Influence of Temperature and Reaction Time on the Performance of Thermal Pyrolysis of Compact Polystyrene Waste.

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Abstract. The purpose of this study is to determine the influence of the temperature and reaction time on the thermal pyrolysis process of compact polystyrene residues based on the percentage of liquid obtained at a heating cup of 15 °C min⁻¹ and cooling system for the condensation of pyrolytic gases at 10 °C. It worked with temperatures between 375 and 425 °C and times of 5 and 10 minutes. The results showed that the reaction time has no representative influence on the liquid fraction, while the temperature has a great importance in the liquid yield reaching a maximum contribution at 400 °C, after this the percentage of liquid oils tends to decrease by guiding the formation of the gas fraction. The maximum production was 81.4% with a kinematic viscosity of 1,026 mm² s⁻¹, relative density 0.9352, flash point 24 °C and a caloric power of 48.5 MJ kg⁻¹. The mixture of aromatic hydrocarbons obtained, with carbon chains between C6 and C20, are present in 75% by mass.

1. Introduction
The production of plastics is increasing rapidly in recent years due to its high demand, versatility, low cost and its use in a number of industrial and commercial applications giving counterproductive environmental result by the generation of waste, which is one of the fractions of greater attention in municipal solid waste (MSW) for its long time of degradation and high volume used for final disposal [1]. In the MSW exist a mixture of plastics that can be considered as recyclable that constitute several thermoplastics such as PET polyethylene terephthalate, PP polypropylene, PE polyethylene, PS polystyrene, among others. Plastic waste is managed through various techniques including recycling, reuse, reduction of use and handling - disposal in landfills as conventional techniques or non-conventional techniques such as chemical recycling [2]. In recent years chemical recycling has become one of the most important methods in several countries with techniques such as glycolysis, gasification, hydrolysis, among others to convert waste into fuels [3], technologies such as gasification and pyrolysis have been the subject of researches in recent years. [4].

Pyrolysis is a process of converting organic material including plastic waste into energy (liquid oils) and value-added products (coal) by the controlled addition of heat with or without catalytic agents that guide the formation of compounds similar to conventional fuels [5]. Polystyrene pyrolysis is mainly performed as a tool for depolymerization of macromolecule strictly controlled conditions and...
subsequent recovery of styrene monomer of great commercial interest. Furthermore, if a complete pyrolysis of the polystyrene plastic molecule is carried out, the breaking of the chains into lighter fractions [6], which follows a reaction mechanism in a single step for most plastics except PVC, data verified by means of the DTG curve in the thermogravimetric analysis where there is only one peak in the derivative of the mass versus the temperature with respect to time [7]. The objective of this article is to identify the temperature and time of greater production of liquids in the thermal pyrolysis of compact polystyrene, a plastic used mainly in the food industry as a container; and the characterization of said product according to its chemical composition and physical-chemical properties.

2. Materials and methods

2.1. Sample preparation and reactor conditions

A thermal pyrolysis reactor designed and built for the effect was used, of batch type with heating by electrical resistances and a system of valves to purge with a continuous flow of nitrogen the present. The heating cup is controlled through the temperature control system. The gases coming from the reaction are cooled in a system with cooling water at 10 ºC. The reactor pressure at the time the plastic degradation begins is maintained at pressures below 550 kPa for safety and control of the equipment, which is heated to a fixed rate of 15 ºC min⁻¹, a common speed in a slow pyrolysis where the effect of other variables can be evaluated. For each test, 100 grams of sample were weighed and 4 temperature levels (375, 400, 425 and 450 ºC) were carried out to determine the effect of this variable on the production of the liquid fraction, at two different residence times that were 5 and 10 minutes once the working temperature was reached, with three repetitions by experiments to ensure its repetitiveness in the different levels and treatment, having a set of 24 data used to study the influence of the two input variables on the amount of liquid generated, which will determine the percentage of the fraction at the end of each of the repetitions by weighing it and then by means of a mass balance according to the plastic fed.

2.2. Analytical methods

The polystyrene residues were analyzed by thermogravimetry (TGA 1 STAR System METTLER TOLEDO) establishing the limits of temperature of the experimentation that served in the experimental design established in a range from 25 to 900 ºC with neutral atmosphere of nitrogen and a heating rate of 15ºC/min. The pyrolytic products are condensed at a temperature of 10ºC; where the non-condensable gas fraction is collected in Tedslar casings through a gas trap and the liquid fraction sampled in amber containers and maintained at temperatures of 15ºC. At least three repetitions of the experiment were performed to obtain a significant sample size and to analyze the effect of temperature and time variables. Temperature and pressure control is performed by taking data every thirty seconds to determine the tendency of gas production at the time of increasing the temperature Figure 1.

![Figure 1](image-url). Reactor temperature versus pressure produced by the gases generated.
3. Results and Discussion

3.1. Raw material analysis

The recycling of polystyrene is rare in recycling campaigns due to its difficult identification concerning waste from other types of plastics, which is why it is necessary to characterize the material sampled. In addition to the physical tests of solubility and flame color, the FTIR of the compact PS was carried out, where four groups of pronounced bands belonging to the multiple tension movements are presented: a) C-H bonds to 2919,7 cm\(^{-1}\), b) C-C bond between 1400, 1600 cm\(^{-1}\) aromatic ring with -CH2 bending movement, c) aromatic ring tensions with values of 748,245 cm\(^{-1}\) and d) ring deformation vibrations outside the plane at a length of 1027 cm\(^{-1}\), as shown in Figure 2; confirming the majority presence of styrene in the structure of the polymer [8], [9]. The band present in 1341 cm\(^{-1}\) shows the presence of N-C and N-H bonds corresponding to amines and amides that are UV protective additives or antistatic additives, very common in the manufacture of plastics to give better characteristics. The band in 1027 cm\(^{-1}\) corresponds to the vibration of methylbenzene bonds that are characteristic of plasticizing agents.

![Figure 2. Infrared Spectroscopy Results.](image)

![Figure 3. TGA Y DTG of the Polystyrene](image)

In order to determine the thermal degradation temperature that provides the best performance of the liquid fraction, the TGA and DTG curve in Figure 3 establishes the initial degradation temperature for PS at 370\(^\circ\)C and a maximum temperature of 425\(^\circ\)C, worked under dynamic conditions with a heating rate of 15\(^\circ\)C, which compared with data shown by [10] verifies that the displacement of the TGA curves to the high temperature region when the heating speed increases. That is, at a faster heating rate, the equilibrium is reached slowly and, as such, the curve moves towards the high temperature region.

3.2. Pyrolysis performance

During the first stage of thermal degradation of PS a cracking of volatile substances occurs at relatively low temperatures (<150\(^\circ\)C) due to the rupture of bonds in the structures as additives or contaminating agents of the material, followed by a series of parallel decomposition reactions such as reforming, dehydration, condensation, polymerization, oxidation and gasification [11]. The performance averages of pyrolytic products with a constant heating rate of 15 \(^\circ\)C min\(^{-1}\) are shown in the table 1.

The elemental analysis of the PS is characterized by the low ash content producing a low percentage of solid product after pyrolysis at different temperatures [12], a reference that explains the values lower than 3% in the experiments of the solid fraction. At temperatures close to 375\(^\circ\)C there is a favourable effect of this parameter on the performance of the liquid fraction when the residence time increases from 5 to 10 minutes, however as the temperature increases to 450\(^\circ\)C the residence time has no significant effect on any of the product fractions. In similar studies carried out at 450\(^\circ\)C and heating rates lower than 10\(^\circ\)C per minute, a fraction similar to that of this research was obtained in the liquid product, i.e. 80%, however the gas fraction decreases to 13% and the percentage of solids increases to 6.2% [4]; this
is possibly attributed to the regrouping of compounds to form long chains of higher molecular weight, when the residence time increases.

**Table 1.** Pyrolysis results of Polystyrene at different time and temperature treatments.

| T (°C) | t(min) | % LIQ | % SOL | % GAS | t(min) | % LIQ | % SOL | % GAS |
|--------|--------|-------|-------|-------|--------|-------|-------|-------|
| 375    | 5      | 73.79 | 1.84  | 24.37 |        | 76.56 | 0.90  | 22.54 |
| 400    | 5      | 80.60 | 0.56  | 18.84 | 10     | 81.41 | 1.16  | 17.43 |
| 425    | 5      | 78.35 | 0.64  | 21.01 |        | 79.08 | 2.28  | 18.64 |
| 450    | 5      | 80.63 | 2.16  | 17.21 |        | 79.28 | 2.30  | 18.42 |

3.3. Effect of reaction time on percentage of liquid.

The effect of time at four temperature levels was studied. At a time of 5 minutes at 400°C it gives a yield of 80.6% and at 10 minutes a yield of 81.41% showing that there is no significant difference in the production of liquids at the reaction times of 5 minutes and 10 minutes in the reactor conditions. The amount of total hydrocarbons in the 5-minute sample presented a greater dispersion of data due to the fact that the effect of time is a function of the dimensions of the reactor and the transfer of heat through the elements of the equipment. Therefore a time of 10 minutes is suggested as an optimal time in which the distribution of hydrocarbons in the sample is stabilized, this being the time necessary for the total degradation of the PS. Similar analysis was observed and reported by [4] and [13].

3.4. Effect of temperature on percentage of liquid.

The quantity of gas is closely related to the quantity of liquid pyrolysis products, from 425 °C the liquid fraction begins to decrease to favour the gaseous fraction [14]. A high temperature causes the C-C bonds to have a greater rupture generating lighter hydrocarbons with a short chain, behaviour explained by [15]. Thus, for every 1% that the liquid fraction decreases, the fraction of gas generated increases by 0.97%.

The different temperature levels at a time of 10 minutes in the batch reactor gave the yields presented in Figure 4. At that time at a temperature of 375°C gave a liquid fraction of 76.6% with a gas production of 22.5% and 0.9% solids which was the lowest yield obtained. The highest production value was at 400 °C with 81.4%, 17.4% and 1.2% of liquid, gaseous and solid fraction respectively.

It is determined as the optimum temperature of greater production of liquid percentage at the operating conditions defined above, 400 °C; different to that predicted by the thermogravimetric analysis (450°C) due to the fact that in the TGA there are controlled conditions with small amounts of sample, which in comparison with the conditions of the pyrolysis reactors can be, even in occasions, particular for each case [4].

The yield of the produced liquid oil rose at the beginning of the process, after a certain temperature and time, the yield of the oil began to decrease (Figure 4). This is due to the fact that after reaching the temperature of maximum generation of liquid compounds certain secondary reactions such as poly aromatic formation reactions are initiated during the pyrolytic process which decreases the performance of oils [16] and [17].
The pyrolysis of PS at a temperature of 400º C and residence time of 10 min, produced 41% of carbon chain components between C12 and C 20. Compounds that are formed possibly due to the reactions that occur at the time of production of styrene which is the hydrocarbon that is first generated in the decomposition of PS [18]. As can be seen in Figure 5 up to 425º C a similar behavior is seen in the production of light compounds, however at 450º C a greater production of compounds between C20 and C28 is observed as opposed to the other temperatures. Particularly evident at both 5 and 10 minutes of reaction but much more pronounced at 10 minutes congruent with [4] where it mentions that the longer the residence time facilitates that the chains again interlace and form linear compounds of higher molecular weight. Previous studies have reported an increase in the generation of styrene at higher temperatures up to a maximum point, with a subsequent decrease due to the formation of compounds originating between several aromatic radicals [19].

3.5. Characteristics of the liquid obtained
Different parameters of the liquid fraction obtained for the best pyrolysis conditions were analyzed, as shown in table 2. The kinematic viscosity presents a value of 1.026 mm² s⁻¹ at 40°C, which is lower than that specified in the ASTM D975 standard for conventional diesel, however it is consistent with the value reported by [4]. The low viscosity of the liquid fraction is attributed to the variation in the structure and composition of PS that differentiates it from other monomers [20]. A low viscosity favors the pulverization and atomization of the fuel, contributing to engine performance, even at low temperatures [21]. The relative density at 15.6°C of the liquid fraction obtained is 0.9352 g cm⁻³, which resembles the
values reported by [4]; this density is slightly higher than that reported for conventional diesel (0.81-0.87 g cm$^{-3}$), as reported by [22]. The sulfur content of the liquid fraction obtained is extremely high, 1120 ppm, which means that for its use as fuel must first undergo a previous desulfurization process, however, when applied as an additive to reduce viscosity, for example the cutter stock, the sulphur content is within permissible limits. The HHV of the liquid fraction obtained at the best pyrolysis conditions is one of the most important parameters for the identification of a fuel, the value obtained was 48.5568 MJ kg$^{-1}$, which is higher than the reference value for conventional diesel (43.06 MJ kg$^{-1}$) [23]. Several researchers have studied the liquid fraction of PS pyrolysis as an individual energy source or as a mixture with conventional diesel [24], due to the high content of aromatic compounds that raise the flash point. However, there are other applications in which the main objective is the recovery of monomers mainly styrene, and other compounds such as toluene and ethylene benzene that can be used as a chemical source in industries for the polymerization of PS polymer [15].

| Test                      | Units                  | Results Authors | Miandad (2016) | Cutter Stock Parameters |
|---------------------------|------------------------|-----------------|-----------------|-------------------------|
| API Gravity at 60 °F      | °API                   | 19.8            | NR              | NR                      |
| Relative Density 15.6°C   |                        | 0.9352          | 0.91 - 0.92     | NR                      |
| Sulfur content            | % W                   | 0.112           | NR              | Max 2.5                 |
| Kinematic viscosity at 40°C | mm² s$^{-1}$               | 1.026           | 1.92 - 3.24     | Max 7                   |
| Water and sediment content | % V                 | 0.5             | NR              | Max 0.2                 |
| Distillation of 90%       | °C                    | 325             | NR              | NR                      |
| Flash point               | °C                    | 24.1            | 28.1 – 30.2     | Min 60                  |
| Calculated cetane number  | -                     | 20.06           | NR              | NR                      |
| Higher Heating Value (HHV)| MJ/kg                | 48,5568         | 41.4 – 41.8     | NR                      |

*NR: Not Reported

4. Conclusions
The results of obtaining liquid hydrocarbons from PS in a 3 L capacity batch reactor with a coupled cooling system for the condensation of pyrolytic gases at 10°C were studied. In which the effect of time and temperature variables on the performance of liquid products was analysed. The reaction time taken since it reaches the working temperature has no influence and is worked at 10 minutes. The temperature has high significance in the liquid yield until reaching a maximum contribution of 400 °C after this the percentage of liquid oils decreases as the temperature increases generating an increase in the formation of the gas fraction. 81.4% of liquid products are obtained with a kinematic viscosity of 1,026 mm2 s$^{-1}$, relative density 0.9352, flash point 24 °C and a caloric power 48.5 MJ kg$^{-1}$.

Due to the high content of styrene, toluene and ethylene benzene in pyrolytic oils according to [16] and [15]. The monomer generated can be used in the chemical industry [25]; [4] or for its high content of aromatic hydrocarbons and mixture of carbon atoms between C9 and C25 and flash point lower than 100°C [26]; as well as for the chromatographic analysis that shows a composition of C6 to C20 of 75%. the fuel obtained from the liquid fraction has composition and properties similar to those of the cutter stock and can be used as diluent in refineries to adjust the viscosity of fuel oil.

5. References
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