Catalytic pyrolysis of plastic materials using natural zeolite catalysts synthesized from volcanic ash

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Abstract. Plastic waste and its inadequate final disposal are a serious problem of environmental pollution, which has increased considerably in this time of pandemic due to the use of masks, gloves, food packaging or others, which will eventually reach the oceans, increasing the problem of the islands that are made up of plastic waste. Since the final disposal techniques of plastic waste are insufficient, in this research the catalytic pyrolysis has been evaluated using zeolites synthesized from volcanic ash of the Ubinas volcano (Peru), as catalysts. For this, two catalysts were synthesized, Z1 and Z2 zeolite, made at 150 and 180 °C in a 5 M NaOH solution, respectively. The pyrolysis was carried out at a catalyst/polymer ratio of 10 and 20 % and it was compared with a synthetic zeolite (ZSM-5) and without catalyst at a reaction temperature of 450 °C. The essays were carried out with PP virgin and plastic waste. It was determined that catalytic pyrolysis using natural zeolites synthesized from volcanic ash are appropriate for the treatment of plastic materials and that they tend to generate a higher proportion of pyrolytic gases and do not generate carbonaceous residues.

1. Introduction
Pyrolysis or cracking is a tertiary recycling technique through which organic polymers decompose at high temperatures into components of lower molecular weight in the form of fuel gases, oils and solid residue under conditions of an oxygen-free atmosphere, therefore, dioxin is not produced and carbon monoxide and dioxide emissions are reduced [1], [2], [3]. Currently, the pyrolysis is being studied to be an alternative for the mitigation of urban plastic waste in the environment. There are two types of pyrolysis, the thermal and the catalytic, of them, the catalytic pyrolysis has multiple advantages over thermal since it improves the efficiency of the process by reducing the residence time and affects the selectivity of the pyrolytic products, in addition, the use of catalysts such as zeolites generates high-quality products that do not require subsequent downstream stages [4], [5]. The performance of pyrolytic
products will depend on the type of plastic waste used as raw material since this will determine the boiling point of pyrolytic products [4]. The main factors that affect the pyrolysis process are the temperature, the retention time, the composition of the raw material and the catalyst [2], as well as, the type of reactor, pressure, residence time, type of circulating gas and heating rate [6]. The control of these factors will determine the performance and distribution of the products [6]. Despite all the potential advantages of catalytic pyrolysis, the process has some limitations such as the high energy demand that requires, the cost of the catalyst and the low reuse of the catalysts [2]. So, the recommended solutions for these challenges are the search for cheaper catalysts, the regeneration of catalysts and the general optimization of the process.

Catalysts are chemical substances that accelerate chemical reactions, decrease the residence times and the reaction temperature (requiring less energy), and in the case of polymer pyrolysis, they improve the conversion and quality of fuels, increasing their efficiency against the thermal pyrolysis [2], [5], [7]. The characteristics of the catalyst will influence the performance and quality of the pyrolytic products to be obtained [8]. The heterogeneous catalysts are the most widely used because they are easy to separate from pyrolytic products (gases, liquids or solids) and also resist temperatures up to 1300 °C [4]. The main characteristics that are sought in catalysts is that they have the presence of Lewis and Brønsted acid sites since both are involved in the mechanism of polymers degradation. The physical properties of the catalysts are also important, such as the surface area, the pore size and the pore volume [6]. Among the catalysts used for polymer pyrolysis are natural and synthetic zeolites (ZSM-5, HUSY, Hβ and HMOR), silica-alumina, alumina and FCC (Fluid Catalytic Cracking) [2], [4], [6].

Zeolites are crystalline aluminosilicates that, when are dehydrated, they develop a porous structure with ion exchange capacity [6]. Due to their high crystallinity, surface area and selectivity they are very active in catalytic processes. The potential and economic use of natural zeolite was tested for the catalytic pyrolysis of polypropylene, polyethylene, polystyrene and polyethylene terephthalate against synthetic zeolite, this despite of the low surface area of natural zeolite, its microporous structure and low acidity [7]. There have been studies of natural zeolites with a low surface area, where their surfaces were modified by impregnating them with Ni, Ni-Mo, Co and Co-Mo and they observed that the modification improved their catalytic properties by increasing their activity and selectivity [9].

Volcanic ash is a residue that contains silica and alumina, being the ash from the Ubinas volcano rich in silica (45.26%) and alumina (13.40%) [10], the flame-retardant activity of polymeric of this volcanic ash has been studied [11]. So, in the present research it was sought to take advantage of its composition as a source of raw material for the synthesis of natural zeolites, which would lower the cost of the catalysts in the pyrolysis process. Therefore, two types of zeolites were synthesized that were tested in the pyrolytic process for virgin polypropylene (PP) and for plastic waste, comparing it with thermal pyrolysis.

2. Experimental procedure

2.1. Materials

The raw material for the synthesis of natural zeolites was the volcanic ash from the Ubinas volcano located in Moquegua, Peru. The composition of volcanic ash is 45.26% SiO$_2$, 13.40% Al$_2$O$_3$, 6.72% Fe$_2$O$_3$ which has a SiO$_2$/Al$_2$O$_3$ molar ratio of 5.73 [12]. For the comparison of the pyrolysis process, the synthetic zeolite, ZSM-5, of the ZEOLYST INTERNATIONAL brand and CBV 5524G model was used with a composition of 100 % w/w zeolite, SiO$_2$/Al$_2$O$_3$ molar ratio of 50 and a surface area of 425 m$^2$/g. In the pyrolysis process, an extra pure grade nitrogen gas (99.99%) (PRAXAIR P-4631-H) was used as recirculating gas and the polypropylene PP 5707N from SABIC brand and the collected plastic waste containing polypropylene as the main component were used as polymers.

2.2. Synthesis of natural zeolites
The collected volcanic ash was dried and ground in a mono planetary mill at 450 rpm for 25 min until obtaining a powder with a particle size of 75 μm. Subsequently, 10 g of volcanic ash was placed in a teflon with 60 ml of 1.5 M NaOH and then it was taken to a batch reactor. The batch reactor was placed into the oven at 150 or 180 °C for 12 h, which corresponds to Z1 and Z2, respectively. The sample was left to rest for 2 days at room temperature and then it was washed with 500 ml of distilled water and rest for 1 day for its sedimentation. Then the vacuum filtration of the sample was proceeded to eliminate the greatest amount of water and finally to be dried in the stove at 100 °C for 3 h. The dried sample was ground and placed in a bottle.

2.2.1. Characterization of natural zeolites. Z1 and Z2 natural zeolites were texturally characterized, their surface area (S\textsubscript{BET}), pore size and pore volume were determined by BET adsorption and desorption isotherms in an ASAP 2020 Micromeritics apparatus with N\textsubscript{2} gas flow at 77 K.

2.3. Pyrolysis process
The natural zeolites and polymers were weighed on a RADWAG brand analytical balance, model AS 220.R2 with readability of 0.1 mg. The catalyst/polymer ratio (% w/w) of 10 and 20 was used for each of the zeolites. Fast pyrolysis was carried out in a NanYang XinYu model SK2-2-12TPB3 tubular furnace with a 60 x 200 mm chamber at 450 °C, with a heating rate of 10 °C/min and with a continuous circulation of N\textsubscript{2} gas. Arriving at the set point temperature, the crucible containing the zeolite and the polymer was introduced, which was kept in the oven for 20 min. The gas generated passed through a cooling trap contained in a thermos with liquid nitrogen where the liquids were recovered, and the gases were received in the extractor hood. After the process, the crucible and the cooling trap were weighed to determine the percentage of yield (wt%) of the solids, liquids and waxes pyrolytic. The pyrolysis was carried out with the virgin polymer (polypropylene) and the zeolite with the highest yield was selected for the pyrolysis of plastic waste. Table 1 shows the coding of the samples used in the pyrolysis process and their conditions.

| Sample code | Zeolite type | Polymer type | Catalyst/polymer ratio (% p/p) | Reaction temperature | Residence time | Polymer weight (g) |
|-------------|--------------|--------------|-------------------------------|----------------------|----------------|--------------------|
| T           | None         | PP           | -                             | 450                  | 20             | 1                  |
| Z1-C1       | Z1           | PP           | 10                            | 450                  | 20             | 1                  |
| Z2-C1       | Z2           | PP           | 10                            | 450                  | 20             | 1                  |
| ZSM-5-C1    | ZSM-5        | PP           | 10                            | 450                  | 20             | 1                  |
| Z1-C2       | Z1           | PP           | 20                            | 450                  | 20             | 1                  |
| Z2-C2       | Z2           | PP           | 20                            | 450                  | 20             | 1                  |
| ZSM-5-C2    | ZSM-5        | PP           | 20                            | 450                  | 20             | 1                  |
| PW-Z2-C1    | Z2           | Plastic waste| 10                            | 450                  | 20             | 1                  |

3. Results and discussion

3.1. Characterization of zeolites
Table 2 shows the textural properties of the natural zeolites synthesized from the volcanic ash of the Ubinas volcano.
Table 2. Textural properties of natural zeolites from Ubinas volcano.

| Sample | Pore size (Å) | Pore volume (mm$^3$/g) | Micropore area (m$^2$/g) | $S_{BET}$ (m$^2$/g) |
|--------|---------------|-------------------------|---------------------------|----------------------|
| Z1     | 96.84         | 47.12                   | 8.08                      | 25.91                |
| Z2     | 146.81        | 39.70                   | 8.60                      | 11.43                |

The pore size, shown in table 1, point out the Z1 and Z2 natural zeolites are mesoporous catalysts while the ZSM-5 synthetic zeolite is microporous as indicated by other authors [13], [14]. These characteristics will determine the distribution of the pyrolytic products as indicated in figure 1.

3.2. Yields of pyrolytic products

The pyrolytic products obtained were carbonaceous solids (char), liquids, waxes and gases. Figure 1 shows the performance of solids, liquids and waxes by varying the catalyst/polymer ratio and it is observed that there is a difference between the thermal pyrolysis with the catalytic pyrolysis (using the zeolites synthesized from volcanic ash and with the synthetic zeolite ZSM-5). Being the percentage of the gaseous product higher in the catalytic pyrolysis with a maximum value of 76.42 ± 4.95% with the ZSM-5 zeolite and the minimum value of 47.26 ± 2.30% without the use of a catalyst. Therefore, it could be inferred that the use of zeolites favors a greater generation of gases.

![Figure 1. Pyrolytic residues (%) obtained in the catalytic and thermal pyrolysis process using PP and plastic waste.](image)

It is observed that the ZSM-5 zeolite, which is the one with the highest surface area (425 m$^2$/g), is the one that has produced the greatest amount of gases, this due to the fact that catalysts with a high surface area ($S_{BET}$) allows a greater contact between the reactants and the catalyst surface, which leads to an increase in the cracking reaction rate, producing more gases than liquids [2]. However, despite the high difference in $S_{BET}$ compared to Z1 and Z2 zeolite, with these ones an increase in the conversion to gases has also been achieved and it is much higher with the Z2 zeolite, which has a larger pore size with a higher micropore area. This is probably because it has zigzagging channels, typical of zeolites, that hinders the formation of larger molecules, such as wax and liquids, within the pores. In addition,
considering that in the catalytic pyrolysis mechanism, in its initial stages thermal cracking occurs on the external surface of the catalyst, where the wax is mainly generated and later, the pores act as selective channels, whose size influences, and where the gases will generate [2]. This would corroborate that the catalytic activity depends on the structural characteristics of the zeolites, among them, the pore size [2], [15], which are influenced by their synthesis conditions. This would explain the reason why there is a lower gas yield with Z1 zeolite whose pore size is smaller than Z2 zeolite. This behavior was also observed by a natural zeolite with a low S\textsubscript{BET} (3.21 m\textsuperscript{2}/g), a pore size of 8.34 Å with a microporous structure and low acidity whose pyrolytic yield was 75.4% gas, 14% liquid and 10.7% solid residue. This is probably due to the fact that the catalyst supports the initial degradation of PP, which would increase the generation of gases but not that of liquids [14], [16].

Additionally, a variation is observed between catalytic pyrolysis when treating PP and plastic waste, this occurs because the plastic waste also present other additives aside from the PP that can affect the process. This is the reason why when treating plastic waste, washing and segregation according to their typology, is important [17], [18]. However, in the present study, no major difference in performance has been observed both in obtaining liquids (34.36 ± 3.20% and 32.80 ± 3.29% for Z2C1 and PW-Z2C1), waxes (14.30 ± 5.93% and 15.85 ± 1.55%, for Z2C1 and PW-Z2C1) and gases (51.52 ± 5.32% and 50.29 ± 3.92%, for Z2C1 and PW-Z2C1); while if there was carbonaceous residue generation with the PW-Z2C1 (1.06 ± 0.22%). Moreover, it should be noted that when using plastic waste there was the generation of solid carbonaceous residue while there was no generation when using virgin polypropylene, this due to the presence of other additives in addition to polypropylene. It is worth mentioning that according to Santella \textit{et al.} [15] a small pore size favors the generation of solid waste (coke) which is typical of the ZSM-5 zeolite which in all cases has produced char.

4. Conclusion
It is concluded that the natural zeolites synthesized from the Ubinas volcano have a catalytic activity, in addition the type of zeolite and the catalyst/polymer ratio influence on the performance and distribution of the pyrolytic products. A higher yield of pyrolytic gases was obtained with the catalytic pyrolysis reaching a maximum of 76.42 ± 4.95% (with the ZSM-5 zeolite) compared to 47.26 ± 2.30% (thermal pyrolysis). Between Z1 and Z2 zeolites, a higher gas yield was obtained with the Z2C1 sample (51.52 ± 5.32%). The highest yield of pyrolytic liquids was obtained with thermal pyrolysis (37.78 ± 1.64%). In the case of pyrolytic waxes, the highest yield was obtained with Z1C2 sample with a value of 21.69 ± 2.21%. No solid residues (coke) were obtained with Z1 and Z2 zeolite; however, if was obtained it with ZSM-5 zeolite and with thermal pyrolysis. When using plastic waste and Z2C1 sample, a higher gas yield was obtained (50.29 ± 3.92%).

Reference
[1] Jin Z, Chen D, Yin L, Hu Y, Zhu H. Molten waste plastic pyrolysis in a vertical falling film reactor and the influence of temperature on the pyrolysis products. Chinese Journal of Chemical Engineering. 2018; 26(2): p. 400-406.
[2] Miandad R, Barakat MA, Aburiazaiza AS, Rehan M, Nizami AS. Catalytic Pyrolysis of Plastic Waste: A Review. Process Safety and Environmental Protection. 2016;102: p. 822-838.
[3] Singh R, Raj B. Time and temperature depended fuel gas generation from pyrolysis of real world municipal plastic waste. Fuel. 2016; 174: p. 164-171.
[4] Al-Salem SM, Antelava A, Constantinou A, Manos G, Dutta A. A review on thermal and catalytic pyrolysis of plastic solid waste (PSW). Journal of Environmental Management. 2017; 197: p. 177-198.
[5] Kunwar B, Cheng HN, Chandrashekar SR, Sharma BK. Plastics to fuel: a review. Renewable and Sustainable Energy Reviews. 2016; 54: p. 421-428.
[6] Sharuddin S, Abnisa F, Daud W, Aroua M. A review on pyrolysis of plastic wastes. Energy Conversion and Management. 2016;115: p. 308-326.
[7] Miandad R, Barakat MA, Rehan M, Aburiazaiza AS, Ismail IMI, Nizami AS. Plastic waste to liquid oil through catalytic pyrolysis using natural and synthetic zeolite catalysts. Waste Management. 2017; 69: p. 66-78.

[8] Till Z, Varga T, Sója J, Miskolczi N, Chován. Kinetic identification of plastic waste pyrolysis on zeolite-based catalysts. Energy Conversion and Management. 2018; 173: p. 320-330.

[9] Sriningsih W, Saerodji MG, Trisunaryanti W, Tryono, Armunanto R, Falah II. Fuel Production from LDPE Plastic Waste over Natural Zeolite Supported Ni, Ni-Mo, Co and Co-Mo Metals. Procedia Environmental Sciences. 2014; 20: p. 215-224.

[10] Vargas M, Hermoza-Gutiérrez M, Tupayachy-Quispe DP, Almirón J, Huanca Z. PK, Velasco-Lopez FJ. Manufacture of geopolymeric mortars from ash coming from the ubinas volcano, assessment of its mechanical, physical and microstructural properties. Revista Boliviana de Química. 2020; 37(3): p. 148-159.

[11] Almirón J, Roudet F, Duquesne S. Influence of volcanic ash, rice husk ash, and solid residue of catalytic pyrolysis on the flame-retardant properties of polypropylene composites. Journal of Fire Sciences. 2019; 37(4-6): p. 434-451.

[12] Calderón N, Vargas M, Almirón J, Bautista A, Velasco F, Tupayachy-Quispe D. Influence of the Activating Solution and Aggregates in the Physical and Mechanical Properties of Volcanic Ash Based Geopolymer Mortars. IOP Conference Series: Materials Science and Engineering. 2021; 1054(012003): p. 1-9.

[13] Ratnasari DK, Nahil MA, Willi PT. Catalytic Pyrolysis of Waste Plastics using Staged Catalysis for Production of Gasoline Range Hydrocarbon Oils. Journal of Analytical and Applied Pyrolysis. 2017; 124: p. 631-637.

[14] Miandad R, Barakat MA, Aburiazaiza AS, Rehan M, I.M.I. I, Nizami AS. Effect of plastic waste types on pyrolysis liquid oil. International Biodeterioration & Biodegradation. 2017; 119: p. 239-252.

[15] Santella C, Cafiero L, De Angelis D, La Marca F, Tuffi R, Vecchio Ciprioti S. Thermal and catalytic pyrolysis of a mixture of plastics from small waste electrical and electronic equipment (WEEE). Waste Management. 2016; 54: p. 143-152.

[16] Almeida D, Marques M. Thermal and catalytic pyrolysis of plastic waste. Polímeros: Ciência e Tecnologia. 2016; 26(1): p. 44-51

[17] Wong SL, Ngadia N, Abdullah TAT, Inuwa IM. Current state and future prospects of plastic waste as source of fuel: A review. Renewable and Sustainable Energy Reviews. 2015; 50: p. 1167–1180.

[18] Sogancioglu M, Ahmetli G, Yel E. A Comparative Study on Waste Plastics Pyrolysis Liquid Products Quantity and Energy Recovery Potential. Energy Procedia. 2017; 118: p. 221-226.

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