



Short communication

On the intrinsic reaction rate of polyethylene pyrolysis and its interplay with mass transfer

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ARTICLE INFO

Keywords:

Pyrolysis
Intrinsic kinetics
Polymers
Polyolefins

ABSTRACT

An attempt to determine the the intrinsic kinetic of polyolefins pyrolysis is presented. For this, pyrolysis experiments of polyethylene were performed in a screen heater reactor, where the effects of mass and heat transfer on the pyrolysis process are minimized. First-order mass loss rate constants obtained at 500 °C were circa 0.5 and 1.3 s⁻¹ for HDPE and LDPE, respectively, which are significantly higher than the majority of the values reported in the literature. At 450 °C, the mass loss rate of HDPE was lower, circa 10⁻² s⁻¹. Additionally, we have observed that the interplay between mass transfer and the depolymerization reactions can be used to steer the product distribution. For instance, in a 50 g scale batch reactor, the product obtained at 420 °C (only oil) is much lighter than at 500 °C (mixture of oil and wax), which can be attributed to the much lower evaporation rate of larger cracking products at 420 °C as a result of which these fragments crack further in the reacting liquid phase.

1. Introduction

Pyrolysis is a technology advocated to play a role in chemical recycling of plastic waste [1–5]. A detailed understanding of the pyrolysis process at in the of intrinsic reaction rates and their interplay with mass and heat transfer is instrumental for designing pyrolysis technology. Feasible productivities in kg per reactor volume per time, as well as the yield and composition of the products of pyrolysis technologies are related to intrinsic reaction and transfer rates. In this short communication we focus on measuring the intrinsic reaction rate by minimizing mass and heat transfer limitations. For this we have used an in-house developed screen-heater reactor which has proven its worth for biomass and lignin pyrolysis in the last decades [6–11]. In addition, a selection of experimental results are presented to show the interplay between mass transfer and chemical reactions.

To our knowledge, very little information on the intrinsic reaction rate of plastic pyrolysis is currently available due to heat and mass transfer limitations caused by the experimental equipment used, such as thermogravimetric analysis (TGA) and batch packed beds [12–17]. The obtained kinetic parameters are then often referred to as “apparent” pre-exponential factor and activation energy [18].

Pyle and Zaror introduced a method to analyse whether the pyrolysis rate is controlled by heat transfer or chemical kinetics [19]. Mettler et al. [20] visualized this in a graph, as shown in Fig. 1. The method makes use

of the Biot ($Bi = \frac{hL_c}{\lambda}$) and Pyrolysis numbers ($Py_1 = \frac{\lambda}{k_p C_p L_c}$ & $Py_2 = \frac{h}{k_p C_p L_c}$), where the Biot number relates the external heat transfer rate through convection to the intraparticle heat transfer rate via conduction, and the Pyrolysis number relates the internal or external heat transfer rate to the reaction rate [19,21]. It is important to note that for the reaction rate the mass loss rate of the pyrolyzing sample is considered, because this is what is experimentally measured. The reaction rate does not have to be equal to the mass loss rate; the two are related by the transport rate of molecules away from the reaction zone on/in the pyrolyzing sample. This will be discussed in more detail later.

$Bi > 1$ is undesirable when attempting to measure intrinsic kinetics due to the presence of a temperature gradient inside the reacting particle (sample). For a very high pyrolysis number ($Py > 10$), heat transfer to and in the particle is considerably quicker than the reaction rate. Therefore, both $Bi \ll 1$ and $Py > 10$ are the requirements needed to be in a so-called kinetically-limited isothermal regime, where the process is essentially free of heat transfer limitations [20,22,23]. We estimated Biot and Pyrolysis numbers of polyolefins pyrolysis in the screen-heater reactor at different characteristic lengths (1–150 μm) and the results are also plotted in Fig. 1. The overall heat transfer coefficient used for the calculation was obtained from the literature [8], and the kinetic constant (k) value of 0.5 s⁻¹ was based on the measured mass loss rate of HDPE (see Results and Discussion). It can be seen from the graph that at

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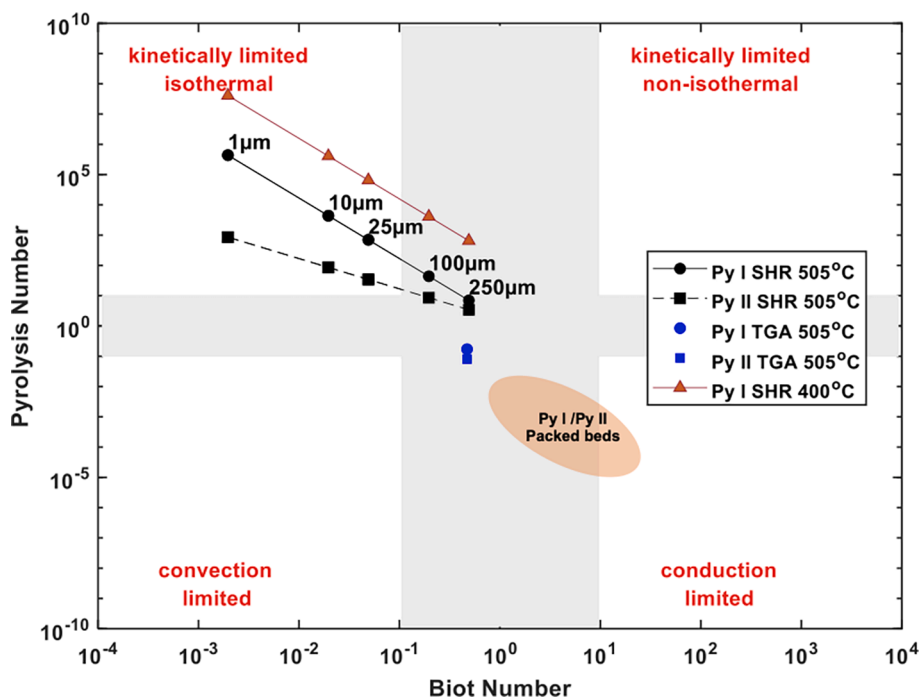


Fig. 1. Pyrolysis reaction and heat transfer regime map. Plotted values are estimated Bi and Py of HDPE pyrolysis in a screen heater reactor (SHR) with different characteristic lengths. The map is adapted from [20].

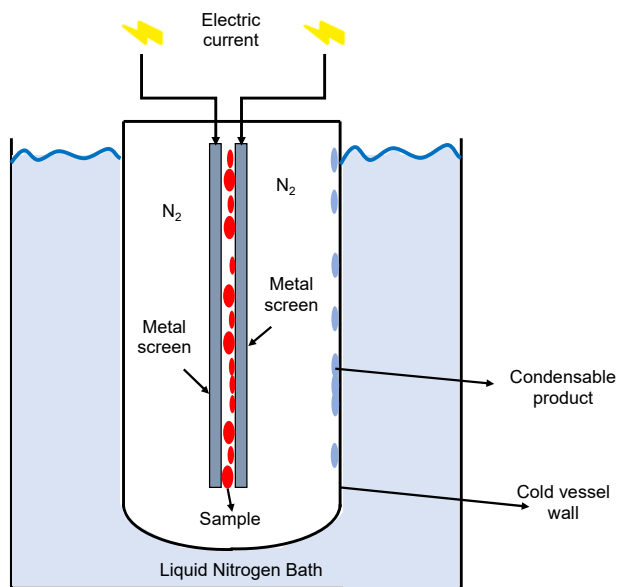


Fig. 2. Screen-heater reactor used in the pyrolysis experiments of polyolefins.

the used characteristic length of $25 \mu\text{m}$ [8], which is the half thickness of the sample, the reaction is kinetically limited and isothermal at 500°C . This regime is not possible to achieve in TGA and packed beds, see Fig. 1.

Mass transfer is, next to heat transfer, also important in the pyrolysis process. When pyrolyzing polyolefins the feedstock undergoes cracking reactions and the products of these reactions will have to leave the reaction zone (particle or a liquid pool), before they are collected in the condenser system. Leaving the reaction zone can be via evaporation, sublimation, or ejection of aerosols. For brevity we will use evaporation as the general term to denote all these phenomena. If the evaporation rate is low, like in a TGA [12–15], the measured mass loss rate is not representative for the reaction rate. At 500°C , the evaporation rate in the screen-heater is $>10 \text{ s}^{-1}$ for molecules up to 1000 Da

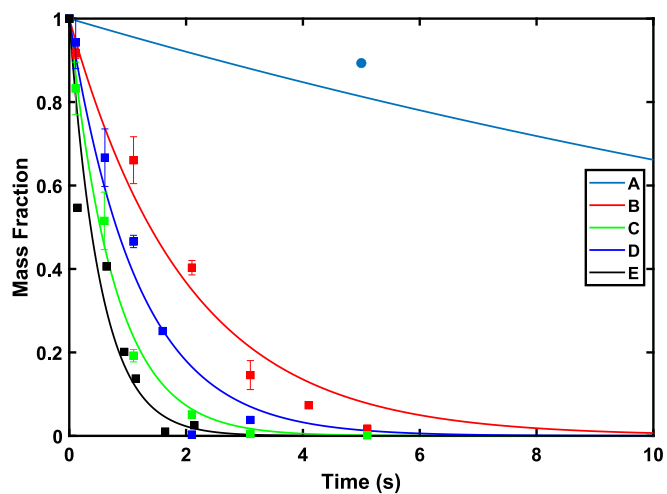


Fig. 3. Mass loss with time in the pyrolysis experiments of polyethylene under different conditions. Legend: A) HDPE (450°C , 5 mbar); B) HDPE (505°C , 5 mbar); C) LDPE1 (505°C , 5 mbar); D) LDPE1 (505°C , 1 bar); E) LDPE2 (505°C , 5 mbar). The lines are first order mass loss regression lines.

(Supplementary Information, Fig. S2), to be compared to 1 s^{-1} for the reaction rate, as a result of which the measured mass loss rate is a better estimate of the reaction rate.

In this context, to illustrate the interplay of chemical reactions and mass transfer, we present experimental data on the effects of the pyrolysis temperature, pressure, and the molecular weight of the feedstock, using a screen heater reactor, to reduce mass and heat transfer limitations.

2. Materials and methods

In this present study, virgin high-density polyethylene (HDPE) with an average initial molecular weight of 74 kDa and two different low-

Table 1
Comparison of rate constant (s^{-1}) obtained from different works.

Source	Material	T (°C)	$k_{overall}$ (s^{-1})
This Work	HDPE	505	0.50
	HDPE	450	0.02
	LDPE1	505	1.31
	LDPE2	505	1.88
	LDPE1 (1 bar)	505	0.86
Jiang et al. [26]	HDPE	500	0.018
	LDPE	500	0.008
Li et al. [16]	HDPE	500	0.005
Zhang et al. [27]	PP	370	0.003
Ding et al. [28]	HDPE	420	0.002
Al-Salem et al. [29]	HDPE	500	0.004
Schubert et al. [30]	LDPE	450	$<10^{-3}$
Till et al. [31]	RPW	455	0.002
Elordi et al. [32]	HDPE	500	0.022
Westerhout et al. [25]	LDPE	500	0.36
	PP	500	0.34

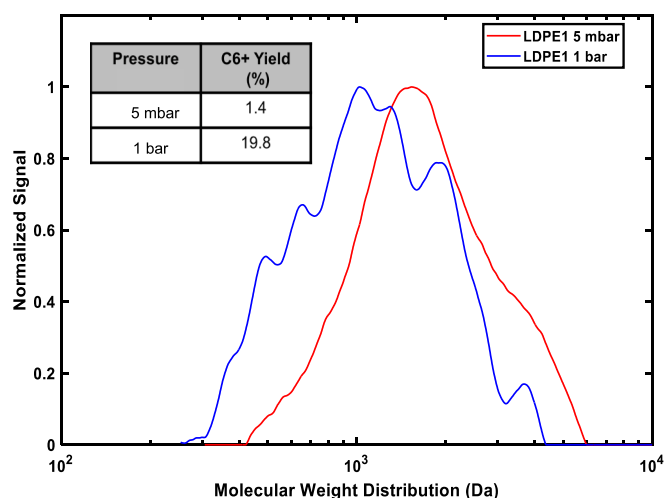


Fig. 4. Molecular weight distribution of the condensed product and the C6 + gases in the pyrolysis experiments of LDPE1_186kDa performed at 505 °C, heating rate of 5000 °C/s, and two different pressures, 5 mbar and 1 bar.

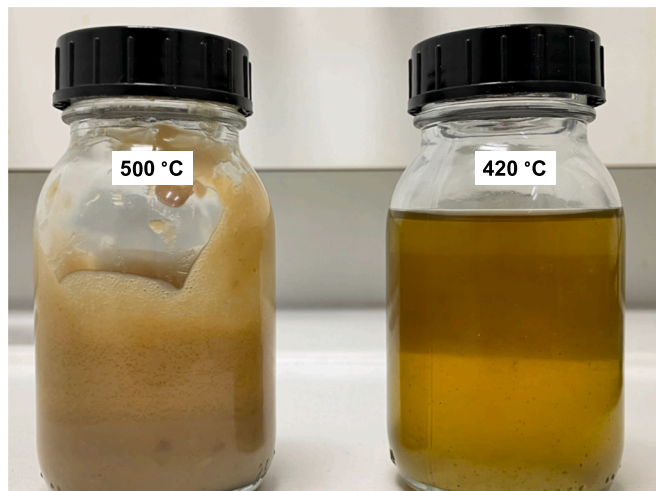


Fig. 5. Picture of the condensed products obtained in the pyrolysis experiments of LDPE1_186kDa performed in a 50 g-scale batch reactor at 1 bar and two different temperatures, 500 °C (left) and 420 °C (right).

density polyethylene (LDPE1 and LDPE2) with an average initial

molecular weight of 186 kDa and 4 kDa, respectively, were used. A detailed description of the screen heater reactor has been previously described elsewhere [6,7,10]. The set-up is illustrated in Fig. 2. Here we describe shortly the general principles of the reactor. 50 mg of solid sample (with particle size between 250 and 600 μm) is rapidly heated by screens with a rate of up to 5000 °C/s. The sample is placed in a chamber with walls cooled by liquid nitrogen. Due to the cooling with liquid nitrogen the environment outside the screen is ca. -180 °C and as a consequence, reaction products that leave the reacting sample will quench chemically (do not further react). The chamber is filled with nitrogen and can be depressurized down to 5 mbar. Evaporated products condense on the walls of the cooled chamber. Condensed and solid yields are measured by measuring differences in weight of the screens, vessel and clamps before and after reaction. It is worth mentioning that the solid product is the product that has not evaporated during the reaction. Gas yield is determined by difference and gas samples analyzed in GC-FID. The condensed product is collected by washing with tetrahydrofuran (THF) and analyzed by Gel-Permeation Chromatography (GPC). The temperature profile of a typical experiment is shown in the [Supplementary Information](#).

To discard any potential catalytic effect of the metallic screens, we performed experiments using screens with different mesh sizes, which could allow us to see any effect of changing the contact area between the metal screens and the plastic sample. Details on the experiments and procedure followed can be found in the [Supplementary Information](#) (Table S1). The results under the same operation conditions were similar for both screens, thus indicating a negligible effect of the screens used. This result coincides with Hoekstra et al. who performed biomass pyrolysis using gold-sputtered screens in the same set-up [7]. Similar product yield, gas composition, and molecular weight distribution were obtained from the experiments using both gold-sputtered screens and stainless steel screens, removing the possibility of catalytic activity by the metallic screens [7].

Two additional pyrolysis experiments of LDPE (186 kDa) were run in a 50 g-scale batch reactor at two different temperatures, 420 and 500 °C. Details on this set-up are described in a previous work from our group [24].

3. Results and discussion

The measured mass loss in the screen heater is plotted in Fig. 3. Mass loss data are fitted to a first order isothermal model to obtain a first order mass loss rate constant. Reported rate constants are listed in Table 1. The mass loss rate LDPE of 186 kDa (LDPE_1) at 5 mbar and 505 °C is ~ 1.3 s^{-1} , which is much faster than measured rates in TGA (see Table 1). Hence, indeed in the screen-heater mass transfer limitations are low and the measured mass loss rate approaches closer the intrinsic reaction rate. Strikingly speaking this is then the reaction rate towards molecules that can easily evaporate. To the best of our knowledge, only Westerhout et al. [25] reported a rate constant close to ours, 0.3 s^{-1} , but they disregarded their own measurement. They also used a screen-heater and ascribed, but did not prove, the high rate to catalytic activity of the screens. We have shown that this is not the case for our system (see Experimental section).

By changing the pressure inside the chamber the evaporation rate of reaction products can be steered. Pyrolysing LDPE_1 (186 kDa) at 1 bar instead of 5 mbar resulted in a slightly lower mass loss rate ($k \sim 0.9$ s^{-1}), see Fig. 3. The chemical reactions inside the pyrolyzing sample are not affected by the pressure. Here also the interplay between reactions and mass transfer plays a role. That is, at 1 bar larger molecules evaporate less fast as a result of which that stay longer in the hot reaction front cracking further to smaller molecules that evaporate faster. This was confirmed by the differences in molecular weight distribution of the condensed product obtained at two different pressures, 5 mbar and 1 bar (Fig. 4). The product from pyrolysis at 1 bar is lighter and richer in components of the naphtha range than the product obtained at 5 mbar.

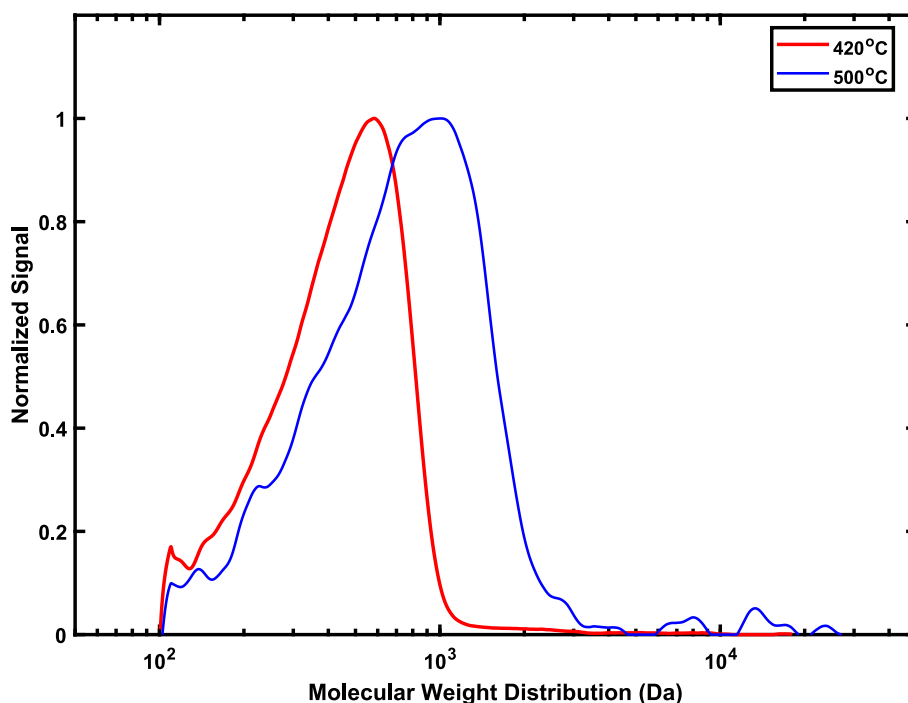


Fig. 6. Molecular weight distribution of the condensed product in the pyrolysis experiments of LDPE1_186kDa performed in a 50 g-scale batch reactor at 1 bar and two different temperatures, 420 and 500 °C.

Temperature is another parameter that influences the kinetics in pyrolysis. Experiments run at different temperatures (Supplementary Information, Fig. S4) show a major change in polymer conversion, from 10% to almost 80%, when increasing the temperature by 25 °C, from 450 to 475 °C. These results correspond to a first order mass loss rate constant of 0.06 and 0.7 s⁻¹, respectively.

The initial molecular weight of the polymer also has an effect on the mass loss rate measured. The mass loss rate of LDPE_2 of 4 kDa is, at holding times below 2 s, higher than the rate of LDPE_1 of 186 kDa (Fig. 3). This can be explained by the fact that a fraction of the low molecular weight LDPE can evaporate without the need for cracking reactions.

When comparing the type of polyolefins, the mass loss rate of HDPE is lower than the one of LDPE (Fig. 3). This agrees with literature findings as LDPE is expected to degrade quicker than HDPE due to the higher branching degree and less crystallinity [33,34].

Based on the results presented, it is possible to conclude that the interplay between transport (evaporation) and cracking reactions plays a major role in the product distribution of pyrolysis. To further confirm our hypothesis, we ran experiments in a grams-scale batch reactor with LDPE (186 kDa) at two different temperatures, 420 and 500 °C. At 420 °C and after 4 h of reaction, 9 % of solid residue remained, which corresponds to a mass loss rate constant of 10⁻⁴ s⁻¹. It was also observed that the condensed product obtained at 420 °C was much lighter (no waxes but liquid oil) than the one obtained at 500 °C (rich in waxes), see Figs. 5 and 6. Thus, at lower temperatures, evaporation is less fast and the cracking reactions can proceed in the liquid phase to a larger extent, leading to lighter products.

4. Conclusions

Measuring the intrinsic kinetics of polyethylene pyrolysis is only possible in experimental set-ups such as the screen heater, where mass and heat-transfer limitations are limited. Using that set-up, we have observed a mass loss rate of polyethylene pyrolysis at 500 °C of circa 1 s⁻¹, which is much higher than previously reported (10⁻³ – 10⁻² s⁻¹). Those reported low rates are a result of the mass and heat transfer

limitations. However, such high rates of 1 s⁻¹ imply that in practical process the productivity in kg per unit of volume per unit of time is limited by heat addition, as 1 s⁻¹ corresponds to ca. 1 GW per m³ reacting liquid (considering a heat of reaction of 1.5 MJ/kg).

The activation energy is high because at lower temperature, 450 °C, the mass loss kinetic constant drops to circa 10⁻² s⁻¹.

We have also shown that the interplay of mass transfer and the depolymerization reactions can be used to steer the product distribution. Lower temperature and higher pressure lead to vapours leaving the reacting particle/liquid (initial) with lower molecular weight. When targeting naphtha range feed to be (co-)fed to a steam cracker, this is preferred.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

The authors gratefully acknowledge the Institute for Sustainable Process Technology (ISPT) of the Netherlands and the Dutch Polymer Institute (DPI) within the framework of the INREP project (MOOI plan, 2020, *An Integrated approach towards Recycling of Plastics*) and partners. They also thank Benno Knaken and Ronald Borst from the University of Twente for their technical support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2023.143886>.

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