

## CO-PYROLYSIS OF OLIVE RESIDUE WITH POLY(VINYL CHLORIDE) USING THERMOGRAVIMETRIC ANALYSIS

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Pyrolytic process has a promising potential for the environmentally friendly upgrading of lignocellulosic materials and plastic waste. The co-pyrolysis of olive residue and poly(vinyl chloride) was investigated under nitrogen atmosphere by dynamic thermogravimetric analysis in the temperature range of 300–975 K. Two main stages of mass loss have been evidenced by TG analysis. The first occurs in the temperature range of 420–684 K, and the second occurs at 631–840 K. This research was focused on the interaction between olive residue and poly(vinyl chloride) during the pyrolysis process. Discrepancies between the experimental and calculated TG/DTG profiles were considered as a measurement of the extent of interactions occurring on co-pyrolysis. It was found that reactivity of olive residue was increased in olive residue/PVC mixture. In addition, a kinetic analysis was performed to fit thermogravimetric data, the mixture is considered as multistage process. A reasonable fit to the experimental data was obtained for all materials and their mixture by isoconversional Friedman method.

**Keywords:** co-pyrolysis, kinetics, olive residue, poly(vinyl chloride)

### Introduction

Co-processing of biomass and plastic is presently being considered as an alternative means of reducing CO<sub>2</sub> emissions and replacing of fossil fuels [1–4]. The thermal utilization of biomass can contribute to the reduction of CO<sub>2</sub> emissions as the same amount of CO<sub>2</sub> that is extracted from the atmosphere during the growth period of the plants as it is released by combustion (CO<sub>2</sub> balance).

Major components of municipal solid waste were biomass and plastics, followed by putrescibles and incombustibles. The application of co-pyrolysis technologies involving biomass and plastics for energy generation requires a proper understanding of the thermal properties and reaction process of biomass and plastic mixtures.

Thermogravimetric analysis (TG) is one of the commonly used techniques to study thermal events during the pyrolysis process of fuel [5–9]. The thermal decomposition of biomass derived materials has been studied [10–12]. Two peaks that appear in thermogravimetric curves are due to hemicellulose (the first one) and cellulose (the second one), whereas lignin decomposes in a broad range of temperatures. Numerous studies on the thermal decomposition of plastic and, in particular, PVC have been carried out, especially in inert atmosphere [13–16]. Two major

stages occur between 200–550°C, the first stage of degradation is connected to the release of the high amount of chlorine in PVC. This first step of degradation occurs in the same temperature range as for the hemicellulose and cellulose fractions of biomass. The second stage, which is believed to be the degradation of remaining hydrocarbons, occurs at higher temperatures.

Several studies have been devoted to the study of the thermal decomposition of mixtures of polymers and lignocellulosic materials [17–23]. Sharypov *et al.* [17] examined the combination of biomass with synthetic polymer mixtures and reported that biomass is thermal degraded at a lower temperature than the polyolefin and independent thermal behaviours were observed for each component of biomass/plastic mixtures. Jakab *et al.* [18, 19] analysed the effect of the presence of cellulose derivatives on thermal decomposition of vinyl polymers. The presence of lignocellulosic materials slightly affects high-density polyethylene decomposition, as the main degradation processes of cellulose derivatives have ended before high-density polyethylene begins to degrade. On the other hand, the effect of the presence of polypropylene on the thermal decomposition of cellulose derivatives was negligible. When degradation of biomass and polystyrene mixtures was evaluated, the yield of monomer, dimer and trimer from polystyrene decom-

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position was reduced, indicating that the radical chain reactions and intramolecular hydrogen transfer reactions were hindered by the presence of lignocellulose char [18]. In some cases, the polymeric matrix can influence the thermal degradation of cellulosic materials. Matsuzawa *et al.* [20] reported that poly(vinyl chloride) (PVC) and poly(vinylidene chloride) (PVdC) may affect the cellulose thermal degradation. HCl evolution in the dehydrochlorination reaction of vinyl chlorides seems to act as acid-catalyst to promote the dehydration reaction rather than the depolymerization reaction in cellulose pyrolysis. Sorum *et al.* [21] explored the pyrolysis characteristic and kinetics of Municipal Solid Wastes (MSW). The results indicated that the cellulosic fraction of MSW was modeled by three independent parallel reactions describing the degradation of hemicellulose, cellulose and lignin. The reactivity of cellulosic matter was increased in a mixture with polyvinyl chloride (PVC). Li *et al.* [22] investigated the pyrolysis products of MSW components (paper, paperboards, PVC, PE, rubber, vegetal materials, wood and orange husk) by a laboratory-scale rotary kiln. The effects of heating methods, moisture contents and size of waste on the pyrolysis gas and compositions were evaluated. However, and in spite of the above mentioned studies, there is a lack of information about the influence of cellulosic materials on the thermal degradation of polymers. The analysis of the thermal behaviour of mixtures of lignocellulosic materials and polymers is important not only from the recycling but also from the processing point of view.

Interactions between polymers and biomass are not well known. The main goal of this paper is to evaluate the interaction between olive residue and PVC during pyrolysis. Thermal analysis of pure components and mixture was performed by thermogravimetric analyser under dynamic conditions. The calculation of apparent activation energies was based on the application of the isoconversional Friedman method [24].

## Experimental

### *Materials and samples preparation*

The olive residue (mixture of all solid components) was obtained from Marrakech area which located about 300 km of Rabat. Olive residue was obtained from the solid product of traditional olive oil process (Maâsra in Morocco). Air-dried olive residue was ground to obtain a uniform material of an average particle size (0.2 mm). The chemical composition of the olive residues are given in Table 1.

**Table 1** Chemical composition of olive residue

Biopolymer composition	Mass%
Cellulose	27.3
Hemicellulose	32.7
Lignin	33.8
Holocellulose	60.0
Extractives	06.2

The samples of PVC were provided by Plador (Marrakech, Morocco). The olive residue:PVC (1:1 mass ratio) mixture was blended by tumbling for 30 min in order to achieve homogeneity. In all experiments, samples of around 20 mg with particle sizes ranging approximately from 0.1 and 0.2 mm were placed in the thermobalance.

### *Experimental techniques*

Olive residue, PVC and their mixture samples were subjected to thermogravimetric analysis in a nitrogen atmosphere. Rheometric Scientific STA 1500 TGA analyzer was used to measure and record the sample mass change with temperature over the course of the pyrolysis reaction. Thermogravimetric curves were obtained at four different heating rates (2, 10, 20 and 50 K min<sup>-1</sup>) between 300 and 975 K; the precision of reported temperatures was estimated to be  $\pm 2^\circ\text{C}$ . Nitrogen gas was used as an inert purge gas to displace air in the pyrolysis zone, thus avoiding unwanted oxidation of the sample. A flow rate of around 60 mL min<sup>-1</sup> was fed to the system from a point below the sample and a purge time of 60 min (to be sure the air was eliminated from the system and the atmosphere is inert). The balance can hold a maximum of 45 mg; therefore, all sample amounts used in this study averaged approximately 20 mg. The reproducibility of the experiments is acceptable and the experimental data presented in this paper corresponding to the different operating conditions are the mean values of runs carried out two or three times.

## Results and discussion

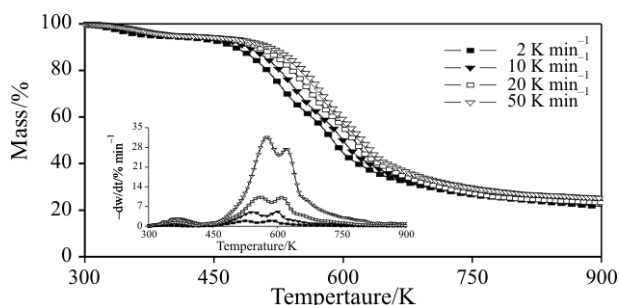
### *Thermal degradation of olive residue*

Figure 1 shows the TG/DTG curves at four different heating rates of 2, 10, 20 and 50 K min<sup>-1</sup> from room temperature to 975 K. Table 2 shows the temperatures of the start ( $T_I$ ) and finish ( $T_F$ ) of the main mass loss, the temperatures of maximum rate of mass loss for the two main peaks of the DTG curves and the intermediate temperatures for all the heating rates.

The TG curves showed a slight mass loss occurring from ambient temperature to about 420 K due to

**Table 2** Different temperature values of the olive residue, PVC and their mixture

Sample	Heating rate/K min <sup>-1</sup>	First step/K			Second step/K		
		T <sub>1</sub>	T <sub>max</sub>	T <sub>F</sub>	T <sub>1</sub>	T <sub>max</sub>	T <sub>F</sub>
Olive residue	2	430	499	537	537	558	608
	10	447	543	572	572	600	622
	20	453	562	587	587	611	644
	50	463	576	602	602	623	662
PVC	2	486	514	610	610	689	740
	10	498	543	642	642	726	806
	20	510	560	659	659	745	823
	50	530	588	684	684	771	861
Olive residue/PVC	2	420	531	631	631	690	740
	10	443	555	656	656	723	776
	20	477	582	671	671	734	805
	50	488	605	685	685	757	840

**Fig. 1** TG curves of olive residue at different heating rates. Inset: corresponding DTG curves

the loss of water present in the material and external water bounded by surface tension. The thermal degradation of olive residue starts at approximately 430 K, and there follows a major loss of mass where the main devolatilization occurs and is essentially complete by approximately 660 K. This is followed by a slow further loss of mass until 970 K, after which there is essentially no further loss of mass. The residual mass amounted around of 19–24% and was decreased when the heating rate increased (Table 3).

In the DTG curves, there are clearly two overlapping peaks and as the heating rate was increased, the two peaks become progressively merged. The composition of the biomass was cellulose, hemicellulose, lignin and extraneous components and the thermal degradation of individual components has been to extrapolate to the overall degradation of the original biomass [25]. In the thermal degradation of olive residue, the lower temperature peak was mainly represented by the decomposition of hemicellulose, and the higher temperature peak was mainly represented by cellulose. The peak corresponding of lignin is overlapping by the other two peaks; lignin decom-

poses slowly over a very broad range of temperatures, providing a gently sloping baseline [12]. It appears that the second peak is a prolongation of the first peak. This point is in accordance with the idea that lignin begins to decompose at low temperatures (similar to those at which hemicellulose begins to decompose) but its range of thermal decomposition extends to higher temperatures.

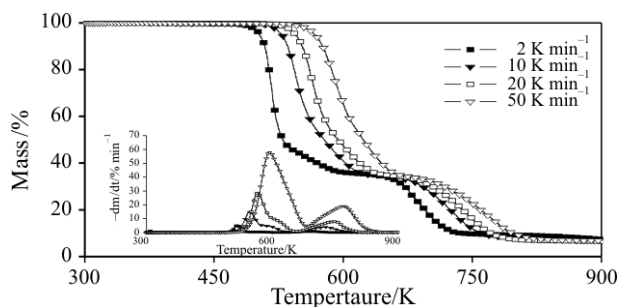
Table 2 shows that there was a lateral shift to higher temperatures  $T_{\max_1}$  and  $T_{\max_2}$  for olive residue as the heating rate was increased. The lateral shift is also illustrated in Fig. 1. The lateral shift has been reported for different types of biomass [25–27] and has been assigned as being due to the combined effects of the heat transfer at different heating rates and the kinetics of the decomposition resulting in delayed decomposition.

#### Thermal degradation of PVC

Figure 2 shows the TG/DTG curves of the PVC decomposition recorded at different heating rates. A two main stage mass loss is observed. For example, the TG curve measured at 10 K min<sup>-1</sup>, shows that the first stage, lo-

**Table 3** The residual mass of olive residue, PVC and their mixture at 900 K

Heating rate/ K min <sup>-1</sup>	The residual mass/%		
	Olive residue	PVC	Olive residue/ PVC
2	18.9	5.9	9.3
10	21.5	6.4	16.1
20	21.9	6.5	16.6
50	24.1	6.7	19.3



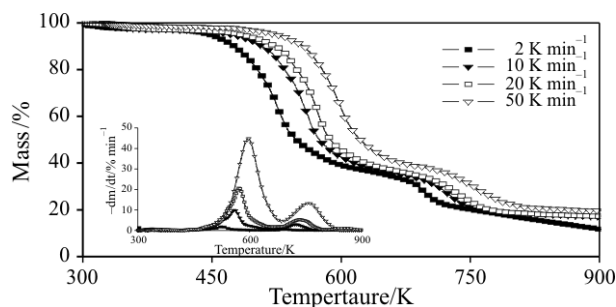
**Fig. 2** TG curves of PVC at different heating rates. Inset: corresponding DTG curves

cated between 498 and 642 K, represents a 64 mass% mass loss. The second stage, ranging from 642 to 806 K, represents a 28.6 mass% mass loss with 6.4 mass% for the mass of the final solid residue (Table 3). Corresponding to the two-stage mass loss on the TG curves, two peaks are observed on the DTG curves. For example, on the DTG curve at  $10 \text{ K min}^{-1}$  where the stages are more clearly visible, the first peak is observed at 543 K. The second peak is observed at 726 K. These results are presented in Table 2.

As shown in Fig. 2, between 486 and 684 K the main reaction involves a dehydrochlorination step with the subsequent formation of conjugated double bonds in polyene chains [28, 29]. On the other hand, only one DTG peak appears in the 610–861 K temperature range, which corresponds to the decomposition of the polyene chain formed during the first stage of PVC degradation. At the end a black carbonaceous residue is obtained. Many studies have shown that the thermal degradation of PVC proceeds in two distinct stages of mass loss [10, 20]: a stage in the temperature range of 473–653 K and another stage occurring in the range 653–823 K. It has been suggested that the first stage corresponds to dehydrochlorination with subsequent formation of conjugated double bonds [28], accompanied by the formation of small amounts of hydrocarbons, mainly aromatics such as benzene, toluene, naphthalene, indene, anthracene, *o*-xylene etc. [30, 31]. The second stage was reported to correspond to the scission of polyene sequences formed during the first stage [32].

#### Thermal degradation of the mixture

The TG/DTG curves of mixture of olive residue and PVC at heating rates of 2, 10, 20 and  $50 \text{ K min}^{-1}$  are presented in Fig. 3. In general, we can note that the domains of degradation of the first step of PVC and olive residue are overlapped. It can be seen that no separation of the DTG peaks of dehydrochlorination of PVC and olive residue. It should be added that the characteristic temperatures for the mixtures change in comparison with those for each component (Table 2). PVC in a mix-



**Fig. 3** TG curves of mixture at different heating rates. Inset: corresponding DTG curves

ture degrades at higher temperatures than pure PVC, while the olive residue in a mixture degrades at the lower temperatures than pure olive residue.

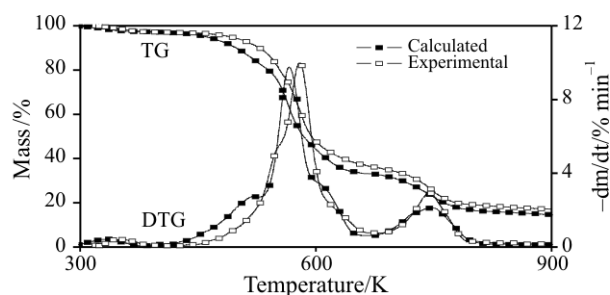
The TG/DTG curves show clearly two main steps. The first step, obtained in the temperature range (420–685 K), is attributed to the decomposition of hemicelluloses, cellulose and dehydrochlorination of PVC. The second step occurs between 631 and 840 K, which corresponds to the decomposition of remaining PVC and lignin from olive residue. The residual mass amounts are presented in Table 3.

To investigate whether interactions existed between the olive residue and PVC, a theoretical TG/DTG curves was calculated. This curve represented the sum of individual components behaviour in the mixture:

$$W_{\text{sum}} = x_1 W_{\text{olive residue}} + x_2 W_{\text{PVC}}$$

where  $w_{\text{olive residue}}$ ,  $w_{\text{PVC}}$  are mass loss of each material in same operational condition and  $x_1$ ,  $x_2$  are the mass fraction of olive residue and PVC in the mixture. The calculated and experimental curves for olive residue/PVC mixture at  $10 \text{ K min}^{-1}$  are illustrated in Fig. 4.

In all mixture, co-components show a different behaviour from that of the pure materials. A significant interaction is observed in the first stage of degradation at 443–656 K, while the second major stage of degradation is not affected. The dehydrochlorination of PVC increases the reactivity of olive residue (Table 2). However, the interactions at lower temper-



**Fig. 4** Comparison between experimental and calculated TG/DTG values for the olive residue/PVC mixture at  $10 \text{ K min}^{-1}$

atures have no significant impact on the degradation of remaining PVC and lignin from olive residue at higher temperatures. The difference in the remaining fraction at 900 K can be caused by irregularities between experiments and/or influence of char formation of olive residue and/or PVC at lower temperatures. Probably, PVC has particularly strong effect on the degradation of olive residue. HCl evolution from PVC occurred initially in major reactions of the mixture with PVC and olive residue, suggesting HCl gas to influence olive residue degradation. Other authors have observed interaction between PVC and cellulose materials [10, 20, 33, 34]. According to Matsuzawa *et al.* [10], HCl gas released from PVC accelerates cellulose degradation and production of aldehyde compounds (H-C=O). Moreover, Saeed *et al.* [33] reported that many additional compounds are released during co-pyrolysis of PVC and wood compared with pyrolysis of single parent fuels. These include mainly aldehydes and higher hydrocarbons. Sorum *et al.* [20] explored the pyrolysis characteristic and kinetics of MSW. The results indicated that the reactivity of cellulosic matter was increased in a mixture with polyvinyl chloride (PVC). McGhee *et al.* [34] investigating the co-pyrolysis of PVC with straw also found evidence of interaction during the dehydrochlorination step. One probable explanation of the interaction between straw and PVC was that the liberated HCl may be interacted chemically with the cellulose, catalysing an acid hydrolysis type of reaction making it less stable.

#### Determination of kinetic parameters

The kinetics of thermal decomposition reactions of carbonaceous materials is complex, in that decomposition of carbonaceous materials involves a large number of reactions in parallel and in series. Although thermogravimetry provides general information on the overall reaction kinetics, rather than individual reactions, it could be used as a tool for providing comparison of kinetic data of various reaction parameters such as temperature and heating rate. So the biomass and plastic pyrolysis reaction equation may simply be expressed as the following formula:

$$\frac{dx}{dt} = A \exp\left(-\frac{E}{RT}\right) f(x) \quad (1)$$

where  $A$  is pre-exponential factor,  $E$  is activation energy,  $T$  is temperature,  $t$  is time,  $f(x)$  is function of conversion,  $x$  is pyrolysis conversion.

The Friedman method [18] was adopted in this work for the kinetic analysis of the thermogravimetric curves of these materials. This method is directly based on Eq. (1) whose logarithm is

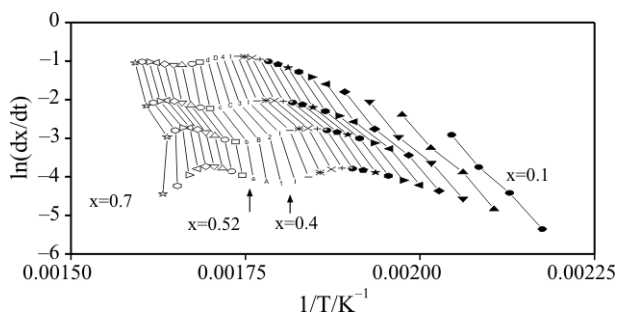
$$\ln\left(\frac{dx}{dt}\right) = \ln[Af(x)] - \frac{E}{RT} \quad (2)$$

Plotting  $\ln(dx/dt)$  vs.  $1/T$  at a given conversion yield a straight line of slope  $-E/R$ .

Isoconversional Friedman plots obtained for olive residue are shown in Fig. 5, where two regions can be clearly identified. It is assumed that the first process ( $0.08 < x < 0.4$ ) corresponds to the hemicellulose degradation, while the second one ( $0.52 < x < 0.72$ ) corresponds to the cellulose degradation. As the lignin degradation process is observed for a wide range of  $x$ , it is not considered in the  $E_a$  calculation as well as those values in the transition region ( $0.4 < x < 0.52$ ). The average  $E_a$  calculated in such way for the first region was  $165 \text{ kJ mol}^{-1}$ , while  $E_a$  for the second region was  $219 \text{ kJ mol}^{-1}$  (Table 4). These results seem to confirm the existence of two different processes in the olive residue thermal degradation. Garcia Perez *et al.* analysed the thermal degradation of sugarcane bagasse, a lignocellulosic derivative [11]. The global pyrolysis of sugarcane bagasse was assumed to be the sum of the contribution of each component (hemicellulose, cellulose and lignin), and they used an algorithm to predict the kinetic parameters as the best fitting to the proposed equation.  $E_a$  values found by them were  $105$  and  $235 \text{ kJ mol}^{-1}$  for hemicellulose and cellulose respectively.

**Table 4** The activation energy for pyrolysis of olive residue, PVC and their mixture

Sample	Activation energy/ $\text{kJ mol}^{-1}$	
	First step	Second step
Olive residue	165	219
PVC	116	235
Olive residue/PVC	137	231



**Fig. 5** Friedman plots for olive residue thermal degradation

A similar study was carried out for the PVC. Figure 6 shows the isoconversional Friedman plots for PVC. From the Fig. 6, two regions were clearly identified: the first process ( $0.05 < x < 0.6$ ) corresponding to the dehydrochlorination of PVC had an  $E_a$  of  $116 \text{ kJ mol}^{-1}$ , while for the second ( $0.7 < x < 0.9$ ) corresponding to the decomposition of remaining PVC, an average  $E_a$  of

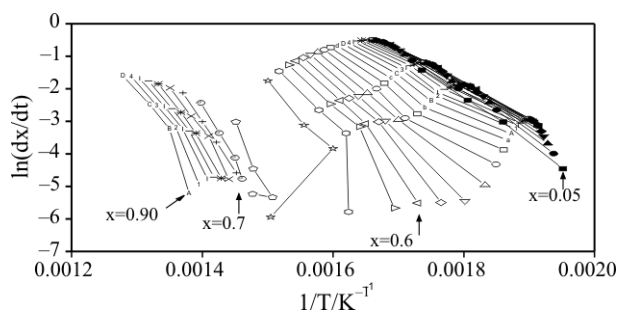


Fig. 6 Friedman plots for PVC thermal degradation

235  $\text{kJ mol}^{-1}$ , was found (Table 4). Most of the kinetic parameters reported in the literature were evaluated considering two main stages in the temperature range 200–550°C during PVC thermal decomposition. Wu *et al.* [16] applied the Friedman method in this temperature range and reported an  $E_a$  value of 164–190  $\text{kJ mol}^{-1}$  in the temperature range 200–327°C, and an  $E_a$  of 218–267  $\text{kJ mol}^{-1}$  in the range 327–527°C. Marcilla and Beltran [15], applying numeric integration, reported an  $E_a$  value of 137–147  $\text{kJ mol}^{-1}$  in the range 200–327°C, and an  $E_a$  of 239  $\text{kJ mol}^{-1}$  in the range 327–550°C. Miranda *et al.* [14] studied the thermal degradation of PVC under vacuum. The degradation activation energy was reported to be 153–200  $\text{kJ mol}^{-1}$  in the range 200–375°C and 243  $\text{kJ mol}^{-1}$  in the range 375–520°C. Bockhorn *et al.* [35] found an activation energy of 140  $\text{kJ mol}^{-1}$  for the first step degradation of PVC (dehydrochlorination), and has been reported an activation energy of 260 for the second step of degradation.

Friedman method was also applied to the study of thermal degradation of the olive residue/PVC mixture. The isoconversional Friedman plots are shown in Fig. 7. It is possible to take two major regions corresponding to both degradation processes. The first stage, obtained in the temperature range (420–685 K), is attributed to the decomposition of hemicelluloses, cellulose and dehydrochlorination of PVC. The second stage occurs between 631 and 840 K, which corresponds to the decomposition of remaining PVC and

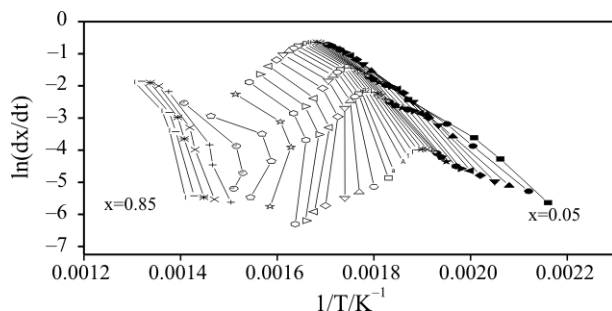


Fig. 7 Friedman plots for olive residue/PVC thermal degradation

lignin from olive residue in the mixture. The activation energy found for the first stage is calculated to be 137  $\text{kJ/mol}$ . The activation energy calculated for the second stage is 231  $\text{kJ mol}^{-1}$  (Table 4). When comparing these results with those of the pure materials, it is easy to note that the presence of olive residue does not significantly change the apparent activation energy of the second step of thermal decomposition of PVC (with- in the error of the method), but the  $E$  value for first step mixture degradation was higher and lower than for the PVC and olive residue pure, respectively. The dehydrochlorination of PVC increases the reactivity of olive residue. However, the interactions at lower temperatures have no significant impact on the degradation of remaining PVC and lignin from olive residue at higher temperatures.

## Conclusions

The TG/DTG curves show clearly two major steps. The first step, obtained in the temperature range (420–685 K), is attributed to the decomposition of hemicelluloses, cellulose and dehydrochlorination of PVC. The second step occurs between 631 and 840 K, which corresponds to the decomposition of remaining PVC and lignin from olive residue.

Comparing the TG/DTG curves, discrepancies between experimental and calculated curves are observed: PVC in a mixture degrades at higher temperatures than pure PVC, while the olive residue in a mixture degrades at the lower temperatures than pure olive residue. These experimental results indicate a significant synergistic effect during co-pyrolysis of olive residue with PVC.

The degradation of olive residue/PVC mixture was modelled with two main reactions describing the degradation of hemicelluloses, cellulose, dehydrochlorination of PVC and degradation of remaining PVC and lignin from olive residue with activation energies of 137 and 231  $\text{kJ mol}^{-1}$ . When comparing these results with those of the pure materials, it is easy to note that the presence of olive residue does not significantly change the apparent activation energy of the second step of thermal decomposition of PVC (within the error of the method), but the  $E$  value for first step mixture degradation was higher and lower than for the PVC and olive residue pure, respectively. Consequently, co-pyrolysis in mixture of olive residue and PVC should be considered as an economically favourable alternative for the pyrolysis treatment of solid wastes because lower energy will be required. It seems that the co-pyrolysis process could have potential for the environmentally friendly transformation of lignocellulosic and plastic materials.

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