

Enhancement of BTX production via catalytic fast pyrolysis of almond shell, olive pomace with polyvinyl chloride mixtures



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ABSTRACT

This work addresses enhanced benzene, toluene and xylene (BTX) production by catalytic fast co-pyrolysis from agroindustrial biomass blended with PVC and the use of prepared NaZSM-5 and HZSM-5. Results from catalytic fast pyrolysis of biomass indicates that oxygen-containing compounds decreased whereas aromatics increased. The catalytic effect of mineral content altered the co-pyrolysis intermediates by increasing the formation of mono-aromatics while reducing poly-aromatic hydrocarbons. Furthermore, the addition of PVC strongly influenced thermal decomposition of agricultural waste biomass, where BTX yields were enhanced up to 26.6% and 25.1% for 1:2 OP/PVC-HZ and 1:2 AS/PVC-HZ, respectively. Yields of toluene and xylene peaked at 19% and 10.5% hydrocarbon yields with 1:2 OP/PVC-HZ blend. Additionally, from the pyrolytic gas, CH₄ yields increased while the CO₂ yield fell due to oxygen removal by decarboxylation. These findings could provide a great insight into the olive pomace and almond shell valorization through an inexpensive and straightforward easy process.

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1. Introduction

Depletion of fossil fuels, growing concern for reducing pollution and political commitment have made it crucial to harness renewable energy to a greater extent (Kumar et al., 2020; Liu et al., 2014). Thus, biomass as an energy source has emerged as one possible option with great potential applications in the future (Patil et al., 2022). Lignocellulosic biomass is an abundantly renewable feedstock for producing bio-oil with aromatic hydrocarbons via fast pyrolysis (Xiao et al., 2021). However, the bio-oil yielded has certain disadvantages in comparison to petroleum-derived oil: low calorific value, high viscosity, and thermal instability (Patil and Baral, 2021). This is because it is made up of a mixture of oxygenated compounds (such as acids, phenols and short chain oxygen compounds) (Oh et al., 2021). Moreover, the hydrogen-deficient nature of lignocellulosic biomass yields undesirable features in the bio-oil. Therefore, co-pyrolysis with hydrogen-rich material has become a simple way of enhancing both bio-oil quality and yields (Qian et al., 2021). To tackle the problems posed by bio-oil, plastic waste is presented herein as a solid feedstock for blending with lignocellulosic biomass residue: in the process this is beneficial from both a financial and environmental perspective. Furthermore, the continuous increase in plastic waste needs to be disposed of harmlessly (Lin et al., 2020). Among the most used types of

plastics, polyvinyl chloride (PVC) has attracted attention due to rising consumption of it in recent years. In fact, it currently accounts for 12% of total human demand (Wang et al., 2021; Yu et al., 2016). Worldwide demand for PVC is expected to grow by 3.2% annually until 2023 (Zhou et al., 2020). To counter harmful emissions in PVC combustion by traditional plastic waste disposal techniques, enhanced recycling techniques that convert solid waste blends into high value-added products are urgently needed. Thus, co-pyrolysis of biomass and plastics would help conserve the environment and fossil fuels reserves by recovering hydrocarbon compounds from waste in the form of biofuels.

To enhance the bio-oil obtained from co-pyrolysis, firstly, it must undergo catalytic upgrading using efficient catalysts to reduce its oxygen content and heavy hydrocarbons (Cai et al., 2020; Chaihad et al., 2021). Catalysts may be incorporated into co-pyrolysis to remove oxygenated fractions via decarboxylation, dehydration and decarbonylation, to produce enhanced bio-oil. The use of an acid catalyst over the catalytic co-pyrolysis can improve bio-oil quality via the Diels-Alder reaction. This is expected to occur with biomass-derived and plastic olefins (Dada et al., 2021a). Among different catalysts, there has been great interest in zeolites due to their relatively low cost and availability. Traditional zeolites vary in porosity and acidity that could influence their cracking catalytic effect in biomass pyrolysis (Cai et al., 2020; Chaihad et al., 2021; Dada et al., 2021b). Lazaridis et al. found that the branches of phenols can be removed easily with Brønsted acids and transformed into olefins (ethylene, propylene). These could directly form monocyclic aromatic hydrocarbons through aromatization (Lazaridis et al., 2018). Acidic, basic

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Table 1
Feedstock characteristic data analysis.

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		79.92	15.31	49.9	6.1	0		20.1	0.2
AS	3.11	3.39	78.48	14.16	47.21	5.71	0.45	44.1	18.3	0.3
PVC	0.23	4.24	98.73	0.04	40.03	5.09	0	46.6	19.9	0.1
		1.04						0		
	Mineral content (wt%)									
	Ca		K		Mg		Na			
OP	0.45		3.48		0.068		0.059			
AS	0.29		1.16		0.032		0.058			
	Chemical composition (wt%) ^{db}									
	Klason lignin		Lignin		Cellulose		Hemicellulose		Extractives	
OP	21.2		–		–		31.5		38.1	
AS	–		13.4		28.1		39.7		–	

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

and neutral catalysts have been used to increase the amount of hydrocarbon bio-oil production through pyrolysis of plastics and biomass waste mixtures (Terry et al., 2021). Among various traditional zeolites, protonic type Zeolite Socony Mobil-5 (HZSM-5) is the most active deoxygenation catalyst with high selectivity for producing aromatic hydrocarbons such as BTX (benzene, toluene and xylene) and PAHs (polycyclic aromatic hydrocarbons) (Hu and Gholizadeh, 2019; Wei et al., 2020). The acid sites of HZSM-5 promote deoxygenation, decarbonylation and decarboxylation of oxygenate compounds (Liang et al., 2015). Lin et al. reported a synergistic increase in yields of aromatics and valuable mono-aromatics selectivity during the catalytic co-pyrolysis of corn stover and waste plastic over a HZSM-5 zeolite (Lin et al., 2020).

However, in combination with zeolites, some internal minerals in biomass, such as alkali and alkaline earth metals (AAEMs) could interact as catalysts and influence bio-oil yields and their composition (Alcazar-Ruiz et al., 2021c; Lin et al., 2020). In previous studies it was reported that the presence of potassium favours the formation of low-molecular weight compounds through catalytic depolymerization and by cracking anhydrosugars during the thermal decomposition of biomass (Lin et al., 2020; Zhang et al., 2017). Many studies have reported on the catalytic effect of AAEMs on biomass pyrolysis by itself. However, there has been little research into the catalytic effect of AAEMs when biomass and plastics are used in co-pyrolysis. Moreover, little attention has been paid to assessing the catalytic coupling effect of AAEMs and zeolites on the production of aromatics during co-pyrolysis. This work will focus on the catalytic action of zeolites in conjunction with the inherent metals founded in biomass without the need for synthetic addition of catalytic metals.

Thus, in this study, two important agroindustrial biomass residues (olive pomace and almond shell) were mixed with PVC to show their hydrocarbon production synergies in fast co-pyrolysis. Biomasses and PVC were blended with ZSM-5 in sodium and acid form (NaZSM-5 and HZSM-5) and analyzed through Py-GC/MS. The aim of this paper was to research the effect of catalytic fast co-pyrolysis on hydrocarbon product selectivity, aimed at enhancing value-added compounds, such as BTX. Moreover, the coupling effect of the AAEMs inherent to the biomass and zeolite on the production of aromatics was evaluated.

2. Materials and methods

2.1. Feedstock samples

Residue from two agroindustrial biomass, olive pomace (OP) and almond shell (AS), were used as feedstocks. OP was supplied by Aceites García de la Cruz oil mill (Madridejos, Castilla-La Mancha, Spain) and AS

was collected from Castilla-La Mancha, Spain. Prior to the experiment, the biomass samples were oven-dried for 24 h at 100 °C, and then milled and sieved. With this an average particle size ranging from 100 to 150 µm was obtained. Polyvinyl chloride (PVC) was purchased from Sigma-Aldrich, US and grounded and sieved to a particle size under 0.1 mm.

2.2. Sample characterization

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 information about moisture, ash, volatile matter and fixed carbon content. Also, the ultimate analysis was carried out to find the quantity of carbon, hydrogen, nitrogen, oxygen and sulphur concentrated in the sample. In addition, metal content was determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) with Varian 720-ES equipment (previously calibrated using standard stock solutions).

From the ultimate analysis, the hydrogen to carbon effective molar ratio (H/C_{eff}) was determined with the following equation (Eq. 2), (Zhang et al., 2018):

$$H/C_{eff} = \frac{H - 2 \cdot O - 3 \cdot N - 2 \cdot S}{C} \quad (1)$$

where H , C , O and N are the moles of hydrogen, carbon, oxygen and nitrogen.

The higher heating value (HHV) shown in Table 1 was calculated from the elemental analysis based on an ultimate data analysis with the following empirical correlation (Eq. 1), (Alcazar-Ruiz et al., 2021c):

$$HHV \left(\frac{MJ}{kg} \right) = 0.3491 \cdot C + 1.1783 \cdot H + 0.1005 \cdot S - 0.1034 \cdot O - 0.0151 \cdot N - 0.0211 \cdot A \quad (2)$$

where C , H , S , O , and N are the weight percentages of carbon, hydrogen, sulphur, oxygen and nitrogen, and A is that of ash.

For the OP sample, the content of extractives, hemicellulose and Klason lignin was determined following this experimental methodology: firstly, the extractives content was determined with the Soxhlet successive exhaustion method using dichloromethane (6 h), ethanol (16 h) and water (16 h), as an adaptation from TAPPI 204 om-97. After extraction, the sample was dried at 110 °C for 1 h and cooled to room temperature in a desiccator. The extractives solubilised by the solvents were determined by the mass difference in the solid (Miranda et al., 2019). Lignin content was then found by the Klason method (TAPPI T 222

om-02) (TAPPI, 2018). The samples (350 mg) of extractive-free material were added to 3 mL of H₂SO₄ (72%) at 30 °C for 1 h, then diluted to 3% w/w H₂SO₄ and reacted in an autoclave for 1 h at 120 °C. The residue was filtered, washed until neutralised, dried at 110 °C until a constant weight was reached and cooled to room temperature. The difference in weight after treatment determined the amount of Klason lignin (Miranda et al., 2019). For determining the hemicellulose content, 150 mL of NaOH solution (0.5 M) were added to 1 g of extractive-free material and boiled for 3.5 h with recycled water. The product was filtered, washed until neutralised, dried at 110 °C for 1 h and cooled to room temperature. The difference in weight after treatment determined the amount of hemicellulose. For AS, lignin, hemicellulose and cellulose content were calculated following this experimental methodology reported elsewhere (López-González et al., 2013) whose results are given in Table 1.

2.3. Catalyst preparation

The zeolite ZSM-5 was supplied in ammonium form by Zeolyst International (SiAl = 25). To obtain it in protonic form HZSM-5, it was calcined at 550 °C for 15 h. The sodium form NaZSM-5 was obtained by ion-exchange with 5 M NaNO₃ (35 mL g⁻¹). Then, the slurry was filtered, washed with deionized water and dried at 110 °C overnight. This procedure was repeated three times and finally the sample was calcined for 4 h at 550 °C. The total content of sodium in NaZSM-5 (determined by atomic absorption spectrophotometry using a Spectra 220FS analyzer) was 2.04 wt.%.

The BET surface area was determined by adsorption and desorption data acquired with a Micromeritics ASAP 2010 apparatus, whereas the concentration of acid sites was measured by temperature-programmed desorption of ammonia using a Micromeritics TPD/TPR analyzer. A detailed description of both techniques is given elsewhere (Dorado et al., 2001) whose results can be found in Table 2.

2.4. Catalytic co-pyrolysis procedure analysis

The catalytic fast co-pyrolysis of OP and AS mixed with PVC were performed in a Py-GC/MS-FGA (CDS Pyroprobe 6200 and Agilent Technologies 7890B/5977B GC/MS, and CDS Analytical Model 5500 Fixed Gas Analyser).

In the first step, the biomass feed and zeolite catalyst were studied preparing blends with different biomass/zeolite mass ratios (2:1, 1:1 and 1:2). For example, 2:1 OP-NaZ refers to a blend ratio of 2:1 between olive pomace (OP) and NaZSM-5 (NaZ) zeolite. Secondly, different experiments were performed mixing biomass and PVC with a fixed mass ratio of 1:1.5. This proportion had been optimized in a previous study (Alcazar-Ruiz et al., 2021a, 2021b). These samples are named as 1:1.5 biomass/PVC. For instance, 1:1.5 AS/PVC refers to a mixture of almond shell and PVC. To better understand the influence of co-pyrolysis on blends of PVC and agricultural waste biomasses, predictable and experimental data for hydrocarbon selectivity were compared. The predictable (Pred 1:1.5 (OP, AS)/PVC) and the experimental (1:1.5 (OP, AS)/PVC) results for each compound detected after fast pyrolysis were calculated as follows (Alcazar-Ruiz et al., 2021a, 2021b):

$$CY_{th} = CY_{WB} \cdot F_{WB} + CY_{PVC} \cdot F_{PVC} \quad (3)$$

Table 2
Characterization data of NaZSM-5 and HZSM-5.

Sample	NaZSM-5	HZSM-5
S _{BET} (m ² /g)	437	441
Total acidity (mmol NH ₃ /g)	0.39	0.61
Weak acid (mmol NH ₃ /g)	0.39	0.02
T desorption (°C)		295
Strong acid (mmol NH ₃ /g)	0.00	0.59
T desorption (°C)		400

where CY_{th} is theoretical carbon yield; F_{WB} and F_{PVC} are the mass fraction of the agricultural waste biomass studied and PVC; and CY_{WB} and CY_{PVC} are the carbon yields (%) obtained from fast pyrolysis. If the experimental values are higher than the predictable ones, it is indicative of a synergistic effect in which more hydrocarbons are produced.

Finally, zeolite was blended with the biomass-PVC mixture varying the biomass/PVC-zeolite mass ratio (2:1, 1:1 and 1:2). In this case, sample 1:2 OP/PVC-HZ refers to a mixture of olive pomace/PVC (1:1.5 OP/PVC) and HZSM-5 (HZ) zeolite in a ratio of 1:2. All the experiments were carried out 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. Fast pyrolysis was conducted at 650 °C at a heating rate of 20 °C/ms and a residence time of 20 s. These operational conditions as well as the biomass/PVC ratio selected had been optimized previously in an earlier study (Alcazar-Ruiz et al., 2021a, 2021b).

For the analysis, the GC/MS injector temperature was kept at 280 °C. An Elite-35MS capillary column (30 m × 0.25 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 enabled the chemical composition of the bio-oil to be separated and identified. The oven temperature was programmed from 40 °C to 280 °C at a heating rate of 5 °C/min. The chromatograms were integrated, and relative peak areas were calculated. These peaks were identified using the National Institute of Standards & Technology (NIST) library as a reference and only those whose matching quality surpassed 80% were taken into consideration. The FGA used a 1/8" packed column and a 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 pyrolyzer collected the organic products from pyrolysis and transferred them to the GC/MS as usual. All the experiments were carried out in triplicate to ensure reproducibility.

The peak area based on a Py-GC/MS and Py-FGA analysis could not reveal the real content of the target compounds. However, if the sample masses matched in each fast pyrolysis experiment, the corresponding chromatographs could be compared to reveal the proportions and selectivities of the components in the bio-oils produced.

3. Results

3.1. Agricultural waste biomass characterization

Table 1 shows the characterization data for the two agroindustrial waste biomasses (OP and AS) used. In the proximate analysis, both biomasses showed high volatile matter content, which was higher in OP. However, OP had the highest carbon content (49.88%) and lowest oxygen content (43.99%), which resulted in a high calorific value of 20.01 MJ/kg. Both biomass feeds were higher in oxygen and hydrogen which might have been caused by the higher content of hydroxyl (-OH) group in their organic structure (Huang et al., 2021).

Alkali and alkaline earth metal (AAEMs) content is a key factor to consider, as they can act as indigenous catalysts in fast pyrolysis to modify the final composition of the bio-oil (Fermoso et al., 2017). Potassium was the most abundant metal, which was higher in OP (3.48 wt.%). Regarding the chemical composition, extractives were the main fraction in OP. They include the fat (approximately 2%) still in the olive pomace after olive oil was produced. With AS, hemicellulose was the main fraction obtained, as expected (Schmitt et al., 2020).

Converting feedstocks with a H/C_{eff} ratio under 1 into hydrocarbon aromatics without using a catalyst is a highly complex task (Chen et al., 1986; Zhang et al., 2011). As shown in Table 1, the H/C_{eff} of the two biomasses are under 0.29. Thus, a catalyst is essential for converting rich oxygen waste biomass into valuable hydrocarbons.

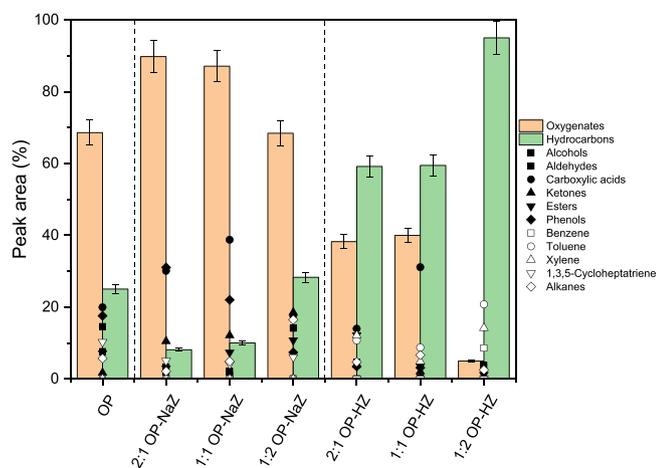


Fig. 1. Product yield obtained from the catalytic fast pyrolysis of OP over NaZSM-5 (OP-NaZ) and HZSM-5 (OP-HZ) zeolites.

3.2. Catalytic fast pyrolysis of agroindustrial waste from biomasses

The product yield from the pyrolysis of biomass/zeolite, as well as those from the raw materials (OP and AS), are shown in Figs. 1 and 2.

The components detected in the bio-oil were divided into two groups: hydrocarbons and oxygenates. Hydrocarbons were mainly composed of olefins, cyclic hydrocarbons and aromatics. These, in turn, were divided into monocyclic aromatic hydrocarbons (MAHs) mainly benzene, toluene and xylene (BTX); and polycyclic aromatic hydrocarbons (PAHs). Moreover, oxygenates production was based on alcohols, aldehydes, carboxylic acids, esters, ketones and phenols. Fig. 1 shows that yields of hydrocarbons in the non-catalytic fast pyrolysis of OP peaked at 25%, while the remainder were oxygen-containing compounds. The most representative oxygenate groups detected were phenolics (17.6%) and carboxylic acids (20%). The former come from the thermal decomposition of lignin (Wang et al., 2015), whereas the latter stemmed from the acidic nature of the feed (Dorado and Silva, 2020). When NaZSM-5 was added to the sample, hydrocarbon compounds fell and oxygenated products rose, thus increasing the percentage of phenolics and acids. The formation of hydrocarbons might have been limited due to the catalytic effect of the extra sodium apported by the zeolite. The catalytic effect of Na promotes intermolecular and intramolecular dehydration, protonation and aromatization. This could have formed more phenolic compounds (Alcazar-Ruiz et al., 2021c; Hernando et al., 2017), and probably enhanced the catalytic action of the AAEMs, inherent to the

raw OP. Among the phenolic compounds, guaiacols (a benzene ring containing at least one methoxyl and one hydroxyl substituted oxygen-containing group) were enhanced from 6.5% to 13.7% in 2:1 OP-NaZ. Phenolic compounds from lignin pyrolysis are known to undergo repolymerization in order to form char and a coating of coke on the catalyst surface, and led to catalyst deactivation (Elfadly et al., 2017). Yields of carboxylic acids (mainly acetic acid) reached 39% in the 1:1 OP-NaZ sample. According to the literature, the main factor behind this high yield was the large amount of hemicellulose in the biomass matrix, which underwent ring scission to produce it (Alcazar-Ruiz et al., 2021a, 2021b; Chen et al., 2019). Furthermore, hydrocarbon production fell on adding NaZSM-5 zeolite, in comparison to the raw biomass. The only hydrocarbons detected were olefins and cyclic hydrocarbons. The total percentage of hydrocarbons reached yields of 28.3% for 1:2 OP-NaZ, which was made up of 16.5% and 11.8% of olefins and cyclic hydrocarbons, respectively. This might have been due to the combined catalytic action of AAEMs inherent in OP and the sodium contribution from NaZSM-5. In this case, the zeolite in the sample combined with the catalytic effect of the inherent AAEMs (especially K, 3.48 wt.% (Table 1)) led to a fall in oxygenates at the expense of a slight rise in the formation of hydrocarbons. It should be noted that aromatics were not obtained, which indicates the lack of acid sites in NaZSM-5. Even though the number of Brønsted acid sites inside were low, they could still catalyze oxygen compound bonds to form hydrocarbons.

When HZSM-5 was used as a catalyst, oxygen content dropped whereas aromatics rose in comparison with the raw biomass. This is known to be caused by the acid sites in HZSM-5, which promoted deoxygenation, decarbonylation and decarboxylation of the oxygenate components. In addition, it enhanced cracking, oligomerization, alkylation, isomerization, cyclisation and aromatization via a carbonium ion mechanism which promoted the formation of hydrocarbons (Liang et al., 2015). With a greater ratio of zeolite in the mixture, hydrocarbon production was enhanced, which peaked at 95% in 1:2 OP-HZ. The yield of MAHs was higher than that of PAHs, as can be shown in OP-HZ blends. Lazaridis et al. (2018) found that the branches of phenols can be removed easily with Brønsted acids and transformed into olefins (ethylene, propylene). These could easily form monocyclic aromatic hydrocarbons (MAHs) through aromatization. However, BTX appeared in the bio-oil with toluene being the most prevalent. The high BTX yields obtained with HZSM-5 were attributed to its suitable pore structure and acidic strength which acted over OP. Aromatic hydrocarbons were mainly derived from the shape-selective catalytic fast pyrolysis of oxygenated intermediates (especially G and S- type phenols) via dihydroxylation and demethoxylation. These intermediate oxygenates entered the zeolite channels, and underwent a series of deoxygenation reactions at the acid sites (Huang et al., 2021). From the results, it was found that the selective yields of toluene and xylene in 1:2 OP-HZ were 20.8% and 14.2% respectively, which were much higher than those in benzene (8.6%). Toluene and xylene can be directly produced from dehydration (-OH) and demethoxylation (-OCH₃) of the oxygenated precursors (especially phenolics). However, to produce benzene an additional step is required to those needed for toluene and xylene: demethylation (-CH₃) of toluene and xylene (Huang et al., 2021, 2020). Therefore, benzene is more difficult to obtain than toluene and xylene, hence the lower yield.

The product yield obtained from the catalytic fast pyrolysis of AS is shown in Fig. 2. The raw material showed an extremely high production of oxygenates. With NaZSM-5, there was a slight fall in oxygenates, from 97.1% (AS) to 84.4% (1:2 AS-NaZ). However, the distribution of oxygenates was quite different from OP, and varied with the action of NaZSM-5. Thus, yields of phenol compounds strongly decreased from 48.3% for AS to 30.9%, 19.1% and 13% for 2:1, 1:1 and 1:2 AS-NaZ, respectively. This tendency revealed how this extra sodium addition supplied by NaZ action affects to phenolic

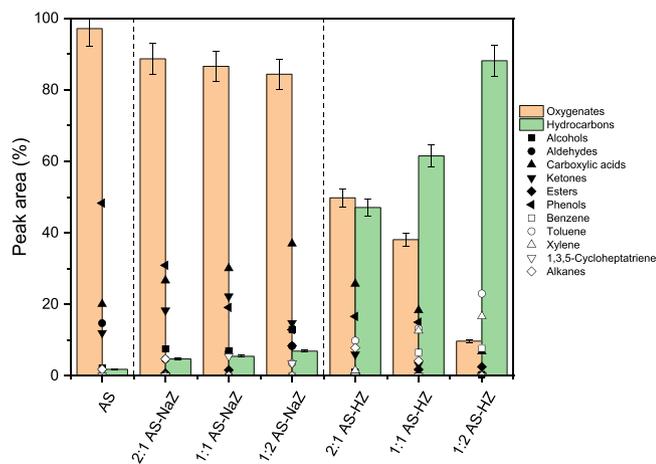


Fig. 2. Product yield obtained from the catalytic fast pyrolysis of AS over NaZSM-5 (AS-NaZ) and HZSM-5 (AS-HZ) zeolites.

compound production. In this case, guaiacols and syringols (benzene ring with two methoxyls and one hydroxyl oxygen-containing substituted) were the main phenolic molecules detected. Therefore, the distribution of benzene radicals changed as more zeolite was added to the blend. Acid content remained constant on adding NaZSM-5, whose main product was acetic acid. This could have been due to the high amount of hemicellulose (39.7 wt.%) in the AS organic matrix (Table 1) (Schmitt et al., 2020). Finally, after increasing the proportion of zeolite in the blend, the yield of low molecular weight (LMW) oxygenates compounds (such as alcohols, aldehydes and ketones) clearly increased. This was due to the catalytic action of AAEMs (such as potassium and calcium) and the presence of free hydroxyl radicals from phenol decomposition (Chen et al., 2019). However, the catalytic effect of Na tended to be higher due to the combination of the sodium inherent in AS and that added from NaZ. The catalytic effect of AAEMs promoted intermolecular and intramolecular dehydration, protonation and aromatization, thereby increasing yields of LMW (Hernando et al., 2017). Moreover, oxygenate yields were higher in AS in comparison to OP when the NaZ zeolite was present. This was because the amount of AAEMs inherent in AS were lower than in OP (Table 1). Hydrocarbon yields fell slightly on adding NaZSM-5 and peaked at 7% in 1:2 AS-NaZ. Toluene and 1,3,5-cycloheptatriene were the main hydrocarbons in that sample, each of which had yields of 3.5%. Thus, a catalytic effect was observed in the rise in aromatic hydrocarbons and a decrease in phenols as the amount of zeolites increased (Alcazar-Ruiz et al., 2021a, 2021b; Cai et al., 2020; Chagas et al., 2016).

After adding HZSM-5, there was a clear decrease in oxygen-containing products. Oxygenates yields decreased from 97.1% to 9.7% for AS and 1:2 AS-HZ. This was especially remarkable in phenolic compounds, whose production became null in 1:2 AS-HZ. The same catalytic trend was observed in both biomasses. When the proportion of HZSM-5 zeolite increased, more hydrocarbons were produced, from 1.8% to 88.2% for AS and 1:2 AS-HZ, respectively. These were fundamentally aromatics (toluene followed by xylene and benzene). Note that this kind of compounds has not been found in the obtained AS bio-oil through fast pyrolysis. The results revealed that toluene yields increased, which peaked in 1:2 AS-HZ at 22.9%. The same trends were obtained for xylene and benzene, with yields of 16.6% and 7.6%, respectively.

The higher catalyst to biomass feed ratio provided more acid sites of the catalyst which led to a great deal of contact between pyrolysis oxygenate intermediates and the catalyst. This enhanced catalytic conversion of fast pyrolysis intermediates into aromatic hydrocarbons. In general, BTX yield is enhanced for 1:2 AS-HZ and OP-HZ blends, with toluene and xylene yields being higher for AS blends and benzene for OP blends. To further enhance BTX production, an external hydrogen donor could have blended to have a synergistic effect on the catalytic fast pyrolysis of biomass.

3.3. Fast co-pyrolysis of PVC and agricultural waste biomasses

3.3.1. Hydrocarbon selectivity in non-catalytic fast co-pyrolysis

As a special polymer, PVC was selected to be studied in co-pyrolysis with biomass despite its low H/C_{eff} in comparison to other polyolefins. In addition, PVC has low HHV, which may not help to reduce oxygen content at first in blend with agricultural waste biomasses. Moreover, from PVC and biomass mixtures, the biomass with higher H/C_{eff} ratio could act as a hydrogen donor for PVC in fast pyrolysis (Zhang et al., 2016). Thus, it was selected to demonstrate how beneficial it is in hydrocarbon production. However, biomass samples (OP and AS) had a higher H/C_{eff} ratio than PVC (Table 1), which acted as a hydrogen donor in co-fast pyrolysis blends. The water evolved from biomass pyrolysis could have acted as a reactive compound, thereby accelerating PVC cracking, which promoted bio-oil yields (Zhang et al., 2016; Zhao et al., 2021).

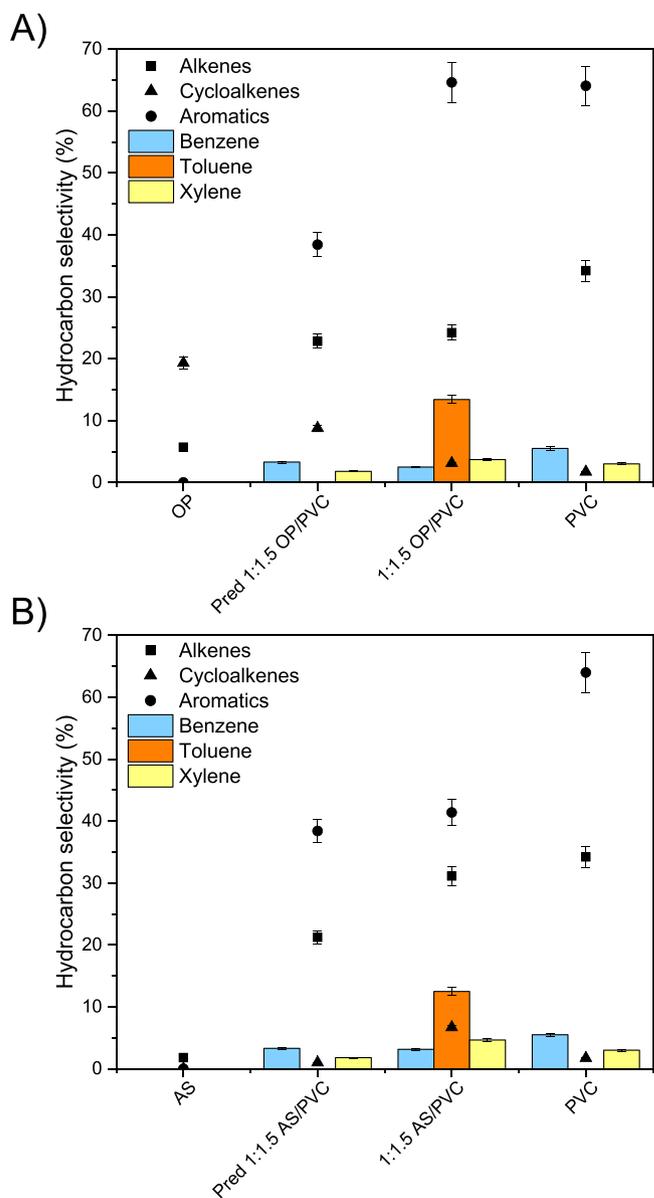


Fig. 3. Hydrocarbon selectivity obtained from the fast co-pyrolysis of bio-oil of A) 1:1.5 OP/PVC and B) 1:1.5 AS/PVC blends.

Fig. 3 summarized this comparison for OP and AS in co-pyrolysis with PVC after fast pyrolysis at 650 °C.

The results revealed that hydrocarbon compounds were largely obtained from PVC pyrolysis, the most representative of which was the aromatics hydrocarbon group with a selectivity of 64%. Regarding MAHs, benzene and xylene were the only BTX compounds detected. Previous studies demonstrated that the formation of aromatics can be ascribed to a molecular rearrangement and cyclisation of fragments of polyene (Alcazar-Ruiz et al., 2021a, 2021b; Zhou et al., 2020). The water evolved from them during pyrolysis could have acted as a reactive compound to accelerate PVC cracking, and hence, promote the production of aromatics (Zhang et al., 2016). Interestingly, dehydrochlorinated and chlorinated hydrocarbons (typically obtained in thermal PVC degradation) should be expected at temperatures above 500 °C, but they were not detected. Previous works have shown that at a high pyrolysis temperature AAEMs could prevent generation of chlorinated hydrocarbons (Karayıldırım et al., 2005; Zhou et al., 2020, 2004). This is because, if formed, they would be adsorbed by the carbon char produced. This effect was already observed in a previous study (Alcazar-Ruiz et al., 2021a, 2021b).

Therefore, the biomass materials studied would act as a catalyst which would inhibit dehydrochlorination and promote the chain scission of PVC to form aromatics (Zhou et al., 2015).

The comparison of theoretical and experimental results shown in Fig. 3 also demonstrated that there is a synergistic effect during the co-pyrolysis of biomass and PVC. Thus, there is a decrease in oxygen-containing products, whereas hydrocarbon selectivity, especially aromatic compounds, is favored. This trend was mainly observed when OP was used as the biomass. Thus, compared to the predictable data, sample 1:1.5 OP/PVC showed very high aromatic selectivity data (Fig. 3A), similar to that for the raw PVC, but without emissions of Cl-containing compounds. Therefore, co-pyrolysis of OP and PVC enhanced the bio-oil end product, with a higher amount of valuable chemicals produced, such as BTX, than with raw OP or PVC. Curiously, toluene was the main BTX formed with a selectivity of 13.4%, even though it was not detected in the raw materials. In 1:1.5 AS/PVC (Fig. 3B), there were less improvements in the formation of aromatics. However, BTX production, mainly toluene, was still enhanced in a similar way as in 1:1.5 OP/PVC. The difference observed was the amount of PAHs produced, which was higher in the OP with PVC combination than in AS with PVC. Thus, this indicated that the formation of oxygen-containing compounds was still higher in 1:1.5 AS/PVC with a yield of 20.2% in comparison with 4.8% in 1:1.5 OP/PVC. With the latter, the synergistic effect during the co-pyrolysis of biomass and PVC was demonstrated by way of hydrocarbon formation (sum of MAHs and PAHs) which was highly improved in 1:1.5 OP/PVC. In conclusion, it could be determined that the strong presence of inherent metals such as K in OP rather than AS, could have promoted a PVC chain scission to form aromatics (Zhou et al., 2015).

The main pyrolytic gases given off during the fast co-pyrolysis of these samples were also analyzed with FGA. Fig. 4 shows the fixed gas compounds that passed through the trap.

The gases obtained were CO, CH₄, CO₂, C₂H₂, C₂H₄ and C₂H₆, with the main ones being CH₄ and CO₂ in all the samples. Light hydrocarbons come from thermal cracking and methanation (Widyawati et al., 2011). Consequently, with PVC, a polymer with high hydrogen content (Table 1), more light hydrocarbon gases (C₂H₂, C₂H₄ and C₂H₆) were produced than with the biomass waste. It is noteworthy that CH₄ and C₂H₂ emissions were enhanced in the biomass/PVC blends. This was due to the AAEMs inherent in the biomass organic matrix. Thus, potassium is known to be an active catalyst for methanation (Alcazar-Ruiz et al., 2021a, 2021b; Puig-Gamero et al., 2020) and can attack the polymeric chains of PVC. However, CO and CO₂ are formed by the thermal decomposition of oxygen functionality in the lignocellulosic organic matrix (Nasir Uddin et al., 2013; Puig-Gamero et al., 2020). Generally speaking, CH₄ yields increased in pyrolytic gas, while the CO₂ yield was concurrently reduced due to the removal of oxygen by decarboxylation (Zhao et al., 2021).

3.3.2. Hydrocarbon selectivity in catalytic fast co-pyrolysis

As the most valuable products obtained from the fast co-pyrolysis of biomass and PVC belonged to the hydrocarbon family, this section focused on their selectivity. The hydrocarbons were distributed into three groups: alkanes, cycloalkenes and aromatics, among which the latter were the main products obtained. As commented above, aromatic hydrocarbons were composed of BTX, MAHs and PAHs. In this study, PAHs were categorized as naphthalene and its derivatives, indene and its derivatives, and multi-ring aromatic components with over two rings.

Fig. 5 shows the catalytic effect of NaZSM-5 and HZSM-5 on hydrocarbon selectivity in the fast co-pyrolysis of the blend of OP and PVC (1:1.5 OP/PVC).

In general, as commented above, aromatic compounds were the main group of hydrocarbons detected. On comparison with the non-catalytic experiment (1:1.5 OP/PVC), selectivity of aromatics decreased on adding NaZSM-5. Benzene was the only BTX enhanced by

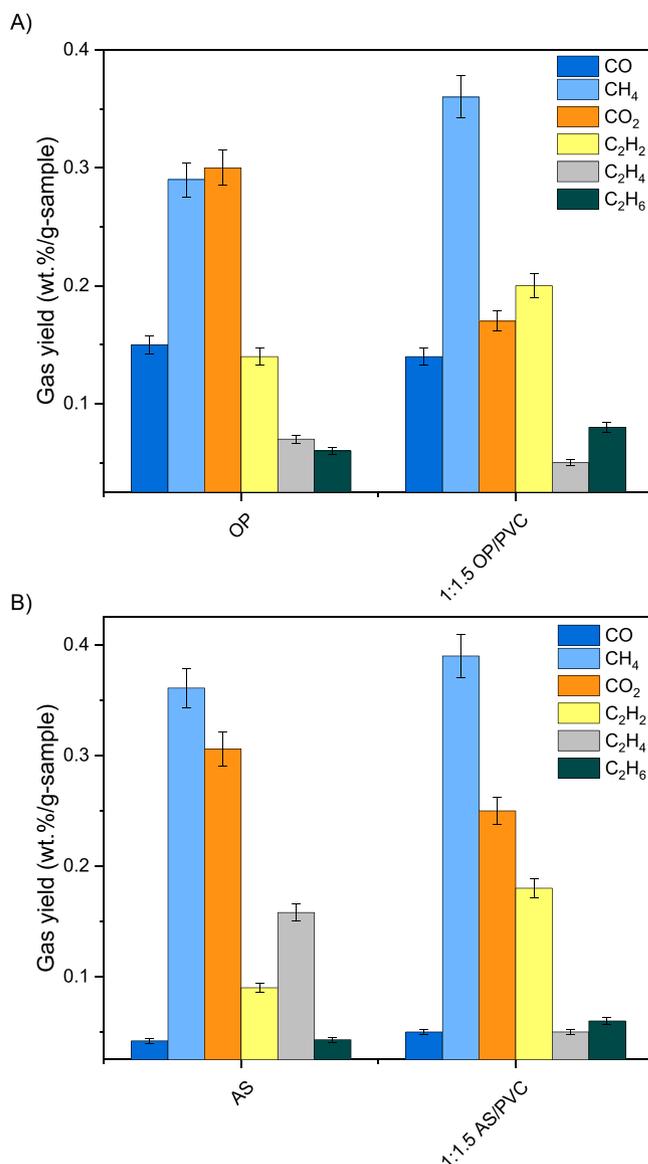


Fig. 4. Pyrolytic gas yields (wt.%/g-sample) obtained from fast co-pyrolysis for A) OP/PVC and B) AS/PVC blends.

the catalytic effect of NaZSM-5, which peaked at a 5% yield in 2:1 and 1:1 OP/PVC-NaZ. The sum of the BTX yielded was smaller than that with PAHs, an undesirable group of compounds (Praveen Kumar and Srinivas, 2020; Zhang et al., 1995). It has been shown in the literature that adding potassium decreases the bio-oil yield during co-pyrolysis of the biomass and plastic blends (Hassan et al., 2016). Furthermore, it causes additional cracking and deoxygenation (Fermoso et al., 2017), catalyzing the formation of low molecular weight components (Li et al., 2021). As the zeolite adds sodium, another alkaline metal, there may have been a similar effect here.

Compared to the non-catalytic fast co-pyrolysis of the OP/PVC blend, the presence of the HZSM-5 zeolite promoted the formation of aromatics while decreasing the amount of aliphatic hydrocarbons and oxygenate compounds. As expected, the OP/PVC co-pyrolysis vapours diffused into the pores in HZSM-5 and underwent a series of deoxygenation, isomerization, and oligomerization reactions at the acid site to form aromatics (Lin et al., 2020). However, in Fig. 1 it was observed that aromatic compounds were promoted by action by HZSM-5. Yields of aromatics peaked in 1:2 OP-HZ. Moreover, more of this compound was produced by mixing biomass with PVC, as shown in Fig. 3. Therefore, as observed in Fig. 6, the combined action

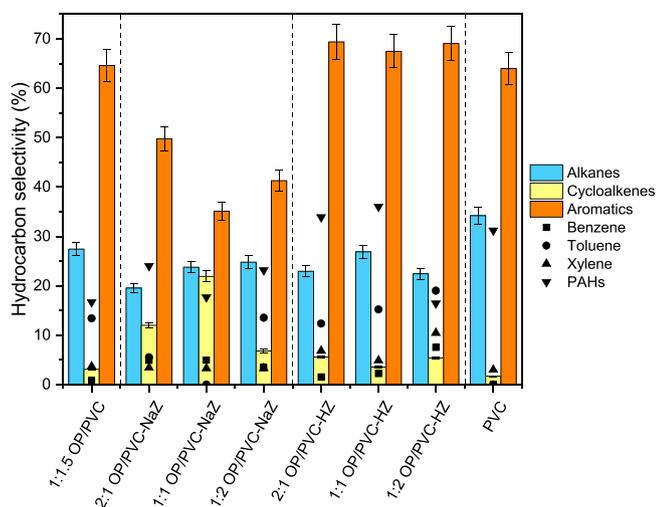


Fig. 5. Hydrocarbon selectivity obtained for the catalytic fast co-pyrolysis of 1:1.5 OP/PVC over NaZSM-5 (OP/PVC-NaZ) and HZSM-5 (OP/PVC-HZ) zeolites.

of biomass-PVC and HZSM-5 seemed to promote aromatic compounds, for which MAHs (specifically BTX) were obtained in higher amounts than PAHs. HZSM-5 promoted and facilitated the formation of MAHs, especially value-added compounds like toluene and xylene, whereas they inhibited the formation of PAHs (Lazaridis et al., 2018). Production of aromatics in OP/PVC experiments was high, and was slightly enhanced with HZSM-5, from 64% in 1:1.5 OP/PVC to 70% in 1:2 OP/PVC-HZ. Nevertheless, if BTX distribution is considered, a clear catalyst effect can be observed. In this case, BTX selectivity significantly increased, with toluene being the main aromatic detected. Thus, in 1:2 OP/PVC-HZ, a maximum yield of 19% was obtained, higher than that in the raw materials OP (12%) and PVC, which was not detected. Meanwhile, yields of PAHs fell, especially in 1:2 OP/PVC-HZ (in which selectivity for BTX was much higher than that for PAHs).

Fig. 6 shows the zeolite catalytic effect on the fast co-pyrolysis of the AS/PVC blend. As for the catalytic OP/PVC experiments, aromatics were the main hydrocarbon group obtained.

On comparing the results for both biomasses, aromatic selectivity was higher for the OP/PVC blends than for AS/PVC ones. This was mainly due to the nature of the raw feedstock. As aromatic

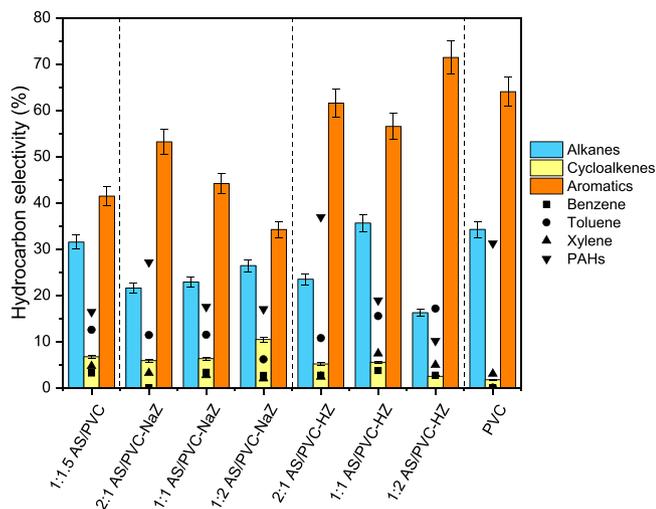


Fig. 6. Hydrocarbon selectivity obtained from the catalytic fast co-pyrolysis of 1:1.5 AS/PVC over NaZSM-5 (AS/PVC-NaZ) and HZSM-5 (AS/PVC-HZ) zeolites.

compounds are fundamentally derived from lignin decomposition, and this content is higher in OP than in AS (Table 1), this is logical (Alcazar-Ruiz et al., 2021a, 2021b).

On adding NaZSM-5 to AS/PVC a similar trend was seen as with OP/PVC. As already commented, aromatic selectivity fell as the sodium from the zeolite favoured production of low molecular weight components. Regarding action by HZSM-5, the formation of aromatics was again promoted while production of aliphatic hydrocarbons and oxygenate compounds dropped. Selectivity of aromatic compounds strongly increased from 41.4% in AS/PVC to 71.4% in 1:2 AS/PVC-HZ. BTX were also enhanced, and toluene was highly promoted in comparison with the non-catalytic results. Also, production of PAHs decreased, showing that the combined effect of HZSM-5 and PVC over product distribution could be extrapolated to different kinds of biomasses.

Finally, the results revealed that a higher HZSM-5 catalyst to biomass/PVC blend ratio enhanced catalytic conversion of fast pyrolysis intermediates into aromatics. Additionally, the 1:2 HZSM-5 proportion in OP/PVC and AS/PVC blends displayed the optimum bio-composition, in terms of higher BTX selectivity (especially toluene) in comparison with PAHs. Valuable chemicals such as toluene and xylene were further enhanced and obtained in the bio-oils. Moreover, useful aromatics like styrene or ethylbenzene were broadly formed.

4. Conclusions

Results have revealed that co-pyrolysis of OP and AS with PVC increased production of aromatic compounds, especially BTX. PVC strongly influenced the thermal decomposition of agricultural waste biomass. Also, biomass could have acted as an active catalyst for inhibiting the dehydrochlorination of PVC and promoting the chain scission of PVC to form aromatics. This study determined that hydrocarbon selectivity was enhanced with HZSM-5. This catalytic effect was observed in the 1:2 Hz ratio, in which BTX yields were higher than PAHs. Under the conditions of the study optimum BTX yields were obtained: 26.6% and 25.1% in 1:2 OP/PVC-HZ and 1:2 AS/PVC-HZ, respectively. The presence of toluene and xylene were enhanced whose yields peaked at 19% and 10.5% respectively in 1:2 OP/PVC-HZ. However, the presence of AAEMs altered the co-pyrolysis intermediates by increasing the formation of mono-aromatics while reducing PAHs. In short, the combined effect of the OP/PVC experiments, followed by catalytic HZSM-5 action was to enhance the production of aromatics. The exploration on other zeolites would results a key factor to improve aromatic production. Finally, this study showed that by combining the feedstocks in the study, waste could be reduced in order to produce valuable compounds through environmental-friendly catalytic fast pyrolysis technology.

CRediT authorship contribution statement

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

Declaration of Competing Interest

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

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