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Research Article

Marble sludges as environmentally friendly catalyst in olive pomace pyrolysis: Effect of sludge composition on pyrolysis product distribution and biochars

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ABSTRACT

Waste management of olive pomace is difficult because of the high production amount and non-biodegradable organic substances. Catalytic pyrolysis process is one of the effective methods for olive pomace (OP) management and for obtaining valuable organic substances from it. Therefore, in this study, different types of marble sludge were used as catalyst in the olive pomace pyrolysis process at 500 °C temperature and 40% catalyst dose. While K1, K2, K3 are the sludges obtained from physicochemical treatment of travertine type marble processing wastewater with alum, $FeCl_3$ and PEL, respectively, K4,K5 and K6 are the corresponding physicochemical treatment sludges of natural stone type marble processing wastewater. Pyrolysis product yields and characteristics of pyrolysis biochars were investigated. The highest product yield for biochar liquid and gas fractions was obtained with the K1 catalyst. The biochar obtained for OP+K1 pyrolysis has the highest initial decomposition temperature. Biochar obtained by using K6 was more granular. Biochar having the highest calorific value (1193 cal/g) was obtained with the catalytic pyrolysis of OP with K4 catalyst. Biochars obtained with the K1 and K6 catalysts have similar calorific values. Besides calorific values, the characteristics of biochars indicated that these biochars can be used for diverse purposes either as additive or feedstock. Consequently, K1 catalyst can be recommended for olive pomace catalytic pyrolysis when biochars are evaluated in terms of product yield and biochar characteristics.

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INTRODUCTION

Türkiye is among the Mediterranean countries where olive and olive oil production is high. Approximately 225,000 tons of olive oil was produced in Türkiye in 2020 [1]. Olive pomace (OP), which is a solid waste consisting of olive seed, the pulp of the olive, water and oil, is generated during the olive oil production process. Waste management of OP is very difficult due to the high production amount of pomace, the difficulties in the treatment, and the presence of non-biodegradable organic substances in it. One of the effective methods for OP management and obtaining valuable organic substances from it is pyrolysis. Especially catalytic pyrolysis process has been studied commonly since it has important advantages over conventional pyrolysis process such as selectivity of valuable substances formed during the pyrolysis, enhancement of quality and quantity of pyrolysis products [2]. Although in OP pyrolysis various catalyst types were studied, carbonate-derived catalysts, such as dolomite ($CaMg(CO_3)_2$), potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3),

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iron carbonate ($FeCO_3$), calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$), calcium oxide (CaO), calcium hydroxide ($Ca(OH)_2$), magnesium oxide (MgO) and lithium carbonate (Li_2CO_3), are mostly preferred among them since they are readily available and low cost [3, 4]. Thermal and mechanical strength of dolomite catalyst is high and therefore it can be used more than once with little performance degradation. In a study, it was emphasized that catalytic efficiency of dolomite in the pyrolysis process remain almost constant [5]. As for other catalyst types, performance on the product yields can be changed. For instance, in the study about catalytic effects of K_2CO_3 and Na_2CO_3 in OP pyrolysis process stated that catalytic effect of these on product yields are irregular but mostly K_2CO_3 had a better catalytic effect than the Na_2CO_3 [6]. Similarly, catalytic effect of $Ca(OH)_2$ and CaO vary with pyrolysis temperature and the material being pyrolyzed. In the pyrolysis process of OP and $Ca(OH)_2$, biochar quantity increased and liquid fraction decreased with catalyst [7]. Although various catalysts have been used to improve the process in OP pyrolysis, there are very few studies that partially place the waste material in the catalyst.

Marble processing plant wastewater is formed with the combination of marble dusts released during marble processing and the water used during marble cutting processing. These wastewaters are an important source of pollutants for the environment, agricultural lands, and water resources [8, 9]. For this reason, physicochemical treatment, such as coagulation-flocculation-sedimentation process, is applied commonly for the treatment of these wastewaters. It is important that the marble sludge produced as a result of this treatment process should not be released directly to the environment, as it will have adverse effects on the environment. It is important to apply economical and feasible alternatives that will provide recycling of these sludges to the system. Moreover, the properties of marble sludge varied based on the coagulant type used in the coagulation-flocculation-sedimentation process. Different coagulants and flocculants have been studied for andesite and travertine type marble processing wastewaters and it has been observed that the characteristics and structures of the physico-chemical treatment sludge obtained with each of them are different from each other [8, 9]. Therefore, in this study, first, different type of marble sludges were obtained as physico-chemical treatment sludge by applying alum and $FeCl_3$ as coagulant to travertine and natural stone type of marble processing effluents. Additionally, the sludges produced by using polyelectrolyte in the processing facility were collected. The prepared six types of marble sludges were studied as catalyst in the OP pyrolysis process. Thereby, marble sludges were utilized as environmentally friendly catalysts in OP pyrolysis by prevention of negative effects of marble sludges on environment and by providing conversion waste material to the useful products via pyrolysis. Pyrolysis biochars obtained from catalytic pyrolysis of OP-marble sludge mixtures were investigated in terms of surface morphology, surface acidity, thermal behavior, heating, and ash value. In this way, a symbiotic, sustainable, and environmentally friendly approach has been applied in the disposal of OP and marble sludge wastes.

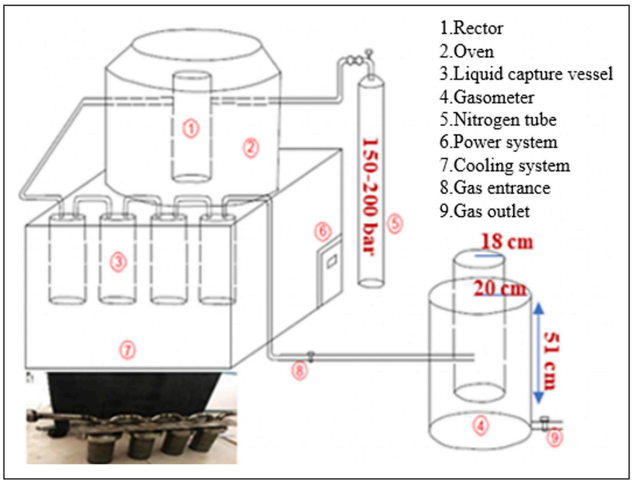


Figure 1. Fixed bed batch pyrolysis system.

Table 1. Types and given codes of the marble sludges

The type of marble whose processing wastewater was used	Chemical used in coagulation-flocculation treatment	Code of marble sludge in this study
Travertine	$Al_2(SO_4)_3$.18H2O	K1
Travertine	$FeCl_3$	K2
Travertine	PEL*	K3
Natural stone	$Al_2(SO_4)_3.18H_2O$	K4
Natural stone	$FeCl_3$	K5
Natural stone	PEL*	K6

*: Sludges produced by using polyelectrolyte in the processing facility.

MATERIALS AND METHODS

The studied OP samples were obtained from the Ernar Ind. Trade. Co. Ltd. olive oil production facility operating in Mersin/Erdemli-Türkiye. Travertine and natural stone type marble processing effluents were taken from the marble processing facility of REMAR Co.Ltd. (Konya-Türkiye). The coagulation-flocculation and sedimentation processes were carried out on the marble processing effluents with the help of alum ($Al_2(SO_4)_3.18H_2O$) and iron (III)chloride ($FeCl_3.6H_2O$) coagulants in a Jar test setup (VELP-FC6S model). Conditions determined in previous studies were used for the coagulation-flocculation and sedimentation process [8, 9]. After the coagulation-flocculation and sedimentation, the supernatant part of the samples was withdrawn, the remaining settled sludge was dried at 40–50°C and sieved through a 300-micron-sized sieve. The abbreviations of the marble sludge samples used in the study were indicated in Table 1.

Catalytic pyrolysis process of OP-marble sludge mixtures was conducted in fixed bed batch pyrolysis system (Fig. 1) with at least two replicates at 500°C temperature, 40% catalyst dose and with 100 g total weight of OP-marble sludge mixtures. The pyrolysis char and oil obtained after pyrolysis were collected separately, weighed on a precision balance, and recorded as a percentage. The pyrolysis gas was collected in the gasometer and the volume of the collected pyrolysis gas was calculated

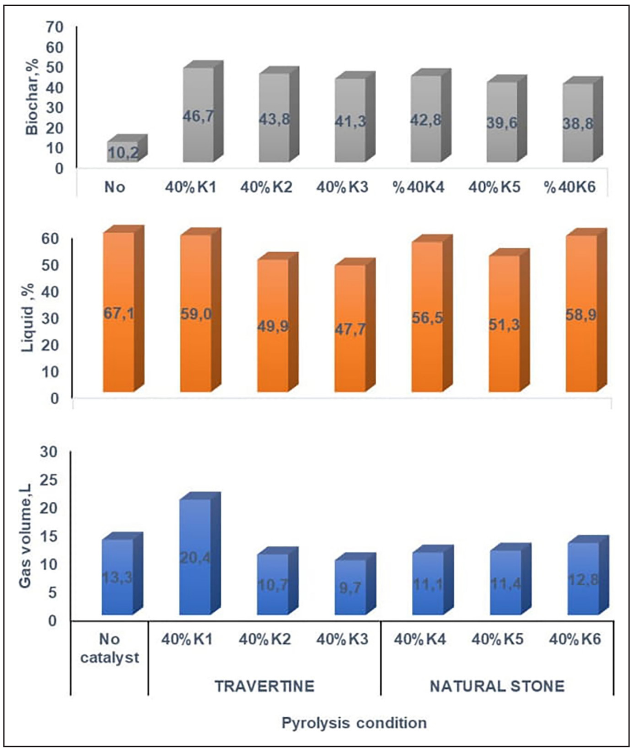


Figure 2. Pyrolysis product fractions obtained from the pyrolysis of OP with different catalysts at 40% dose and 500°C temperature.

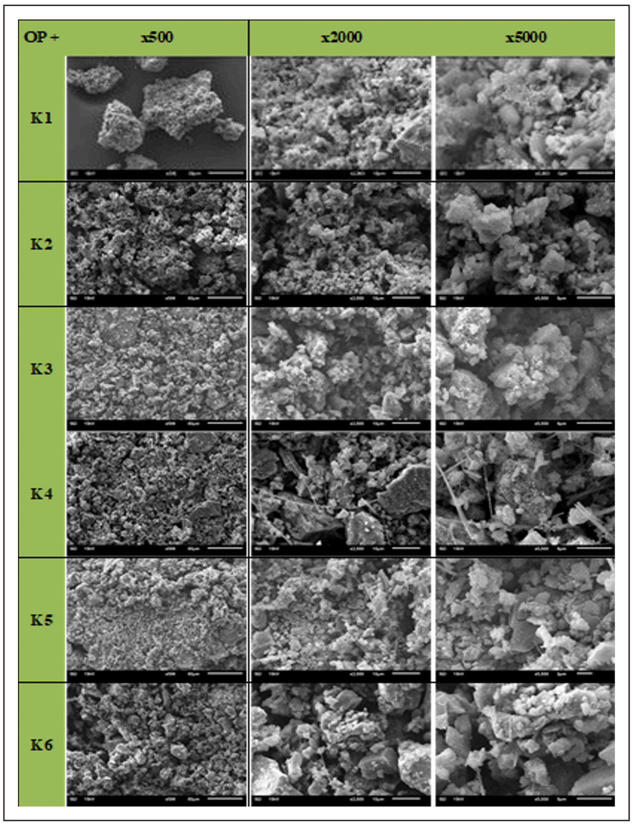


Figure 3. SEM images of pyrolysis biochars obtained from the pyrolysis of OP with different catalysts at 40% dose and 500°C temperature.

by measuring the rise in the gasometer and gasometer surface area. SEM imaging, acidity analyzes, and thermogravimetric analysis (TGA) were performed for the characterization of the obtained pyrolysis biochars. Furthermore, ash content and calorific value of biochars were revealed. SEM analyses were conducted at JEOL-JSM-6610 model device, at 15 kV acceleration voltage. Surface acidity of the biochars were determined titrimetrically as follows: Isopropyl alcohol-toluene mixture (v/v; 1:1) and 1% phenolphthalein solution prepared with isopropyl alcohol was added to the sample as solvent and 0.1% N KOH solution was used for the titration of sample up to observing pink color. Equation 1 was used for acid value calculations.

$$\text{Acid value (mmol/g)}=(A-B)N/W \qquad (1)$$

A: Standard alkali volume used in titration (mL)

B: Standard alkali volume used in titration of blank (mL)

N: Standard alkali normality

W: Sample weight (g)

As for TGA analyses, PerkinElmer TGA4000 Model device was used at a rate of 20 mL/min nitrogen gas flow, 20°C/min heating rate and 900°C target temperature. Leco AC-350 Model Calorimeter Device was used for the determination of heat values of biochars at 15–20 atm pressure.

RESULTS AND DISCUSSION

Pyrolysis Product Yields

The product amounts of OP obtained at 500°C, 40% catalyst dose with different catalysts were shown in Figure 2. Travertine marble sludges (K1, K2, K3) had higher pyrolysis biochar product amount compared to marble sludges obtained from natural stone (K4, K5, K6). Catalysts obtained by using alum chemical (K1 and K4) had higher biochar amount than catalysts obtained with $FeCl_3$ and PEL for both types of marbles. The highest amount of OP biochar belonged to K1 catalyst. Similar to biochar findings, pyrolysis liquid product quantities were very close to each other. The most obvious difference between the catalysts was observed for the pyrolysis product gases. The gas product volume of K1 catalyst was higher than other catalysts. The main components of all of the marble sludge samples are Ca, C, O, and Mg, and minor components were Al and Fe inorganics which come from the used coagulants in the physicochemical treatment process. Since the catalytic effects of each inorganic in the catalyst structures are different from each other, this also affected the amount of pyrolysis products. When all pyrolysis products were evaluated in general, the highest product yield in OP pyrolysis biochar liquid and gas was obtained with the K1 catalyst.

Characteristics of Pyrolysis Biochars

SEM images of biochars formed from catalyzed OP pyrolysis generally showed a rough and amorphous structure (Fig. 3). It has been reported that some amorphous carbon structures are formed during pyrolysis due to the degradation of cellulose and that these structures can form micropores [10]. It can be said that the biochar obtained from the OP

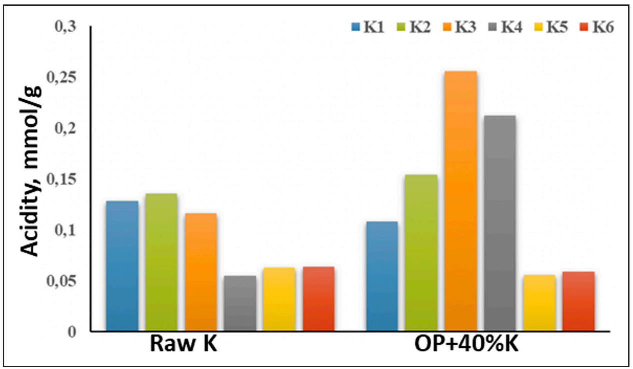


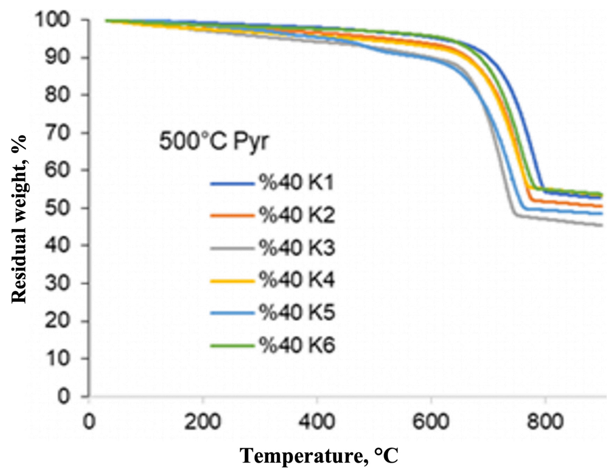
Figure 4. Surface acidity of biochars.

pyrolysis using K6 catalyst had a more granular distribution, and the lignocellulosic structures are more decomposed by the effect of this catalyst. A similar situation was observed in SEM images of biochars obtained with other catalysts.

The surface acidity values of the pyrolysis biochars obtained as a result of the pyrolysis of OP with different catalysts at 40% dose and 500°C were presented in Figure 4. According to the graph, acidity of raw catalysts generated from the travertine was higher than the raw catalysts of natural stone. However, this situation was not valid for the pyrolysis biochars. As for biochars, the highest surface acidity was observed at biochars obtained pyrolysis of OP with K3 and K4 catalysts. Therefore, it can be emphasized that used chemicals as coagulant during the physicochemical treatment of marble wastewater have effect on the biochar surface acidity.

The TGA thermograms and thermal resistance values of the pyrolysis biochars were presented in Figure 5. It can be stated that the thermal strengths up to about 420°C were close to each other and the residual masses of biochars obtained from pyrolysis with K1, K4 and K6 were similar to each other. Residual percentages ranged from 46 to 54.5%. DT1 (565°C) and T10 (701°C) values of OP+K1 pyrolysis biochars were higher than biochars obtained with other catalysts.

The heat values and ash percentages of raw catalysts, raw OP+K mixtures and pyrolysis biochars obtained at 40% dose, 500°C were presented in Table 2. The heating values of the raw catalysts were close to each other and vary in the range of 5.8–7.08 cal/g. Due to the high moisture content of the OP waste, the heating values of the raw OP+K mixtures



Sample		Thermal resistance values					Residual
Type	40% catalyst	DT1* (°C)	DT2** (°C)	T_5 (°C)	T_{10} (°C)	T_{50} (°C)	at 850°C (%)
OP pyrolysis biochars, 5°C/min	K1	565	-	612	701	-	53.35
	K2	402	593	523	664	-	51.09
	K3	391	559	339	600	743	46.22
	K4	319	596	462	659	-	54.29
	K5	391	566	423	583	764	48.97
	K6	511	-	625	685	-	54.33

*DT1-first decomposition temperature; **DT2-second decomposition temperature; T5, 10, 50: Temperatures at which 5%, 10% and 50% decomposition occurs

Figure 5. Thermal characteristics of biochars.

were quite low and close to each other. While the biochar sample with the highest calorific value in OP+K pyrolysis was obtained with the K4 catalyst with a calorific value of 1193 cal/g, the biochar obtained with the K1 and K6 catalysts gave a similar calorific value. However, the calorific values of all biochars were mostly lower than the conventional fuel. This can be attributed to the high catalyst ratio found in the biochars. Therefore, usage of produced biochars as fuel is not recommended but they can be used as catalysts for another pyrolysis cycle thanks to high catalyst ratio.

Table 2. Heating value and ash percentages of raw catalysts, raw OP+K mixtures and pyrolysis biochars

Catalyst	K1	K2	K3	K4	K5	K6
Raw catalyst heat value (cal/g)	7.08	8.6	6	5.8	6.9	6.5
Raw catalyst ash content (%)	63.9	56.4	58.7	55.4	56.2	87.1
			OP+40%K heating value (cal/g)			
Raw mixture	7.3	19.2	8.6	11.4	13.4	9.5
500°C Pyr	1041.1	800.2	781.1	1193.4	967.6	1087.6
			OP+40%K ash content (%)			
Raw mixture	24.2	25.0	23.2	24.3	21.7	19.0
500°C Pyr	51.1	49.4	50.9	49.5	51.5	50.5

The ash contents of the raw catalysts vary between 55.38% and 87.06%, and the highest ash content belongs to the K6 catalyst. There was no direct reflection of the ash contents of the raw catalysts to the ash contents of the mixtures. In OP samples, no significant difference was observed in terms of ash contents for all catalysts and close values were obtained (Table 2). Pyrolysis biochar contained higher ash quantity than raw mixtures. This can be connected to the presence of the catalyst and increased concentration of inorganic components and organic matter pyrolytic reaction residues in the biochar content.

CONCLUSIONS

In this study, different marble sludge types were used in the OP pyrolysis process as catalyst and biochars obtained at catalytic pyrolysis process were examined in terms of surface morphology, surface acidity, thermal behavior, heating, and ash value. While the pyrolysis biochars and liquids quantity were close to each other for all catalyst type, obvious difference was observed in the gas volumes. The highest gas volume obtained at OP-K1 pyrolysis process. All biochar samples had rough and amorphous structure and OP pyrolysis using K6 catalyst had a more granular distribution, and the lignocellulosic structures are more decomposed by the effect of this catalyst. Although no systematic effect was obtained for the surface acidity of the biochars, an increment was observed in the surface acidity values of the biochars compared to the raw catalyst. As for thermal characteristics of biochars, it can be stated that OP-K1 biochars have higher DT1 (565°C) and T10 (701°C) values comparing to the others. The highest calorific values in OP+K pyrolysis biochars were obtained with K4 (1193 cal/g), K6 (1087 cal/g) and K1 (1041 cal/g), respectively. Usage of produced biochars as fuel is not recommended since their heat values are not high as much as conventional fuels, however; they can be used as catalysts for another pyrolysis cycle thanks to high catalyst ratio. All in all, K1 catalyst can be recommended for olive pomace catalytic pyrolysis when biochars are evaluated in terms of yield and characteristics.

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DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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