

# Catalytic Pyrolysis of Municipal Plastic Wastes (MPW) for the Production of Valuable Chemical Products

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The work was focused on converting plastic mixtures of LDPE (low density polyethylene), PP (polypropylene), and PS (polystyrene) with incorporation of small amounts of organic matter and paper, via catalytic pyrolysis into valuable products. The small incorporation of these materials was due to its low presence in the MPW used in this study. The results were compared with those of thermal pyrolysis. Mixture composition was set to obtain olefins/aromatic ratio of approximately 1 for the success of the next alkylation step. As in thermal pyrolysis, this ratio was difficult to obtain, FCC catalyst was tested. No significant impact in product yields and composition was observed with the incorporation of small amounts of the mentioned materials and with the use of this type of catalysts. The solid seems to contain the incorporated materials in the initial plastic waste mixture. The use of FCC increased the gas and solid content of about 3.7 % and 27.1 %. The liquid-oil decreased 30.8 %. Regarding liquid-oil composition, the use of FCC increased the aromatic compounds. Catalyst increased the quality of the liquid-oils, however it was not observed a significant impact in other products.

## 1. Introduction

Thermoplastics are made of synthetic and organic polymer resins of high molecular mass. Nowadays, thermoplastics are largely used in most sectors of activity. The most frequent thermoplastics are LDPE, PP, PS, PET and PVC. As most of these synthetic plastics are resistant to biodegradation, they may generate huge amounts of undesirable wastes, unless they are converted into valuable products. Around 70 % of European plastic waste is not recycled due to technical or economic reasons and end up in landfills (27 %) or are incinerated (42 %) (Ian Tiseo, 2021). There is also a risk associated with the release of hazardous chemicals and potential contamination of water bodies (Narancic and O'Connor, 2019). In fact, around 64 % of the waste found in several water bodies is plastic (Verma et al., 2016). The disposal of plastic waste not only damages the aquatic and terrestrial ecosystem, but also increases air pollution and accelerates climate change (Robaiana et al., 2020). The low percentage of recycled plastic waste is due to the high management costs associated with the treatment of plastic waste derives from the presence of other compounds such as metal and paper in this type of wastes (Qureshi et al., 2020).

Several valorisation processes have been studied for plastic waste and pyrolysis has proven to be a suitable one to deal with contaminated wastes (Miandad et al., 2016). Pyrolysis is a tertiary recycling technique that has several economic advantages over other technologies such as gasification and incineration (Miandad et al., 2017). Pyrolysis conditions can be optimised to produce the desired product yield and composition, namely operation temperature and pressure and retention time. The most suitable temperatures values range from 400 °C to 500 °C. Alongside temperature, pressure also influences the cracking process in which organic polymers of high molecular weight are converted into lower molecular weight compounds (Al-Salem et al., 2017). Plastic waste is thermally decomposed into three main products, liquid-oil, gaseous and solid fraction. The liquid-oil is the primary product and the quality and quantity of this product depends on various factors such as: the type of the feedstock, type of reactor used and process parameters. The liquid-oil derived from plastic waste is mainly composed by hydrocarbons, including paraffins, olefins or aromatics, and can be used in multiple applications such as furnaces, boilers, turbines and diesel engines (Sharuddin et al., 2016) and it may also be used as raw material in several industries. The gaseous fraction is composed by carbon dioxide and other low

molecular weight hydrocarbons that can be converted into energy, for example, to be used in pyrolysis processes. Pyrolysis solid fraction is mainly composed by recalcitrant carbon and remaining inorganic matter (Almeida and Marques, 2016), it may be used in applications such as agronomic valorisation and remediation of soils. The pyrolysis of plastic waste has been studied for some decades, including the thermal decomposition of LDPE, PP and PS. However, the effect of contaminants and the presence of PET and PVC may cause problems due to the formation of undesirable components and of oxygenated and chlorinated compounds (Lopez et al., 2011), which increases the complexity of liquid-oil upgrading before their utilisation. This subject still needs further studies and research. Another important research area is catalytic pyrolysis, as it presents numerous advantages over thermal pyrolysis, as catalysts enable the reactions to proceed at a faster rate and may allow using less severe operation parameters such as lower temperature and shorter retention time. Catalytic pyrolysis may improve products yield or trigger other desirable reactions to improve the quality of the product (Anene et al., 2018). A wide range of catalysts have been developed and tested in pyrolysis process, including zeolites, especially ZSM-5 (zeolite sonony mobil-5), FCC (fluid catalytic cracking), Co-Mo (cobalt-molybdenum) and other aluminosilicates (Budsareechai et al., 2019). Indeed, ZSM-5 is a promising catalyst due to the high cracking activity and high selectivity towards gasoline range aromatic hydrocarbons (Zhou et al., 2021). One of the disadvantages of the use of catalysts is the usual high catalyst cost, however, the advantages can often surpass the commercial price. After a previous study done by the authors in catalytic pyrolysis of various LDPE, PP and PS mixtures and in thermal pyrolysis of this plastic waste mixtures with incorporation of different materials (Costa et al., 2021), it was decided to test the catalytic pyrolysis using FCC catalyst in mixtures with incorporation of small amounts of cardboard and organic matter present in MPW. The results obtained were compared with those of thermal pyrolysis.

## 2. Experimental Description

Pyrolysis tests were performed in a 5.5 L autoclave batch reactor from Parr Instrument Company. Plastic waste mixed with the catalyst were placed inside the reactor that was closed, afterwards, and purged with N<sub>2</sub> to guarantee an inert atmosphere. The main parameters of all experiments were optimised by previous studies done in the same installation to be published soon. The initial pressure was atmospheric pressure, the pyrolysis temperature was about 440 °C and the reaction time was 30 min. The heating rate was about 5.5 °C/min.

At the end of the experiment, the autoclave was cooled down to room temperature. The gases were collected, measured and analysed by gas chromatography (GC-FID-TCD Hewlett Packard 6890). The autoclave was opened and the solid and liquid fractions were separated and weighted to calculate the yield of these two products. The liquid fraction was distilled to obtain three fractions: one with a distillation point lower than 150 °C, other that distilled between 150 and 270 °C and the residual liquid with higher molecular weight. The first two fractions were characterized by GC/MS (Hewlett Packard). The quantitative analysis was performed by external calibration using a hydrocarbon standard mixture. The solid fraction was extracted with hexane.

Plastic waste mixtures contained LDPE, PP and PS with incorporation of organic matter and paper, with the compositions presented in Table 1. The catalyst used was FCC. Catalyst / plastic waste ratio was 1:3.

*Table 1: Composition of plastic mixtures tested.*

Test N°	LDPE	PP	PS	Incorporation		Catalyst Type
				Paper	Organic matter	
1	30	60	10	0	0	Without
2	30	60	10	0	0	With
3	28	60	10	2	0	Without
4	28	60	10	2	0	With
5	28	60	10	0	2	Without
6	28	60	10	0	2	With

## 3. Results discussion

All the tests of thermal and catalytic pyrolysis performed in this study led to similar products yields. The highest liquid-oil yield was obtained when the mixture without incorporation but with the presence of catalyst was used (Figure 1). This value was of about 93.1 wt.%. On the other hand, the incorporation of cardboard and organic matter led to an increase of gas and solid content, especially when FCC was used. The use of catalyst led to a significant effect of the products yield. In the incorporation experiments, the use of FCC increased the gas and solid content of about 3.7 wt.% and 27.1 wt.%. The liquid-oil decreased 30.8 wt.%. It was observed that the liquid-oil yield only reached values of about 53.8 wt.% with the use of catalyst in the incorporation experiments. The large amounts of solids produced in these two experiments, about 35.1 wt.%, showed that the increase in

the cracking reactions in the presence of the catalyst did not occur, in contrary to what was expected. Probably, as the decomposition of the cardboard and of the organic matter is not favoured at the experimental conditions used, the not converted material may deactivate rapidly the FCC catalyst, preventing the cracking reactions. The gaseous fraction was always below 12 wt. %.

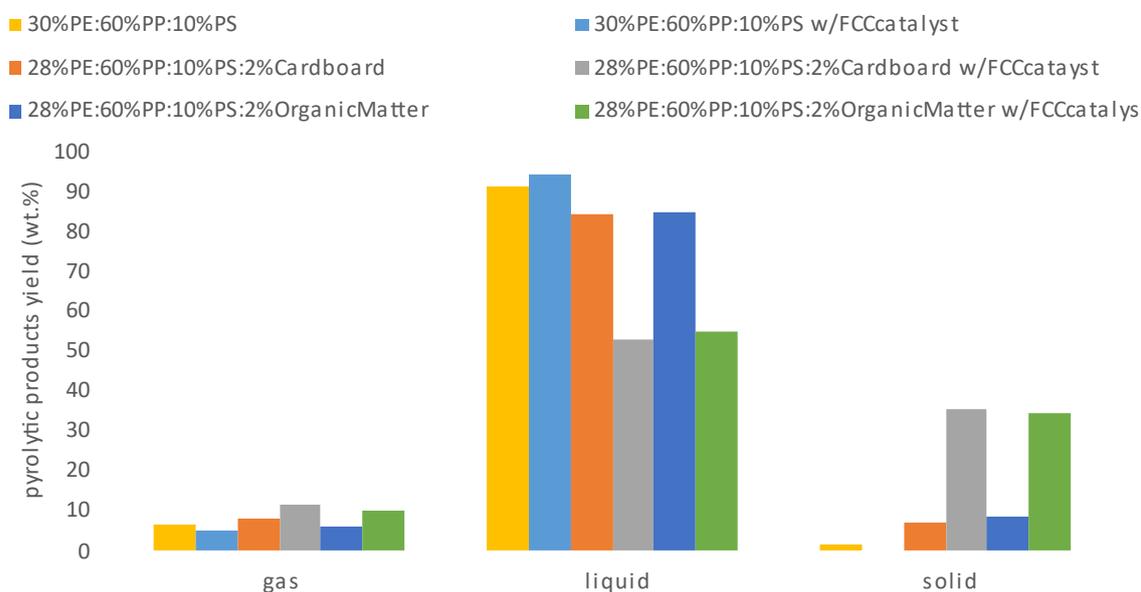


Figure 1: Products yield of the thermal and catalytic pyrolysis (Reaction temperature = 440 °C; reaction time = 30 min; autogenous pressure)

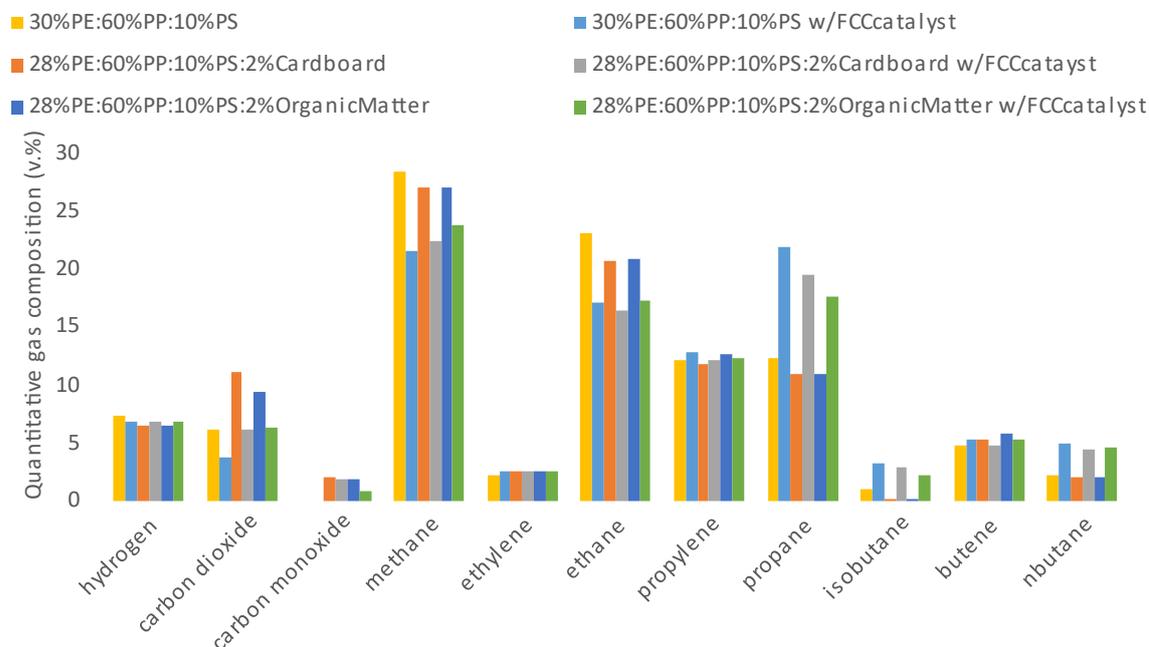


Figure 2: Gases product composition (Reaction temperature = 440 °C; reaction time = 30 min; autogenous pressure)

Regarding gas composition, hydrogen, carbon monoxide, carbon dioxide and hydrocarbons until C<sub>4</sub> were detected. Hydrogen, ethylene, propylene and butene were very similar in all experiments, representing around 6.8 v.%, 2.5 v.%, 12.3 v.% and 5.2 v.%. The compounds produced in lower amounts were carbon monoxide, ethylene and C<sub>4</sub> hydrocarbons. The production of carbon monoxide (around 1.7 v.%) was due to the pyrolysis of cardboard and organic matter. Overall, the application of this plastic waste mixture ratio produced more alkanes compared to alkenes. Volumetric percentages of methane reached values between 21.55 to 28.47 v.%. It is clearly observed that the use of FCC decreased carbon dioxide, methane and ethane contents. The propane, isobutene and n-butane increased. So, probably the presence of FCC in the pyrolysis process increases the formation of higher molecular weight compounds of the gas produced. These results were not expected, because FCC is a cracking catalyst so, the formation of lighter compounds was not predicted.

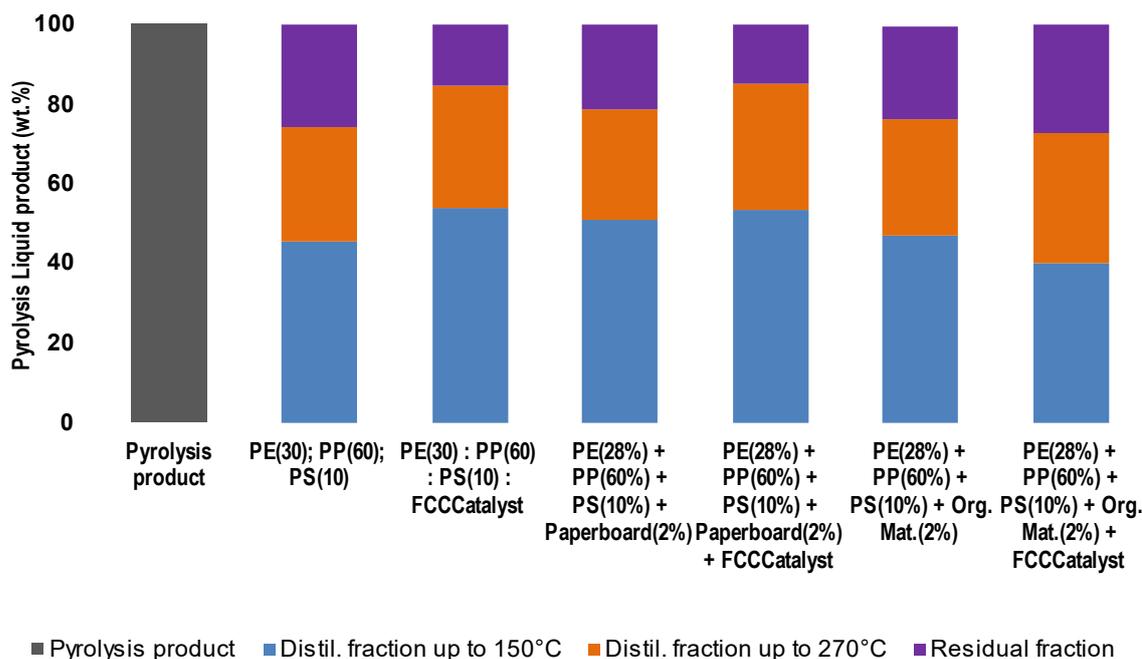


Figure 3: Boiling point distribution of the thermal and catalytic pyrolysis liquids (Reaction temperature = 440 °C; reaction time = 30 min; autogenous pressure)

As it can be observed in Figure 3, the use of catalysts led to the production of a lighter liquid phase, i.e. containing compounds with smaller carbon chains (lower molecular weight). The use of catalysts resulted in smaller production of residual fractions and more quantity of lighter distillates (consisting of compounds with boiling point under 150 °C).

Pyrolysis of polyolefin residues mixture – PE (30 wt.%): PP (6 wt.%): PS (10 wt.%) – without incorporation of other different types of residues, (Figure 3) clearly shows that the FCC presence led to an increase of the distillate fractions (volatile compounds) of about 19 wt.% (b.p. 150 °C) and 6 wt.%, w/w, (150 °C < b.p. < 270 °C) and to a significant decrease (65 wt.%) in the distillation residual fraction (b.p. > 270 °C).

Regarding the incorporation of cardboard in the plastic mixture, it was observed that its presence essentially resulted in a higher production of more volatile compounds (from 45 to 51 wt.%). The addition of the catalyst in this mixture also led to higher volumes of distillate fraction and an evident decrease in the residual fraction of the distillation (from 21 wt.% to 15 wt.%).

Regarding the incorporation of organic matter in the mixture of plastics, it was observed that the results were not promising either in the absence or in the presence of the catalyst, as the residual fractions was higher when this material was incorporated.

The liquid fraction is a complex mixture composed by, mainly hydrocarbons. In the Figure 4 is presented the liquid main identified compounds grouped into paraffins, olefins and aromatics. About 54 v.% of liquid compounds were identified. The unidentified compounds can be heavier hydrocarbons and a small amount of heavy oxygenated compounds. The results did not show a clear relation between the use of catalyst and the

quality of the liquids. The influence of FCC is not clear and highly depends on the feedstock used. For instance, for the mixture with only plastics the presence of the catalyst decreased the paraffin content (from 24.1 v.% to 16.1 v.%) and increased olefins (from 12.8 to 15.8 v.%) and aromatic compounds (from 18.1 v.% to 23.5 v.%). However, for the mixture with incorporation of cardboard and organic matter (OM) the tendency was the opposite, with a decrease in the olefins and aromatic compounds. Also, several cyclic and branched hydrocarbons were detected. The aromatic compounds detected in higher concentrations were ethylbenzene, toluene and xylenes. The ration olefins/aromatics was always below 0.5, which do not allow the direct alkylation reaction once this parameter has to be close to one.

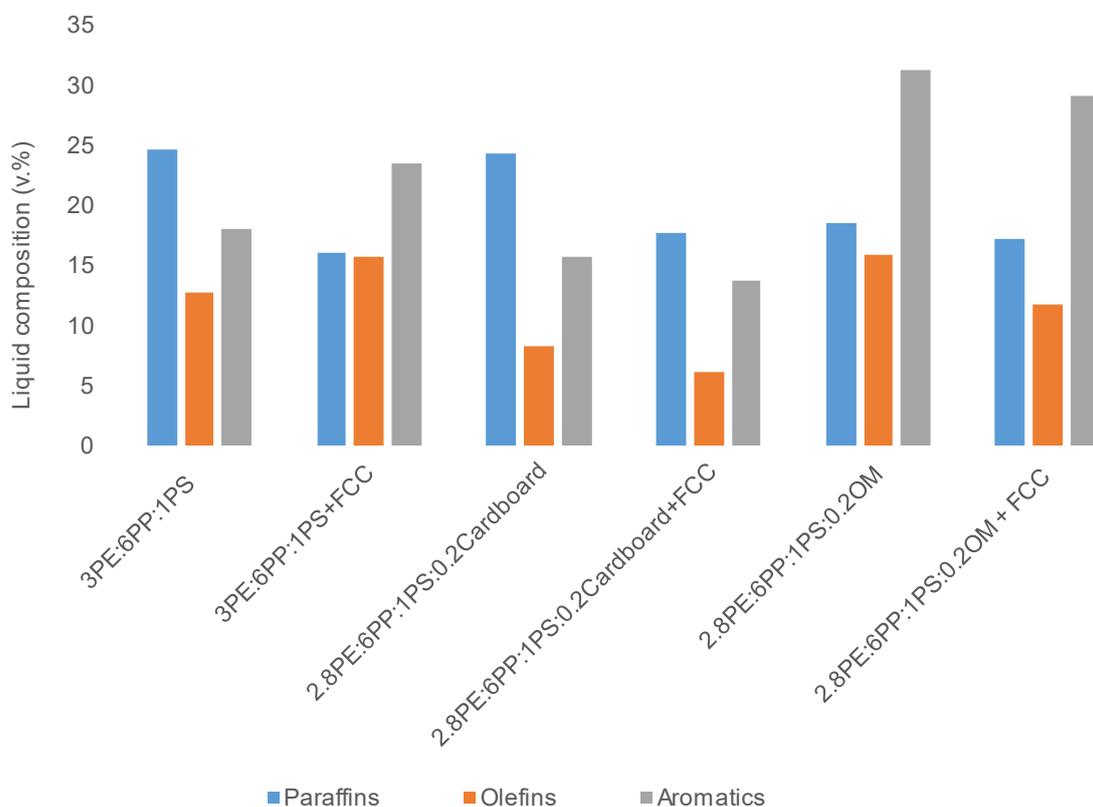


Figure 4: Liquid product composition (Reaction temperature = 440 °C; reaction time = 30 min; autogenous pressure)

The oxygenated liquid compounds were detected in very small amounts and only in the tests where cardboard and organic matter were used. Probably these results, are due to the small amount of these materials used, only 2 wt.%. However, more tests are needed to prove these assumptions.

#### 4. Conclusions

For all the pyrolysis tests performed similar products yield were observed, being the highest liquid-oil yield obtained when the mixture without incorporation and in the presence of catalyst was used (around 93.1 wt.%). On the other hand, the incorporation of cardboard and organic matter led to an increase of gas and solid content, especially when FCC was used. The use of catalyst showed a significant effect of the products yield, especially in experiments where the incorporation of cardboard and organic matter were used. The presence of FCC increased the gas and solid content of about 3.7 % and 27.1 %. The liquid-oil decreased 30.8 % (to the yield of about 53.8 wt.%). The large amounts of solids produced in these two experiments, showed that the increase in the cracking reactions in presence of catalyst did not occur in opposition to what was expected. Regarding the gas composition, the production of hydrocarbons was favoured by the presence of the FCC.

The liquids were composed by, mainly, hydrocarbons (paraffins, olefins and aromatics). About 54 v.% of liquid compounds were identified. Oxygen content in the mixtures used were, probably removed in the form of CO<sub>2</sub> and CO and some was retained in the solid product. The results did not show a clear relation between the use

of catalyst and the quality of the liquids. The influence of FCC is not clear and highly depends on the feedstock used. The ratio olefins/aromatics was always below 0.5, which do not allow the direct alkylation reaction once this parameter has to be close to one. As the main objective of this study was to obtain liquids able to be used in the alkylation process, the results obtained did not allow achieving the objectives. More tests should be done, using other types of catalysts. The effect of small amounts of other types of plastics and impurities, usually present in recycled plastics will be also studied in future research studies.

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