



# Article Catalytic Pyrolysis of High-Density Polyethylene: Decomposition Efficiency and Kinetics

Hadas Raveh-Amit <sup>1,\*</sup>, Florent Lemont <sup>2</sup>, Gabriela Bar-Nes <sup>1,3</sup>, Ofra Klein-BenDavid <sup>1,4</sup>, Nissim Banano <sup>1</sup>, Svetlana Gelfer <sup>1</sup>, Patrice Charvin <sup>2</sup>, Tahriri Bin Rozaini <sup>2</sup>, Johann Sedan <sup>2</sup> and François Rousset <sup>2</sup>

- <sup>1</sup> Department of Chemistry, Nuclear Research Centre Negev, P.O. Box 9001, Beer Sheva 8419000, Israel; gabi.barnes@gmail.com (G.B.-N.); ofrak1@googlemail.com (O.K.-B.); nissoba@gmail.com (N.B.); gelfersveta1973@gmail.com (S.G.)
- <sup>2</sup> DES, ISEC, DE2D, SEVT, LPTI, CEA, Centre de Marcoule, BP17171, 30207 Bagnols sur Cèze, France; florent.lemont@cea.fr (F.L.); Patrice.charvin@cea.fr (P.C.); Muhamad-Tahriri.BINROZAINI@cea.fr (T.B.R.); Johann.Sedan@cea.fr (J.S.); francois.rousset@cea.fr (F.R.)
- <sup>3</sup> Department of Civil and Environmental Engineering, Ben-Gurion University of the Negev, P.O. Box 653, Beer-Sheva 8410501, Israel
- <sup>4</sup> Department of Geological and Environmental Sciences, Ben-Gurion University of the Negev, P.O. Box 653, Beer-Sheva 8410501, Israel
- \* Correspondence: hadasa@nrcn.gov.il; Tel.: +972-8656-7852

Abstract: Organic waste is generally characterized by high volume-to-weight ratios, requiring implementation of waste minimization processes. In the present study, the decomposition of high-density polyethylene (HDPE), was studied under thermal and catalytic pyrolysis conditions on two experimental systems. Firstly, pyrolytic conditions for HDPE decomposition were optimized in a laboratory-scale batch reactor. In order to maximize gas yields and minimize secondary waste, the effects of aluminosilicate catalysts, catalyst loading, and reaction temperature on decomposition efficiency were examined. Secondly, kinetics and reaction temperatures were studied on a large capacity thermobalance, especially adjusted to perform experiments under pyrolytic conditions at a larger scale (up to 20 g). The addition of catalysts was shown to enhance polymer decomposition, demonstrated by higher gas conversions. Condensable yields could be further minimized by increasing the catalyst to polymer ratio from 0.1 to 0.2. The most prominent reduction in pyrolysis temperature was obtained over ZSM-5 catalysts with low Si/Al ratios; however, this impact was accompanied by a slower reaction rate. Of the zeolites tested, the ZSM-5 catalyst with a Si/Al of 25 was found to be the most efficient catalyst for waste minimization and organic destruction, leading to high gas conversions (~90 wt%.) and a 30-fold reduction in solid waste mass.

**Keywords:** waste minimization; plastic decomposition; catalytic pyrolysis; zeolites; macro thermogravimetric analysis

# 1. Introduction

Organic waste is characterized by high volume to weight ratios, requiring implementation of waste minimization processes. When organic waste is contaminated with radionuclides, it may further pose a hazard due to radiolysis and the generation of combustible and explosive gases. Thus, minimizing waste volume as well as forming a chemically stable and conditioned matrix are of high importance in the treatment of contaminated polymers. Effective volume reduction of solid organic waste can be achieved by thermal treatments, such as incineration, gasification, pyrolysis and plasma treatments. Moreover, thermal treatments can improve the homogeneity and stability of the waste produced following treatment [1,2].

Pyrolysis, i.e., the process of thermal decomposition of organics in the absence of oxygen, produces three main products: solid char, condensable oils and organic and



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). inorganic gases [3]. The metal radionuclides are expected to remain in the char solid waste fraction and not to migrate into the condensable and gas fractions [1]. Pyrolysis has several key advantages over other thermal processes. Firstly, it is considered more environmentally compliant than incineration due to the limited carbon dioxide and significantly lower NOx and SOx levels emitted during the process. Secondly, unlike incineration treatment, pyrolysis is performed at moderate temperatures and thus, it is less challenging with respect to the volatilization of radionuclides.

Pyrolysis for solid organic waste contaminated with radionuclides has not been extensively studied, in contrary to the 30 years of research on the valorization of plastic waste into valuable fuels and chemicals [3–6]. This technology is considered promising for recovering non-recyclable plastics and obtaining valuable products [6]. Analysis of the thermo-gravimetric profiles, kinetic parameters and product composition of plastic pyrolysis was examined on various reactor types and for different waste compositions, of which high- and low-density polyethylene, polypropylene, and polystyrene have been mostly studied, as these polymers represent real-world plastic waste composition [6–8]. Such studies provided useful information on the decomposition mechanisms involved and on the optimization of olefins and aromatics product generation. Product selectivity and conversion yields can be enhanced by adding catalysts, i.e., catalytic pyrolysis. It also allows operating at lower reaction temperatures and, thus, lowering the energy consumption of these processes. Among the different catalysts, the ZSM-5 zeolite and Zeolite Y, are widely used in hydrocarbon cracking due to their acidity, pore structure, and thermal stability [9,10]. Product selectivity and conversion yields are also influenced by the reaction conditions, including temperature, heating rate, residence time in the reaction zone, and reactor type, as previously reviewed in detail [11].

Whereas product selectivity and the generation of valuable products are critical goals for the pyrolysis of municipal solid waste [6], it is not required for volume reduction of radioactively-contaminated plastics [1]. To be considered a suitable thermal treatment for the minimization of radio-contaminated organic waste, three main goals need to be met: (i) significantly reduce waste volume into char; (ii) minimize secondary waste and (iii) maximize gas yields. The first goal is set to concentrate all the refractory radionuclides in the char fraction. The two other goals are aimed to increase the treatable gas volume and decrease the complex condensed hydrocarbons, reducing the risk of blocking and scaling in the experimental system. Hu et al. studied the product conversion of typical solid wastes (polyethylene, paper towels, and textile) by thermal pyrolysis at different temperatures ranging from 475 °C to 550 °C [12]. Increasing the pyrolysis temperature resulted in increased conversions to gas (~20 wt% to ~40 wt%) and decreased liquid yields (~60 wt% to ~50 wt%) when the mixed wastes were treated. Similar trends in product conversions were observed when polyethylene only was treated at identical reaction conditions. However, high liquid yields were produced (for polyethylene) at all temperatures tested. Klein-BenDavid et al. studied polyethylene pyrolysis at different reaction temperatures up to 600 °C in order to reduce the liquid yields by maximizing the gas yields [13]. Even at the highest temperature tested, the wax and oil fractions could not be reduced to less than ~35 wt% of the product yields. This study demonstrated that although the solid waste mass was effectively reduced (the char fraction was ~1–2 wt%), additional improvements are required to minimize condensable yields if pyrolysis is to be considered a suitable thermal treatment for the minimization of contaminated solid waste. The present study aims to fill this gap by examining the use of catalytic pyrolysis as a means to optimize product conversions for solid organic waste contaminated with radionuclides.

Here, polymer decomposition by catalytic pyrolysis was explored as a method for waste minimization for solid organic waste contaminated with radionuclides. Two types of catalysts were studied, Zeolite Y and ZSM-5, which were previously shown to enhance gas yields of the polymers pyrolyzed, regardless of the reactor type [9,10]. In the first set of experiments, the effects of different catalysts, reaction temperature and catalyst loading on decomposition efficiency were studied in order to optimize product conversions. In

the second set of experiments, the impact of the catalysts on the reaction temperature and decomposition kinetics was studied on a large capacity thermobalance system, especially adjusted to perform experiments under pyrolytic conditions on up to 20 g of polyethylene.

## 2. Results and Discussion

## 2.1. Impact of Aluminosilicate Catalysts and Reaction Temperature

To study the catalytic effects on polymer decomposition, HDPE was treated by thermal (no catalyst) and catalytic pyrolysis at mild temperatures (450 °C and 525 °C) in the presence of different catalysts (Table 1). A description of the pyrolysis system and a schematic diagram are presented in Section 3.2. Product conversions into gas, condensable, and char were calculated to evaluate the decomposition efficiency of the treatment. Product distribution of pyrolyzed HDPE following thermal and catalytic conditions performed at a reaction temperature of 450 °C and 525 °C are presented in Figures 1 and 2, respectively.

Catalyst SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Ratio Surface Area [m<sup>2</sup>/g] Pore Radius [nm] 900 0.74 Zeolite Y 5.1 25 425 0.56 ZSM-5 (25) ZSM-5 (200) 200 400 0.56 ZSM-5 (800) 800 405 0.56



Figure 1. Product distribution following HDPE polymer decomposition in the presence of catalysts at 450 °C. Si/Al ratios of the catalysts are depicted in brackets. (a) Gas yields. (b) Condensable yields. (c) Char yi elds. (Note: *y*-axis scale ranges are different).

(25)

(800)

Table 1. Chemical and physical properties of catalysts used in this study.



**Figure 2.** Product distribution following HDPE polymer decomposition in the presence of catalysts at 525 °C. Si/Al ratios of the catalysts are depicted in brackets. (**a**) Gas yields. (**b**) Condensable yields. (**c**) Char yields. (Note: *y*-axis scale ranges are different).

Under thermal pyrolysis conditions, increasing the reaction temperature from 450 °C to 525 °C promoted conversions to gas (~30 wt% to ~70 wt%) and reduced condensable yields (~65 wt% to ~30 wt%). Catalytic pyrolysis resulted in higher decomposition efficiency than thermal pyrolysis, as evidenced by higher gas yields. Higher gas yields correlated with lower condensable yields, indicating that the zeolites promoted secondary decomposition of the condensable vapors. Char yields (3–4 wt%), representing the waste product, confirmed that pyrolysis resulted in 25- to 30-fold reduction in solid waste mass. No significant differences in waste minimization were observed at the different conditions.

The highest conversions to gas were obtained over ZSM-5(25) (~90 wt%). Zeolite Y or ZSM-5(800) enhanced gas yields to similar extents (~50 wt%), whereas only ~30 wt% gas yield was obtained without the addition of a catalyst. The two ZSM-5 catalysts share similar structures and pore sizes, but differ in their Si/Al ratios (25 vs. 800). Si/Al ratios are inversely correlated with the catalyst acidity and polymer decomposition efficiency [14], supporting that this difference accounts for the higher decomposition efficiency achieved over ZSM-5(25) at 450  $^{\circ}$ C.

Increasing the reaction temperature to 525  $^{\circ}$ C (Figure 2), increased gas conversions for all treatments, except for treatment over ZSM-5(25). In the case of the latter, which was proven as highly efficient at 450  $^{\circ}$ C, increasing temperature was not beneficial as no further improvement in polymer decomposition was observed. At a reaction temperature of 525  $^{\circ}$ C (Figure 2), Catalytic pyrolysis conditions over zeolite Y resulted in similar product distributions as obtained by thermal pyrolysis, while catalytic pyrolysis over each of the two ZSM-5 zeolites resulted in slightly higher gas yields (~10 wt%).

Comparing the structural and chemical properties of zeolite Y and ZSM-5 showed that they have similar surface areas (Table 1). Zeolite Y has a lower Si/Al ratio than ZSM-5, and thus is more acidic, suggesting it may have better catalytic performance [15]. Nevertheless, ZSM-5 has smaller pores (0.55 nm) than zeolite Y (0.74 nm), which likely accounts for their improved catalytic performance by allowing the access and breakdown of smaller molecules, in accordance with previous studies [14,16].

## 2.2. Impact of Catalyst Loadings

To study the effects of the catalyst loading (i.e., catalyst to polymer ratio) on the decomposition efficiency, HDPE was pyrolyzed over various catalyst to polymer ratios ranging from 0.05 to 0.2. This set of experiments was focused on catalytic pyrolysis treatments over ZSM-5(25), since it resulted in the highest polymer decomposition efficiency. Experiments were performed at a reaction temperature of 450 °C, since increasing the temperature in the presence of this catalyst did not yield significantly higher gas conversions. Product conversions into gas, condensable, and char of pyrolyzed HDPE over different catalyst loadings are presented in Figure 3. Higher catalyst loading resulted in increased polymer decomposition, as depicted by elevated gas conversions, ranging from ~75 wt% to 95 wt%. Higher gas yields correlated with lower condensable yields, and no significant differences in char yields were obtained. Condensable yields were nearly eliminated (~2 wt%) by pyrolyzing HDPE over ZSM-5(25) and catalyst to polymer ratio of 0.2. Due to the efficient decomposition resulting from catalyst to polymer ratios of 0.1 and 0.2, these ratios were chosen for further testing.



**Figure 3.** Effect of catalyst to polymer ratios on product distribution in the decomposition of HDPE at 450 °C. Si/Al ratios of the catalysts are depicted in brackets. (**a**) Gas yields. (**b**) Condensable yields. (**c**) Char yields. (Note: *y*-axis scale ranges are different).

#### 2.3. Thermogravimetric Analysis: Onset of Decomposition and Reaction Rate

Preliminary thermogravimetric tests were carried out on the macro-thermobalance with polyethylene and zeolite Y. Figure 4 shows the mass loss and decomposition rates over time, of either 5 g or 20 g of HDPE, with or without the addition of the catalyst. In accordance with the results obtained on the laboratory decomposition system, for both 5 g and 20 g of HDPE loads, the pyrolysis initiation temperature was significantly decreased in the presence of the catalyst. In the case of treating 5 g of HDPE, the use of 10% of zeolite Y lowered the initial decomposition temperature of the pyrolysis from 475 °C to 430 °C, whereas treatment of 20 g of HDPE, with the same catalyst loading, lowered the initial decomposition temperature from 485 °C to 390 °C. However, lower weight loss rates were

obtained in the presence of the zeolite, according to the DTG curves (Figure 4c). Zeolite Y therefore acts as a catalyst by lowering the activation energy of the overall pyrolysis reaction, resulting in decomposition at lower reaction temperatures and reduced energy consumption. On the other hand, this impact is accompanied by a significant drop in the overall reaction rate.



**Figure 4.** TGA and DTG curves of HDPE pyrolysis performed with and without zeolite Y. (**a**) TGA curves for 5 g of HDPE. (**b**) TGA curves for 20 g of HDPE. (**c**) DTG curves for 5 g and 20 g of HDPE.

Tests were carried out on different types of ZSM-5 zeolites for different masses of HDPE (5 g and 20 g) and different catalyst loadings (0.1 and 0.2 catalyst to polymer ratios). Figures 5 and 6 show the mass loss over time or temperature for the treatment of 5 g or 20 g of HDPE with different ZSM-5 catalysts, respectively. As was observed for Zeolite Y, all ZSM-5 zeolites lowered the pyrolysis temperature. The most predominant effect was obtained with ZSM-5 with a Si/Al ratio of 25, which reduced the initiation temperature by 120 °C on average. Pyrolysis kinetics were slowed down over the zeolites ZSM-5 (25) and ZSM-5 (200) (Figure 7). However, for ZSM-5 (800) the effect was reversed as pyrolysis rates increased at a catalyst loading of 0.2. These results can be explained by differences in sorption/desorption kinetics of pyrolysis gases over zeolites with different Si/Al ratios. Previous studies showed that increased Si/Al ratio content is associated with a reduced specific surface area of the zeolites as well as lower gas adsorption properties [17]. This can explain the dual impact of the zeolites, depending on their differences in Si/Al ratios. Zeolites with a lower Si/Al ratio yield higher surface reactivity in gas-solid processes, and hence result in a more prominent decrease in the overall activation energy of the pyrolysis reaction. On the other hand, lower Si/Al ratio also result in limited gas desorption (higher retention properties) and therefore in slightly slower decomposition rates.



**Figure 5.** TGA curves of 5 g of HDPE pyrolysis performed with and without ZSM-5 catalysts (different grades). (a) ZSM-5 (25). (b) ZSM-5 (200). (c) ZSM-5 (800).



**Figure 6.** TGA curves of 20 g of HDPE pyrolysis performed with and without ZSM-5 catalysts (different grades). (a) ZSM-5 (25). (b) ZSM-5 (200). (c) ZSM-5 (800).



**Figure 7.** DTG curves of 20 g of HDPE pyrolysis performed with and without ZSM-5 catalysts (different grades). (a) ZSM-5 (25). (b) ZSM-5 (200). (c) ZSM-5 (800).

## 3. Materials and Methods

## 3.1. Materials

HDPE was supplied by Metzerplas Ltd. (Kibbutz Metzer, Israel) and shredded to 5 mm flakes. Zeolite Y ( $SiO_2/Al_2O_3$  molar ratio = 5.1) and ZSM-5 catalysts with different  $SiO_2/Al_2O_3$  molar ratios (25, 200 and 800) were produced by Zeolyst (Conshohocken, PA, USA). Chemical and physical properties of the catalysts were provided by the manufacturer and are shown in Table 1.

## 3.2. Laboratory-Scale Pyrolysis System, Experimental Conditions and Product Conversion

Pyrolysis treatments and product conversion analysis were performed using the previously described laboratory-scale system [13] with minor modifications described herein (Figure 8). Briefly, the experimental system consisted of a quartz tubular reactor (550 mm long with a diameter of 60 mm) positioned in a temperature-controlled electric oven and a cooled glass trap for condensable. Two thermocouples were placed in the system. The first was located in the cooled glass trap and the second inside the reactor near the sample. In each experiment, a blend of the HDPE polymer (5.0 g) and the catalyst (0.5, 1.0 or 2.0 g) was manually mixed and placed in the reactor for the thermal treatment. To eliminate oxygen from the system prior to the thermal treatment, nitrogen was purged into the reactor at a rate of 200 standard cc/min (sccm) for one hour. Then, the nitrogen flow rate was set to a rate of 20 sccm and the oven was heated at a rate of 20 °C/min. The oven was kept at a constant temperature for 180 min after reaching the target temperature (450 °C or 525 °C depending on the experiment). A list of the experiments performed on the pyrolysis system is given in Table 2. It should be noted that a low inert gas flow rate

was used in order to enhance gas yields by increasing the residence time in the reactor and, in turn, promoting secondary reactions of the decomposition products. The actual temperature measured at the center of the reactor was 25 °C higher than the set-point (e.g., 475 °C when set to 450 °C). Solid and liquid products were collected and weighed after the reactor cooled down. Char and condensable yields were calculated based on their post-treatment mass, relative to the initial polymer mass, while the gas yields were calculated according to the mass balance. All experiments were repeated at least twice and their average and standard deviation (less than 6% between replicates) are presented.



**Figure 8.** The laboratory-scale pyrolysis system. (**a**) A schematic diagram of the system. (**b**) A picture of the system.

Reaction Temperature	HDPE Mass	Catalyst (SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> Ratio)	Catalyst Loading
450 °C	5 g	No catalyst added Zeolite Y (5.1) ZSM-5 (25) ZSM-5 (800)	0.5 g 0.5 g 0.5 g
525 °C	5 g	No catalyst added Zeolite Y (5.1) ZSM-5 (25) ZSM-5 (800)	0.5 g 0.5 g 0.5 g
450 °C	5 g	ZSM-5 (25) ZSM-5 (25)	0.25 g 1.0 g

Table 2. Experiments carried out on the pyrolysis system.

## 3.3. Macro-Thermogravimetric System, Experimental Conditions and Analysis

Thermogravimetric analysis was performed using the DANTE experimental device [18] shown in Figure 9. The large capacity thermobalance was equipped with a camera, to observe phenomena that may affect the measurements, and multiple thermal sensors that do not impact the weighing. The complete setup included a 1500 mm long Haynes 214 alloy tube, 155 mm in diameter, which can be heated by a furnace up to 1200 °C; a crucible containing the sample suspended from a hollow alumina rod, through which a thermopile (with up to eight thermocouples) was connected to a load cell in the upper chamber; an array of 13 thermocouples in the lower part of the furnace, arranged in the shape of a cross to measure the temperature in different locations; an isolation valve separating the atmospheres in the upper chamber and the furnace; and a gas treatment

system to cool and clean the gaseous effluents of the heat treatment processes under study. The upper chamber was high enough (1350 mm) to accommodate the rod and the sample before it was introduced into the furnace at a given temperature. The load cell (HBM SP4M, 5 kg) was connected wirelessly to the acquisition system via a transponder, thus avoiding wire-related mechanical constraints. The furnace can be swept vertically at different rates with either air, nitrogen or oxygen. This setup has been calibrated and validated for studies of organic and inorganic materials [9].



**Figure 9.** The DANTE macro-thermobalance. (**a**) A schematic diagram of the system. (**b**) A picture of the system.

The experimental system described above had to be adjusted to perform experiments under pyrolytic conditions. Thus, a special pyrolysis device consisting a stainless-steel enclosure was designed in order to ensure inert conditions around the sample (Figure 10). The device consisted a 12.5 cm high cylindric crucible (internal diameter 3.6 cm), into which a tube was introduced in order to evacuate the pyrolysis gaseous products from the system without interfering with the internal organic charge. The oxygen circulating in the oven was required to allow the combustion of the pyrolysis gases leaving the device. Two thermocouples were placed in the device. The first was located inside the crucible, 100 mm from its upper part and the second was in the gas evacuation tube. Before introducing the polymer into the oven, the internal atmosphere of the device was inerted by the introduction of liquid nitrogen before sealing the unit. Once the temperature and pressure had stabilized in the thermobalance, the unit was lowered to the center of the oven. The tests were carried out under the following conditions: temperature in the furnace 670  $^{\circ}$ C, pressure -8 mbar, inerting gas (in the crucible)  $N_2$ , gas in the furnace: 50 sccm air and 150 sccm  $O_2$ . Tests were carried out with 5 g and 20 g of polyethylene with and without catalyst. Different types of zeolitic catalysts were tested: zeolite Y and ZSM-5 with different  $SiO_2/Al_2O_3$  ratios (25, 200, 800) at different catalyst to polymer ratios of 0.1 and 0.2. A list of the experiments performed on the DANTE macro-balance is given in Table 3.



**Figure 10.** The pyrolysis device. (**a**) A schematic diagram of the reaction, profile view. (**b**) A schematic diagram of the reaction, upper view. (**c**) A picture and of the device.

HDPE Mass	Catalyst (SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> Ratio)	Catalyst Loading
5 g	No catalyst added	-
	Zeolite Y (5.1)	0.5 g
	ZSM-5 (25)	0.5 g
	ZSM-5 (25)	1.0 g
	ZSM-5 (200)	0.5 g
	ZSM-5 (200)	1.0 g
	ZSM-5 (800)	0.5 g
	ZSM-5 (800)	1.0 g
	No catalyst added	-
	Zeolite Y (5.1)	2.0 g
	ZSM-5 (25)	2.0 g
20 g	ZSM-5 (25)	4.0 g
20 g	ZSM-5 (200)	2.0 g
	ZSM-5 (200)	4.0 g
	ZSM-5 (800)	2.0 g
	ZSM-5 (800)	4.0 g

Table 3. Experiments carried out on the DANTE macro-balance.

## 13 of 14

## 4. Conclusions

In the present study, the influence of two key parameters, the addition of catalysts and reaction temperatures, on polyethylene decomposition were studied to enhance gas conversions and reduce char and condensable yields. Of the catalysts tested, ZSM-5 (25) obtained the highest gas conversions at mild reaction temperatures. Both the addition of catalysts and increasing the reaction temperature were shown to enhance polymer decomposition, demonstrated by higher gas conversions. Either condition resulted in a substantial reduction of condensable yields while the char, representing the solid waste product, was not significantly affected. Reduction of the condensable yields can be further enhanced by increasing the ZSM-5 catalyst loading up to a catalyst to polymer ratio of 0.2.

Tests carried out on the DANTE macro-thermobalance allowed us to gain a closer insight into the reaction mechanism and kinetics, showing that adding ZSM-5 catalysts significantly decreased the pyrolytic decomposition temperature of polyethylene, which can possibly limit the energy consumption of such treatment. Among the zeolites tested, ZSM-5 (25) had the most significant impact on temperature reduction, which gives this zeolite an additional advantage. However, it was demonstrated that the use of this zeolite caused a twofold reduction in the kinetics of pyrolytic decomposition, probably due to a retention effect of the pyrolysis gases by limiting their desorption from the catalysts [17]. Additional studies could be undertaken in order to examine the solid-gas mechanisms involved in this process and to optimize the treatment parameters in order to find the best compromise between lowering treatment temperature and affecting the kinetics of pyrolysis.

Overall, ZSM-5(25) was identified as the most suitable catalyst for HDPE pyrolysis in terms of waste minimization (product composition) and energy consumption (treatment temperature).

Since the advantage provided by the catalysts at 450 °C was "over-ridden" by increasing the reaction temperature to 525 °C, it is therefore recommended to decompose HDPE either in the presence of ZSM-5 at 450 °C or without the catalyst at 525 °C. These two types of treatments present a tradeoff: adding the catalyst yields secondary waste, whereas operating at higher temperatures increases energy consumption and affects material selection and system design.

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