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Comparison of Ca-Based Commercial and Natural Catalysts Performance on Olive Pomace Pyrolysis Process

Gamze GÖKTEPELİ[1*], Esra YEL[1]

Highlights:

- Catalytic effect of $Ca(OH)_2$ and marble sludges on pyrolysis process were compared
- Marble sludge showed a comparable catalytic effect with $Ca(OH)_2$
- Using marble sludges in olive pomace pyrolysis process contribute waste management with sustainable, zero waste and upcycling approaches

Keywords:

- Ca-based catalyst
- Marble waste
- Olive pomace
- Pyrolysis

ABSTRACT:

Physicochemical treatment was applied with 20 mg/L alum to the marble processing effluents as 5 minutes 200 rpm mixing, 25 minutes 15 rpm mixing and 60 minutes settling and marble sludge (MS) was produced. Catalytic performance of MS in olive pomace (OP) pyrolysis process was evaluated and compared to commercial $Ca(OH)_2$ since it mainly comprises of different AAEMs (especially Ca and its forms such as $CaCO_3$, CaO) functioned as catalyst. Catalytic pyrolysis was conducted at 600°C and 5°C/min heating rate with 5% and 10% catalyst (MS or $Ca(OH)_2$) dosages. Although both catalysts had important effect on pyrolysis product yields, $Ca(OH)_2$ was found as good alternative for higher gas production and MS was introduced as better option for the higher char production comparing to the conventional OP pyrolysis. Pyrolysis biochars produced with MS were in higher thermal strength than the biochars generated with $Ca(OH)_2$. Moreover, biooils of OP+MS include different organic compounds, such as 9 heptadecanol, 1-eicosanol, ethyl linoleate, ethyl oleate, addition to the compounds observed in pyrolysis liquids of OP and OP+ $Ca(OH)_2$. All detected organic components have diverse usage areas. $Ca(OH)_2$ provided more decrement in the percentages of oxygenated compounds as compared to the MS. Consequently, it can be stated that MS can be used successfully as an alternative to Ca-based commercial catalyst in OP pyrolysis.

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This study was produced from the PhD thesis of Gamze GÖKTEPELİ.

INTRODUCTION

Olive pomace (OP) is the solid by-product of the olive oil extraction process. OP includes oil, pulps, pits and skin. Although characteristics of OP depend on many factors related to the conditions that olive tree has grown, such as topography, climate, soil types etc., polysaccharides, proteins, other pigments, lignocellulosic polyalcohol, polyphenols, and fatty acids are the main organic components of it. If it is not well managed, OP is a waste which may cause adverse effects on the environment because of its high moisture content, acidic pH and non-biodegradable organic components (Ayadi et al.,2021). In the case of land disposal, it can increase the soil hydrophobicity and infiltration rate because of its oil and polyphenols content (Ayadi et al.,2021). These problems can be prevented when OP is converted into economically valuable products and/or fuel with the thermochemical processes, such as pyrolysis.

Pyrolysis is one of the suggested methods in proper waste management in which the thermochemical fractioning of organic structures into solid, liquid and gas fractions provide recovery of economically valuable products. It has been widely used for lignocellulosic biomasses, such as OP, by researchers (Caglar et al.,2002; Kumar et al.,2017; Dinc et al.,2018). The end products of biomass pyrolysis, namely pyrolysis biochar, biooil and gas, can be evaluated in many different areas with diverse purposes. Pyrolysis biochar can be used as adsorbent, composite filler material, fuel, soil improver etc. (Kumar et al.,2017). Pyrolysis biooil and gases can be evaluated in recovering valuable compounds and/or in producing energy (Dinc et al.,2018).

Catalysts have been used in biomass pyrolysis process for several purposes, such as for the reduction in pyrolysis temperature, time and cost of achieving the same products; also for the production of the more value-added products. Alkaline earth metals (AAEMs) are one of the commonly used, effective, and attractive catalyst types. Cost is a very critical parameter for the catalyst selection since catalysts can easily be coked and cause to deactivation in pyrolysis process. Ca is cheaper and effective catalyst at lignocellulosic biomass pyrolysis as compared to other common catalysts Co and Ni (Luo et al.,2020). In a study conducted by Chen et al., (2017) pyrolysis biooil quality was enhanced with CaO catalyst by decreasing tar content and oxygenated compound quantity in fluid products. Similarly, Mohammed et al. (2017) indicated that the value-added chemicals in the pyrolysis liquids increased with $Ca(OH)_2$ usage in *Napier grass* pyrolysis. Zhang et al. (2022) emphasized that agglomeration in pyrolysis due to the lignin particles of lignocellulosic biomasses can be prevented with $CaOH_2$ and/or $Ca(HCOO)_2$ addition. Likewise, catalytic effect of CaO and/or $CaCO_3$ on pyrolysis tar via cracking, deoxgenation, deacidification reactions was emphasized in the literature (Zhao et al.,2019; Li et al., 2021). Furthermore, Ban et al., (2022) indicated that the distribution of the pyrolysis products, especially oxygenated compounds, considerably affected from Ca additives during coal pyrolysis. $CaO/CaCO_3$ can be used in catalytic pyrolysis in three forms: pure, modified and waste $CaO/CaCO_3$ (Li et al., 2021). Among these forms, waste $CaO/CaCO_3$ was highly recommended for catalytic pyrolysis when considered from economic aspects. Ca containing wastes that especially generated during the industrial applications can be evaluated as catalysts in biomass pyrolysis due to both their high production quantities and low costs. However, most of these wastes are just being landfilled, even disposed via simple dumping and they have not been efficaciously evaluated in large scale. In addition, Ca-based catalysts used in the pyrolysis were mostly commercial catalysts (Mutlu, 2012; Aysu et al., 2016; Yang et al., 2018) and there are very few studies that use the waste material in the Ca-based catalyst. In pyrolysis, catalytic effect varies based on the Ca form (such as oxides, hydroxides, phosphate etc.). For instance, Luo et al., 2020 emphasized that catalytic effect of

$Ca(OH)_2$, $CaCO_3$, $CaCl_2$, CaO, $Ca(H_2PO_4)_2·H_2O$ on municipal sludge during the pyrolysis differ based on bond energy and solubility in water. Therefore, it can be inferred that Ca-containing wastes have potential vital importance for catalytic pyrolysis process.

Marble sludges (MSs) are being produced at high quantity at the end of the physicochemical treatment process (coagulation-flocculation-sedimentation process) of marble processing effluents and they are accumulated mostly onto the land of the marble processing plant. Therefore, they cause pollution in the environment, agricultural lands, and water resources (Onen et al., 2022; Goktepeli, 2023). On the other hand, MSs contain different AAEMs (especially Ca and its forms such as $CaCO_3$, CaO) that can function as catalyst for pyrolysis process depending on the marble structure and physicochemical process. It can be emphasized that these physicochemical treatment sludges can have a potential as being catalysts for agricultural biomass pyrolysis process. However, to the best of authors' knowledge there have not been any study evaluated the catalytic performance of these wastes in OP pyrolysis without any pre-treatment by investigating both yield and characteristics of pyrolysis end products. Therefore, in the presented study, catalytic performance of marble sludge, generated from physicochemical treatment of marble processing industry effluents with alum, in OP pyrolysis process were revealed by comparing with commercial $Ca(OH)_2$. Catalytic performances of both waste and commercial Ca-containing materials were compared in terms of pyrolysis product yields, thermal characteristics of pyrolysis biochars and valuable organic compounds in pyrolysis biooils. Ca-containing waste materials are environmental problems in the environment when disposed without control. However, by the suggested evaluation method in this study, it is aimed to introduce them as economical values and environmental solutions via proper waste management approach.

MATERIALS AND METHODS

Waste Materials

OP lignocellulosic biomass samples were obtained from a two-phase olive mill facility (Mersin/Türkiye) soon after olive picking season and they were stored in freezer.

Marble processing effluents were collected from a marble processing facility (Konya/Türkiye) and physicochemical treatment was applied to produce marble sludge (MS). In the process, coagulation-flocculation and sedimentation was applied by using alum ($Al_2(SO_4)_3.18H_2O$) as coagulant in VELP-FC6S model Jar test setup. Optimum conditions for physicochemical treatment process were selected based on the previous literature on the same wastewater as follows: 1.5 minutes rapid mixing with 200 rpm, 25 minutes slow mixing with 15 rpm and 60 minutes settling under 20 mg/L alum chemical dosage (Onen et al.,2018; Onen et al.,2022). After physicochemical treatment, the settled sludge was collected, dried at 40-50°C and sieved through 300-micron-sized sieve (Onen et al.,2018).

The catalytic effect of different types of Ca-based catalysts were compared at two different OP and MS/$Ca(OH)_2$ mixing ratios as 95:5 and 90:10 (w/w) respectively. Pyrolysis temperature and heating rate was set as 600°C and 5°C/min respectively, in the fixed bed batch pyrolysis system. Pyrolysis gas, biooil and biochar fractions were collected separately, quantified and characterized by analyses. TGA analyses for biochars were conducted with PerkinElmer - TGA4000 Model device at 20 mL/min nitrogen flow as carrier gas, 900°C target temperature and the heating rate was 20°C/min. Shimadzu QP2020 GC-MS device with DB-5MS capillary column with 30m x 0.25µm x 0.25µm (length x diameter x film thickness respectively) were used for GC-MS analyses of pyrolysis liquids.

RESULTS AND DISCUSSION

Pyrolysis Product Yields

Pyrolysis product yields of OP obtained with/without $Ca(OH)_2$ or MS addition were given in Figure 1. Liquid decrement and char increment for both 5% and 10% $Ca(OH)_2$ were observed in catalytic OP pyrolysis with $Ca(OH)_2$. These results are comparable with the literature. For example, Aysu et al., (2016) emphasized that Na_2CO_3, $ZnCl_2$ catalysts increased pyrolysis liquid quantities in *Anchusa azurea* pyrolysis, $Ca(OH)_2$ affected vice-versa. Similarly, $Ca(OH)_2$ resulted in biooil decrement and enhanced gas and biochar formation in sugarcane bagasse pyrolysis. $Ca(OH)_2$ dehydration process caused changes in the product yields. Pyrolysis process and product yields are affected from the water released in Ca dehydration process (Wang et al.,2010). However, since this dehydration process is affected by both pyrolysis temperature and biomass type, reverse effects can also be seen when the pyrolysis conditions changed. For instance, biooil quantity of pine wood pyrolysis with $Ca(OH)_2$ firstly decreased at 350 and 400°C temperature and then started to increase after 700°C (Wang et al.,2010). Similar effects were observed in this study at MS addition for pyrolysis biochar and biooil. Encinar et al., (2009) indicated that biooil quantity decreased with increment in dolomite dosage in OP pyrolysis at 500°C-700°C temperatures. Pyrolysis gas percentages decreased with 10% MS as compared to non-catalyzed OP pyrolysis (Figure 1). The pyrolysis biochar and biooil quantities fractioned with MS were slightly higher than the quantities produced with $Ca(OH)_2$. Increment in the pyrolysis biochar with MS addition can be attributed to the thermal resistance of the MS since its structure is similar to the dolomite ($Ca{\bullet}Mg(CO_3)_2$). It can be emphasized that instead of noncatalytic OP pyrolysis, $Ca(OH)_2$ can be used as catalyst if higher gas production was aimed. However, MS is better option for the higher biochar production.

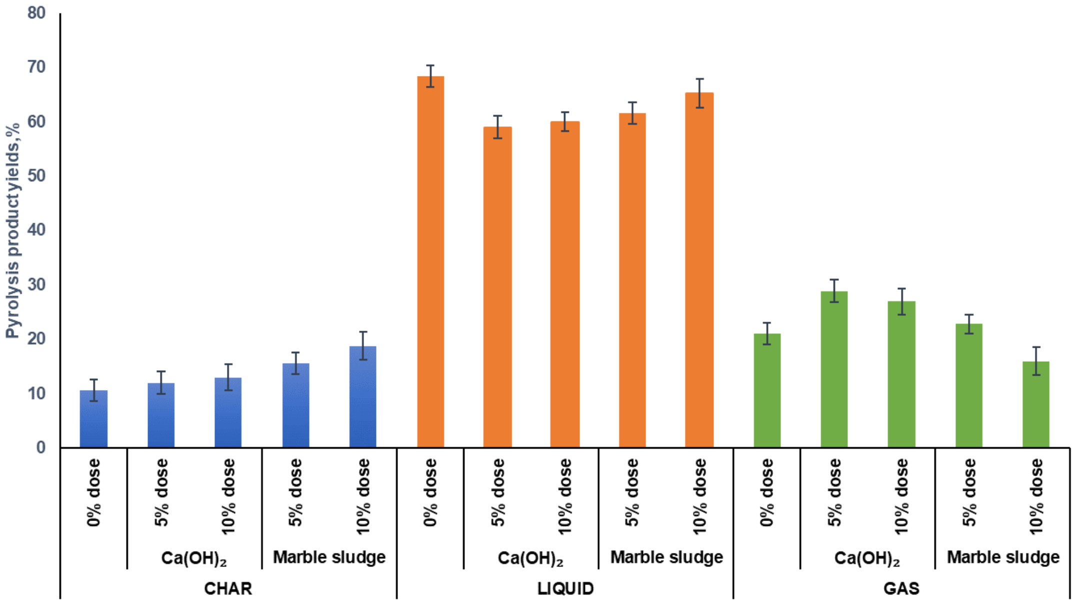

Figure 1. Comparison of Catalytic Effects of $Ca(OH)_2$ and Marble Sludges on OP Pyrolysis Product Yields (adapted from Goktepeli,2023)

Thermograms of pyrolysis biochars obtained with $Ca(OH)_2$ and MS addition to the OP waste were indicated that the initial mass losses were observed at 400-450°C for all pyrolysis chars (Figure 2). However, mass loss in pyrolysis biochars obtained with MS were lower than others and the highest mass loss was detected with 10% $Ca(OH)_2$. This result can be attributed to the thermal dehydroxylation of $Ca(OH)_2$. Khachani et al., (2014) indicated that around 476°C is the temperature which was observed thermal dehydroxylation of $Ca(OH)_2$ and the maximum weight loss occurred at

Tmax=459.3°C based on the DTG curves of $Ca(OH)_2$. The second mass losses were obtained at higher temperature (>600°C) for all biochars (Figure 2). It can be stated that biochars fractioned with MS had higher thermal strength than the others since the temperature at which maximum second mass loss observed increased with the usage of MS instead of $Ca(OH)_2$. While second mass loss was observed at temperature between 600-650°C for noncatalytic pyrolysis biochars and biochars obtained with $Ca(OH)_2$, mass loss occurred at around 700°C for pyrolysis biochars with MS (Figure 2).

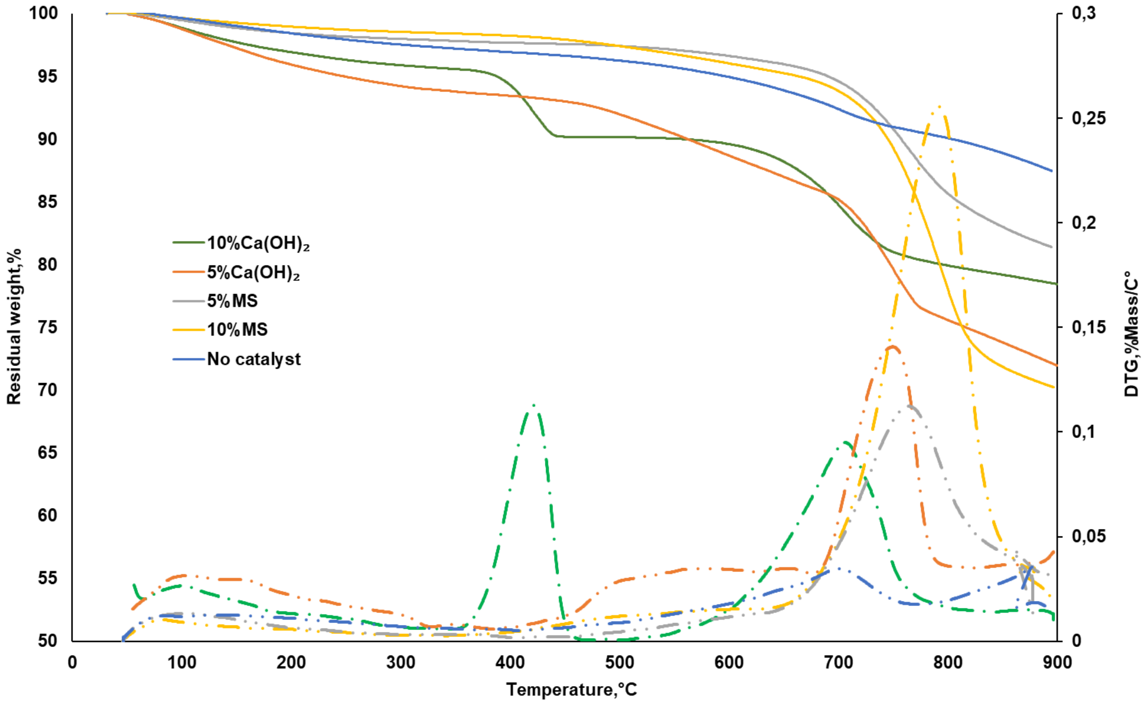

Figure 2. Thermal Behaviour of Noncatalytic and Catalytic Pyrolysis Biochars of OP

Fractions and types of organic compounds in the biooils were given in Figure 3 and Table 1, respectively. Aliphatic, oxygenated and aromatic compounds were observed in biooils of all conditions (Table 1). However, $Ca(OH)_2$ and MS addition to the OP made a significant difference in the percentages of organic compounds in biooils (Figure 3). Pyrolysis biooils obtained with $Ca(OH)_2$ and MS led to increment in the fractions of aliphatic compounds and decrement in fractions of oxygenated compounds prominently (Figure 3). These changes in oxygenated and aliphatic compounds in biooils were more as compared to the aromatic compounds in the presence of $Ca(OH)_2$. Similarly, Wang et al., (2010) indicated that new aliphatic compounds were produced in the case of catalytic pyrolysis of pine wood with $Ca(OH)_2$. Edeh et al., (2019) emphasized that dolomite type catalysts have an important effect on the decarboxylation and hydrocracking reactions which results in increment of aliphatic compounds during the lignocellulosic biomass pyrolysis. Furthermore, in *Anchusa azurea* and $Ca(OH)_2$ catalytic pyrolysis, the quantity of oxygenated compounds in the biooil decreased as compared to conventional pyrolysis process (Aysu et al.,2016). Therefore, although it can be emphasized that both $Ca(OH)_2$ and MS exhibited catalytic property during the OP pyrolysis, $Ca(OH)_2$ provided more decrement in the percentages of oxygenated compounds as compared to the MS (Table 1, Figure 3). It was investigated that pyrolysis biooils of lignocellulosic biomasses have mostly low H/C ratio, high viscosity and high oxygen content because of the large molecules and these properties were resulting in limitation to direct uses of pyrolysis biooils (Yel, 2022). Biooils with less oxygenated compounds and more aliphatic compounds have more stable characteristics (Liu et al.,2014). While some aliphatic compounds, such as nonane, decane, tetradecane, pentadecane, heptadecane etc., were observed in all biooils; organic compounds, such as 9 heptadecanol, 1-eicosanol, ethyl linoleate, ethyl oleate etc., were found only in OP+MS biooils (Table 1). These organic compounds have diverse usage areas. For instance, ethyl linoleate is commonly used in cosmetic sectors due to its antibacterial and anti-inflammatory characteristics (Ko et al.,2018). Similarly, 1-Eicosanol can be used in lubricants, plastics, textiles, emulsion stabilizers etc. (URL 1). Therefore, it can be stated that in addition to the compounds observed in biooils of OP and OP+$Ca(OH)_2$, different organic compounds having wide usage area can also be produced from pyrolysis of OP+MS.

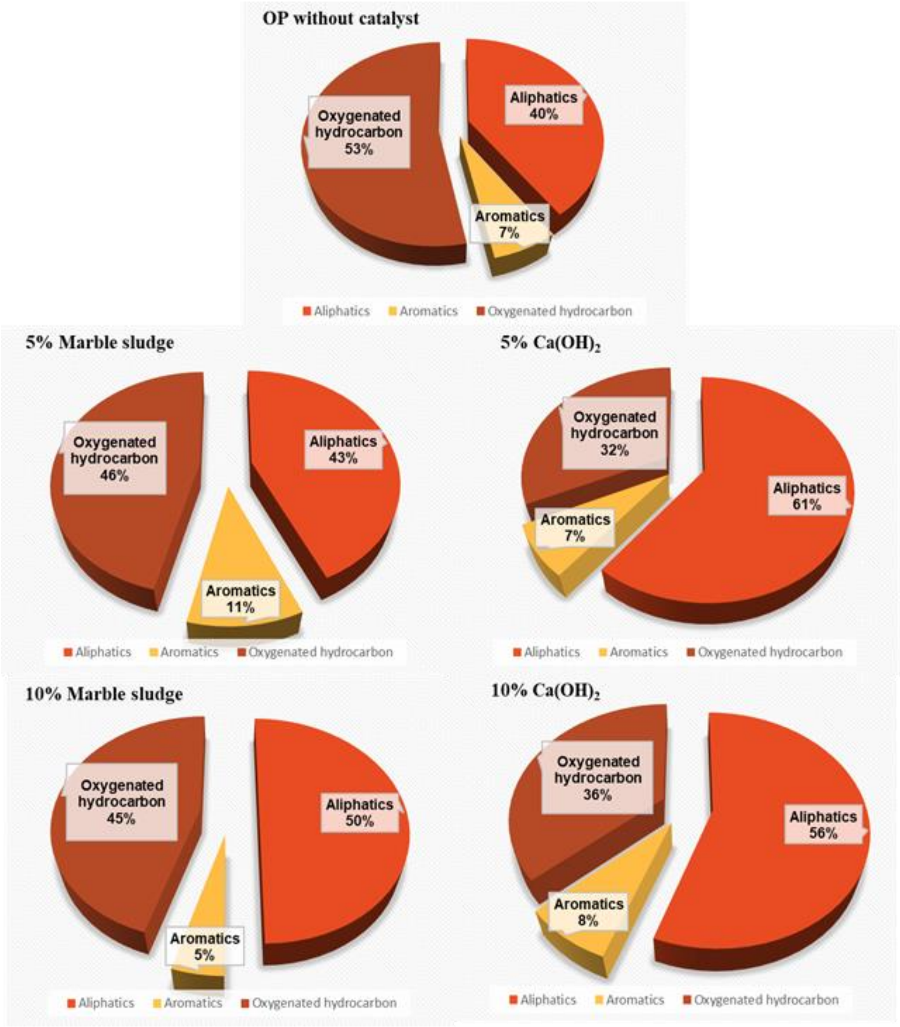

Figure 3. Fractions of Organic Compounds in OP Pyrolysis Oils Obtained with/without Catalyst

Pyrolytic gas densities of catalytic and conventional pyrolysis processes were compared in Figure 4. The pyrolytic gas densities were in the range of 1-1.5 g/L for conventional OP pyrolysis, 2-3 g/L for OP+$Ca(OH)_2$ and 1.5-2 g/L for OP+MS. The higher gas densities obtained in the presence of Ca-based catalysts. The compounds formed in fluid phase during the pyrolysis were more volatile and since the higher volatility cause less condensation, the condensed fractions were lower in catalytic pyrolysis compared to the conventional pyrolysis. Moreover, primary and secondary pyrolysis are the main stages of the pyrolysis process and catalysts have important effect on the secondary pyrolysis reactions. The oil compounds produced during primary pyrolysis process continue to thermally cracking in secondary pyrolysis process via catalyst, thereby gas and hydrocarbon products (C_nH_m) are generated. This results in change in the pyrolysis gas densities (Xu et al.,2022). Lu et al., (2022) emphasized that Ca, Ni, Fe catalysts promote combustible gas formation during biomass pyrolysis, and this can change catalytic pyrolysis densities as compared to the conventional pyrolysis.

Table 1. Organic Compounds in Catalytic OP Pyrolysis Oils at 600^{o}C (+): Compounds Exist in Pyrolysis Oils; (-): Compounds Do Not Exist in Pyrolysis Oils

Compounds	**Pyrolysis conditions**					**Compounds**	**Pyrolysis conditions**				
	0%	5% Ca(OH)$_2$	10% Ca(OH)$_2$	5% MS	10% MS		0%	5% Ca(OH)$_2$	10% Ca(OH)$_2$	5% MS	10% MS
Alkanes						**Alkenes**					
Nonane	+	+	+	+	+	1-Nonene	+	+	+	+	+
Decane	+	+	+	+	+	1-Decene	+	+	+		+
Cyclopropane, 1-hexyl-2-methyl-	-	+	+	-	-	1-Nonadecene	-	-	-	+	-
Octane, 3,5-dimethyl-	+	+	+	-	-	1-Heptene	-	-	-	+	+
Cyclopropane, 1,2-dibutyl-	-	+	+	-	-	1-Undecene	+	+	+	+	-
Cyclopropane, 1-pentyl-2-propyl-	-	+	+	-	-	5-Undecene	-	+	+	-	+
Undecane	+	+	+	-	-	2-Dodecene, (Z)-	-	+	+		-
Nonane, 2,5-dimethyl	+	+	+	-	-	Cyclododecene	-	-	-	+	-
Cyclododecane	+	+	-	-	-	Cyclohexene, 1-octyl-	+	+	-	-	+
Tridecane	+	+	+	-	-	7-Tetradecene	+	+	-	-	-
Decane, 2,5,6-trimethyl	+	+	+	-	-	1-Hexadecene	+	+	+	+	+
Tetradecane	+	+	+	+	+	1-Heptadecene	+	+	+	+	+
Pentadecane	+	+	+	+	+	7-Heptadecene, 1-chloro-	+	-	+	-	+
Cyclododecane	-	-	-	+	+	1-Octadecene	+	+	+	-	
Hexadecane	+	+	+	+	+	9-Eicosene, (E)-	+	-	-	-	+
Heptadecane	+	+	+	+	+	1-Docosene	+	-	-	-	-
Octadecane	+	+	+	-	-	9-Tricosene, (Z)-	+	-	+	-	-
Dodecylcyclohexane	-	+	+	-	-	**Esters**					
n-Pentadecylcyclohexane	+	+	+	-	-	Hexadecanoic acid, methyl ester	+	-	+	+	-
Heneicosane	+	-	+	-	-	Hexadecanoic acid, ethyl ester	+	+	+	+	+
Cyclohexane, nonadecyl-	-	+	+	-	-	9,12-Octadecadienoic acid, methyl ester, (E,E)-	+	+	+	-	+
Alcohols						9-Octadecenoic acid (Z)-, methyl ester	+	+	-	+	-
1-Nonanol	+	+	+	-	-	8-Octadecenoic acid, methyl ester, (E)-	+	-	+	-	+
1-Decanol	-	-	+	+	+	9-Octadecenoic acid, methyl ester, (E)-	+	+	+	-	-
1-Undecanol	+	+	+	-	-	Octadecanoic acid, methyl ester	-	+	+	+	-
1-Dodecanol	+	+	+	-	-	Ethyl linoleate	-	-	-	+	+
n-Tridecan-1-ol	+	+	+	-	-	Ethyl Oleate	-	-	-	+	+
1-Tetradecanol	+	+	+	-	+	Butanoic acid, ethenyl ester	-	-	-	+	+
9-Octadecen-1-ol, (E)-	+	-	+	-	-	**Benzenes**					
9-Heptadecanol	-	-	-	+	+	Ethylbenzene	+	+	+	-	-
1-Octadecanol	+	+	+		+	o-Xylene	+	+	+	-	-
n-Nonadecanol-1	+	+	+	-	+	Benzene, 1,4-dimethyl	+	+	+	-	-
2-Isopropyl-5-methyl-1-heptanol	-	-	-	+	+	Benzene, methyl	-	-	-	+	-
1-Eicosanol	-	-	-	+	+	Benzene, 1,3-dimethyl	+	+	+	-	-
Ketones						**Phenols**					
2-Heptadecanone	+	+	+	-	-	Phenol, 4-methoxy	-	+	+	-	-
3-Octadecanone	-	-	+	-	+	Phenol, 4-ethyl-2-methoxy-	+	+	+	+	+

Table 1. Organic Compounds in Catalytic OP Pyrolysis Oils at 600oC (+): Compounds Exist in Pyrolysis Oils; (-): Compounds Do Not Exist in Pyrolysis Oils (Devamı)

Compounds	**Pyrolysis conditions**					**Compounds**	**Pyrolysis conditions**				
	0%	5% $Ca(OH)_2$	10% $Ca(OH)_2$	5% MS	10% MS		0%	5% $Ca(OH)_2$	10% $Ca(OH)_2$	5% MS	10% MS
Cyclotridecanone	-	-	-	+	+	Phenol, 2-methoxy	+	+	+	-	-
2-Cyclopenten-1-one, 2-methyl	-	-	-	+	+	Phenol, 2,6-dimethoxy	-	-	-	+	+
Cyclotridecanone	-	-	-	+	+	**Acids**					
2-Octanone	-	-	-	+	+	Pentadecanoic acid	+	+	-	+	+
Cyclopentadecanone, 2-hydroxy-	+	-	-	-	-	n-Hexadecanoic acid	+	+	-	+	-
						Oleic Acid	+	-	+	-	-

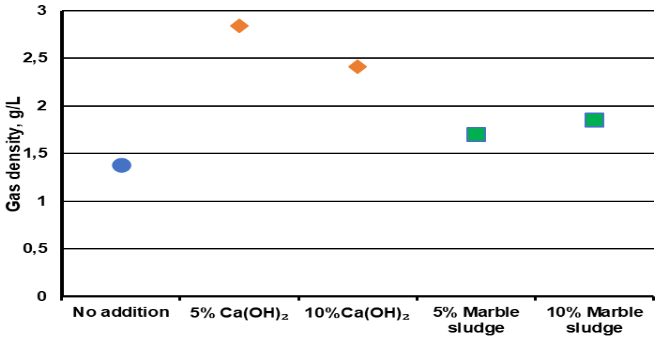

Figure 4. Comparison of conventional and catalytic pyrolysis gas densities (adapted from Goktepeli, 2023)

CONCLUSION

The use of waste material in another process to produce valuable resultant products can contribute waste management with sustainable upcycling with zero waste approaches. This study indicated that MS can be used as an alternative Ca-based catalyst in OP pyrolysis. OP catalytic pyrolysis applied with both MS and $Ca(OH)_2$ had some important advantages over conventional OP pyrolysis. Firstly, higher pyrolysis biochar and gas quantities were obtained with both MS and $CaOH_2$ catalysts. Secondly, characteristic of pyrolysis end products showed an explicit alteration with catalyst usage. For instance, thermal strength of biochars were increased, pyrolysis biooil qualities enhanced with decrement in oxygenated compounds etc. Moreover, the biooils produced with both MS and $Ca(OH)_2$ were including organic compounds having diverse usage areas. This means the produced biooils were new generation feedstock. If the biochar at higher quantity and higher thermal strength is aimed, MS catalyst should be preferred in OP pyrolysis. $Ca(OH)_2$ is a better catalyst option for obtaining more organic structures and better quality in pyrolysis fluid phase fractions.

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Conflict of Interest

The article authors declare that there is no conflict of interest between them

Author’s Contributions

The authors declare that they have contributed equally to the article.

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