



Full Length Article

Petrochemical feedstock from pyrolysis of waste polyethylene and polypropylene using different catalysts

Bianca Pedroso S. Santos^a, Débora Almeida^a, Maria de Fatima V. Marques^{a,*},
Cristiane A. Henriques^b

^a Instituto de Macromoléculas Eloisa Mano, Universidade Federal do Rio de Janeiro – UFRJ, Av. Horácio Macedo, 2030, Centro de Tecnologia, Bloco J, Rio de Janeiro, Brazil

^b Instituto de Química, Universidade do Estado do Rio de Janeiro, Rua São Francisco Xavier, 524, Maracanã, Rio de Janeiro, Brazil



ARTICLE INFO

Keywords:

Catalytic degradation

Thermal degradation

Plastic waste

Polypropylene

Polyethylene

Zeolites

ABSTRACT

In this work, thermal and catalytic pyrolysis of urban plastic waste composed of a mixture of polyethylene (PE) and polypropylene (PP) was studied. The catalysts investigated were HZSM-5, USY, NH₄ZSM-5 (ZSM-5 in ammonium form), and their corresponding alkaline-treated (BHZSM-5, BUSY, and BNH₄ZSM-5) or acid-leached (LHZSM-5, LUSY, and LNH₄ZSM-5) forms. The catalytic pyrolysis using BHZSM-5 (ZSM-5 in alkaline form), USY, BUSY, and NH₄ZSM-5 resulted in higher amounts of liquid fraction, which was composed of alkylbenzenes, naphthalenes, and olefins. Acid leaching of zeolite NH₄ZSM-5 increased both the specific area and the mesopore volume, allowing an increase in the liquid and gas fractions, and a reduction in the solid fraction. BHZSM-5 zeolite showed the best catalytic performance for the production of a high amount of liquid fraction, which was virtually composed of olefinic hydrocarbons without the formation of solid products. Moreover, BNH₄ZSM-5 zeolite (alkaline-treated NH₄ZSM-5) was a good pyrolysis catalyst also due to its high specific area and pore volume, resulting in higher gas formation in comparison with the liquid fraction (composed mostly of alkylbenzenes), and almost no solid fraction.

1. Introduction

Plastics make a fundamental contribution to society because of their versatility and relatively low cost. As a result, the amounts of synthetic plastic waste generated have been increasing steadily, causing environmental problems since these plastics do not degrade rapidly and can remain in the environment for long periods [1,2].

Another problem is that plastic waste is bulkier than organic waste, thus taking up more space in landfills, so adequate disposal is expensive. Indeed, the use of landfills is not an appropriate option to dispose of these wastes due to their low degradation rate [3–5].

Moreover, the incineration of these plastic wastes results in environmental problems due to increased emissions of harmful compounds such as sulfur and nitrogen oxides, dust, dioxins and other toxins, depending on the nature of the plastic [6,7].

Incineration and disposal in landfills cause the loss of chemical species that would be required to synthesize the polymers again [8]. Therefore, it is necessary to find other solutions that are more sustainable than incineration or disposal in landfills [9]. Numerous studies in the area of recycling and reuse of these polymers have been carried

out with the objective of producing raw materials and energy [10–12]. Various types of recycling have been found to be good options for controlling the increase of plastic waste because they are environmentally friendly compared to incineration and disposal in landfills. In fact, from recycling it is possible to recover raw materials, energy, and fuels in addition to minimizing the consumption of natural resources and inputs, and consequently reducing the environmental impacts of industrial activity [13–15].

Plastic recycling methods, according to ASTM D5033-00, are divided into four types depending on the final result obtained: primary (mechanical reprocessing into a product with equivalent properties), secondary (mechanical reprocessing into products requiring lower properties), tertiary (recovery of chemical constituents) and quaternary (recovery of energy). High-value polymers are normally mechanically recycled successfully, such as to make PET bottles. However, a major portion of plastics produced each year, composed essentially of polyolefins, is used to make disposable items for packaging or other short-lived products that are discarded within few months after manufacture. This indicates that the current use of plastics is not sustainable. Also, because of the durability of the polymers involved, substantial

* Corresponding author.

E-mail address: fmarques@ima.ufrj.br (M.d.F.V. Marques).

quantities of discarded plastics are accumulating in landfills worldwide.

On the other hand, in chemical recycling, chemical degradation leads to the production of liquid fuels and chemical compounds with a high added value from fragments of residual or segregated plastic material [1,16]. One of the methods of tertiary recycling is pyrolysis. This process can be thermal or catalytic and is a promising alternative that allows the conversion of low-value polymers into gaseous and liquid hydrocarbons [6].

Catalytic pyrolysis of plastics shows slightly higher levels of inert residue generation than mechanical recycling options, but much lower volumes than generated by other thermal and oxidative processes (incineration, gasification to methanol, gasification to syngas, gasification combined with combustion). Unlike the gasification processes, it produces a char, not a vitrified slag, which explains the higher hazardousness of its processing. Nevertheless, it is superior to the other thermal feedstock recovery processes in the cumulative energy demand balance (it is almost as energy efficient as conventional mechanical recycling processes) and ranks intermediate in the range of global warming potential, with lower CO₂ emission than achieved by other treatments [17].

The pyrolysis process is not expensive, and a wide range of final products can be obtained. In this process, heating occurs without the presence of oxygen. Depending on the material that will be pyrolyzed, organic compounds can be obtained as the final result, which will be cracked to generate mainly gaseous and liquid products. Also obtainable at the end of the process is an inorganic material which will remain unchanged in the solid fraction (char). The gas and liquid fractions can be used as a source of chemical products [18,19]. The catalyst has to be developed to reduce the char amount.

Thermal pyrolysis requires high temperatures, which usually results in products with low final quality, making this process unfruitful. This is because uncatalyzed thermal degradation gives rise to low molar mass substances, requiring further separation processes to result in new products [20,21].

This method can be improved by the addition of catalysts, which will reduce the temperature and the reaction time and allow the production of higher value-added hydrocarbons such as fuel oils and petrochemicals [22,23].

Both the physical and chemical properties of the catalysts will determine their cracking efficiency. These characteristics together promote the disruption of the C–C bonds and determine the type of product formed [24].

Catalyzed cracking has been widely used due to several advantages when it is compared to the thermal process since it more efficient concerning reactor use, reaction temperature, and residence time. However, catalytic cracking also has some disadvantages, such as the difficulty of recovering the catalyst after use, which increases its cost. Furthermore, the direct contact of the catalyst with the plastic residue deactivates it rapidly due to the deposition of matter and the poisoning by other elements such as chlorine, sulfur, and nitrogen contained in some additives that may be present in the plastic residue [25].

Thus, the development of more effective catalysts for the pyrolysis of polyolefins is essential to make pyrolysis more effective, allowing the formation of high-value chemicals [26,27].

The catalysts most used in the catalytic degradation of polymers are zeolites and amorphous materials [8]. The difference in the catalytic activity of these solids is mainly related to their acid sites, including their strength and quantity. The textural properties, such as specific surface area and pore volume, as well as particle size, also influence the performance of the catalytic process since these characteristics control the accessibility of large polyolefin molecules to the catalytically active internal sites of these solids [21,22].

In this work, two zeolites with different framework structure were selected for study: ZSM-5 and USY with MFI and FAU structure, respectively. ZSM-5 is a medium pore zeolite, which has a three-dimensional porous structure formed by a 10-MR straight channels

($5.6 \times 5.3 \text{ \AA}$) interconnect by 10-MR sinusoidal channels ($5.5 \times 5.1 \text{ \AA}$). It does not have cavities but the interconnections between the channels have a free diameter of about 9 \AA . This zeolite is thermally and chemically stable and possesses strong acid sites that are important for catalytic cracking. On the other hand, Y is a large pore zeolite whose three-dimensional framework structure is formed by sodalite cages connected by hexagonal prisms in a tetrahedral arrangement that forms supercavities ($\approx 11 \text{ \AA}$ diameter) which are interconnected by 12-MR apertures of about 7.1 \AA . USY zeolite (the ultra-stable form of Y zeolite) has mainly weak and medium strength acid sites, which are less effective in cracking than the strong ones. However, the presence of the supercavities with apertures of 7.1 \AA favors the accessibility of the large plastic molecules to the acid sites located into the pore structure.

Thus, in the present work, the objective was to study the behavior of catalytic pyrolysis of urban plastic waste composed of polyethylene (PE) and polypropylene (PP) at 1:1 wt/wt ratio mixture using different types of zeolite as catalyst to obtain petrochemical inputs with high added value. The selected parent zeolites were ZSM-5, in both acid (HZSM-5) and ammonium (NH₄ZSM-5) forms, and USY. To the best of our knowledge, no study has been published regarding the comparison of micro/mesoporous ZSM-5 and USY zeolites for the catalytic pyrolysis of plastics, associating their catalytic properties with the PE:PP pyrolysis products distribution.

2. Experimental

2.1. Materials

Two types of municipal plastic waste (MPW) composed of post-consumed polyethylene (PE) and polypropylene (PP) were used in this study. They were obtained from a recycling company in the form of flakes and were washed three times with ethanol and dried overnight.

The parent zeolites investigated in the pyrolysis experiments were zeolite HZSM-5, provided by PQ Corporation in the acid form, ultra-stable Y zeolite (USY), and ZSM-5 in ammonium form (NH₄ZSM-5), supplied by Petrobras Research Center (CENPES). These zeolites were grounded and sieved and the fraction with particle size less than 200 mesh ($74 \mu\text{m}$) was separated for study, treated and used as catalysts for pyrolysis of plastics.

Samples of PE and PP were mixed with synthetic zeolites using a twin-screw mini-extruder in the counter-rotating mode at 60 rpm and $180 \text{ }^\circ\text{C}$ for 7 min, obtaining samples weighing 5 g with well distributed catalyst particles in the polymer. The proportion was 1:1 wt./wt. in PE:PP mixture with and without zeolites. The amount of zeolite in the samples was 5% wt.

2.2. Treatment of the original zeolites

Mesoporosity can be introduced into the original zeolite samples through post-synthesis treatments such as acid leaching (L) and alkaline treatment (B).

For the alkaline treatment, the zeolite was suspended in a 0.2 mol/L NaOH solution using a zeolite (g)/NaOH solution (mL) ratio equal to 0.008, at $75 \text{ }^\circ\text{C}$, for 30 min, as previously established by Alves et al. [28]. After, the solid was separated by filtration and washed with deionized water until neutral pH. Then it was dried at $200 \text{ }^\circ\text{C}$, for 1 h. The alkaline-treated samples were converted into the acid (H) form by ion-exchange with a 2 mol/L NH₄Cl solution. Then, the zeolite was separated by filtration, washed with deionized water and calcined in a muffle furnace at $450 \text{ }^\circ\text{C}$, for 4.5 h. The samples were named Bzeolite, where B means the alkaline treatment.

The leaching treatment was carried out in two steps. In the first step, the zeolite was suspended in an 1 mol/L NH₄Cl solution using a zeolite (g)/solution (mL) ratio of 0.04, at $80 \text{ }^\circ\text{C}$, for 24 h. At the end of the treatment, the solid was separated by centrifugation, washed with distilled water and dried for 20 h at $110 \text{ }^\circ\text{C}$; the solid was then heated in

Download English Version:

<https://daneshyari.com/en/article/6632383>

Download Persian Version:

<https://daneshyari.com/article/6632383>

[Daneshyari.com](https://daneshyari.com)