



Development of sustainable resource recovery approach from agro-industrial wastes by revealing the economic added value potential

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Abstract

The physicochemical sludge generated from treatment of effluents from marble processing facilities should be managed properly due to their adverse effects on the environment. These sludges can be evaluated as catalyst in pyrolysis since they consist of some inorganics such as CaCO_3 and Al or Fe salts which come from marble structure and coagulation–flocculation treatment of the effluent, respectively. Therefore, in this study, an approach for sustainable resource recovery from agro-industrial wastes (olive pomace) was developed by offering a solution to the two different waste types via pyrolysis and by revealing economic value-added potential of the process. Olive pomace-marble sludge catalyst mixtures were pyrolyzed in a laboratory-scale fixed bed batch pyrolysis system by using four catalyst dosages (10, 20, 30 and 50%) and three pyrolysis temperatures (300, 500 and 700 °C) at 5 °C/min heating rate. Pyrolysis oils and gases were analyzed with GCMS-FID and FTIR for evaluating the potential of economically valuable organic compounds. Organic compounds having extensive usage areas, such as feedstock for surfactants production, emollient, flavoring and softening, and high economic value in the market, such as 1-Pentadecanol, 2-Pentadecanone and Octane, were identified especially in catalytic pyrolysis liquid products. For instance, the potential profit that can be obtained from the conversion of olive pomace to ‘2-pentadecanone’ compound found in catalytic pyrolysis oil produced in this study is around 2.46×10^{13} USD for 2021/22 years at ideal conditions. Consequently, the presented approach contributes to sustainable circular economy via converting wastes into economic value instead of conventional waste disposal methods.

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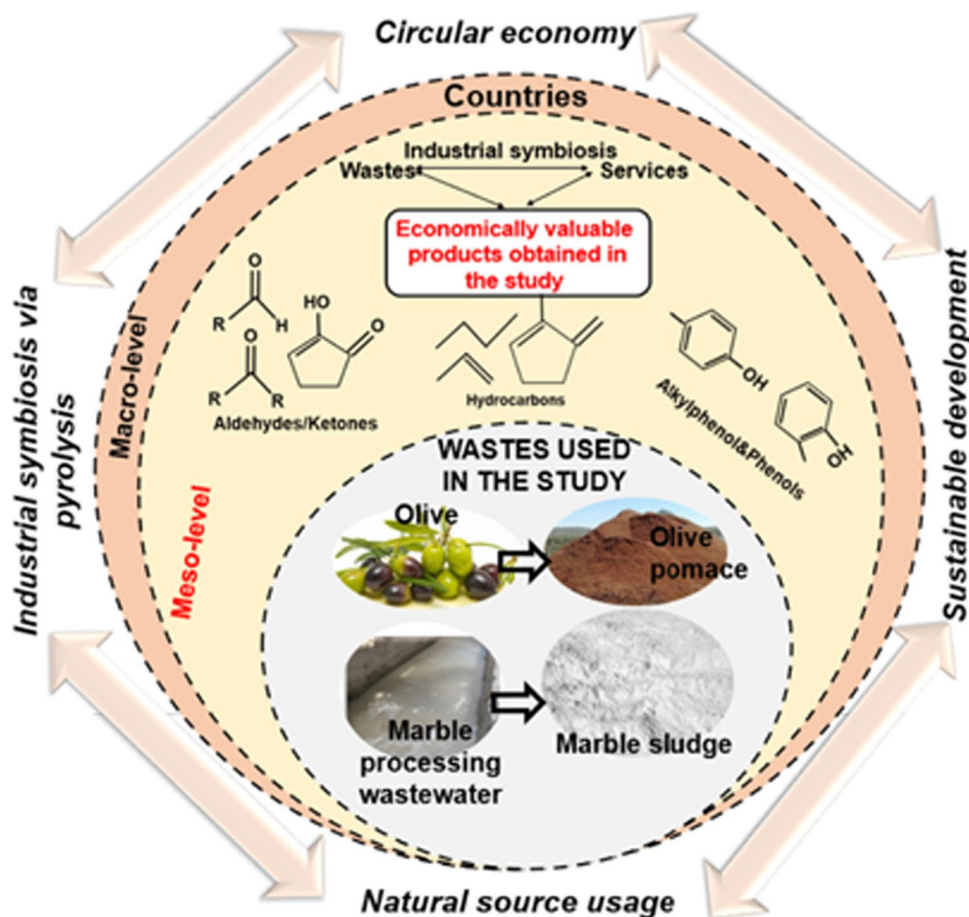
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Graphical abstract



Keywords Agro-industrial wastes · Catalytic pyrolysis · Economically valuable compounds · Marble · Sustainable resource recovery

Introduction

Fossil fuels have been depleted sharply because of global population increment resulting in more energy consumption. Moreover, fossil fuels have significant impacts on global warming and climate change. According to Soeder (2021), fossil fuels and industries cause 89% of global CO₂ emissions. Therefore, researchers have been got into focus on renewable energy sources for a long time. Particulate matter emission and low efficiency are the main problems for solid fuels in comparison with liquid biofuels. As for liquid biofuels, they can be transported easier because of their density, and they can be stored at more controlled conditions compared to solid fuels. Among the renewable liquid fuels, biomass pyrolysis fluid fractions (bio-oil and gas) can be utilized successfully as a substitute of fossil fuels. Research showed that pyrolysis fluid phase with high quality can be obtained especially for lignocellulosic biomass depending

on the characteristics of cellulose, hemicellulose, lignin structures and inorganic elements in the contents of lignocellulosic biomasses (Panchasara and Ashwath 2021). Pyrolysis fluid phases of lignocellulosic biomasses, such as hazelnut shell, wood, sugarcane bagasse as well as olive pomace, can be used effectively for producing value-added products such as ketones, alkanes, alkenes, phenols, benzenes, esters and terpenes. For instance, n-decane compounds found in lignocellulosic biomass pyrolysis fluid phase can be utilized as solvent and they are active components of automotive fuels. In another example, one of the compounds commonly found in pyrolysis fluid phase is methyl oleate that is used in various sector such as detergents, cosmetics, wetting agents, stabilizers, textile treatments, emulsifiers plasticizers for duplicating inks and rubbers (Frankel 2012). The price of terpene compounds, such as α -Pinene, varies between 45 USD and 13,800 USD/kg, depending on the purity level in the US market (URL 1). Similarly, ketone compounds can be



observed at high quantity in pyrolysis fluid phases which are used in many sectors such as oil extraction from vegetables, coating industry, refining process, chemical production, etc. (Shang et al. 2022).

Olive pomace (OP) is the solid residue of the olive oil extraction process which consists of the olive pit, the pulp of the olive, water, and oil. Production rate of OP is noteworthy high in Türkiye, e.g., approximately 650,000 tons OP generation per season (TUBITAK 2015). OP contains 10–56% lignin, 12–24% cellulose, 7–22% hemicellulose, metal and polyphenol (Dinc 2018). It is a type of waste that exhibits phytotoxic and antimicrobial effects. Moreover, OP is non-biodegradable and contains many organic components. For all these reasons, OP disposal is both an economic and technical problem, and there is a need to implement safe and economical solutions for its disposal. On the other hand, OP contains many valuable compounds and significant inorganic components. Therefore, new technological solutions and productive approaches have the importance for bringing OP to economy.

In the pyrolysis process, a variety of catalysts is widely used for both improving the quality of pyrolysis fluid fraction and increasing the economically valuable compounds in this fluid fraction. Studies showed that potential and organic compound selectivity of catalysts in catalytic pyrolysis changes based on the catalyst type (Ding et al. 2018; Shang et al. 2022). Acidic catalysts (ZSM-5, metal modified-ZSM-5, Al-MCM-41, etc.), basic catalysts (CaO, MgO and KOH), metals and their oxides and low cost-catalysts (clay, red mud, etc.) are widely studied catalysts in the literature. Among these, basic catalysts provide reduction of oxygenates and acidic fractions in fluid phases of catalytic pyrolysis and their selectivity for the deoxygenation compared to the acidic catalyst is high. In other words, basic catalysts convert acid compounds to the mainly ketone compounds during catalytic pyrolysis (Ding et al. 2018).

The marble industry is quite developed both in the world and in Türkiye. A high amount of marble dust–water suspension (effluent) is produced from large-scale marble processing facilities during the extraction, processing and polishing stages. These effluents can reach to the surface water and groundwater if they are not managed properly (Ersoy et al. 2005; Dede et al. 2020). The commonly used method in the treatment of this effluent is coagulation–flocculation which produces physicochemical sludge (Yılmaztürk 2011). The treatment sludges should not be released directly to the environment as they will have adverse effects. It is necessary to find other economical and feasible alternatives that will enable the recycling of treatment sludge into the system. Physicochemical sludges produced in marble processing facilities consist of inorganic compounds, such as CaCO_3 , and Al or Fe precipitates, which come from structure of marble and

the coagulation–flocculation process, respectively. These sludges can be evaluated in the catalytic pyrolysis process as catalyst as can be emphasized in the literature information above. However, to the best of the authors' knowledge, there had not been any study in the literature on using marble sludge as catalyst in the OP catalytic pyrolysis. Furthermore, the effects of marble sludge on characteristic properties and recoverable component contents of pyrolysis fluid phases, possible pyrolysis reaction pathways and economically valuable organic compounds in fluid phases had not been studied up to now.

In this regard, in this study, economically valuable compounds in the fluid phase fractions of OP pyrolysis were produced by the marble sludge catalyst obtained from physicochemical treatment of marble processing effluents. Moreover, possible reaction stages occurred during the catalytic pyrolysis process by marble sludge catalyst and change in the quantity of economically valuable organic compounds found in fluid phase fractions of pyrolysis process were evaluated in detail. With this study, sustainable resource recovery approach from agro-industrial wastes were developed by offering a solution to the two different waste types and by revealing economic value-added potential of wastes. The novelty of this study was using heterogenic, non-uniform structure of the catalyst which was the marble sludge containing not only marble dusts but also other processing wastes and treatment chemicals. Although calcite–dolomite structures have been separately used as catalysts in pyrolysis, marble processing effluents physicochemical treatment sludge including alkaline earth elements, oxide/hydroxide structures together with calcite–dolomite particles had not been studied directly in OP pyrolysis.

Materials and methods

Waste samples

OP samples were received from the Ernar Inc. Co. Ltd olive oil production facility (Mersin/Türkiye) at which 2-phase olive squeezing operation is applied. OP quantity at the facilities operating in Türkiye increased in recent years since it become mandatory for 3-phase olive oil production facilities to switch 2-phase systems by the year 2023. Nearly 2500 tons/season OP is being generated in the facility.

Marble sludge catalyst (K1) was obtained with the physicochemical treatment of the marble processing effluent by using alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) as chemical coagulant (Onen et al. 2023). The detailed experimental conditions for physicochemical treatment process of the marble processing effluent are presented in Fig. 1. K1 contains mainly Ca (19.25%),

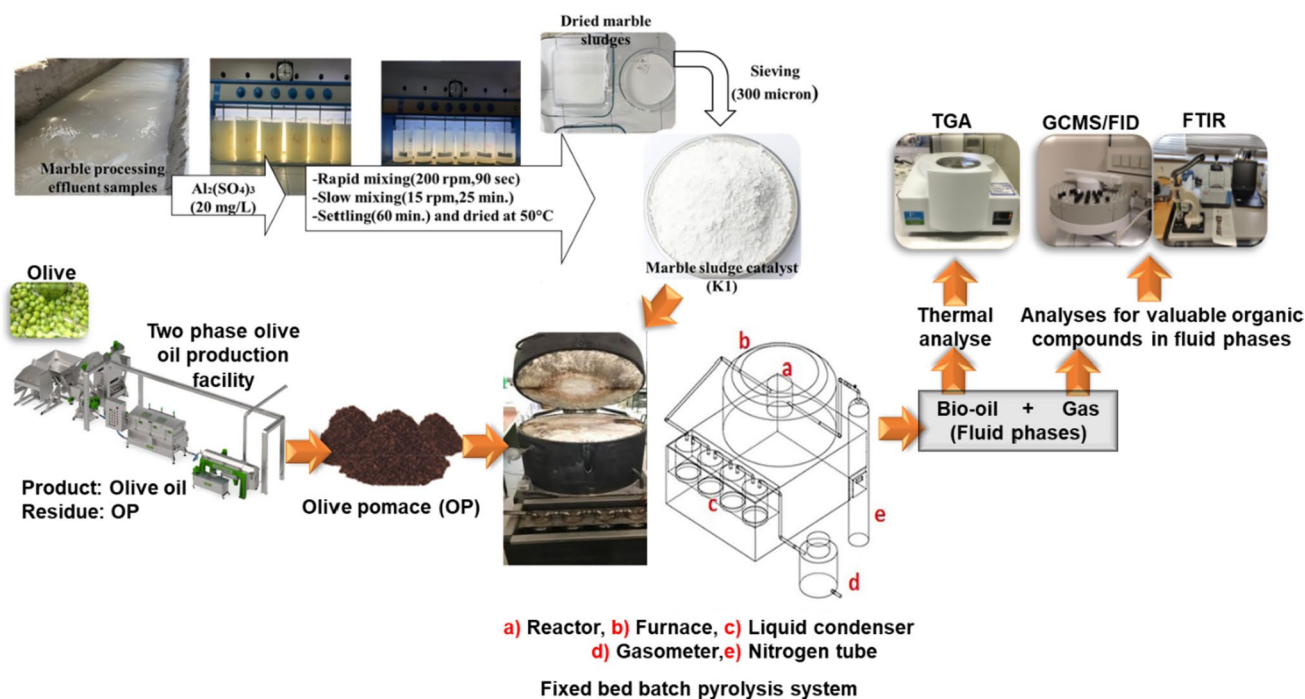


Fig. 1 Flowchart of experimental study and pyrolysis system components

C (13.63%), O (65.25%) elements and oxide/hydroxide precipitates of the coagulant (Onen et al. 2023). Other characteristic features of K1 catalysts, such as particle size, thermal resistance and heat values, were presented in another study published by the authors (Onen et al. 2023).

Pyrolysis experiments

OP + K1 mixtures were pyrolyzed in the laboratory-scale fixed bed batch pyrolysis system (Fig. 1) by using four catalyst dosages (10, 20, 30 and 50%) and three pyrolysis temperatures (300, 500 and 700 °C) at 5 °C/min heating rate. In the literature, different ratios between 10% (López et al. 2011) and 50% (Kumagai et al. 2015) have been suggested for catalyst types containing calcite, dolomite or oxide/hydroxide structures. Since OP is a lignocellulosic biomass, the lowest pyrolysis temperature was selected as 300 °C considering degradation temperatures for hemicellulose and cellulose in its structure (degradation temperatures for hemicellulose: 157–357 °C and cellulose: 240–390 °C) (Al bkoor Alrawashdeh et al. 2017; Ghouma et al. 2017). The upper temperature level for pyrolysis experiments was chosen considering that the degradation rate of K1 increases above 700 °C (Onen et al. 2023). Pyrolyzed total mass of OP + K1 mixtures was 100 g. Pyrolysis fluid phase products (bio-oil and gas) were collected separately.

Analyses

Pyrolysis fluid phase products were characterized by injecting into SHIMADZU brand GCMS/FID (GCMS was used as abbreviation in the study) device after extracting organic structures into n-hexane (GC-grade). Pyrolysis gas fractions were collected in the gasometer during each experiment and at the end of each run gas samples has passed through activated carbon tubes containing 0.5 g of powdered activated carbon with the help of a vacuum pump (Abiko 2015). These activated carbon tubes were then washed with 10 mL of n-hexane, and the obtained extracts were injected into SHIMADZU GCMS/FID. Pyrolysis oil fractions were collected in condensed liquid traps, known volume of oil samples were placed in the separatory funnels for the extraction process, 10 mL of n-hexane was added to them and shaken well, and then, the extracts were collected from the lower part of the separating funnel and injected into GCMS/FID. Details of the method and program applied in GCMS/FID analyses are presented in Table 1.

TGA of pyrolysis oils were carried out in PerkinElmer Brand TGA4000 Model device with nitrogen gas flow at 20 mL/min as inert atmosphere and heating rate of 5 °C/min. The upper TGA temperature for the analyses was 900 °C. ATR method was applied for FTIR analyses of pyrolysis fluids. For the ATR method, the monolithic diamond crystal ID 7 module of the FTIR device was used.

Table 1 GCMS methods applied in qualitative analysis of fluid phases

GCMS/FID qualitative analysis method			
Device	SHIMADZU GCMS/FID		
Column (length × inside diameter × thickness)	Restek Rxi-5 Sil MS (30 m × 0.25 mm × 0.25 μm)		
Column flow	0.48 mL/min		
Carrying gas	Helium		
Injection mode	split 10/1		
Injection temperature	250 °C		
Column heating program	Velocity (°C/min)	T (°C)	Retention (min)
	–	40	2
	4	240	5

Results and discussion

Catalytic pyrolysis mechanism of olive pomace and organic fraction of pyrolysis oils

Two different phases, namely tar and liquid phase, were observed in pyrolysis oils of OP + K1 mixtures. Organic structures found in the pyrolysis oils were evaluated from the findings of GCMS and FTIR analyses. The distribution of organic compounds having peak area higher than 1% in the GCMS analysis of pyrolysis bio-oils of OP + K1 mixtures was given in the supplementary material (Figure SM1). Pyrolysis fluids of lignocellulosic biomass mostly consist of organic acids, ketones, esters, phenols, alcohols and dehydrated compounds due to the cellulose, hemicellulose and lignin structures (Lyu et al. 2015). Similarly, aliphatic (alkanes and alkenes), aromatic (benzene and phenols) and oxygenated compounds (acids, aldehydes, alcohols, esters and ketones) were detected in all OP pyrolysis oils obtained in this study. However, distribution of the organic compounds changed clearly with pyrolysis temperature and the less variety in organic compound was observed at 300 °C pyrolysis temperature compared to the liquid products of 500 and 700 °C temperature (Figure SM1). A variety of the organic compounds for the 500 and 700 °C temperature was similar to each other.

The reaction steps during the catalytic pyrolysis of OP with K1 were estimated as in Scheme 1 by considering the findings of different studies in the literature and adapting to the waste used in this study. Possible steps and reactions in which the K1 catalyst has a catalytic effect were also indicated in Scheme 1 based on GCMS findings of pyrolysis oils presented in Figure SM1. Phenols are formed as a result of the degradation of lignin in the structure of OP by primary and secondary pyrolysis reactions. Some phenol species are formed because of secondary pyrolysis reactions such as dehydration, isomerization and decarboxylation during the pyrolysis of OP + K1 (Scheme 1). Methoxy phenol species

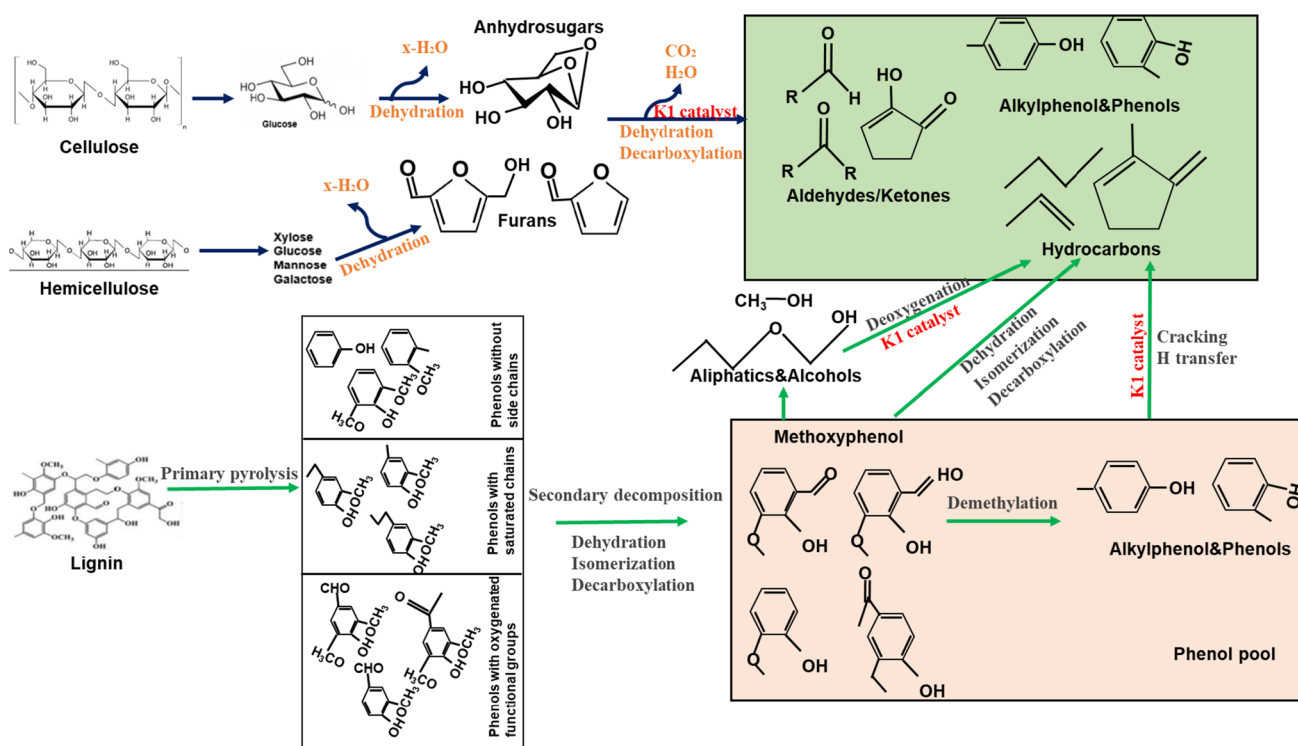
are converted into phenol and alkylphenol groups by demethylation reaction. These phenol species cause the formation of benzene and derivative groups in OP + K1 pyrolysis bio-oils by catalytic decomposition and H transfer (Scheme 1).

The most detected alkane compounds in OP + K1 pyrolysis bio-oils were Octane (C₈H₁₈), Nonane (C₉H₂₀), Decane (C₁₀H₂₂), Hendecane (C₁₁H₂₄), Dodecane (C₁₂H₂₆), Tetradecane (C₁₄H₃₀), Cyclohexane eicosyl (C₂₆H₅₂), Cyclododecane (C₁₂H₂₄), Pentadecane (C₁₅H₃₂), Hexadecane (C₁₆H₃₄) and Heptadecane (C₁₇H₃₆). The lowest carbon number observed in the components of pyrolysis bio-oils was 7 (C7) and the highest carbon number was 26 (C26). The carbon number of most of the alkane compounds was in the range of 7(C7)–17(C17) (Figure SM1). Alkane compounds with high carbon numbers, such as Cyclohexane eicosyl, 9-Cyclohexylnonadecane and Cyclohexane nonadecyl, were cycloalkane groups. Although the diversity of alkane groups was quite high in both catalytic and non-catalytic pyrolysis bio-oils of OP, n-alkane compounds found also in diesel oil, such as ‘hexadecane, heptadecane, octadecane nonadecane’ (Muhammad et al. 2015) were observed mostly in catalytic pyrolysis bio-oils. This finding is also consistent with the catalytic pyrolysis results of OP in the literature. Hani and Hailat (2016) reported that the bio-oils obtained with OP + zeolite catalytic pyrolysis had more n-alkane compounds.

Another aliphatic group found in pyrolysis bio-oils was alkenes. The alkene compounds mostly observed in pyrolysis bio-oils were 1-Nonene (C₉H₁₈), 1-Tetradecene (C₁₄H₂₈), 1-Nonadecene (C₁₉H₃₈), 1-Hexadecene (C₁₆H₃₂), 1-Heptene (C₇H₁₄), 1-Octene (C₈H₁₆), 1-Undecene (C₁₁H₂₂) and 1-Heptadecene (C₁₇H₃₄). The diversity of alkene compounds in catalytic pyrolysis bio-oils was less than alkanes. Therefore, it can be concluded that the compounds obtained during the catalytic pyrolysis process were predominantly saturated aliphatic structures. This can be attributed to the conversion of alkenes (olefins), which are in the unsaturated aliphatic hydrocarbon class, to saturated hydrocarbons (alkanes) (Hani and Hailat 2016).

The presence of alkane and alkene compounds in pyrolysis bio-oils was supported by FTIR analyses besides GCMS





Scheme 1. Reaction steps for OP+K1 catalytic pyrolysis [prepared with evaluation of this study results by adapting the findings of Zheng et al. (2014), Zadeh et al. (2020), Wang et al. (2021)]

analyses (Fig. 1). In uncatalyzed pyrolysis bio-oils, double band of alkane C–H stretch in the range of 2920–2850 cm^{-1} and bands of alkane compounds at 1455–1375 cm^{-1} were detected for all temperatures (Fig. 2). In the FTIR spectra of the bio-oils obtained at 300 °C the double band of alkane C–H stretch at 2920–2850 cm^{-1} were observed for 0–30% K1 doses. The same bands were observed in pyrolysis liquid obtained at 700 °C and 0–30% K1 doses when compared to 300 °C. This can be interpreted as an increase in alkane formation with increasing pyrolysis temperature. For 50% K1 doses at 300 °C, the double band alkane C–H stretch was detected as a smaller single band only around 2850 cm^{-1} . CH₂ bending of alkane at 1453–1454 cm^{-1} in 300 °C pyrolysis bio-oils were not observed for 50% K1 doses. This result indicates less alkane formation with increasing K1 dose. In the pyrolysis bio-oils of 300 °C, bands belonging to the unsaturated ketone and alkene group were detected for all K1 doses (0–50% K1) at 1633–1629 cm^{-1} (Fig. 2). It was detected aliphatic C–H out-of-plane bending or alkene C=C bending for CH₂ with a C number of 4 or more at 724–719 cm^{-1} at 300 °C (10–30% K1), 500 °C (0–30% K1) and 700 °C (0–50%K1). New bands formed around 885 cm^{-1} for all K1 doses at 700 °C indicated the meta-substituted benzene ring or alkene. The bands observed at 1455–1375 cm^{-1} at all doses of 700 °C also belong to alkane compounds. Bands of double band alkane C–H stretching in

the range of 2920–2850 cm^{-1} at 500 °C were observed at non-catalyzed and all catalytic pyrolysis bio-oils (Fig. 2).

The variety of benzene and phenol compounds was much less compared to aliphatic compounds. Benzene compounds detected at the highest percentage were Benzene methyl (Toluene, C₇H₈) and Benzene ethyl (C₈H₁₀). Toluene and ethyl benzene were observed more frequently at higher temperatures (500 and 700 °C) compared to lower pyrolysis temperatures (300 °C). This can be explained by the fact that higher temperatures are better for hydrogen production, which helps condense and rearrange the aromatic ring (Uzun et al. 2007). Phenols were detected more in the pyrolysis bio-oils of OP as compared to benzenes. Phenol 2-methyl (C₇H₈O), Phenol 4-ethyl-2-methoxy (C₉H₁₂O₂) and Phenol 2,6-dimethoxy (C₈H₁₀O₃) were the most detected phenol compounds at different pyrolysis conditions and catalyst doses. Besides these compounds, Phenol (C₆H₆O) and Phenol 3-ethyl (C₈H₁₀O) compounds were also encountered in the bio-oils of some pyrolysis conditions. Phenolic compounds can be classified into three main categories: Guaiacol type (G-type), Syringol type (S-type) and Phenol type (H-type) (Shen et al. 2015). Phenol and Phenol 2-methyl compounds were H-type; Phenol 2,6-dimethoxy were S-type; Phenol 4-ethyl-2-methoxy were G-type phenols in the pyrolysis bio-oils of OP+K1 mixtures. In the presence of K1 more phenol compounds were detected in OP



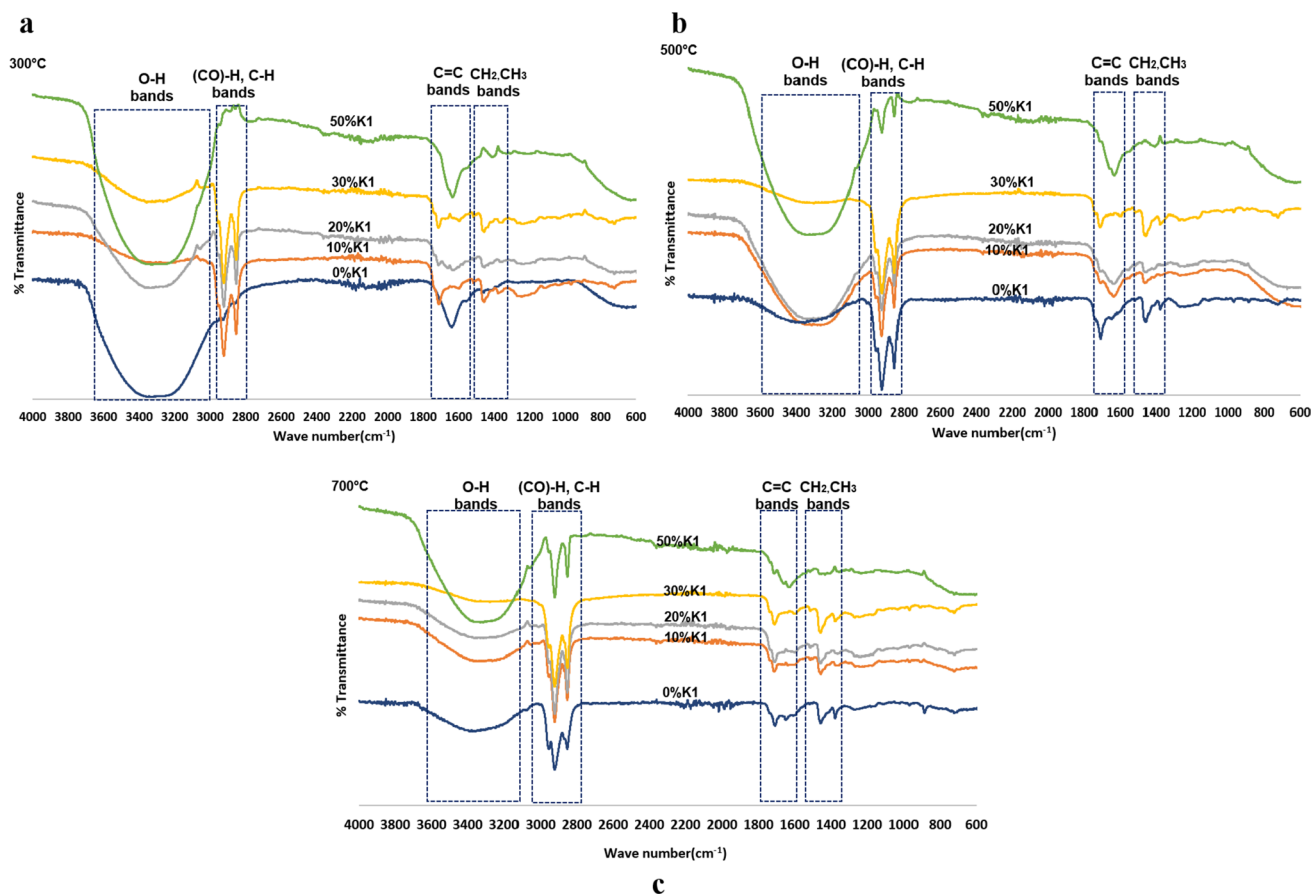


Fig. 2 FTIR spectra of pyrolysis bio-oils obtained with pyrolysis of OP and K1 at **a** 300 °C; **b** 500 °C; **c** 700 °C

pyrolysis liquids, and this was confirmed with FTIR findings. Phenol, ester or vinyl ether compounds were present at all catalyst doses (%10–50 K1) of all pyrolysis temperatures at 1226–1221 cm^{-1} . The only exception was 50% K1 doses at 300 °C pyrolysis temperature since a sharp decrease in these bands was observed at that pyrolysis condition. This may be due to less phenol formation at these doses. Moreover, aromatic C-H out-of-plane bending around 1600 cm^{-1} was also detected for all temperatures, indicating that aromatic compounds are formed at lower temperatures by the effect of catalyst. The fact that more common phenol compounds in pyrolysis liquids with the effect of K1 is a positive result since phenols are chemicals with high added value.

One of the groups of oxygenated compounds in pyrolysis bio-oils was acids. The commonly detected acid compound in catalytic and non-catalytic pyrolysis bio-oils of OP was oleic acid. Butanoic acid ($\text{C}_4\text{H}_8\text{O}_2$), Hexanoic acid ($\text{C}_6\text{H}_{12}\text{O}_2$) and cyclohexanecarboxylic acid ($\text{C}_6\text{H}_{11}\text{CO}_2\text{H}$) were other acid compounds in pyrolysis bio-oils apart from oleic acid. During the pyrolysis of lignocellulosic biomass, acid compounds are mostly formed with the degradation of cellulose and hemicellulose (Scheme 1). Acids are difficult to use in the engine as they cause corrosion. They catalyze

polymerization reactions, thereby reducing the stability of the bio-oil. For these reasons, the low amount of acid compounds in pyrolysis bio-oils is important for the quality of the pyrolysis bio-oil (Christoforou et al. 2018). As shown in Figure SM1, acid compound numbers in pyrolysis bio-oils decreased with the addition of K1 especially at 300 °C pyrolysis temperatures. Moreover, the number of acid compounds in the pyrolysis bio-oils obtained with K1 was quite low for most catalyst doses. This situation can be attributed to the neutralization of the carboxylic groups in the hemicellulose by the $\text{Ca}(\text{OH})_2$ and CaO compounds, which occur when the CaCO_3 in the structure of the K1 catalyst starts to decompose during the pyrolysis (Wang et al. 2010).

Other groups of oxygenated compounds observed in pyrolysis bio-oils were alcohols, esters, and ketones. 1-Dodecanol ($\text{C}_{12}\text{H}_{26}\text{O}$), 1-Decanol ($\text{C}_{10}\text{H}_{22}\text{O}$) and 1-Undecanol ($\text{C}_{11}\text{H}_{24}\text{O}$) were among the most detected alcohol compounds in OP + K1 pyrolysis bio-oils. Sulfate esters of 1-dodecanol, also known as lauryl alcohol, are widely used as surfactants. 1-Decanol has a role as metabolite and protic solvent. 1-undecanol has a flowery odor, an oily taste and is used as a flavoring agent in cooking (National Center for Biotechnology Information 2021). Since alcohol compounds can be used in



many industrial areas, they are generally among the desired compounds in pyrolysis oils (Christoforou et al. 2018). In OP pyrolysis bio-oils obtained both with and without K1 had a high alcohol diversity, and this diversity increased for most pyrolysis conditions with the use of K1 (Figure SM1). This is a desirable result as it enhances the use of pyrolysis bio-oils for different purposes and the potential to recover valuable organic substances from bio-oils. While dotriacontyl pentafluoropropionate ($C_{35}H_{65}F_5O_2$), hexadecanoic acid, methyl ester ($C_{17}H_{34}O_2$), hexadecanoic acid and ethyl ester ($C_{18}H_{36}O_2$) were the most observed ester groups, Propyl methyl ketone ($C_5H_{10}O$), 2-cyclopenten-1-one, 2-methyl (C_6H_8O) and 2-pentadecanone ($C_{15}H_{30}O$) were the most common ketone compounds in OP + K1 pyrolysis bio-oils. Furan and anhydrosugar compound groups were decomposed by decarboxylation and dehydration reactions with the help of K1 and formed ester and ketone compound groups in pyrolysis bio-oils (Scheme 1).

In FTIR spectrum, oxygenated compounds were also detected conformably GCMS analysis. The bands seen around 1710 cm^{-1} for 10–30% K1 doses in the FTIR spectra of the bio-oils obtained at $300\text{ }^\circ\text{C}$ pyrolysis temperature of OP belong to acid or aliphatic ketone in dimer form; bands at this wavelength were not detected when the 50% K1 doses were applied (Fig. 2). Small bands were detected for 10–30% K1 doses at 1365 cm^{-1} . The aldehyde (CO)-H stretch occurs as a pair of weak bands at $2860\text{--}2800\text{ cm}^{-1}$, usually masked by alkane C-H absorptions. Ketone, quinone, acid, aldehyde, etc., around $1708\text{--}1704\text{ cm}^{-1}$ groups were observed in pyrolysis bio-oils at $500\text{ }^\circ\text{C}$ and $700\text{ }^\circ\text{C}$ for doses of 0–30% K1 and 0–20% K1, respectively (Fig. 2). The formation of these bands starting from $300\text{ }^\circ\text{C}$ can be interpreted as both the increase in alkane formation and the formation of oxygenated compounds at lower temperatures due to the catalyst effect. The intensity of these bands decreased sharply as the catalyst dose increased at the same temperature. At $1630\text{--}1600\text{ cm}^{-1}$, unsaturated ketone groups, aromatic C=C or alkene groups were observed for 10–50% K1 doses in $500\text{ }^\circ\text{C}$ pyrolysis bio-oils, and for all catalyst doses of $700\text{ }^\circ\text{C}$ bio-oils (Fig. 2).

O–H stretch bands of phenol or alcohol were observed between 3600 and 3300 cm^{-1} (Şensöz et al. 2006) at all K1 doses (0–50%) of all pyrolysis temperatures. The intensity of double bands of alkane C–H stretching increased in the range of $2920\text{--}2850\text{ cm}^{-1}$ in 10% K1 dose of OP and $300\text{--}700\text{ }^\circ\text{C}$ pyrolysis temperature bio-oils (Fig. 2). According to the FTIR results, there was no significant change in the oil composition by increasing the pyrolysis temperature from 500 to $700\text{ }^\circ\text{C}$, whereas oxygenated compounds and more alkenes formed at temperatures of $500\text{ }^\circ\text{C}$ and above when the catalyst was not used.

In Fig. 3a, the distributions, and total numbers of organic compound groups in the OP and OP + K1 mixtures pyrolysis bio-oils were presented. The diversity of most of the organic structures decreased with high K1 doses (50%) at

all pyrolysis temperatures. However, the most significant difference was observed in 50% K1 doses at $300\text{ }^\circ\text{C}$ pyrolysis temperatures (Fig. 3a). This can be explained by the incomplete degradation of OP at $300\text{ }^\circ\text{C}$ pyrolysis temperature and lower portion of OP in the total pyrolysis mass. While there was not much difference in the organic compound diversity in the pyrolysis bio-oils with the increase in pyrolysis temperature at 0–20% K1 doses, a significant difference was observed at 30 and 50% K1 doses. Compound diversity at 30% and 50% K1 doses at $300\text{ }^\circ\text{C}$ pyrolysis temperature was considerably lower compared to higher temperatures (Fig. 3a). It can be noted that the addition of K1 increased the diversity in organic compounds for most experimental conditions as compared to the 0%K1 pyrolysis condition. In addition, the effect of K1 on pyrolysis bio-oils was visually examined. Bio-oils were poured into 100 mL graduated cylinders, volumes of tar and liquid portions were recorded (Fig. 3b). The ‘tar’ consists of heavier molecular weight compounds and the ‘liquid’ part consists of lighter compounds. The quantities of the tar and liquid phases in the bio-oils in the beakers were recorded and these values were compared on the same plot (Fig. 3b). The tar level in pyrolysis bio-oils obtained from the pyrolysis of OP with K1 was lower than that of uncatalyzed pyrolysis bio-oils. As the K1 ratio increased, the tar content in the bio-oils decreased for most pyrolysis conditions. As a result, it can be stated that K1 had a catalytic effect during the pyrolysis process of OP based on both GCMS results and visual findings. Moreover, K1 converted heavy molecular structures in bio-oil into shorter chained, light organic compounds.

Effect of marble sludge catalyst (K1) on thermal characteristics of OP pyrolytic bio-oil

Thermal properties of pyrolysis bio-oils were evaluated for both the tar and liquid phase of pyrolysis bio-oils. Thus, organic compounds found in tar and liquid phase observed in GCMS and FTIR were interpreted separately. In Fig. 4, TGA curves of liquid and tar phase of pyrolysis bio-oil varying according to different pyrolysis temperatures at the same K1 dose were given. The thermal resistance values obtained from Fig. 4 are summarized in Table 2.

Major thermal decomposition of all pyrolysis liquids of 0%K1 occurred up to about $123\text{--}125\text{ }^\circ\text{C}$ and their complete decomposition ended at about $185\text{--}200\text{ }^\circ\text{C}$. Residue values at the end of $300\text{ }^\circ\text{C}$ ranged between 0.13 and 1.25%, and T_{50} values varied between 74.7 and $100.3\text{ }^\circ\text{C}$. As the pyrolysis temperatures increased, the decrement in the DT1 values of the liquids was observed. That indicates more decomposition and the formation of smaller molecular compounds at higher temperatures (Table 2). The same trend continued in T_5 , T_{10} and T_{50} values. The main decomposition temperatures for 10% and 20% K1 doses were approximately $94\text{--}122$ and $101\text{--}111\text{ }^\circ\text{C}$, respectively

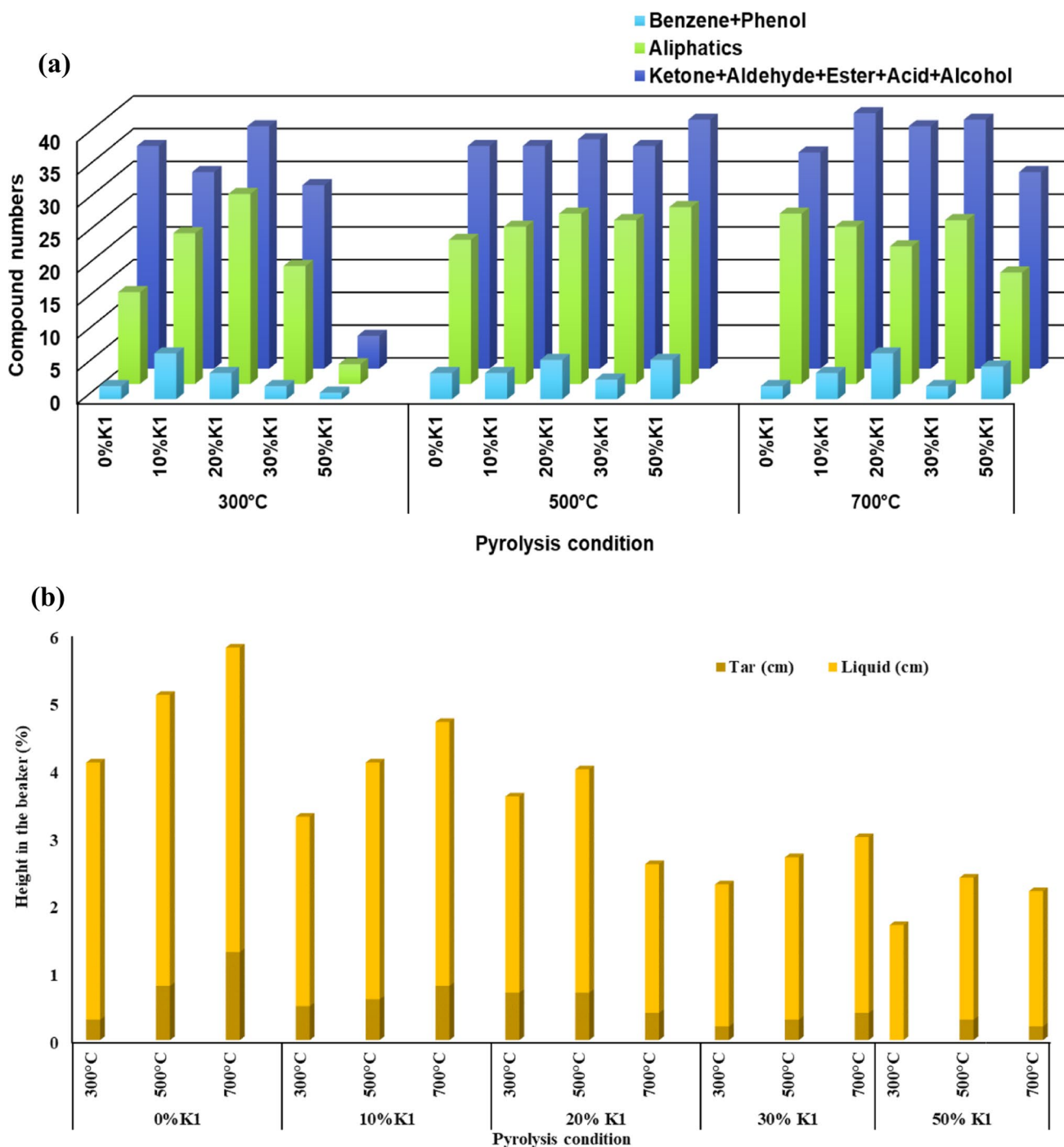


Fig. 3 **a** Changing in the organic compounds in the pyrolysis bio-oils of OP with catalyst dose. **b** Comparison of tar and liquid phases of OP+K1 pyrolysis bio-oils

(Fig. 4). At these doses, as the pyrolysis temperatures increased, the DT1 values of the liquids decreased. For the 30% K1 dose, the TGA curves obtained all pyrolysis temperatures, except for the 700 °C, were very close to each other. It is seen that there was a decrease in DT1, T₅, T₁₀ and T₅₀ values at this dose. The same trend was

valid for the 50% K1 dose. Moreover, the TGA curves for the 50% K1 dose were closer to each other and there was almost no visible difference between the curves. This result can be explained by the fact that the pyrolysis liquids obtained at all temperatures at high catalyst dose have close thermal resistance. The DT1, T₅, T₁₀ and T₅₀ values

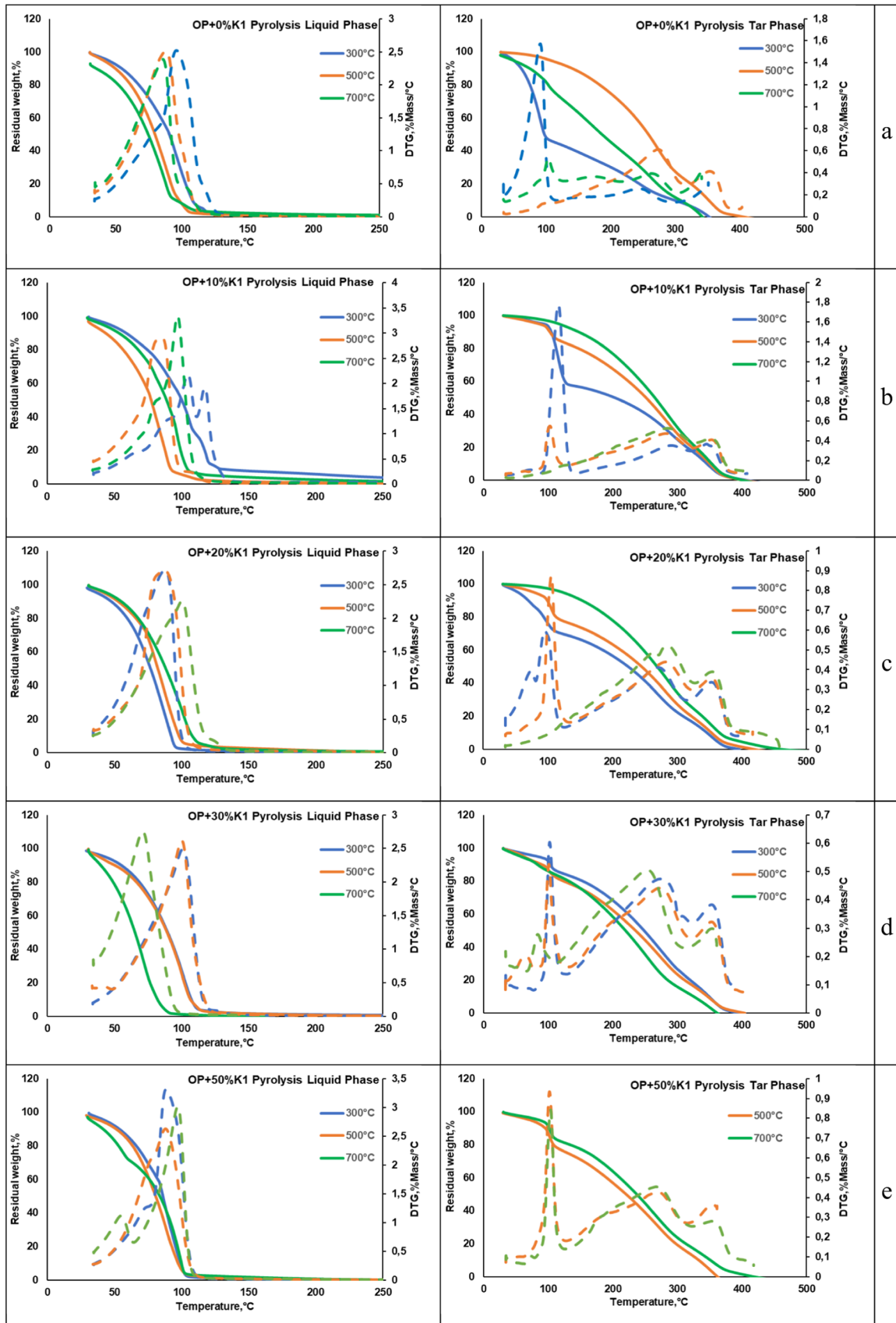


Fig. 4 TGA and DTG thermograms of liquid and tar phase of pyrolysis bio-oils obtained at different pyrolysis temperatures and K1 ratio a 0%K1, b 10% K1; c 20% K1; d 30%K1; e 50%K1

found for the 50% K1 dose were the lowest compared to all other doses. Also, no residues were formed for the 50% K1 doses (Table 2). The absence of residue can be interpreted as that the low or no high boiling point aromatic components in the liquid composition remained at these doses due to catalyst effect.

There are not many studies investigating the structure of pyrolysis tar in the literature. In one of the pyrolysis studies, 43.58% of the tar obtained with chestnut bark pyrolysis at 400 °C was dissolved in n-pentane. Moreover, 6.36, 61.72 and 31.92% of the n-pentane soluble were aliphatic, aromatic and polar compounds, respectively. The sum of the aliphatic and aromatic subfractions was 68.08% (Demiral and Çemrek Kul 2015). Therefore, it is likely that aliphatic and aromatic compounds will form the majority in the OP pyrolysis tar due to the lignin and cellulose in its structure.

The tar residual for all K1 dosages was higher at 300 °C which means a higher proportion of aromatic compounds was found in their composition (Table 2). Major decomposition of all pyrolysis tars of OP without catalyst (0% K1 dose) took place up to about 339–367 °C, while their complete decomposition ended at about 341–404 °C (Fig. 4). The DT1 values of the tars were low in the range of 37–44 °C, while the DT2 values varied in the range of 95–123 °C. In addition, there was a slight decrease in DT1 and DT2 values of tars as the pyrolysis temperature increased. In addition, the decrease in T_5 , T_{10} and T_{50} values above 500 °C pyrolysis temperature can be explained by the formation of compounds with smaller molecules at high temperatures and increment in compound diversity. These results also line up with the GCMS results. Diversity in organic compounds was considerably lower at 300 °C and 50%K1 dosage compared to higher temperatures (Fig. 3a). Particularly, at doses above 20% K1, a slight decrease in DT1 and DT2 values was observed as the dose increased, indicating the formation of compounds with smaller molecules by the catalyst effect. Also, at doses above 20% K1, the percentage of residues at 300 °C generally decreased as the dose increased. From this, it can be inferred that the thermal resistance of pyrolysis tars at 10% K1 and 20% K1 doses were slightly higher.

Economic potential of valuable compounds recovery from catalytic pyrolysis liquid

Organic compounds presented in Figure SM1 were categorized to interpret effects of K1 on quantity of organic compounds in pyrolysis bio-oils (Table 3). ‘1-Pentadecanol,

2-Pentadecanone and 9-Octadecenoic acid (Z) methyl ester’ compounds had the highest area percentage for all studies temperatures and catalyst dose (Table 3). 1-Pentadecanol is used widely for many purposes such as feedstock for production of surfactants, emollient, flavoring and softening (URL 2). 2-Pentadecanone is one of the main compound agents for flavoring like 1-Pentadecanol. Furthermore, new studies showed that 2-Pentadecanone can be successfully used as an active ingredient for diabetic wound healing cream since it shows antibacterial activity, collagen deposition and wound closure (Siyumbwa et al. 2019). Similar to this study, Zhang et al. (2017) reported that 2-Pentadecanone is one of the main ketone compounds for rice husk pyrolysis oil obtained with CaCO_3 catalyst. CaCO_3 is the main component of K1. Furthermore, percent peak area of 2-Pentadecanone mostly increased with the catalyst ratio increment and the highest area was observed at 50%K1 ratio for all pyrolysis conditions (Figure SM1). This can be interpreted as that K1 affects decarboxylation reactions for converting acid compounds to ketone in pyrolysis bio-oils. Little or no acid compounds formation in catalytic pyrolysis bio-oils also support this argument. Another organic compound having high peak area (%) in pyrolysis bio-oils for all studied temperature was 9-Octadecenoic acid (Z) methyl ester (Methyl oleate). It arises from condensation of the carboxy group of oleic acid with methanol and it is a methyl ester of fatty acid. Since oleic acid is one the main compounds found in olive and olive oil, formation of methyl oleate during pyrolysis process was an expected result. Moreover, the percentage of this compound in pyrolysis bio-oil decreased with the catalyst usage for all studied temperatures (Figure SM1). Methyl oleate is commonly used in many industries to make detergents, waxes, stabilizers, rubbers, drying oils. Furthermore, it is used as emulsifier in the cosmetic industry, plasticizer, lubricant in the leather industry and so on (URL 3). Additionally, ‘Heptadecane, Pentadecane, Hexadecanoic acid methyl ester and Olealdehyde dimethyl acetal’ were the organic compounds commonly observed at relatively high percentage for 500 and 700 °C pyrolysis temperature and all catalyst dosage (Table 3). Although Heptadecane, Pentadecane, Hexadecanoic acid methyl ester and Olealdehyde dimethyl acetal were not detected in non-catalytic pyrolysis bio-oils obtained at 300 °C, they were observed at all catalytic pyrolysis bio-oils at the same pyrolysis temperature (Table 3). This shows that these organic compounds can be generated at lower temperatures by using K1. Heptadecane and Pentadecane (n-decane compounds) most probably formed from oleic acid with the reaction of hydrogenation, decarboxylation and hydrocracking (Scheme 2). Increment in the GCMS peak area percentage of these compounds with K1 catalyst can be related to the impact of K1 catalyst on decarboxylation and hydrocracking reactions (Scheme 2) (Edeh et al. 2021). Heptadecane can be utilized in a variety of applications such as generation of detergents or proteins, chlorination



Table 2 Thermal resistance findings of liquid and tar phase of pyrolysis bio-oils obtained from the pyrolysis of OP + K1 mixtures

Sample		Thermal resistance value					Residue at 300 °C (%)
K1 ratio (%)	Pyrolysis temperature	DT1* (°C)	DT2** (°C)	T_5 (°C)	T_{10} (°C)	T_{50} (°C)	
<i>Liquid phase of pyrolysis oils of OP + K1 mixtures</i>							
0	300 °C	42	–	44.0	54.6	90.8	0.51
	500 °C	41	–	40.5	49.7	79.9	0.13
	700 °C	32	–	<30	35.2	74.7	0.87
10	300 °C	40	131	46.7	58.8	100.3	2.55
	500 °C	34	107	33.6	43.4	77.5	0.35
	700 °C	34	108	41.4	53.4	88.9	1.25
20	300 °C	33	–	37.2	47.5	76.8	0.00
	500 °C	35	105	42.5	52.6	82.2	0.08
	700 °C	33	–	44.5	55.0	88.2	0.65
30	300 °C	34	–	43.1	55.2	89.7	0.60
	500 °C	32	–	38.6	50.4	89.3	0.14
	700 °C	31	–	33.8	39.8	65.4	0.00
50	300 °C	35	–	43.3	53.5	86.1	0.00
	500 °C	31	–	39.5	51.2	80.7	0.00
	700 °C	29	–	32.6	41.5	83.7	0.00
<i>Tar phase of pyrolysis bio-oils of OP + K1 mixtures</i>							
0	300 °C	37	107	49.4	61.4	97.5	9.88
	500 °C	44	123	105.3	140.2	258.5	27.46
	700 °C	42	95	48.3	74.4	186.6	11.81
10	300 °C	38	94	91.1	104.6	203.7	24.85
	500 °C	39	96	84.3	102.5	251.8	28.32
	700 °C	52	90	115.5	147.1	265.4	32.19
20	300 °C	43	117	53.5	69.7	224.0	22.57
	500 °C	45	87	77.9	99.1	244.9	27.47
	700 °C	54	108	122.4	152.9	268.9	34.45
30	300 °C	44	89	82.4	103.1	248.7	26.72
	500 °C	40	108	61.8	90.3	235.5	23.52
	700 °C	41	93	56.8	83.7	219.9	16.03
50	300 °C	–	–	–	–	–	–
	500 °C	37	79	71.7	95.4	220.5	19.33
	700 °C	41	91	85.5	101.5	236.9	23.75

$T_{5, 10, 50}$ Temperatures at which 5, 10 and 50% degradation occurs

*DT1-first degradation temperature

**DT2-second degradation temperature

reactions, stock for hydrocracking processes while Pentadecane is widely used as solvent for the inks and degreasing and organic synthesis (Schmidt et al. 2014). Hexadecanoic acid methyl ester (methyl palmitate) is used as flavoring agents, emollient and skin conditioning (URL 4).

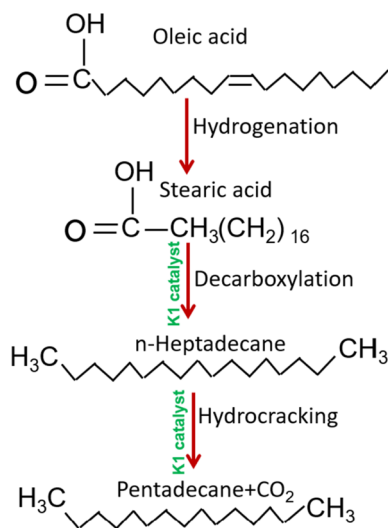
2-phase and 3-phase centrifuge systems are used during olive oil production from olive in Türkiye and OP quantity, water consumption, pollution load and olive oil quality change based on these production technologies. OP quantity is much higher in 2-phase systems compared to 3-phase systems. By the year 2023, a total of 1264 olive oil production facilities are being operated in Türkiye, 816 of them are

2-phase, 444 of them are 3-phase, and 4 of them are traditional systems (URL 5). It has been made mandatory for 3-phase olive oil production enterprises to switch 2-phase systems in year 2023 since olive mill wastewater produced by the 3-phase systems has very complex structures with highly acidic characteristics and high COD values (URL 5). This means that the produced OP quantity will increase in the forthcoming years for Türkiye, and finding new solutions to OP waste to turn into economic value is becoming more important. From this point of view, the income obtained by existing olive oil production facilities from OP and the economic return when 2-Pentadecanone compound is recovered



Table 3 Comparison of GCMS peak area percentage of organic compounds found in pyrolysis bio-oils (high quantity: compounds with area (%) ranging from 1 to 10; intermediate quantity: compounds with area (%) ranging from 0.1 to 1.0)

Temperature	300 °C	500 °C	700 °C
Compounds observed in all pyrolysis bio-oils at high quantity	–1-Pentadecanol –2-Pentadecanone –9-Octadecenoic acid (Z)-, methyl ester –Cyclotridecanone	–1-Pentadecanol –2-Pentadecanone –9-Octadecenoic acid (Z)-, methyl ester –Heptadecane –Hexadecane –Hexadecanoic acid, methyl ester –Olealdehyde, dimethyl acetal –Pentadecane –Tetradecane	–1-Nonadecene –1-Pentadecanol –2-Pentadecanone –9-Octadecenoic acid (Z)-, methyl ester –Heptadecane –Hexadecane –Hexadecanoic acid, methyl ester –Olealdehyde, dimethyl acetal –Pentadecane
Compounds observed in only catalytic pyrolysis bio-oils at high quantity	–Heptadecane –Hexadecanoic acid, methyl ester –Olealdehyde, dimethyl acetal –Pentadecane	–Cyclohexene, 1-nonyl-	–Hexadecane –Octadec-9-enoic acid –Pyridine 3-ethyl-4-methyl- –Tetradecane
Compounds observed in only catalytic pyrolysis bio-oils at intermediate quantity	–Tridecane	–9-Octadecen-1-ol, (Z)	–Dodecane (CAS) –Octadecanoic acid, methyl ester
Compounds observed in all pyrolysis bio-oils at intermediate quantity	–	–1-Decanol –Decane –Dodecane –Hendecane –Octadec-9-enoic acid	–

**Scheme 2.** Possible formation steps of n-decane compounds [adapted from Edeh et al. (2021)]

from pyrolysis oil at ideal conditions were compared for 2021–22 season (Fig. 5). In Türkiye, 2.35×10^5 -ton olive oil produced in 2021/22 season (TEPGE 2022) which corresponds to 9.40×10^5 -ton OP production for 2-phase centrifuge systems (Fig. 5). Most of the olive oil production

facilities in Türkiye reuse OP for secondary oil extraction from pomace or for fuel production. Approximately 52 USD per ton of OP can be driven profit in this way (means that 47.94×10^6 USD profit for 2021/22 season) (Ministry of Industry and Technology 2021). Within the scope of the study, approximately 60 g of pyrolysis oil (nearly 6 g of which is 2-Pentadecanone compound) was produced from 100 g of OP pyrolysis. In line with this information, the potential profit that can be obtained from the conversion of OP produced in Türkiye to 2-Pentadecanone compound between 2021/2022 is around 2.459×10^{13} USD (Fig. 5). Therefore, it can be emphasized that even if pyrolysis system and recovery processes of valuable compounds from pyrolysis oil have additional cost and time, the difference in profit is very significant. Moreover, this sample calculation was performed for only one compound found in pyrolysis oils. For this reason, it can be stated that the study findings are quite instructive for future studies which should focus on the recovery of valuable compounds from pyrolysis oils.

Economically valuable compounds in pyrolysis gases

The distribution of organic compounds in catalytic and conventional pyrolysis gas of OP with catalyst dose and



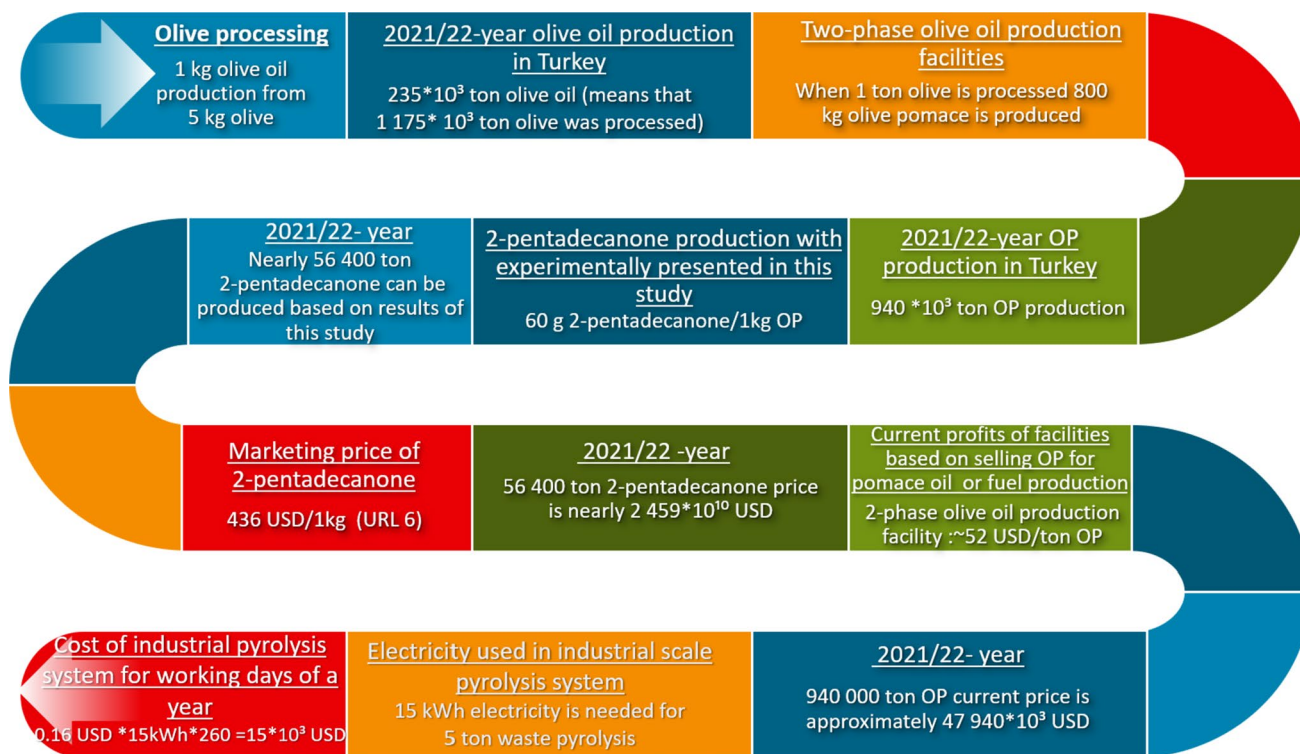
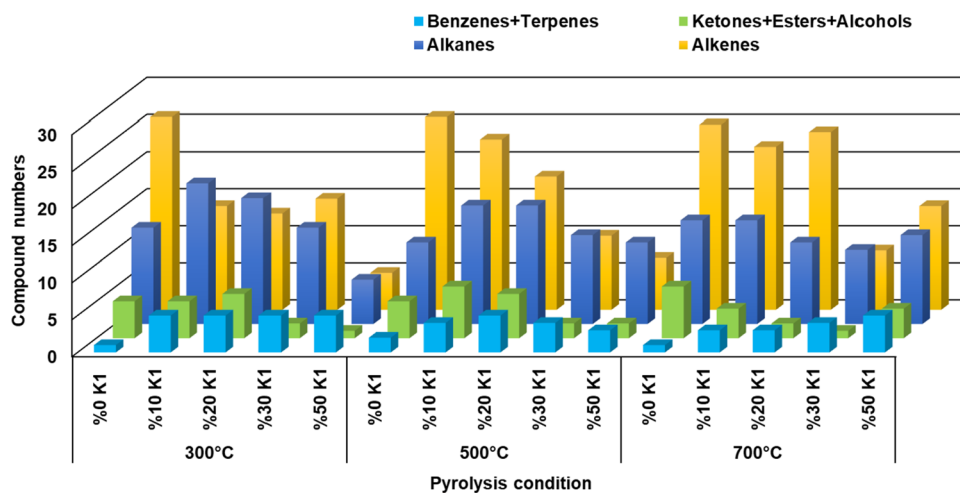


Fig. 5 Potential profit rate of recovery of 2-Pentadecanone compound from pyrolysis oils of OP produced in Türkiye between 2021/22

Fig. 6 Variation of organic compounds in catalytic and conventional pyrolysis gas of OP with catalyst dose and temperature



temperature is presented in Fig. 6. Most of the pyrolysis gases at all catalyst dosages comprised of aliphatic compounds. Similar to OP + K1 pyrolysis bio-oils, aliphatic and other compound numbers in pyrolysis gases obtained at 50% catalyst doses also mostly showed a reduction compared to other K1 doses. At high K1 doses less amount of pyrolyzed OP and higher amount of catalyst may affect decomposition of OP and may explain the decrease in component diversity detected in both pyrolysis liquids and pyrolysis gases. When the aliphatic groups in the OP + K1 pyrolysis gases were compared, the diversity of the alkene groups was greater

than the alkanes for most pyrolysis conditions. Moreover, the alkene number increased with temperature for most pyrolysis conditions. This can be attributed to the increase in cleavage reactions with temperature and the formation of more alkene compounds. Similarly, it has been emphasized by different researchers that mostly alkene compounds are more common in pyrolysis gases than alkanes and the increment in the temperature increases the alkene diversity (Miskolczi and Czégény 2016; Xue 2017). For other organic compounds (ketone, ester, terpene, benzene and alcohol), no clear change was observed with catalyst dose and temperature.

Table 4 Comparison of GCMS peak area percentage of organic compounds found in pyrolysis gases (high quantity: compounds with area (%) ranging from 1 to 10; intermediate quantity: compounds with area (%) ranging from 0.1 to 1.0)

Temperature	300 °C	500 °C	700 °C
Compounds observed in all pyrolysis gases at high quantity	–1-Heptene –1-Octene –1-Octene 3-ethyl –2-Pentanone, 3[(acetyloxy) methyl] 3,4-dimethyl- (.+ –.) –Octane	–1-Heptene –1-Octene –1-Octene, 3-ethyl –2-Heptene –2-Pentanone, 3 [(acetyloxy) methyl] 3,4-dimethyl- (.+ –.) –Disulfide dimethyl –Octane –Dimethyl trisulfide	–1-Heptene –1-Octene –1-Octene, 3-ethyl –2-Heptene –Octane
Compounds observed in only catalytic pyrolysis gases at high quantity	–Pinene < alpha->	–	–
Compounds observed in only catalytic pyrolysis gases at intermediate quantity	–	–Heptane –Benzene, methyl- –Pinene < alpha->	–Benzene, methyl
Compounds observed in all pyrolysis gases at intermediate quantity	–2-Heptene	–1,3-Heptadiene, 2,3-dimethyl –Cyclohexane, methyl-	–

The distribution of organic compounds having peak area greater than 1% in the GCMS analysis of pyrolysis gases of OP + K1 mixtures is given in Figure SM2. Moreover, organic compounds presented in Figure SM2 were also categorized as Table 4 to interpret K1 effects on quantity of organic compounds in pyrolysis gases. The organic compound diversity in the pyrolysis gases of OP + K1 was less compared to the pyrolysis bio-oils.

The most common organic compounds in pyrolysis gases were alkane and alkene aliphatic compounds (Fig. 6). While Hexane 3-methyl (C₇H₁₆), Heptane (C₇H₁₆), Cyclohexane methyl (C₇H₁₄), Cyclopentane ethyl (C₇H₁₄), Octane (C₈H₁₈), Cyclohexane 1,3,5-trimethyl (C₉H₁₆) and Decane (C₁₀H₂₂) were the most common alkane compounds, Trichloroethene (C₂HCl₃), 1-Hexene 2-methyl (C₇H₁₄), 1-Heptene (C₇H₁₄), 2-Heptene (C₇H₁₄), Cyclohexene 3-methyl (C₇H₁₂), 1-Heptene 2-methyl (C₈H₁₆), 1-Octene (C₈H₁₆) and 1-Octene 3-ethyl (C₁₀H₂₀) were the most common alkene compounds in the pyrolysis gases. The observation of aliphatic compounds, whose physical characteristics are normally liquid phase, in OP + K1 pyrolysis gases can be explained by the fact that the part of the hot fluid phase leaving the pyrolysis reactor, which cannot be condensed in the liquid capture vessels, has passed into the gas phase. Among the aliphatic compounds in the pyrolysis gas, 1-Heptene (C₇H₁₄), 1-Octene, Octane (C₈H₁₈) and 1-Octene 3-ethyl (C₁₀H₂₀) had the highest area (%) for all temperature and all catalysts dosage (Table 4). The usage area of all these organic compounds is extensive all over the world.

1-Heptene can be utilized in the organic synthesis of flavors, dyes, oils etc. (URL 7). 1-Heptane peak area (%) in catalytic pyrolysis gas was higher compared to non-catalytic gas for all studied pyrolysis temperatures (Figure SM2). 1-Octene can be utilized as surfactants, plasticizer, organic synthesis and in polyethylene production (URL 8). Octane is one of the major components of gasoline and it is volatile and very flammable. Its usage area is very wide such as solvent, lacquer diluent, antiknock agent for engine fuels, carrier solvent and blowing agent for foam (URL 9). Compared to the other organic compounds, 1-Octene 3-ethyl has less usage area in the manufacturing sector.

In addition to the compounds observed in all pyrolysis gases at high quantity, compounds which observed at 500 and 700 °C for some catalysts dosages such as Heptane (Table 4) was detected mostly in catalytic pyrolysis gas instead of conventional pyrolysis gas of OP (e.g., 39.71% for pyrolysis gas of 10%K1 and 700 °C). It is highly flammable so it can be utilized in many industries, including use as fuels. Moreover, it can be used as standard for determination of octane rating, solvent and organic synthesis (URL 10) (Figure SM2).

Other compounds observed in pyrolysis gases apart from aliphatics were ketone, ester, terpene, benzene and alcohol. Ketone compounds mostly detected in pyrolysis gases were 2-Hepten-4-one 2-methyl (C₈H₁₄O) and 2-Pentanone 3[(acetyloxy)methyl]-3,4-dimethyl (C₁₀H₁₈O₃). The ester compounds observed in gases were quite low. Pinene alpha (α-Pinene, C₁₀H₁₆), Pinene beta (C₁₀H₁₆) and Limonene (C₁₀H₁₆) were the main terpene compounds detected in



pyrolysis gases (Table 4). Terpene compounds in pyrolysis gases are of great interest due to their relatively high prices and wide applications in the chemical, food, cosmetic, pharmaceutical, fragrance, flavor and biotechnology industries. Especially, α -Pinene has been reported to have the potential to achieve a promising profit margin in a study describing economically promising biobased chemicals (URL 1). Moreover, the sales prices of α -Pinene vary between 45 USD and 13,800 USD/kg, depending on the purity level in the US market (URL 1). Although α -Pinene was not found in pyrolysis gas obtained from pyrolysis of OP without catalyst (in other words 0%K1), it was detected in most of the pyrolysis gases of OP + K1 (Figure SM2, Table 4). Moreover, the highest peak area percentage of α -Pinene were observed in the gases of 50% K1 catalyst dose of 300 and 500 °C, respectively (Figure SM2).

In the benzene group, Benzene ethyl and Benzene methyl (Toluene) were detected under most pyrolysis conditions. Similar to terpenes, benzene groups in gases also have a very important place in the sector. The main use of toluene is by adding it to gasoline to improve octane ratings. Toluene is also used to produce benzene and as a solvent in paints, coatings, synthetic fragrances, adhesives, inks and cleaning agents. In addition to the high number of sectors where toluene is used, its economic value is also quite high. While the global toluene market reached a value of US\$ 21 Billion in 2016, the market is projected to reach a value of more than US\$ 28 Billion by 2022. (URL 11).

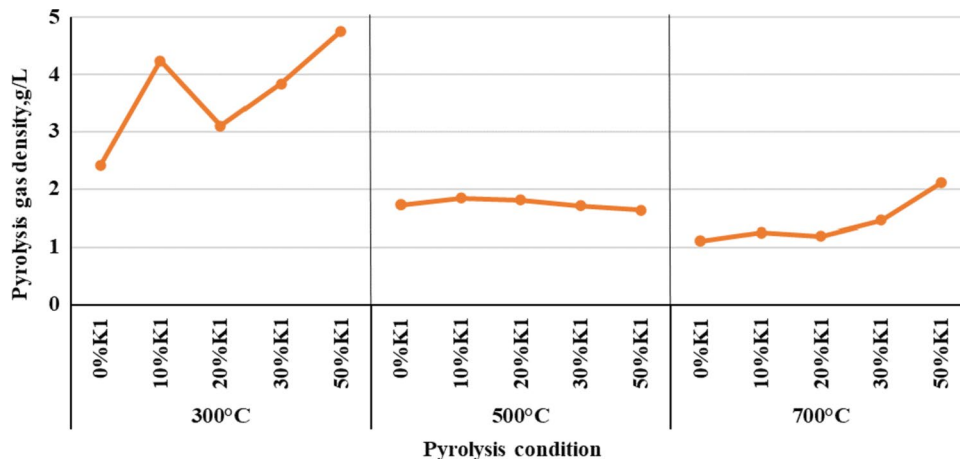
Pyrolysis gas densities change with the organic compound diversity in the pyrolysis gas presented in Figure SM2. Therefore, pyrolysis gas densities were calculated and presented in Fig. 7. While densities for pyrolysis gases obtained at 300 °C pyrolysis temperature changed between 2 and 5 g/L, they ranged between 1–2 g/L for gases obtained at 500 and 700 °C pyrolysis temperature. This indicated that increment in the pyrolysis temperature provided more decomposition of OP biomass, which results in generation of organic compounds having smaller molecular weight and density in the pyrolysis gas. Increment in the pyrolysis temperature from 300 to

700 °C resulted in gas density decrement up to 30%K1 catalyst dosage. As for 50%K1, gas density first decreased with the increment of the temperature from 300 °C to 500 °C and then density increased changing pyrolysis temperature from 500 °C to 700 °C (Fig. 7). This can be correlated with the fact that K1 also starts to degrade at 700 °C and so it affects the gas density as well. The temperature at which the most oscillations were observed in gas densities was 300 °C, and densities at 500 °C were more stable and closer to each other. This can be attributed to the incomplete pyrolysis reactions at 300 °C and the degradation of most of the hemicellulose and cellulose compounds in OP structure at 500 °C.

Conclusion

In this study, marble sludge generated from physicochemical treatment of marble processing facilities was evaluated as catalyst in biomass (OP) pyrolysis to produce economically valuable compounds in fluid phase fractions of OP pyrolysis. Furthermore, sustainable resource recovery approach from agro-industrial wastes were developed by revealing economic value-added potential of wastes. Aliphatic (alkanes and alkenes), aromatic (benzene and phenols) and oxygenated compounds (acids, aldehydes, alcohols, esters and ketones) were observed in all OP pyrolysis bio-oils obtained in this study. ‘1-Pentadecanol, 2-Pentadecanone and 9-Octadecenoic acid (Z) methyl ester’ compounds can be produced at all studied pyrolysis conditions. As for obtaining high-quantity ketone compounds in pyrolysis bio-oils, pyrolysis should be conducted with high K1 dosage since K1 accelerates decarboxylation reactions for converting acid compounds to ketone in pyrolysis bio-oils. If organic compounds, such as Heptadecane, Pentadecane, Hexadecanoic acid methyl ester and Olealdehyde dimethyl acetal, in pyrolysis bio-oils are targeted, catalytic pyrolysis of OP with K1 should be carried. Although these organic compounds were not found in non-catalytic pyrolysis

Fig. 7 Change of pyrolysis gas densities with pyrolysis conditions



bio-oils obtained at 300 °C, they were observed at all catalytic pyrolysis bio-oils at the same pyrolysis temperature. This shows that these organic compounds can be generated at lower temperature by the contribution of K1. Additionally, catalytic pyrolysis bio-oils can be used to produce and/or recovery n-decane compounds (such as Heptadecane and Pentadecane) and n-alkane compounds (i.e., Hexadecane, Heptadecane, Octadecane, Nonadecane) since K1 catalyst had an impact on decarboxylation and hydrocracking reactions. Addition to the quantitative analysis, catalytic effects of K1 on pyrolysis bio-oils were visually observed clearly. The tar content in the bio-oils decreased as the catalyst ratio increased for most pyrolysis conditions, which indicates that K1 converted heavy molecular structures in bio-oil into shorter chained, light organic compounds.

The organic compound diversity in the pyrolysis gases of OP + K1 was less compared to the pyrolysis bio-oils and the most common organic compounds in pyrolysis gases were alkane and alkene aliphatic compounds. Aliphatic compounds having extensive usage areas all over the world, such as '1-Heptene (C₇H₁₄), 1-Octene, Octane (C₈H₁₈) and 1-Octene 3-ethyl (C₁₀H₂₀),' had the highest percentage for all gases produced at all temperature and catalysts dosages. Moreover, terpene and benzene groups having high economic value in the market were observed especially in catalytic pyrolysis gases. All in all, it can be stated that K1 had important catalytic effects on the fluid phase products of OP and various organic compounds having high economic value and extensive usage area can be produced at higher quantity with catalytic effect of the K1 during the OP pyrolysis. The approach presented in this study will contribute establishment of circular economy via the proposed symbiotic waste processing between olive and marble industries.

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Author contributions Original manuscript draft was prepared by Gamze Goktepelı. Experimental studies, material preparation, data collection and analyses were performed by Gamze Goktepelı and Afra Ozgan. Conceptualization, review and editing were made by Gamze Goktepelı, Vildan Onen, Gulnare Ahmetli, Merve Kalem and Esra Yel.

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Availability of data and materials The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Ethical approval The article does not involve human participants and/or animal studies.

Consent to participate All authors of the article agree to participate in the journal submission.

Consent for publication All the authors listed have approved the manuscript that is enclosed.

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