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Catalytic co-pyrolysis of PET/PP plastics and olive pomace biomass with marble sludge catalyst*

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Abstract

Sustainable and efficient waste management requires involvement of symbiotic solutions to various types of wastes, and so to achieve circular economy. Through this motivation, in this study, combined thermochemical conversion (pyrolysis) of plastics, biomass and marble processing effluents physicochemical treatment sludge (K1) were studied. In this combination, plastics were petroleum-based synthetic aromatic (PET) and aliphatic (PP) organics, while olive pomace-OP was natural agricultural residue. K1 was mineral product, which was first introduced in the literature as pyrolysis catalyst by the authors. In the study, co-pyrolysis of polymers and biomass was catalyzed by mineral waste containing $CaCO_3$. The effect of plastic type and pyrolyzed material mixture ratio on pyrolysis fractions were investigated. Moreover, material recovery potential from pyrolysis fractions was discussed. In catalytic co-pyrolysis, by increasing the plastic ratio in the mixture, the pyrolytic liquid and oligomer fraction increased while the solid (char) and gas fraction decreased. For 70%PP+15%OP+15%K1 mixture, liquid product was dominant, whereas with 60%PET+20%OP+20%K1 much more pyrolytic gas fraction was produced. The thermal degradation of char products did not exceed 2-3% up to 600 °C and this stability continues up to approximately 700 °C reveals the potential of the char to be used in alternative areas as a material with high thermal resistance, for example, as adsorbent, in cathodic electrode production, in compost or in composite. The catalytic co-pyrolysis liquid products contain alkanes, alkenes, acids, phenols, benzene, aldehydes, esters, alcohols and ketones. Benzene, acid and alcohol groups were dominant in liquids, while alkane, alkene and alkyne groups were dominant in gases.

Keywords: Biomass, catalytic co-pyrolysis, industrial symbiosis, marble sludge, plastic wastes

1. Introduction

Sustainable and efficient waste management requires involvement of symbiotic solutions to various types of wastes, and therefore, to achieve circular economy. Among the major contributors to carbon footprint the production assemblies and fuels play an important part. Within the scope of circular economy carbon footprint reduction efforts include the upcycling of wastes [1]. Biomass and plastic wastes are natural and synthetic organics, respectively, and their efficient conversion provides mitigation of the pollution caused by them. Instead of produce-use-dispose approach of linear economy, more sustainable approaches are getting popular in terms of circular economy. In circular economy the concept of upcycling is the conversion of waste materials into materials of higher value/quality, lower carbon footprint. Making waste management providing better quality products with upcycling as a more creative approach than recycling. It may be feasible to examine the symbiotic recovery approaches for wastes that can be converted to new generation low-carbon products symbiotically. Post-consumer plastic wastes, which are synthetic polymers make up a sizeable portion of solid wastes. The volume of post-consumer plastic waste is rising due to an increase in the use of plastic in disposable consumer materials [2]. It is projected that by 2050, either landfills or the natural environment will receive about 12,000 Mt of plastic waste [3]. In the two-phase olive oil extraction system approximately 80% of the olive mass becomes OP which is composed of olive pulp, skin, crushed pits and

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residual olive oil as well as a notable moisture content (60–70%) [4]. Marble industry generates inorganic marble particles (mainly in $CaCO_3$ structure) during processing stages, and these are important pollutants either in the air or in water.

Cycling of a single type of waste may produce new products more valuable than the previous, yet, co-processing of more than one type of waste may result in more valuable upcycled products. Pyrolysis is reported as a carbon negative process; the pyrolytic reactions produce oil, gas and char fractions that are able to meet the circular economy and hydrocarbons closed-loop recycling [5]. Strategies for converting biomass and plastic waste in achieving affordable and clean energy in a sustainable manner, which denotes Sustainable Development Goal 7 (SDG7) [6].

It can be emphasized that the industrial symbiosis approach, which focuses on product and resource recycling to create closed-loop systems that essentially aim to produce less waste and consume fewer natural resources, is very important to encourage advanced recycling approaches. One of these approaches is the pyrolysis process. During thermal decomposition, there are chain-breaks and new molecules of different sizes are formed. Since most of these molecules are radical in character, they can turn into gas, liquid and solid products by giving a series of reactions among themselves. The pyrolysis reaction conditions can be inert, oxidative or reductive, catalytic or non-catalytic.

The synergistic effects of co-pyrolysis (pyrolyzing polymers and biomass mixtures together) can improve products quality to valuable hydrocarbons [7–9]. Co-pyrolysis offers an attractive pathway with high potential for mixed wastes by minimizing the requirements on waste separation [10,11]. The use of synthetic polymers with biomass in the co-pyrolysis process can balance the elemental content in the feedstock, improving the properties of degradation products [12]. In their study, Özsin and Pütün [13] co-pyrolyzed walnut shells (WS) and peach stones (PST) were selected as biomass species. They reported that positive or negative synergy depends on the type and contact of components, pyrolysis duration, temperature and heating rate, removal or equilibrium of volatiles formed, and addition of solvents, catalysts, and hydrogen-donors. Among these factors, the types of blending feedstock are the major factor that can significantly influence the synergistic effects [9].

Compared to synthetic polymers, biomass has lower thermal stability and this promotes the degradation of synthetic macromolecules [14]. Biomass is the green source of renewable carbon, but its bio-oil contains a mixture of complex oxygenated compounds such as carboxylic acids, aldehydes, furans, anhydrosugars, ketones, esters, ethers and phenols which gives the bio-oil undesirable properties making its use as a direct substituent for fossil fuel difficult. Plastic wastes contain high H/C ratio and relatively low O/C ratio while its vice versa for biomass and this results in increased quality and uniformity of the products [15]. During co-pyrolysis, plastics serve as hydrogen donors. Hydrogen is transferred to the biomass-derived radicals, which can improve the oil quality and increase its quantity [4,16–19]. Co-prolysis of plastics and OP biomass was reported as innovative solution for sustainable results [1]. By taking advantage of the unique chemical composition of OP biomass and its synergistic interactions with plastics, co-pyrolysis serves the development of new functional materials and additives with improved performance and sustainability credentials [1].

Catalytic pyrolysis processes are widely used for converting polymers into fuel or raw material hydrocarbon mixtures. Catalysts have significant effects on the yield and composition of thermal decomposition products [6,20–22]. Abnisa and Daud [9], Hassan et al. [23] and Zhang et al. [24] reviewed and summarized non-catalytic and catalytic co-pyrolysis and their benefits on biomass and waste plastics co-pyrolysis oil product quality enhancement. Catalytic co-pyrolysis of waste plastic and lignocellulosic biomass can provide superior performance in upgrading pyrolysis oil e.g. produce aromatics along with char reduction [10,23,24]. Catalytic co-pyrolysis of plastic and solid biomass can be developed as in-situ (the catalyst is mixed with the feedstock and placed in the same reactor) or ex-situ (catalyst is separated from the feedstock into a separate downstream reactor) catalysis [25]. The role of plastic to biomass ratio, catalyst, feedstock to catalyst ratio, reaction temperature and co-pyrolysis method are very important in catalytic co-pyrolysis of plastic and solid biomass [10,26]. Mo et al. [26] revealed that future research should focus on the development of efficient catalysts that can effectively convert biomass and plastic waste into useful hydrocarbons. Additionally, research should focus on improving the understanding of the catalytic co-pyrolysis process and the effects of different reaction conditions. Sanchez-Avila et al. [1] inferred that additional research is needed to evaluate the synergistic impact of varying mixing ratios of plastics and OP co-pyrolysis.

Therefore, in this study, as thermochemical conversion, co-pyrolysis of polymers (PET and PP wastes) and lignocellulosic biomass (OP) was catalyzed by mineral waste containing $CaCO_3$ (marble processing wastewater treatment sludge). By this approach, it was aimed to contribute industrial symbiosis solutions. The effect of plastic type and pyrolyzed material mixture

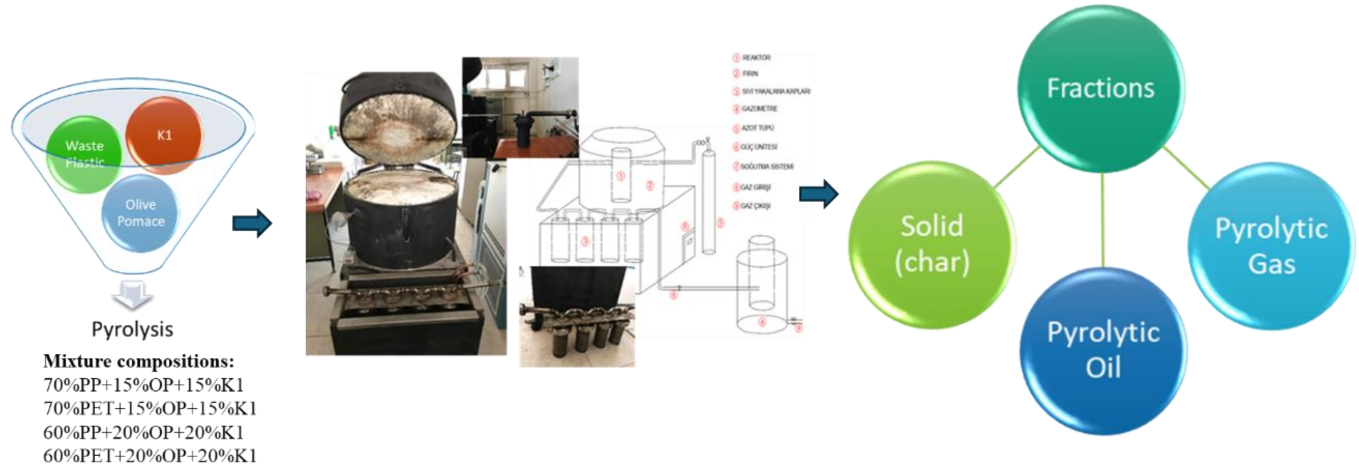


Figure 1. Experimental diagram of in-situ catalytic co-pyrolysis process

ratio on pyrolysis fractions were investigated. Moreover, material recovery potential from pyrolysis fractions was discussed.

2. Materials and method

Co-pyrolysis and catalytic pyrolysis of polymeric material and biomass are among the widely studied applications in the literature. In this study, catalytic co-pyrolysis was applied using three wastes (PET/PP wastes, K1 and OP wastes) and pyrolysis product characterizations were presented. K1 was a mineral product obtained from marble processing industry effluent physicochemical treatment sludge. K1 was first introduced in the literature as pyrolysis catalyst by the authors [27–29]. Co-pyrolysis process was conducted at fixed bed pyrolysis reactor (Fig. 1) at 500 °C pyrolysis temperature with no retention at target temperature. Total mass at each run was arranged as 100 g.

In the previous studies of the authors, it was evaluated that in the catalytic pyrolysis of K1 with plastics, the majority of the reactions were generally completed at the pyrolysis temperature of 500 °C (turning point) in the characterization findings, the most stable pyrolysis products were generally obtained at this temperature, the change in product characteristics was less above 500 °C. Therefore, it was not necessary to work at higher temperatures by spending more energy [27–30]. For this reason, catalytic co-pyrolysis studies were applied as non-retention pyrolysis at the target pyrolysis temperature of 500 °C. In previous studies, it was evaluated that 40% K1 dose in plastic+K1 mixtures provided sufficient maximum fragmentation and that no significant difference was observed in pyrolysis chars at 50% K1 dose, and 40% K1 dose (60% plastic presence in the environment) was recommended for pyrolysis experiments with retention [27–30]. In this study, plastics were selected as the main base material and two different mixing ratios were studied for each plastic (Fig. 1). The mixing ratios studied were 60% PET or PP waste, and 70% PET or PP waste. In each plastic percentages, OP and K1 ratios were kept equal, to prevent changes due to proportional differences.

Char calorific values were determined by bomb calorimeter. For comparison, theoretical calorific values were calculated by using a simple mass balance calculation, in which the calorific values of the char unit mass were assumed to be linear and multiplied by the ratios of the components in the mixture to calculate the theoretically expected calorific values as; %Plastic in mixture*Plastic's heat value + %OP in mixture*OP's heat value = Theoretical cal/g

TGA analyses were performed for the thermal characteristics of the pyrolysis chars and liquid products. FTIR analyses were conducted to analyze the structural differences in the chars and liquid. SEM images were used for the characterization of surface morphology of the pyrolysis chars. GC-MS/FID were used for analyzing the organic compounds found in both pyrolysis liquid and gas products.

3. Results and discussion

3.1. PET/PP+OP+K1 catalytic co-pyrolysis product yields

The product fractions obtained as a result of catalytic co-pyrolysis of PET and PP plastic waste types with OP and K1 at 500 °C were shown in Fig. 2. In catalytic co-pyrolysis with PET, the char and gas fractions decreased while the liquid and oligomer fractions increased by increasing the PET ratio from 60% to 70% and decreasing the OP and K1 ratios from 20% to 15%. In the mixtures containing PP instead of PET, char and gas decreased and the liquid fraction increased with the increasing PP dose. PP was effective in the formation of liquid product, whereas in the mixtures containing PET, the gas product was dominantly higher (Fig. 2). When the OP ratio in the catalytic co-pyrolysis sample, i.e. the decrement of the lignocellulosic structure, the phenolic compounds originating from this structure will also decrease. In the first stage of dehydration and demethylation reactions, compounds with high molecular weight and condensation temperature are formed [31]. Accordingly, since more fluid fraction is concentrated in samples containing less OP, the liquid product yield is higher. It can also be said that the reaction rate increases and the amount of gas increases with more degradation in the case of increment in the amount of K1 in the mixture. The amount of higher solid product in samples containing 60% plastic was primarily related to the higher amount of K1 in the mixture. The lower amount of char in PP containing mixtures was interpreted as PP disintegrating more in the presence of OP and the organic structures in the char were less. This situation was examined in characterization studies. In terms of liquid product yield, it can be recommended to perform catalytic co-pyrolysis in a composition of 70%PP+15%OP+15%K1, whereas, 60%PET+20%OP+20%K1 with PET can be recommended in processes where gaseous product is aimed to be obtained (Fig. 2).

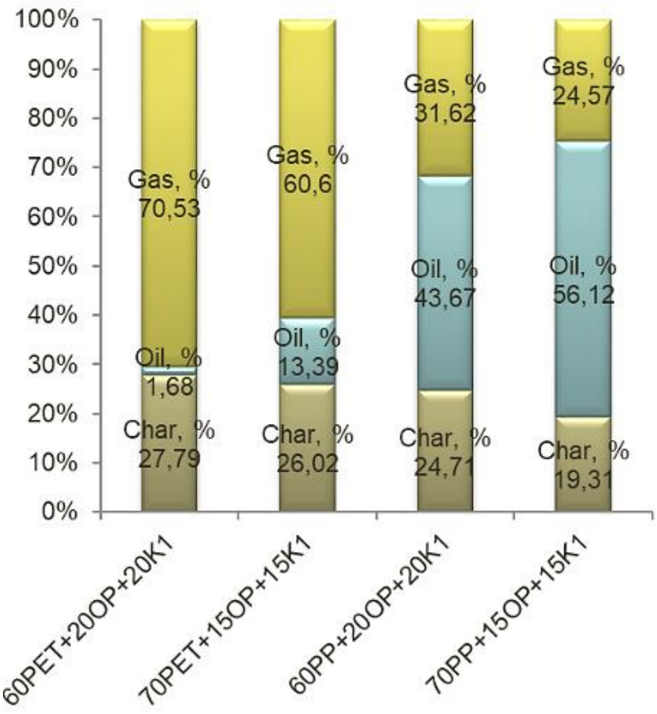


Figure 2. Catalytic co-pyrolysis product yields

The composition of wastes significantly impacts the efficiency and selectivity of catalytic co-pyrolysis. Synergistic effect is the sum of the individual effects or contributions of the co-feeding factors when two or more factors interact. Biomass thermally decomposes through a number of exothermic and endothermic reaction mechanisms. Plastic pyrolysis occurs through radical mechanisms involving initiation, propagation, and revocation through the use of radicals' disproportionation or recombination [26]. Different types of plastics have different chemical structures and properties, that affect their reaction during pyrolysis. PET is aromatic structure which can produce a high yield of aromatic hydrocarbon feedstocks used in the production of plastics, fuels, and chemicals, whereas, PP is aliphatic structure, these compounds can produce a high yield of liquid fuels [23,26]. In their synergistic interaction, biomass and plastics exchange radicals and elemental particles during the co-pyrolysis process and this interaction affects both the quality and quantity of the products [26]. Catalysts exhibit a minor deoxygenation effect on the products compared to the non-catalytic co-pyrolysis process, changing in the hydrocarbon content [4]. CaO, which is the component of catalyst in this study can effectively convert acidic compounds into stable molecules by acting as an absorbent, a reactant, and a catalyst. It can absorb CO_2 from the gaseous product leading to an apparent increase in the H_2 content while reducing the gaseous products [32] (Fig. 2).

In the literature, there has not been exactly similar study with same waste blends and the same catalysts. Grause et al [33] reported 30–50% oil product yield from catalytc pyrolyses under the catalysis of CaO and $Ca(OH)_2$ and It was estimated that the effect of Ca forms change with the type of material pyrolysed [34]. Gulab et al, [35] reported 26.6% oil production in which $CaCO_3$ pyrolysis favors formation of aromatic hydrocarbons. Catalytic co-pyrolysis improve the bio-oil quality by reducing oxygen content through hydro-deoxygenation and liquid yield of 57.0 wt% was reported [36]. High cracking and reforming effects of this low-cost, abundant K1 with its mainly CaCO3 content was intended to increase pyrolytic fluids (oil+gas) quality and quantity. Tang et al [37] reported 32.8% gas, 46.8% oil and 20.4% solid product yields at the same temperature with CaO catalyst, indicating that the addition of CaO during the pyrolysis of waste biomass and plastics significantly enhances the catalytic thermal cracking reactions of tar compounds. By using K1, in the PET catalytic co-pyrolysis, gas product yield could be increased to above 70%, while the oil product yield was increased to above 56% for PP catalytic co-pyrolysis.

3.2. PET/PP+OP+K1 catalytic co-pyrolysis solid product characteristics

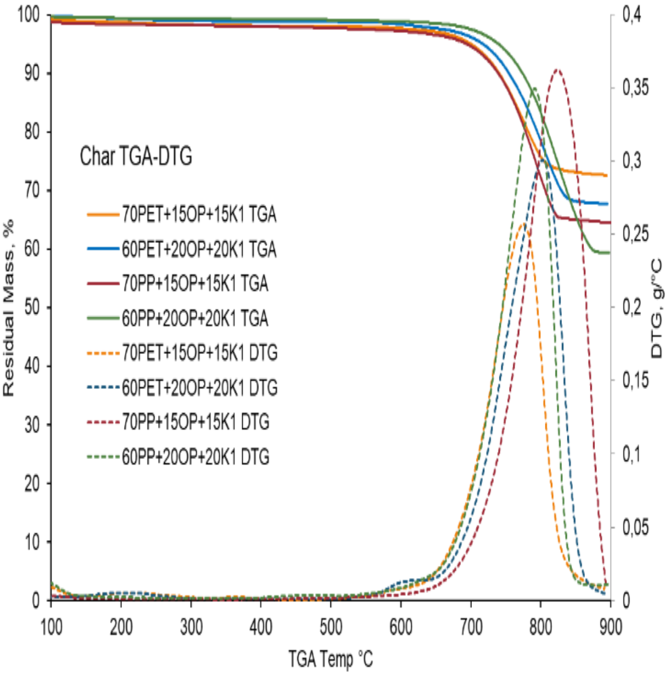
The solid products obtained from PET/PP+OP+K1 catalytic co-pyrolysis are expected to be structurally dominated by carbon and calcium carbonate. According to the findings of the authors' previous studies, the surface acid values of the char products obtained from the mixtures of PET+20%K1, PP+20%K1 and OP+20%K1 at 500 ° C pyrolysis temperature were determined as 0.16 mmol/g, 0.10 mmol/g and 0.06 mmol/g, respectively [30]. In PET+OP+K1 catalytic co-pyrolysis studies, the chars obtained with 60PET+20OP+20K1 and 70PET+15OP+15K1 mixtures at the same temperature had higher surface acid values (Table 1). In catalytic co-pyrolysis, it was observed that the decrease in the ratio of K1 in the alkaline structure caused a slight increase in the surface acid value of the char sample. Surface acidity represents the oxygenated components in the structure of the sample and affects its thermal properties. High acidity favors overreaction of reactants and increases repolymerization of molecules leading to the formation of poly-aromatics. In summary, acid sites promote deoxidation, cleavage, oligomerization, alkylation, isomerization, cyclization and aromatization [4].

Table 1. Calorific values and ash contents of catalytic co-pyrolysis char products at 500 °C

Mixture, %			Char			
			Surface Acidity, mmol/g	Theoretical Heat value (cal/g)[!]	Measured Heat value (cal/g)	Ash (%)
60PET	20OP	20K1	0.18	2905	3103.8	37.91
70PET	15OP	15K1	0.24	3183	3669.5	34.04
60PP	20OP	20K1	0.05	640	818.3	72.43
70PP	15OP	15K1	0.06	540	971.7	69.08

[!] 0.6*4015 + 0.20*2480 = 2905 cal/g
0.7*4015 + 0.15*2480 = 3182.5 cal/g
0.6*239.8 + 0.20*2480 = 640 cal/g
0.7*239.8 + 0.15*2480 = 539.9 cal/g

The calorific values of chars were significantly higher in mixtures containing PET compared to those containing PP (Table 1). In the authors' previous studies, the calorific values of char products obtained at 500 °C pyrolysis temperature of PET+20%K1, PP+20%K1 and OP+20%K1 mixtures were determined as 4015 cal/g, 239.8 cal/g and 2480 cal/g, respectively [30]. The char obtained at 60%PET+20OP+20K1-500 °C pyrolysis condition had a calorific value of 3103.8 cal/g. It was observed that the calorific value of the char product obtained at 70%PET+15OP+15K1-500 °C pyrolysis condition increases slightly by increasing the PET ratio, which provides higher calorific value, and decreasing the OP and K1 ratios. With a simple mass balance calculation, the calorific values of the char unit mass were assumed to be linear and multiplied by the ratios of the components in the mixture to calculate the theoretically expected calorific values (Table 1). The measured calorific values of the char were significantly higher than the calculated values, and in addition, the char calorific value of the sample containing 60% PP was expected to be higher than the one containing 70% PP, but it was lower (Table 1). Compared to the situation in chars obtained in binary combinations of wastes, the fact that the higher calorific value was reached when the OP in the mixture decreases when the three wastes were pyrolyzed together indicates that the catalytic co-pyrolysis reaction mechanisms operate differently. The calorific value depends on the carbon, hydrogen and oxygen content, as well as the H/C ratio. When plastics were used in the reaction, this ratio increased due to the contribution of the H atoms provided by the plastic and accordingly the O atoms decreased, thus the calorific value increased [38]. Co-pyrolysis of PET with biomass can lead to complete suppression of crystallites in PET and minimize the formation and growth of polycyclic aromatic hydrocarbons (PAHs) at 500 °C. However, at extreme temperatures, the formation and growth of PAHs increases due to the increase in the concentration of radicals. Radical formation on biomass is essential for synergistic improvement of the calorific value of char by affecting other carbon structures during co-pyrolysis [39]. Similarly, the ash contents of char products obtained from PET+%20K1, PP+%20K1 and OP+%20K1 mixtures were 30%, 56.6% and 57%, respectively. Contrary to the calorific values, ash contents were higher in ternary mixtures containing PP compared to those containing PET (Table 1). It was observed that as the OP and K1 ratio in the mixture increases, calorific values decrease, and ash contents increase. A systematic difference can also be mentioned between PET and PP.



Mixture, %			Tonset, °C*	Tend, °C**	T_5,°C	T_{10},°C	T_{50},°C	Residue at 900 °C (%)
60PET	20OP	20K1	560	875	700	740	>900	72.5
70PET	15OP	15K1	550	843	717	754	>900	67.7
60PP	20OP	20K1	595	857	694	739	>900	64.4
70PP	15OP	15K1	620	893	739	774	>900	59.3

*T_{onset}: degradation begins; **T_{end}: degradation finishes; $T_{5, 10, 50}$: temperatures of 5, 10 and 50% degradation

Figure 3. TGA-DTG curves and thermogravimetric findings of catalytic co-pyrolysis chars

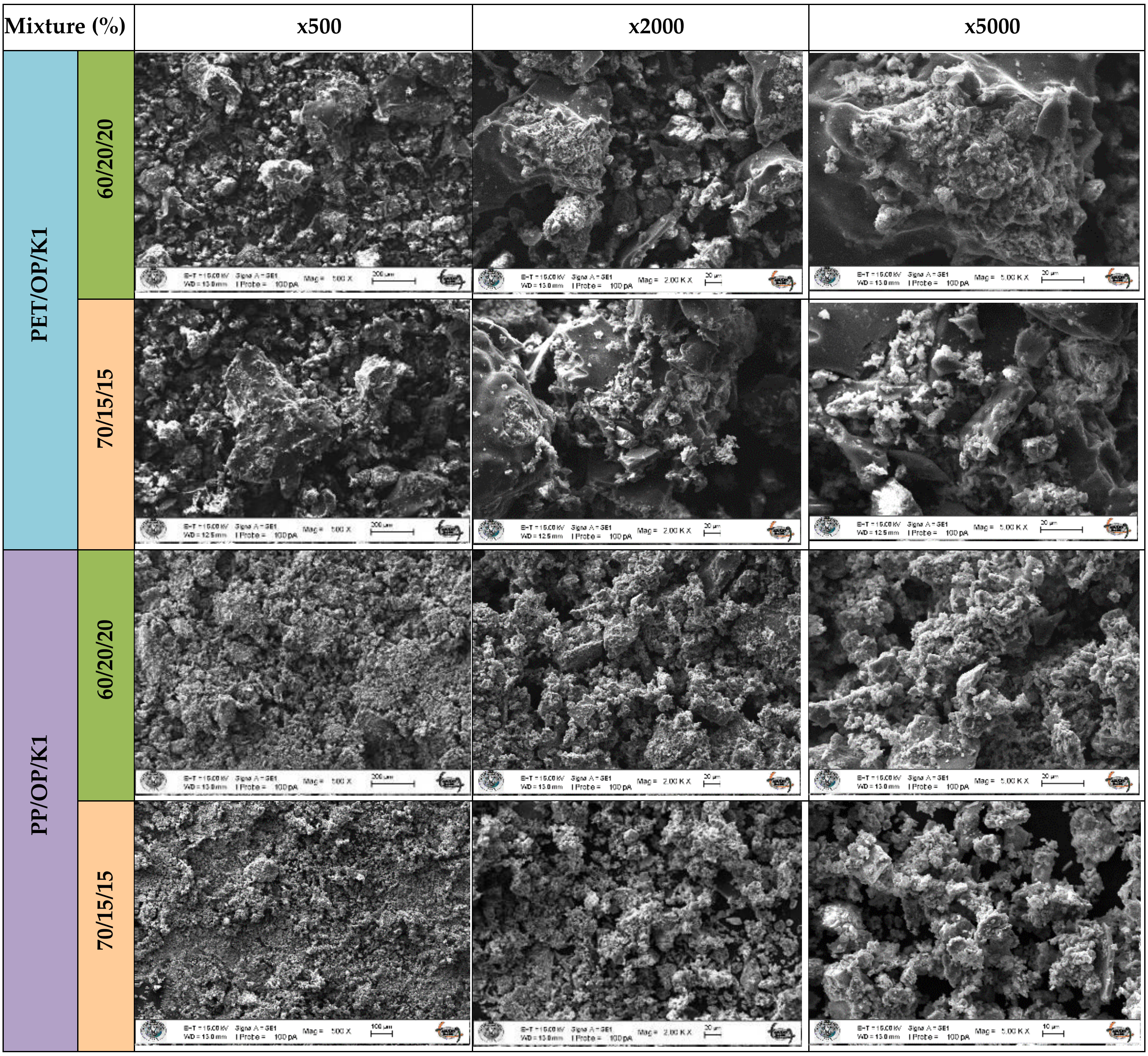


Figure 4. SEM images of char products obtained from the catalytic co-pyrolysis of PET and PP with OP and K1

Thermochemical properties of the solid products were presented in Fig. 3. With the increase in OP and K1 doses in pyrolysis mixtures there was an increase in T_{onset} and T_{end} values for PET and vice versa for PP plastics. In mixtures with higher K1 doses, the char obtained became more thermally resistant. The reason for this situation can be explained as the increase in the amount of mineral structured catalyst in the solid product and the acceleration of the decomposition reaction, making this product inert composition. This situation was also observed in studies where mineral catalysts with a similar structure to K1 were used [40,41]. At the same time, the increase in OP amount plays a role in the increase in thermal resistance for both plastic types. The majority of hemicellulose, cellulose and volatile substances in the OP decompose between 177–380 °C. Hemicellulose decomposes between 157–357 °C under the influence of volatile substances with low molecular weight. Cellulose in the OP structure also begins to decompose between 240–390 °C [42]. The amount of residue left by all samples at 900 °C is more than 50%. According to this residue value, it was determined that the chars obtained in the catalytic co-pyrolysis carried out with PET type plastic wastes were thermally more resistant than PP. However, this finding in the final residue value showed the opposite throughout the degradation reaction. The thermogram of PP-60, which progresses above all curves in Fig. 3 from 600 °C where the decomposition starts, continued as the most resistant char up to 850 °C, but resulted in the lowest residue at the end of the decomposition. Similarly, the thermogram of PET-60 was the second curve from the top, and it resulted in a lower residue than PET-70 at the end. The fact that the decomposition does not exceed 2–3% up to

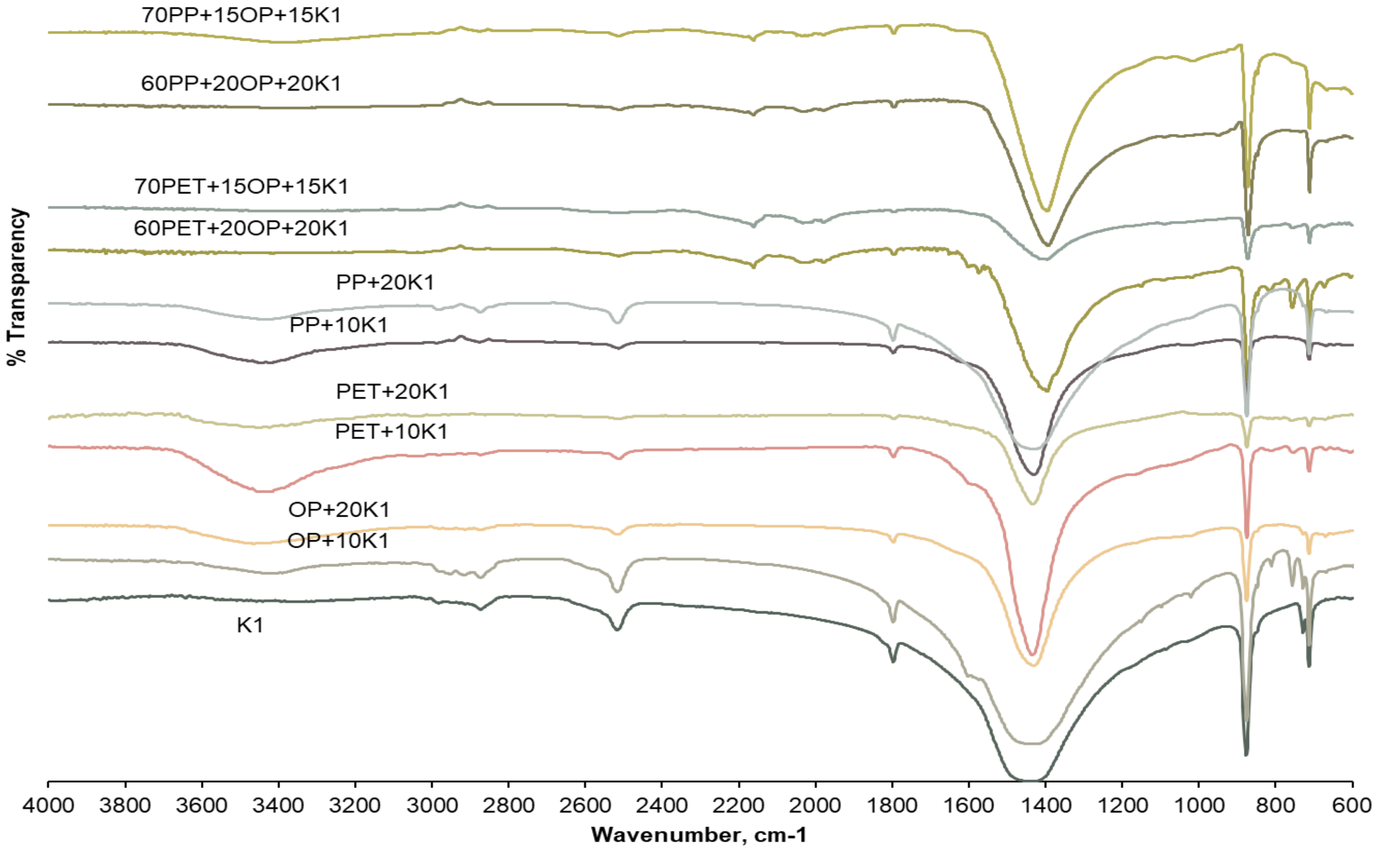


Figure 5. FTIR spectra of PET/PP+OP+K1 catalytic co-pyrolysis chars

600 °C in all thermograms and this stability continues up to approximately 700 °C reveals the potential of the chars obtained with the ternary mixture to be used in alternative areas as a material with high thermal resistance.

SEM images of chars were given in the Fig. 4. In SEM images (Fig. 4), while the agglomeration was more in samples containing PET and the sticky surface image between particles was more apparent. However, in PP chars, more separate and powdery surfaces were noticeable. Char products of PET type plastics at 500 °C for 15% OP and K1 doses, it was observed that the particles were stuck to each other and had a granular structure. It was determined that with the increase in the dose of OP and K1, smaller agglomerations were formed as a result of the non-degradable lignocellulosic structures that caused the adhesion between the particles and the better decomposition of PET fibers (Fig. 4). In the pyrolysis of PP with 15% OP and K1, it was determined that the particle distribution formed by the breakdown of the polymer structure was more homogeneous than PET; the surface roughness and agglomeration of the char increased slightly with the increase of the OP and K1 dose to 20% (Fig. 4). PP is an aliphatic polymer, and the breakdown of PP is almost completed at 500 °C [27–29], but the lignin ratio increases with the increase of the OP ratio in the mixture and not all of the lignin is broken down at this temperature. The increase in agglomeration and surface roughness can be associated with the increase in the lignin ratio remaining from the breakdown in the char structure.

The structural differences in the chars obtained at 500^{0}C catalytic co-pyrolysis of PET/PP+OP+K1 blends were compared with their FTIR spectra (Fig. 5). The bands belonging to the components in the calcite and travertine structure seen at 712 cm^{-1}, 872 cm^{-1}, 1795 cm^{-1} and 2509 cm^{-1} in the FTIR spectra of the chars obtained from the catalytic co-pyrolysis of 60PET+20OP+20K1 and 60PP+20OP+20K1 were an indication that the K1 initially present in the mixture can be completely or partially recovered. Disubstituted benzenes with carbonyl groups at 756 cm^{-1}, C-H bond at 673 cm^{-1}, mono o-substituted benzene at 756 cm^{-1}, trisubstituted double bond at 816 cm^{-1}, mono p-substituted benzene at 847 cm^{-1}, C=C ring stretching of lignin at 1397 cm^{-1}, amine at 1557 cm^{-1}, benzene ring C=C bond at 1574 and 1594 cm^{-1}, aromatic C=C at 1600 cm^{-1}, Si-O and Si-H stretching due to 1979 and 2027 were observed. Most of these bands were also present in the odor spectrum of 70PET+15OP+15K1 catalytic co-pyrolysis, but some band intensities are decreased. The decrease in the band intensity of the C=C ring stretching of lignin at 1397 cm^{-1} can be interpreted as the decrease in the OP ratio in the mixture; the decrease in the band intensities at 872 cm^{-1} and 712 cm^{-1} can be interpreted as the decrease in the K1 ratio in the mixture.

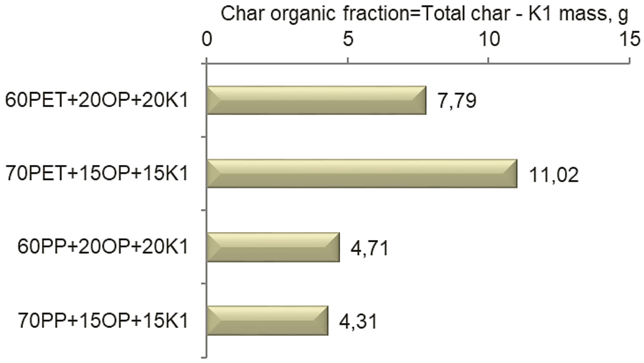


Figure 6. Differences between the initial K1 masses of pyrolysis solid products for PET/PP+OP catalytic co-pyrolysis

The formation of the new bands, the aromatic C-H at 1091 cm^{-1} and the alkyne group at 2161 cm^{-1}, may be due to the higher PET ratio in the mixture (Fig. 5). In the mixture of 60PP+20OP+20K1, mono p-substituted benzene at 848 cm^{-1}, C=C ring stretching of lignin at 1394 cm^{-1}, aromatic C=C at 1600 cm^{-1}, alkyne at 2161 and 2511 cm^{-1}, and aromatic unsaturated compound at 2034 cm^{-1} are observed (Fig. 5). The same bands belonging to the catalytic co-pyrolysis char containing 60%PP were also observed in the catalytic co-pyrolysis spectrum of 70PET+15OP+15K1 and changes were observed in some band intensities.

3.3. Sustainable utilization of pyrolysis solid products

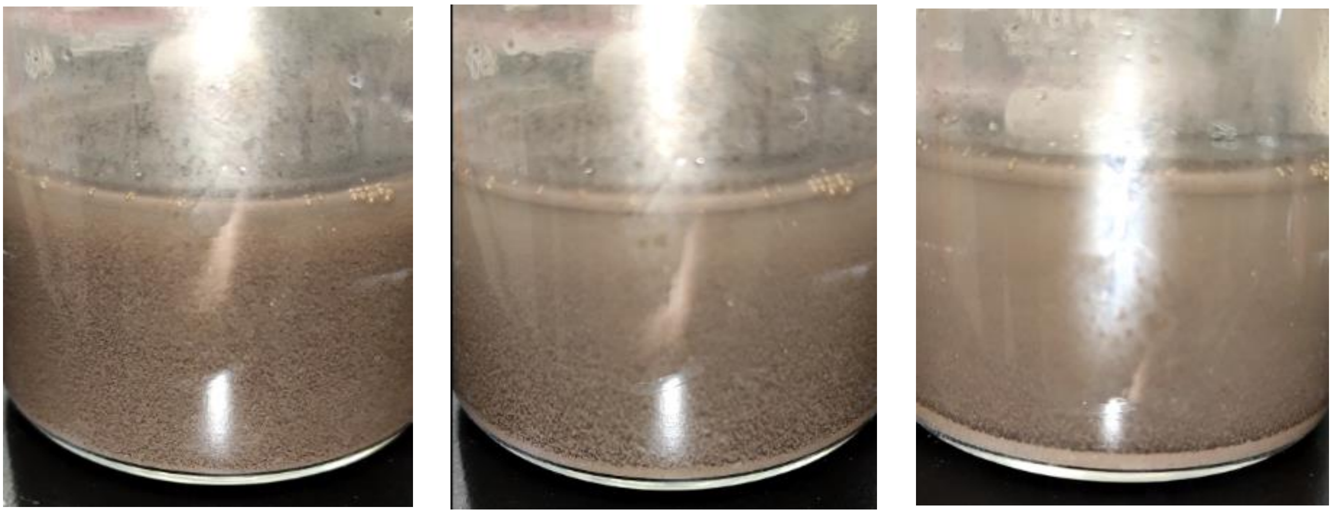
Both carbon structure and K1 were present in pyrolysis chars as mentioned in previous sections. For this reason, in this section, the amounts of K1 initially put into the reactor were deducted from the amounts of solid products and the remaining masses were compared (Fig. 6). The amount and quality of organic components in the solid product affect the usage of the catalyst. Fig. 6 shows how much difference there was in the solid product content after pyrolysis, in addition to the amount of catalyst used at the beginning. The char in the PET+OP+K1 solid product content was higher than the PP+OP+K1 char. The degradation at high K1 doses was also associated with the pyrolytic reactions of the excess K1.

The presence of K1 in the solid product will ensure the reusability of the catalyst. There are some studies indicating that the catalyst must be separated from the char for reusability [43]. On the other hand, some studies in the literature emphasize that pyrolysis chars themselves can be used as catalysts [44–46]. Moreover, the effectiveness of char and CaO together as a catalyst has also been emphasized in the literature [47]. Another common application for pyrolysis solid product is biochar derived from coprolysis holds promise as soil amendment [1]. In the light of this information, two alternative approaches can be mentioned: the separation of char and K1 structures of solid products; or the use of the solid product as it is.

Some preliminary experiments have been carried out for the separation of K1 and carbon part of pyrolysis solid products. It was put into water, mixed in an ultrasonic bath and left to settle; the particles started to settle in a short time as seen in Fig. 7. During settling, the white K1 particles, which were heavier than the carbon structures, first settled at the bottom and the carbon structures formed a black layer phase on top. Although it is important for this situation to appear as in Fig. 7 in 50 seconds in terms of ease of separation, it is highly likely that the other structure will remain, especially between the particle pores during this separation. For this reason, it was evaluated that a short-term ultrasound pretreatment would be beneficial.

3.4. PET/PP+OP+K1 catalytic co-pyrolysis oil product characteristics

The calorific values of the pyrolytic liquid products obtained under other conditions were presented in Table 2.



t=10 seconds t=30 seconds t=50 seconds

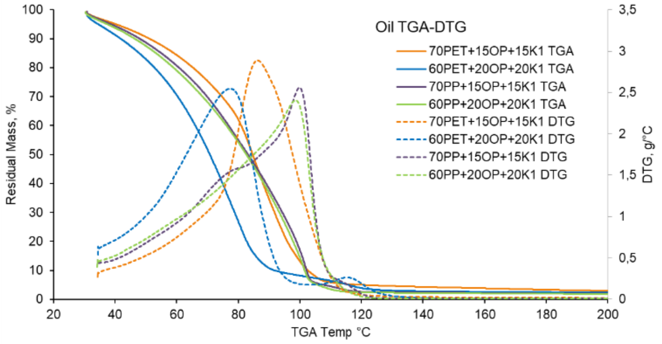
Figure 7. Separation of pyrolysis solid products as they precipitate in water

Table 2. Catalytic co-pyrolysis liquid product calorific values at 500 °C

Mixture, %			Tar/Oil Heat value (cal/g)
60PET	20OP	20K1	N/A (oil not produced)
70PET	15OP	15K1	36.2 (oil) 4448 (oligomer)
60PP	20OP	20K1	9340
70PP	15OP	15K1	10147

Separate measurements were made for the oligomer and oil product obtained under the 70PET+15OP+15K1 condition. The calorific values of the liquid product for PP+20K1 and OP+20K1 pyrolysis at 500 °C were found to be 10147 cal/g and 154.3 cal/g, respectively [29,30]. Approximately 10000 cal/g calorific value was measured in PP+OP+K1 pyrolysis liquid products. It was seen in Fig. 2 that the catalytic co-pyrolysis mixtures provided high amounts of liquid product in the presence of PP. In this case, it was shown that catalytic co-pyrolysis with PP provided higher performance in terms of both quantity and thermal content in the liquid product.

The thermal resistances of the liquid products obtained from PET/PP+OP+K1 catalytic co-pyrolysis were presented in Fig. 8. The curves were quite close to each other. However, the difference in the location of the peak point in the DTG curves shows the difference in the degradation reaction. All liquid products started to decompose at very low temperatures and were exhausted before reaching 200 °C, leaving no residue. The fact that the decomposition started at 30-35 °C can be interpreted as the presence of excessive volatile components in the liquid product. While the IDT and SDT values of the liquid product for PET decrease with the increase in the K1 and OP amounts, the opposite is the case for PP. The reason for this increase in PP can be explained by the fact that the increasing K1 dose creates lower molecular weight groups in PP depolymerization. For both K1 doses, the T_5, T_{10} and T_{50} values were quite close to each other. The fact that the syringyl rings in the lignin structure of OP were reduced and that it becomes more stable in terms of degradation also supports the increase in thermal resistance seen in the TGA curves of PP chars.



Mixture, %			Tonset, °C *	Tend, °C **	T_5, °C	T_{10}, °C	T_{50}, °C
60PET	20OP	20K1	36	123	40	51	85
70PET	15OP	15K1	35	105	35	42	71
60PP	20OP	20K1	36	106	39	48	83
70PP	15OP	15K1	39	110	37	46	82

Figure 8. TGA-DTG curves and thermogravimetric findings of catalytic co-pyrolysis liquids of PP/PET blends with OP and K1

Volatile components have an important role in these liquid products with low thermal resistance (Fig. 8). Chemical structures were evaluated via FTIR spectra (Fig. 9). The oil product of 60PET+20OP+20K1 condition was in too low quantity to characterize. In the FTIR spectrum of the catalytic co-pyrolysis liquid of 70PET+15OP+15K1 and 60%PP+20OP+20K1 mixtures, OH group at 3322 cm^{-1}, alkyne group at 2161 cm^{-1}, aryl substituted C=C at 1634 cm^{-1}, –CH_3 group at 1386 cm^{-1}, vinylidene group C-H or aromatic ether aryl-O stretching at 1278 cm^{-1} were observed. These results showed that the liquid product contains mainly olefinic and aromatic hydrocarbons and oxygenated compounds such as paraffinic and alcohol. According to the GC-MS scans performed to detect this, the liquid product formed by the 70%PET+15OP+15K1 catalytic co-pyrolysis contains alkane, alkene, acid, phenol, benzene, aldehyde, ester, alcohol, ketone and other organic compound groups (Fig. 10). Benzene groups with higher carbon numbers were formed as a result of the condensation of alkene groups in the gas product in the liquid product and were richer in terms of the number of compounds compared to other groups. CaO can react with acids and other carboxyl groups to form calcium carboxylates which would decompose at higher temperatures to form linear ketones, CO_2 and H_2O. As a result, the ketones content of pure CaO increased [4]. While Propanoic acid ($C_3H_6O_2$), Oxalic acid ($C_2H_2O_4$) and Benzoic acid ($C_7H_6O_2$) were the acid compounds encountered, the presence of alcohol and its derivatives in the highest number and variety in pyrolysis liquids can be mentioned. Ethanol, 2-chloro-,acetate (C_2H_5OH), Mequinol ($C_7H_8O_2$); 1-Heptanol, 2,4-diethyl ($C_9H_{20}O$); 2-Isopropyl-5-methyl-1-heptanol ($C_{11}H_{24}O$); Tridecanol ($C_{13}H_{28}O$) were observed as important alcohol compounds and Benzene (C6H6), Dotriacontyl pentafluoropropionate ($C_{35}H_{65}F_5O_2$), Nonadecyl heptafluorobutyrate ($C_{23}H_{39}F_7O_2$) were observed as benzene group (Fig. 11). Consistent with the literature, both the plastics, and biomass polymers crack to produce small compounds involving short chain alkenes and furan derivatives from cellulose and hemicellulose which then react together to produce nonoxygenated aromatic compounds [24]. It can be said that the calorific value of these liquids is higher due to the presence of more components in alkane and alkene groups in the liquid product composition obtained from the catalytic co-pyrolysis of PET waste compared to the liquid product obtained from the catalytic co-pyrolysis of PET waste (Table 2).

3.5. PET/PP+OP+K1 catalytic co-pyrolysis gas product compositions

Considering the distribution of pyrolysis products (Fig. 2), the gas product of the catalytic co-pyrolysis condition, which can produce the highest amount of

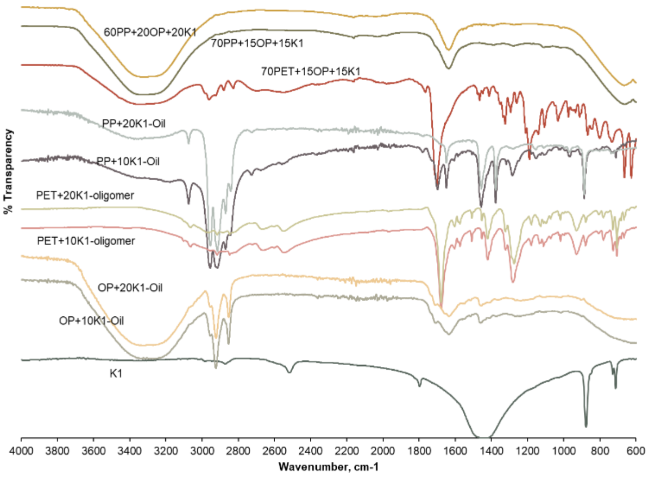


Figure 9. FTIR spectra of PET/PP+OP+K1 no-hold catalytic co-pyrolysis liquids

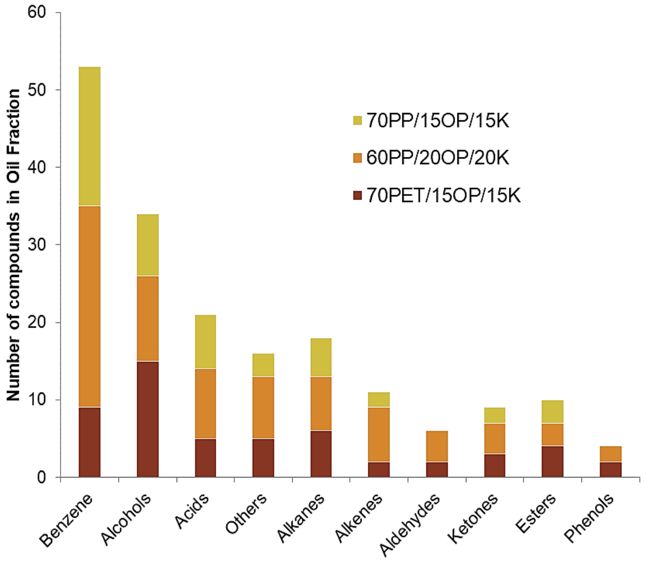


Figure 10. Organic composition of liquid products obtained from catalytic co-pyrolysis of PET/PP waste with OP and K1

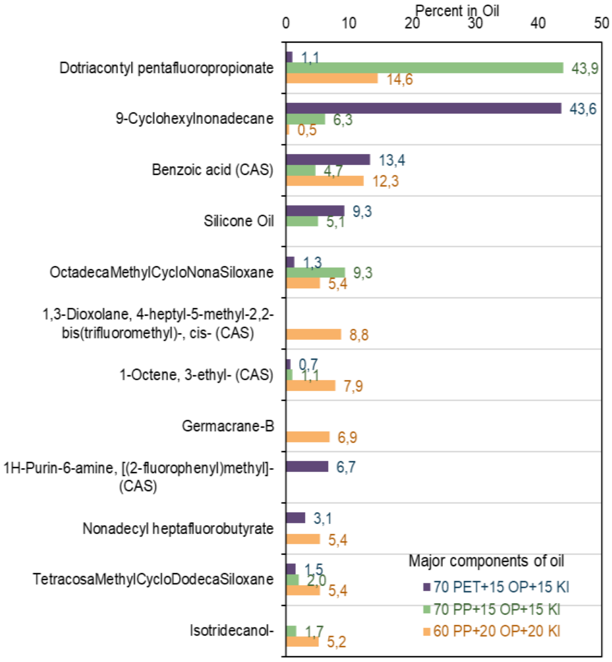


Figure 11. Major components of co-pyrolysis liquids

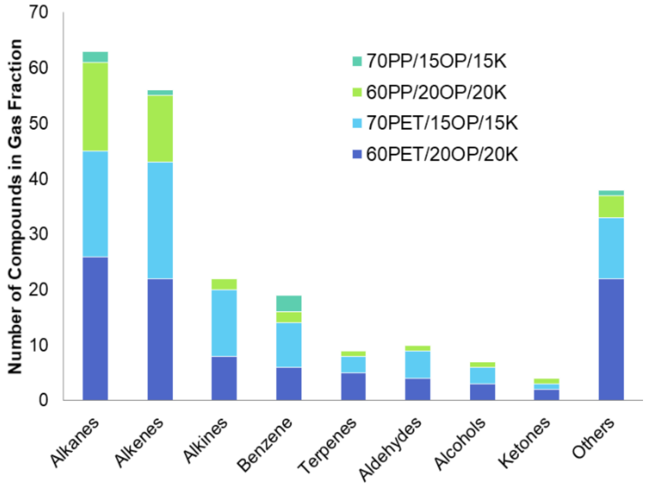


Figure 12. Organic composition of gaseous products obtained from catalytic co-pyrolysis of PET/PP waste with OP and K1

gaseous product, was also the product with the highest component diversity (Fig. 12). In the case of higher OP and K1 doses in PET catalytic co-pyrolysis, an increment in the number of alkane, alkene, terpene and ketone group compounds was also observed. The alkane compounds observed in the majority of the pyrolysis gases obtained with different OP and K1 doses of PET waste were Hexane 2-methyl (C_7H_{16}), Cyclohexane methyl (C_7H_{14}), Cyclopentane ethyl (C_7H_{14}), Cyclobutane (1-methylethylidene) (C_7H_{12}), Heptane 4-methyl (C_8H_{18}), Cyclopentane 1,2,3-trimethyl (C_8H_{16}), Octane (C_8H_{18}), Heptane 3,4,5-trimethyl ($C_{10}H_{22}$), Cyclohexane 1,3,5-trimethyl (C_9H_{18}), Decane ($C_{10}H_{22}$) (Fig. 12 and Fig. 13). In these pyrolysis experiments, the carbon numbers of the gases with a high frequency varied between 7-10 (C7-C10), while the carbon numbers of the gases observed rarely were higher (Fig. 12). Again, with the increase in OP and K1 doses for PET, the presence of the same alkene group compounds was detected.

Although the carbon numbers of alkenes in gases generally vary between 5-12 (C5-C12), the vast majority have 7 and 8 (C7-C8) carbons. Compared to alkane compounds, the carbon numbers of alkenes in gases were lower. In addition to alkane and alkene compounds, other aliphatic groups found in pyrolysis gas were alkynes. Although alkyne groups do not have a wide range of diversity as much as alkanes and alkenes, the most common compounds in PET/OP/K1 catalytic co-pyrolysis gas are 1,1'-Bicyclohexyl and 1-Cyclohexyl-1-propyne. New alkane, alkene, alkyne, terpene, aldehyde, alcohol and ketone group compounds were observed with the increase of OP and K1 doses in PP catalytic co-pyrolysis (Fig. 12). The carbon numbers of alkene compounds observed in the pyrolysis gases of PP+K1 mixtures are between 2 and 13 (C2-C13). When the compositions of the liquid and gas products of catalytic co-pyrolysis are compared with each other, benzene, acid and alcohol groups were predominant in liquids, while alkane, alkene and alkyne groups were dominant in gases.

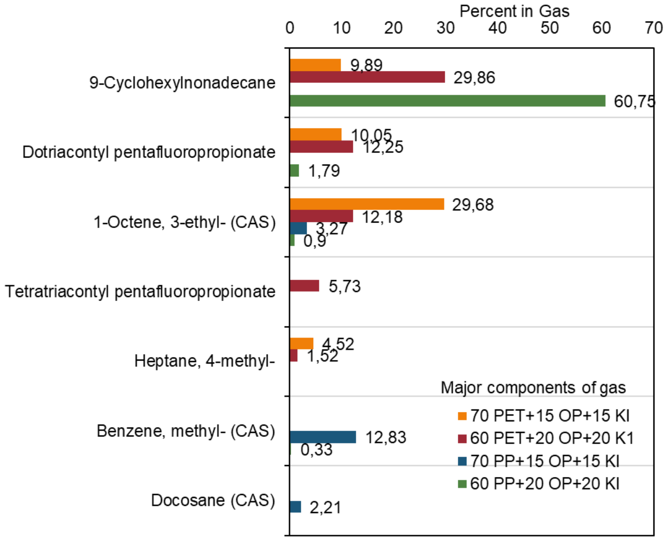


Figure 13. Major components of co-pyrolysis gases

The density of the pyrolysis gas of co-pyrolysis was compared in the Fig. 14. In catalytic co-pyrolysis experiments, as the plastic ratios in both PET+OP+K1 and PP+OP+K1 mixtures increase, the density of the gas product decreases (Fig. 14). The higher density in both in the presence of 60% plastic was related to the fact that the number and variety of compounds in the gas product were higher compared to the mixtures with 70% plastic. In these pyrolysis experiments, the carbon numbers of the gases with a high frequency of observation varied between 7–10 (C7–C10), while the carbon numbers of the rarely observed gases were higher. Compared to the catalytic pyrolysis findings, high carbon numbers and high-density values were decisive in the density of the compound carbon numbers.

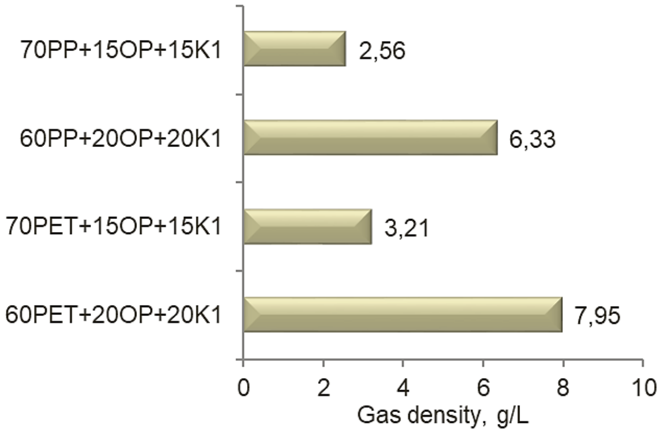


Figure 14. Comparison of the densities of pyrolysis gases obtained by PET/PP+OP catalytic co-pyrolysis

4. Conclusion

In this study, wastes of three different structures were symbiotically recycled via catalytic co-pyrolysis. Two types of polymers (PET and PP) were co-pyrolyzed with lignocellulosic biomass (olive pomace) together with catalytic contribution of marble processing effluent treatment sludge (K1). The effect of plastic type and pyrolyzed material mixture ratio on pyrolysis fractions were investigated. Waste PET or PP can be thermally degraded together with OP and K1 via catalytic co-pyrolysis. While pyrolytic liquid product was dominant for 70%PP+15%OP+15%K1 mixture, much more pyrolytic gas fraction was produced in the pyrolysis of 60%PET+20%OP+20%K1. The thermal stability of char fractions reveals the potential of the char to be used in alternative areas as a material with high thermal resistance, for example, as adsorbent, cathodic electrode production, in compost or in composite. The studies on the details of the conditions of char evaluation and utilization are recommeded as further studies.

The catalytic co-pyrolysis liquid products contained benzene, alcohols, acids dominantly. High number of group components in the liquid product resulted in the higher calorific value, indicating the potential of fuel production. Dotriacontyl pentafluoropropionate, 9-Cyclohexylnonadecane, Benzoic acid, 1-Octene3-Ethyl and Methyl benzene were the chemicals that had the highest recovery potential from catalytic co-pyrolysis fluid fractions. Each of these potentially recoverable chemicals were important feedstock chemicals in diverse number of industries including cosmetics, chemicals etc. The most important output of this study was investigating the potential recovery products via processing of three different types of wastes together. This will help reducing carbon footprint, contribute to achieve circular economy and increasing sustainability. As further studies, the separation and purification technologies for these chemicals need to be studied under the criteria of low energy and material consumption and low cost.

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References

[1] D.T.Sekyere, J. Zhang,Y. Chen, Y. Huang, M. Wang, J. Wang, N. Niwamanya, A.Baridye, Y. Tian, Production of light olefins and aromatics via catalytic co-pyrolysis of biomass and plastic, Fuel, 333, 2023,126339.

[2] N.Sánchez-Ávila, A. Cardarelli, M. Carmona-Cabello, M.P. Dorado, S. Pinzi, M. Barbanera, Kinetic and thermodynamic behavior of co-pyrolysis of olive pomace and thermoplastic waste via thermogravimetric analysis, Renew Energ, 230, 2024,120880.

[3] Z.Murti, D. Dharmawan, S. Siswanto, D. Soedjati, A. Barkah, P. Rahardjo, Review of the circular economy of plastic waste in various countries and potential applications in Indonesia, IOP Conf. Ser. Earth Environ. Sci, 2022,

[4] R. Aguado, A. Escámez, F.Jurado, D. Vera, Experimental assessment of a pilot-scale gasification plant fueled with olive pomace pellets for combined power, heat and biochar production. Fuel, 344, 2023, 128127.

[5] M.S.Qureshi, A. Oasmaa, H. Pihkola, I. Deviatkin, A. Tenhunen, J. Mannila, H.Minkkinen, M. Pohjakallio, J. Laine-Ylijoki, Pyrolysis of plastic waste: Opportunities and challenges, J Anal Appl Pyrol, 152, 2020, 104804.

[6] A.L.K.Chee, B.L.F. Chin, S.M.X. Goh, Y.H. Chai, A.C.M. Loy, K.W. Cheah, C.L. Yiin, S.S.M. Lock, Thermo-catalytic co-pyrolysis of palm kernel shell and plastic waste mixtures using bifunctional HZSM-5/limestone catalyst: Kinetic and thermodynamic insights, J Energy Inst, 107, 2023, 101194.

[7] J. Choudhary, B. Alawa, S. Chakma, Insight into the kinetics and thermodynamic analyses of co-pyrolysis using advanced isoconversional method and thermogravimetric analysis: a multi-model study of optimization for enhanced fuel properties, Process Saf Environ 173, 2023,

[8] S.Y.Oh, Y.D. Seo, Polymer/biomass-derived biochar for use as a sorbent and electron transfer mediator in environmental applications, Bioresour Technol, 218, 2016, 77–83.

[9] F.Abnisa, W. M. A. W. Daud, A review on co-pyrolysis of biomass: an optional technique to obtain a high- grade pyrolysis oil. Energ Convers Manage, 87, 2014, 71–85.

[10] Z.Wang, K.G. Burra, T. Lei, A.K. Gupta, Co-pyrolysis of waste plastic and solid biomass for synergistic production of biofuels and chemicals-A review, Prog Energ Combust, 84, 2021,100899.

[11] A.C.Johansson, L.Sandström, O.G. Öhrman, H. Jilvero, Co-pyrolysis of woody biomass and plastic waste in both analytical and pilot scale, J Anal Appl Pyrol, 134, 2018, 102–113.

[12] K. Yang, K. Wu, F. Li, L. Jia, S. Wang, H. Zhang, Investigation on the co-pyrolysis of bamboo sawdust and low-density polyethylene via online photoionization mass spectrometry and machine learning methods, Fuel Process Technol 240, 2023,

[13] G. Özsin, A.E. Pütün, A comparative study on co-pyrolysis of lignocellulosic biomass with polyethylene terephthalate, polystyrene, and polyvinyl chloride: Synergistic effects and product characteristics, J Clean Prod, 205, 2018, 1127–1138.

[14] F.A.Al-Balushi, K.G. Burra, Y. Chai, M. Wang, Co-pyrolysis of waste tyre and pine bark: Study of reaction kinetics and mechanisms. Biomass Bioenerg, 16T8, 2023,106654.

[15] J. Chattopadhyay, T.S. Pathak, R. Srivastava, A.C. Singh, Catalytic co-pyrolysis of paper biomass and plastic mixtures (HDPE (high density polyethylene), PP (polypropylene) and PET (polyethylene terephthalate)) and product analysis, Energy, 103, 2016, 513–521.

[16] A.C. Dyer, M.A. Nahil, P.T. Williams, Catalytic co-pyrolysis of biomass and waste plastics as a route to upgraded bio-oil, J Energy Inst, 97, 2021, 27–36.

[17] K.G. Burra, A.K. Gupta, Kinetics of synergistic effects in co-pyrolysis of biomass with plastic wastes, Appl Energ, 220, 2018, 408–418.

[18] P.Lu, Q. Huang, A.T. Bourtsalas, Y. Chi, J. Yan, Synergistic effects on char and oil produced by the co-pyrolysis of pine wood, polyethylene and polyvinyl chloride, Fuel, 230, 2018, 359–367.

[19] M.V.Navarro, J.M, L´opez, A.Veses, M.S. Call´en, T.García, Kinetic study for the copyrolysis of lignocellulosic biomass and plastics using the distributed activation energy model, Energy, 165, 2018, 731–42.

[20] J.R.Kim, J.H. Yoon, D.W. Park, Catalytic recycling of the mixture of polypropylene and polystyrene, Polym Degrad Stab, 76(1), 2002, 61–67.

[21] S. Kumagai, I. Hasegawa, G. Grause, T. Kameda, T. Yoshioka, Thermal decomposition of individual and mixed plastics in the presence of CaO or Ca(OH)2, J Anal Appl Pyrol, 113, 2015, 584–590.

[22] S. Gopinath, P.K. Devan, K. Pitchandi, Production of pyrolytic oil from ULDP plastics using silica-alumina catalyst and used as fuel for DI diesel engine, RSC Adv, 10(61), 2020, 37266–37279.

[23] H. Hassan, J.K. Lim, B.H. Hameed, Recent progress on biomass co-pyrolysis conversion into high-quality bio-oil, Bioresource Technol, 221, 2016, 645–655.

[24] X. Zhang, H. Lei, S. Chen, J. Wu, Catalytic co-pyrolysis of lignocellulosic biomass with polymers: a critical review. Green Chem, 18(15), 2016, 4145–4169.

[25] B. Muneer, M. Zeeshan, S.Qaisar, M.Razzaq, H.Iftikhar, Influence of in-situ and ex-situ HZSM-5 catalyst on co-pyrolysis of corn stalk and polystyrene with a focus on liquid yield and quality, J Clean Prod, 237, 2019, 117762.

[26] F. Mo, H. Ullah, N. Zada, A.A. Shahab, Review on Catalytic Co-Pyrolysis of Biomass and Plastics Waste as a Thermochemical Conversion to Produce Valuable Products, Energies, 16, 2023, 5403.

[27] V.Onen, A. Ozgan, G. Goktepeli, M. Kalem, G. Ahmetli, E. Yel, Marble processing effluent treatment sludge in waste PET pyrolysis as catalyst-I: pyrolysis product yields and the char characteristics, Int J Environ Sci Technol, 20(4), 2023,3965-3986.

[28] G. Ahmetli, A. Ozgan, V. Onen, M. Kalem, G. Goktepeli, E. Yel, Marble processing effluent treatment sludge in waste poly (ethylene terephthalate) pyrolysis as catalyst–II: recovery from pyrolytic fluids, Int J Environ Sci Technol, 21(7), 2024, 6021–6042.

[29] G. Goktepeli, A. Ozgan, V. Onen, G. Ahmetli, M. Kalem, E. Yel, Alternative green application areas for olive pomace catalytic pyrolysis biochar obtained via marble sludge catalyst. Biodegradation, 35, 2024, 907–938.

[30] E.Yel (Director), Development of upgrade recycle system by environmental-benign functional materials using waste materials (marble sludge and olive oil wastes) in Turkey, Tübitak-JSPS Joint Research Programs, Bilateral JRP Final Report, 2022.

[31] D. Duan, H. Lei, Y. Wang, R. Ruan, Y. Liu, L. Ding, Y.Zhang, L. Liu, Renewable phenol production from lignin with acid pretreatment and ex-situ catalytic pyrolysis, J Clean Prod, 231, 2019, 331–340.

[32] X. Chen, Y. Chen, H. Yang, W. Chen, X. Wang, H. Chen, Fast pyrolysis of cotton stalk biomass using calcium oxide, Bioresource Technol, 233, 2017, 15–20.

[33] G.Grause, S.Matsumoto, T.Kameda, T.Yoshioka, Pyrolysis of Mixed Plastics in a Fluidized Bed of Hard Burnt Lime, Ind. Eng. Chem. Res. 50(9), 2011, 5459–5466.

[34] S. Kumagai, I. Hasegawa, G. Grause, T. Kameda, T. Yoshioka, Thermal decomposition of individual and mixed plastics in the presence of CaO or $Ca(OH)_2$, J Anal Appl Pyrol 113(2015), 584–590.

[35] H.Gulab, K.Hussain, S. Malik, Z. Hussain, & Z. Shah. Catalytic co-pyrolysis of E Crassipes biomass and polyethylene using waste Fe and CaCO3 catalysts. Int J Energy Res, 40(7), 2016, 940–951.

[36] T. A.Vo, H. V. Ly, I. Hwang, H. T. Hwang, J.Kim, & S. S. Kim, Enhancement of biofuel quality via conventional and catalytic co-pyrolysis of bamboo with polystyrene in a bubbling fluidized bed reactor: Coupled experiments and artificial neural network modeling. Fuel, 346, 2023, 128403.

[37] Y.Tang, J.Dong, Y. Zhao, G. Li, Y.Chi, E.Weiss-Hortala, ... & C.Ye, Hydrogen-rich and clean fuel gas production from Co-pyrolysis of biomass and plastic blends with CaO additive. ACS omega, 7(41), 2022, 36468–36478.

[38] A. Alcazar-Ruiz, F. Dorado, L. Sanchez-Silva, Fast pyrolysis of agroindustrial wastes blends: Hydrocarbon production enhancement, J Anal Appl Pyrol, 157, 2021, 105242.

[39] F.Abnisa, P.A. Alaba, Recovery of liquid fuel from fossil-based solid wastes via pyrolysis technique: A review, J Environ Chemical Eng, 9(6), 2021, 106593.

[40] B. Saha, P.K. Reddy, A.C.K. Chowlu, A.K. Ghoshal, Model-free kinetics analysis of nanocrystalline HZSM-5 catalyzed pyrolysis of polypropylene (PP), Thermochim Acta, 468(1-2),2008, 94–100.

[41] C. Covarrubias, F. Gracia, H. Palza, Catalytic degradation of polyethylene using nanosized ZSM-2 zeolite, Appl Catal A-Gen, 384(1-2), 2010, 186–191.

[42] K. Al bkoor Alrawashdeh, K. Slopiecka, A.A. Alshorman, P. Bartocci, F. Fantozzi, Pyrolytic degradation of olive waste residue (OWR) by TGA: thermal decomposition behavior and kinetic study, J Energ Power Eng, 11(8). 2017, 497–510.

[43] J.Shah, M.R. Jan, Z. Hussain, Catalytic pyrolysis of low-density polyethylene with lead sulfide into fuel oil, Polym Degrad Stab, 87(2), 2005,329–333.

[44] A.S. Al-Rahbi, J.A. Onwudili, P.T. Williams, Thermal decomposition and gasification of biomass pyrolysis gases using a hot bed of waste derived pyrolysis char, Bioresource Technol, 204, 2016, 71–79.

[45] D.Q. Fu, X.H. Li, W.Y. Li, J. Feng, Catalytic upgrading of coal pyrolysis products over bio-char, Fuel Process Technol, 176, 2018, 240–248.

[46] K.Sun, N.J. Themelis, A.T. Bourtsalas, Q. Huang, Selective production of aromatics from waste plastic pyrolysis by using sewage sludge derived char catalyst, J Clean Prod, 268, 2020, 122038.

[47] H.Weldekidan, V. Strezov, T. Kan, R. Kumar, J. He, G. Town, Solar assisted catalytic pyrolysis of chicken-litter waste with in-situ and ex-situ loading of CaO and char, Fuel, 2019, 246, 408–416.