Corrigendum to "Kinetic analysis for thermal cracking of HDPE: A new isoconversional approach" [Polymer Degrad. Stab. 129 (2016) 306–318]

A B S T R A C T

Converting waste plastic into marketable hydrocarbons is a promising way to protect the environment and earn financial gain. While several kinetic studies have examined the cracking of waste plastic, they are often oversimplified or inappropriate for designing an industrial reactor. This work proves the necessity of using isoconversional methods by using Differential Scanning Calorimetry (DSC). DSC verified that cracking of waste plastic involves the production of several intermediates, indicating that the kinetics is more complex and requires further studies. Several isoconversional methods such as Friedman, Ozawa, Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS) and model-free were applied to estimate the apparent activation energy and frequency factor of thermal cracking of high-density polyethylene (HDPE) using non-isothermal and isothermal Thermogravimetric Analysis (TGA). The determined kinetic parameters from each method were evaluated against the experimental data. In order to overcome the failures and shortages engaged with the employed methods, a new isothermal isoconversional model was proposed and good matching results were observed.

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The article presented a new approach for determining the kinetic parameters of thermal cracking of plastics using thermal cracking of high-density polyethylene as an example. After publication it was observed that oxygen exists in the chamber of Thermogravimetric Analyzer (TGA), despite the fact that the conventional protocol available in open literature for purging air in the chamber was followed. The protocol has been extended to 24 hour purging with nitrogen to ensure that no oxygen was left in the chamber.

Using the new protocol all the data related to thermal cracking of high-density polyethylene were obtained again. The results presented in the published article as a sample calculation for thermal cracking are changed and not valid to be considered for pure thermal cracking. The results present partial oxidation and cracking instead.

The publication has been corrected with the new data as given below.

Summary of changes

1 All the Figures in the main body and manuscript have changed.
2 Table 2, A1, A2 and A3 have changed.
3 According to the new results, in isothermal mode, the preheating rate before the desired temperatures does not have any effect on the rate of reaction and involved mechanisms.

It is important to note that still the proposed method in this study has a better match with the experimental data.
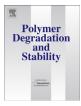
1. Introduction

1.1. Waste plastic cracking

Nowadays, plastics can be found almost everywhere on our planet. Since plastics are produced in a variety of shapes, weights and strengths, and with different levels of durability, they have a wide range of applications in the packaging, automobile, construction, electrical and electronics industries [1]. The global production of plastic increased by 300 times between 1950 and 2013 [2], generating a dramatic increase in waste plastic generation. Globally, 65–70% of waste plastic is buried in landfills, and the remaining 20–25% is incinerated [3]. Neither of these disposal methods are completely environmentally friendly; however, landfilling causes more environmental problems than incineration. As plastics are not biodegradable, they take hundreds of years to decompose in landfill sites. Moreover, pollutants in landfill sites may leak into underground water resources and soil and cause more problems such as contaminating drinking water [4].

Cracking of waste plastic is a promising process for converting waste plastic into fuel. This process decreases the landfilling of waste plastics, enhances the recycling industry and preserves virgin fuel resources [5]. Thermal cracking of waste plastic needs to meet high temperatures to produce more calorific products in the range needed for kerosene and diesel. Using a catalyst in thermo-catalytic

cracking reduces the operating temperature and increases the production of more valuable hydrocarbons such as gasoline, ethylbenzene and styrene [6,7].

Since 1984, a number of studies have been performed on thermal and thermo-catalytic cracking of pure and waste plastics. Most researchers have focused on the product distribution and effect of operating conditions such as temperature, reaction time, type of catalyst and catalyst-to-plastic ratio on the yields of products [6–15].

Besides the operating conditions, the reactor's configuration, size and internals can also affect the product yields. However, an industrial reactor design for the cracking of waste polymers has not been studied in depth. Known reliable kinetic parameters including reaction order (n), apparent activation energy (E_a) and frequency factor (A_0) are the most important requirements for designing a reactor. While several kinetic studies have investigated the cracking of waste plastic [3,9,16–22], most have employed uncertain methods. As a result, they are not quite suitable to be employed in the design of an industrial reactor. Moreover, these studies failed to evaluate the agreement of the estimated kinetic parameters with the experimental data [3,9,16–18].

Most pyrolysis studies have focused on virgin and waste polystyrene (PS), high-density polyethylene (HDPE) and low-density polyethylene (LDPE); however, different kinetic parameters were reported even for one kind of polymer [e.g. 18,19]. Apart from the experimental factors and instrumental accuracy, this diversity could be caused by the molecular structure of the plastic, as even one type of plastic, such as HDPE, is available in different ranges of molecular weight, density and specification. Consequently, characterizations such as the melting point [23], crystallinity [23,24], fusion heat [24], molecular weight and ash content should be reported to demonstrate a fingerprint of the plastic sample in every study.

1.2. TGA and kinetic study

TGA, which uses a high temperature furnace measuring the weight (or weight loss) of a sample at different times and temperatures, is widely used for kinetic studies. TGA uses a very small sample weight to ensure the mass and heat transfer barriers are negligible. For this reason, TGA may find the net rate of the reactions and provide more accurate and reliable data compared with other methods [25].

TGA can essentially be employed in two different modes, isothermal and non-isothermal [26,27]. The choice of mode depends on the nature of the reactions [25]. Non-isothermal TGAs are considerably less time-consuming than isothermal TGAs, and are thus attractive for quick investigations [27]. In isothermal methods, the temperature of the sample after reaching a specified value remains constant during the decomposition of the sample. As fewer experimental variables are used in isothermal methods, compared to non-isothermal TGAs, the results are more reliable [27,28]. In addition, the isothermal approach is recommended for observing the reaction with the production of different intermediates, such as the decomposition/pyrolysis of waste plastics [28].

Isoconversional and non-isoconversional methods can be used to analyze TGA datasets in order to estimate the kinetic parameters. In the non-isoconversional methods, kinetic parameters are constant throughout the reaction, whereas the isoconversional methods generate kinetic parameters as a function of the extent of the reaction [16,17,19–22,29,30]. Considering the nature of thermal/catalytic cracking, it can be concluded that polymer decomposition is not a single reaction and that it produces different intermediates. For this reason, several polymer researchers have applied isoconversional methods to conduct kinetic studies of

polymer decomposition [16,17,19–22].

Polymer researchers have mostly studied non-isothermal TGAs by applying the isoconversional methods of Coats-Redfern, the modified Coats-Redfern [17,31], Friedman [16,18,21], Ozawa [16], Kissinger–Akahira–Sunose (KAS) [21], Flynn–Wall–Ozawa (FWO) [21] and model-free [19,20,29,30] to determine the kinetic parameters. In these methods, the activation energy slightly increases or decreases during the cracking of waste plastics, but the difference between the levels of activation energy at different conversion factors is not significant [16,17,19,20].

Nevertheless, the estimated kinetic parameters from non-isothermal TGAs are not applicable for isothermal measurements [30]. While most researchers confirm that pyrolysis reactors work under constant temperature [20], few have studied isothermal TGAs of waste plastics [3,19,20,22]. The common methods to analyze isothermal TGAs are the conventional method which generates constant kinetic parameters over the entire decomposition [3], and the isoconversional model-free method which is highly recommended in different works [19,20,22].

Despite the rich content of research on the kinetic study of polymer decomposition, it is difficult to find a reliable model for designing an industrial reactor. One question remains unanswered regarding which method is more precise for predicting the kinetic parameters of polymer decomposition. In this work, we attempt to bridge this gap by focusing on a comprehensive kinetic study of pyrolysis of HDPE and comparing different methods. The isothermal-differential method presented in this paper better fits the real case and provides more consistent results. This method involves fewer assumptions and thus prevents more errors. The findings of this paper are a step forward in the design of an industrial reactor.

This article employs and analyzes the following isoconversional methods for non-isothermal and isothermal TGAs to determine the kinetic parameters: Friedman, Ozawa, FWO, KAS, and model-free methods. We evaluate the results against the experimental data and discuss their reliabilities. Considering the limitations of the employed methods, we present a new differential isoconversional method to estimate the kinetic parameters.

2. Materials and methods

2.1. Plastic (raw material)

Table 1 shows the typical properties of the virgin HDPE used in this study. DSC and TGA were used to determine the melting point, fusion heat, crystallinity and ash content.

2.2. TGA

Non-isothermal and isothermal TGAs were carried out for 13 mg of the HDPE in disposable aluminum pans by Perkin Elmer TGA7 under an inert atmosphere of 30 mL min^{-1} N$_2$. Before each measurement the TGA was purged with N$_2$ for 2 hrs to avoid any oxidation. If there was any interruption for TGA test in order to stop purging of nitrogen through TGA apparatus nitrogen purging was set at 24 hours before testing a new sample. This method guarantees that there is no oxygen in the reaction zone. The weight and furnace calibration were performed according to the Perkin Elmer TGA 7 instruction manual. Different heating rates of 40, 45, 50 and 55 °C min^{-1} were applied in non-isothermal TGAs from 40 to 575 °C. Two sets of isothermal decompositions were studied at constant temperatures of 390, 400, 410, 420 and 430 °C. The heating rates before reaching the target temperatures (which could be called the pre-heating rate) were set at 50 and 25 °C min^{-1} during the first and second attempts to obtain isothermal measurements, respectively. These isothermal measurements enabled us to predict