

# Characterization of the Thermal Pyrolysis Process of Waste Derived from Mechanical Recycling of Plastics

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The various strategies for recycling and valorization of plastic waste are an alternative to reduce the large amounts of garbage available worldwide. Specifically, obtaining reusable plastics through mechanical recycling represents a viable and economically sustainable option. However, this process results in waste that is impossible to recycle by conventional methods. Therefore, an alternative is proposed for processing this waste from the mechanical recycling of plastics, obtaining value-added fuels that can complement conventional ones. In this work, the thermal pyrolysis of a random waste is presented, finding that it is possible to obtain 82.4% of the initial mass of the waste in crude pyrolytic oil at a temperature of 425 °C. This raw pyrolytic oil is fractionated and characterized, finding that at these temperature conditions, 27.49% is a light fuel like gasoline, 49.29% is a medium fuel like diesel, and 23.22% is a heavy fuel like heavy diesel.

## 1. Introduction

Recycling plastic has become a critical issue globally as plastic waste continues to accumulate in landfills and oceans. In Latin America, the plastic recycling industry has grown significantly in recent years, but it still faces challenges in terms of collection and processing. Latin America generates over 16 million tons of plastic waste annually, but only a small percentage is properly collected and recycled. In Brazil, for example, only 8% of plastic waste is recycled, while in Mexico the rate is slightly higher at 15% (Patti et al., 2022).

Despite these challenges, governments and private companies in Latin America are taking steps to promote plastic recycling and reduce plastic waste. In Colombia, for instance, a few cities have implemented successful recycling programs, with Bogotá leading the way with its "Recicla Ya" initiative (Vega, 2020). The benefits of plastic recycling are numerous, including reducing greenhouse gas emissions, conserving natural resources, and creating jobs in the recycling industry. A report by (Symeonides et al., 2019) indicates that for every ton of plastic that is recycled, 5.7 jobs are created, and carbon dioxide emissions are reduced by 3.6 tons.

There are several types of recycling, including mechanical, chemical, and biological recycling. Mechanical recycling involves grinding and melting down plastic waste to create new products, while chemical recycling involves breaking down plastic into its constituent chemicals to be used as feedstocks for new plastic production. Biological recycling uses microorganisms to break down plastic into biodegradable materials (Riesco et al., 2022).

Globally, the use of plastic continues to rise, with estimates suggesting that by 2050, the plastic industry will consume 20% of all oil production and 15% of the annual carbon budget. Despite efforts to increase recycling rates, only 9% of the plastic produced globally is being recycled, with the rest ending up in landfills or the environment (Mai et al., 2020). Therefore, we must prioritize recycling and reduce our reliance on single-use plastic to protect our planet and future generations.

In particular, the mechanical recycling of plastic produces several types of waste, including plastic dust, fragments of non-recycled material, and residual additives and pigments. These waste products can pose significant environmental risks, as they can release toxic chemicals into soil and water systems if not properly managed. In addition, the melting process involved in mechanical recycling can also result in the release of fumes and particulate matter into the air, contributing to air pollution. Increased recycling can help to mitigate the negative impacts of plastic waste on the environment.

The combination of two types of recycling such as mechanical and chemical increases the efficiency of the process and reduces the amount of waste generated. Thermal pyrolysis is a thermal process that significantly improves the production of liquid, solid and gaseous products and has proven promising in various studies such as those presented by (Riesco et al., 2022). Research works on the evaluation of thermal pyrolysis are presented by various authors, where only the effect on the yield of liquid obtained is studied, but distillations for refining and purification in search of obtaining commercial fuels such as gasoline and diesel are not developed (Riesco et al., 2022) (Yansaneh et al., 2022). For this reason, this work presents an alternative to processing the waste generated through a plastic mechanical recycling company. Specifically, the waste is revalued by obtaining commercially valuable fuels that can be used in the generation of electricity or the company's vehicles.

## 2. Materials and methods

### 2.1 Raw materials characterization

The raw material used in this article comes from a traditional mechanical recycling company in Mexico. This company processes between 1200 and 1500 tons of plastic waste per month, mainly polypropylene (PP), high-density polyethylene (HDPE), and low-density polyethylene (LDPE). However, during the recycling process, approximately 5 to 10% of the generated waste is no longer valuable and must be returned to the landfill or stored, causing a high cost. Figure 1 shows the plastic recycling process. The randomness of these waste products makes it impossible to carry out homogeneous characterization tests, such as thermogravimetry, for which a methodology is needed to estimate the composition of the mixture.

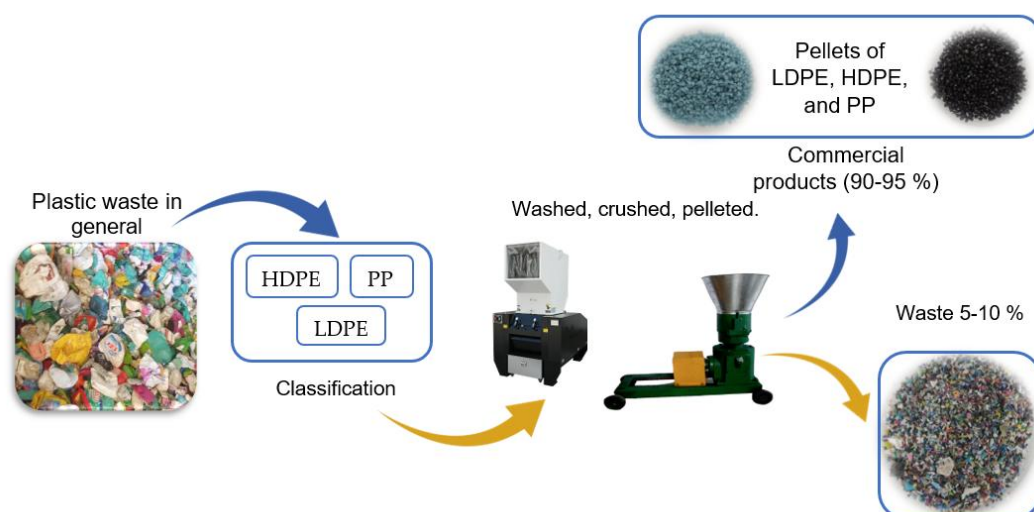


Figure 1: Plastic recycling process.

Initially, the combined waste was placed in a tank filled with water at 4°C (density of 1000 kg/m<sup>3</sup>) to distinguish the plastic waste from dust particles and any other unwanted materials in the mixture. Next, the mixture of plastic waste without dust and other substances was put in a container with a mixture of ethyl alcohol and water (density of 0.93) to separate the HDPE (density of 0.94 to 0.97). Finally, the separated portions were put in an oven set at 120°C for 8 hours to remove any remaining water and alcohol.

### 2.2 Experimental Setup and Procedure

The used equipment is a semi-batch reactor with a 1 kg raw material loading capacity (see Figure 2). Once the safety commands indicated have been sealed and verified, such as the verification of settings and valves, the pyrolysis process is started. The test temperatures were 425°C and 475°C. The test time was two hours, heating is carried out by two 1 000 W resistors. The temperature ramp is 15 °C/ min.

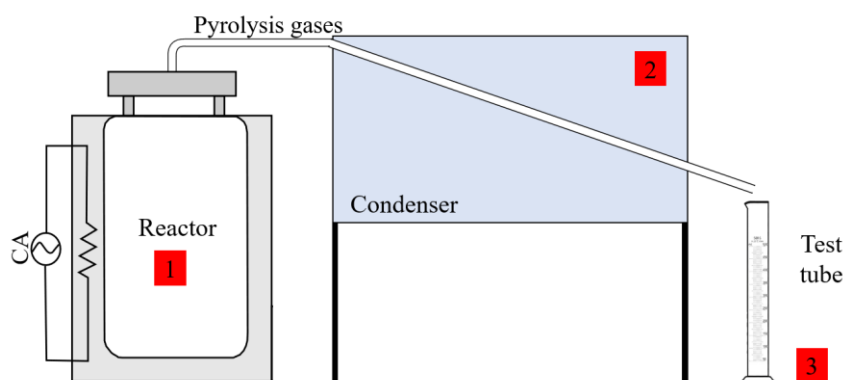


Figure 2: Test facility of pyrolyzer (1. Reactor, 2. Condenser, 3. Test tube).

### 2.3 Fractionation of raw pyrolytic oil

Pyrolytic oil due to its physical and chemical characteristics can be used as fuel in boilers, burners, or incinerators. But it cannot be used directly in an internal combustion engine or a turbine. For this reason, the fractionation process is performed as any hydrocarbon. Where the separation between the different fractions is known as gasoline between 20 and 180 °C, diesel between 180 and 320 °C, and the rest of the components known as heavy diesel or fuel oil in products above 320 °C. This process is carried out in a distillation unit under ASTM D86 regulations that allow the use of a condenser with a large heating capacity and storage of products. The test facility used is presented the Figure 3.



Figure 3: Test facility of distillation of ASTM D 86

### 2.4 Characterization of products

The liquid products were also characterized to study their physical properties and composition. The composition was analyzed using a Varian 450GC chromatographer, with a 100 m × 0.25 mm × 0.25 μm column, a flow rate of 3 mL/min, and saturated alkanes C<sub>7</sub>-C<sub>30</sub> as a standard. The split-type injector was set to 280 °C and the FID-type detector to 340°C. The heating ramp of the furnace was 40°C for three minutes, followed by a speed of 20 °C/min until reaching 320°C, and was maintained for 8 min. Kinematic viscosity was measured with a Cannon-Fenske viscometer with a time and temperature uncertainty of ±0.1 s and ±0.1 °C, respectively, according to ASTM D 445 standard. Density was determined with a floating densitometer applying the ASTM D 1298 standard. Calorific values were determined with an IKA C3000 calorimeter pump, applying the isoperibolic method, following the ASTM D 240 standard. Distillation temperatures were determined for 100 mL samples, at atmospheric pressure, under the ASTM D 86 standard.

### 3. Results

#### 3.1 Raw materials composition

Table 1 shows the results of the raw material characterization, according to the methodology described in Section 2.1. The raw material is mainly made up of  $11.3 \pm 0.8\%$  HDPE, a mixture of LDPE and PP ( $85.2 \pm 1.3\%$ ), and  $3.5 \pm 0.5\%$  of other materials, not plastics.

Table 1: Results of raw materials characteristics

Type of Plastics	% wt
LDPE	$44.6 \pm 0.1$
PP	$40.6 \pm 0.1$
HDPE	$11.3 \pm 0.1$
Other materials <sup>a</sup> , not plastics	$3.5 \pm 0.1$

<sup>a</sup>Paper labels, Soil residues, Metallic particles

#### 3.2 Yields of pyrolysis

The yield of each of the products (oil, gas, and solid) shows behavior as reported in the literature (Riesco et al., 2022). The behavior displayed in Figure 4 shows that at higher temperatures, gas formation increases and liquid product decreases. Additionally, solid products are close to 10% wt, with this high percentage being due to the possibility that non-plastic materials do not degrade at this temperature.

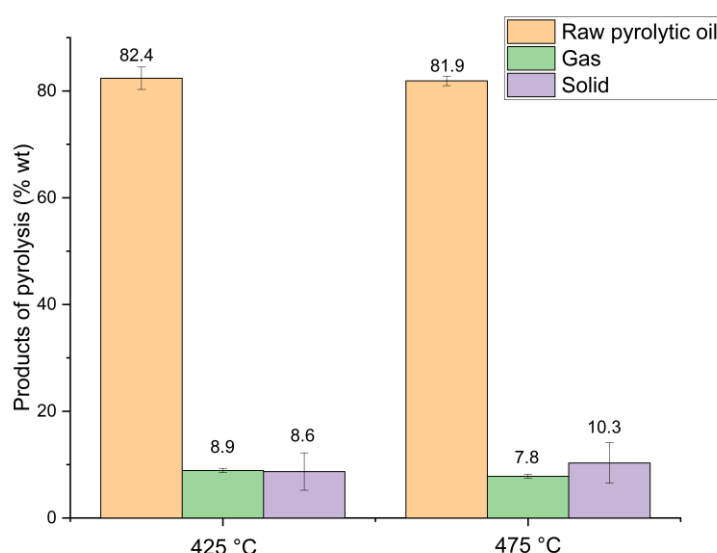


Figure 4: Yields of pyrolysis.

#### 3.3 Fractionation of raw pyrolytic oil

The raw pyrolysis oil obtained is distilled, obtaining three fractions as described in subsection 2.3. The results show a liquid yield with a higher presence of medium pyrolytic oil (180-320 °C) (diesel-like) of  $50.30 \pm 1.02\%$  wt, followed by light pyrolytic oil (20-180 °C) (gasoline-like) with  $25.64 \pm 1.84\%$  wt; and finally, heavy pyrolytic oil (320-400 °C) (heavy diesel-like) with  $24.05 \pm 0.82\%$  wt. These results are shown in Figure 5 and the Figure 6, the appearance of each fraction and the raw pyrolysis oil can be observed.

As seen in Figure 5, the liquid product yields are not a function of the pyrolysis temperature. This proves the hypothesis that the oil obtained from pyrolysis is independent of degradation temperatures, resulting in the same amount of petroleum byproducts. Light pyrolytic oil can be an additive for spark-ignited engines, while medium pyrolytic oil can be an additive for compression-ignited engines. Finally, heavy pyrolytic oil can be an additive in incinerators or boilers. To verify this claim, the physic-chemical characterizations are presented in subsection 3.4. The products obtained from the pyrolysis are mixed since their yields when fractionated are very similar. For this reason, only each of these is analyzed.

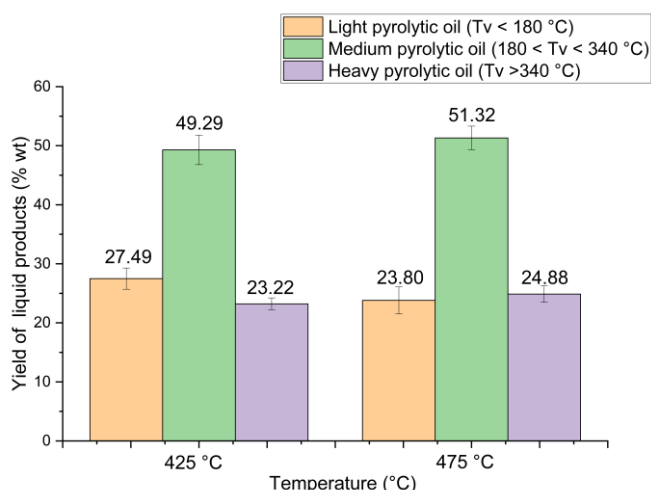


Figure 5: Yield of fractionation of raw pyrolytic oil ( $T_v$  = Vapor temperature)

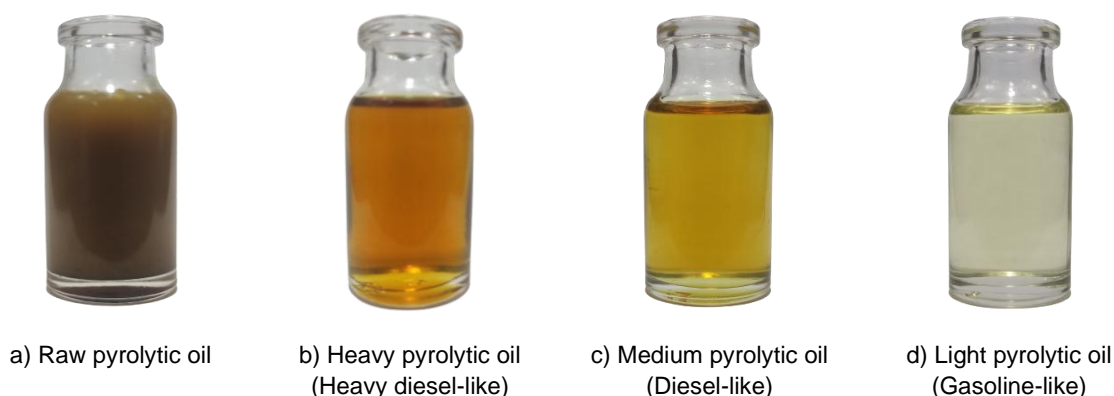


Figure 6: fractionated pyrolytic oil.

### 3.4 Liquid Product Analysis

Despite having performed separation with analytical equipment for each of the different fractions, an effect of particle carry-over is observed at the initial and final evaporation temperatures for each characterized sample presented in Table 2. In addition, there is a significant division in the carbon percentages of each fraction, which allows us to conclude that an adequate separation of the various hydrocarbons occurs by an atmospheric distillation method. Likewise, Table 2 shows temperatures within the range of commercial hydrocarbons such as gasoline for gasoline-like, diesel for diesel-like, and heavy diesel for heavy diesel-like. Values such as density and viscosity are of the same order as each of the compared commercial fuels. In turn, the cetane number is presented for the light fraction reaching a value similar to commercial gasoline showing adequate resistance to self-detonation. Also, the raw pyrolytic oil has a cetane index of 47.57 and the medium fraction of 68.37. These obtained products can serve as a basis to complement commercial fuels or to produce additives. Since no significant differences are observed concerning the results presented by various authors (Riesco et al., 2022, Gonzalez-Aguilar et al., 2022).

### 3.5 Energy analysis

The energy consumption in the production of alternative fuels has a significant advantage over traditional petroleum processes. Since most raw materials for these fuels come from waste and their primary goal is resource valorization, this method is no exception. As there is no cost for the raw material in the process, it is beneficial. However, the energy consumption for this low-scale thermochemical transformation system is 30% higher, averaging at 9.60 [kW h/L], compared to 12.55 [kW h/L] for this process.

Table 2: Results of physic-chemical characterizations

Properties	Raw pyrolytic oil	Fraction			Standard
		Light	Medium	Heavy	
Density at 20 °C [kg/m <sup>3</sup> ]	-	728.1±0.2	792±0.7	-	ASTM D 1298
Kinematic viscosity at 40 °C [mm <sup>2</sup> /s]	-	0.72±0.01	1.98±0.08	-	ASTM D 445
Initial Boiling Point	36±1	35±1	184±1	321±1	
T <sub>10</sub> (°C)	96±1	55±1	201±1	341±1	
T <sub>50</sub> (°C)	216±1	90±1	254±1	374±1	ASTM D 86
T <sub>90</sub> (°C)	389±1	159±1	326±1	397±1	
Final Boiling Point	415±1	210±1	338±1	417±1	
Heat value [MJ/kg]	45.51±0.31	42.70±0.18	46.39±0.29	46.18±0.52	ASTM D 240
Chromatographic analysis [wt%]					
C <sub>8</sub> -C <sub>10</sub>	58.82±0.56	76.47±0.57	77.18±0.75	1.18±0.27	
C <sub>11</sub> -C <sub>15</sub>	35.07±0.89	14.18±0.59	79.49±0.80	14.12±0.35	-
C <sub>16</sub> -C <sub>30</sub>	6.11±0.12	9.35±0.16	13.33±0.48	84.70±0.55	
Other properties (Calculated with correlations)					
Octane Index	-	90.59	-	-	(Riesco et al, 2022)
Cetane Index	47.57	-	68.37	-	ASTM D4737

#### 4. Conclusions

The pyrolysis alternative for the valorization of waste generated by mechanical recycling is viable, as despite consuming 30% more energy compared to traditional petroleum-derived fuels, they are fuels that can be burned in emissions-controlled systems. This allows for proper disposal compared to storage or incineration. Additionally, the obtained results for calorific value show values higher than conventional diesel and heavy diesel from petroleum.

#### Nomenclature

%wt – weight to weight percentage

PP – Polypropylene

LDPE – low-density polyethylene

HDPE – high-density polyethylene.

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