

Hydrocarbon selectivity enhancement through catalytic fast co-pyrolysis of almond shell and plastic wastes blends

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Biomass has emerged as an energy potential option which great future applications. Different thermochemical methods such as pyrolysis have been promoted as one solution. Fast pyrolysis leads to high bio-oil production (approximately 75 wt.%) and occurs at high heating rates, moderate temperatures, and short residence times (Salvilla et al., 2020). Lignocellulosic biomass is an abundantly renewable feedstock to produce bio-oil containing aromatic hydrocarbons via fast pyrolysis process (Xiao et al., 2021). Moreover, the hydrogen-deficient nature of lignocellulosic biomass results in unenviable features in bio-oil. The produced bio-oil presents undesirable properties, such as low calorific value, high viscosity, and thermal instability since it is made of a mixture of oxygenated compounds (like acids, phenols and short chain oxygen compounds) compared to petroleum-derived oil. Therefore, co-pyrolysis with hydrogen-rich material has become an easy way in operation for improving both, quality and yield of bio-oil. To tackle the problems of bio-oil, plastic waste is presented as a solid feedstock to blend with lignocellulosic biomass residues because of adding economic and sustainable benefits to the process. Furthermore, the continuous increase of waste plastic needs to be disposed harmlessly. Plastic materials have similar properties to those in fossil fuels in terms of heating value and lack of oxygenates compounds. To upgrade the obtained bio-oil from co-pyrolysis, it must firstly undergo a catalytic upgrading process with the use of efficient catalysts to reduce oxygen content and heavy hydrocarbons (Cai et al., 2020). Catalysts may be incorporated into the co-pyrolysis process to remove oxygenated fractions via decarboxylation, dehydration and decarbonylation reactions, resulting an upgrade bio-oil version.

In this work, an agricultural biomass residue, almond shell (AS), collected from the Castilla-La Mancha region (Spain) was mixed with polyethylene (PE) and polystyrene (PS), both typical agricultural plastic wastes, and subjected to catalytic fast co-pyrolysis. AS and plastic wastes were blended with ZMS-5 in sodium and acid form (NaZSM-5 and HZSM-5, named as NaZ and HZ, respectively) and the analyzed through Py-GC-MS. The proportion between AS and plastic wastes was optimized in a previous study (Alcazar-Ruiz et al., 2021). Zeolite was blended with the AS-PE and PS mixtures varying the mass ration (2:1, 1:1 and 1:2). Thus, as an example of the notation, the sample 1:2 AS/PE-HZ refers to a mixture of almond shell/PE (1.5:1 OP/PE) and HZSM-5 (HZ) zeolite in 1:2 proportion. Fast pyrolysis reaction was conducted at 650 °C with a heating rate of 20 °C/ms and a residence time of 20 s.

The objective of this work was to investigate the effect of catalytic fast co-pyrolysis on hydrocarbon product selectivity, looking for enhancing the production of value-added compounds, such as benzene, toluene and xylene (BTX). Furthermore, the coupling effect of inherent alkali and alkaline earth metals (AAEMs) from biomass and zeolite addition on the aromatic production was evaluated.

The obtained product yields for the studied blends are shown in Figure 1. Plastic in blend with AS feedstock was expected to reduce the oxygen content at the organic phase whilst carbon yield increased, leading to a higher calorific value. The detected components in the bio-oil have been divided into two groups, hydrocarbons and oxygenates. Hydrocarbons are mainly composed of olefins, cyclic hydrocarbons and aromatics, which were also divided into: monocyclic aromatic hydrocarbons (MAHs), being mainly benzenes rings; and polycyclic aromatic hydrocarbons (PAHs), categorized as naphthalene and its derivatives, indene and its derivatives, and multiring aromatic components having more than two rings. On the other hand, oxygenates production is based on alcohols, aldehydes, carboxylic acids, esters, ketones and phenols.

Aliphatic hydrocarbons derived from pyrolysis of PE could interacted with the oxygenated fraction present in AS through a series of cracking, cyclization and isomerization reaction, thereby increasing hydrocarbon diversity (alkenes and cyclic hydrocarbons). Without catalyst, 1.5:1 AS/PE produced around an 80 % of hydrocarbon compounds, being mostly aliphatic in the range of C₆-C₂₀. When NaZSM-5 is added to that blend, hydrocarbon compounds were reduced and oxygenated products are slightly enhanced, increasing phenolics and acids. The formation of hydrocarbons could be limited due to the catalytic effect of the extra sodium apported by the zeolite. The only hydrocarbons detected were olefins in the carbon numbers C₆-C₂₀, for which more than a half of that detected components were in the range of C₇-C₁₀. After adding HZSM-5, hydrocarbon production was enhanced, and a diversity of hydrocarbon compounds was produced. In that case, the total percentage of hydrocarbons increases in comparison to non-catalytic blend due to aromatic production was enhanced as much HZSM-5 in blend. From Fig. 1 a) it is observed how aromatic selectivity increased in detriment of a reduction on aliphatic fraction. Aromatic presence increased being produced in largest (45% of total hydrocarbons) for 1:2

AS/PE-HZ, in which MAHs were promoted than PAHs. PAHs are considered an undesirable group of bio-oil compounds due to its highly coke formation in the presence of an acid catalyst.

Regarding PS, the results are shown in Fig. 1 b). Bio-oil composition obtained from PS fast pyrolysis was shown to be oxygen-free. In comparison to PE, PS has a low aliphatic content due to the aromatic ring nature of the styrene monomer. The general catalytic effect over 1:1.5 AS/PS blend was an increased aromatic production, in which toluene was enhanced as compared to the raw feedstock. After adding NaZSM-5, the yield increased around 12% for 1:2 AS/PS-NaZ. The catalytic effect of Na tends to be higher due to combination of inherent sodium already found in AS and the added one from NaZSM-5. The presence of AAEMs altered the co-pyrolysis intermediates by increasing the formation of mono-aromatics while reduced PAHs. They could promote intermolecular and intramolecular dehydration, protonation, and aromatization reactions. Hydrocarbon yield increased with HZSM-5 mixing blends, for which aromatics were the most abundant compounds, being toluene and 1,3,5-cycloheptatriene production enhanced. In this case, PAHs were obtained in higher proportion than MAHs. As expected, the AS/PS co-pyrolysis vapors diffused into HZSM-5 pores and underwent to a series of deoxygenation, isomerization, and oligomerization reactions at the acid sited to form aromatics.

In conclusion, hydrocarbon selectivity was enhanced for AS/PE and AS/PS blends, and even improved due to the catalytic action of the zeolites. The present study showed that the catalytic fast co-pyrolysis of the combination of the studied feedstocks is a promising technology to decrease wastes disposal and to produce, in an environmental-friendly way, valuable-added products through.

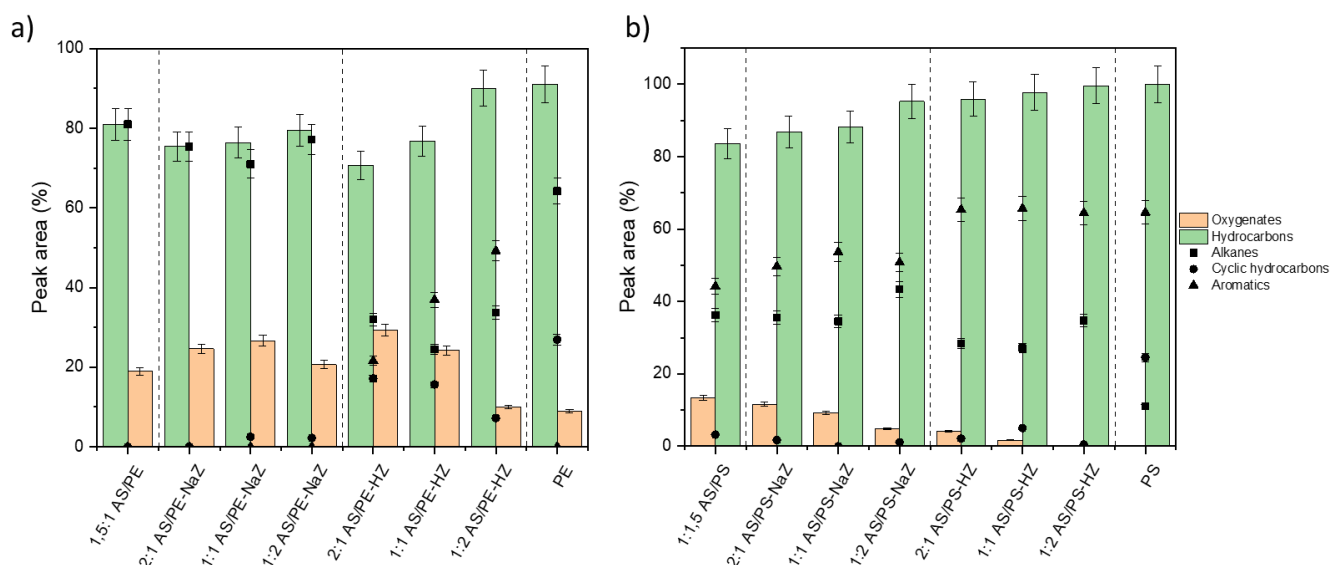


Figure 1. Product yield obtained from the catalytic fast pyrolysis of a) AS/PE and b) AS/PS over NaZSM-5 (NaZ) and HZSM-5 (HZ) zeolites.

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