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Pyrolysis of Grape Marc from Tunisian Wine Industry: Feedstock Characterization, Thermal Degradation and Kinetic Analysis

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Abstract: Despite the huge amounts of grape marc generated in Tunisia from the wine industry, very few efforts have been exerted to manage this harmful waste. Therefore, thermal processes may contribute to an environmental friendly management and also help winemakers to create new economic profitable circuits in an increasingly competitive context. Among the various thermochemical conversion process, pyrolysis is suitable for the recovery of food processing residues, due to their high minerals content and ability to create high added values of the derived products (biochar, bio-oil and syngas). In this context, the aim of this work is to optimize the pyrolysis process in order to benefit from the grape marc potential for achieving highest product yields. Therefore, physico-chemical and energy characteristics of grape marc issued from a Tunisian wine cooperative were determined according to international standards. Thermogravimetric analyzes were also performed to predict the grape marc behavior during degradation under an inert atmosphere. The profile of the mass loss rate shows two decomposition peaks corresponding to the cellulose and lignin decomposition. These peaks are shifted to lower temperatures comparing to several lignocellulosic biomass feedstocks due to high content of minerals that may play a catalytic role in the thermal degradation process. The biochar yield was about 40%, which was never met in literature for agricultural biomass in slow pyrolysis. Such behavior may be attributed to high lignin content in grape marc. Activation energies were calculated using integral Flynn-Wall-Ozawa and Kissinger-Akahira-Sunose methods and differential Friedman method. The obtained values were 226.8, 224.2 and 229.5 kJ/mol, respectively. Such kinetics data are crucial in the design of the pyrolyzer for Tunisian grape marc recovery.

Keywords: grape marc; kinetic models; characterization; pyrolysis

1. Introduction

Grape is one of the most important fruit crops in the world with over 74 million tons produced annually [1]. Pressing grapes give juice, which is mostly for fermentation, and marc, which is also called pomace (solid product) [2], containing skins, seeds and stalks [3]. Although the pressing grape method depends strongly on the type of wine (white or red), Toscano et al. [3] described a general process giving the following proportions of grape products: 73% of juice and 27% of grape marc. The grape marc is distributed as follows: 19.5% of skins, 4.5% of seeds and 3% of stalks [3]. Grape marc may be processed further in distilleries in order to extract alcohol and the generated waste is called the exhausted grape marc residues. Wine cave (fresh grape marc) and alcohol distilleries (exhausted grape marc) produce large amounts of wastes, which are estimated at 7 million tons worldwide per year [4].

Grape marc characteristics depend strongly on the climatic conditions [5]. In general, grape marc is a wet (60% of moisture content) and heterogeneous waste [2]. Fresh grape marc are considered as a non-contaminated material with harmful characteristics, such as low pH and high organic matter (90%), including phytotoxic and antibacterial phenolic substances [6]. The most common methods to recover these residues include production of alcohol, tartar, pharmaceuticals, cosmetics [6], feedstuff [7], yeast [8], extraction of phenolic compounds [9], production of oil [10] or energy [11], decontamination of effluents containing metals, such as copper and nickel [12], composting [13] and direct use as an organic fertilizer [14]. According to the European Council Regulation EC1493/1999 involving the common organization of wine market, fresh grape marc (except stalks) must be transferred to alcohol distilleries [6]. In Spain, several studies showed that exhausted grape marcs have a high content of lignin and tannin and are not easily digested. Therefore, they are not appropriate as nutritional supplements for animals. Besides, their high C/N ratio limits their potential as soil fertilizers [14]. In this way, Italian laws (2010) require wine producers to send their wastes to distilleries [3]. Thus, some recovery methods are no longer permitted. In the same context, composting was also declared to not be economically viable in France and is gradually disappearing. Therefore, 60% of distilleries in France are using grape marc as combustible [4]. In fact, grape marc has interesting physical and thermal properties and energy contents [2,15]. However, a particular attention should be paid to the ash accumulation and pollutants emissions factors during grape marc combustion.

Similar to other Mediterranean countries, Tunisia is committed to finding a solution for environmental and economical disposal of their wastes and to participate further to reduce the global greenhouse effect. The wine industry in Tunisia generates annually about 25,000 tons of grape marc issued from internationally-known varieties, such as Grenache, Syrah, Cinsaut, Muscat of Alexandria, and from 54 aboriginal varieties, such as Razzegui, Tebourbi, Asli, Bazzoul Khaddem, Sakalsi, Garrat, Hamri, Chetoui and Chaouch. The grape plantations and the wine extraction processes are spread almost all over the country, although they are mainly located in the North East [16]. The discharge of the generated grape marc is usually centralized and seasonal in a short period of the year (August–October) [16]. Furthermore, only 10% from the generated grape marc are used as nutritional ferment. A small part is used for compost production or dried and used as fertilizer [5]. The rest is either dumped or used as a traditional combustible in an uncontrolled manner, leading to the release of hazardous pollutants.

Currently, there is no sustainable strategy for the grape marc recovery in Tunisia. Recently, Kraiem et al. [17,18] showed that despite suitable lower heating, high mineral contents and low bulk densities limit their direct use as biofuels in a combustion appliance for the residential heating sector. Authors had then resort to the densification and the blend of grape marc with woody biomass, which has low ash content [17,18]. However, combustion tests showed the high particular matter emissions, which limit the recovery of grape marc in domestic heating [17,18]. Therefore, the pyrolysis process could be a promising issue for the grape marc valorization since their mineral contents may be blocked in the residual char. This pyrolysis process could be interesting for wine, juice or jam-making industries [19,20]. However, as far as we know, a similar survey was never conducted in Tunisia, despite big potential gains. In fact, storage, handling and transport costs may be reduced with nearby, decentralized pretreatment establishments. Moreover, the pyrolytic gases can provide the power required for the endothermic pyrolysis process, ensuring self-sufficient operating system. In addition, the bio-oil and the biochar obtained from the pyrolysis process could be recuperated by winemakers for biofuels or soil amendments applications.

Consequently, the aim of this experimental work is to contribute to the understanding of the Tunisian grape marc behavior within an industrial processed pyrolysis. In particular, characteristics, including proximate and ultimate analyses, are determined. Thermogravimetric analyzes are also performed to predict the behavior of this waste during thermal degradation under different inert types of atmosphere. The obtained data are used for determining kinetic parameters that are subsequently used for determining the optimum pyrolysis process parameters.

2. Materials and Methods

Grape marc used in this study was collected from a wine cooperative located in the north of Tunisia (Bou Argoub, Nabeul). The sample was fresh with 60% (wb) of moisture, which was reduced to 10%. The sample was characterized through moisture content (EN 14774-1), ash content (EN 14775) and Low Heating Value, LHV (EN 14918) determination. Volatile matters and fixed carbon were determined using the Thermogravimetric analysis method [21]. Furthermore, elemental analysis was performed using a CHNOS analyzer (ThermoFisher Scientific, Villebon, France).

Thermogravimetric analyses (TGA) were carried out using a Mettler-Toledo TGA/DSC3+ (Mettler-Toledo, Columbus, OH, USA) thermobalance apparatus and repeated at least three times, with good reproducibility. The experiments were performed under nitrogen with flows of 12 Nl·h^{-1} according to different linear heating programs (5, 10, 20 and 30 °C/min) in the range of 20–950 °C.

3. Kinetic Approach

Many works have focused on the data analysis method for extracting reliable kinetic data from TGA experiments. There are three types of kinetic methods used for the analysis of biomass pyrolysis kinetics: differential, isoconversional, model-fitting and pseudo-components kinetics methods [22–25].

The fundamental rate equation used in all kinetic studies is generally described as:

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

where k is the rate constant and $f(X)$ is the reaction model that describes the reaction mechanism. The conversion rate X is given by Equation (2):

$$X = \frac{W_0 - W_t}{W_0 - W_f},\tag{2}$$

where W_t, W_0, and W_f are time t, initial and final weights of the sample, respectively.

The Arrhenius equation (Equation (3)) expresses the rate constant k:

$$k = Aexp\left(\frac{-Ea}{RT}\right),\tag{3}$$

where 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).

Energy activation is defined as the minimum energy requirement that must be overcome before molecules can get close enough to react and form products. Accordingly, the reactions with a high Ea need a high temperature or a long reaction time.

By combining Equations (1) and (3), we obtain:

$$\frac{dX}{dt} = Aexp\left(\frac{-Ea}{RT}\right)f(X).\tag{4}$$

If the temperature is varied by a constant designed by β, which is the heating rate ($\beta = \frac{dT}{dt}$), the introducing of β in the Equation (4) gives:

$$\frac{dX}{dT} = \frac{A}{\beta}exp\left(\frac{-Ea}{RT}\right)f(X).\tag{5}$$

By taking the logarithms of both sides of Equation (5), the first proposed differential Friedman method (Equation (6)) is obtained [26]:

$$Ln\frac{dX}{dt} = Ln\left(\beta\frac{dX}{dT}\right) = Ln[Af(X)] - \frac{Ea}{RT}.$$ (6)

If we rearrange Equation (6), we can obtain:

$$L\frac{dX}{f(X)} = \frac{A}{\beta}exp\left(\frac{-Ea}{RT}\right)dT.$$ (7)

After integrating Equation (7), it can be obtained:

$$g(X) = \int_0^X \frac{dX}{f(X)} = \frac{A}{\beta}\int_0^T exp\left(\frac{-Ea}{RT}\right)dT$$ (8)

By taking logarithms and using the Doyle approximation, Equation (8) can be rewritten as Equation (9). This equation is known as the Flynn-Wall-Ozawa method (FWO) [27]:

$$Ln\beta = Ln\frac{AEa}{g(X)R} - 2.315 - \left(\frac{1.0516Ea}{RT}\right).$$ (9)

By using the derivation of Equation (3), and applying the logarithmic scale with the temperature data for each conversion rate (X) at different heating rates ($\beta_j = \frac{dT}{dt}$), the Kissinger method (KAS) calculates activation energy by plotting Equation (9) [28]:

$$Ln\frac{\beta}{T^2} = Ln\frac{AR}{Eag(X)} - \frac{Ea}{RT}.$$ (10)

The kinetic methods used in this study are Friedman, Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) and their principles are listed in Table 1.

Table 1. Isoconversional Kinetic methods used in evaluating activation energy in this study.

Method	Expression	Plots	Reference
Friedman	$Ln\frac{dX}{dt} = Ln\left(\beta\frac{dX}{dT}\right) = Ln[Af(X)] - \frac{Ea}{RT}$	$Ln\left(\beta\frac{dX}{dT}\right)$ vs. $\frac{1}{T}$	[26]
FWO	$Ln\beta = Ln\frac{AEa}{g(X)R} - 2.315 - \left(\frac{1.0516Ea}{RT}\right)$	$Ln\beta$ vs. $\frac{1}{T}$	[27]
KAS	$Ln\frac{\beta}{T^2} = Ln\frac{AR}{Eag(X)} - \frac{Ea}{RT}$	$Ln\frac{\beta}{T^2}$ vs. $\frac{1}{T}$	[28]

4. Results and Discussions

4.1. Grape Marc Characterization

Table 2 shows the proximate and ultimate analyses of the Tunisian grape marc. Moisture is reduced to 10%, since it was very high after the wine extraction process (60 wt %). Furthermore, the direct use of the grape marc has a negative effect on the thermochemical process efficiency and temperature [29].

Table 2. Proximate and ultimate analyses of grape marc.

	This Study	Miranda et al. [15]	Gonzalez-Vazquez et al. [30]	Makela et al. [31]
Proximate Analysis	%			
Moisture [wb]	10	7.49	-	1.4
Fixed Carbon [db]	31.1	24.73	19.7	-
Volatile matter [db]	55.6	67.80	67.6	-
Ash [db]	13.3	7.47	12.7	8.23
LHV [db] (MJ·kg^{-1})	18.02	19.54	18.7	19.6
Elemental Analysis [db]	%			
C	42.2	42.97	45.5	48.7
H	3.5	9.28	5.1	5.57
O	37.7	-	34.7	35.9
N	3.0	2.05	1.8	1.66
S	0.3	0.17	0.17	-

[wb] Wet basis, [db] dry basis.

The ash content is 13.3%, which is higher than wood chips, at the same level as the grape marc was found by other authors, although this was lower than wheat straw [3]. The fixed carbon (31.1%) is higher than the value obtained by Miranda et al. (25%) for grape marc and higher than several biomass resources, such as olive husk (19%) and pine sawdust (17%). However, as expected, the volatile matter (55.6%) is lower than the grape marc of Miranda et al. (67.8%), olive husk (76%) and pine sawdust (69%) [15,32–34]. The high ash and fixed carbon contents confirm that slow pyrolysis is the suitable thermochemical conversion process for the grape marc recovery. In particular, the char yield (fixed carbon fix and ash contents) was about 44.4%, which was never met in literature for agricultural biomass under slow pyrolysis conditions. This feature distinguishes Tunisian grape marc from European ones and even from Chinese and American pomace. Many factors can explain these differences, such as local wine making practices and Tunisian grapevine specificity. The pyrolytic char derived from the Tunisian grape marc may have several applications, including soil amendment, adsorbents, biocoal, etc.

Elemental analysis also shows some differences with values met in literature, although this is consistent with the wide range of biomass composition that would undergo efficient pyrolysis. Carbon, hydrogen and oxygen are lower than the mean reported values, while N and S are quite high. This repartition is close to the composition of grape skins, although it is quite different from that of its seeds or stalks [32–34]. If nitrogen remains in char, this would be a supplementary argument in favor of pyrolysis against combustion, as biochar can be used as nutrients for soils.

4.2. Thermal Degradation of Grape Marc under Inert Atmosphere

The thermal degradation of biomass feedstocks was well described in the literature, which serves the main purpose of ensuring that from an energy standpoint, the pyrolysis process is self-sufficient [24–28,33,35]. Many factors affect the kinetic parameters based on the processing of TGA data, including processing conditions; heat and mass transfer limitations; physical and chemical heterogeneity of the sample; and systematic errors.

Figure 1 shows the mass loss (*X*) and the derivative (DTG) of mass loss (*dX/dt*) curves obtained during the pyrolysis of Tunisian grape marc. Thermogravimetric analysis could evaluate the thermal behavior of fuels under an inert atmosphere. The results are helpful in the fundamental understanding of biomass fuels when developing biomass utilization for the pyrolysis plant.
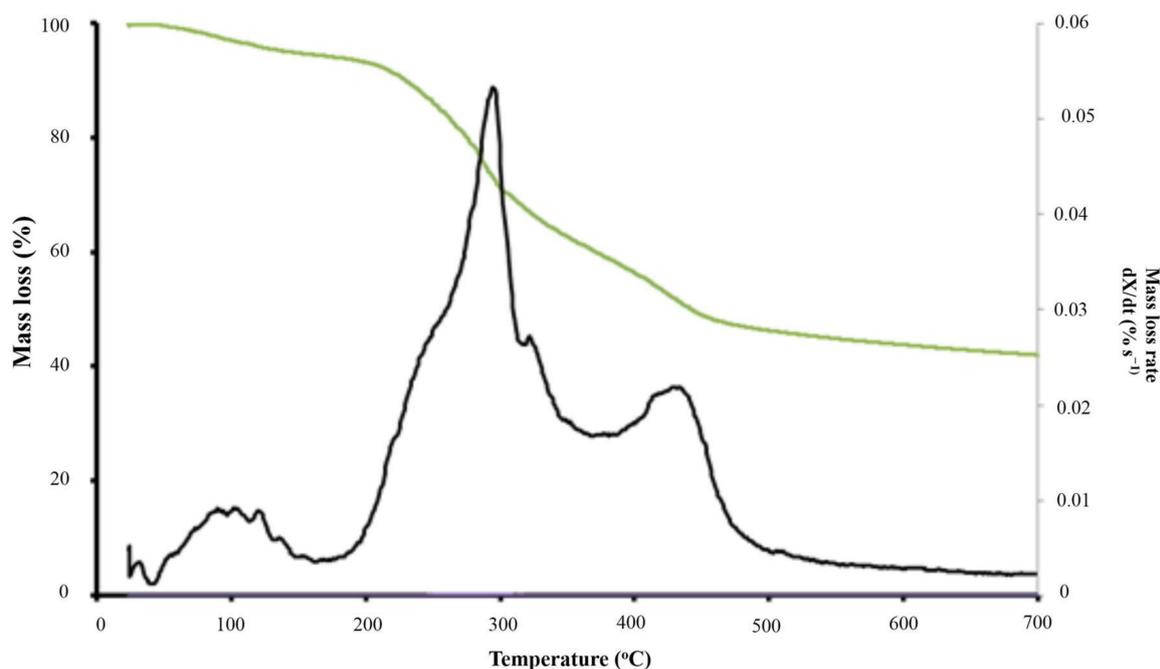
Figure 1. TG and DTG curves of Grape Marc under an inert atmosphere at 5 °C/min.

The shape of Derivative Thermo-Gravimetric (DTG) curve includes three regions in ascending order of temperature variation, corresponding to three degradation steps. The first region occurred between 23 and 166 °C, which corresponds to the biomass drying by moisture loss and the departure of light volatiles. The second region corresponds to the devolatilization step, which occurs between 166 °C and 500 °C. This step was called in the literature as the active pyrolysis includes two zones. The first one occurs between 166 and 362 °C, which corresponds to the decomposition of cellulose and hemicellulose. A clear peak at 288 °C is attributed to the decomposition of cellulose with an overall maximum rate of 0.055 %·s^{-1}. A second zone occurs between 362 °C and 500 °C, which corresponds to the lignin degradation. After the devolatilization step, a third step of passive pyrolysis is observed. This step characterized by a low and a continuous mass loss rate corresponds to the end of lignin degradation as well as char formation and rearrangement.

Several phenomena occur within grape marc pyrolysis and to varying extents: cracking, reforming, dehydration, condensation, polymerization and even oxidation and gasification reactions, which take place after the release of the oxygen and the vapors present in the product.

The obtained TG data, T (temperature), X (mass loss), T_{peak} (peak temperature), dX/dt (mass loss rate) and R_M (mean reactivity) are shown in Table 3. One may remind that reactivity is calculated as follows:

$$R_M = 100 \sum \left(\frac{R_{peak}}{T_{peak}} \right) . \tag{11}$$

The comparison of the obtained values with those found in literature for various lignocellulosic biomass feedstocks shows several differences. First, the peak temperature obtained at 288 °C is lower than the reported peak temperatures for cellulose decomposition, which is between 310 and 320 °C. Furthermore, this is lower than the peak temperature of 332 °C for pure cellulose [36] and for various lignocellulosic biomass in the literature [22,35,37]. However, this peak was at 261 °C for palm kernel shells for example [38]. The high content of minerals initially present in the Tunisian grape marc [20,21] is thought to be responsible for the shift to lower levels of temperatures as they may play a catalyzing role in the process. The impact of these minerals, especially Na, K and Mg, were evidenced in previous investigations [39].

Table 3. TG under inert atmosphere (5 °C/min).

	Pyrolysis Zone	T (°C)	166–750
		X (%)	94.5–41.3
Active Pyrolsis	**Zone 1**	T (°C)	166–362
		X (%)	94.5–61.2
		$T_{peak\ 1}$ (°C)	288
		R_1 (%·s^{-1})	0.032
	Zone 2	T (°C)	362–500
		X (%)	64.81–46.4
		$T_{peak\ 2}$ (°C)	423
		R_2 (%·s^{-1})	0.021
		$R_M \times 10^3$ (%·s^{-1}·°C^{-1})	0.14
Passive Pyrolysis		T (°C)	500–750
		X (%)	46.4–41.3

Hemicellulose decomposition is identified through the shoulder between 238 and 257 °C, which is in the interval of 195–306 °C. Such behavior is well-known in the literature and the hemicellulose decomposition step appears usually as a more or less pronounced shoulder instead of a well-defined peak [38]. Similar to cellulose decomposition, during the grape marc thermal degradation, hemicellulose decomposition occurs at a lower temperature due to the catalytic effect of alkali and alkali-earth metals [39].

The lignin degradation step also shows a clear difference compared to the usual shape of the DTG curve of lignocellulosic biomasses. In particular, the DTG curve of the Tunisian grape marc shows a specific region occurring between 362 and 500 °C, with a peak at 425 °C that yields an overall rate around 0.021 %·s^{-1}. This peak is attributed to the high contents of lignin. Otherwise, the zone corresponding to the cracking of the polymeric structure of C–C or C–O–C bonds in lignin would result in only a flat tailing section. Generally, the thermal degradation of lignocellulosic biomass is not characterized by a sharp peak for lignin decomposition.

The reactivity value (0.14 × 10^{-3} %·s^{-1}·°C^{-1}) is in the same magnitude as those of various biomasses, such as the coffee husk around 0.19 × 10^{-3} %·s^{-1}·°C^{-1} [38] or palm residues (0.23 × 10^{-3} %·s^{-1}·°C^{-1}) [40] for the same heating rate.

The char yield of 39.68% is expected in view of the proximate analysis, although this is higher than any agricultural waste. The char resulting from the first stages also probably contributed to the secondary reactions, which mainly occurred by catalyzing cracking and polymerization reactions that promoted recombination reactions among the volatile species to yield more condensed char structures [39].

In order to extract the kinetic parameters of the thermal degradation of Tunisian grape marc under pyrolysis conditions, the impact of different heating rates was investigated. Figure 2 showed that increasing the heating rate leads to a shift in the peak temperature towards higher values together with higher mass loss rates. Indeed, when heating rate is increased from 5 to 30 °C/min, the maximum peak temperature moves from 288 to 322 °C. The explanation is that the material reaches the cracking temperature in a shorter time when higher heating rates are considered. Due to the heat and mass transfer limitations inside the particle, these higher heating rates are a consequence of inner temperature gradients. In fact, increasing the reactor temperature ramp does not allow good temperature stabilization within the grape marc, which causes a delay in the volatile matter departure. The same behavior has been reported in the literature for numerous biomasses [40–42].
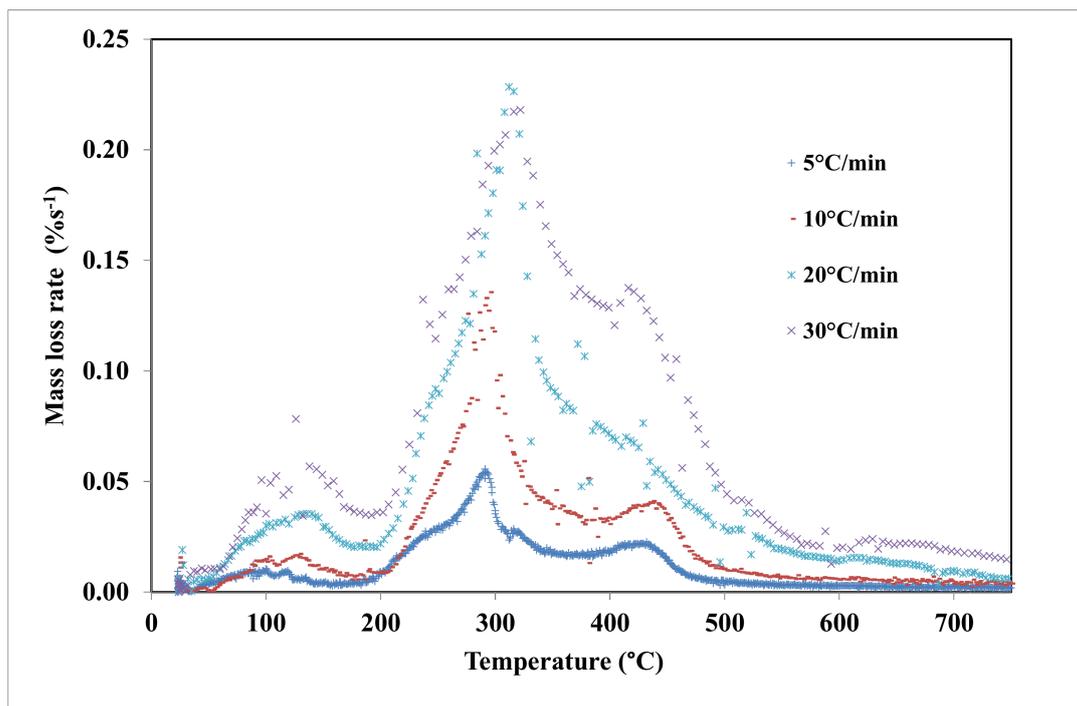
Figure 2. Mass loss rate for different heating rates.

4.3. Kinetic Study

The linear plots of KAS, FWO and Friedman are shown in Figure 3. As the initial mass loss is attributed to the moisture loss, the first conversion rate selected to determine the kinetic parameters is 0.2, while the final point is taken at 0.65. Above this value, no good determination coefficients were obtained, which may be attributed to the complexity of the char production and rearrangement.
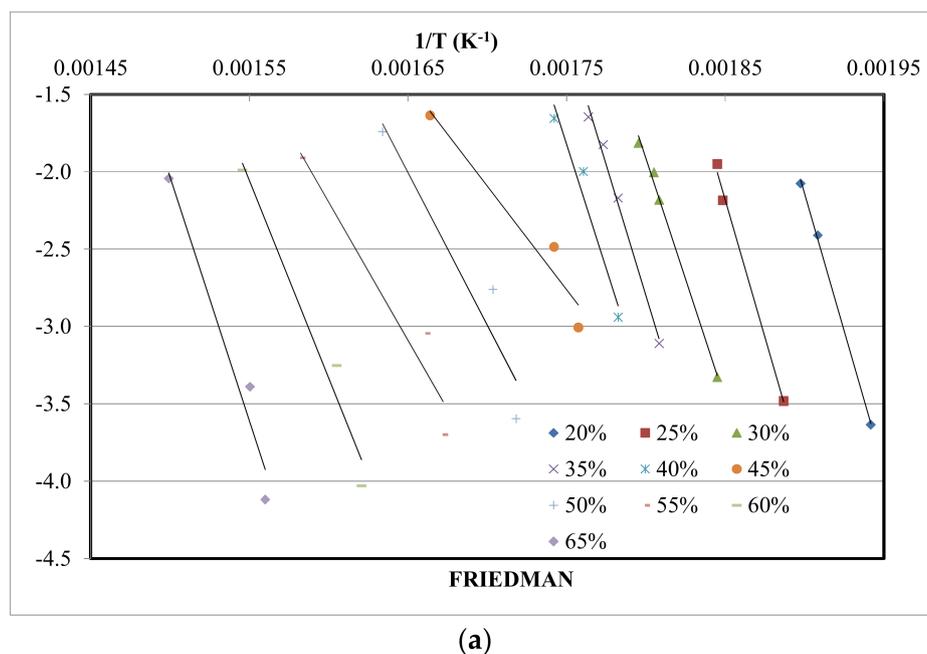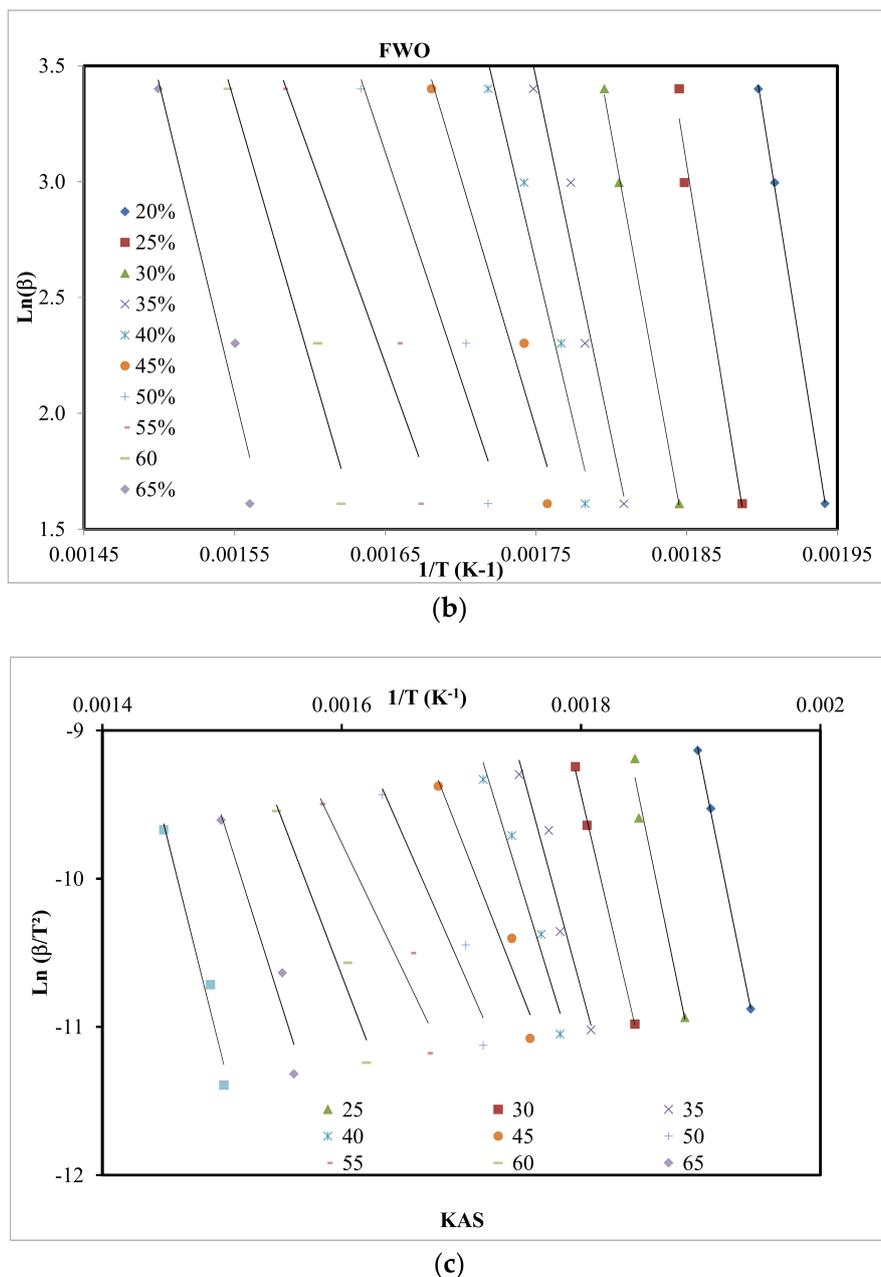

(**a**)

Figure 3. *Cont.*

(b)

(c)

Figure 3. Plots for kinetic models. (**a**) Friedman; (**b**) FWO; (**c**) KAS.

The calculated corresponding values are presented for each conversion ratio in Table 4. The mean activation energy values for GM with the use of the KAS, FWO and Friedman methods were 224.2, 226.8 and 229.5 kJ/mol, respectively. Table 4 depicts that the activation energy decreases when the conversion increases. It is assumed that a good biomass thermal degradation meets low activation energy values. In the initial stages and for KAS, FWO and Friedman methods, the *Ea* values were high (333.3, 323.3 and 295.9 kJ/mol, respectively, at $X = 0.2$). However, these values gradually decrease as the conversion rate X goes up until it reaches 55%, before increasing again (an exception point around 45% is probably due to an experimental error). This phenomenon was not reported in other works, where *Ea* was decreasing continuously, for several cellulosic biomasses [43,44]. This is explained by the quick and first scission of the weakly bonded amorphous cellulose and hemicelluloses. Once all-crystalline cellulose has decomposed, lignin accounted for a further decrease in activation energy [44].

Table 4. Calculated Energy activation with R^2 values from Friedman, FWO and KAS models (E, kJ/mol).

X	Friedman		FWO		KAS	
	Ea	R^2	*Ea*	R^2	*Ea*	R^2
0.20	295.9	0.999	323.3	0.999	333.3	0.999
0.25	295.0	0.995	316.9	0.979	324.4	0.978
0.30	259.2	0.995	282.0	0.999	287.4	0.999
0.35	280.5	0.991	244.4	0.947	247.7	0.943
0.40	267.5	0.955	217.0	0.964	218.8	0.961
0.45	111.4	0.947	172.1	0.959	171.3	0.954
0.50	163.8	0.911	154.5	0.948	157.6	0.941
0.55	148.5	0.936	142.9	0.939	140.0	0.930
0.60	212.3	0.965	176.9	0.962	175.3	0.958
0.65	262.2	0.959	212.1	0.941	212.1	0.935
Mean	229.5		226.8		224.2	

In our case and according to previous studies [2–5,14,31,41], lignin content in grape marc is much higher than cellulose. Consequently, the whole pyrolysis is thought to be mainly controlled by the lignin and its intermediate products.

In another hand, it is noticed that the activation energy for grape marc is greater than the values obtained for the pyrolysis of lignin [45,46] and other biomass [32,47–50]. These activation energies are high even when compared to other grape marc that originated from Italy. Fiori et al. found values between 171 and 178 kJ/mol for heating rates between 3 and 30 °C/min [51].

The isoconversional methods were applied to four different experimental data sets (5, 10, 20 and 30 °C/min). The results are presented in Figure 4. KAS and FWO are very close. The calculated *Ea* at the different conversion levels can be attributed to a different macro-component decomposition. At low conversion levels (0.2–0.3), the activation energies between 250 and 340 kJ/mol can be regarded as being related to hemicelluloses degradation. The lower *Ea* in the range of 140–240 kJ/mol are obtained for the conversion levels of 0.25 and 0.50, which can be attributed to cellulose cracking. The activation energy increases to 212 kJ/mol for KAS and OFW models and to 262 for the Friedman model at higher conversion levels, for which lignin is thought to be responsible. At higher temperatures, activation energies decrease, which may be explained by an overlapping of cellulose and lignin continuing degradation as well as by char rearrangement through secondary and more complex reactions, which was found in literature [52–55].
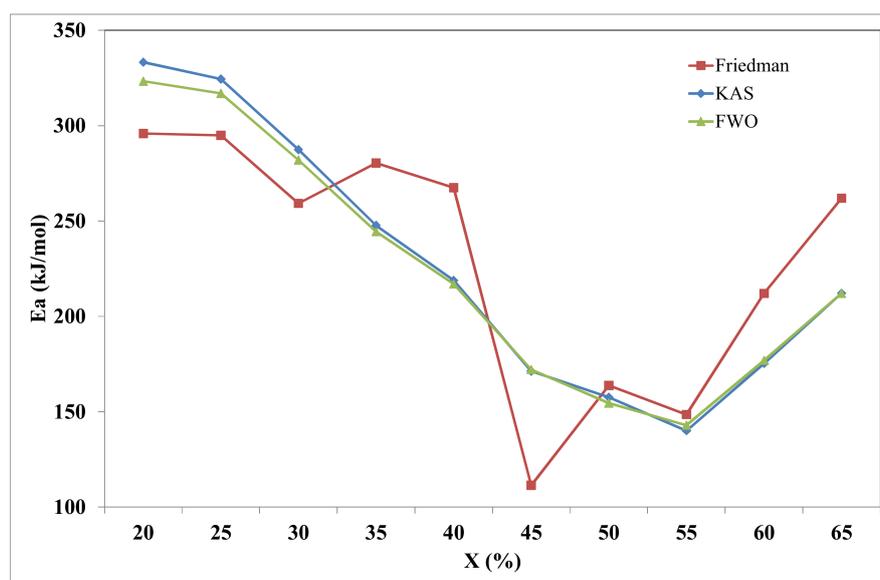
Figure 4. Activated Energies for Friedman, FWO and KAS method for conversion from 20 to 65%.

5. Conclusions

In these times, where the circular economy is at the service of the economic actors, the slow pyrolysis of grape marc can be an advantage in the wine industry and distilleries on more than one level, especially in the Tunisian context. Furthermore, as better environmental management of grape marc is increasingly necessary, this study is required to achieve a better understanding of the economics of grape marc pyrolysis for bio-fuel production and for resolving issues related to the capabilities of this technology in practical applications. Indeed, the pyrolysis process applied to these residues provides a high biochar yield of around 40%, which was never reached by any other agricultural waste. This fact is explained by the inhibition of hemicellulose and cellulose decomposition on one hand and by high lignin content on the other hand. With the same aim to improve some characteristics of grape marc by increasing its bulk density and reducing its ash content, densification and blending with woody biomass can help to solve the problem. The biochar is interesting as it may be used as nutritional ferment for soils or may undergo direct and efficient gasification. Minerals, which were an obstacle in combustion operations, become a major asset in pyrolysis. Furthermore, their presence played a catalytic role and shifted the cracking temperatures to lower values, thus reducing the operation cost.

To optimize this and to achieve high energy recovery from grape marc, kinetics data were calculated and helped in the design of pyrolysis reactors for grape marc. Integral and differential methods used in the frame of this work showed very close and reliable kinetic parameters.

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Conflicts of Interest: The authors declare no conflict of interest.

Nomenclature

A	pre-exponential factor (s^{-1})
Ea	activation energy (kJ/mol)
k	rate constant (s^{-1})
R	universal gas constant (J/K mol)
R_M	mean reactivity ($\%{\cdot}s^{-1}{\cdot}^{\circ}C^{-1}$)
t	time (s)
T	absolute temperature (K)
T_{peak}	peak temperature (K)
W_0	initial weight of the sample (mg)
W_f	final weight of the sample (mg)
W_t	time t weight of the sample (mg)
X	mass loss (%)
β	heating rate (K/s)

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