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The use of exhausted grape marc to produce biofuels and biofertilizers: Effect of pyrolysis temperatures on biochars properties

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Abstract

The wine industry represents an important economic sector in the Mediterranean countries. Currently, grape marc is valorized for ethanol production by distillation process generating a second residue called exhausted grape marc (EGM) that should be properly managed in order to avoid any related negative impacts onto the environment. In the present investigation, an innovative strategy was proposed to convert EGM into biofuels and biofertilizers through thermochemical conversion process such as carbonization/pyrolysis technique. In order to select the appropriate operating parameters, the impact of the slow pyrolysis temperatures of EGM (from 300 to 700°C) on biochar production yields as well as their physico-chemical characteristics were assessed. The experimental results showed that the biochars yields production decrease with increasing the pyrolysis temperature and reach a plateau above 500°C. The biochar yield at 500°C is around 33%, which is amongst the highest values obtained for food processing residues. The biochar physico-chemical characterization showed a higher surface area (253.4 m²/g) was obtained for the char prepared at 600°C. However, the

maximum nutrients contents, namely potassium, nitrogen and phosphorus were registered at 500°C. Based on the biochar yields and characteristics, it seems that EGM biochar produced through slow pyrolysis at 500°C could be considered as a promising biofertilizer for agricultural purposes.

Highlights:

- Exhausted grape marc (EGM) wastes were pyrolysed under various temperatures;
- Biochar production decreases with temperature and the yield reaches 33% at 500°C;
- Physico-chemical, textural, structural properties of EGM biochars were determined;
- The produced biochar at 500°C (EGM-B500) has high nutrient contents and porosity;
- The EGM-B500 is very attractive for agricultural and/or environmental applications.

Keywords : Exhausted Grape marc; pyrolysis; biochar; nutrients availability; textural properties

Words count :5018

1.0 INTRODUCTION

In the Mediterranean countries, agriculture and food processing activities produce huge amounts of by-products and wastes. These residues are generally not basically harmful, but their seasonal production and their high organic matter contents could represent serious environmental concerns. Thus, an efficient recovery of these wastes is very important for global sustainability, higher profitability of agriculture and agri-food industry and promotion of the circular economy concept.

Grape marc (GM) is one of the main food processing industries residues available worldwide since about 70 million tons of wine grape are annually produced [1]. Up to 20 % of the harvested wine grape becomes waste during wine production [2]. This residue originating from vineyard includes the skins, stalks and seeds grape. The implementation of environmental strategies for the grape marc treatment, in order to avoid various ecologic

hazards such as bad smells, surface and groundwater pollution, was pointed out as the main concern by various socio-economic actors.

Various disposal methods were proposed for grape marc recovery, including feedstock for pharmaceutical and cosmetics products [3], feedstuff [4], compost [5], and fertilizer [6]. However, these methods have several drawbacks such as bad smells, economic viability, thus some among them are abandoned or no longer permitted.

Recently, biochemical and thermochemical conversion processes were proposed as promising technologies for grape marc valorization. In particular, grape marc can act as a raw material for biogas production [7]. However, the related involved biochemical processes were quite sensitive to the inlet feedstock; indeed, the microorganisms growth might be easily inhibited by the toxic substances potentially present in the substrate. Additionally, biochemical processes generally need very long residence times, and involve big volumes, which cause high design and manufacturing costs. Alternatively, thermochemical conversion through combustion was tested since GM can be burned on-site at the winery for heat generation that could be used in the winemaking process itself. However, heterogeneity, high humidity, and high mineral contents have strongly diminished the combustion efficiency and also caused important emissions of particulate matters in the exhaust gas [8]. Therefore, examining the recovery of grape marc through an optimized pyrolysis processes could be an interesting alternative. In fact, this technique is well adapted to heterogeneous feedstock or substrates with high mineral contents, such as grape marc. Furthermore, it has the advantages to produce three different fractions (gas, liquid, solid) that could be valorized separately. The gaseous and liquid fractions could be used as biofuels in the pyrolysis plant for heating or electricity production. The solid fraction (char) could be used directly for agricultural soils amendment (called biochar) or activated in order to produce efficient adsorbents for pollutants removal from aqueous and gaseous effluents [9].

Only few investigations have examined the recovery of grape marc through pyrolysis techniques. Xu et al. [2] have examined the flash pyrolysis (from 300 to 600°C) at different vapor residence times (2.5, 5, and 20 s) of grape skins and the mixture of grape skins and seeds for bio-oil production. Authors showed that the optimum pyrolysis temperature for grape skin was 550°C, and 450°C for the mixture [2]. Khiari and Jeguirim [10] have examined the pyrolysis of grape marc provided by the Tunisian wine industry. The authors found that biochar production yield was close to 40 %. Such value was not mentioned in previous investigations for agricultural biomasses during slow pyrolysis experiments. Authors have attributed this result to high lignin and ash contents and affirmed the good potential of the use of grape marc for biochar production [10].

Biochars recovery for soil amendment has received widespread attention since it contributes to carbon sequestration, therefore decreasing the CO₂ emissions into the atmosphere [11]. Furthermore, benefits of soils amendment with biochars were not only limited to climate change mitigation, but also to agronomic soils' physical, chemical, hydrodynamic and biological properties improvements [12-13]. Indeed, biochars are highly rich in carbon (C), but contain also significant amounts of oxygen (O), hydrogen (H), sulfur (S), nitrogen (N), and non-negligible concentrations of various inorganic elements such as calcium (Ca), potassium (K), phosphorus (P) that are very useful for plants growth. A wide range of raw and pre-treated biomass feedstocks were pyrolysed for biochars production (Table 1). These feedstocks include woody biomass resources, agriculture residues, food processing residues, green waste, wastewater sludge, and dairy manures [14-20]. During these investigations, biochar properties including pH, ash contents, elemental composition, specific surface area and micropores volume were generally determined. These properties were found to be very dependent on the feedstock type as well as on the operating parameters such as the final temperature, the residence time, and the heating rate. Indeed, these investigations showed that

with increasing the pyrolysis temperature, the aliphatic components of the feedstock are progressively decomposed and transformed into aromatic compounds [19]. Furthermore, the biochar yields, acidic functional groups concentration, volatile matter content, total oxygen content, and cation exchange capacity (CEC) decreased with the increasing of the applied temperatures. In contrast, the aromatic character, the basic functional groups, the pH, the fixed carbon, the carbon stability, the ash contents, the exchangeable and soluble cations, and the specific surface area of biochars increased with the applied temperature [19, 20]. Generally, the biochars pH values increase by increasing the pyrolysis temperature due to the elimination of oxygen surface groups including $-\text{COOH}$ and $-\text{OH}$ [21]. These basic properties allow the use of biochars as an alternative of lime for the improvement of acidic-soils quality [22].

The heating rate and the residence time play also an important role during biochar production [18]. The residence time not only influences the biochar production yields, but also their textural properties. Tsai et al. [23] indicated that the residence time increase leads to an increase in the biochar pore sizes distribution. Besides, the heating rate strongly affects the composition and the nature of the pyrolysis products, including biochars. In fact, low heating rates during biochar production allows the limitation of the thermal cracking of biomass and therefore higher biochar yields are obtained. In contrast, a high heating rate promotes the fragmentation of biomass and increases the gaseous and liquid yields, limiting the biochar formation [24].

The biochars production yields and properties also depend on the biomass composition. Generally, high biochar yields are obtained for pyrolysis of solid wastes and animal litters compared to those obtained from crop residues and woody biomasses [21]. These higher yields are related to the presence of the main inorganic constituents of the feedstock [2]. Furthermore, the raw lignocellulosic biomass structure and its composition in terms of

cellulose, hemicellulose and lignin could also significantly influence the pyrolysis products. In particular, cellulose and particularly lignin considerably increase the biochars production yields [23].

This study aims to examine the potential of grape marc as a feedstock for biochar production. Therefore, its slow pyrolysis was performed at different temperatures ranging between 300 and 700°C. Then, the produced biochars' physicochemical properties including their surface chemistry, as well as their textural and structural properties were analyzed using different analytical techniques. The determined features are essential to decide about the suitability of the produced chars for agronomic soil amendment.

Table 1. Main feedstocks, operating conditions and the produced biochars characteristics.

Feedstock	Pyrolysis Temperature (°C)	Heating rate (°C min ⁻¹)	Residence time (h)	Yield (%)	pH	Surface area (m ² g ⁻¹)	Ash (%)	C (%)	H (%)	C/H	C/O	Reference
Bagasse	500	10	1	43.7	9.3	-	8.57	85.59	-	30.35	8.17	[14]
Rapeseed plant	800	5.0	-	28.2	-	19.0	15.3	79.51	0.72	-	-	[15]
Poplar wood	400	8	-	32	9	3.0	3.5	67.30	4.42	-	-	[16]
Pine wood	700	10	-	-	6.6	29.0	3.8	95.30	0.82	-	-	[17]
Conocarpus wastes	200	-	4	51.33	7.37	-	4.53	64.19	-	16.21	2.42	[14]
	400	-	4	31.86	9.67	-	5.27	76.83	-	27.15	5.43	
	800	-	4	23.19	12.38	-	8.64	84.97	-	137.05	17.45	
Straw	200	-	1	84.95	5.34	-	11.9	45.57	-	7.90	1.19	[18]
	200	-	4	78.24	6.11	-	12.78	46.52	-	8.46	1.29	
	400	-	1	37.30	10.82	-	25.74	57.59	-	17.14	3.46	
	400	-	4	36.65	10.78	-	28.4	59.17	-	19.05	3.77	
	600	-	1	32.48	10.93	-	32.33	59.09	-	38.42	5.36	
	600	-	4	30.89	10.99	-	34.31	60.8	-	45.71	5.73	

2.0 MATERIALS AND METHODS

2.1 Samples preparation

The grape marc selected for this study is a mixture of different grape varieties available in the Alsace Region (France). It was provided from the Sigolsheim distillery (France), after ethanol extraction by distillation process. This residue of distillation is called exhausted grape marc (EGM). Prior to its use, the EGM was manually sorted to remove the branches. Then, EGM was grounded using a laboratory crusher and sieved to obtain a uniform sample with an average particle size ranging between 0.25 and 0.4 mm.

2.2 Exhausted Grape marc Characterization

The elemental analysis of EGM was carried out by a CHONS analyzer (FlashEA 1112, Thermo Scientific, Villebon, France) for the major elements, according to standard NF EN ISO 16994 for the chlorine determination. The inorganic elements concentrations were determined by ICP (720 ES, Varian, Les Ulis, France) according to standard NF EN ISO 17294-2.

The proximate analysis were determined using various methods [25]. The moisture, ash contents, and volatile matters were determined according to NF EN ISO 18134-3, NF EN 14775 and NF EN ISO/IEC 17025:2005 standards, respectively. Fixed carbon were then deduced from the previous analyses.

In order to follow the thermal behavior of the EGM under pyrolysis conditions, a thermogravimetric analyzer TGA/DSC3+ apparatus ((Mettler-Toledo, Columbus, OH, USA) was used. During these tests, 10 mg of EGM were inserted in an alumina crucible and introduced inside the thermobalance, then heated under N₂ at a flow rate of 6NL/h. This heating process occurred from 20 to 800°C at a constant heating rate of 5 °C min⁻¹.

2.3 Biochar Production

The biochar production was realized in a vertical tubular furnace already described in previous investigation [26]. During each test, 2 kg of grape marc was distributed in the different pyrolyzer drawers. N₂ flow of 5 NL h⁻¹ was constantly fed at ambient temperature during 30 minutes to eliminate the residual oxygen. Then, the temperature was increased to the settled value (300-700°C), at a constant heating rate of 5°C min⁻¹. Once stabilized, the temperature was maintained constant during 1 h, and then natural cooling was performed under N₂ flow. During these experiments, the exhausted gases passed through a condensing system constituted of refrigerant connected to a liquid collector. The exhausted gases were cooled by circulating cold water in order to recover the liquid fraction (bio-oil).

2.4 Biochar characterization

The physico-chemical, textural and structural properties of biochars were assessed using the different following analytical methods.

The particle size distribution was determined on a water suspension of biochars using a laser granulometer (Mastersizer Malvern Instrument, Worcestershire, UK).

The produced biochars' pH values were determined by mixing 1 g of biochar with 10 mL of deionized water for 1 h by using a magnetic stirrer. The pH of the filtered aqueous solution was measured with a pH-meter (HI2211, HANNA Instrument, Woonsocket, RI, USA).

The elemental and proximate analyses of the biochars were determined according to the same procedures of the EGM (see section 2.2).

Scanning Electron Microscopy (SEM) was used in order to assess the produced biochars morphology. SEM images were carried out using a Philips model FEI model Quanta 400 apparatus (Amsterdam, The Netherlands). Prior to the observation, the samples were covered with a tinny gold layer by using an Agar automatic sputter coater. During the analyses, three magnification levels (x1000, x5000 and x20000) were selected.

Energy Dispersive X-Ray (EDX) (Oxford Inca Si, Oxford Instruments, Concord, MA, USA) analyses have been also performed for the identification of the main mineral species and for the observation of their dispersion through the biochar matrix.

The specific area and porosity of the EGM biochars were determined by carbon dioxide adsorption using gas adsorption analyzer (ASAP 2020, Micrometrics, Norcross, GA, USA). Before the measurements, biochars were out-gassed under vacuum during 24h at 150°C. This step is required to eliminate the surface water as well as the volatile organic compounds. During these analyses, the CO₂ adsorption was performed at a controlled temperature (0°C) by using an ice-water bath.

X-ray Photoelectron Spectroscopy (XPS) also known as Electron Spectroscopy for Chemical Analysis (ESCA), which is a surface-sensitive quantitative spectroscopic technique was used to determine the elemental composition of the produced biochars. The average depth of analyses for the XPS measurements was approximately 5 nm. The measurements were made with a vacuum (UHV) spectrometer (Thermo-VG, Thermo Fisher Scientific, Dreieich, Germany) equipped with a CLAM4 hemispherical electron analyzer (CDM).

The structural properties of the different produced EGM chars were analyzed by Raman spectroscopy. During this analysis, the Raman spectra were recorded with a BX40 LabRam, Jobin Yvon/Horiba spectrometer (Kyoto, Japan). Raman spectra were obtained in a backscattered configuration with an excitation laser at 632.8 nm. The analyses parameters were selected as follows: microscope objective 50x, acquisition time 300 s, 1 accumulation. During this analysis, different parameters related to the biochar structure could be obtained. Details on their calculations and significance could be found in previous investigations [27, 28].

3.0 RESULTS AND DISCUSSION

3.1 Characterization of the Exhausted Grape Marc

Table 2 displays the ultimate and proximate analyses as well as the inorganic elements concentrations in the EGM. The obtained values are in the range of typical composition of agriculture and food processing residues reported in literature [29-32].

The elemental composition analysis shows that carbon content (50.75%) is higher than the mean values reported in the literature. In addition, the fixed carbon value (24.35%) is also greater than the ones obtained for various lignocellulosic biomasses [33]. The high fixed carbon content found in this biomass sample can be explained by the exhaustion of sugars in the ethanol production, remaining a residue with higher content of lignin. Lignin is the component in biomass which provides a higher yield of solids after pyrolysis and therefore high char yields during the slow pyrolysis of EGM. The analysis of the inorganic elements indicates that potassium (K), calcium (Ca) and phosphorus (P) exist in EGM with relatively high contents compared to other biomasses (Table 2). Indeed, the contents of K, Ca and P were assessed to 0.677%, 0.622% and 0.257%, respectively (Table 2). These elements, if still present in the produced chars after the slow pyrolysis of EGM, they would be very useful for plants growth and development.

Table 2. EGM Proximate and Ultimate analyses (db : dry basis, ar : as received)

Elemental composition ^{db} (%)		Mineral composition ^{db} (mg/kg)	
C	50.75	Al	50
H	6.40	Ca	6220
N	1.18	Fe	110
S	0.02	K	6770
O	38.40	Mg	890
Proximate analysis (%)		Na	40
Moisture^{ar}	7.55	Cl	140
Volatile matter^{db}	72.40	P	2570
Fixed Carbon^{db}	24.35	Si	330
Ash^{db}	3.25	Ni	-

3.2 Exhausted Grape Marc Thermal degradation

The thermal degradation behavior of the used EGM was examined under inert atmosphere at a heating rate of $5^{\circ}\text{C min}^{-1}$. Figure 1 presents the Normalized Anhydrous Weight (NAW) and the Normalized Anhydrous Weight Loss Rate (NAWLR) of EGM. The degradation of dry EGM begins around 150°C lower than the initial degradation temperature of the most of the lignocellulosic biomasses. Such behavior is attributed to the degradation of lignin that starts at low temperature and occurs in a large temperature range [34]. Furthermore, alkali metals, like potassium, may catalyze the thermal degradation of EGM.

In the temperature interval ranging between 210 and 290°C , two small shoulders are observed at 225 and 266°C , respectively. Such observation was discussed in details in previous investigation and was attributed to the hemicellulose decomposition. In particular, the curve shape looks generally as a more or less pronounced shoulder instead of an intense peak depending on the hemicellulose content in the raw biomass. During the EGM thermal degradation, the presence of a first shoulder at 225°C may be attributed to different hemicellulose compounds or to the catalytic effect of alkali elements on its decomposition [33].

The NAWLR curve shows a sharp peak observed at 320°C with maximum loss rate of $0.039\% \text{ s}^{-1}$. This well-known peak is attributed to the cellulose decomposition. Various peak temperatures and maximum loss rates are reported in the literature depending on the raw biomass characteristics. In this study, the maximum peak temperature of EGM is higher than that reported in the literature for grape marc (288°C), while the maximum mass loss rate is lower ($0.039\% \text{ s}^{-1}$ against $0.055\% \text{ s}^{-1}$ in the literature) [10]. Such results indicate that EGM reactivity is lower than that of the raw grape marc, which can be related to the difference in the inorganics content. In fact, the higher reactivity was obtained for grape marc with an ash content of $13 \text{ wt.}\%$, while the EGM ash content is $3.25 \text{ wt.}\%$ (see Table 2). The distillation process may decrease the mineral contents of the grape marc and therefore affect the biochar production.

After the sharp peak, a slow and a continuous mass loss rate, named in the literature passive pyrolysis, occurs above 500 °C. This step corresponds also to the lignin degradation and the char formation and rearrangement. At a temperature of 800°C, the char percentage for EGM was assessed to 28.9 wt% (30.9 wt.% at 700 °C) which is relatively higher than that of woody biomasses and several agriculture residues. This observation is very important for the economic viability of the biochar production from exhausted grape marc. However, the obtained value is lower than that obtained for Tunisian grape marc (not distilled) [10]. Such results suggest that an economic study for the selection between exhausted grape marc and raw grape marc for biochar production needs to be undertaken.

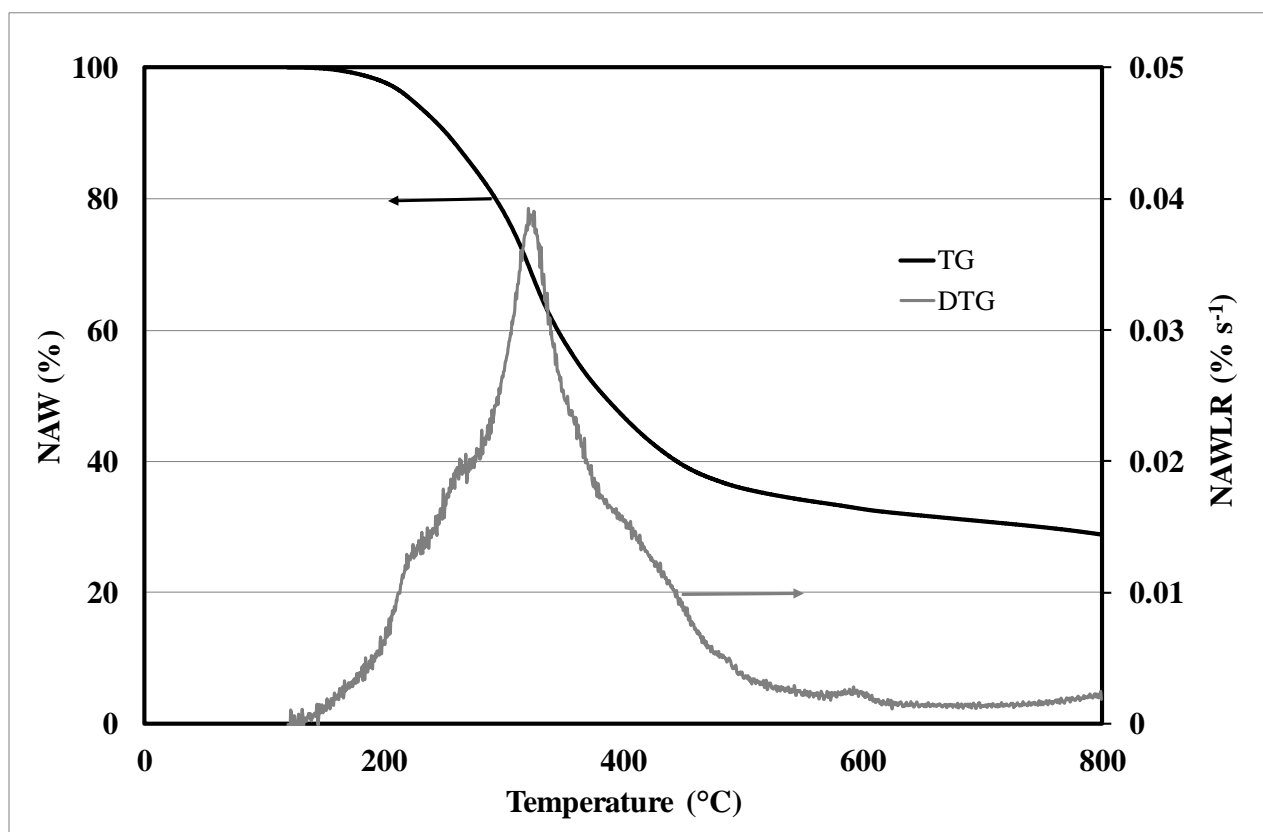


Figure.1. Normalized Anhydrous Weight (NAW) and Normalized Anhydrous Weight Loss Rate (NAWLR) of Exhausted Grape Marc (EGM) in N₂ atmosphere at heating rates of 5°C min⁻¹.

3.3 Biochar Yields

EGM biochars were elaborated at various temperatures, ranging from 300 to 700°C, in a pilot scale pyrolyzer, according to the experimental protocol given in section 2.3. The obtained biochar yields are presented in Figure 2.

As expected, the biochar yields were relatively important below 500 °C. The obtained values were 65.8% and 59.1% at 300 and 400 °C, respectively. These values are in agreement with EGM thermal degradation behavior during thermogravimetric analysis. In fact, the devolatilization step was not ended at these temperatures. When the pyrolysis temperature was further increased, the biochar yields production dramatically decreased and reached 33.8%, 32.6% and 30.8% for temperatures of 500°C, 600°C and 700°C, respectively. Such results indicate that a pyrolysis temperature of 500 °C may be suitable for biochar production at large scale since the devolatilization step is finished and no significant EGM mass loss occurs above.

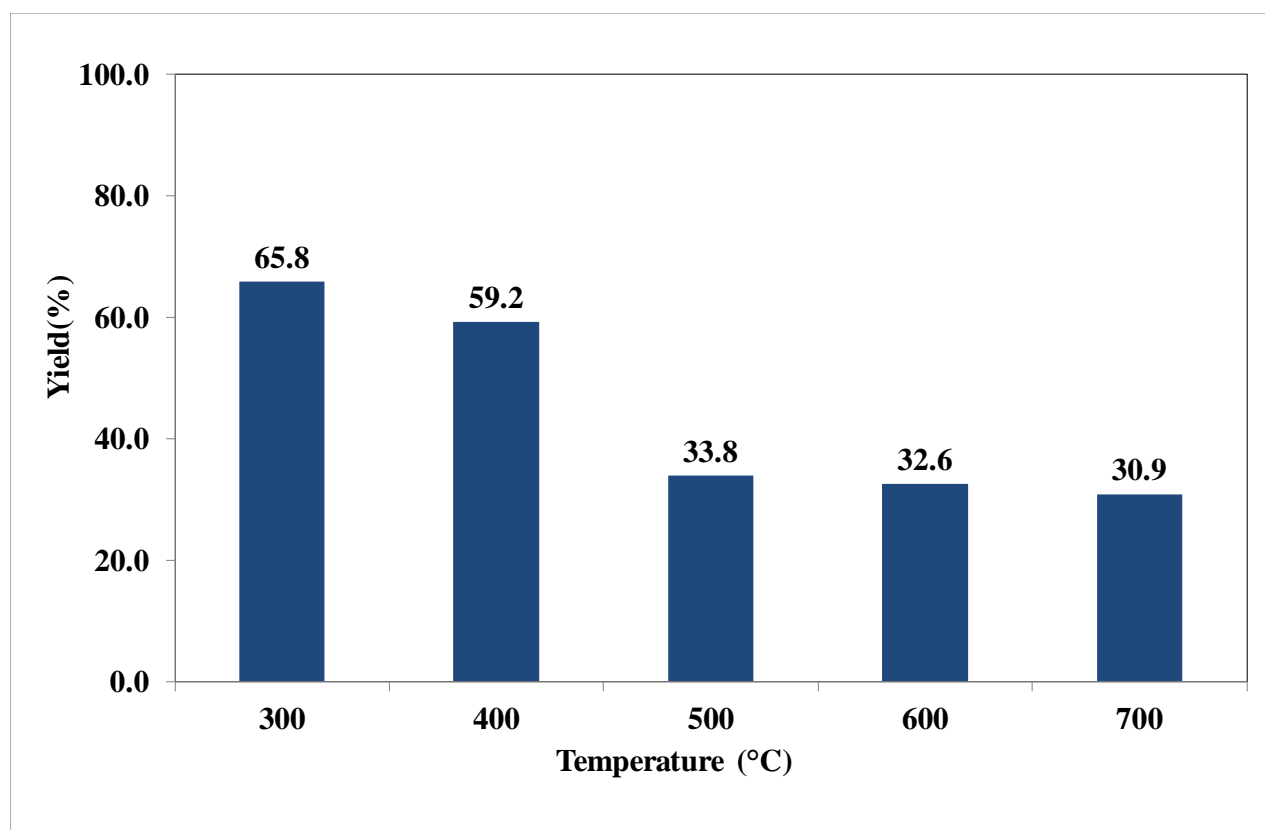


Figure.2. Effect of pyrolysis temperature on biochar yields

Similar results for biochar yields were observed for various agricultural biomass such as peanut-shell (36.80%–25.80%), corn-straw (35.50%–24.90%), and wheat-straw (32.40%–22.8%) in the temperature interval of 400 to 700 °C [35]. The EGM char yield obtained in the present study are higher than those reported in literature for pyrolysis performed in similar conditions. This observation could be related to the high lignin content in grape marc. In fact, in the pyrolysis process, lignin is the most important constituent responsible for higher char formation, while hemicelluloses and cellulose contribute more to volatile compounds emissions [36]. The high content of lignin in the exhausted grape marc is attributed to the exhaustion of sugars during the ethanol production. Furthermore, the relatively high presence of alkali metals (see Table 2) tends to increase the char yields during the pyrolysis process, as abundantly discussed in the literature [33].

3.4 Biochars characterization

Figure 3 shows the distribution curves (logarithmic scale) of the biochars prepared at different temperatures. It can be clearly seen that the average particle sizes is ranging from 120 μm to 150 μm , and an increase of the smallest particles ratio (average 25 μm) was observed at higher pyrolysis temperatures. A small variation of the average particle size is also observable with the pyrolysis temperature increase (Table 3), with a maximum value for the biochar prepared at 600 °C (146 μm) and a strong decrease for the biochar prepared at 700 °C (129 μm).

Table 3. Particle Size Distribution of the different biochars

Pyrolysis temperature	300 °C	400 °C	500 °C	600 °C	700 °C
d10 (μm)	33	28	44	32	22
d50 (μm)	117	113	147	146	129
d90 (μm)	219	221	238	254	230

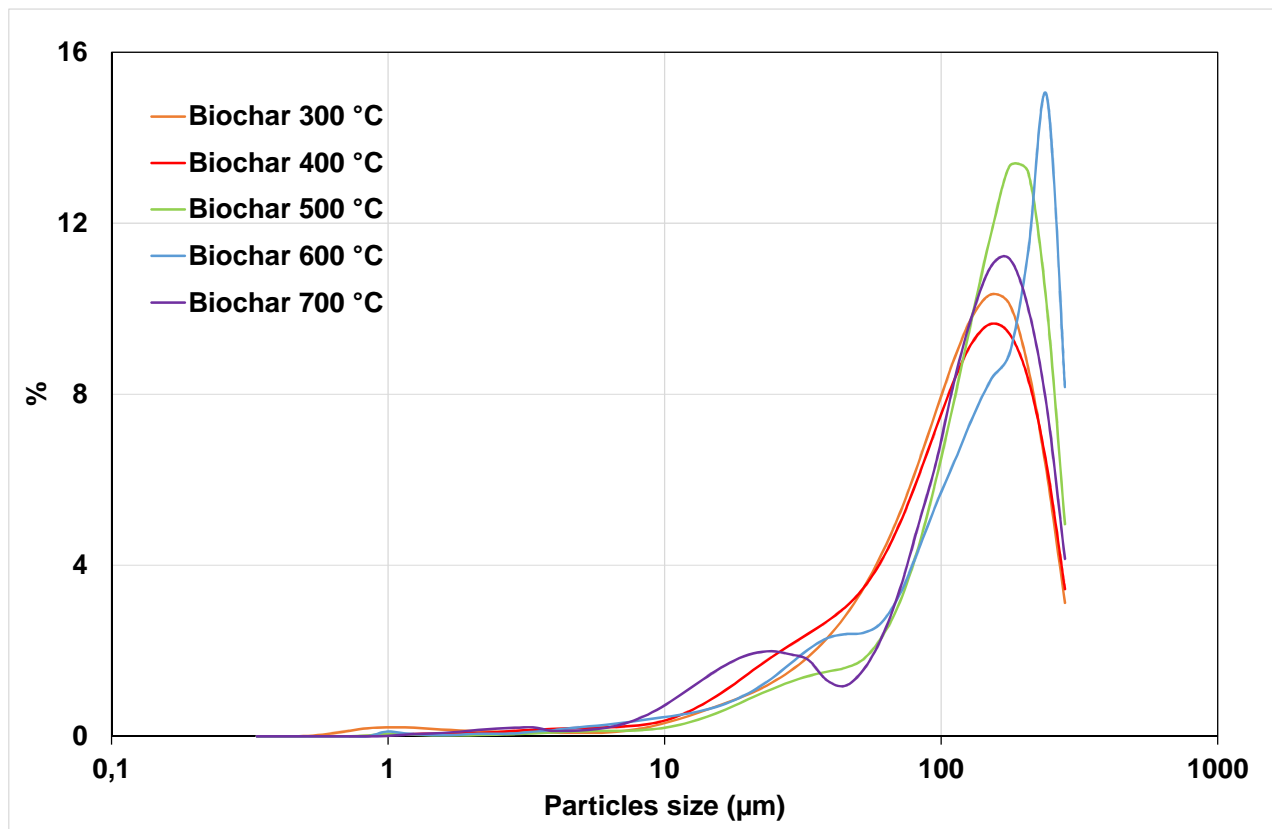


Figure. 3. Particle size distribution of biochars produced from EGM at different temperatures

Proximate analysis was conducted for the four biochars (300, 400, 500 and 600 °C). The obtained results (Table 4) show that all biochars samples have volatiles matters contents decreasing from 64.7 % to 15.7 % when the temperature increases from 300 to 600°C. The higher fixed carbon amounts are observed for pyrolysis temperature of 500 and 600 °C, when compared to the other pyrolysis temperature tested. In similar way, ash contents increase with the increase of pyrolysis temperature, except for the biochar obtained at 600 °C. Such result is attributed to the high mineral and lignin contents in EGM. It is well known that lignin is difficult to decompose during biomass pyrolysis, thus generating a high amount of solid residue [36].

The knowledge of the fixed carbon and volatile matter contents is very important for the selection of the most suitable thermochemical conversion process. Therefore, biomass with high fixed carbon engender higher production of biochars [36].

Table 4. Proximate analyses of the produced biochars (as received basis)

Pyrolysis Temperature (°C)	300	400	500	600
Moisture (%)	3.4	3.7	4.4	4.5
Volatile matter (%)	64.7	45.2	27.9	15.7
Fixed carbon (%)	27.0	43.4	58.2	71.3
Ash (%)	4.9	7.7	9.5	8.5

The chemical composition of the grape marc biochars are reported in the Table 5. It shows that the biochar gets richer in C and poorer in H and O as the pyrolysis temperature increases. Indeed, the C content increased from about 60.21% to 72.89 % with increasing temperature from 300 to 700°C. The obtained values are in the same order of magnitude as the ones experimentally and numerically obtained by Debiagi et al for peanut shell and wood waste chars [37].

The O and H contents significantly decrease from about 26.20% and 6.04% to 15.00% and 1.23% for the biochars produced at 300 °C and 700 °C, respectively. This behavior can be attributed to the dehydration and decarboxylation reactions that become more important when the applied temperature increases. Therefore, the H/C ratios of the EGM biochars decrease with the increase of the pyrolysis temperature. This decrease is closely related to the augmentation of the hydrophilic character of the biochar and therefore to the enhanced water retention capacity. A similar trend was observed for the O/C ratio, up to 500 °C. The lower values obtained at higher temperatures indicate the presence of aromatic rings forming very stable graphite-like structures. The low percentage of S observed after pyrolysis at 300 °C and its absence at higher temperatures can be probably assigned to the decomposition of sulfur compounds into volatile SO₂ [38, 39].

Most of the other elements studied (P, Ca, Mg, Na, and K) are still present after pyrolysis at different temperatures. Such behavior is attributed to the low volatility of the corresponding oxides. Indeed, compared to the raw EGM (see Table 2), the nutrients (Ca, K and P) contents have significantly increased reaching values of 1.84%, 2.13% and 0.83%, respectively (Table 5). This observation highlights the opportunity offered by these biochars to be used as amendments in agriculture and supports the choice of pyrolysis instead of combustion for EGM thermochemical conversion.

Table 5. Ultimate Analysis of EGM biochars produced at different temperatures (DL: detection limit)

Pyrolysis Temperature (°C)	300	400	500	600	700
Elemental composition (%)					
C	60.21	67.42	72.91	72.13	72.89
H	6.04	5.07	3.15	2.16	1.23
N	2.51	2.71	2.72	1.71	1.57
S	1.09	<DL	<DL	<DL	<DL
O	26.2	20.1	12.9	15.3	15.0
H/C	0.10	0.08	0.04	0.03	0.02
O/C	0.44	0.30	0.18	0.21	0.21
Mineral composition (mg/kg)					
Al	554	433	471	326	357
Ca	7010	10300	13400	17961	18381
Fe	512	771	930	718	724
K	11000	16400	21700	20095	21281

Mg	1150	1430	1900	2929	3159
Na	199	299	407	422	427
Ti	19	-	40	-	-
P	3370	4940	6230	8194	8322
Si	3150	4590	6150	1326	1539
Ni	-	-	-	0	4.5

The measured pH of the produced biochars increased with the increase of the pyrolysis temperature (Table 6). Indeed, these values rose from a relatively neutral pH (7.2) to a very alkaline one (10.1) for the biochars produced at 300 °C and 600 °C, respectively. This behavior is due to removal of acidic function groups with increasing the thermal treatment. Similar results were reported in the literature for bagasse and straw [14, 18].

Table 6. pH of biochars produced at different temperatures

Pyrolysis Temperature (°C)	300	400	500	600
EGM (This study)	7.2	8.7	9.9	10.1
Straw [18]	*	10.8	*	10.9
Bagasse [14]			9.3	

The BET specific surface area (SSA) of the produced biochars from EGM significantly increased with the increase of the pyrolysis temperature. Indeed, the measured specific surface areas increased from about 25 m² g⁻¹ to more than 253 m² g⁻¹ when the pyrolysis temperature increased from 300°C to 600°C (Table 7). A similar trend was obtained also for the micropores volume where its value at a temperature of 400 °C (0.03 cm³ g⁻¹) increased by a factor of more than 2.6

when the applied temperature passed to 600°C. This improvement of the biochars textural properties can be attributed to the fact that, at higher temperature, volatilization is more important, and consequently the biochar obtained is more porous, due to the creation of empty spaces into the carbon matrix. Similar results have been reported by several authors [40, 41]. For example, Cui et al. [41] have characterized biochars obtained from the pyrolysis of *Canna Indica* biomass (China) at pyrolysis temperatures of 300, 400, 500 and 600°C, a residence time of 2 hours and a constant heating rate of 5°C min⁻¹. They demonstrated that the increase of the pyrolysis temperature from 300°C to 600°C enhanced their specific surface area from 3.46 to 10.4 m² g⁻¹ due to the development of the microporous structure [41]. Besides, Kim et al. [42] reported that increasing the pyrolysis temperature of a local Korean biomass (*Miscanthus sacchariflorus*) from 300 to 600°C, has considerably increased the BET surface areas of the produced biochars from 0.56 to about 381 m² g⁻¹ [42].

It is worth mentioning that the relatively high measured surface areas of the EGM biochars produced at temperatures of 500 and 600°C is a real advantage for the use of these chars in environmental applications, and especially for the removal of toxic pollutants from aqueous and gaseous effluents.

Table 7. Textural Properties of EGM biochars produced at different temperatures

Pyrolysis Temperature (°C)	300	400	500	600
SSA (m ² g ⁻¹)	25	130	205	253
Micropores volume (cm ³ g ⁻¹)	-	0.03	0.06	0.08

Figure 4 gives the SEM images at the three magnifications of 1000, 5000 and 20000 times of the four EGM biochars. The images obtained at 1000 and 5000 magnifications show that, when the

pyrolysis temperature increases, the degradation of the biochars is more pronounced and the related porosity becomes more important. Indeed, the biochar produced at 300°C presents a smooth surface with some pores that are not clearly defined. At the opposite, the biochars obtained at 500 and 600°C present irregular surfaces with well-developed porosities, characterized by the presence of tubular structures that were clearly visible in the related images at a magnification of 5000. These results confirm the BET analyses that proved the development of microporosity with the increase of temperature. EDX analyses (data not shown) indicated the presence of various minerals, mainly potassium and calcium, while phosphorous and silicon are also present in the biochars. We can also observe the appearance of small needles on the surface of biochar produced at 400, 500 and 600°C (x20000), and associated to the decomposition of calcium tartrate that, as well as potassium tartrate, is naturally present in grapes. This observation is supported by the shape of the crystals which is characteristic of calcium tartrate and oxalate [41].

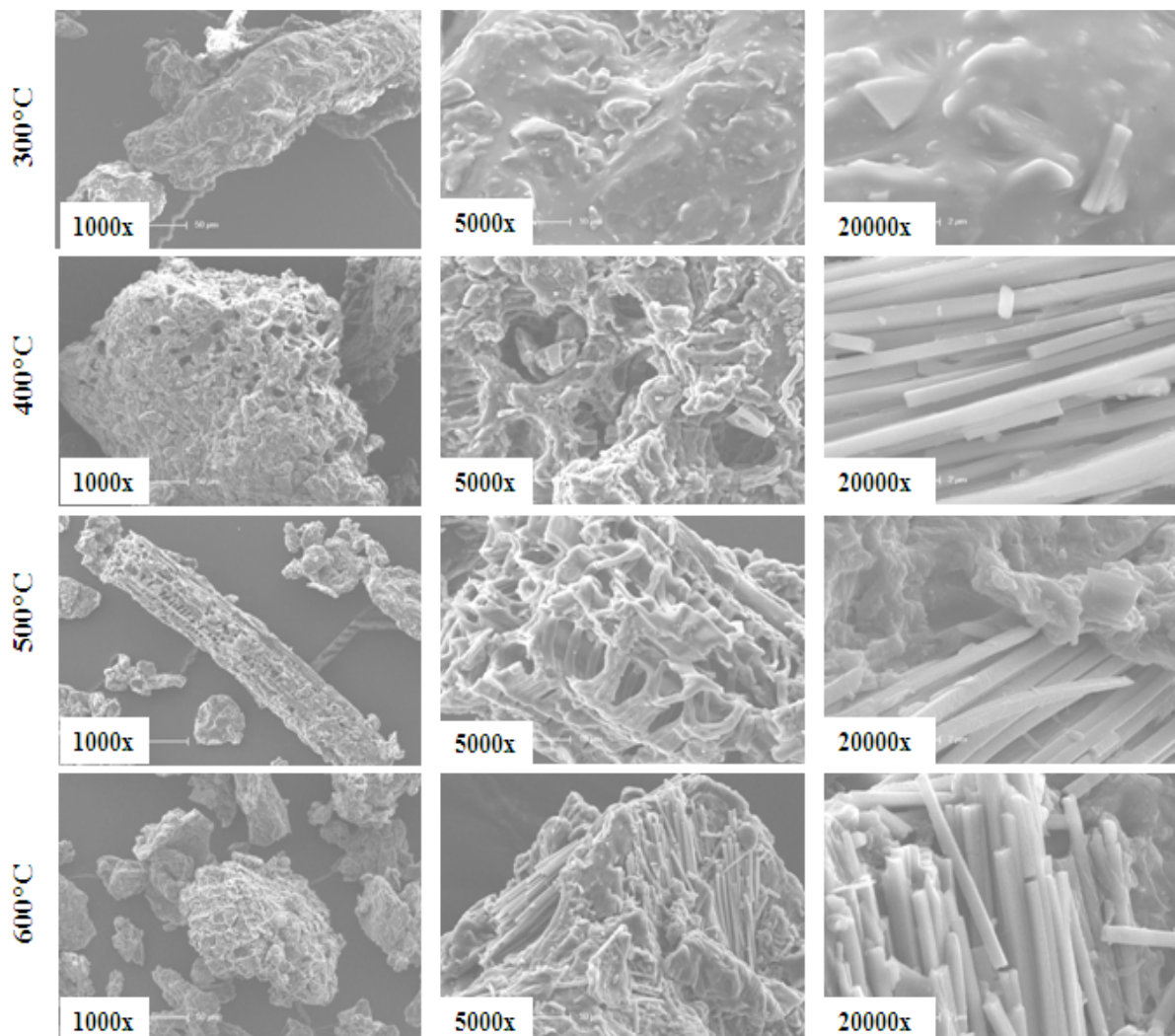


Figure.4: SEM images of EGM biochars pyrolysed at different temperatures (300-600 °C).

Figure 5 gives the XPS spectra of the four biochars generated by the pyrolysis of EGM performed at various (300, 400, 500, 600 and 700°C) temperatures. For a pyrolysis temperature of 300 °C, only carbon and oxygen were detected with respective percentages of 57.1% and 42.9%. These values decrease to 15.3 % and 38.5 % for the biochar produced at a temperature of 700°C. Indeed, with the increase of the applied temperature, other elements were detected on the surface of the biochar, particularly Ca and K whose percentages at 700°C reached 21.5 and 22.3 %, respectively. This result is attributed to the removal of some volatile organic compounds from the EGM by increasing the pyrolysis temperature, leading to higher concentrations of Ca and K. Moreover, Ca

and K are not completely transferred in the gas phase during the thermal treatment, even at relatively high temperatures (700°C). These relatively high nutrients contents are very important if these chars are valorized as biofertilizers in agricultural soils.

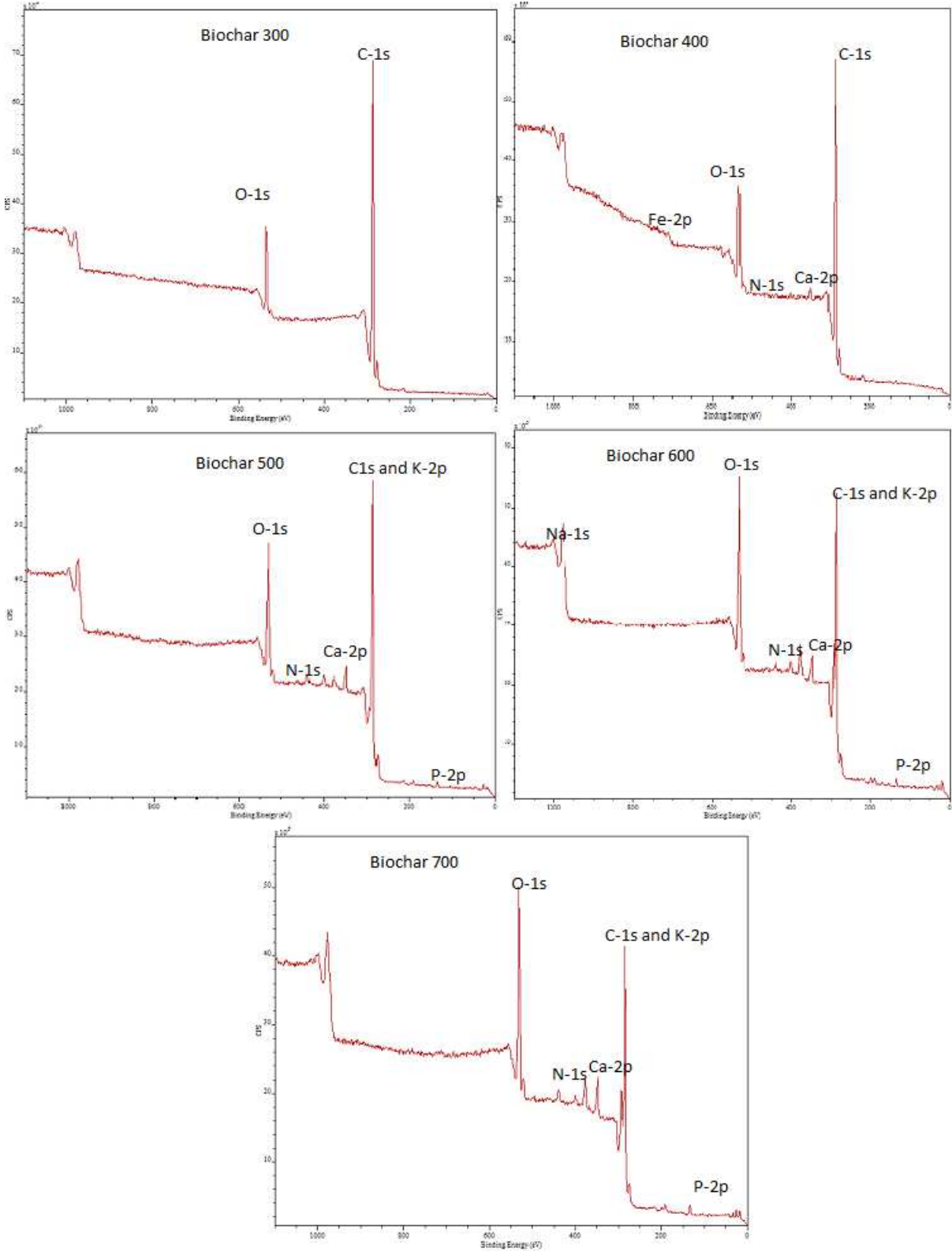


Figure 5. XPS spectra of the produced biochars from EGM at different pyrolysis temperatures

Raman spectrometry was used to further analyze the structure of the biochars produced at different temperatures. At 300 and 400°C, the Raman spectra exhibited a signal without distinguishable peaks (not shown). Such behavior is attributed to high proportion of amorphous carbon structures obtained during the pyrolysis at low temperatures. Above 500°C, the Raman spectra exhibited two relatively broad Raman bands at around 1330-1370 cm^{-1} and 1590-1610 cm^{-1} (Figure 6). These bands correspond to the D-band and G-band, respectively. The D-band is related to sp^2 -bonded carbon with structural defects, while the G-band is related to the in-plane vibrations of the sp^2 -bonded graphitic carbon structures. The region between D-band and G-band, called the valley region “V”, is related to the amorphous carbon structure. From these spectra, structural parameters such as ID (D band intensity height), IG (G band intensity height), IV (Valley region intensity height) as well the different ratios ($\frac{ID}{IG}$, $\frac{IV}{IG}$, $\frac{IV}{ID}$) have been derived in order to get valuable information regarding the char structure.

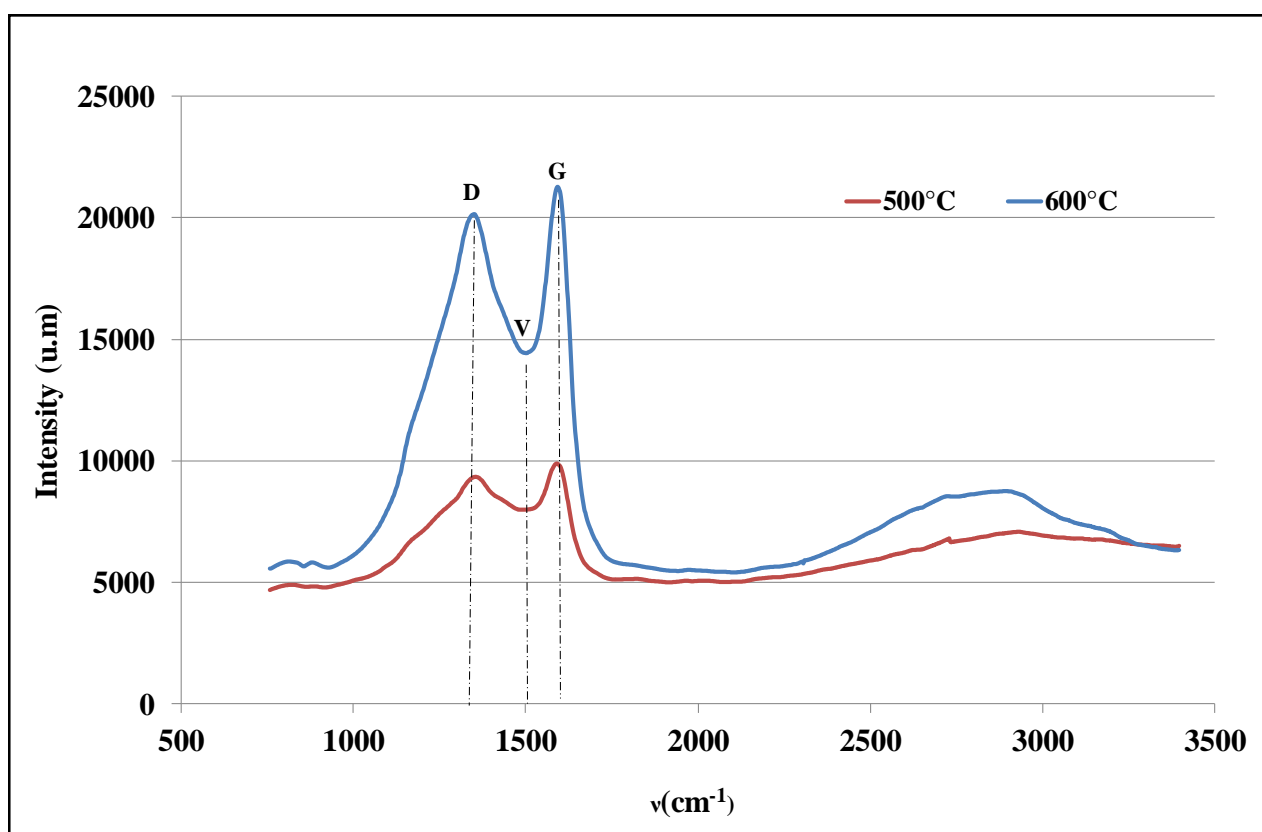


Figure.6. Raman spectra of the EGM biochars produced at different temperatures

The values derived from Figure 6 show that the IV/IG ratio decreases from 0.814 at 500°C to 0.682 at 600°C. Similar trend is also observed for the IV/ID ratio from 0.865 at 500°C to 0.715 at 600°C. Such behavior is attributed to the char evolution structure with pyrolysis severity from the amorphous carbon to an organized carbon (turbostratic char). Furthermore, the IG/ID ratio decreases from 1.063 at 500°C to 1.048 at 600°C indicating the increase of the proportion of condensed aromatic ring structures having defects. The D structures are created by the condensation of small aromatic amorphous carbon structures. These findings are in accordance with the ones obtained during the analysis of the structural parameters evolution of wood char under different thermal treatment [28].

3.5 Practical Implication

Several information could be derived from the EGM biochar production and characterization. In fact, experimental results showed that the chars yields production were approximately constant for pyrolysis temperatures above 500°C with an average value close to 33% which is higher than the ones obtained for lignocellulosic biomass feedstocks. This behavior is attributed to the higher lignin and alkali minerals contents. The biochars characterization indicated that the biochar obtained at 500°C has the highest amount of potentially available minerals with an interesting value of surface area and microporosity. These properties make this biochar as a suitable candidate for soil amendments and also pollutants adsorption. However, further investigations regarding their agronomic potential use through controlled plant growth, soil structure improvements and nutrients release/adsorption tests are required.

4.0 CONCLUSION

In this study, slow pyrolysis of exhausted grape marc was carried out at temperatures of 300, 400, 500, 600 and 700 °C and a constant heating gradient rate of 5 °Cmin⁻¹ in perspective of obtaining

specifically featured biochars for potential uses in agriculture as soils amendment and/or in environmental applications as pollutant adsorbent. For this purpose, in depth characterization of the produced biochars including various complementary physico-chemical parameters was performed.

Obtained results indicated that the optimal temperature was 500°C with a chars yield value close to 33%. In addition, the characterization study confirmed the EGM biochar prepared at 500°C has an interesting minerals amount as well as a developed surface area and microposity. These properties make EGM biochar a promising material that could be used as biofertilizers as well as efficient adsorbents.

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