

# Pyrolysis of Real-World Waste Plastics in a Thermo-Catalytic Two-Stages Fixed-Bed Reactor

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Real-world waste plastics obtained from its final disposal on the municipal landfill of San Diego de la Unión (Guanajuato, México) were processed in a thermo-catalytic two-stage fixed-bed reactor using a commercial zeolite H-ZSM-5 catalyst. Single plastic low-density polyethylene (LDPE) was also processed and used as a reference. The physic composition of the real-SDU sample was PETE: HDPE: PVC: LDPE: PP: PS: OTHER= 14: 6: 2: 38: 24: 4:12. For non-catalytic pyrolysis, a liquid yield product was 85 and 65 wt.-% for single LDPE and the real-SDU sample, respectively. Real-SDU sample produced 3-fold more solid than LDPE (16 vs. 5 wt.-%). The proximate and ultimate analyses showed that solid residues would be composed mainly of ashes due to source contamination. The thermo-catalytic pyrolysis, using H-ZSM-5 as the catalyst, significantly increased the fraction of the light-gas products at the liquid fraction cost, compared to thermal pyrolysis. The solid yield was independent of the non-catalytic or thermo-catalytic reactions, so changes in yield distribution were related to the hydrocarbon's catalytic reformation during the thermal-pyrolysis first-stage reactor. In both LDPE and the real-SDU cases, the liquid yield decreased around 34 wt.-% concerning the non-catalytic reaction. Still, it improved the oil fraction's quality. The H-ZSM-5 catalyst promotes the cracking of heavier hydrocarbons produced in the thermal-pyrolysis stage reactor into lighter hydrocarbons, influencing the liquid products' chemical composition by 2-fold increasing the fuel range fraction (C<sub>7</sub>-C<sub>16</sub>). This process could be considered a technological option for the remediation of urban plastic wastes by producing hydrocarbons in the fuel range such as gasoline, jet, and diesel fuels.

## 1. Introduction

Plastic is an indispensable material in modern human life. Due to its mass production, widespread use, and difficulty in disposal, the waste generated by its mass use brings severe ecological challenges. The strategy to solve this problem focuses on converting these wastes into valuable products, mainly liquid hydrocarbon fuels. Existing technologies for recycling various plastics, such as polypropylene (PP), low-density polyethylene (LDPE), high-density polyethylene (HDPE), polystyrene (PS), and polyethylene terephthalate Ester (PETE), has matured and been widely used worldwide. However, the technology for the chemical conversion of municipal mixed plastic waste (MMPW) has not yet been fully developed. MMPW is a mixture of various dirty plastics that are not suitable for primary recycling. Among the technologies that can be used to process MMPW, pyrolysis technology is a promising option to achieve high yields of valuable products (including liquid hydrocarbon fuels) (Williams & Stanley, 2007). In view of ecological safety and the global trend of reducing the production and use of conventional non-renewable fuels, the conversion of MMPW to hydrocarbons as a technology option has attracted attention.

There are many studies on the pyrolysis of individual plastics, but few studies have focused on municipal mixed plastic waste (Lu et al., 2020). Given the complexity of these kinds of residues' chemical compositions,

it is challenging to describe the decomposition process's behavior and define its thermal difference. These factors limit the development of commercial plants for the commercial production of liquid fuels from MMPW. Several recycling methods have been proposed to reduce municipal plastic waste (Al-Salem et al., 2010). Several ways of thermochemical conversion of plastic waste have been reported in the literature: incineration, gasification, plasma gasification, combustion, pyrolysis, glycolysis, hydrolysis and ammonolysis, and hydrogenation. Among them, thermochemical pyrolysis is considered a reliable solution for adding value to non-recyclable plastic waste.

Pyrolysis is a thermochemical conversion process that involves heating a mixture of waste plastics to a moderate temperature (300-550 °C) and an inert atmosphere to produce oil, gas, and coke. Pyrolysis is a flexible process, and process performance can be adjusted by adjusting process parameters (such as temperature, pressure, heating rate, reactor design, and catalyst) (Lopez et al., 2017). In this regard, previous studies have shown that in optimizing liquid hydrocarbon fractions, the two-step configuration of thermal decomposition followed by catalytic decomposition has multiple advantages (Muhammad et al., 2015). The use of catalysts adds value to pyrolysis because a suitable catalyst can improve product quality and guide the process to provide selectivity to more valuable products, even at temperatures below the pyrolysis temperature (Serrano et al., 2012). The most studied catalysts to increase the selectivity to light olefins, gasoline, jet, and diesel fuels fractions are conventional acidic solids used to crack petrochemical raw materials, such as zeolites (H- $\beta$ , H-Y, H-ZSM-5, among others) (Aguado et al., 2009), FCC catalysts (Barbarias et al., 2015), and non-zeolite mesoporous solids (Sakata et al., 2009). The results reported in the literature indicate that the cracking ability of the catalyst depends on its physical and chemical properties. Therefore, ZSM-5 zeolite has become one of the most commonly used catalysts due to its acidity and unique texture characteristics (structure and pore size). These characteristics promote breaking C–C bonds and determining the resulting product's chain length (Serrano et al., 2012).

In this work, the effect of incorporating successive catalysis stages into the thermochemical pyrolysis stage of municipal mixtures used for real-world plastic waste on the performance and composition of liquid product fractions was evaluated.

## 2. Experimental

### 2.1 Raw material classification

A real mixed municipal plastics waste (MMPW) was recollected from the San Diego de la Unión's (SDU; México) municipal landfill and classified according to the Resin Identification Code (RIC; ASTM D7611). The identity of each plastics type was verified through the characteristic functional groups determined by infrared spectroscopy. PVC and miscellaneous materials were discarded from MMPW to avoid health and environmentally hazardous pyrolysis by-products, such as dioxins, furans, cyanogens, amines, and hydrochloric acid).

### 2.2 Characterization of the plastic waste samples

Moisture, matter volatiles, fixed carbon, and atomic composition were determined for the municipal mixed plastic waste and individual components according to the ASTM D4931, D7582, D5373/D1552, respectively. For C, H, N, and S determination, a Thermo Scientific FLASH 2000 analyzer and methionine (C: H: N: S: O= 40.3: 7.45: 9.39: 21.95: 21.45) as standard were used; oxygen was determined by difference. The measurements were made with four repetitions obtaining standard errors >3%.

### 2.3 Reaction test

Thermal and thermo-catalytic pyrolysis experiments were carried out in a vertical two-stages fixed bed reactor (Figure 1) manufactured in SS316 and equipped with an oil condenser, liquid-gas separator, and a sorbent-gas sampler. Each reactor section of 300 mm length and an internal diameter of 19 mm was connected in a series configuration and independently heated with PID controlled tube irradiation furnaces. Around 20 g of plastic sample (1.0-2.8 mm) was loaded into the first reactor, while 5 g of catalyst (0.08-0.13 mm) was packed in the second reactor. The plastic sample and catalyst were packed between silicon carbide (SiC) fixed-beds to improve heat transfer into the reactors. The first reactor was purged with a vacuum pump at room temperature for 1 h to remove moisture and volatile matter, and then, the whole reaction system was oxygen-purged with nitrogen. The nitrogen flow and the second reactor's temperature were set at 100 mL·min<sup>-1</sup> and 500 °C throughout the experiment. The plastic samples' thermal pyrolysis took place in the first reaction with a heating rate of 10 C·min<sup>-1</sup>, from room temperature to 500 °C, and then, the temperature was held at 500 °C for 1 h. The volatile products produced in the pyrolysis stage passed directly to the second-stage reactor

containing the catalyst at 500 °C. The liquid products were collected in a condenser unit, while thermal desorption sampling tubes with Tenax TA polymer sorbent were used for incondensable fractions.

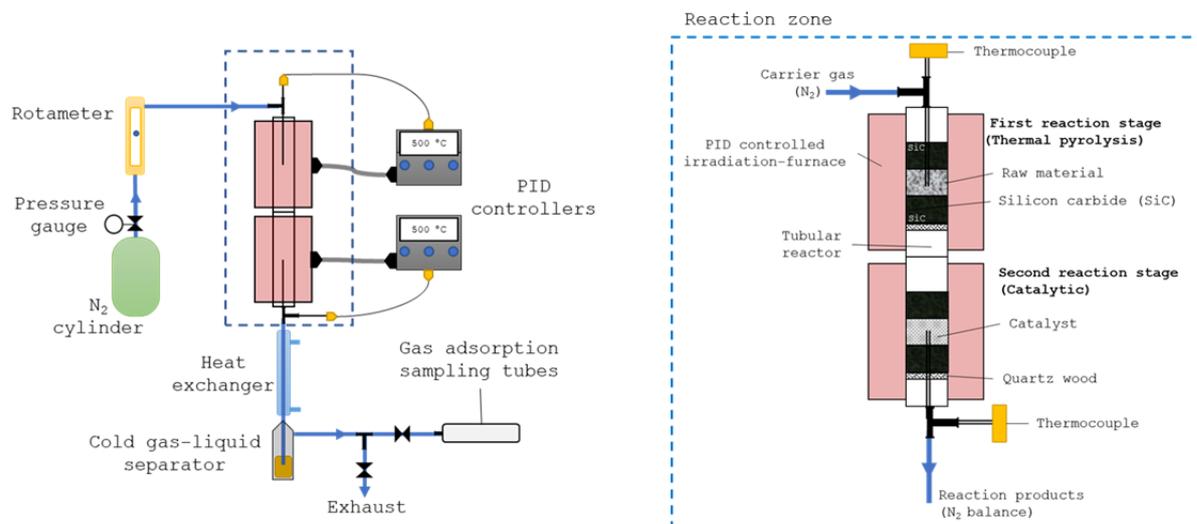


Figure 1: Scheme of the experimental test bench for thermal and thermo-catalytic pyrolysis.

## 2.4 Liquid product analysis

Oil samples were characterized by gas chromatography with mass spectrometry (GC-MS). Analyzes were performed using an Agilent 7890B model high-performance gas chromatograph equipped with an HP-5-MS capillary column and coupled to a Waters Quattro model triple quadrupole mass spectrometer. Compounds identification was based on the Mass Spectrum Library of the National Institute of Standards and Technology (NIST).

## 3. Results and discussion

### 3.1 Raw material characteristics

The municipal solid waste collected was initially classified into organic matter (46 wt.-%), plastics (30 wt.-%), glass and metals (4 wt.-%), paper (4 wt.-%), and miscellaneous (16 wt.-%). This composition is consistent with the commonly reported municipal mixed solid waste (Kumar & Samadder, 2017). The composition profile for paper, metal, glass, and miscellaneous waste corresponds to the typical rural zone, while the organic/plastic ratio represents urban strata.

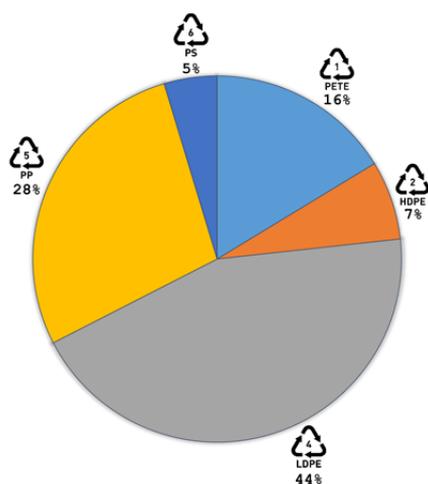


Figure 2: Composition of the mixed municipal plastic sample (SDU sample) used in this work.

The characteristic composition of the plastic fraction for the San Diego de la Unión landfill was: low-density polyethylene (LDPE, 38%), polypropylene (PP, 24%), polyethylene terephthalate (PETE, 14%), high-density polyethylene (HDPE, 6%), polystyrene (PS, 4%), polyvinyl chloride (PVC, 2%), and miscellaneous polymer (12%). In this case, PVC and miscellaneous plastics were discarded from the mixed plastic sample to avoid damage to infrastructure and highly toxic emissions due to corrosive and hazardous by-products generated at pyrolysis conditions. Finally, the mass composition for the mixed plastic sample used in this work (called as SDU sample) was represented in Figure 2.

*Table 1: Properties (in wt.-%) of individual plastics and the SDU sample. N.D.: non-detected*

| Material | Moisture  | Volatile matter | Fixed carbon | Ashes     | Carbon     | Hydrogen   | Oxygen     | Nitrogen    |
|----------|-----------|-----------------|--------------|-----------|------------|------------|------------|-------------|
| PETE     | 2.4 ± 0.1 | 84 ± 4          | 7.4 ± 4      | 5.6 ± 0.2 | 64.1 ± 0.6 | 3.4 ± 0.6  | 32.1 ± 0.3 | N.D.        |
| HDPE     | 2.4 ± 0.1 | 97 ± 2          | N.D.         | 1.4 ± 0.4 | 73.2 ± 0.4 | 13.3 ± 0.6 | 13.4 ± 0.2 | N.D.        |
| LDPE     | 2.3 ± 0.1 | 98 ± 2          | N.D.         | 1.6 ± 0.3 | 74.7 ± 0.6 | 12.7 ± 0.5 | 12.6 ± 0.6 | 0.02 ± 0.01 |
| PP       | 2.4 ± 0.1 | 95 ± 4          | 1.6 ± 0.3    | 3.5 ± 0.2 | 85.5 ± 0.8 | 13.7 ± 0.1 | 2.3 ± 0.6  | N.D.        |
| PS       | 2.5 ± 0.1 | 97 ± 3          | 0.6 ± 0.2    | 1.7 ± 0.3 | 89.0 ± 0.4 | 10.8 ± 0.6 | 0.6 ± 0.1  | N.D.        |
| SDU      | 2.4 ± 0.1 | 93 ± 4          | 0.7 ± 0.4    | 6.1 ± 0.2 | 75.6 ± 0.7 | 11.4 ± 0.7 | 12.8 ± 0.3 | 0.03 ± 0.01 |

Table 1 summarizes the properties determined for individual plastics and the SDU sample. The moisture percentage is affected by the materials' physical and chemical properties that allow them to absorb water from the environment. It should be considered that, given the origin of the samples, the humidity of the sample could be affected due to contamination by organic matter and exposure to environmental conditions. In this case, the moisture fraction in the recollected plastic samples did not exceed 3 wt.-%, which could be caused by conditions of high exposure to solar radiation. Volatile matter refers to the weight fraction of a sample that turns into gas for annealing up to 950 °C under an inert atmosphere. The remaining residues correspond to the mixture of the inorganic matter fraction and the fixed carbon. The volatile matter fraction exceeded 90 wt.-% for individual plastics, except for PET, which presented 84 wt.-%. For the SDU sample, the volatile matter reached 91 wt.-%, a value located in the lower limit within the individual plastics range. This difference could be explained due to the sample's contamination with inorganic fractions from the sampling site, according to the percentage of ashes in the SDU sample, 6.1 wt.-%.

Polyethylene samples (HDPE and LDPE) showed a similar atomic composition (C, H, O, N and S), averaged in 74, 13, and 13 wt.-% of carbon, hydrogen, and oxygen, respectively. In this case, a theoretical high heat value (HHV) around 11,050 MJ·kg<sup>-1</sup> was determined. Polyethylene terephthalate (PETE) has the lowest carbon (64.1 wt.-%) and hydrogen (3.4 wt.-%) but higher oxygen fraction (32.1 wt.-%) compared to other plastics samples. In this case, the theoretical HHV value of PETE was 30 % lower than HDPE and LDPE. In contrast to the different varieties of polyethylene (HDPE, LDPE, and PET), propylene and polystyrene show lower oxygen concentrations (<3 wt.-%) but higher carbon fraction (~90 wt.-%). In these cases, the HHV was determined at 11,300 MJ·kg<sup>-1</sup>. The composition determinations made in this work for individual plastics were consistent with the typically reported in the literature. Usually, the analyzed plastic wastes contain a molar composition between 20 and 60 wt.-% of carbon, <50 wt.-% of oxygen, and <80 wt.-% of hydrogen (Vuppaladadiyam et al., 2019). The atomic composition of the SDU sample was representative of non-oxygenated plastic materials (LDPE, HDPE, PP, and PS), which is consistent with its composition (~72 wt.-% of LDPE and PP). The presence of sulfur was not detected in any of the samples.

### 3.2 Product yield

Figure 3 shows the gas-liquid-solid yield values obtained in the thermo- and thermo-catalytic pyrolysis for the SDU sample and LDPE. In thermochemical pyrolysis, without catalyst, LDPE presented the maximum liquid yield with 85.4 wt.-%, while solid- and gas-yield reaches 5.2 and 9.4 wt.-%, respectively. The liquid- and gas-yields obtained in this work were consistent with those commonly reported in the literature, except for the solid fraction. In this regard, the samples' source contamination by organic matter and inorganic pollutants evidenced in the proximate analysis (Table 1; ~1.6 wt.-% ashes) should be considered. The thermal pyrolysis of the SDU mixture reached a liquid yield of 64.7 wt.-%, with 13.5 and 21.8 wt.-% of solids and gaseous products, respectively. This result shows a liquid yield 24 % lower than obtained for LDPE, at the cost of increasing the gas and solid fraction. The difference could be explained in terms of the composition of the SDU sample, composed mainly of LDPE (44%), PP (28%), and PET (16%). Although individually LDPE and PP commonly report high liquid-yields in thermal pyrolysis (> 80%), conversely, PET pyrolysis favors the

formation of carbon and light gases (>50 %) (Al-Salem et al., 2017). Therefore, the presence of PET in the SDU sample could be detrimental to pyrolysis liquids' performance.

The incorporation of the H-ZSM-5 zeolite in the post-pyrolytic stage decreases the liquid fraction in products. For both raw materials, LDPE and SDU, the liquid product yield was up to 35 % less than non-catalytic processes. It should be mentioned that the fraction of solids was not significantly modified. Therefore, the yield variation would be related to a catalytic effect, which would favor the reformation of hydrocarbons generated during the first reaction stage (thermochemical pyrolysis), forming lighter products and increasing the gaseous fractions.

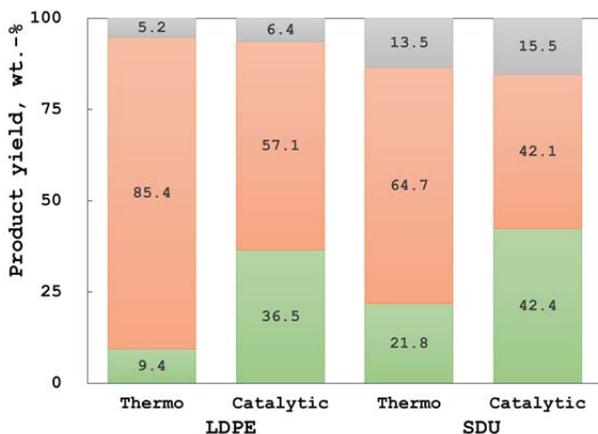


Figure 3: ● Solid, ● liquid, and ● gaseous product yield obtained in the thermal and thermo-catalytic pyrolysis of SDU and LDPE samples.

The liquid fractions generated by thermal pyrolysis of LDPE and SDU presented a semi-fluid appearance with a waxy appearance and a light-brown color, while the products obtained from the thermo-catalytic process showed a more fluid and oily appearance. These visual differences suggest modifications in the compounds' chemical nature possibly caused by heavy hydrocarbons cracking into lighter fractions. In this regard, the composition of the pyrolysis oil obtained for both SDU and LDPE were similar to each other, consistent with the fact that the main component in the SDU sample is LDPE. However, traces of alkyl-hydrocarbon compounds related to the decomposition of polypropylene were identified, and a fraction of styrene due to polystyrene's thermal decomposition. Comparing the fractions obtained from thermal and thermo-catalytic pyrolysis (Figure 4), we can realize that the liquid fraction components' nature is maintained, only with variation in their proportion. In this sense, the oil obtained in the thermal pyrolysis of the SDU mixture presents a majority fraction of hydrocarbons with more than 16 carbon atoms (69 %; C<sub>16+</sub>) and a minor fraction of intermediate hydrocarbons (32%; C<sub>7</sub>-C<sub>16</sub>).

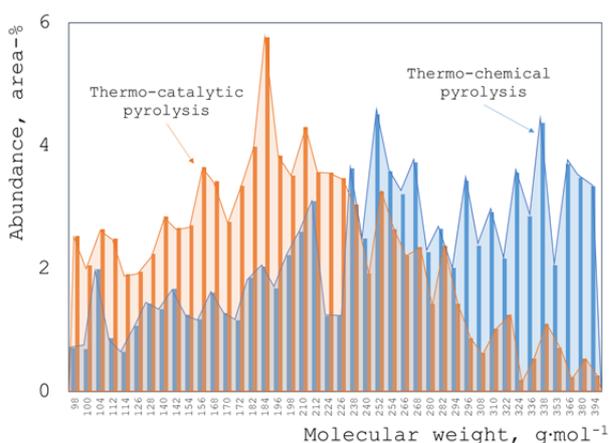


Figure 4: ● Molecular weight distribution of the liquid products obtained by thermal and thermo-catalytic pyrolysis of the SDU sample.

Thermo-catalytic processing, using a zeolite type H-ZSM-5, showed a significant effect on the hydrocarbons molecular weight. The abundance of intermediate hydrocarbon compounds ( $C_7$ - $C_{16}$ ) doubled compared to that obtained by the thermochemical process. In this regard, the H-ZSM-5 catalyst would be promoting C–C bond-breaking reactions, favored the conversion of heavy hydrocarbons formed in the thermochemical stage to lighter hydrocarbon fractions, both intermediate ( $C_7$ - $C_{16}$ ) and light hydrocarbons ( $C_1$ - $C_6$ ). The above would be consistent with the increase in the yield of gaseous products observed as an effect of the catalyst. In this sense, even though the implementation of a second catalytic reaction stage decreases the liquid yield and increases the gas fraction, this would improve the liquid fraction quality. It is also important to mention that chlorinated or cyanogenic compounds were not detected in the GC-MS analysis of liquid fractions.

#### 4. Conclusions

The implementation of a second catalytic reaction stage, using zeolite H-ZSM-5 as a catalyst, sequential to thermochemical pyrolysis of the mixed municipal plastic waste of the San Diego de la Unión landfill (México), increases the liquid fraction's quality, with a higher proportion of intermediate hydrocarbons within the gasoline range but at the cost of liquid-yield. H-ZSM-5 catalyst promoted C–C bond-breaking reactions and favored the production of lighter hydrocarbon fractions. The thermo-catalytic pyrolysis process represents a viable technological option for processing municipal mixture plastic waste. This option, if feasible, would reduce the volume of waste disposed of in the sanitary landfill and provide a fuel source.

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