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Fast pyrolysis of agroindustrial wastes blends: Hydrocarbon production enhancement

A. Alcazar-Ruiz, F. Dorado, L. Sanchez-Silva *

Department of Chemical Engineering, University of Castilla – La Mancha, Avda. Camilo José Cela 12, 13071 Ciudad Real, Spain

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ABSTRACT

Fast pyrolysis of waste from agroindustry may be an alternative choice for sustainable use of enhanced biofuels. Plastics are one option for improving the hydrogen to carbon efficiency ratio (H/C_{eff}) of biomass feedstock. Waste from agroindustry in blends with biomass could modify the reaction mechanism for removing oxygen by substituting decarbonylation and decarboxylation with dehydration. Firstly, fast pyrolysis was performed to find the optimal mass blending ratio for olive pomace (OP) and agroindustrial polymers (polyethylene (PE), polystyrenes (PS) and polyvinyl chloride (PVC)) according to hydrocarbon production. Experimental results for the 1.5:1 OP/PE, 1:1.5 OP/PS and 1:1.5 OP/PVC mass blending ratios at 500 °C, showed synergistic enhancement of hydrocarbon yields. Alkenes yield were enhanced for 1.5:1 OP/PE, where the light hydrocarbons fraction (C_6-C_{10}) first increased and then decreased with temperature, reaching a maximum at 650 °C. For 1:1.5 OP/PS and 1:1.5 OP/PVC, it was improved the aromatic compounds formation, being 500 °C and 650 °C the optimal reaction temperature for the former and the later, respectively. Benzene, toluene and xylene were in large quantities obtained for PS and PVC blends with OP. Additionally, the synergistic effect on pyrolysis of the blends did not show any clear trend for pyrolytic gas emissions. In general, as reaction temperature increased, CO and CO_2 emissions fell and CH_4 was enhanced. Finally, olefin and aromatic yields were promoted for blends with a higher H/C_{eff}.

1. Introduction

Growing concerns with the imminent depletion of fossil fuels and their adverse environmental effects have led to a focus on using renewable lignocellulosic biomass as an alternative energy resource. Olive oil production and related industries are of great importance in terms of wealth, health and tradition in the Mediterranean area [1]. However, this industry generates olive pomace in high amounts as waste from agroindustry and there have been moves to valorise this. Dried olive pomace contains a high amount of organic matter, water-soluble fats, proteins, water-soluble carbohydrates and water-soluble phenolic substances [2]. Therefore, this olive waste could be used as a sustainable biomass feedstock for creating valuable products, thereby reducing the impact the olive oil industry has. In addition, the hydrogen to carbon effective (H/C_{eff}) ratio plays a significant role in the conversion efficiency of biomass into valuable products. Thus, it is logical to add high hydrogen yield co-reactants to lignocellulosic biomass, hence modifying the reaction mechanism of oxygen removal by substituting decarbonylation and decarboxylation with dehydration, which enhances the hydrogen deficient biomass [3].

Plastic waste is seen as one option for improving the hydrogen to carbon efficiency of sustainable biomass feedstock due to its hydrogen-rich nature [4]. Furthermore, plastic materials have similar properties to those in fossil fuels in terms of heating value and lack of oxygenated compounds. Currently, the most widespread plastics used are polyethylene (PE), polypropylene (PP), polystyrenes (PS), polyvinyl chloride (PVC) and polyethylene terephthalate (PET). For over 50 years, plastics have been made for improving our standard of living [5]. Consequently, annual global consumption of plastics has surpassed 300 million tonnes [6]. Due to its high consumption, managing this waste material is of great social and environmental concern. At present, recycling these residues is a growth area. In Europe, only 32.5 % of plastic waste generated in 2019 was recycled, while the rest was landfilled or used in energy recovery processes [7]. To be specific, plastic waste from agroindustry represents 2% of total plastic waste generated [8].

To reduce such wastes, different thermochemical methods such as pyrolysis have been promoted as one solution. Pyrolysis of plastic waste in an inert atmosphere is regarded as one of the most viable recycling

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* Corresponding author.
E-mail address: marialuz.sanchez@uclm.es (L. Sanchez-Silva).

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methods for obtaining valuable products [9]. Three pyrolysis processes can be differentiated depending on operating conditions, each of which is aimed at producing desirable products. Fast pyrolysis leads to high bio-oil production (approximately 75 wt.%) and occurs at high heating rates, moderate temperatures and short residence time [4,10,11]. Operating conditions for fast pyrolysis can easily be adjusted to maximise bio-oil production and the quality of the products obtained [12]. Furthermore, in this process plastic could act as a source of hydrogen atoms, producing hydrocarbons with a similar composition found in conventional gasoline [13]. Therefore, co-pyrolysis could be a promising solution since it can easily process waste from biomass and plastics, tackling different challenges simultaneously and converting them into high value fuels or chemicals [14]. In co-pyrolysis, high oil yields are achieved at temperatures from 400 to 600 °C, and the optimum temperature for maximum oil yield depends on the proportions and characteristics of the feedstock [4]. Moreover, co-pyrolysis of woody biomass and plastic waste produces high yields in terms of forming hydrocarbons while oxygenated compounds such as ketones, aldehydes and acids are suppressed [15]. However, any improvements in the yield and quality of bio-oil is attributed to various synergistic interactions between the feedstocks [4,16,17].

Research data on biomass and plastic pyrolysis usually focus on bio-oil properties and yield, rather than the synergistic mechanism. The synergy effect between biomass and polymers in co-pyrolysis is the main factor behind bio-oil quality and any improved quantity [3]. It usually occurs when the combined effects of the components are greater than the sum of their individual ones. Ephraim et al. analysed the synergistic effect and product yield for various plastic materials and saw that product composition depends on feedstock [18]. Li et al. studied the maximum content of hydrocarbons from catalytic fast co-pyrolysis of rice husk and plastic films waste from greenhouses, at a maximum temperature of 600 °C with a mass ratio of 1:1.5 [19]. Mixtures of biomass sawdust and waste polyolefins from packaging for dairy products revealed maximum hydrocarbon production were achieved with 75 % of PS blends [13]. In general, the literature has established a positive synergy between biomass and plastics, which results in enhanced aromatic hydrocarbon yields due to the higher calorific values and H/C_{eff} ratio in plastics compared to biomass [20,21]. Nevertheless, there are no studies that focus on the synergistic enhancement of olive pomace in blends with plastic wastes in which pyrolysis product distribution is valorised.

In this study, olive pomace is co-pyrolysed with waste polymers (PE, PS and PVC) to valorise these agroindustrial subproducts and to research the influence of plastic content on bio-oil properties. Furthermore, olive pomace and the polymers mass ratio (OP/P ratio) and the effect of reaction temperature were studied to evaluate the synergies, hydrocarbon composition in bio-oils, and the hydrogen to carbon effective ratios derived from fast pyrolysis mixtures.

2. Materials and methods

2.1. Materials

Olive pomace (OP) was supplied by Aceites García de la Cruz olive oil mill (Madridejos, Castilla-La Mancha, Spain). Prior to the experiments, OP was first oven-dried for 24 h at 100 °C and milled and sieved to a obtain an average particle size ranging from 100 to 150 μm. The polymers used (PE, PS and PVC) were purchased from Sigma-Aldrich, US. The plastics received were ground and sieved to a particle size of under 0.1 mm.

2.2. Sample characterisation

Materials were first characterized by elemental and thermogravimetric analysis in a TGA apparatus (TGA-DSC 1, Mettler Toledo). The ultimate and proximate analysis were carried out according to standards UNE 15104:2011, UNE-EN ISO18123:2016, UNE 32-004-84 and UNE 32-002-95, in a Thermo Fischer Scientific Flash 2000 elemental analyser, equipped with a thermal conductivity detector. The proximate analysis provided data on moisture, ash, volatile matter and fixed carbon content. Also, the ultimate analysis was used to find the concentration of carbon, hydrogen, nitrogen, oxygen and sulphur in the sample. The higher heating value (HHV) can be calculated using the ultimate analysis data with the following empirical correlation (Eq. 1, [22]; Table 1):

$$HHV\,(MJ/kg) = 0.3491\ x\ C + 1.1783\ x\ H + 0.1005\ x\ S - 0.1034\ x\ O\ -0.0151\ x\ N - 0.0211\ x\ A \tag{1}$$

In which C, H, S, O and N are the weight percentages of carbon, hydrogen, sulphur, oxygen and nitrogen respectively, whereas A is the weight percentage of ash.

In addition, metal content was determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) with Varian 720-ES equipment (which was previously calibrated using standard stock solutions). The ratios of extractives, hemicellulose and Klason lignin in OP were tested according to the TAPPI 204 om-97 and TAPPI T222 om-02 method [23,24] whose results are shown in Table 1.

The chemical structure of the obtained residual carbon after fast pyrolysis was characterized by: Resolution Scanning Electron Microscope (HRSEM), carried out using a Gemini SEM 500 High from ZEISS brand (Oberkochen, Germany); Energy Dispersive X-Ray Analyses (EDX), carried out in an Oxford brand instrument at 15.00 kV accelerated voltage and 127x magnifications; and finally, FTIR spectroscopy, performed with a Perkin-Elmer FTIR Spectrum-two spectrophotometer provided with a Universal Attenuated Total Reflectance accessory (UATR). The spectra accumulated 64 scans with a range between 500 and 4000 cm^{-1} and a resolution of 8 cm^{-1}.

2.3. Fast co-pyrolysis experiments, conditions and procedure analysis

The co-pyrolysis experiments were performed with OP and PE, PS and PVC via Py-GC/MS-FGA (CDS Pyroprobe 6200 pyrolyser; Agilet Technologies 7890B/5977B GC/MS, and CDS Analytical Model 5500 Fixed Gas Analyser). A schema of the experimental setup is presented in Fig. 1.

The GC/MS injector temperature was kept at 280 °C. An Elite-35MS capillary column (30 m x0.25 μm) was used for chromatographic separation. Helium (99.999 %) was selected as the carrier gas at a constant flow rate of 1 mL/min and a 1:80 split ratio. This was carried out to separate and identify the chemical composition of the bio-oil. Oven temperature was programmed from 40 °C (3 min) to 280 °C at a heating rate of 5 °C/min. The chromatograms were integrated, and relative peak areas were calculated and subsequently identified using the NIST library as a reference and only those with over an 80 % matching quality were considered. The FGA used a 1/8″ packed column and thermal conductivity detector to analyse the gases produced during fast pyrolysis that were not easily assayed using capillary GC/MS. The absorbent trap of the pyrolyser collected the organic products from pyrolysis and transferred them to the GC/MS as usual.

Different experiments were performed by varying the OP/P ratio (1.5:1, 1:1, 1:1.5, and 1:2), by keeping the total feedstock mass at 1 mg ± 0.05 mg and placing it in the middle of a quartz tube (2 mm diameter and 20 mm long) with a quartz wool base. The heating rate and the reaction time of fast pyrolysis were optimized, set at 20 °C/ms, and 20 s [2]. Firstly, fast pyrolysis took place at 500 °C to determine the optimum mass ratio. Subsequently, the influence of temperature on product distribution was performed at 500, 550, 600, 650, and 700 °C. The experiments were carried out in triplicate for each sample to ensure reproducibility.

The peak area based on the Py-GC/MS and Py-FGA analysis could not show the real content in the target compounds. However, if the mass of

Table 1
Characteristic data analysis of the materials.

Sample	Proximate analysis (wt.%)^{*daf}				Ultimate analysis (wt.%)^{*daf}				HHV (MJ/kg)	H/C$_{eff}$
	Moisture	Ash	Volatile matter	Fixed carbon^{*diff}	C	H	N	O^{*diff}		
OP	1.36	3.39	79.92	15.31	49.88	6.12	0	43.99	20.01	0.15
PE	0.45	0.22	99.27	0.06	85.70	14.20	0.05	0.05	46.63	1.98
PS	0.26	2.39	97.30	0.04	92.31	7.72	0	0	41.27	1.01
PVC	0.23	1.04	98.73	0.04	40.03	5.09	0	0.65	19.87	0.09
OP Chemical composition (wt.%)^{*db}										
Klason Lignin	21.2									
Hemicellulose	31.5									
Extractives	38.1									
OP Mineral Content (wt.%)										
Ca	0.45									
K	3.48									
Mg	0.068									
Na	0.059									

^{*daf}: dry and ash free basis.
O^{diff}: % of oxygen calculated from difference in C, H, N and S.
Fixed carbon^{*diff}: % of fixed carbon calculated from differences in moisture, ash and volatile matter.
^{*db}: dry basis.

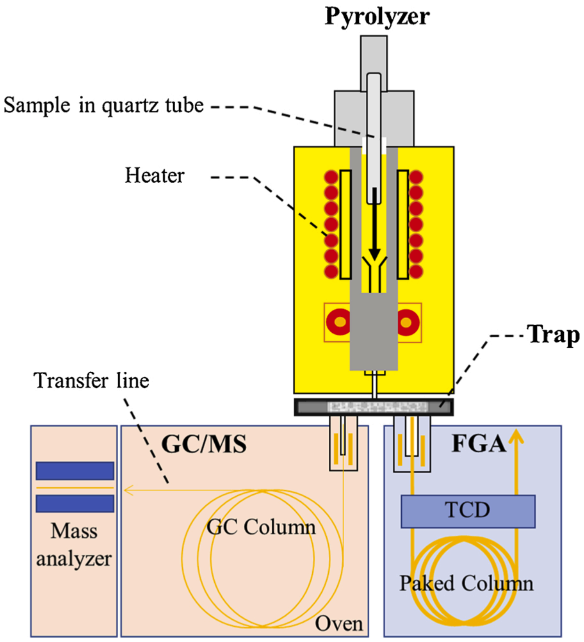

Fig. 1. Schematic experimental setup of Py-GC/MS-FGA used for co-pyrolysis experiments.

the sample was the same in each pyrolysis experiment, the corresponding chromatographs could be compared to reveal the proportion of components in the bio-oils produced.

2.4. *Effective hydrogen to carbon molar ratio (H/C_{eff})*

The effective hydrogen to carbon molar ratio (H/C$_{eff}$) is used to describe whether a feedstock can be upgraded or processed at existing refineries [25]. This factor shows the potential the feedstock has for converting it economically to hydrocarbons, and helps estimating the overall yield of olefin and aromatics [26]. The definition of H/C$_{eff}$ is calculated by using the number of moles of the feedstock with the following equation [16]:

$$H/C_{eff} = (H - 2O - 3\,N - 2S)\,/\,C \tag{2}$$

Higher H/C$_{eff}$ ratios in the feedstock implies more efficient conversion at refineries. This ratio is also shown by many researchers to estimate how a feedstock can be economically converted to hydrocarbons using a potential catalyst. The H/C$_{eff}$ ratio of petroleum-derived feedstocks is between 1 and 2 and that for lignocellulosic biomass is between 0 and 0.3 [27]. Therefore, pyrolysis oil from the latter feedstock may be considered to have hydrogen-deficient molecules when compared to those in the feedstock at the current petroleum refinery [25]. Therefore, to obtain pyrolysis oil with a high H/C$_{eff}$ ratio, agro-industrial plastics could be a potential hydrogen donor feedstock, to produce enhanced bio-oil.

2.5. *Synergistic evaluation*

To obtain a comprehensive analysis of the results, theoretical values expected from each experiment were calculated by considering the proportion of mixtures as an arithmetic sum of the values obtained by single-feedstock fast pyrolysis, assuming there were no chemical interactions between either feedstock during devolatilisation. This method may be considered as one of the best approaches for analysing synergistic effects in properties after any pyrolytic process, since bio-oils from lignocellulosic biomass are not miscible with polyolefin oils [28].

3. Results and discussion

3.1. *Thermal behaviour of olive pomace and agroindustrial plastics*

Fig. 2 shows the thermogravimetric (TG) and the derivate thermogravimetric (DTG) curves obtained for OP, PE, PS and PVC. The main pyrolysis stage for OP took place at temperatures between 120 and 450 °C, as seen from their DTG profile in Fig. 2b. For OP, the shoulders observed at around 280 and 350 °C were attributed to hemicellulose and cellulose decomposition, respectively. These peaks were followed by a tail, which was ascribed to lignin decomposition, leading to char formation. However, a small peak was observed for olive pomace at nearly 400 °C, which could be attributed to lipid decomposition of the olive oil [29]. One outstanding observation was that the thermal stability of the biomass was lower than that for the plastics during pyrolysis. Thus, the free radicals arising when the biomass degraded might have promoted decomposition of plastic-derived macromolecules [3]. Moreover, thermal degradation of PE took place at a higher temperature range (410–520 °C) and was completed at 520 °C. As seen with the behaviour of PE, the PS sample was thermally degraded from 350 to 500 °C. In general, thermal decomposition of most synthetic polymers (such as PE

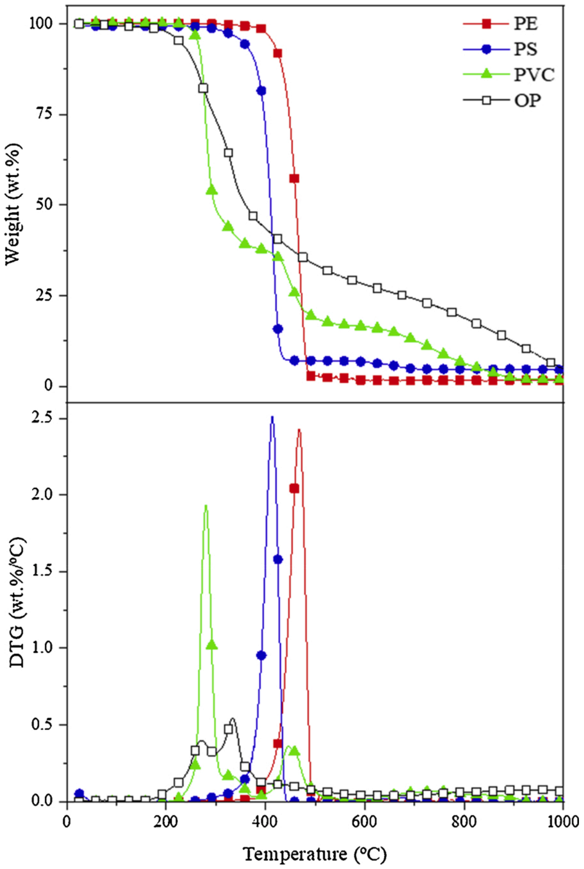

Fig. 2. TG and DTG profiles of OP, PE, PS and PVC; a) TGA curves and b) DTG curves for co-pyrolysis.

and PS) occurs by random scission and radical mechanisms: initiation, propagation and termination [30]. The carbon-to-hydrogen (C—H) bonds of primary, secondary, and tertiary carbon atoms, and carbon-to-carbon (C—C) sigma bond are the only ones that makes probability distribution in bond selection for radical formation or breakage [3]. However, in straight chain polymers, the main products formed are hydrogen gas and hydrocarbons [4]. In contrast with the thermal behaviour seen with PVC, two peaks are observed that correspond to two degradation stages. The first one occurred in the 240−410 °C temperature range. The dominant reaction here was dehydrochloration in which HCl and other chlorinated hydrocarbons were released. The second peak occurred in the 410–540 °C interval, in which rearrangement and cyclisation of conjugated polyene were the main reactions and the benzene derivates generated. This indicates that carbon-chloride bonds during pyrolysis has less energy than that in C—C bonds [31]. Furthermore, note that the loss in mass could have occurred earlier when PVC was in the blend, indicating that promoted pyrolysis products could have occurred at lower temperatures [26]. In conclusion, those polymers selected could provide hydrogen, which is lacking in OP, due to the range of temperatures in fast pyrolysis. Also, there may have been improvements to product distributions for the OP/P blends.

3.2. Effect of OP/P mass ratio on product distribution

To analyse the influence of adding agroindustrial polymers (PE, PS and PVC) to product distribution, different OP/P mass blending ratios were evaluated. The optimal OP/P mass ratio was selected taking into account the hydrogen to carbon effective $(H/C)_{eff}$ ratio which efficiently converted OP into elaborate biofuels. However, this data could demonstrate synergistic enhancement on hydrocarbon product distribution. Also, polymers with different $(H/C)_{eff}$ ratios were selected to be studied in a mixture with OP through fast pyrolysis to observe whether there was an improvement in hydrocarbon production efficiency or not. It must be stressed that fast pyrolysis temperature was set at 500 °C. First, raw samples of the materials under study were pyrolysed to establish their product composition. The results showed significant differences in pyrolysis product distribution for OP and agroindustrial polymer samples. The relative percentage of hydrocarbons in OP bio-oil reached a maximum of 25 %, while the remainder were the oxygenates formed based on alcohol, aldehydes, acids, esters, ketones and phenols. The most representative group identified in OP pyrolysis were phenolics from the thermal decomposition of lignin [23]. In contrast, from pyrolysis product distribution of agroindustrial polyolefins at 500 °C, hydrocarbons were the main functional group detected, and they accounted for nearly 100 %. The theoretical (Theo) and experimental (Exp) data for the carbon yield (%) of each functional group detected after fast pyrolysis of the different OP/P mass ratios were compared to study the synergistic effects. Theoretical carbon yield (CY_{th}) can be calculated as follows [29]:

$$CY_{th} = CY_{OP} \cdot F_{OP} + CY_{P} \cdot F_{P} \tag{3}$$

Where F_{OP} and F_P are the mass fraction of olive pomace and polyolefin used (varied PE, PS and PVC), and CY_{OP} and CY_P are the carbon yields (%) obtained from fast pyrolysis. A positive rise in carbon yield production in comparison with the theoretical value of the blend could be deemed a synergistic effect in which more hydrocarbons are formed. Fig. 3 summarised this effect on hydrocarbon distribution for the different OP/P mass ratios with the fast pyrolysis experiments performed at 500 °C.

Fig. 3 compares theoretical and experimental carbon yields of total hydrocarbons produced from fast pyrolysis for different OP/P mass blending ratios. With PE, its product distribution is mainly based on hydrocarbons, with alkanes being the most representative group detected, with a yield of 64.17 %. The PE composition gave rise to a greater HHV of 41 MJ/kg (Table 1), similar to those in commercial fuels, such as gasoline or diesel [32]. However, PE in blends with biomass feedstock was expected to reduce the oxygen content at the organic phase whilst carbon yield increased, leading to a higher HHV. The synergistic effect between the OP/PE mass blending ratios during fast pyrolysis has been discussed. In Fig. 3a, synergy was detected on comparing theoretical and experimental hydrocarbon formation for OP/PE blends. Aliphatic hydrocarbons derived from pyrolysis of PE might have interacted with the oxygenate fraction present in OP through a series of cracking, cyclization and isomerization reactions, thereby increasing hydrocarbon diversity (alkenes and cyclic hydrocarbons) [16]. According to the results, the 1.5:1 OP/PE mass blending ratio produced the highest percentage of hydrocarbons. The maximum percentage of hydrocarbons reaches a maximum of 89.73 % at 500 °C. The hydrocarbons obtained are mostly aliphatic compounds, especially long chain olefins, and they amount to 79.44 % of total condensable compounds. Thus, it may be concluded that mixtures of OP and PE by fast pyrolysis can modify the reaction mechanism, thereby removing oxygenates by substituting decarbonylation and decarboxylation with dehydration [3]. Previous studies have demonstrated the modification of reaction pathway of the co-feeding of lignocellulosic biomass with hydrogen-rich feedstocks in catalytic pyrolysis [33–35]. In addition, hydrogen abstraction by OP oxygenates and reactive free radicals could facilitate thermal degradation of PE, which explains the synergy on increasing aliphatic hydrocarbons [3].

Regarding Fig. 3b, from the OP/PS blends, positive synergy was observed with an increase in hydrocarbon, specifically the carbon yield of aromatic compounds. Bio-oil composition obtained from PS fast pyrolysis was shown to be oxygen-free. It has significant hydrocarbon content which amount to 64.54 % of carbon yield. In comparison with PE, PS has a low aliphatic content due to its aromatic ring. Also, PS has a similar HHV to commercial liquid fuels, and has the capacity to reducing

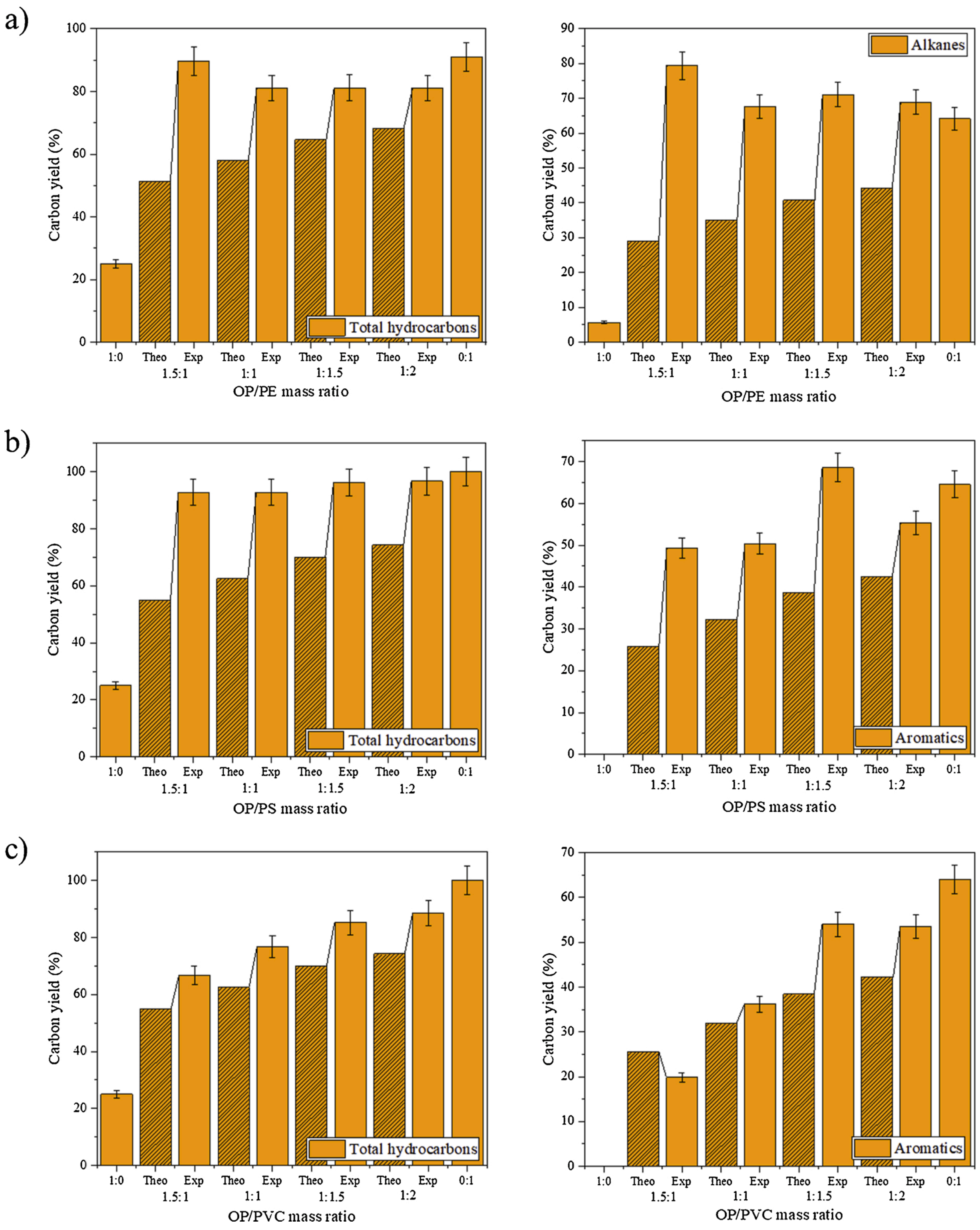

Fig. 3. Mass ratio effect on fast pyrolysis hydrocarbon production at 500 °C of a) OP/PE, b) OP/PS and c) OP/PVC.

oxygen increasing carbon yield. Different OP/PS mass ratios were studied to observe the synergistic effect in fast pyrolysis by comparing theoretical and experimental results. The aromatic yields obtained are discussed between ratio blends. Moreover, the 1:1.5 OP/PS mass blend ratio provided the highest percentage of hydrocarbons. The relative content of hydrocarbons in this blend represented 96.23 % of carbon yield at 500 °C, in which 68.57 % of the condensable compounds detected were aromatics. These results were coherent with the literature, in which adding PS in blends with lignocellulosic biomass enhanced the quality of the bio-oil obtained, as oxygenated compounds transformed into aromatics [36–38].

Some special polymers, such as PVC, has attracted attention for use in co-pyrolysis. PVC was selected despite its low H/C_{eff} in comparison with other polyolefins. In Fig. 3c, a synergistic effect in the OP/PVC blends by fast pyrolysis at 500 °C was assumed. Results revealed hydrocarbon compounds were the main product obtained from PVC pyrolysis, with aromatics being the most representative hydrocarbon with 53.43 % of total carbon yield. Zhou et al. researched the pyrolysis mechanism for PVC, and explained that formations of aromatics can be ascribed to molecular rearrangement and cyclisation of fragments of polyene [31]. PVC has low HHV, which may not help to reduce oxygen content in blends with OP. Moreover, OP has a higher H/C_{eff} ratio in comparison to PVC. The hydrogen content in OP could act as a hydrogen donor for PVC in fast pyrolysis. In this case, water evolved from OP pyrolysis could also act as a reactive compound, thereby accelerating further cracking of PVC, and hence, promoting yields of bio-oil [3]. Furthermore, PVC chloride atoms are unstable and easily split at higher temperatures. Dehydrochlorinated and chlorinated hydrocarbons were formed at temperatures below 500 °C. As the pyrolysis temperature was set at 500 °C, chloride compounds were not detected in this study. Additionally, removing HCl typically includes alkali and alkaline earth metal substances as absorbents, as the inherent metals presents in the organic matrix of OP [31]. This will be discussed in more detail below. The blend with the 1:1.5 OP/PVC mass ratio produced the highest carbon yield of hydrocarbon compounds (85.23 %) at 500 °C, in which 54.04 % of the components detected were aromatics.

These results demonstrated the synergy observed on comparing theoretical and experimental data. This proved to have an apparent effect on bio-oil hydrocarbon production, thus enhancing use of OP [16]. Additionally, one of the forms to evaluate the bio-oil quality is through its calorific value. Closely, this depends on carbon, hydrogen and oxygen contents, as well as the H/C_{eff} ratio. When plastics are used in the reaction, this ratio increases due to the contribution of the H atoms that the plastics provide, and consequently the O atoms decrease, thus increasing the calorific value [39]. For this reason, synergy was obtained between OP and agroindustrial polyolefins (PE, PS and PVC), where the oxygenates were reduced and hydrocarbon compounds fomented. Indeed, this effect was supported by the effective hydrogen to carbon ratio values obtained for the blends. The carbon yields of hydrocarbon compounds in bio-oil with H/C_{eff} ratios are given in Fig. 4. The convex parabolic curves in Fig. 4a and 4b demonstrate there is a synergistic effect between OP and PE or PS blends in fast pyrolysis. Alkenes production reached a maximum carbon yield for the 1.5:1 OP/PE blend ratio, in which the H/C_{eff} mixture marked 0.88. This result suggests that the 1.5:1 OP/PE ratio should mean there is enough hydrogen added to the blend to maximise hydrocarbon products. However, this small amount of PE in the blend could stabilize most of the unstable compounds in the bio-oil by hydrogenation. The unstable molecules that tend to increase coke formation include oxygenates with unsaturated bonds [27]. Conversely, aromatic compounds reached maximum yields when OP/PS and OP/PVC blend ratios were 1:1.5, in which H/C_{eff} was 0.66 and 0.11, respectively. Remarkably, in OP/PVC mixtures aromatic production synergy was observed in the bio-oils produced, even though PVC showed a low hydrogen to carbon effective value. Despite this, PVC was characterised as hydrogen-rich and intermediate in a blend with OP during fast pyrolysis. Furthermore, oxygenated chemical bonds from the OP organic matrix could favour chain scission and breakages in long-chain organic matter in polyolefins [3]. The convex curves shown demonstrate synergy in the OP/P blends. Thus, this may indicate that thermochemical processes efficiently convert more undefined oxygenates into hydrocarbons when producing bio-oil from these blends. The best options for OP/P mass blending ratios were 1.5:1 OP/PE, 1:1.5 OP/PS and 1:1 OP/PVC. These were the optimal proportion of polyolefins and OP feedstock for enhancing olefin and aromatic compounds production yields.

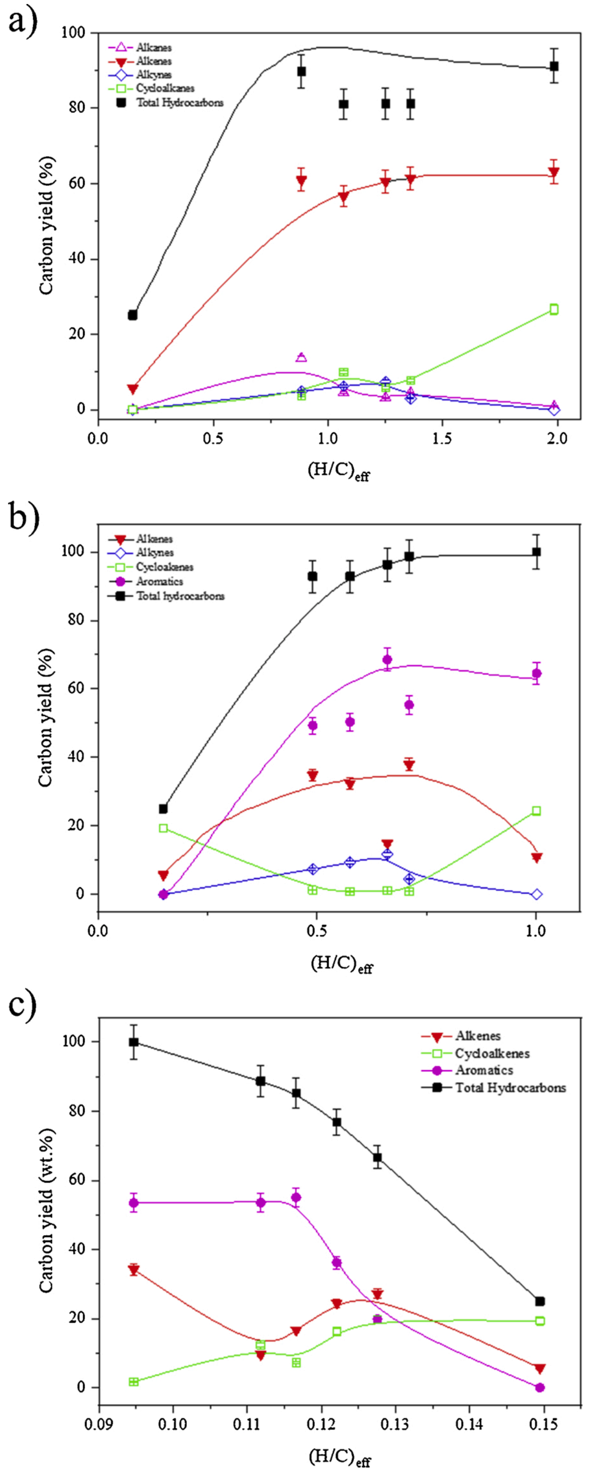

Fig. 4. Hydrocarbon composition in the bio-oil obtained through fast pyrolysis with different H/C_{eff} ratios of a) OP/PE, b) OP/PS and c) OP/PVC feedstock blend ratios.

3.3. *Influence of reaction temperature on fast pyrolysis products for the OP/P mass ratios selected*

To study the influence of fast pyrolysis temperature on hydrocarbon composition, 1.5:1 OP/PE, 1:1.5 OP/PS and 1:1.5 OP/PVC blends were evaluated at a range of 500–700 °C. The experimental hydrocarbon composition obtained by varying reaction temperature are shown in Fig. 5.

Fig. 5 shows how hydrocarbon production is promoted as fast pyrolysis temperature increases. This trend varied in carbon yields depending on the feedstock selected. From the literature, higher temperatures in fast pyrolysis indicate that more energy is available for rupturing organic bonds. This could promote devolatilisation in feedstocks and facilitate endothermic co-pyrolysis reactions [16]. Regarding

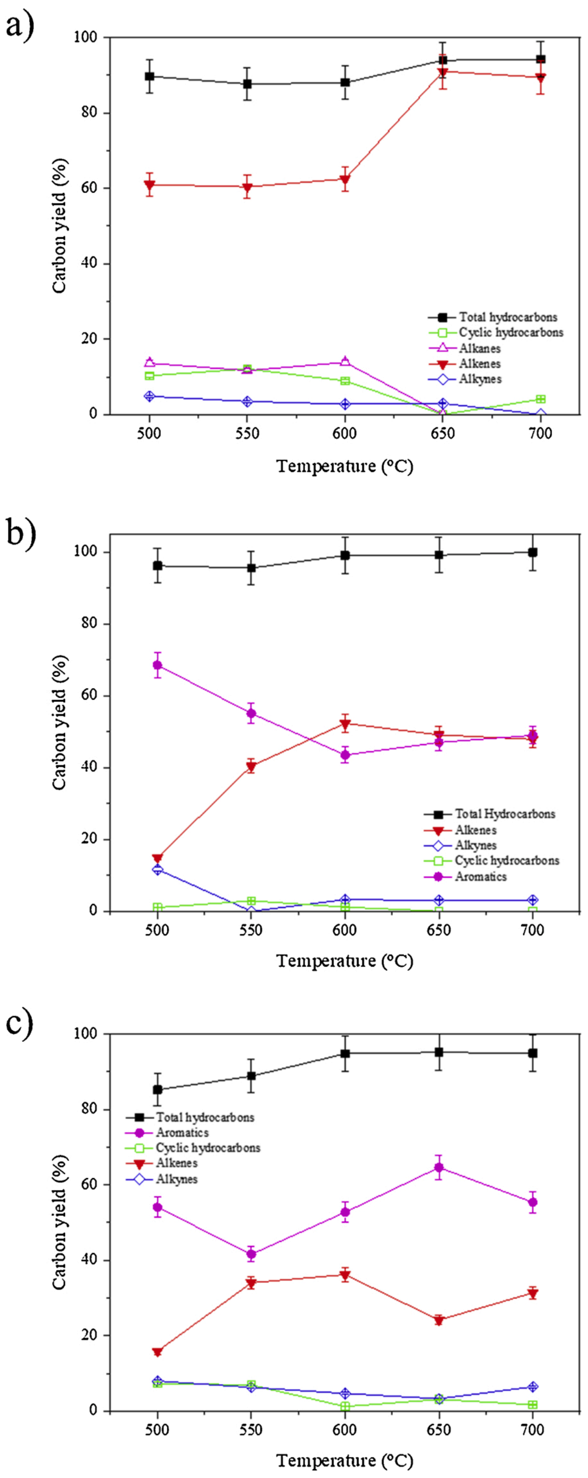

Fig. 5. Influence of temperature fast pyrolysis on a) 1.5:1 OP/PE, b) 1:1.5 OP/PS and c) 1:1.5 OP/PVC feedstock blend ratios.

the1.5:1 OP/PE mass blend ratio, maximum carbon yield was detected at 650 °C, with a maximum production of aliphatic compounds (93.97 % of total hydrocarbons). Remarkably in Fig. 5a for 1.5:1 OP/PE at 650 °C the following carbon yields were observed: 91.02 % of alkenes and 2.94 % of alkynes. Alkene yields initially accounted for 61 % at 500 °C and reached a maximum value at 650 °C. Strikingly, in the case of 1:1.5 OP/PS blend (Fig. 5b), 500 °C was selected as the optimal temperature due to the positive results obtained in aromatic hydrocarbons production yields. When PS was used in the blend, aromatic carbon yields declined as temperature increased, reaching minimum yields at 600 °C. By contrast, at 600 °C alkene yields reached a maximum (52.35 %) for the 1:1.5 OP/PS mass blending ratio. Further studies on pyrolysis established that 500–550 °C was the optimum temperature range for maximising hydrocarbon composition from waste plastic based on polystyrene [5]. In Fig. 5c, carbon yields obtained from a temperature analysis of the 1:1.5 OP/PVC mass blending ration is shown. The results revealed a maximum yield for the total sum of hydrocarbons at 650 °C which accounted for 95.16 %. Aromatics were the main product detected with 64.62 % of carbon yield. At lower temperatures they fell to the detriment of alkenes. In contrast, when pyrolysis temperature increased, this trend was reverted. This might have been due to reforming and aromatisation of alkenes, and the side chains of the aromatic ring structure cracking during depolymerisation under high temperature conditions [31]. In this study, no organic chloride compounds were found above 500 °C for OP/PVC blends. According to the research of Chen et al. [40], interactions might occur between the pyrolysis products of PVC and the volatiles of biomass pyrolysis, or between the products of PVC and the solid char residue of biomass pyrolysis. To clarify this finding, ultimate and mineral content analysis were carried out to the solid char residue generated by 1:1.5 OP/PVC at 650 °C sample (Table 2). The carbon content greatly increased (76.40 wt.%) while oxygen content was reduced (17.25 w.%) in comparison with the data from raw OP (Table 1). In addition, HSEM coupled with EDX was carried out to study the residual carbon obtained after fast pyrolysis at 650 °C for OP/PVC blends. As shown in Fig. 6a, the carbon residue obtained for 1:1.5 OP/PVC showed a porous structure. It is due to the amount of volatile matter, as well as the chemical composition of OP, in which hemicellulose content was detected in higher proportion (Table 1) [2,41,42]. EDX results (Fig. 6b) demonstrate that carbon, in agreement with ultimate analysis (Table 2), was the major contributor to the sample. Interestingly, chlorine was detected in the same weight percentage as inherent AAEMs (K). Fig. 6c shows the FTIR spectrum of the obtained carbon residue. A strong absorption peak at 3100−2600 cm^{-1} corresponding to the asymmetrical stretching of H-Cl was observed. Moreover, an absorption peak at 750−660 cm^{-1} verified the existence of -C-Cl bonds in the char residue [31]. Thus, these results suggest that the rests of chlorinated compounds from PVC were retained by the char residue. It has been proposed that biomass materials can act as catalyst which inhibits the dehydrochlorination process or promotes the chain scission of PVC. Thus, dehydrochlorination during PVC fast pyrolysis is only partly completed [43]. Similar results were obtained from Kuramochi et al. [44], where chlorine emissions were reduced by the presence of wood during pyrolysis of PVC. The reason suggested by these authors was that hemicellulose may reduce HCl emission by fixing the Cl into the pyrolyzed residue. As commented, our results also indicates that chlorinated compounds were retained in the carbon residue. Thus, it would be an effective method for degradation and dechlorination of chlorine-containing plastics to produce high quality liquid products. The generation of chlorinated hydrocarbons would be avoided increasing the pyrolysis temperature and with the presence of inherent alkali and alkaline earth metals (AAEMs) from lignocellulosic biomass, acting as adsorbents. Indeed, one the typical methods to remove HCl involves the use of AAEMs as adsorbents [31,45–47].

Regarding the hydrocarbon distribution in the bio-oil, a significant increase in the yield of aliphatic compounds for PE and aromatic

Table 2
Characteristic data analysis of 1:1.5 OP/PVC char residue at 650 °C.

Ultimate analysis (wt.%)^{*daf}			
C	H	N	O^{*diff}
76.40	5.67	0.68	17.25
Mineral content (wt.%)			
Ca	K	Mg	Na
0.24	1.58	0.057	0.049

^{*daf}: dry and ash free basis.

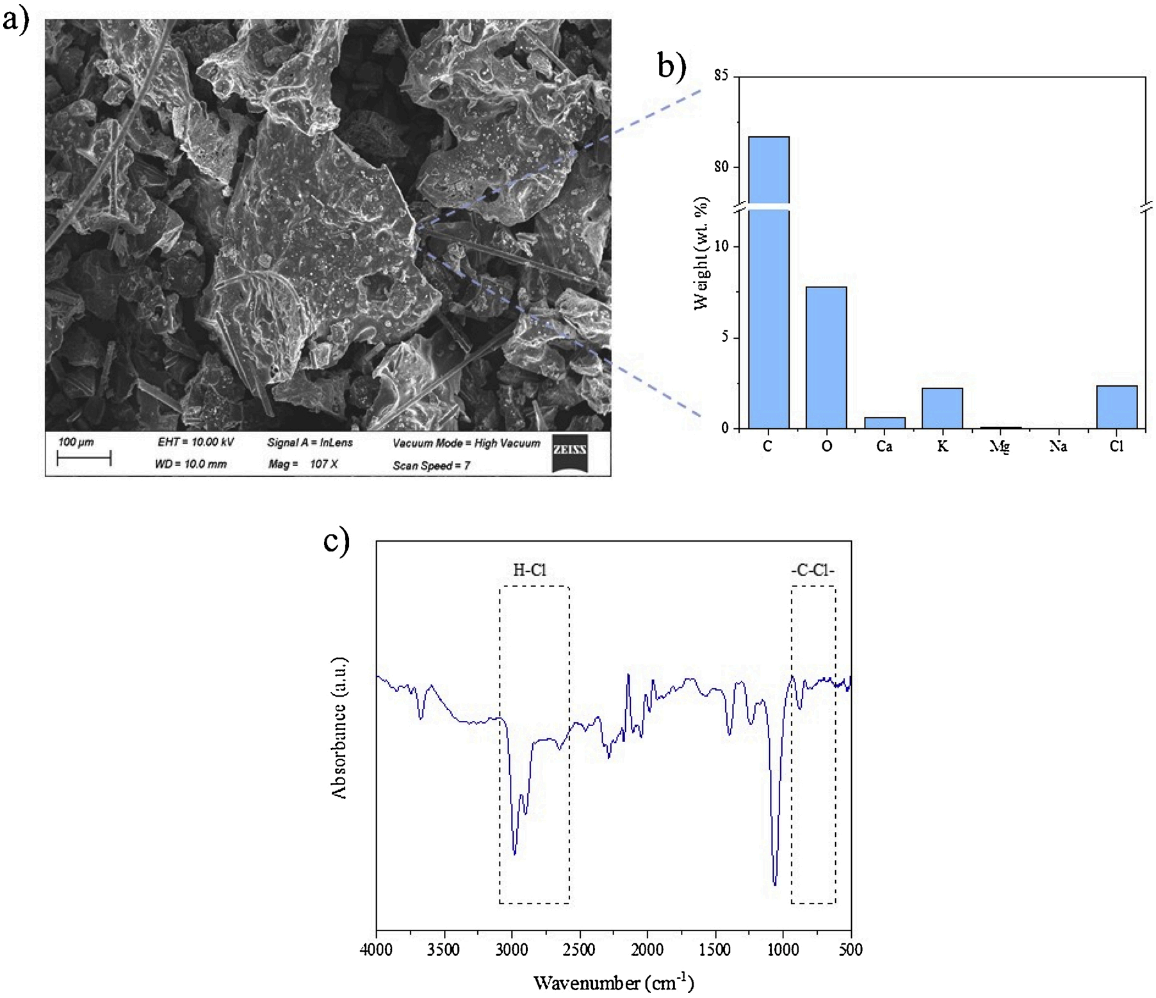

Fig. 6. Characterisation analysis of the obtained 1:1.5 OP/PVC char residue after fast pyrolysis at 650 °C: a) HRSEM image, b) EDX analysis and c) FTIR spectra.

hydrocarbons for PS and PVC in blend with OP can be noted as reaction temperature increased. Moreover, aromatics were the main products for OP with PS and PVC blends, including monocyclic aromatic hydrocarbons (such as benzene, toluene and xylene) and polycyclic aromatic hydrocarbons (PAHs). Both aromatics and olefins are essential as feedstock for the manufacture of valuable products, such as pharmaceutical compounds, paints, solvents, among others [39]. Moreover, light olefins together with BTX (benzene, toluene and xylene) are the most common preliminary petrochemicals [48]. To further investigate the effect of temperature on the production of that valuable components, an analysis of the major fraction obtained in the bio-oils were carried out. Table S1 shows a detail breakdown of the hydrocarbon distribution in the bio-oils obtained at different reaction temperatures. The effect of temperature on the carbon number distribution of aliphatic hydrocarbons for 1.5:1 OP/PE blends is shown in Fig. 7. The aliphatic fraction was in the range of C_6-C_{20}, which were mainly derived from the random chain scission of the PE [39,48]. As temperature increase, the relative content of light hydrocarbons (C_6-C_{10}) first increased and then decreased, reaching the maximum at 650 °C, accounting C_6 and C_7 maximum carbon yields. On the other hand, the hydrocarbon fractions between C_{11} and C_{20} exhibited a different trend, first decreasing and then increasing with reaction temperature. These results suggest that the long C-C chains cracking to form light hydrocarbons (C_6-C_{10}) was favoured as reaction temperature increased, being optimum at 650 °C.

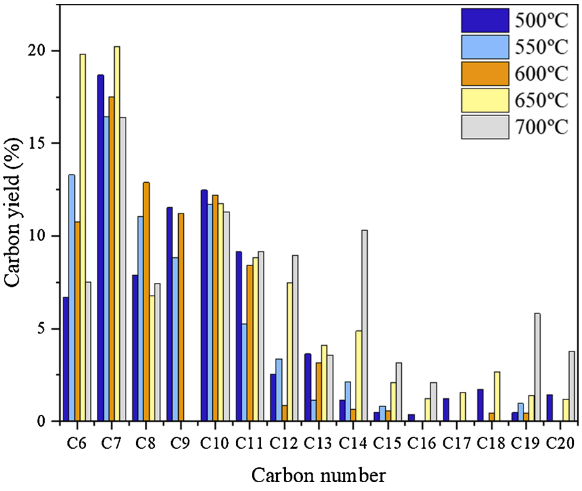

Fig. 7. Effect of reaction temperature on the carbon number distribution of aliphatic hydrocarbons in the bio-oil obtained for the 1.5:1 OP/PE sample.

The influence of reaction temperature for 1:1.5 OP/PS was done focused on aromatic distribution. Both PS and OP (specially lignin, one of its major chemical fractions) are aromatic in nature. Additionally, there is a possibility of PAHs formation from their degradation products. In this work, PAHs are categorized as naphthalene and its derivatives, indene and its derivatives, and multiring aromatic components having more than two rings. Fig. 8a shows the aromatic selectivity of 1:1.5 OP/PS blend as reaction temperature increased. The obtained aromatic

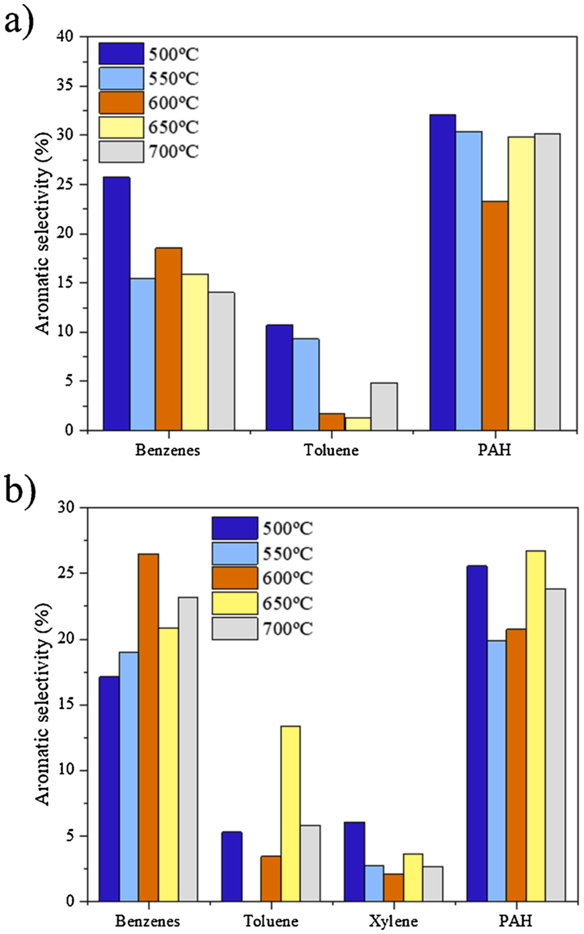

Fig. 8. Effect of reaction temperature on the aromatic compounds distribution in the bio-oil obtained for the a) 1:1.5 OP/PS and b) 1:1.5 OP/PVC sample.

compounds were divided into benzenes (benzene derivatives include ethylbenzene, propylbenzene, 2-propenylbenzene, 1-propenylbenzene, cyclopropylbenzene, biphenyl, terphenyl, etc.), toluene and PAHs. The presence of naphthalene and indene derivatives could be attributed to the generation of methyl groups during lignin depolymerization [49]. In general, benzenes and toluene selectivity decreased while PAHs were in the same percentage yield when reaction temperature increased. As PAHs are undesirable in the bio-oil because they are highly susceptible to coke formation [49–51], a reaction temperature of 500 °C would be the best for this blend.

For the 1:1.5 OP/PVC blend, the effect of temperature was studied dividing the obtained aromatic fraction into benzenes and its derivatives, toluene, xylene and PAHs. For this sample, it was obtained a higher yield of aromatics than the pyrolysis of the raw biomass. Interestingly, the most valuable monocyclic aromatics (toluene and xylene) were found for the OP/PVC blend, but not for the raw PVC. Thus, the combination of OP and PVC improves the final product, generating valuable chemicals like BTX. The aromatic selectivity of 1:1.5 OP/PVC blend at different reaction temperature is shown in Fig. 8b. BTX were obtained in a major proportion at 650 °C, accounting 37.9 % of aromatic selectivity. Among the PAHs observed, two-ring PAH, naphthalenes and indenes, dominated in all the samples. Naphthalene selectivity was decreased as reaction temperature increased, from 9.7 to 6.4 %. In general, monocyclic aromatics were favoured versus PAHs fractions as reaction temperature increased.

To sum up, the fraction of light hydrocarbons (C_6-C_{10}) was favoured as reaction temperature increased for 1.5:1 OP/PE, being the optimum temperature 650 °C. On the other hand, valuable chemicals like toluene or xylene were found abundant in the bio-oils, and useful aromatics like styrene or ethylbenzene were amply formed for PS and PVC mixed with OP. They increased with temperature for 1:1.5 OP/PVC, but not for 1:1.5 OP/PS, being therefore the optimum temperature 650 °C for the former and 500 °C for the later.

Pyrolytic gas was collected during fast pyrolysis experiments and analysed with FGA. The fixed gas compounds that passed through the trap in fast pyrolysis at 500 °C for the materials under study are shown in Fig. 9. The thermochemical processes involved high rates of temperature conducive to endothermic reactions, such as Boudouard, water-gas, and steam-methane reforming [29]. The main gases given off during pyrolysis were CO, CH_4, CO_2, C_2H_2, C_2H_4 and C_2H_6 and the main ones obtained throughout the whole process were CO, CO_2 and CH_4 for all samples. Olive pomace had the highest CO_2 yield and CH_4 emissions, which correlated with the elemental analysis (Table 1). CO and CO_2 are formed from thermal decomposition of oxygen functionality in their inner lignocellulosic organic matrix [52]. The light hydrocarbons detected came from thermal cracking and methanisation [53]. The highest CH_4 yield may have been promoted by the inherent amount of potassium content in the OP sample (Table 1). This metal is reported in the bibliography as an active catalyst for methanation [29]. However, there is a close correlation between the H/C_{eff} ratio and pyrolytic gas emissions yields. Zhang et al. stated that as the H/C_{eff} ratio feedstock rose, CO and CO_2 emissions also increased [27]. For that reason, as PE is one of the polyolefins with the highest ratios of H/C_{eff}, high amounts of CO and CO_2 emissions were observed. For OP, the sum of the oxygenated gases represented the most important fraction detected. Furthermore, as polymers are abundant sources of hydrogen, a greater amount of light hydrocarbons gases (C_2H_2, C_2H_4 and C_2H_6) were detected in comparison with lignocellulosic OP. However, these gases might have evolved in aromatisation, thereby enhancing carbon efficiency yields of aromatic compounds in blends with OP [6].

Using biomass and polymers to improve fast pyrolysis product yields and quality is an important issue for research on pyrolysis gas emissions. The pyrolytic gas produced from the combination of biomass-polymer pyrolysis comes into contact swiftly before cooling, and is catalysed into CO_2 or CO. Synergy is observed after these processes, when oxygen is removed, and high-quality bio-oil is obtained [54]. Regarding the pyrolytic gas emission results for the blends used, it might be concluded that they did not follow any clear trend due to the synergy between the raw materials. Table 3 shows the effect of temperature on yields of the gases given off which were detected for the previously selected mass blending ratio samples. Overall, a reduction in CO and CO_2 product yields was seen, when OP was mixed with polymers. Blends with a low H/C_{eff} ratio should produce more CO by decarbonylation, as they are hydrogen-deficient compounds, which probably limit the amount of

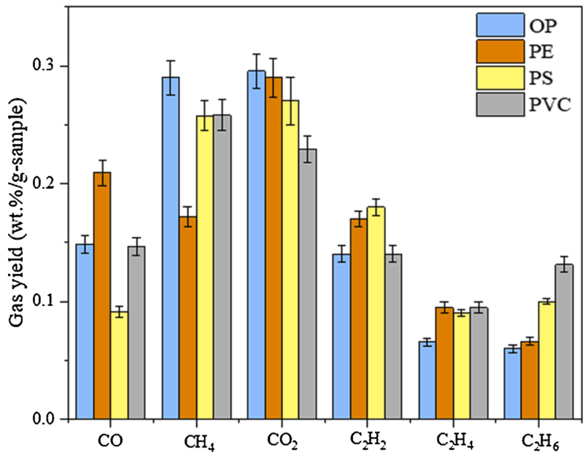

Fig. 9. Pyrolytic gas yields obtained (wt.%/g-sample) from fast pyrolysis of OP, PE, PS and PVC at 500 °C.

Table 3
Pyrolytic gas composition results at different fast pyrolysis temperatures.

Sample	Reaction temperature (°C)	wt.% / g-sample					
		CO	CH_4	CO_2	C_2H_2	C_2H_4	C_2H_6
1,5:1 OP/ PE	500	0.17	0.21	0.26	0.16	0.13	0.09
	550	0.11	0.21	0.26	0.18	0.16	0.09
	600	0.18	0.29	0.17	0.07	0.21	0.08
	650	0.16	0.24	0.17	0.15	0.16	0.12
	700	0.15	0.10	0.26	0.23	0.12	0.13
1:1,5 OP/ PS	500	0.30	0.35	0.19	0.11	0.03	0.03
	550	0.26	0.35	0.19	0.11	0.03	0.06
	600	0.07	0.31	0.36	0.14	0.04	0.09
	650	0.06	0.34	0.14	0.33	0.06	0.08
	700	0.14	0.55	0.11	0.07	0.09	0.04
1:1,5 OP/ PVC	500	0.34	0.06	0.29	0.21	0.06	0.07
	550	0.32	0.09	0.29	0.17	0.06	0.07
	600	0.62	0.15	0.07	0.05	0.05	0.06
	650	0.14	0.36	0.17	0.20	0.05	0.08
	700	0.19	0.52	0.16	0.06	0.02	0.04

oxygen transferred into water and favour CO production [27]. Also, CO_2 formation by the water-gas shift reaction as a function of H/C_{eff} shows the same trend as that for CO [27,55]. For the 1.5:1 OP/PE, the range of temperatures between 600–650 °C, limited CO_2 emission was observed. These results are coherent with hydrocarbon compounds yields at those temperatures at which oxygenates were suppressed. Moreover, CH_4 became the most representative gas in PE blends, due to the features this plastic has, as it is a carbon chain. The effect of temperature on the 1:1.5 OP/PS displayed ever increasing formation of CH_4 and reached 0.55 wt.%/g-sample at 700 °C. CO and CO_2 formation was largely constant throughout the range of temperature, although lower gas yields were detected as temperature increased. These were in keeping with the previously described trend in hydrocarbon yields. With the 1:1.5 OP/PVC sample, a reduction in CO and CO_2 were observed while temperature increased. Maximums oxygenate gas yields were given off in the 500–600 °C range, where hydrocarbon yields ranked low. However, PVC samples displayed similar trends for CH_4 with maximum yields reached as temperature increased. This was related to the decrease in alkanes yields obtained.

In general, results indicated that CO and CO_2 formation were both reduced during co-pyrolysis. While olefin and aromatic carbon yields increased for higher H/C_{eff} ratio blends, CO and CO_2 carbon yields decreased. However, these outcomes implied that hydrogen transfers from polymers to biomass-derived oxygenates may have mitigated polymerisation and cross-linking reactions and suppressed decarbonylation and decarboxylation reactions to generate CO and CO_2 [3]. According to these results, thermal decomposition of CO and CO_2 fell as temperature increased. Also, light hydrocarbon emissions were promoted with temperature, especially for CH_4. Thus, in conclusion, as temperatures rose, thermal cracking and methanisation were promoted as the inherent potassium in OP become more active as a catalyst.

4. Conclusions

The effects of fast pyrolysis temperature and olive pomace (OP) and agroindustrial polymers (PE, PS and PVC) mass blending ratios on product distribution and hydrocarbon composition were researched. Experimental results demonstrated an apparent synergy with hydrocarbon yields in fast pyrolysis bio-oil at 500 °C for the 1.5:1 OP/PE, 1:1.5 OP/PS and 1:1.5 OP/PVC mass ratios. Moreover, alkenes are maximised for OP/PE and aromatic compounds for OP/PS and OP/PVC blends. Total hydrocarbon yields increased as temperatures rose from 500 to 700 °C. For the 1.5:1 OP/PE blend, alkenes formation was improved, where the light hydrocarbons fraction (C_6-C_{10}) first increased and then decreased with temperature, reaching a maximum at 650 °C. On the other hand, aromatic compounds production was enhanced for 1:1.5 OP/PS and 1:1.5 OP/PVC, with optimal temperatures at 500 and 600 °C, respectively. The more valuable aromatic chemicals like benzenes, toluene and xylene were found to be abundantly formed for both blends. As for pyrolytic gas composition, they did not follow any trend, owing to the synergy in the blends. In general, while temperature increased, CO and CO_2 decreased and CH_4 was promoted. Finally, H_2-rich feedstocks (plastics) and a H_2-deficient (OP) offers synergy in improving aliphatic and/or aromatic carbon yields of the bio-oils formed.

Authorship statement

All persons who have made substantial contributions to the work reported in the manuscript, but who do not meet the criteria for authorship, are named in the Acknowledgements and have given us their written permission to be named. If we have not included an Acknowledgements, then that indicates that we have not received substantial contributions from non-authors.

CRediT authorship contribution statement

A. Alcazar-Ruiz: Conceptualization, Investigation, Writing - original draft, Data curation, Supervision. **F. Dorado:** Formal analysis, Methodology, Funding acquisition, Writing - review & editing. **L. Sanchez-Silva:** Validation, Resources, Writing - review & editing.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jaap.2021.105242.

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