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ADVANCES & PROSPECTS IN THE FIELD OF WASTE MANAGEMENT

Tunisian tomato waste pyrolysis: thermogravimetry analysis and kinetic study

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Abstract

This paper aims to set up viable units of thermal processing of numerous agricultural wastes in a sustainable development and eco-friendly approach that could create new economic profitable circuits in an increasingly competitive context. One of the most problematic food wastes are tomato processing by-products; concentrating and canning industrial activities generate important amounts of them, particularly in the Tunisian context. As no reference was found in literature dealing with these last residues, this work intended to explore their potential as biomass fuels. Pyrolysis is then applied in thermogravimetric conditions for different heating rates (5, 10, 20, and 30 °C/min) in order to recover energy on one hand and to extract the corresponding kinetic parameters for an accurate design of reactors on the other hand. Main results include suitability of the tomato residues to a thermal valorization thanks to high contents of volatiles and fixed carbon and low ash percentage as well as an interesting heating value comparable to lignocellulosic biomass. Mass loss profiles indicate consecutive and overlapping stages of drying, active pyrolysis, and passive pyrolysis. The experimental profiles of conversion rate were well fitted by the three isoconversional methods; the best fitting is recorded by the Flynn-Wall-Ozawa associated with a first-order model for the intermediate pyrolysis and with a contracted sphere ($n = 1/3$) for the slowest studied pyrolysis.

Keywords Tomato waste · Kinetics · Thermogravimetric analysis · Pyrolysis

Introduction

Tomato (*Solanum lycopersicum* L.) is a term that designates both the herbaceous plant and the fleshy fruit. The worldwide consumption of tomatoes is up to 100 million tons. These fruits might be found in almost all continents, with a leading rank of China. Tunisia is a producing and exporting country of tomatoes. Especially, Tunisia is the first consumer country in concentrated canned forms, generating consequently around 35,000 tons annually of tomato pulps, seeds, skins, etc. (Kraiem et al. 2016). Worldwide, tomato processing by-products are over than to 1 million tons. Unfortunately, these residues are not sufficiently valorized, the land filling being almost the only and scarce pathway of recovery, although it was declared not viable (Khiari et al. 2019). Even more serious, seasonal and centralized discharges of tomato wastes from agri-food industries have harmful effects on the environment especially because of the chemical products used during the growth. These same chemical products limit the usage of tomato wastes in pharmaceutical and cosmetic fields except in case of biological and organic farming of tomatoes. First for better management and then to respond to energy demand, thermochemical valorization could be a possible solution. Yet, very few academic works addressed this issue and the only industrial-scale manifestation of thermal recovery of this ignored residue is some combustors, the operating of which is more or less controlled. Moreover, and like many other biomasses, combustion of tomato residues still poses the problematic of minerals (Khiari and Jeguirim 2018). However, this particular issue can be avoided with pyrolysis and even better can become an interesting asset to get valuable nutrients for soils. Pyrolysis could take land over combustion, due also to

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the chemical and physical properties of the tomato processing by-products on one hand and to the multiple forms of recovered energy by the degradation in inert atmosphere on the other hand (Kordoghli et al. 2017a).

Despite these attractive features and as far as we know, only two Spanish papers have dealt with the pyrolysis of tomato residues in thermogravimetric conditions (Font et al. 2009; Mangut et al. 2006). Some more works could be found concerning this biomass characterization. More precisely, the interesting thermochemical properties of the tomato residues include high volatile matters, high levels of carbon, hydrogen, and oxygen and low mineral content. Calculations of ratios such (H/C) and (O/C) obtained from previous works indicated also the suitability of tomato wastes to thermal degradation by pyrolysis. These ratios ranged from 12.9 to 14.9% and from 37 to 78.6% respectively. In reported literature, more arguments could be in favor of tomato wastes by pyrolysis: low contents of mineral salts such as N, K, Cl, and Ca; small quantities of metals such as Fe and Mn; and low percentages of sulfur (S), especially in comparison with conventional fossil fuels. These aspects are interesting from an environmental and technical point of view.

Besides, unsaturated fatty acids in tomato residues (mainly in seeds) are high with more than 80%, in which C16 and C18 make up over 96% of total fatty acids (Rossini et al. 2013). Such contents are close to those of other agro-biomasses that have proved being excellent fuels such as in olive seeds (Souilem et al. 2017) or in grape seeds (Crews et al. 2006). The high heating values reported (ranging between 19.5 and 22.4 MJ/kg) are comparable to sawdust (Jeguirim et al. 2014; Kraiem et al. 2016; Mangut et al. 2006; Yargıç et al. 2015).

As for pyrolysis, it is well known that the process is carried out for temperatures above 200 °C. The by-products (volatiles, tar and char) composition is largely influenced by the operating conditions and by again the physical and chemical characteristics of the samples. For most biomasses, thermogravimetric and derivative thermogravimetric (TG/DTG) profiles are made of three more or less pronounced zones corresponding to drying, devolatilization, and char formation.

In the two mentioned papers dealing with the pyrolysis of the tomato waste, the degradation occurred in successive and/or overlapping steps that thermogravimetric analysis (TGA) could characterize.

For example and according to Font et al., the low inorganic material content in the tomato plant sample is the reason why the peak corresponding to water vaporization is small for the three tested heating rates (5, 10, 20 °C/min). The consecutive wide band in the DTG curve might be attributed to the overlapping of the different fraction decomposition. Molecules such as CO, CO_2, CH_4, and CH_3^+ ion were detected with thermogravimetry coupled with mass spectroscopy (TG/MS). Contents of hemicelluloses (28.8%) within tomatoes are comparable to sawdust (27%) (Jeguirim et al. 2017); its degradation within tomato plants occurs in almost the same range, i.e., between 200 and 325 °C. Cellulose and lignin continue cracking until 700 °C where char production starts and continues until 1100 °C (Font et al. 2009).

As for Mangut et al., TGA comparison was made between samples made of sole tomato peels, sole tomato seeds, and mixed seed and peels from tomato residues. The thermochemical conversion of these materials combined numerous processes based on the cracking of biomolecules under the effect of heat. For a better monitoring, the mixture of tomato skins and seeds was the residue materials retained for their next kinetic study (Mangut et al. 2006).

In fact, the goal of the two papers was to bring out the pyrolysis kinetics with the ultimate objective of improving the efficiency of commercial pyrolysers.

In their kinetic investigations, Font et al. have considered five solid fractions in their model and calculated the kinetic parameters by integration of the differential equations by the Euler method. First-order models were used during the kinetic parameters extraction. Main results brought out that the initial small fraction (7–8.5%), with small activation energies (Ea), ranging between 64 and 67 kJ/mol, correspond to the humidity of the sample. The second fraction decomposes at 200–323 °C. Activation energies being between 117 and 122 kJ/mol, the authors thought of it to be essentially hemicelluloses, whereas the following range 150–250 kJ/mol is attributed to cellulose. For the authors, the fraction that starts decomposing at 525 °C with activation energy around 64–80 kJ/mol corresponded to lignin; even they admitted that is only the fraction that decomposes at high temperature. Since lignin normally decomposes in a wide interval of temperatures, some of it was surely included in the previous fractions (Font et al. 2009). Mangut et al. found activation energies close to afore obtained values: 130.9–257.5 kJ/mol for cellulose, around 115 kJ/mol for hemicelluloses, 56.2–208.7 kJ/mol for lignin (Mangut et al. 2006).

It is important here to precise that the residues used in these works are either issued from a tomato juice-making industry or from a farm raw activity. No references have been found in literature concerning the pyrolysis of wastes issued from tomato concentrating and canning factories, which is the main industrial activity of tomato processing in the Tunisian context, so the contribution of this paper can be important. Indeed, this investigation is part of a sustainable development approach, the aim being to develop a thermochemical energy recovery pathway while reducing the increasing tomato waste quantities issued from Tunisian tomato processing industries. The methodology is based on experimental campaigns in a thermobalance in order to identify the optimum operating conditions to get the best calorific pyrolytic by-products on one hand and to extract the kinetic parameters for a most accurate design of a pyrolysis reactor on the other hand.

Materials and methods

Fresh tomato residues were provided by a Tunisian local tomato concentrating and canning industry. Water content was reduced from 60 to 10% before carrying out the characterization campaign and prior to the TGA runs.

Characterization study

Tomato samples were prepared according to UNI EN 14780:2011 standard and characterized through the determination of their moisture content (EN 14774:2009), their ash content (EN 14775:2010), and their low heating values (EN 14918:2010).

Elemental analysis was performed using a CHONS analyzer (ThermoFisher Scientific, Villebon, France) according to the UNI EN 15104:2011 standard.

TGA study

Tomato processing by-products mass loss during pyrolysis can be followed by thermogravimetric analysis (TGA). In this study, runs were conducted with TGA/DSC3 + (Mettler-Toledo, Columbus, OH, USA) and repeated at least three times. The inert gas used was nitrogen with a 12 NL/h flowing rate. Four heating rates were applied (5, 10, 20, and 30 °C/min). Initial sample weights were ranging from 18.9 to 23.6 mg and final temperature was fixed at 950 °C.

Kinetic models

Various physical and chemical phenomena occur during the thermal degradation of any lignocellulosic material: crystallographic structure destruction, chemical bonds breaking, solid product recrystallization, gases desorption, etc. may take turn or take place simultaneously (Khiari et al. 2007). The reaction rate equation is then formalized by considering the geometry and the global kinetics of progression of the reaction interface (Khiari et al. 2008). The fundamental rate equation usually applied in kinetic studies is

$$\frac{\mathrm{dX}}{\mathrm{dt}} = k(\mathrm{T})\,\mathrm{f}(X) \tag{1}$$

where X is the conversion rate (%), k is the rate constant (s^{-1}), and $f(X)$ is the reaction model that describes the reaction mechanism.

The rate constant is calculated given by the Arrhenius equation:

$$\mathrm{k} = \mathrm{A}\exp\left(\frac{-\mathrm{Ea}}{\mathrm{RT}}\right) \tag{2}$$

in which Ea is the activation energy (kJ/mol), R is the universal gas constant (8.314 J/K mol), A is the pre-exponential factor (s^{-1}), and T is the absolute temperature (K).

The conversion rate X is given by

$$X = \frac{\mathrm{W}_0 - \mathrm{W}_\mathrm{t}}{\mathrm{W}_0 - \mathrm{W}_\mathrm{f}} \tag{3}$$

where W_t, W_0, and W_f are sample weights at t, initial and final time.

As for the function $f(X)$, several kinetic models have been proposed, according to the mechanism described by the decomposition reaction.

In non-isothermal conditions, kinetics can be determined by plotting the conversion rate X vs. time t or time derivative conversion rate versus vs. time t while keeping temperature constant. However, in non-isothermal conditions, kinetic parameters are calculated thanks to the plot of X or dX/dt vs. the temperature T.

This way, if the heating rate designed here after by (β) is constant ($T = \beta \times t + T_0$ where T_0 is the initial temperature), one can write

Table 1 Some kinetic models $f(X)$ and their integral forms $g(X)$

Model	$f(X)$	$g(x)$
First order	$1 - X$	$-\ln(1-X)$
Pseudo *n*th order	$(1-X)^{\mathrm{n}}$	$1/(n-1)\,[(1-X)^{(1-\mathrm{n})} - 1]$
Contracted cylinder	$2(1-X)^{1/2}$	$1-(1-X)^{1/2}$
Contracted Sphere	$3(1-X)^{2/3}$	$1-(1-X)^{1/3}$
Energy law	$\nu X^{(\nu-1)/\nu}$	$X^{1/\nu}$
Avrami-Erofe’eve	$\mathrm{p}\,(1-\mathrm{X})\,[-\ln(1-X)]^{(\mathrm{p}-1)/\mathrm{p}}$	$[-\ln(1-X)]^{1/\mathrm{p}}$
Extended Prout-Tompkins	$(1-X)^{\mathrm{n}} X^{\mathrm{m}}$	No analytical solution
1D diffusion	$½X - 1$	X^2
2D diffusion	$[-\ln(1-X)]^{-1}$	$(1-X)\ln(1-X) + X$
3D diffusion (Jander)	$3/2(1-X)^{2/3}[1-(1-X)^{1/3}]^{-1}$	$[1-(1-X)^{1/3}]^2$
3D diffusion (G-B)	$3/2[(1-X)^{-1/3} - 1]$	$1 - 2X/3 - (1-X)^{2/3}$

Table 2 Isoconversional kinetic models

Method	Expression	Plots
Friedman	$\mathrm{Ln}\frac{dX}{dt}=\mathrm{Ln}\left(\beta\frac{dX}{dT}\right)=\mathrm{Ln}[\mathrm{A}f(X)]-\frac{\mathrm{Ea}}{RT}$	$\mathrm{Ln}\left(\beta\frac{dX}{dT}\right)$ **vs.** $\frac{1}{T}$
FWO	$\mathrm{Ln}\beta=\mathrm{Ln}\frac{\mathrm{AEa}}{g(X)R}-2.315-\left(\frac{1.0516\mathrm{Ea}}{RT}\right)$	$\mathrm{Ln}\beta$ **vs.** $\frac{1}{T}$
KAS	$\mathrm{Ln}\frac{\beta}{T^2}=\mathrm{Ln}\frac{AR}{\mathrm{Ea}g(X)}-\frac{\mathrm{Ea}}{RT}$	$\mathrm{Ln}\frac{\beta}{T^2}$ **vs.** $\frac{1}{T}$

$$\mathrm{Ln}\frac{dX}{f(X)}=\frac{\mathrm{A}}{\beta}\exp\left(\frac{-\mathrm{Ea}}{RT}\right)dT \tag{4}$$

Some of these models as well as their integral forms are displayed in Table 1 where $g(X)$ is the integral function of $\mathrm{Ln}\frac{dX}{f(X)}$. These functions are classified into several categories, depending on the geometric progression of the reaction interface, the nucleation and growth process or the diffusion phenomenon.

$g(X)$ is the integral function of $\mathrm{Ln}\frac{dX}{f(X).}$

In order to extract reliable kinetic data from TG experiments, differential isoconversional methods, adjustment models, and pseudo-component methods are often used in biomass kinetic pyrolysis studies. The variants of the first category of models (isoconversional) are Friedman (1964), Flynn-Wall-Ozawa (FWO) (Flynn and Wall 1966), and Kissinger-Akahira-Sunose (KAS) (Kissinger 1956). The corresponding equations are given in Table 2.

Results and discussions

Characterization results

The proximate and ultimate analyses of tomato wastes are given in Table 3. These result values are comparable to values met in literature (Table 3) and show that tomato waste may be an interesting source of energy. Indeed, as water content is an important economic and energy factor especially during the drying operation, its relative low value of around 8% on wet basis (wb) is an encouraging first parameter. The ratio of volatile matter and fixed carbon (VM/CF) (9.5) being more than 4 and volatile matters being around 76%, tomato residues might be considered as very reactive (Tillman 2000). The energy content of 19.5 MJ/kg is interesting even if it is lower than high heating values (HHV) of conventional fuels (Almeida et al. 2014). The heating value calculation is crucial as low values associated with the low mass density (50 kg/m^3) means that greater biomass volumes are needed at the inlet of the reactors. Compaction or densification as well as mixing with other (bio)fuels might be considered as possible ways to increase energy density and reduce handling problems. This conclusion was also reached by other researchers who then used pellets of tomato residues in their works (González et al. 2004; Ruiz Celma et al. 2012).

TGA results

TG and DTG results are shown in Fig. 1 and Table 4. One can note the same profile for the four heating rates. The only difference lies in the decay rate of the residual mass. For 5 and 10 °C/min, the masses decrease in a progressive and slow manner. On the other hand, at heating rates of 20 and

Table 3 Physical and chemical properties of tomato wastes

	Kraiem et al. (2016)	Mangut et al. (2006)	Yargıç et al. (2015)	This work
Moisture (%, wb)	10	4.22	7.18	8
Ash (%, db)	11	4.58	4.49	8
CF (%, db)	–	12.51	10.98	8
Volatiles (% db)	–	78.68	77.35	76
ρ (kg.m^{-3})	52.2	–	–	50
HHV (MJ kg^{-1})	19.5	22.4	20.47	19.5
Energy density (GJ m^{-3})	10.2	–	–	9.75
C (%, db)	54.2	49.52	49.69	59.4
H (%, db)	7	6.74	7.43	7.6
N (%, db)	1.5	2.41	3.78	1.6
O (%, db)	20.2	–	39.1	23.4
S (%, db)		0.038	–	0.35

wb wet basis, *db* dry basis

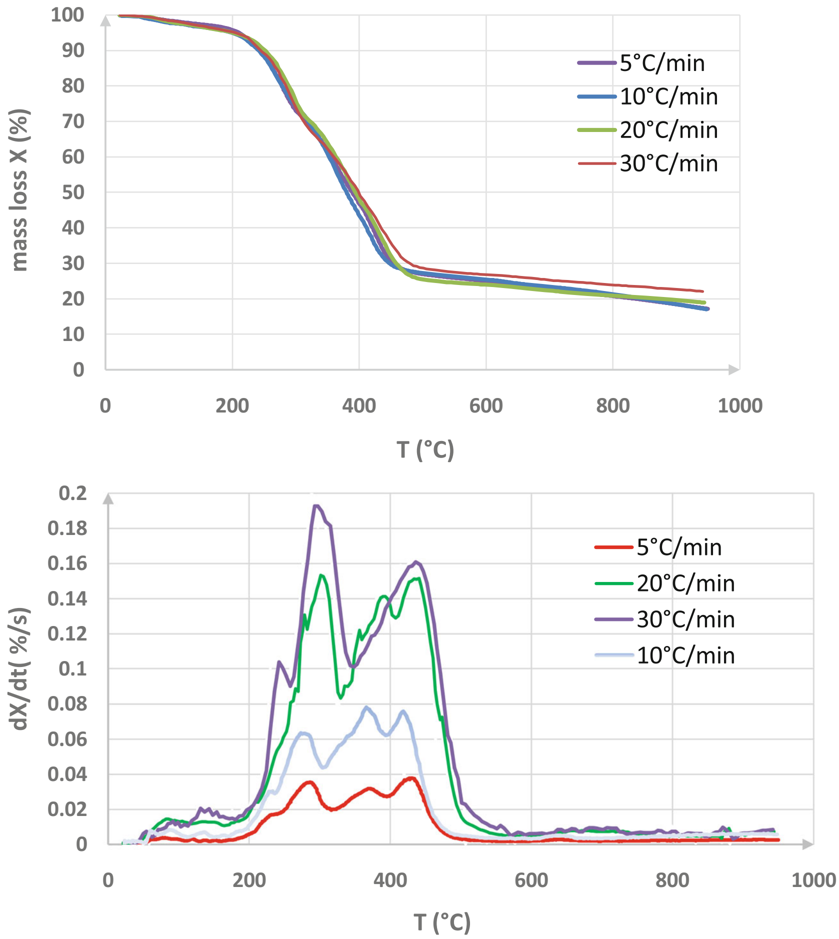


Fig. 1 TG and DTG profiles of tomato waste pyrolysis for different heating rates

30 °C/min, the mass falls down suddenly within a very short time. This can be explained by the fact that slow pyrolysis promotes cracking of most weak bonds and less stable molecules that are easier to degrade whereas the more stable molecules are degraded during the intermediate pyrolysis (Encinar et al. 2008; Kordoghli et al. 2017b).

Three main zones are observed: the dehydration phase, which corresponds to a slight hyperpolarization is explained by the elimination of water molecules. The mass loss during the drying stage continues up to 200 °C. The consecutive devolatilization phase is characterized by a significant weight loss. It begins at around 200 °C, which is often reported for

Table 4 TG of tomato wastes pyrolysis for different heating rates

Heating rate (°C/min)			5	10	20	30
Drying zone		T (°C)	100–198	100–169	100–181	100–199
		X (%)	0.1–4.9	0.1–5.1	0.1–5.14	0.1–5.1
Active pyrolysis	Zone 1	T (°C)	22–325	255–325	275–340	200–250
		X (%)	37–51	15.5–37.4	16.5–41.3	4.9–10.9
		$T_{peak\ 1}$ (°C)	272	267	296	230
		R_1 ($\%{\cdot}s^{-1}$)	0.034	0.062	0.15	0.10
	Zone 2	T (°C)	325–400	325–410	340–425	250–330
		X (%)	54.4–59.4	37.4–71.4	41.3–72.9	10.9–33.9
		$T_{peak\ 2}$ (°C)	359	358	380	288
		R_2 ($\%{\cdot}s^{-1}$)	0.031	0.076	0.14	0.20
	Zone 3	T (°C)	350–440	385–670	425–700	330–490
		X (%)	46.4–41.3	62.5–91.7	72.9–95.8	33.9–70.9
		$T_{peak\ 3}$ (°C)	421	409	423	426
		R_3 ($\%{\cdot}s^{-1}$)	0.037	0.073	0.15	0.16
Passive pyrolysis		T (°C)	650–950	670–950	700–950	490–950
		Char (%)	17.1	17.0	18.9	21.9

Fig. 2 KAS, FWO, and Friedman kinetic models

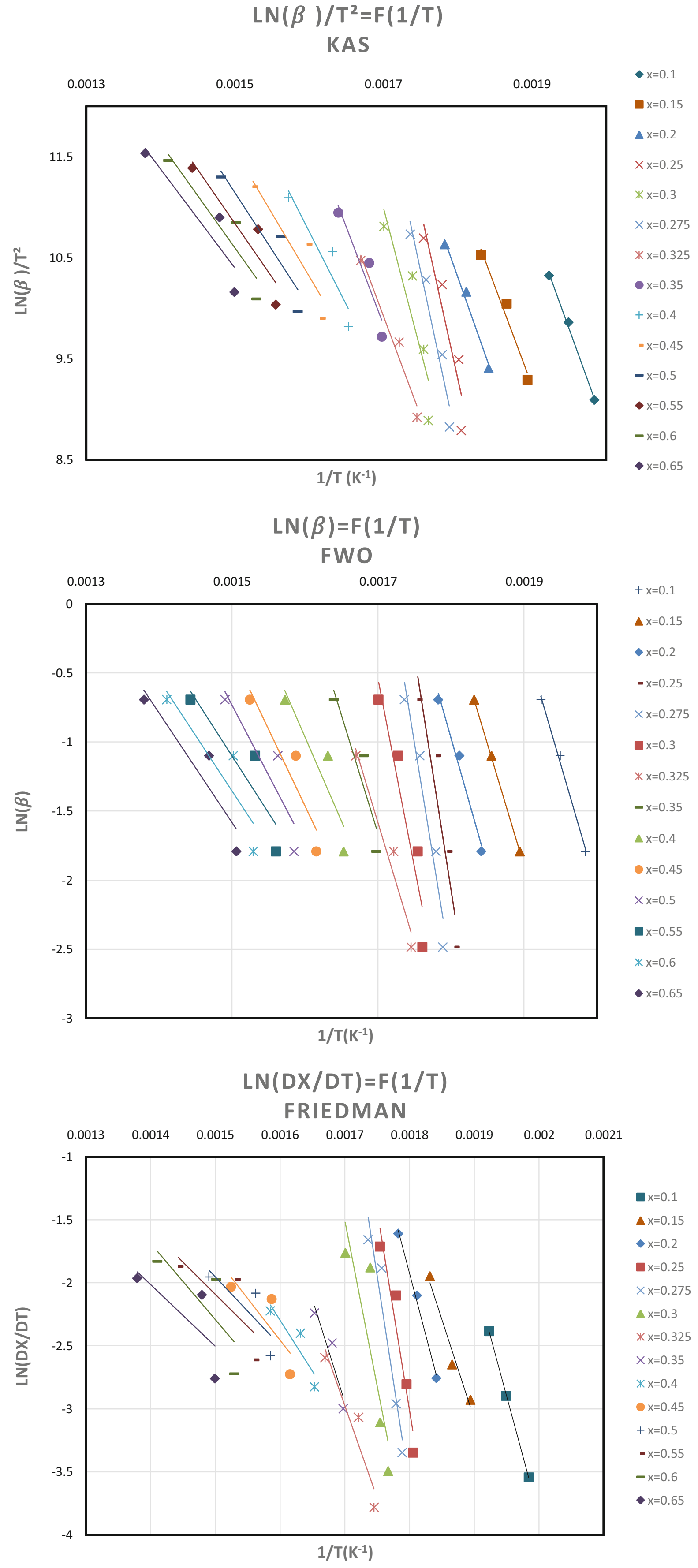


Table 5 Activation energies according to KAS, FWO, and Friedman models

	KAS		FWO		Friedman	
X (%)	Ea (kJ/mol)	R^2	Ea (kJ/mol)	R^2	Ea (kJ/mol)	R^2
10	168.7	0.996	143.075	0.995	157.874	0.999
15	162.8	0.967	139.4	0.999	132.0	0.965
20	172.9	0.984	147.2	0.980	161.6	0.994
25	277.7	0.878	268.1	0.905	263.0	0.923
27.5	287.5	0.938	256.1	0.938	278.5	0.930
30	235.1	0.817	214.9	0.898	218.4	0.749
32.5	163.9	0.966	138.5	0.957	121.6	0.898
35	160.8	0.886	135. 5	0.859	133.9	0.882
40	119.9	0.879	96.5	0.839	66.8	0.816
45	103.2	0.842	87.9	0.871	54.7	0.670
50	94.5	0.859	80.2	0.813	40.1	0.662
55	88.4	0.861	65.2	0.821	42.5	0.601
60	85.9	0.876	63.7	0.810	46.2	0.529
65	81.5	0.840	62.6	0.862	45.3	0.662
Average	135.64		157.35	125.91		

agricultural residues (Jeguirim et al. 2014) and shows three distinctive, large, irregular, and exothermic peaks attributed to the degradation of hemicelluloses, cellulose, and oils, respectively (Ruiz Celma et al. 2012). Char is yielded from 500 to 950 °C, inducing a slight decrease that tends to cancel out. The final percentage of the char at the end of the process ranges between 17.0 (for 10 °C/min) and 21.9% (for 30 °C/min).

In addition, it is clear that the heating rate affects the yields of solid, volatile, and liquid pyrolysis products. In general, increasing the temperature and/or the heating rate decreases the char yield and promotes the formation of incondensable volatiles. At high temperature, the high yield of non-condensable gases is mainly attributed to secondary reactions of thermal cracking or pyrolysis vapor reactions in the gas phase (Yan et al. 2014).

For the Spanish tomato residues, during 5 °C/min pyrolysis, all of these stages ended slightly earlier in comparison with the present work: drying (100–150 °C), hemicelluloses (225–325 °C), cellulose (325–375 °C), and lignin (417–607 °C) (Encinar et al. 2008). As for the temperature peaks, the highest ones are recorded during the third phase of the active pyrolysis stage (421, 409, 423, and 426 °C for 5, 10, 20, and 30 °C/min respectively). The corresponding reactivities increase with heating rates; conversion rates are also at their maximum levels in this zone. Values of the same order of magnitude were obtained for other agricultural wastes such as grape marcs (Khiari and Jeguirim 2018) and olive pomace (Chouchene et al. 2010).

Kinetic results

The kinetic study of the thermal decomposition of tomato processing by-products aims to calculate the kinetic parameters in order to get the reaction rates. Linear diagrams of KAS, FWO, and Friedman are shown in Fig. 2. Since the initial mass loss is attributed to moisture loss, the first conversion rate selected to determine the kinetic parameters is 10%, while the last point is taken at 65% for KAS and FWO and at 40% for Friedman. Above this value, no good coefficient is obtained, which can be explained by the complexity of char production and rearrangement.

The calculated values of activation energies E_a are then presented in Table 5, their evolution, while the conversion is in progress is seen in Fig. 3. The activation energy calculated at the different conversion rates is attributed to the

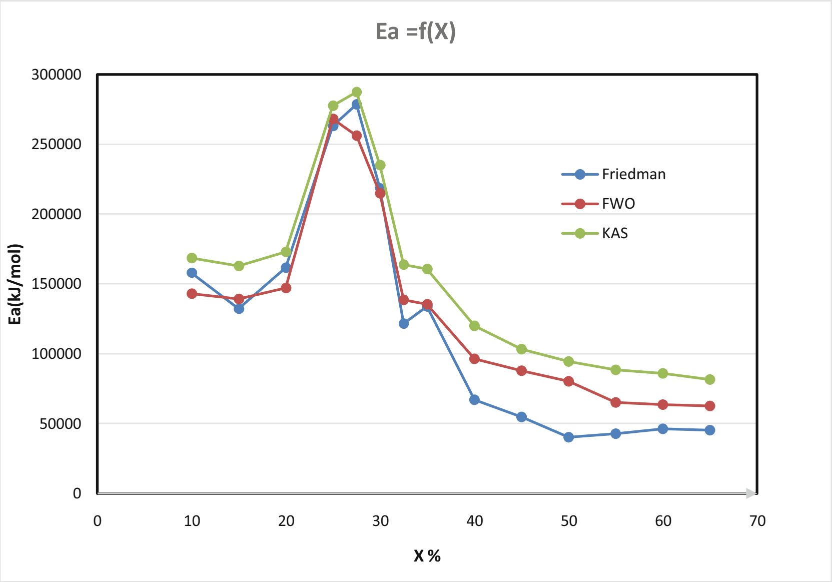


Fig. 3 Activation energies versus conversion rate according to KAS, FWO, and Friedman models

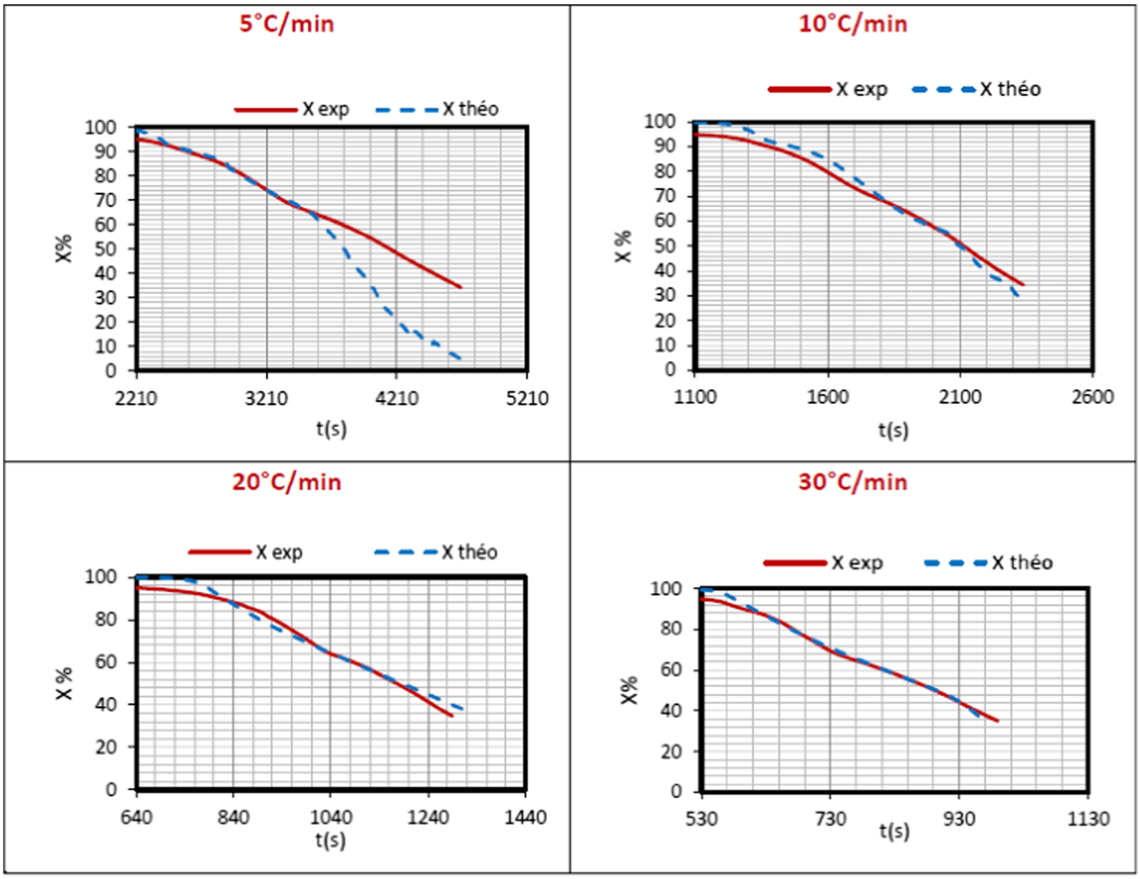


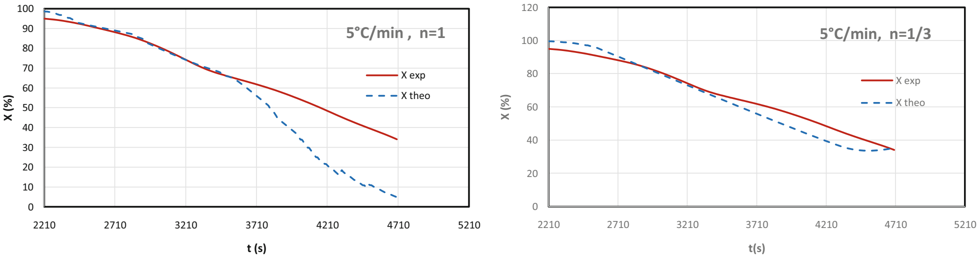
Fig. 4 Experimental and calculated conversion rates of tomato waste pyrolysis for different heating rates

decomposition of macro-components within the tomato residue. KAS and Friedman give similar average values but lower than that calculated by FWO (respectively 135.64, 125.91, and 157.35 kJ/mol). At low conversion levels (10–20%), activation energies between 132 and 172 kJ/mol can be related to hemicellulose degradation. Activation energies increase to 268.1 and 263.1 kJ/mol for FWO and Friedman and to 277.7 kJ/mol for KAS model at higher conversion rates, which can be attributed to cellulose cracking.

Table 5 shows that the activation energy increases as the conversion rate increases to X = 30%. At higher temperatures, the activation energies decrease. The degradation of the lipid content mainly in the tomato seeds is characterized by an activation energy of about 138.5 and 121.6 kJ /mol respectively for FWO and Friedman and 163.9 kJ/mol for KAS model at 32.5%. Beyond this rate, the Ea decreases again. This decrease is also explained by the continuous degradation of cellulose and lignin as well as the rearrangement of the char through secondary and more complex reactions, which some authors have assumed (Antal et al. 1980; Chouchene et al. 2010).

In addition, the activation energy distribution during the Tunisian tomato wastes differs from the Spanish's, the energies of which are 130.9–257.5 kJ/mol for cellulose, 115 kJ/mol for hemicelluloses, and 169.4–173.2 kJ/mol for oil, while lignin decomposition takes place over the entire temperature range with activation energies ranging from 56.2 to 208.7 kJ/mol (Mangut et al. 2006). This discrepancy may be due to the difference in texture and variety of the samples studied as well as the climatic conditions of planting. Moreover, the industries

Fig. 5 Experimental and numerical conversion rate calculated by $n = 1$ and $n = 1/3$ kinetic nth model for 5 °C/min pyrolysis



from which are issued the materials are substantially different: tomato juice units would leave behind more peels and seeds than concentrating tomato units. Finally and most likely, the integration of their kinetic equations was carried out analytically.

One can also add that Fig. 3 confirms that the process is composed of multi-step complex reactions. In addition, one can draw attention to the perfect concordance between the three models during the active pyrolysis phase with correlation coefficients R^2 higher than 0.90 in all cases and between KAS and FWO models during the passive pyrolysis (with $R^2 > 0.81$). The difference observed with the Friedman model during the passive pyrolysis is less than 10%, but the corresponding values of R^2 are the farthest to unity (around 0.60).

In order to validate the above results, fitting between experimental and calculated values is assessed. As explained earlier, this is related to the choosing of $f(X)$. As most of agri-food pyrolysis kinetic models are first order, this last was applied for the four heating rates (Fig. 4).

After having tried the three isoconvertional methods, FWO method was the one that represents the closest values to the experimental ones. For the intermediate pyrolysis (10, 20, and 30 °C/min), experimental and numerical profiles coincide, with a slight difference of nearly 4% during the beginning of the drying phase and a small decay of 5% at the end of the devolatilization stage.

However, for the slow pyrolysis (5 °C/min), a good match is observed until 3500 s. Beyond, conversion rates are undervalued by the first-order model. Therefore, n^{th} order models are tested (Fig. 5). For $n = 1/3$, the calculated and experimental values are closer during the passive pyrolysis than with $n = 1$. But, drying and active pyrolysis are not well fitted. One can conclude that moisture departure as well as hemicelluloses, cellulose, and oil cracking reactions are better described by a first-order model whereas lignin decomposition is more faithfully simulated by a contracted sphere model with $n = 1/3$.

Conclusions

The implementation of the pyrolysis processes depends largely on a reliable design of large-scale units where the pyrolysis reactor plays an important role. This requires among other aspects the determination of the pyrolysis kinetics which, with additional experimentation on a pilot scale, is useful for the design of industrial reactors.

However, as far as we know, tomato concentrating and canning by-products have never been investigated with the view to transform them into added value. In this paper and for ultimate purposes of energy recovery on one hand and volume reduction on the other hand, these residues underwent degradation in an inert atmosphere of N_2 at different heating rates, ranging from slow (5 °C/min) to intermediate (30 °C/min) pyrolysis. Suitability of the tomato wastes as a potential bioenergy source and the applicability of pyrolysis as a profitable way of processing were confirmed. Besides, different calculations could help extracting the best fitting kinetic parameters with perfect match for all the process stages, except at the end of the lignin decomposition phase, where the gap between simulated and experimental values was about 4%. This adequacy can help in the efforts of biomass-food pyrolysis optimization and ultimately in the design of dedicated reactors as well as of co-pyrolysis units that might be run with other lignocellulosic agro-industrial residues. Such sustainable development and eco-friendly approach could then reduce costs and create new economic profitable circuits in an increasingly worldwide competitive context.

In fact and based upon the numerical date given in this work, the possible energy recovery from tomato wastes in the Tunisian context may contribute by 16.3 kTOE (tons oil equivalent) which represents 0.6% of the deficit in the energy balance of Tunisia. However, it is important here to point out that these calculations are rough and very approximate mainly because they do not take into account the logistic costs of transport and collection. Indeed, these wastes are available in a lot of small quantities spread out over a large area, throughout the country, making the aggregation challenging.

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