting-model and the free-model methods [11]. The fitting-model is based on the prior choice of the appropriate kinetic model among those listed in the literature. This method seeks to find the best parameters of a proposed kinetic model to represent the experimental data.

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The risk that no model in a set can describe the process should be taken into consideration [12]. The uncertainty in estimating kinetic parameters caused by the use of fitting-model methods can be avoided with the use of isoconversional methods. The isoconversional methods do not consider any kinetic model. These methods use experimental data obtained at different heating rates. The foundation of the method assumes that at constant conversion, the reaction rate depends only on the temperature. Hence, the activation energy varies with the conversion rate. Based on this assumption, the free-model methods can indicate complex multi-step processes by varying the activation energy with the conversion rate. The main disadvantage of these methods is the oversimplification of the integral temperature approximation used [10].

These models were successfully used for different biomass fuels to understand the reaction kinetics of the pyrolysis process [13]. Kissinger-Akahira-Sunose (KAS), Flynn Wall Ozawa (FWO), Distributed activation energy model (DAEM), and Friedman methods belong to the free-model. Several researchers [14]-[17] have used these methods to extract kinetic parameters from different agricultural residues. Jayaraman et al. [14] studied the kinetic pyrolysis and gasification of sugarcane bagasse using isoconversional models such as Friedman, KAS, and FWO methods. They concluded that FWO and KAS methods are more appropriate to explain the pyrolysis and gasification processes [14]. The found kinetic parameters were applied to predict the pyrolysis process. Results were in a good concordance with the experimental data. Khiari and Jeguirim [15] studied the decomposition of Tunisian grape marc, under an inert atmosphere, at temperatures ranging between 20-700°C. To determine the activation energy value, they used different isoconversional methods (FWO and KAS). They signed that the integral and differential method used on their work leads to reliable kinetic parameters of the pyrolysis process. Martín-Lara et al. [16] explored pyrolysis kinetic of olive stones by isoconversional methods (KAS, FWO and Friedman methods) using thermogravimetric analysis at three heating rates of 5°, 10° and 20°C/min for a final temperature of 800°C. Activation energies varied for a conversion rate ranging from 10 to 90%. They found that results are similar for FWO and KAS methods.

In contrast, the application of Friedman led to slight deviations in the activation energies. The thermochemical decomposition of coffee grounds residues was studied by a thermogravimetric analyzer [17]. Activation energies were determined by two model-free methods namely, KAS and FWO methods. Similar results were obtained with both models. Other results found in the literature on date residues use the adjustment model, but these results are not satisfactory [18].

This work presents a recent kinetic study of Tunisian agricultural residues. The kinetic parameters were calculated using different methods to compare their performances and limits:

a. A not isoconversional free-model method: Kissinger method;
b. Four isoconversional free-model methods: FWO, KAS, Friedman and DAEM methods.

This study aims to evaluate the kinetics of the degradation of four Tunisian agricultural biomasses; date stems, date seeds, olive stones and spent coffee grounds using data from non-isothermal thermogravimetry. These results will provide helpful information for pyrolysis researchers to model the degradation of these biomasses and optimize the pyrolysis process conditions.

Experimental

Material

Date seeds, date stems, olives stones, and spent coffee grounds used in this study were collected from Tunisia. Ash content, heating value, volatile matter, fixed carbon, fat and the C, H, N contents were determined using the protocols reported in a previous work of the GEPEA laboratory [19]. The TG experiments were performed under an inert atmosphere of N_2 (100 mL.min^{-1}) [20]-[21] at four heating rates of 5, 10, 15 and 20°C.min^{-1} [22]-[24]. In all cases, approximately 10 mg of powder samples were thermally treated [25]-[27]. For all used biomasses, the lignocellulosic composition was extracted from thermogravimetric analysis. All analyzes were performed in three replicates. The uncertainties were less than 5%.

Determination of kinetic parameters by model-free methods

Pyrolysis of lignocellulosic biomass is a very complex phenomenon due to variations in the chemical composition within the biomass. So many reactions coincide in a fraction of a second during thermal degradation. Therefore, the prediction of the exact reaction mechanism is not possible. The one-step global model assumes that the devolatilization phenomena proceeds as a single reaction [28],

$$\text{Biomass} \xrightarrow{k} \text{Volatiles} + \text{Char}$$

where volatiles mean the sum of the gases and tars and *k* is defined as the rate constant of the reaction.

The fundamental expression for the decomposition of a solid sample used in all kinetic studies is described as:

$$\frac{da}{dt} = k(T) f(a) \quad (1)$$

a is the degree of conversion defined as:

$$\alpha = \frac{W_0 - W_t}{W_0 - W_f} \quad (2)$$

where w_0 is the initial mass, w_f is the final mass, and w_t is the mass at time t of the sample analyzed by TGA. *f(α)* is a function of *α* depending on the reaction mechanism.

The Arrhenius law is assumed, and is given by the following equation:

$$k(T) = A.exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

where A is the frequency factor (s^{-1}), E_a is the activation energy ($kJ.mol^{-1}$), *R* is the universal gas constant ($J.K^{-1}.mol^{-1}$) and *T* is the absolute temperature (K).

By combining Equations (1) and (3), we obtain the general expression (4) to calculate the kinetic parameters:

$$\frac{da}{dt} = f(a).A.exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

The heating rate is expressed as:

$$\beta = \frac{dT}{dt} \quad (5)$$

The introduction of *β* in the equation (4) gives the differential form of the non-isothermal reaction rate:

$$\frac{da}{dT} = \frac{f(a)}{\beta} Aexp\left(\frac{-E_a}{RT}\right) \quad (6)$$

Significant explanations of different used methods are shown in Table 1.

Table 1 Mathematical equations of Kissinger, FWO, KAS, Friedman and DAEM methods

Method	Equation	Remarks
Kissinger [29]	$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_m}$	Kissinger method assumed that activation energy does not vary according to the conversion rate.
Flynn-Wall-Ozawa (FWO) [30]	$\ln(\beta) = \ln\left(\frac{AE_a}{g(a)R}\right) - 5.331 - 1.052\frac{E_a}{RT}$	The precision of the FWO method is not satisfactory due to the crude temperature integral approximation.
Kissinger-Akahira-Sunose (KAS) [31]	$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{g(a)E_a}\right) - \frac{E_a}{RT}$	KAS method represents all the chemical and physical reactions that occur as thermal decomposition proceeds.
Friedman [32]	$\ln\left(\frac{da}{dt}\right) = \ln[Af(a)] - \frac{E_a}{RT}$	This method considerer that the conversion functions f (α) remain constant, which indicates that biomass decomposition is independent of temperature. It depends only on the loss of mass rate.
Distributed activation energy model (DAEM)	$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E_a}\right) + 0.6075 - \frac{E_a}{RT}$	The simplified DAEM method admits that various irreversible first-order parallel reactions that have different rate parameters occur at the same time.

Results and Discussion

Biomass analysis

Tables 2 and 3 show the chemical and physical properties of the Tunisian biomass wastes used in the experiment. Fibre, proximate and ultimate analysis of date residues, olives stones, and spent coffee grounds are compared with the values of several lignocellulosic biomass samples: one wood-based biomass samples (wood chips) [34], four agricultural wastes (date residues [35], olive stones [36], spent coffee grounds [17] and sugar cane bagasse [14]), and one energy crop (bamboo [37]) (*See* Table 2). The cellulose, hemicelluloses and lignin content of the biomasses studied are slightly different from those reported by other studies. This behaviour can be related to the structure, the generic composition of lignocelluloses and the diversity in soil.

It can be noted that date seeds, olive stones, and spent coffee grounds in this work contain more carbon and less oxygen (therefore lower O/C~0.8-0.9) than wood chips and dates residues studied by Nasser et al. [35] (O/C~1-1.1) as explained by the higher lignin contents in the tested biomass [38]. Cellulose and hemicelluloses contribute to the bio-oil production yield, while lignin produces more significant proportion char [39]. So, these biomasses are a suitable candidate for the production of biochar by pyrolysis — this hypothesis proved that their fixed carbon contents are similar to those of lignin coal. Besides, catalyst supports could be obtained with theses biomasses. In this context, Prati et al. [40] used activated carbons produced from three different wood species for the preparation of supported platinum catalysts. At the same time, Liew et al. [41] studied activated carbon derived from palm kernel shell as catalyst support for nickel catalysts.

However, the ultimate analysis shows that both spent coffee grounds studied in this work and that of Fermoso and Masẽk [17] contain more nitrogen (~2.3 wt%) than the other lignocellulosic biomass (0.1-0.9 wt%). This is can be explained by their high protein content. The four studied agricultural residues have a volatile content of ~76.9-77.9 wt%. This high level of volatile matters is very suitable for bio-oil production [9]. The biomass studied does not have the highest volatiles yields, but the difference with the better biomass sample, olives stones (volatiles yield = 89.3 wt%), is lower than 12% [36]. The lower ash content of residues in this work, compared to sugar cane bagasse and lignin coal, decrease the processing costs, increase energy conversion and reduce disposal problems. The high heating values range from 18.9 to 21.5 $MJ.kg^{-1}$ are similar to previous results [17], [36]. The high calorific values of the studied residues aren't high enough to allow their direct use as a commercial fuel. Thus, these materials must be improved through pyrolysis, which seems to be the most appropriate process for concentrating carbon and developing its calorific value. In conclusion, date residues, olives stones, and spent coffee grounds would be a new source of energy after thermal treatment.

The basic elemental constituents of biomass minerals are Si, Ca, K, and Mg with smaller amounts of S, P, Fe, and Cu. The existence of inorganic minerals, especially the alkali (K, Na, etc.) and alkaline-earth metals (Mg, Ca, etc.) influence the mechanism of biomass pyrolysis. For example, K in the biomass mineral matter catalytically favours char formation and lowers bio-oil yield [43]. In our case, date seeds, olive stones and spent coffee grounds contain the highest percentages in K; therefore, they are more suitable for char production. The analysis of Table 2 validates this hypothesis. Contrariwise biomass with high percentages of alkali metals and Cl are less desirable as fuel because it causes fouling, deposition, corrosion, plugging, and agglomeration [44]. According to the EDX analysis (Energy-dispersive X-ray fluorescence), the number of alkali metals and Cl in, date residues, olive stones, and spent coffee grounds is low (less than 10 wt%).

Table 2 Fibre, proximate and ultimate analysis of date residues, olive stones, and spent coffee grounds

Biomass samples	Fiber Analysis (%)			Ultimate Analysis (wt%)					Proximate Analysis (wt%)			Calorific power
	Cellulose	Hémicelluloses	Lignin	C	H	N	S	O*	[db]Volatiles yield	Fixed Carbon	Ash	MJ.kg^{-1}
Date stems	40.1	30.5	20.3	46.5	5.8	0.7	<0.06	46.9	77.7	18.9	3.4	18.9
Date stems [35]	43.1	27.9	29.5	44.5	6.0	0.3	-	49.2	85.3	12.9	1.8	-
Date seeds	22.5	48.2	25.7	47.9	6.6	0.9	<0.06	44.5	77.6	21.2	1.2	19.9
Date seeds [35]	32.8	30.2	37.1	47.1	6.6	0.9	-	45.3	83.3	14.9	1.4	-
Olives stones	42.3	33.2	20.4	51.3	6.2	0.7	<0.06	41.8	76.9	22.9	0.2	21.5
Olive stones [36]	53.5	22.3	22.5	49.5	6.4	0.2	-	40.7	89 .3	10.0	0.6	21.1
Spent coffee grounds	32.0	35.0	25	50.4	6.9	2.4	<0.06	40.3	77.9	20.3	1.8	21.4
Coffee grounds residues [17]	10.6	36.6	40.6	53.9	7.1	2.3	-	35.8	76.4	22.7	0.9	23.4
Wood chips [34]	31.8	31.8	19	46.4	5.9	0.1	-	47.6	82.3	10.2	0.3	20.3
Sugar cane bagasse [14], [42]	50.5	24.5	23.5	44.3	5.7	0.3	-	40.9	71.9	10.6	9.1	18.2
Bamboo[37]	45.1	25.6	22.5	45.1	4.6	0.3	0.20	37.5	73.1	14.4	2.1	17.6
Lignin coal [12]	-	-	-	44.6	4.7	0.6	0.60	49.5	41.2	26.1	19.8	16.2

*Obtained by difference, [db] dry basis

Table 3 Ash Composition Data of date residues, olives stones, and spent coffee grounds (wt%)

	K	Cl	Ca	P	S	Mg	Fe	Si
Date stems	0.054	0.003	0.040	0.013	0.014	0.000	0.002	0.025
Date seeds	0.140	0.044	0.021	0.058	0.031	0.027	0.005	0.004
Olive stones	0.120	0.027	0.052	0.069	0.030	0.001	0.004	0.017
Spent coffee grounds	0.176	0.040	0.063	0.046	0.060	0.000	0.003	0.000

Thermal characterization

Thermogravimetric analysis (TGA) of date residues, olive stone, and spent coffee grounds under an inert atmosphere at 700°C and for four heating rates of 5, 10, 15 and 20°C/min are illustrated in Figure 1.

The volatiles is released mostly in two steps during the pyrolysis of used biomass. Thus, TGA curves of date residues and olive stones show two peaks while the spent coffee grounds decomposition brings out only one peak with a shoulder. The two peaks appearing in the DTG (The derivative thermogravimetry) curve correspond substantially to the thermal degradation of hemicelluloses, which generally occurs between 250 and 350°C, followed by that of cellulose which is between 325 and 400°C. Lignin is the most stable component since it decomposes at a higher temperature range of 300-550°C [45]. The decomposition of hemicellulose is characterized generally by a small peak in comparison to that of cellulose, whereas no characteristic peak is distinguished for lignin decomposition [21].

More precisely, moisture evaporation is recorded from the first stage of analysis (<150°C) in date stems (*See* Figure 1a). The immediate drop in biomass weight after 150°C is attributed to the launching of volatile matter. According to the DTG curve, the thermal degradation of date stems can be divided into two parts; the decomposition of hemicellulose (30.5%) occurs between 220 and 300°C and that of cellulose (40.1%) between 300 and 380°C. Above 500°C, the mass loss of the sample is minimal (<25wt%), indicating the formation of solid (char) about this temperature and the process is achieved. The TG-DTG thermograph obtained for date stems is similar to that presented by Hadoun et al. [46].

Thermal decomposition of date seeds (Figure 1b) begins approximately at 200°C, the major loss of weight is done until 500°C. The first stage of pyrolysis (240-340°C) can be recognized as the hemicelluloses (32%) decomposition with a maximum rate of 21%/min at 304°C. The second decomposition extends between 340° and 450°C and can be identified as the decomposition step of both cellulose (32.8%) and lignin (37.1%) with a characteristic peak of 4.97%/min at 395°C. This interesting phenomenon associated with hemicellulos component, which has a major decomposition peak and even higher than that of cellulose, may be explained by the extractives content in date seeds [21]. A similar result was reported by Fadhil et al. [47]. For olive stones (Figure 1c) all derivative thermogravimetric (DTG) curves presented two peaks between 200° and 500°C in accordance with the decomposition of hemicelluloses and cellulose, respectively. The first peak, which is between 250° and 320 °C, may arise from the decomposition of mainly extractives and hemicelluloses (33.2%), and partly from the decomposition of lignin (20.4%) [48]. The second peak occurs between 315° and 380°C and can be attributed to the decomposition of cellulose and lignin. These temperatures range are in good agreement with the results found by Martín-Lara et al. [16] for the same biomass.

The mass loss of the spent coffee grounds (Figure 1d) occurred at the temperature ranging from 250° to 500°C. TGA curves indicated a large peak with a shoulder corresponding respectively to the hemicellulose (35%) and cellulose (32%) decomposition. It can be concluded that hemicellulose in this biomass are more reactive than the other two polymers. The decomposition process of the studied residues could be identified in three stages. In the first stage, known as the dehydration stage, we note the release of weakly bonded water molecules and the hydrolysis of some extractives at temperature up to 150°C. The second stage involves (active pyrolysis) the decomposition of hemicellulose, cellulose and a small amount of lignin at a temperature range of 220-500°C. The first peak represents the decomposition of hemicellulose and the second peak corresponds to the decomposition of cellulose. In the third stage (passive pyrolysis), the decomposition of lignin was observed at the temperature range of 315-600°C. Char is the major product produced during passive pyrolysis.

The heating rate is a far-reaching parameter as it affects the conversion as well as the distribution of the product. The increase in the maximum degradation temperature is proportional to the heating rate (Figure 1) to ensure an excellent heat transfer inside the load used, it is better to use a low rate of heating.

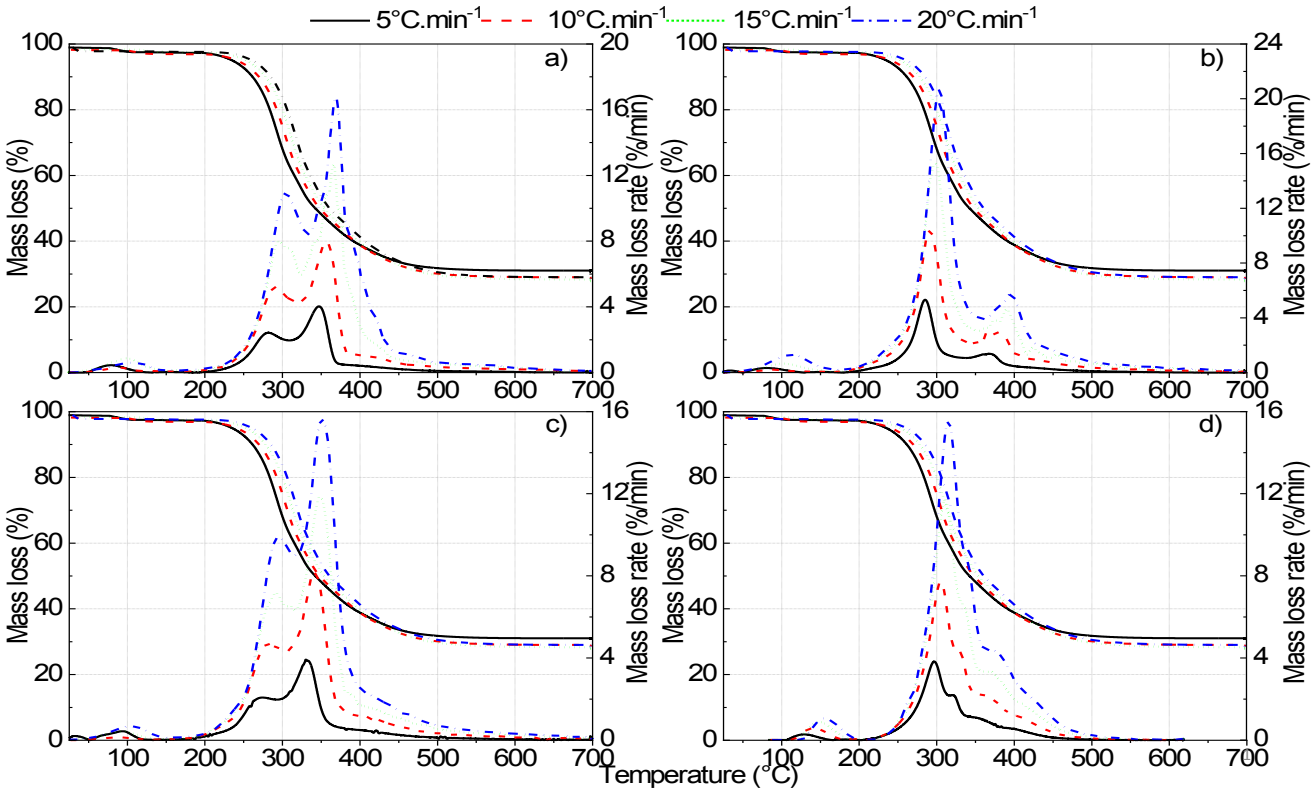

Figure 1 TG profile of (a) date stems (b) date seeds (c) olive stones and (d) spent coffee grounds

Kinetic analysis

Activation energy is distinct as the lowest energy requirement that must be overcome before molecules can get close enough to react and form products. In this respect, the reaction with high activation energy requests a high temperature or a long reaction time. Isoconversional methods are used for the solid-state decomposition since the activation energy (Ea) varies on the reaction progress. Model-free approaches were used to inspect the change in activation energy according to inconstant conversion. The models were applied to the main decomposition region of lignocellulosic components between 200-500°C.

In order to determine the kinetic parameters of date residues, olive stones and spent coffee grounds pyrolysis, conversion fractions moving from 20 to 80% were employed with an increment of 10% at various heating rates [26], [38].

Table 4 Calculated kinetic parameters of Tunisian date seeds and date stems from the four different isoconversional methods

Conversion α (%)	Date stems		Date seeds		Olive stones		Spent coffee grounds	
	Ea	R^2	Ea	R^2	Ea	R^2	Ea	R^2
KAS method								
20	130	0.9813	203	0.9908	143	0.9947	139	0.9934
30	141	0.9850	194	0.9984	162	0.9959	148	0.9953
40	148	0.9784	189	0.9990	176	0.9945	153	0.9967
50	159	0.9883	184	0.9975	183	0.9966	158	0.9962
60	163	0.9965	139	0.9538	191	0.9955	167	0.9979
70	170	0.9983	131	0.9648	190	0.9961	170	0.9995
80	157	0.9696	138	0.9767	219	0.9935	171	0.9999
FWO method								
20	129	0.9837	197	0.9916	142	0.9953	138	0.9942
30	140	0.9868	189	0.9986	159	0.9963	147	0.9959
40	147	0.9809	185	0.9991	173	0.9950	151	0.9971
50	157	0.9896	180	0.9977	180	0.9969	156	0.9967
60	161	0.9969	144	0.9820	187	0.9959	164	0.9982
70	168	0.9985	132	0.9695	186	0.9965	168	0.9996
80	156	0.9733	139	0.9798	213	0.9941	170	0.9993
DAEM method								
20	130	0.9809	203	0.9904	144	0.9945	140	0.9935
30	141	0.9846	195	0.9985	162	0.9958	149	0.9954
40	149	0.9777	190	0.9990	177	0.9943	154	0.9970
50	159	0.9879	184	0.9972	184	0.9965	159	0.9964
60	163	0.9965	170	0.9761	192	0.9955	169	0.9980
70	170	0.9982	132	0.9785	190	0.9961	171	0.9995
80	151	0.9893	139	0.9866	218	0.9929	173	0.9999
Friedman method								
20	153	0.9897	210	0.9955	165	0.9977	160	0.9987
30	154	0.9799	192	0.9940	181	0.9956	161	0.9985
40	156	0.9903	178	0.9981	189	0.9916	160	0.9978
50	180	0.9883	174	0.9596	197	0.9966	174	0.9972
60	179	0.9989	146	0.9660	196	0.9968	178	0.9999
70	173	0.9905	122	0.9704	192	0.9969	176	0.9990
80	120	0.9956	152	0.9807	289	0.9839	183	0.9995

Table 4 lists the activation energy and the correlation coefficients for the isoconversional methods: FWO, KAS, DAEM, and Friedman. A good linear relationship for most of the conversion value was obtained with the designated models, and high R^2 values were achieved. The FWO, KAS, and DAEM methods give similar values of Ea according to α range (Figures 2-5). Contrariwise activation energy values achieved by the Friedman method were slightly higher (<11%) than those previously cited. This difference in calculated Ea values can be caused by the approximation in FWO, KAS, and DAEM equations. Statistical analysis shows that the value of the correlation coefficient is closer to 1.0 in the case of Friedman's method. In this view, it can be inferred that the values calculated with the Friedman method are more accurate and closer to the actual activation energy during the pyrolysis process.

From a global view of Table 4, the fluctuation of the activation energy is observed in all methods. This behaviour is the result of the complexity of the pyrolysis reaction of the different studied residues. The variation in activation energy conversion is also due to the percentage of components present in these residues and their interactions among themselves [38].

Calculated kinetic energy (Table 4) from KAS, FWO, DAEM, and Friedman methods varied within 130-170, 129-168, 130-170, and 120-180 kJ.mol^{-1}, respectively for date stems; 131-203, 132-197, 132-203, and 122-210 kJ.mol^{-1}, respectively for date seeds; 143-219, 142-213, 144-218, and 165-289 kJ.mol^{-1}, respectively for olive stones; and 139-171, 138-170, 140-173, and 160–183 kJ.mol^{-1}, respectively for spent coffee grounds.

The decomposition of date stems (Figure 2) can be divided into three steps. At the beginning of the conversion, 20-60%, the activation energies vary between 129 and 163 kJ.mol^{-1} by KAS, FWO, and DAEM method and between 153 and 180 kJ.mol^{-1} by Friedman method. This is attributed to hemicelluloses degradation. The degradation initially happens on the weakly sites of the hemicelluloses, which required low activation energy. It was observed that date stems have more cellulose content (40.1%) so it requires more activation energy for decomposition, which was increased at α= 60 to 70%. The interaction between hemicelluloses and lignin explains this high level of activation energy. The activation energy calculated from model-free methods is ranging between 163-170, 161-168, 163-170, 179-173 kJ.mol^{-1} for KAS, FWO, DAEM, and Friedman, respectively. This is related to the deterioration of cellulose. For α>70%, the activation energy starts to decrease, announcing the end of lignocellulosic degradation.

As far as that, the decomposition of date seeds (Fig. 3) can be divided into three steps, according to KAS, FWO, DAEM, and Friedman method. Unlike date stems, there was a reduction in Ea in the first stage (20-30%). This initial decrease may be caused by the diffusional limitations of the released gaseous species, generated before and during the pyrolytic cracking [49]. Then a gradual decrease from 30 to 70% followed by an increase from 70 to 80% with all methods (Table 4). The progressive reduction of activation energy in the stage from 30 to 70% is due to the degradation of hemicellulose. Indeed, the average of Ea at this stage is higher than that of date stems. This is explained by the higher percentage of hemicellulose (48.2%) contained in date seeds compared to other compounds [50]. Then the increase in activation energy is associated with simultaneous decomposition of cellulose and lignin, which occurs at a higher temperature. The variation of the activation energy with the conversion rate suggests the existence of a multi-step mechanism that occurs in thermal decomposition [51].

Concerning olive stones (Figure 4), two stages can be identified. In the first stage (20-30%) activation energy increase slightly to an average of 155 kJ.mol^{-1} for KAS, FWO, DAEM, and 173 kJ.mol^{-1} for Friedman method. The second step (30-80%) the average activation energy reaches a higher value of 200 ± 10 kJ.mol^{-1}. The two stages can be identified as the hemicelluloses (33.2%) and the cellulose (42.3%) degradation respectively. A similar result was found by Aboulkas et al. [53].

As for spent coffee grounds (Figure 5), the KAS, FWO and DAEM methods give similar results, while those obtained by the Friedman method are slightly higher. Table 4 shows two maximum values of activation energy. The first maximum is about 163 ± 5 kJ.mol^{-1} according to KAS, FWO and DAEM methods and 178 kJ.mol$^{-1,}$ according to Friedman method. These values correspond to the degradation of hemicelluloses (35%). While the second maximum is 175 ± 5 kJ.mol^{-1} (α = 80%) approximately. This value of activation energy can be attributed to the degradation of cellulose (32%). The average activation energy of spent coffee grounds is around 158, 156, 159, 170 kJ.mol^{-1} for KAS, FWO, DAEM and Friedman methods, respectively.

Lower Ea values of date stem and spent coffee grounds reflect that it may be used for pyrolysis with other biomasses having lower or higher Ea values. The above finding makes these residues suitable for the thermal conversion of biomass to value-added products/ bioenergy.

The Kissinger method gives a single activation energy value for the whole process. The plot obtained from the Kissinger equation (Table 1) shown in Figure 6. By using this method, the activation energy was obtained at the temperature of the maximum reaction rate. The temperature has been determined from the first derivative of the curves at a different heating rate.

The calculated values of activation energies were 161, 198, 225, and 142 kJ.mol^{-1} for date stems, date seeds, olive stones and spent coffee grounds, respectively. The pre-exponential factor is 1.15×10^{10}, 1.73×10^{15}, 8.82×10^{15}, and 3.10×10^{8} s^{-1} for date stems, date seeds, olive stones, and spent coffee grounds correspondingly. When the frequency factor A is less than 10^{9} s^{-1}, it means that the system has a low reactivity [9]. In this case, spent coffee grounds are less reactive biomass. Since activation energy is defined as the energy barrier that reagents must cross to become products, coffee grounds seem to be the right candidate for the thermal decomposition.

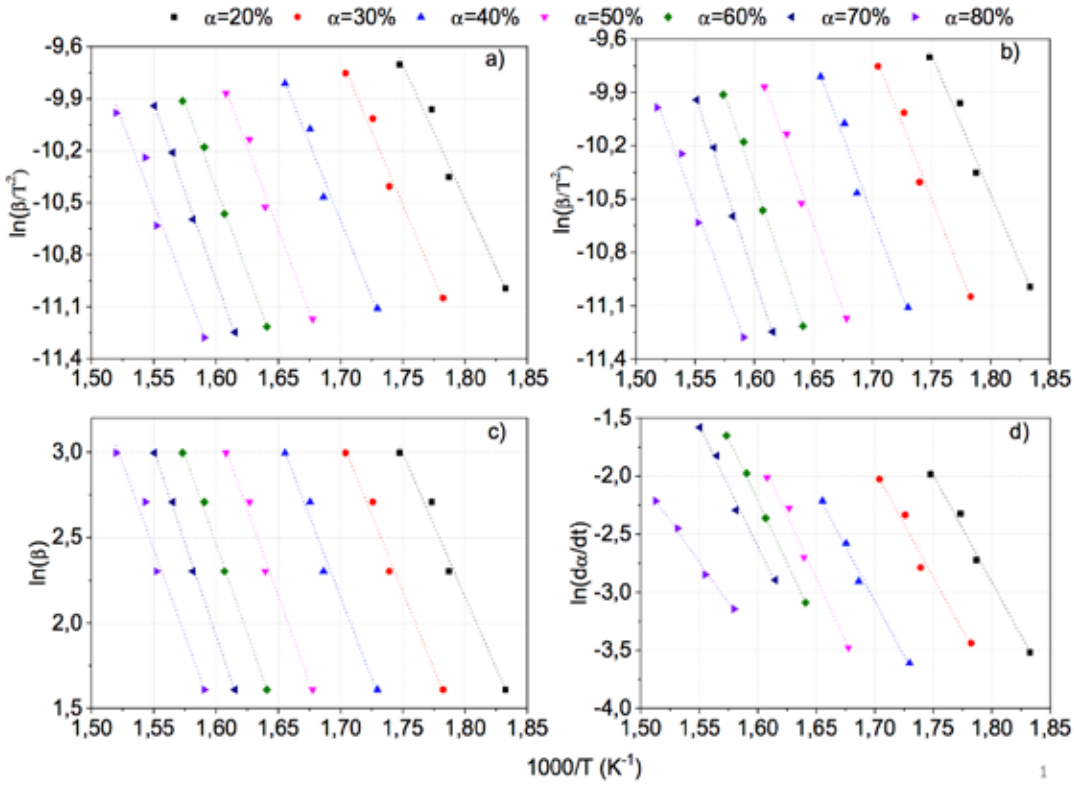

Figure 2 Isoconversional plots of date stem for (a) KAS (b) DAEM (c) FWO and (d) Friedman methods

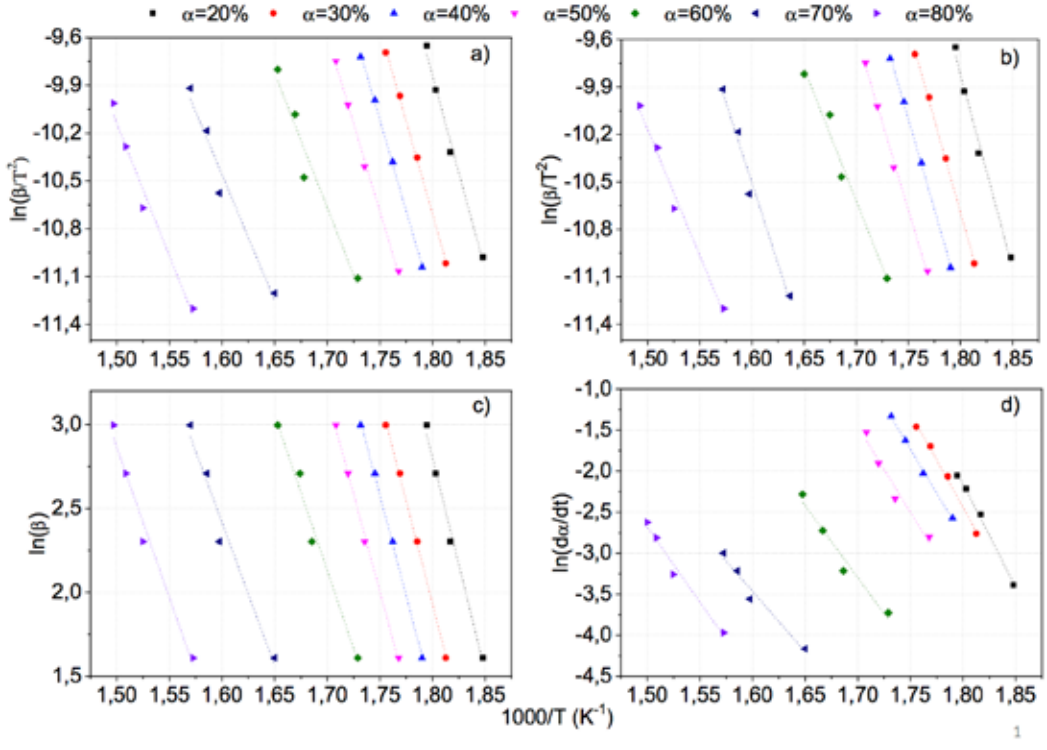

Figure 3 Isoconversional plots of date seeds for (a) KAS (b) DAEM (c) FWO and (d) Friedman methods

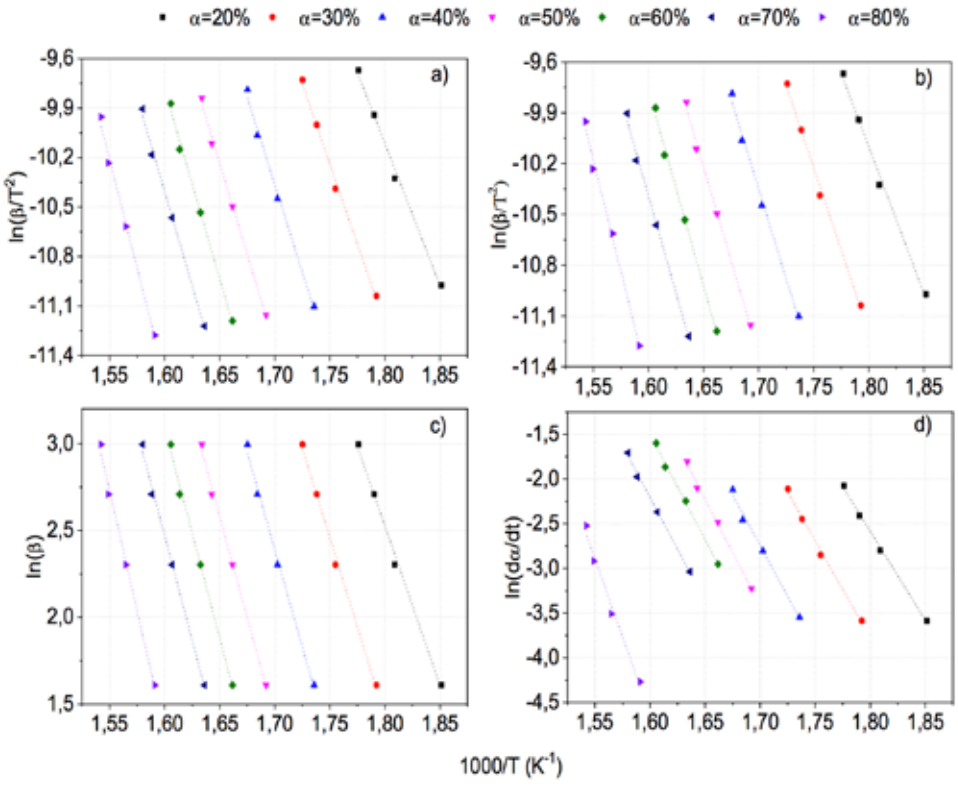

Figure 4 Isoconversional plots of olive for (a) KAS (b) DAEM (c) FWO and (d) Friedman methods

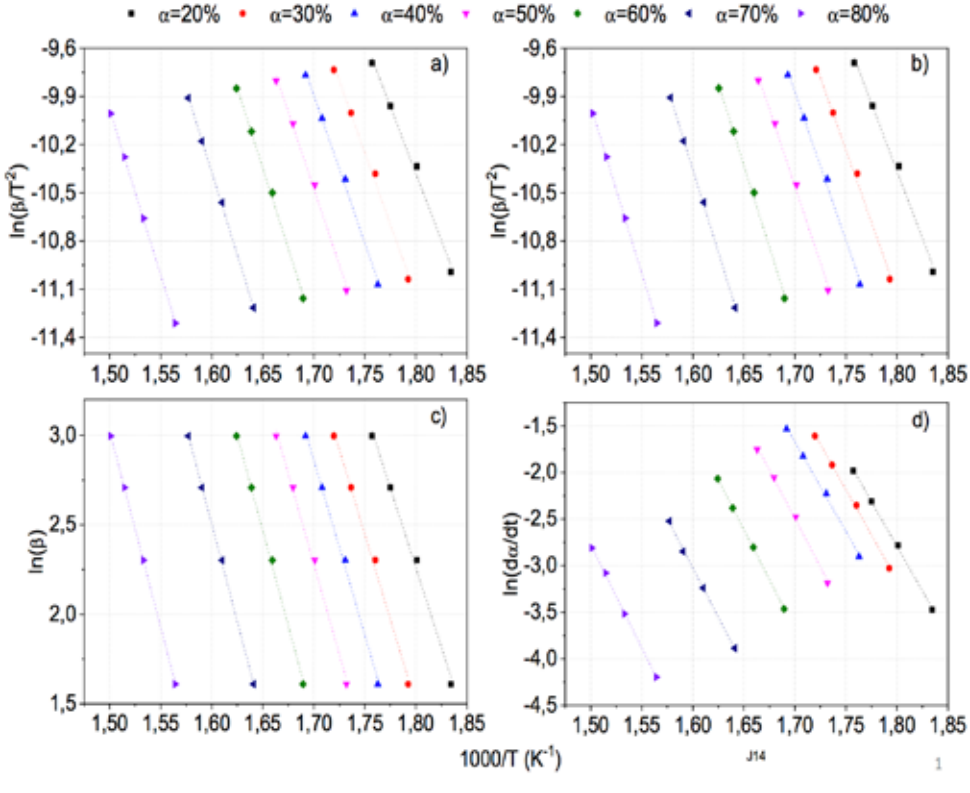

Figure 5 Isoconversional plots of spent coffee grounds for (a) KAS (b) DAEM (c) FWO and (d) Friedman methods

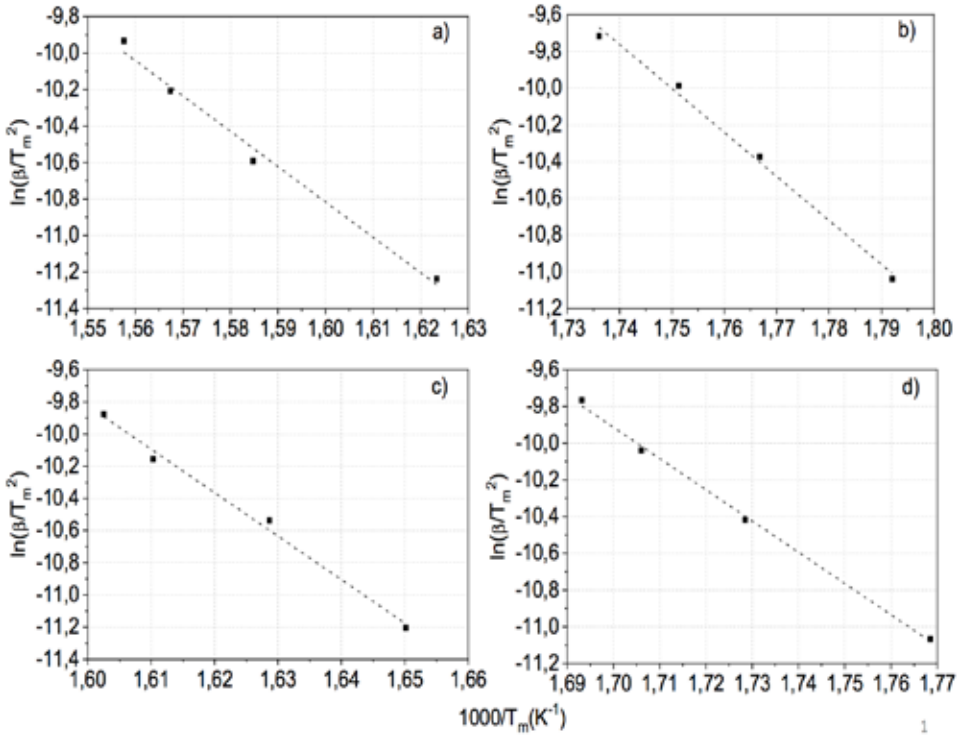

Figure 6 Kissinger plot of biomass: (a) date stems (b) date seeds (c) olive stones and (d) spent coffee grounds

Comparison between the average activation energies values

The comparison between the average values of activation energy obtained in this study and results found by other studies [12],[16],[21],[26],[38],[53]-[54] is summarized in Table 5. The average of activation energy calculated from Kissinger, KAS, FWO, DAEM, and Friedman methods are 161, 152, 151, 152, and 159 kJ.mol^{-1}, respectively for date stems; 198, 168, 166, 173, and 168 kJ.mol^{-1}, respectively for date seeds; 225, 181, 177, 181, and 201 kJ.mol^{-1}, respectively for olive stones; and 142, 158, 156, 159, 170kJ.mol^{-1}, respectively for spent coffee grounds. The calculated activation energy values in the current study evolve in the same order. The difference observed in kinetic values of all presented biomass refers essentially to the gap between the degradation temperatures of these residues and even their inequality percentage of cellulose, hemicelluloses, and lignin. The Ea values obtained by KAS, FWO and DAEM methods are almost equal, while those obtained by Friedman are slightly higher. This behaviour can be explained by the fact that Friedman's method presents no mathematical approximation [55]. It varies only according to the rate of heating. Hence it provides values of activation energies more concrete than the other methods.

Validation of the kinetic parameters

Using the fourth-order Runge Kutta method, and with the application of Friedman's method, we can end up with the rebuilding of the kinetic process [10]. The calculation of the error between the experimental and the simulated results of all tested biomass at different heating rates is illustrated in Table 6. Note that the average error percentage does not exceed 5%. Therefore, the results of the calculated activation energies are acceptable. On the other hand, by increasing the heating rate, the error percentage also increases. Thus, the calculation of the kinetic parameter across the model-free is more reliable at a low heating rate.

Table 5 Comparison of average values of activation energies of different types of biomass

Biomass	Heating rate (°C.min^{-1})	Average value of activation energy (kJ.mol^{-1})				
		Kissinger	KAS	FWO	DAEM	Friedman
Date stems	5-10-15-20	161	152	151	152	159
Date seeds		198	168	166	173	168
Olive stones		225	181	177	181	201
Spent coffee grounds		142	158	156	159	170
Pine sawdust [53]	5-10-15-20-25	-	172	179	207	168
Sal sawdust [53]			148	156	172	182
Areca nuthusk [53]			171	179	160	185
Castor [38]	5-10-15-20-30-40	-	166	167	-	-
Olive pomace [16]	5-10-20	-	195	195	-	193
Prosopis juliflora [54]	2-5-10-15-20-25	165	204	203	-	219
Cattle manure [21]	10-20-30-40-50-60-80	-	185	186	-	199
Herb residue [26]	5-10-20-30	-	-	117	-	-
Lignite Coal [12]	1-6-9-12-15-18	281	282	275	-	283

Table 6 Calculation of maximum and average error according to the heating rate (*See* Figure 7)

Heating rate (°C.min^{-1})	Error calculation (%)							
	Date stems		Date seeds		Olive stones		Spent coffee grounds	
	Average error	Maximum error	Average error	Maximum error	Average error	Maximum error	Average error	Maximum error
5	0.32	0.50	0.60	1.50	0.71	0.95	0.96	2.55
10	1.10	1.90	1.95	4.20	1.85	2.50	1.20	3.50
15	1.95	3.34	2.02	5.35	2.70	6.80	3.50	4.12
20	2.40	5.63	3.16	6.57	3.81	7.91	4.20	6.62

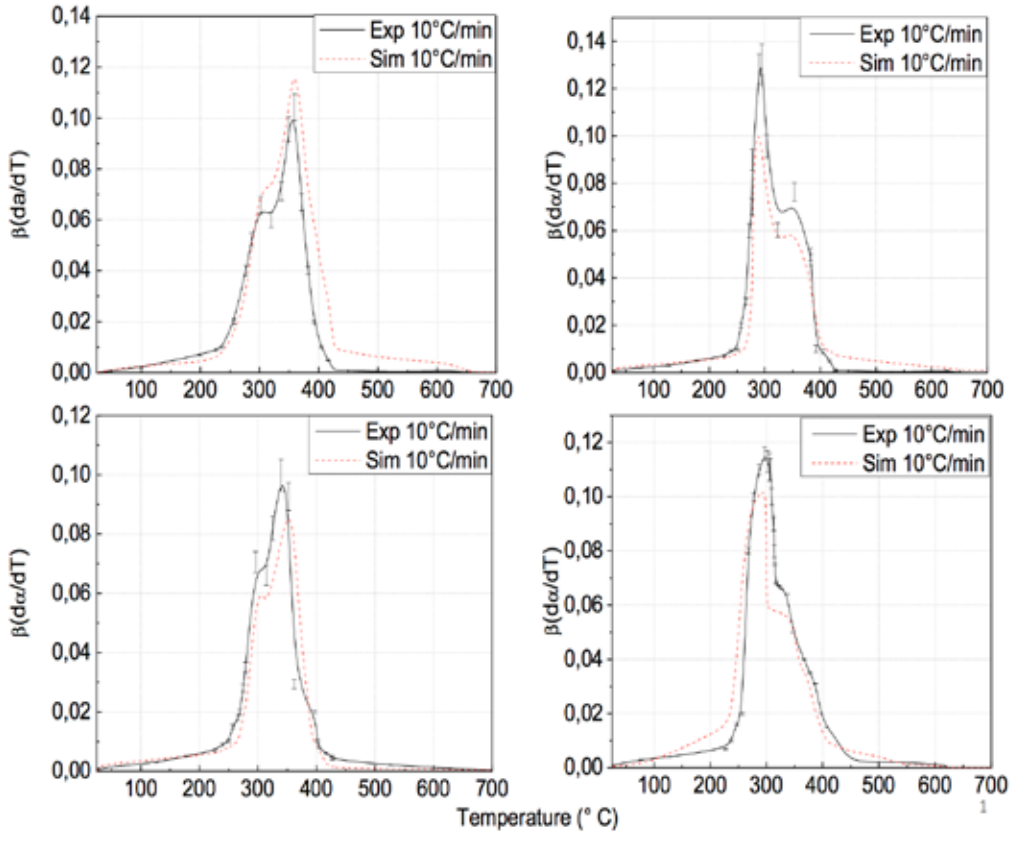

Figure 7 Comparison between Kinetic simulation and experimental data based on Friedman results for (a) date stems (b) date seeds (c) olive stones and (d) spent coffee grounds at 10°C.min^{-1}

Experimental as well as the simulated data based on ln [$A_\alpha f(\alpha)$] and E_α derived from Friedman method at 10°C.min^{-1} for date stems, date seeds, olive stones, and spent coffee grounds are beget in Figure 7. The simulated results have approximately the same curve shape as the experimental results.

Conclusion

In this paper, kinetic parameters of Tunisian agricultural residues: date residues, olive stones, and ground coffee were identified using the free-model (e.g., Kissinger, KAS, FWO, DAEM and Friedman methods). Friedman's method seems to be the most appropriate because it contains no mathematical approximation that reduces the systematic error. For validation, the kinetic process was reconstructed via Eα and Ln (Af(α)) obtained by Friedman and compared with the experimental results. The average error between the experimental values and the simulated values is less than 5% to ensures that kinetic obtained parameters are reliable.

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