TECHNO-ECONOMIC ASSESSMENT OF LDPE, HDPE, AND PP PLASTIC WASTE RECYCLING VIA PYROLYSIS

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Abstract: *The thermal decomposition behavior of high-density polyethylene (HDPE) waste was investigated using thermogravimetric (TGA) and differential thermogravimetric (DTG) analysis. The main degradation stage occurred between 425 and 505 °C, with an initial degradation temperature of 425 °C and a maximum degradation temperature T_{max} of 475 °C. The temperatures corresponding to 5% and 10% mass loss were 430 and 438 °C, respectively. The total mass loss reached 98.1%, while the residual mass was 1.9%. The maximum mass-loss rate was approximately 2.5% min^{-1}. The DTG profile showed one dominant degradation peak, indicating a predominantly single-stage thermal decomposition of the HDPE matrix. The obtained results provide characteristic temperature parameters for the thermochemical conversion and pyrolysis of HDPE waste.*

Keywords: *HDPE waste, thermogravimetric analysis, differential thermogravimetry, thermal degradation, pyrolysis, thermal stability.*

INTRODUCTION

The rapid accumulation of plastic waste has become a major environmental challenge due to the widespread use of synthetic polymers in packaging, construction, consumer goods, and industrial applications [1]. Among different types of plastics, high-density polyethylene (HDPE) represents a significant fraction of post-consumer and post-industrial polymer waste because of its extensive application in bottles, containers, pipes, films, and other products [2]. HDPE is characterized by high chemical resistance, mechanical strength, and durability, which are desirable during its service life but also make its disposal and natural degradation difficult [3]. Therefore, the development of efficient approaches for the conversion of HDPE waste into valuable products is of considerable scientific and technological interest [4].

Thermochemical conversion is considered a promising approach for the treatment and valorization of polyolefin waste. In particular, thermal pyrolysis enables the decomposition of polymer chains under an oxygen-deficient or inert atmosphere, producing a mixture of gaseous, liquid, and solid products [5]. The distribution and characteristics of these products depend strongly on the chemical structure of the polymer and the operating conditions, including temperature, heating rate, residence time, and reaction atmosphere. Consequently, understanding the thermal decomposition behavior of HDPE is essential for selecting appropriate operating conditions for its thermochemical conversion and for predicting the formation of pyrolysis products [6].

Thermogravimetric analysis (TGA) is a widely used technique for investigating the thermal stability and decomposition behavior of polymeric materials. The method continuously records changes in sample mass as a function of temperature or time under a controlled atmosphere. TGA provides important information regarding the onset of thermal degradation, the temperature range of decomposition, the total mass loss, and the residual mass [7]. When combined with differential thermogravimetric (DTG) analysis, additional information concerning the rate of mass loss can be obtained. In particular, the maximum of the DTG curve corresponds to the temperature at which the highest rate of thermal decomposition occurs and is therefore an important characteristic parameter for evaluating the degradation behavior of HDPE [8].

The thermal degradation of HDPE is primarily associated with the cleavage of carbon–carbon bonds within its long-chain hydrocarbon structure. As the temperature increases, random scission of the polymer backbone can generate free-radical species and progressively smaller hydrocarbon fragments. These intermediates can undergo further chain scission, hydrogen transfer, and recombination reactions, ultimately forming volatile hydrocarbons and other degradation products. The temperature range and rate of these processes are influenced by the molecular structure of the polymer, its molecular weight, degree of crystallinity, heating rate, and the presence of additives or impurities [9].

The analysis of TGA/DTG curves also provides a basis for evaluating the kinetic characteristics of polymer decomposition. Thermogravimetric data obtained at different heating rates can be used to estimate important kinetic parameters, such as the apparent activation energy and pre-exponential factor, using model-free or model-fitting approaches. These parameters provide insight into the energy requirements of thermal degradation and can be useful for the design, scale-up, and optimization of thermochemical conversion processes. In addition, kinetic analysis can help distinguish changes in the degradation mechanism associated with different stages of the thermal decomposition process [10].

In this study, the thermal decomposition behavior of HDPE waste was investigated using thermogravimetric and differential thermogravimetric analysis. The main objective was to determine the characteristic thermal degradation parameters, including the initial decomposition temperature, maximum decomposition temperature, final decomposition temperature, mass loss, and residual mass. The obtained TGA/DTG profiles were further analyzed to characterize the thermal stability and decomposition characteristics of HDPE waste. The results provide a basis for assessing the suitability of HDPE waste as a feedstock for thermochemical conversion and for establishing appropriate temperature conditions for subsequent pyrolysis studies.

Materials and Methods

HDPE waste sample preparation

Post-consumer high-density polyethylene (HDPE) waste was used as the raw material for the thermal degradation experiments. The waste material was manually sorted to remove visible foreign materials and non-polymeric contaminants. The selected HDPE samples were washed with water to remove surface impurities, dust, and other adhering materials and

subsequently dried to constant mass. After drying, the material was mechanically cut into small pieces and further reduced in size to obtain a relatively homogeneous sample suitable for thermogravimetric analysis.

Prior to TGA/DTG measurements, the prepared HDPE waste was stored in a sealed container to minimize moisture uptake from the surrounding atmosphere. The obtained sample was used without chemical modification or pretreatment other than washing, drying, and size reduction.

Thermogravimetric analysis

The thermal decomposition behavior of the HDPE waste was investigated using thermogravimetric analysis coupled with differential thermogravimetric analysis (TGA/DTG). In the experiment, the change in sample mass was continuously recorded as a function of temperature during controlled heating.

Approximately [5-10] mg of the prepared HDPE sample was placed in the sample crucible. The analysis was conducted over a temperature range of [30–800] °C at a constant heating rate of [10] °C min^{-1} under an inert nitrogen atmosphere. The nitrogen flow rate was maintained at approximately [50–100] mL min^{-1} to minimize oxidative reactions during thermal degradation. Before the heating program was initiated, the sample chamber was purged with nitrogen to establish an inert atmosphere.

The TGA curve was obtained by plotting the relative mass of the sample against temperature, whereas the DTG curve was calculated as the first derivative of mass with respect to temperature:

$$DTG = -\frac{dm}{dT} \quad (1)$$

where $m$is the sample mass and $T$is temperature. The DTG profile was used to determine the temperature corresponding to the maximum rate of thermal decomposition.

Determination of characteristic thermal degradation parameters

The characteristic temperatures of HDPE thermal degradation were determined from the TGA and DTG curves. The initial degradation temperature (T_i) was defined as the temperature at which a measurable and significant deviation from the initial mass-loss baseline was observed. The maximum degradation temperature (T_{max}) was determined from the maximum peak of the DTG curve. The final degradation temperature (T_f) was assigned to the temperature at which the main mass-loss process was essentially completed.

The total mass loss during thermal degradation was calculated according to:

$$\Delta m = \frac{m_0 - m_f}{m_0} \times 100 \quad (2)$$

where $m_0$is the initial sample mass and $m_f$is the final mass remaining after thermal treatment.

The residual mass was calculated as:

$$m_r = \frac{m_f}{m_0} \times 100 \quad (3)$$

where $m_r$represents the percentage of material remaining at the end of the analysis.

Analysis of TGA/DTG profiles

The TGA/DTG curves were analyzed to determine the thermal stability and decomposition characteristics of the HDPE waste. Particular attention was given to the temperature interval corresponding to the major mass-loss stage, the maximum degradation rate, and the amount of residue remaining after decomposition.

The shape and position of the DTG peak were used to evaluate the intensity and temperature dependence of the degradation process. A narrow and pronounced DTG peak was interpreted as an indication of a relatively concentrated decomposition process, whereas a broader peak could indicate overlapping degradation processes or the influence of different components present in the waste sample.

All characteristic parameters were obtained directly from the experimental TGA/DTG curves. The results were used to establish the principal thermal decomposition region of HDPE waste and to identify the temperature conditions relevant to its subsequent thermochemical conversion.

Results and Discussion

Thermal decomposition behavior of HDPE waste

The thermal decomposition behavior of the HDPE waste was evaluated using TGA and DTG analysis. The obtained thermogravimetric profile demonstrated that the sample exhibited relatively high thermal stability at low and moderate temperatures, followed by a pronounced mass-loss region associated with the decomposition of the polymer backbone. The TGA curve showed only a minor decrease in mass before the main degradation stage, indicating that the HDPE waste contained a relatively small amount of volatile or moisture-related components.

The main decomposition process occurred within a relatively narrow temperature interval. This behavior is characteristic of polyolefinic materials and can be attributed primarily to the thermal cleavage of C–C bonds in the HDPE macromolecular chains. As the temperature increased, random scission of the polymer backbone resulted in the formation of lower-molecular-weight hydrocarbon fragments, which subsequently volatilized from the sample.

The principal thermal degradation parameters obtained from the TGA/DTG analysis are presented in Table 1.

Table 1.

Characteristic thermal degradation parameters of HDPE waste obtained from TGA/DTG analysis

Parameter	Symbol	Value
Initial degradation temperature	Ti	425 °C
Temperature at 5% mass loss	T5%	430 °C
Temperature at 10% mass loss	T10%	438 °C
Maximum degradation temperature	Tmax	475 °C
Final degradation temperature	Tf	505 °C
Total mass loss	Δm	98.1%
Residual mass	mr	1.9%

The initial degradation temperature of approximately 425 °C indicates that the HDPE waste maintained substantial thermal stability up to this temperature. Above this region, the rate of mass loss increased rapidly, reaching a maximum at approximately 475 °C. The \(T_{max}\) value obtained from the DTG curve represents the temperature at which the polymer underwent its most intensive thermal degradation.

The relatively narrow difference between the initial and final degradation temperatures indicates that the major decomposition of the HDPE sample occurred over a comparatively limited temperature range. This is consistent with the predominantly hydrocarbon nature of HDPE and the relatively homogeneous structure of its polymer backbone.

The total mass loss was approximately 98.1%, while only about 1.9% of the initial sample mass remained after the thermal treatment. The low residual mass indicates that the HDPE waste was almost completely converted into volatile degradation products under the applied experimental conditions. The remaining fraction may be associated with inorganic fillers, pigments, stabilizers, mineral impurities, or thermally stable carbonaceous material present in the waste.

DTG characteristics and decomposition rate

The DTG curve provides additional information about the rate of thermal decomposition. In the investigated HDPE sample, the DTG profile was characterized by a dominant degradation peak centered at approximately 475 °C. The presence of a pronounced single peak suggests that the major mass-loss process was associated with the decomposition of the HDPE matrix rather than with several clearly separated degradation processes.

The DTG behavior of the sample is summarized in Table 2.

Table 2.

Main characteristics of the DTG profile of HDPE waste

Characteristic	Value
Main DTG peak temperature, Tmax	475 °C
Approximate onset of DTG peak	425 °C
Approximate end of DTG peak	505 °C
Main decomposition interval	425–505 °C
Maximum mass-loss rate	−2.5 % min^{-1}
Number of dominant DTG peaks	1
Residual mass at the end of analysis	1.9%

The maximum mass-loss rate of approximately 2.5% min^{-1} demonstrates that the decomposition process was particularly intensive around the DTG maximum. The single dominant peak also indicates that the degradation of the HDPE matrix occurred predominantly within one principal temperature region.

The thermal decomposition mechanism of HDPE can be associated mainly with random scission of the polyethylene backbone. At elevated temperatures, C-C bonds undergo homolytic cleavage, generating macroradicals. Subsequent β-scission, hydrogen transfer, and intermolecular reactions produce shorter-chain hydrocarbons. As the molecular fragments

become sufficiently volatile, they leave the sample, resulting in the rapid decrease in mass observed in the TGA curve.

The position of the DTG maximum is particularly important from the perspective of HDPE pyrolysis. The temperature corresponding to the maximum decomposition rate can be considered a characteristic region for intensive conversion of the polymer.

Thermal stability and implications for thermochemical conversion

The TGA/DTG results demonstrate that the HDPE waste possesses relatively high thermal stability before the onset of its main decomposition stage. The limited mass loss below approximately 400-420 °C suggests that substantial conversion of the polymer does not occur in this temperature region under the investigated conditions. A sharp increase in mass loss above the degradation onset indicates that the polymer chains become increasingly susceptible to thermal scission at elevated temperatures.

The almost complete mass conversion observed during the main degradation stage is particularly relevant to the thermochemical valorization of HDPE waste. The low residual fraction suggests that most of the polymeric material can be transformed into volatile products under inert conditions. These products may subsequently condense to form liquid hydrocarbons or remain in the gas phase depending on the reaction temperature, residence time, and reactor configuration.

The results also indicate that temperature control is a critical parameter during the thermal treatment of HDPE waste. Temperatures substantially below the main decomposition region would result in incomplete conversion, whereas temperatures within or above the principal degradation region would promote rapid polymer decomposition. Consequently, the TGA/DTG results can be used as a preliminary basis for selecting the operating temperature range for laboratory-scale pyrolysis experiments.

Conclusion

TGA/DTG analysis showed that HDPE waste has high thermal stability up to approximately 425 °C. The main thermal decomposition occurred in the 425-505 °C range, with a maximum degradation temperature T_{max} of 475 °C. The temperature at 5% mass loss was 430 °C, while that at 10% mass loss was 438 °C. The total mass loss reached 98.1%, and the residual mass was only 1.9%. The maximum mass-loss rate was approximately 2.5% min^{-1}. The presence of one dominant DTG peak indicates that HDPE decomposition occurs mainly through a single intensive degradation stage. The obtained temperature range of 425-505 °C can therefore be considered an important reference interval for the subsequent thermochemical conversion and pyrolysis of HDPE waste. These results confirm the suitability of TGA/DTG analysis for determining the thermal stability and decomposition characteristics of HDPE waste.

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