

Validation of the Application of the Pyrolysis Process for the Treatment and Transformation of Municipal Plastic Wastes

Paula Costa^{a*}, Filomena Pinto^a, Ricardo Mata^a, Paula Marques^a, Filipe Paradelo^a, Luís Costa^b

^aLNEG-UBB, 1649-038 Lisboa, Portugal, Estrada do Paço do Lumiar 22.

^bFCUL, Campo Grande, 1749-016 Lisboa, Portugal
paula.costa@lneg.pt

Only around 30 % of the 27.1 million tonnes of plastic waste recovered annually in Europe is being recycled efficiently into new products. The most common way to recycle plastics nowadays is through mechanical recycling methods that involve sorting plastics by type, melting them and reprocessing into recycled products. Mechanical recycling requires clean, high-purity mono-material streams, that must be obtained by separation at source (by the citizen or industry) or by manual or automated sorting of mixed waste streams. However, this degree of separation is very difficult or even impossible due to composition or contamination of the plastic waste, such is the case for example of complex materials like composites, made of more than one material that in most cases cannot be separated, and of highly contaminated plastic residues (e.g. food packaging). In economic terms, plastic recycling is not always cost-efficient since many times recycling costs are not covered by the prices of the recycled plastics. As a result, approximately 70 % of European plastic waste is not recycled due to technical or economic reasons, so, they are sent to landfill or to incineration. One of the possible solutions to deal with this type of plastic wastes is the pyrolysis process which allows taking profit of plastics organic matter and tolerates a certain degree of contamination. Pyrolysis products have good quality. Gases have high calorific value and liquids have high energetic content and stability characteristics, including well-defined distillation point, stability of physical properties, low acidity, and high miscibility with conventional fuels. However, products obtained by plastic waste pyrolysis depend on the operational conditions and are strongly affected by the type of plastic waste used. The main purpose of this study is to validate the application of the pyrolysis process for treatment and transformation of plastic mix (essentially derived from MSW and from end-of-life composites) into mainly profitable liquids, together with gases and solid by using thermal (or catalytic) pyrolysis. The raw materials studied were waste streams from municipal solid waste (MSW), containing mainly plastic (i.e. PE, PP, PS, and small amounts of PET and PVC) separated from organic waste pool, as well as end-of-life composites (i.e. packages, electrical wastes, vehicles, etc.). After sorting of these waste materials, plastic fractions of different composition were processed in the pyrolysis reactor. The pyrolysis experiments were carried out in batch 5.5 L reactor using different mixtures, operational conditions and catalysts. All gaseous hydrocarbons produced were measured and collected for direct analysis by gas chromatography (GC), whilst liquid hydrocarbons were distilled and solids were extracted with hexane. Liquid fractions were analysed using a GC-MS (gas chromatography-mass spectrometry) to identify their main compounds, which were quantified by GC. The experimental results obtained showed that, for instance, the use of polystyrene favoured highly the formation of aromatic compounds, mainly toluene, ethylbenzene and xylene, while in presence of polyethylene the hydrocarbons produced are mainly paraffins. Also, the presence of PS, PET and PVC increases the solid content, decreasing the liquid yield.

1. Introduction

Plastics are synthetic organic polymer materials that, in the end-of-life, have a very negatively impact in the ecosystems if they are not recovered and valorised. They are derived from petrochemical sources with high calorific value and are mainly composed by carbon and hydrogen, however, depending on the type of plastic, few other undesired elements may be added (e.g. nitrogen, chlorine) (Sharuddin et al., 2016). Moreover, their

production requires 6 % of the oil consumption in a global scale (Quesada et al., 2020). These materials are used in several areas, such as agriculture, automobile industry, electricity and electronics, construction materials, packaging, healthcare and others. The increase of energy demand in our planet, urbanization and economic development are the main factors associated with the high production of plastic waste. Around 25 % of worldwide solid wastes accumulated in landfill are plastics (Saptoadi et al., 2016). In terms of plastic waste management, as most of plastics are non-biodegradable, the European Union is trying to limit the amount of them that go to landfill and incineration (Miskolczi et al., 2009). According to 2017 Eurostat data, for instance, in Portugal only 34.89 % of plastic packaging waste generated were recycled (Eurostat, 2019). Its incineration produces greenhouse gases (CO₂, H₂O, N₂O and CH₄), light hydrocarbons, nitrous and sulphur oxides, dusts, dioxins and other toxins. Landfill is another life-end method of disposal, but leads to a retention and/or leaching of some inappropriate chemicals such as dioxins and heavy metals, causing contamination of soils and, therefore, underground waters (Pinto et al., 1999) if an impermeable structure is not properly constructed. In general, waste plastics are considered the fraction that was separated and rejected from recycling facilities or valorisation into added-value products. The municipal plastic wastes have the average composition of 62 % polyolefins (46 % high and low density of polyethylene and 16 % polypropylene), 16 % polystyrene, 7 % polyvinyl chloride, 5 % polyethylene terephthalate, 5 % acrylonitrile-butadiene-styrene and 5 % of other polymers (Sembiring et al., 2018). They may contain some additives such as flame-retardants, stabilizers and oxidants (Miandad et al., 2019), inorganic compounds (e.g. heavy metals) and composites.

In the last years, several studies about thermo-chemical conversion of plastic waste into alternative-based resource have been reported. Pyrolysis is a thermal decomposition process, at a moderate range of temperatures (usually 400 to 500 °C), of long chain polymers molecules into low molecular weight hydrocarbons through heat and pressure in the absence of oxygen. The process is divided into slow, fast or flash pyrolysis, depending on the primarily conditions that are temperature, retention time and heating rate. There are several reactors designs such as fixed bed, fluidized bed and autoclave, and each one influences differently the behaviour of the feedstock into the reactor and the composition and yield of the products (Guedes et al., 2018). The commonly studied plastic wastes are PE, PP and PS. PE and PP are the largest plastic wastes in MSW, and are characterized essentially by their chain of saturated polymers or polyolefins. On the other hand, PS is a polymer composed by styrene monomers (Vijayakumar & Sebastian, 2018). The three main products, solid, liquid and gas, are composed essentially by hydrocarbons and other organic compounds with high heat value. Their yield depends mainly on the feedstock composition, reactor type, catalyst (for catalytic cracking process) and other parameters such as heating rate, temperature, retention time and pressure (Saptoadi et al., 2016). The addition of PS into a PE and PP feedstock increases the efficiency of the pyrolysis process and the volatile matter produced (Siddiqui & Redhwi, 2009). The solid product, designated as char, is mainly composed by carbon which gives it a great potential to generate heat, to improve soil fertility and increase crops by converting it into active carbon, and can be also used as an absorber or filter for some pollutants, due to its large surface area (Guedes et al., 2018). The liquid produced, composed by saturated (paraffines), unsaturated (olefins) and aromatic hydrocarbons, is the primary objective of the majority of pyrolysis studies, due to its flexible applications such as furnaces, boilers, turbines and diesel engines (Abnisa et al., 2016). Volatile matter and ash content of the feedstock impacts significantly the liquid fraction yield. The gas fraction, known as incondensable hydrocarbons, is composed mainly by carbon dioxide, methane, carbon monoxide, hydrogen and light hydrocarbons. The inorganic compounds (e.g. glass and metals) remain practically unaltered and are free to binding with organic matter and reused as additive or fillers (Adrados et al., 2012). PVC materials contain chloride in their hydrocarbon structure. During the pyrolysis process of chlorinated materials, HCl gas may be formed which is hazardous and poisoning. In order to remove it from the pyrolytic gas, a dechlorination process is needed.

2. Materials and Methods

In this work, different plastic waste mixtures were thermal decomposed via pyrolysis into the three main products (solid, liquid and gas) which were analysed. The plastic used were obtained after sorting of the Municipal Plastic Wastes (MPW). The LDPE was densified, the other types of plastics were only shredded. Overall, the feedstock was composed by higher amounts of low density polyethylene (LDPE), polypropylene (PP) and polystyrene (PS), with a small incorporation of polyvinyl chloride (PVC) and polyethylene terephthalate (PET) in some experiments. The use of higher amounts of LDPE was due to its higher abundance and availability in the MPW and also LDPE is currently disposed into landfills or underexploited through energy recovery. The small incorporation of PVC and PET was due to the low presence of this type of plastics in the MPW used in this study. Also, the chlorinated compounds are undesired in the pyrolysis products, leading to corrosion problems. So, to avoid this unfavourable properties, PVC concentration of raw

materials should be limited. The plastics mixtures chosen cover a wide range of possibilities. The different proportions of feedstock mixtures studied are present in Table 1.

Table 1: Plastic mixtures and their composition used for pyrolysis tests performed

Test	LDPE	PP	PS	PVC	PET
1	100	0	0	0	0
2	90	10	0	0	0
3	90	0	10	0	0
4	80	10	10	0	0
5	60	20	20	0	0
6	58	20	20	2	0
7	58	20	20	0	2

The study was performed in a 5.5 L autoclave (batch reactor) from PARR Instruments CO. with a controller device of autoclave and furnace temperatures, pressure and agitator of the feedstock. Firstly, the feedstock was placed inside the reactor and closed, afterwards was cleaned with N₂ in order to maintain an inert atmosphere inside the reactor. No initial pressure of N₂ was used. As it is a close system the pressure was autogenous and no more than 20 bar was observed. The main experimental parameters of all experiments were chosen based on previous studies done by the authors. The final temperature was set up to 440 °C and the initial pressure was 1 bar (atmospheric pressure). The heating rate was about 5.5 °C/min. The reactor was first loaded, with the plastic waste mixture previously chosen, closed and purged with nitrogen. Then, it was heated until the reaction temperature previously settled was reached, at which it was maintained for 30 minutes. At the end of this period, the autoclave was cooled down immediately to room temperature. The gases were collected, measured and analysed by gas chromatography (GC-FID-TCD Hewlett Packard 6890). Due to the possibility of HCl formation in the pyrolysis test with incorporation of PVC, Mohr's method was used to determinate the amount of chloride ions by their titration with nitrate silver (Meija et al., 2016). A bubbling capture of glass bottles in series with distilled water was placed after the reactor, where the gas passed through before it was collected. Afterwards, the solution was titrated with nitrate silver. Terephthalate acid is, possible to be produced from the decomposition of PET so, as the acid is poorly soluble in water, a similar schematic method to the HCl capture was used, but a solution of 1.6 M NaOH was prepared instead. After the collection, the pH was measured in both solutions to verify any acidic conditions. Finally, the autoclave was opened and its content was weighted and analysed. 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. The liquid samples were characterized by GC/TOFMS (LECO instruments) and their main compounds quantified by GC-FID (Hewlett Packard 6890). The quantitative analyse was performed by external calibration using a hydrocarbon standard mixture.

3. Results presentation and discussion

In this study was assessed the effect of the plastic waste composition on the pyrolysis products. For each test the product yields and its composition were analysed. All the pyrolysis experiments were performed at 440 °C and 30 min of reaction time. In Figure 1 are shown the product yields obtained. In general, the gas yield was similar in all experiments, ranging values between 3.8 and 6 % were obtained. The highest production of liquid was observed with 100 % PE (95.2 %), so, at the experimental conditions used the PE seems to favour the production of liquid products. As it can be observed in Figure 1, the main effect of the different plastic wastes used in the product yield was the increase in the formation of solids when higher amounts of PS were used. This result can be explained by the reaction temperature used and type of reactor. The use of a close system may increase the probability of secondary reactions to occur, this means that the reactions between the lighter molecules initially formed was favoured, originating compounds with higher molecular weight (solid in the PTN conditions). This was also observed at higher pyrolysis temperature (> 400 °C) by Costa et al., 2007, when studied the PS pyrolysis reaction pathway. Also, the presence of PET and PVC has increased the solid product being the highest value obtained when PET was used (9.1 %). Similar trends with the input of PET and PVC in the plastic mixture were reported by Williams & Williams (2007). Sembiring et al. (2018) and Miandad et al. (2019) observed that the consecutive addition of PET decreased the liquid fraction whereas wax and solid mass increased. According to these authors, char is formed due to carbonization and condensation at high temperatures and the presence of oxygen atoms. Indeed, the thermal decomposition of PET can originate oxygenated groups, increasing the potential presence of reactive hydrogen and oxygen

groups, such as $-OH$ and $=O$ (Adrados et al., 2012). Furthermore, the presence of PS and PET originates polyaromatics in the solid fraction (Singh et al., 2019).

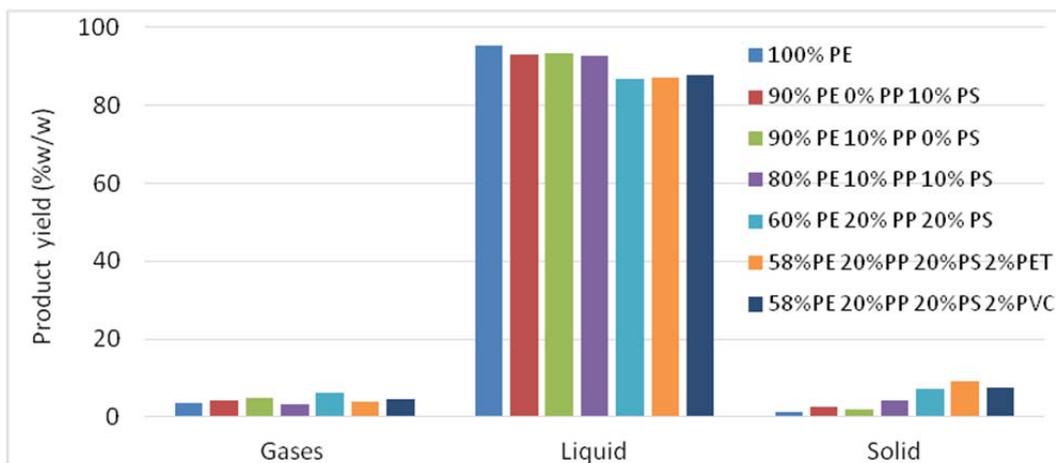


Figure 1: Effect of plastic waste composition on product yields in pyrolysis tests.

Regarding gas composition, overall, the gas produced is composed by around 70 % (v/v) of paraffins and 20 % (v/v) of olefins. The paraffins were, mainly, methane and ethane representing about 50 % (v/v) of the total gas composition and the amount of paraffins decreased with the increase of carbon number being the amount of butane much smaller. Pinto et al. (1999) verified similar results using different plastic mixtures of PE, PP and PS, and explained that the high formation of low weight molecules is due to the fact that, after the cracking process, the reactive species do not tend to react with each other but, instead a quick stabilization of these molecules by hydrogen addition seems to occur. The gas composition is presented in Figure 2. It is, mainly composed by hydrocarbons. The experiments with higher PE content (100 and 90 % of feedstock) led to higher influence in the gas composition, decreasing the methane percentage and increasing butane and butene. The PET incorporation led to a lower production of hydrocarbons, increasing the hydrogen and carbon dioxide. CO_2 increase maybe due to the presence of oxygen in the PET structure. According to Singh et al. (2019), a high carbon dioxide content in the gas sample is linked to the formation of oxygenated compounds during the pyrolysis process. Miskolczi et al. (2009) reported the presence of HCl in the gas products, but no HCl was detected in the gas fraction when PVC was used, so, probably the chloride presence in the PVC structure was not release in the gas phase or as the incorporation was only of 2 % w/w, the HCl was above the detection limit of the analytic method.

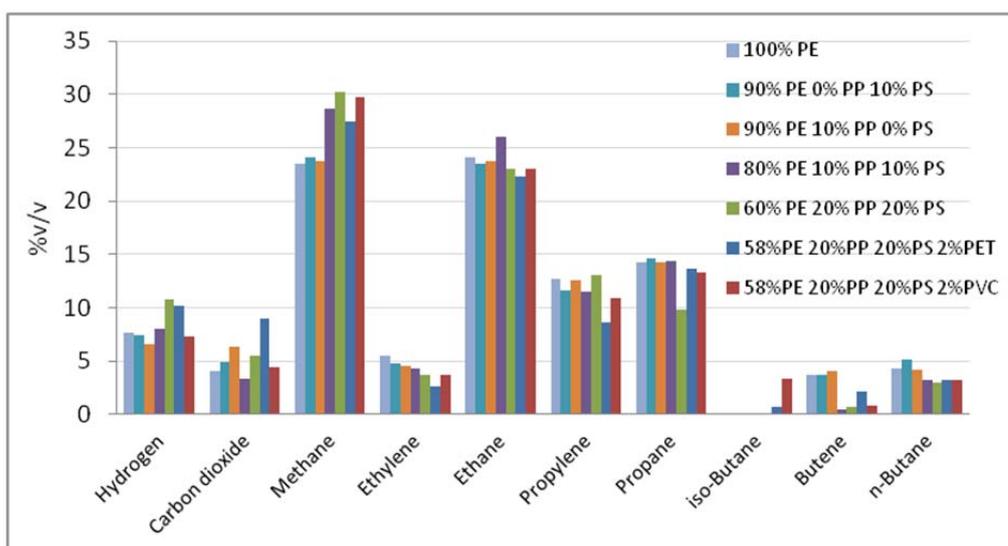


Figure 2: Effect of plastic waste content on gas composition.

Liquid fraction was distilled and three fractions were recovered according to the boiling point distribution. First fraction (1^aF) has boiling point lower than 150 °C, second fraction (2^aF) has boiling point between 150 °C and 270 °C and the third fraction (3^aF) has boiling point higher than 270 °C. For all the pyrolysis testes performed, more than 60% (w/w) of the liquid distilled below 270 °C.

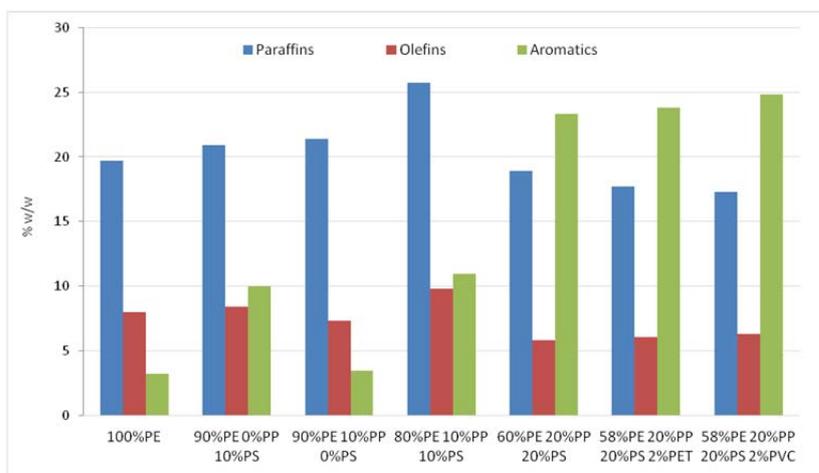


Figure 3. Effect of plastics mixture used in pyrolysis tests on liquid product composition.

The main liquid compounds detected in the 1^aF and 2^aF were n-paraffins from C₆ to C₂₀. Olefins from C₇ to C₁₅ were also found, as well as small amounts of aromatics (Figure 3). The aromatic fraction was mainly constituted by toluene and ethylbenzene, being the highest values obtained when higher percentages of PS were used. The styrene was only detected in very low concentrations. Aromatic compounds are mostly produced from PS pyrolysis, the increase of PS content from 10 % to 20 % in the plastic mixture of LDPE, PP and PS, doubles the aromatic content (from 10.1 % to 20.5 %). PS pyrolysis shows that cracking of the aromatic ring is not favoured. Under these reaction conditions, only the non-aromatic C–C bonds were weak enough to be broken, which was followed by some rearrangement. Furthermore, the presence of PET and PVC in the raw materials also increased the aromatic content, however this trend was more significant in the liquids obtained in the presence of PVC. In this case the aromatic content increased from 22.3 to 24.8 % (w/w). This tendency can be, mainly observed comparing the liquids obtained in the three last testes (60 % PE, 20 % PP, 20 % PS; 58 % PE, 20 % PP, 20 % PS, 2 % PET; 58 % PE, 20 % PP, 20 % PS, 2 % PVC). A similar trend was observed in the case of toluene and ethylbenzene. Probably, radicals from PVC initiated the degradation of PS and promoted the secondary chain scission of PS. The first reaction step of PVC pyrolysis has the lowest activation energy when compared with PE, PP, or PS, because, as the dehydrochlorination of PVC is a free-radical chain reaction, it needs a relatively low temperature (280-350 °C) to occur. Probably, PVC decomposition form lighter products at lower temperatures providing radicals, which, probably, can promote the decomposition of PS and so, forming more light aromatic compounds that were found in the lighter fraction of pyrolysis liquids. Similar results were observed by Miskolczi et al., 2009, when studied the influence of PVC in the MPW pyrolysis process. No oxygenated or chloride compounds were detected by GC/MS analysis. Miskolczi et al., 2009 did not report chlorine liquid compounds in the liquid products of the pyrolysis of a mixture of HDPE, PP, PS with PVC incorporation up to 3 %. Regarding paraffins, a more complex mixture of end products was produced, ranging from C₅ to C₂₀, containing mostly n-pentane, n-hexane and n-heptane. Figure 3 shows that for all tests, the amount of olefins produced was much lower than paraffins concentration. Olefins content increased when higher percentage of PP was used. Probably, because the presence of the methyl group on the PP polymeric structure favoured the stabilisation of the intermediate radicals by the formation of a C=C bond. However, higher values of olefins were expected, so, probably the higher pressures and longer residence times present in the batch reactor do not favour the stabilization of the double bond. In general, the liquid composition is highly dependent on operation conditions used. It was also observed that higher PE content increase the aliphatic compounds (paraffins and olefins), resulting in a lower production of aromatics. Around 34.4 % of alkanes were produced with 100 % of PE in the feedstock. In general, the volume of olefins produced was similar, representing around 8 % (w/w) of total liquid composition. However the increase of PS leads to a decrease in olefins content.

4. Conclusions

Regardless the mixtures used more than 80 % (w/w) liquids and less than 9 % (w/w) solid were produced. In the gases obtained with the mixtures of pure PE, CO₂ was detected, but in small amounts. In the experimental conditions used, especially in a close mode system, PS increases the solid content and decreases the liquid yield. The elementary analysis of the solids showed that the carbon content was between 39 and 52 % and the hydrogen was approximately 3% (w/w). The liquid fraction is composed by paraffins, olefins and aromatics. The feed composition is an important parameter because the decomposition of each type of plastic provides different chemical compounds. For instance, the aromatic content in the liquids increased significantly when PS was used, so, the presence of these compounds seems to be due, mostly, to the decomposition of PS. The aromatics detected were mainly toluene, ethylbenzene and xylene. The presence of paraffins was favoured by the presence of PE. However, the PP presence did not increase the olefins content as much as expected, maybe due to the high pressure attained during the pyrolysis tests in a close mode. Several mixtures of these three kinds of plastics with small incorporation of PET and PVC were tested in order to assess if the pyrolysis technology is adequate to process this kind of plastics and what is its influence on the product yields and composition. No significant impact in product yields and composition was observed with the incorporation of small amounts of PET and PVC in the mixtures.

Acknowledgments

This work was carried out within the scope of the project i-CAREPLAST. This project has received European Union's Horizon 2020 research and innovation funding under grant agreement N° 820770.

References

- Adrados, A., Marco, I., Caballero, B., Lopez-Urionabarrenechea, A., Laresgoiti, M., Torres, A., 2012, Pyrolysis of plastic packaging waste: A comparison of plastic residuals from material recovery facilities with simulated plastic waste. *Waste management*, 32, 826-832.
- Costa P., Pinto F., Ramos A.M., Gulyurtlu I., Cabrita I., Bernardo M., 2007, Kinetic Studies of the Polystyrene Pyrolysis Reaction Pathways, *Chemical Engineering Transaction*, 12, 359-364, ISBN 88-901915-4-6
- European Commission: EUROSTAT, 2019, How much plastic packaging waste do we recycle, *Products Eurostat News*. <https://ec.europa.eu/eurostat/en/web/products-eurostat-news/-/DDN-20191105-2>
- Guedes, R.E., Luna, A.S., Torres, A.R., 2018, Operating parameters for bio-oil production in biomass pyrolysis: A review. *Journal of Analytical and Applied Pyrolysis*, 129, 134-149.
- Meija, J., Michalowska-Kaczmarczyk, A.M. & Michalowski, T., 2016, Mohr's method challenge. *Anal Bioanal Chem*, 408, 1721-1722.
- Miandad, R., Rehan, M., Barakat, M., Aburizaiza, A., Khan, H., Ismail, I., Dhavamani, J., Hassanpour, A., Nizami, A.S.: Catalytic Pyrolysis of Plastic Waste, 2019, *Moving Toward Pyrolysis Based Biorefineries*. *Frontiers in Energy Research*, 7, 1-27.
- Miskolczi, N., Bartha, L., Angyal, A., 2009, Pyrolysis of Polyvinyl Chloride (PVC)-Containing Mixed Plastic Wastes for Recovery of Hydrocarbons. *Energy & Fuels*, 23, 2743-2749.
- Pinto, F., Costa, P., Gulyurtlu, I., & Cabrita, I., 1999, Pyrolysis of plastic wastes. 1. Effect of plastic waste composition on product yield. *Journal of Analytical and Applied Pyrolysis*, 51, 39-55.
- Quesada, L., Calero, M., Martín-Lara, M.A., Pérez, A., Blázquez, G., 2020, Production of an alternative fuel by pyrolysis of plastic waste mixtures. *Energy Fuels*, 24, 1781-1790.
- Saptoadi, H., Rohmat, T., Sutoyo., 2016, Combustion of char from plastic wastes pyrolysis. *AIP Conference Proceedings*, 1737.
- Sembiring, F., Purnomo, C., Purwono, S., 2018, Catalytic Pyrolysis of Waste Plastic Mixture. *IOP Conference Series: Materials Science and Engineering*, 316, 012020.
- Sharuddin, S., Abnisa, F., Daud, W., Aroua, M., 2016, A review on pyrolysis of plastic wastes. *Energy Conversion and Management*, 115, 308-326.
- Siddiqui, M.N., Redhwi, H.H., 2009, Pyrolysis of mixed plastics for the recovery of useful products. *Fuel Processing Technology*, 90, 545-552.
- Singh, R.K., Ruj, B., Sadhukhan, A.K., Gupta, P., 2019, Impact of fast and slow pyrolysis on the degradation of mixed plastic waste: Product yield analysis and their characterization. *Journal of the Energy Institute*, 92, 1647-1657.
- Vijayakumar, A., Sebastian, J., 2018, Pyrolysis process to produce fuel from different types of plastic – a review. *IOP conference series: Materials Science and Engineering*, 396, 012062.
- Williams, E.A. & Williams, P.T., 1997, The pyrolysis of individual plastics and a plastic mixture in a fixed bed reactor. *J. Chem. Tech. Biotechnol.*, 70, 9-20.