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# Kinetic study of pyrolysis of high-density polyethylene (HDPE) waste at different bed thickness in a fixed bed reactor

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**Abstract**

The aim of this study is to investigate the kinetic characteristics of the high-density polyethylene (HDPE) waste pyrolysis process based on thermogravimetric analysis (TGA) and using a fixed bed pyrolytic reactor (FBPR) at different temperatures. In addition, the influence of material bed thickness on the yield distribution and the composition of products was examined over a temperature range of 425–550°C. A higher wax fraction was obtained in the thin bed of the FBPR bed at 425°C. With temperature above 500°C, more oil and wax products were generated in the thick bed of the FBPR. Based on the experimental study, a discrete first-order kinetic lumping model, comprising three independent parallel reactions (lumps), was developed to describe the yield distribution of gases, oil fractions, wax fractions, and solid residue, coupling with secondary cracking reactions of the wax fractions into lighter fractions (i.e., oil and gas). The overall apparent activation energy ($E_a$) and pre-exponential factor ($A_0$) of HDPE pyrolysis were estimated in the FBPR. The results showed that the thickness of the bed of plastics has a pronounced influence on the pyrolysis kinetics of HDPE.

**KEYWORDS**

bed thickness, discrete lumping kinetics, HDPE, pyrolysis

## 1 | INTRODUCTION

The increasing stream of solid plastic waste has resulted in many environmental and social concerns in the world. In the UK, it was estimated that nearly 200 000 tonnes of plastic waste was not properly recycled in 2011[1] due to inherent complexities in the plastic waste stream, including the high cost of collection and separation of post-consumer plastic waste. Additionally, plastic waste is often mixed with

different types and grades together with various additives and contamination from the household, medical, and construction sectors. Hence, it is impossible to reprocess them (especially the mixed ones) directly with conventional mechanical and chemical recycling methods due to the incompatibility among waste constituents. All plastics, derived from fossil resources, are intensive sustainable feedstocks and energy sources. Conversion of unrecyclable end-of-life of plastic into low sulphur hydrocarbon feedstocks

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could be an environmentally friendly solution, especially for post-consumer packaging waste. Trials of technologies, including pyrolysis studied as in this investigation, have been undertaken in many projects.[2–6]

Pyrolysis processes are considered as a promising route for plastic waste recycling due to the relative simplicity of conversion of the heterogeneous plastic waste into lower molecular weight hydrocarbon products which can be used as fuel or chemical feedstock in developing a carbon-efficient circular economy. In particular, pyrolysis processing can deal with mixed unwashed plastic waste contaminated with soil, grease, and other materials.[6] Studies of operational variables have been most prominent in the thermal pyrolysis process literature, such as the effect of residence time, temperature, and catalyst on product distribution[6–11]; the mass change in isothermal[12] or non-isothermal pyrolysis[13,14]; the mechanisms of thermal degradation[3,4]; and the estimation of kinetic parameters of a given pyrolysis process.[4,11,14] However, it is noted that the effect of the fixed bed pyrolytic reactor (FBPR) bed thickness is rarely reported in the study of the pyrolysis process of plastic waste.

Kinetics of polymer decomposition are dependent on the conversion degree and different reaction orders.[15,16] Kinetic parameters are usually associated with operational conditions (e.g., temperature gradient in the sample, residence time), the accuracy of model approximation, the complexity of the reaction mechanism, and the presence of heteroatoms from additives and contaminants.

Thermogravimetric analysis (TGA) is a frequently employed technique to examine the kinetics of thermal degradation as it offers fast, quantitative results under isothermal or non-isothermal conditions. The kinetic information of pre-exponential factors and activation energies for various decomposition reactions can be found via TGA to predict plastic degradation using kinetic models.[3,4,11,12,16–19] Aboulkas et al.[18] applied TGA and a non-isothermal single reaction model to study the kinetic decomposition of mixtures of olive residue and plastic with a nitrogen carrier gas in the temperature range from 300–1273 K at four heating rates of 2, 10, 20, and 50 K min$^{-1}$. Park et al.[11] studied the primary pyrolysis characteristics of refuse derived plastic fuel using a lab-scale furnace and thermogravimetric analysis. They reported the effect of a temperature range of 400–800°C on the product yields of liquid, solid, and gas, and discussed apparent activation energies and pre-exponential factors by single and parallel reaction models to estimate the activation energies of PS, PP, PE, and PVC as 231.83, 193.55, 175.92, and 72.26 kJ mol$^{-1}$ (first degradation of PVC), respectively, and 164.94 kJ mol$^{-1}$ (second degradation of PVC). Al-Salem and Lettieri[4] investigated the pyrolysis kinetics of pure high-density polyethylene (HDPE) at the temperatures of 500, 550, and 600°C in an isothermal

thermogravimetric condition using a micro-thermobalance reactor. They examined the thermal kinetic characteristics for the thermal cracking of the polymer by primary and secondary depolymerization reactions.

TGA only provides meaningful data of the mass change in thermal decomposition reactions in a fixed bed reactor and shows limitations in measuring the gas and liquid fractions and identifying the secondary reactions of heavier fractions produced by primary pyrolysis. Additionally, the TGA technique provides limited information on heat transfer during the pyrolysis process, while the low thermal conductivity of plastics requires high intensity heat and mass transfer in the reactor to minimize the limitations of the physical steps prior to devolatilization and to ensure isothermal conditions.[20]

HDPE, made from petroleum, is a linear and crystalline structured polymer. The main long chain molecules regularly line up with little or no short and/or long side chain molecules. The longer main chain means greater molecular weight, stronger inter-molecular forces, and higher temperature resistance compared with low density polyethylene. HDPE resin is a crystalline polymer. The size and size distribution of crystalline regions influence the tensile strength and environmental stress crack resistance. HDPE resin is perfect for heavy-duty containers such as water tanks, trays, milk and shampoo bottles, and higher temperature and anti-corrosion piping systems. The volume production of HDPE in 2016 was over 51 million tonnes in the world, and will increase to approximately 67 million tons in 2022.[21] While a lot of HDPE packaging is recyclable, there is a large fraction of mixed HDPE waste that cannot be recycled directly. The pyrolysis process breaks the main chains of the HDPE polymer and converts them into small hydrocarbons, so it has become a solution with great growth potential. HDPE waste is generally the third largest component of plastic waste streams. The products from HDPE pyrolysis are mainly hydrocarbon liquids, which may be directly used as fuel or upgraded to valuable chemical feedstock.[4,21] Nevertheless, the complex kinetics and mechanisms of pyrolysis reactions complicate the optimal design of both process and reactor.[10,22] Aguado et al.[7] introduced principal component analysis methodology in order to recognize the trends in the formation rates of the large number of components in the product stream for the HDPE pyrolysis. Ding et al.[14] studied the kinetics of plastic mixture pyrolysis in a low temperature range (between 380–420°C) together with different residence times and developed a four-lump model to describe the product distribution and the rate constants of secondary reactions. Most work has studied the primary pyrolysis of pure plastics (e.g., Al-Salem and Lettieri[4]), and investigated a temperature band lower than 420°C

**FIGURE 1** Schematic of fixed bed reactor
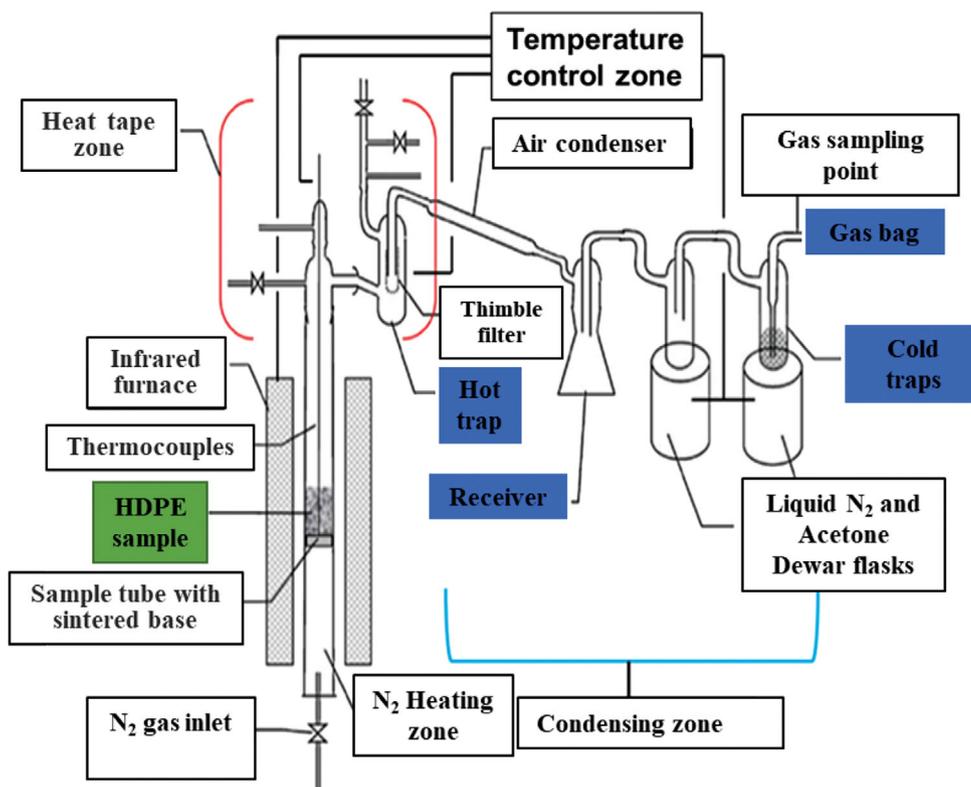
(e.g., Ding et al.[14] and Walendziewski[23]) and higher temperatures over 600°C (e.g., Park et al.[11]; Elordi et al.[24]; Conesa et al.[25]). Thus, an investigation of the pyrolysis characteristics of plastic packaging waste in the temperature range between 400–550°C would be a worthwhile addition to the literature.

The objective of this work is to identify the kinetic characteristics of HDPE pyrolysis at different temperatures, and also the effect of bed thickness on the conversion process and product distribution in two types of reactor (i.e., the TGA and the FBPR). TGA was employed to investigate the thermal degradation behaviour of HDPE in the temperature range between 400–550°C. Identical sample size and bed thicknesses were used in both the TGA and thin bed of FBPR experiments, and different sample sizes were used in the thin bed and thick bed experiments, which examined the effect of particle size on HDPE pyrolysis, and the difference between the TGA and FBPR processes. The overall kinetic parameters for the degradation of HDPE waste were estimated under isothermal conditions assuming first-order reaction. TGA results were further used for the design of the FBPR experimental runs. The effect of bed thickness on product yield and composition of the gas and liquid products was examined at temperatures of 425, 450, 475, 500, and 550°C in a FBPR. The first-order discrete lumping model approach was developed to describe the kinetic behaviour of the HDPE primary pyrolysis and the secondary tar cracking reactions.

## 2 | EXPERIMENT AND MATERIALS

### 2.1 | Materials and their preparation

Samples of HDPE waste were provided by Luxus Limited, a plastic recycling company in England. The HDPE waste consisted of production scrap and rigid post-user polyethylene crates which were cut manually to an approximate size of 8 mm ×8 mm sheet (of negligible thickness). The same material was chosen for all experiments. The sample was further cryogenically shredded for over 3 min under liquid nitrogen atmosphere using a milling grinder (A10, 20 000 L/min, Janke & Kunkel IKA-WERK, GmbH & Co. KG, Staufen, Germany), then particle sizing between 150–250 μm was conducted using bore diameter sieves. The sample was then weighed by electronic analytical balance (Sartorius Analytical Balance, W450E/044, IKA-Werke GmbH & Co. KG, Germany).

### 2.2 | Experimental apparatus

#### 2.2.1 | Thermogravimetric analysis (TGA)

Thermogravimetric experiments were carried out using Mettler-Toledo TGA/DSC1 (temperature range: room

temperature (20°C) to 1100°C, precision of weighing: 0.0025%) programmed to determine the weight change of the sample and heat flow into or out of the samples in a nitrogen atmosphere. Around 20 mg of each sample was weighed into a ceramic crucible; the bed thickness of the sample was less than two-thirds of the height of ceramic crucible to avoid the limitations of heat and mass transfer and contamination of the TGA facility. The samples were heated at 25 K min$^{-1}$ to the set temperature and then maintained in an isothermal condition; nitrogen, as a carrier gas, was circulated through the system at a stable designed flow rate. Data analysis was performed using the STARe software.

### 2.2.2 | Lab-scale FBPR apparatus

The pyrolysis reactor consisted of a vertical quartz tube (50 mm diameter) with a sintered glass plate carrier gas distributor at the base. The sample, fed into the reactor tube with ceramic cavity beads (the beads were used to avoid the blockage of the carrier gas distributor by melted plastic sample), was heated by a 12-kW infrared gold image furnace (P610C; ULVAC-RIKO, Yokohama, Japan) with a proportional–integral–derivative (PID) controller, allowing a reliable wide range of heating rates and holding times. Before each experiment, the glassware apparatus was assembled, and the system was purged with nitrogen (N$_2$) for 10 min. The N$_2$ flow rate was adjusted to the desired stable level before the run start. Nitrogen was used to sweep the volatiles and gases away from the pyrolysis zone and into the condensation system. Immediately after the reactor there was a 160°C zone maintained by wrapped heat tape to maintain the flow of heavy tar components and avoid pipe blockage. A schematic diagram of the experimental FBPR apparatus is reported in Figure 1.

The cooling of the reaction system was achieved through two stages for collection of liquid oil compounds: a room temperature zone; and a low-temperature zone ($-40 \pm 5$°C, measured by HH12B Dual digital thermocouple thermometers), consisting of two cooled traps held in Dewar flask filled by cooled acetone using liquid nitrogen to avoid the entry of condensed products into the gas sample bag. All the remaining non-condensable gases were collected into a 200-L multi-layered gas bag (Jensen Inert Products, Coral Springs, Florida) for further analysis. A more detailed description of the apparatus and of the experimental procedure can be found in Crombie and Mašek.[26]

### 2.3 | The reaction bed

The pyrolysis of a thin bed and thick bed of HDPE was carried out in the FBPR to investigate the difference

**TABLE 1** The thickness of reaction bed

| Bed | Thickness (mm) | Particle size |
|---|---|---|
| Thick | 30–50 | $8 \times 8$ mm$^2$ |
| Thin | 2.0–3.0 | 150–250 μm |
| TGA | 2.0–3.0 | 150–250 μm |

between TGA and FBPR (thin bed) under same nominal conditions, and to investigate the influence of bed thickness (Table 1).

### 2.4 | The collection of products

The wax was collected from the hot trap, then weighed and stored in 28.25-ml snap top vials. The condensed liquid collected from the receiver was weighed and stored in glass bottles, and the light oil from the cold trap (CT-1 and CT-2) was weighed and stored in 7-ml snap top glass vials. All liquid and wax products were kept in a refrigerator to minimize property change before analysis. The gases were preserved in a gas bag and analyzed by totalizing the gas volume obtained by the volumetric flow meter and the carrier gas flow (TG series of Ritter Precision Drum-Type Gas Meters, Germany) with an oxygen and carbon monoxide analyzer (RAPIDOX 3100EB series, Cambridge Sensate Limited, UK). The char-like residue was determined by weight difference between the reactor tube after pyrolysis and the clean reactor after cleaning.

## 3 | EXPERIMENTAL RESULTS AND DISCUSSION

### 3.1 | The thermal degradation behaviour of HDPE waste via TGA

The TGA experiments were undertaken at temperatures of 400, 425, 450, 500, and 550°C with the heating rate of 25 K min$^{-1}$, and the carrier gas (nitrogen) flow rate of 50 ml min$^{-1}$. The TGA results (Figure 2) indicate that the reaction temperature has a significant effect on the thermal degradation process. The lowest conversion rate was measured to be 3.26% at 400°C; the highest conversion rate was obtained at 550°C to be 99.4%, while 99.2% of conversion was observed at 500°C. This result indicates that beyond certain critical level, temperature may not have significant influence on HDPE primary pyrolysis. In this study, HDPE pyrolysis at a temperature of 550°C is considered to examine the influence of higher temperature on yield distribution. The kinetic parameters of HDPE pyrolysis are estimated in terms of the conversion
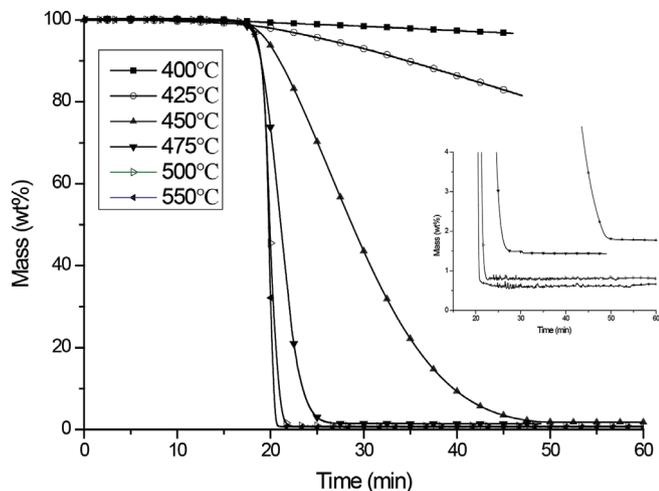
**FIGURE 2** The mass change of high-density polyethylene (HDPE) via thermogravimetric analysis (TGA) at a temperature range between 400–550°C
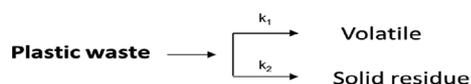


**FIGURE 3** Schematic of single step lumping model of high-density polyethylene (HDPE) pyrolysis

linking to a single-step lumping model (Figure 3) and the Arrhenius law. The activation energy and pre-exponential factor of HDPE thermal decomposing process via TGA are 197.35 kJ mol$^{-1}$ and $4.25 \times 10^{13}$ min$^{-1}$, respectively.

## 3.2 | Effect of bed thickness on conversion of HDPE decomposition via TGA and FBPR

Figure 4 shows the weight percentage of residue in the form of fused plastic aggregates together with some char-like residues at the plateau temperature range of 400–550°C. A clear difference of residue yields between TGA, thin bed, and a thick bed of FBPR can be observed from over 40% to less than 2% through the temperature range of 450–500°C. This may be ascribed to the different performance of reactor heat and mass transfer during the pyrolysis process. When the temperature increased over 500°C, the gap of residue yields between three conditions reduced clearly. The proportion of char residue may be attributed to impurities from the presence of residual additives and contaminants in HDPE waste. Pure HDPE can be converted into nearly 100% of hydrocarbons.[27]

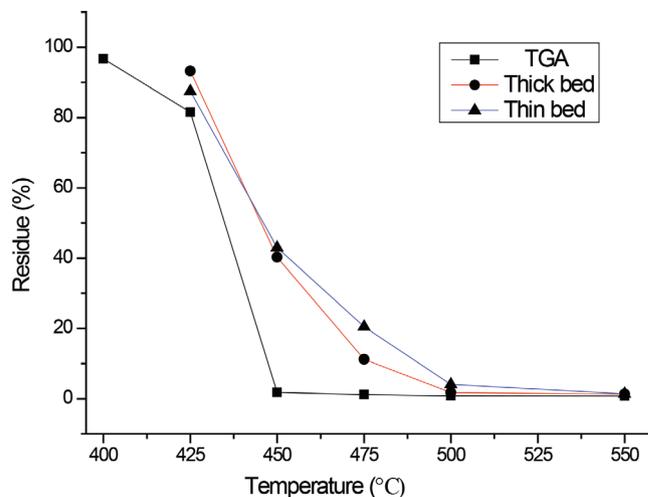Figure 4 also shows that HDPE starts to degrade near the temperature of 400°C, and the conversion increased



**FIGURE 4** The residue yields from thermogravimetric analysis (TGA), thin bed and thick bed at different temperature

from 3.3% to 18.5% with the temperature change from 400 to 425°C. This indicates that the activation energy for bond cleavage in the HDPE hydrocarbon structure can be reached at 400°C, and that the degradation accelerated with the increase in temperature. This is due to the fact that HDPE degradation initially involves scission of tertiary carbon bonds and/or ordinary carbon–carbon bonds in the beta position to tertiary carbons.[28] HDPE degradation significantly intensifies with temperature increase from 475 to 510°C, resulting in a conversion rise from 10% up to 95%. Marcilla et al.[29] reported a similar result for HDPE pyrolysis temperature range of 469–515°C. Higher temperature enhances the chain scission and cleavage of carbon bonds and thereby favours the production of smaller hydrocarbon molecules.

Figure 4 shows that the thermal conversion of HDPE in the thick bed is higher than for the thin bed between 450–550°C. Reactions in the thick bed increase the proportion of the sample involved in the degradation process; the sample amount does affect the pyrolysis outcomes, indicating some heat transfer effects at high mass loadings,[30] and also the possibility of reaction heat dominated by the secondary reactions such as cracking and repolymerization at higher temperature in the thick bed giving exothermic phenomenon effects. Di Blasi et al.[31] observed exothermic effects at the centre of thick samples/beds uniformly heated along the external surface.

## 3.3 | Effect of bed thickness on product yields

Figure 5 and Table 2 show the yield distribution of HDPE pyrolysis obtained from the thin beds and the thick beds

of the FBPR between 425–550°C. At 425°C, more wax was produced in the thin bed indicating that, in such an experimental set-up, at lower temperature the wax conversion is higher. As the temperature increased, higher wax yields were observed in the thick bed between 450–550°C, with a reduction of oil and gas yields. The effect of bed thickness on the product yields might be considered from two aspects. One is linked to particle sizes difference; smaller particle size means a larger surface area for heat transfer. Another aspect is the influence of hot carrier gas passing through the bed, as it is easier to go through a thin bed, which improves heat transfer efficiency. Improvement of heat and mass transfer can result in higher conversion and more gases, especially at a lower temperature, which can be seen in Figure 5. Martínez et al.[32] reported that the bed thickness increase means residence time increase during the study of the HDPE pyrolysis process in fluidized bed reactors.

**TABLE 2** Yield distribution and mass balance of high-density polyethylene (HDPE) pyrolysis for thin beds and thick beds at different temperatures

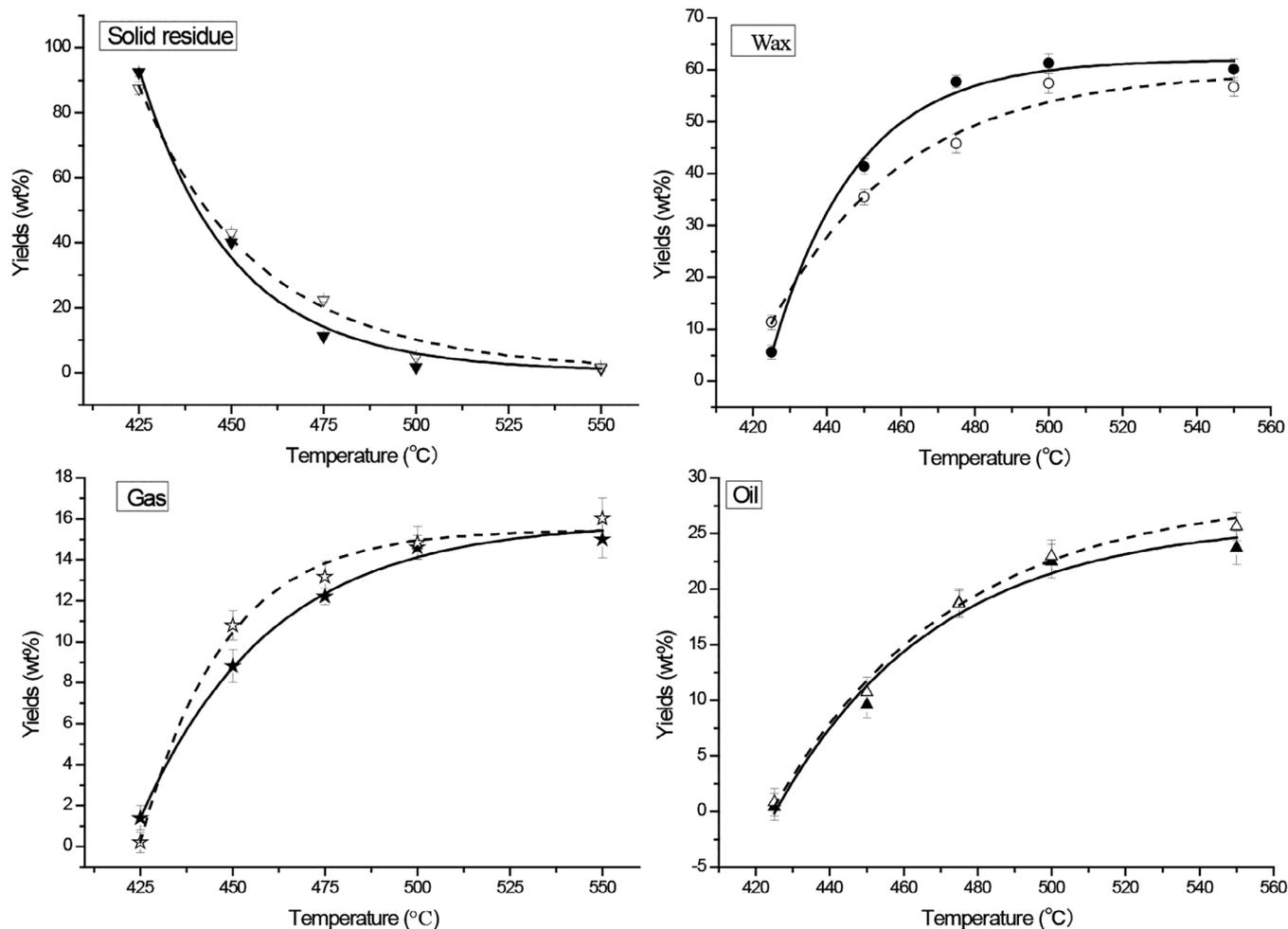|  | Temperature | Wax | Oil | Gas | Residue |
|---|---|---|---|---|---|
|  | (°C) | (%) | (%) | (%) | (%) |
|  | 425 | 5.6 | 0.4 | 1.4 | 92.5 |
|  | 450 | 41.4 | 9.6 | 8.8 | 40.2 |
| Thick bed | 475 | 57.7 | 18.8 | 12.2 | 11.2 |
|  | 500 | 61.3 | 22.5 | 14.6 | 1.7 |
|  | 550 | 60.1 | 23.7 | 15 | 1.3 |
|  | 425 | 11.4 | 0.8 | 0.2 | 87.6 |
| Thin bed | 450 | 35.5 | 10.7 | 10.8 | 43.0 |
|  | 475 | 45.8 | 18.7 | 13.2 | 22.4 |
|  | 500 | 60.2 | 19.3 | 15.2 | 4.0 |
|  | 550 | 53.8 | 22.2 | 21.7 | 1.4 |



**FIGURE 5** High-density polyethylene (HDPE) pyrolysis behaviour from thin beds and thick beds under different temperatures and particle sizes (solid line: thick bed, dash line: thin bed)

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## 3.4 | Effect of temperature on the distribution of product composition from thin bed and thick bed pyrolysis

Temperature is a key process parameter in pyrolysis, affecting both the rate of thermal degradation and the stability of feedstock and reaction products.[6,33–35] As noted earlier, a preliminary study of HDPE pyrolysis in a temperature range between 400–550°C demonstrated the impact of the pyrolysis temperature on the mass change and the thermal stability of the sample. An obvious difference in product distribution between thin bed and thick bed FBPR was observed at the temperatures of 450, 475, 500, and 550°C. The waxes were found to be the predominant fraction with yield over 60% at 500°C for both beds (Figure 5 and Table 2). The yield of the wax, oil, and gaseous products increased with the pyrolysis temperature from 450–500°C. A similar result was also reported by Park et al.[11] However, the wax yield decreased at 550°C as HDPE pyrolysis at higher temperature generates lighter oil fractions, and also the heavier fraction (wax and tar) generated from HDPE pyrolysis is easier to crack into gases.[4,6,8,11,34,35] Williams and Williams[33] described similarly that the cracking reaction of heavier liquid products caused the increase of gas evolution at a higher temperature.

The temperature measurement is another major concern in the pyrolysis process. Flynn[36] mentioned that temperature errors may be the greatest source of uncertainty in the thermal analysis experiments. Different location of temperature sensors may result in a temperature gradient along the apparatus in the same experiment and processing, where the temperature of fused plastic in a fixed-bed batch reactor is much lower than the temperature on the top surface of the reactor.[37] The temperature measurement for a thin bed reactor can cause errors in the estimation of the temperature of the sample since small amounts of sample ($\approx$1 g) in the thin bed may displace thermocouples so that they are not in full thermal contact with samples after the plastic fusion. Thermocouple thermal lag is possible, which causes the difference between true sample temperature and an externally measured sample temperature.[38] This temperature lag may also bring noise in the temperature data so that the actual temperature in the thin bed is higher than the measured temperature; the higher temperature can boost additional cracking of heavier fractions due to the smaller amount of sample in the thin bed and hence a higher fraction of gases can be generated.

## 3.5 | Kinetic analysis

The estimation of the rate constant in the pyrolysis process is of crucial importance in model development.[39] In polymer degradation, pyrolysis processes usually involve a series of elementary reactions with different reaction mechanisms before reaching the final products. These elementary reactions (steps) may show different kinetic parameters. In this study, we adopt the discrete lumping methodology,[40] extrapolating the procedure successfully applied to cognate problems[41,42] to describe the kinetics of HDPE pyrolysis. Additionally, information on the experimental determination of the kinetics can be found in [27].

The different pathways in Figure 6 of HDPE pyrolysis were tested; a best fit to the experimental data from HDPE pyrolysis was proposed, shown in Figure 6B. This model contains three parallel reactions (lumps) and a secondary (wax cracking) reaction when the temperature is high enough; the most important one is the formation of liquids from waxes. To analyze the kinetic model
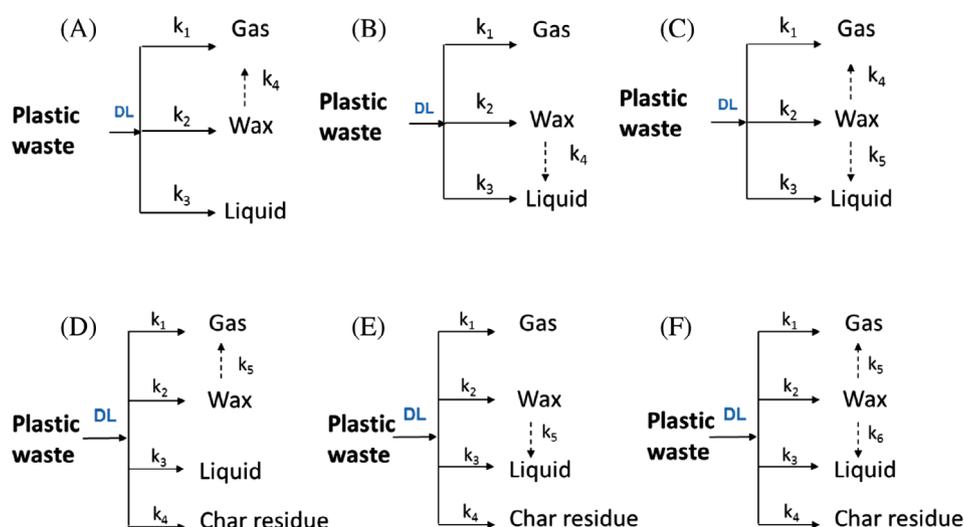


**FIGURE 6** Schematic of different pathways of high-density polyethylene (HDPE) pyrolysis

characteristics of the pyrolysis of plastic waste, the following assumptions were made: (1) all the reactions are assumed to be first-order; (2) all reactions are irreversible; (3) there is no mass transfer resistance and heat resistance limitation in the reactor; (4) the temperature dependence of rate constants follows Arrhenius' law; and (5) the pressure in the reactor is approximately atmospheric. Thus, this proposed model scheme is flexible and predictive to describe other first-order reaction systems such as thermal conversion of other plastics, biomass, and general polymeric material.

The three parallel decompositions and secondary cracking of HDPE pyrolysis for the four lumps scheme could be written as follows:

$$\frac{dx_{plastic}}{dt} = -(k_1 + k_2 + k_3)(1-x) \quad (1)$$

$$\frac{dx_{Gas}}{dt} = k_1(1-x) \quad (2)$$

$$\frac{dx_{wax}}{dt} = k_2(1-x) - k_4 x_{wax} \quad (3)$$

$$\frac{dx_{Liquid}}{dt} = k_3(1-x) + k_4 x_{wax} \quad (4)$$

where $x$, $k_1$, $k_2$, $k_3$, $k_4$, $k_5$, and $k_6$ represent normalized mass fraction of decomposed sample mass, the rate constant (min$^{-1}$) of the pyrolysis of plastic waste to the gas phase, wax fractions, liquid fractions, and wax fractions to oil phase and light liquid fractions during reaction, respectively, as displayed in Figure 6.

The kinetic parameters estimated in these models involve six rate constants, which are determined at three different temperatures. The numerical optimization of a fourth-order Runge–Kutta algorithm of the least square deviations is employed to calculate the parameters based on experimental data by minimizing the error between the experimental and calculated values for nonlinear objective functions. Model development used MATLAB software to determine the optimal parameters.

Table 3 presents the values of the rate constants obtained from the kinetic model. The model results show a good agreement with experimental data (Figure 7). In the primary pyrolysis step, it is clear that the rate constant of HDPE pyrolysis, $k_{HDPE}$ ($k_{HDPE} = k_{Gas} + k_{Oil} + k_{Wax}$), rises as the temperature increases, along with an increase in the rate constants for the production of gas, oil, and wax for both the thin bed and the thick bed. This result corresponds to the yield variation in the experimental study. However, a discrepancy in rate constants can be seen between thin and thick beds at different temperatures. A lower overall rate constant ($k_{Gas} + k_{Oil} + k_{Wax}$) to form gas, oil, and wax was observed in the thin bed at 450°C, while higher rate constants were found at 500 and 550°C. A similar trend of $k_{Oil}$, $k_{Wax}$, and $k_{Wax2Oil}$ (where $k_{Wax2Oil}$ is the rate constant of wax cracked into light oil) can be also seen in Table 3. This indicates that small sample amount and small particle size can enhance thermal conduction efficiency to provide better heat transfer,[31] especially at lower temperatures. The limitation of heat transfer from sample amount and particle size disappears with increased temperature.

The values of $k_{Gas}$ obtained from the thin bed are higher than those from the thick bed between 450–550°C. The values of $k_{HDPE}$ at 550°C from both thin bed and thick bed are far higher than the values at 450°C. The temperature can be a key parameter affecting the product distribution.[3,6] The value of $k_{Wax}$ is obviously larger than the values of $k_{Oil}$ and $k_{Gas}$ at the same temperature. A similar result can be seen in the literature.[4,6,14] The kinetic constant of wax cracking into oil is much lower than $k_{Oil}$. This indicates that the secondary cracking reaction of wax did not dominate the oil yield variation in the temperature range between 450–550°C during the pyrolysis process.

| | Temperature (°C) | Rate constant (s$^{-1}$) | | | | |
| --- | --- | --- | --- | --- | --- | --- |
| | | $k_{HDPE}$ (min$^{-1}$) | $k_{Gas}$ (min$^{-1}$) | $k_{Oil}$ (min$^{-1}$) | $k_{Wax}$ (min$^{-1}$) | $K_{Wax2Oil}$ (min$^{-1}$) |
| Thick bed | 450 | 0.0169 | 0.0035 | 0.0042 | 0.0092 | 0.000 61 |
| | 500 | 0.2716 | 0.0312 | 0.0625 | 0.1779 | 0.000 86 |
| | 550 | 0.8725 | 0.1164 | 0.2079 | 0.5482 | 0.001 73 |
| Thin bed | 450 | 0.0231 | 0.0042 | 0.0068 | 0.0121 | 0.000 51 |
| | 500 | 0.2095 | 0.0340 | 0.0421 | 0.1334 | 0.001 08 |
| | 550 | 0.8239 | 0.1836 | 0.1867 | 0.4536 | 0.002 06 |

**TABLE 3** Kinetic parameters of high-density polyethylene (HDPE) pyrolysis at different bed thicknesses and temperatures
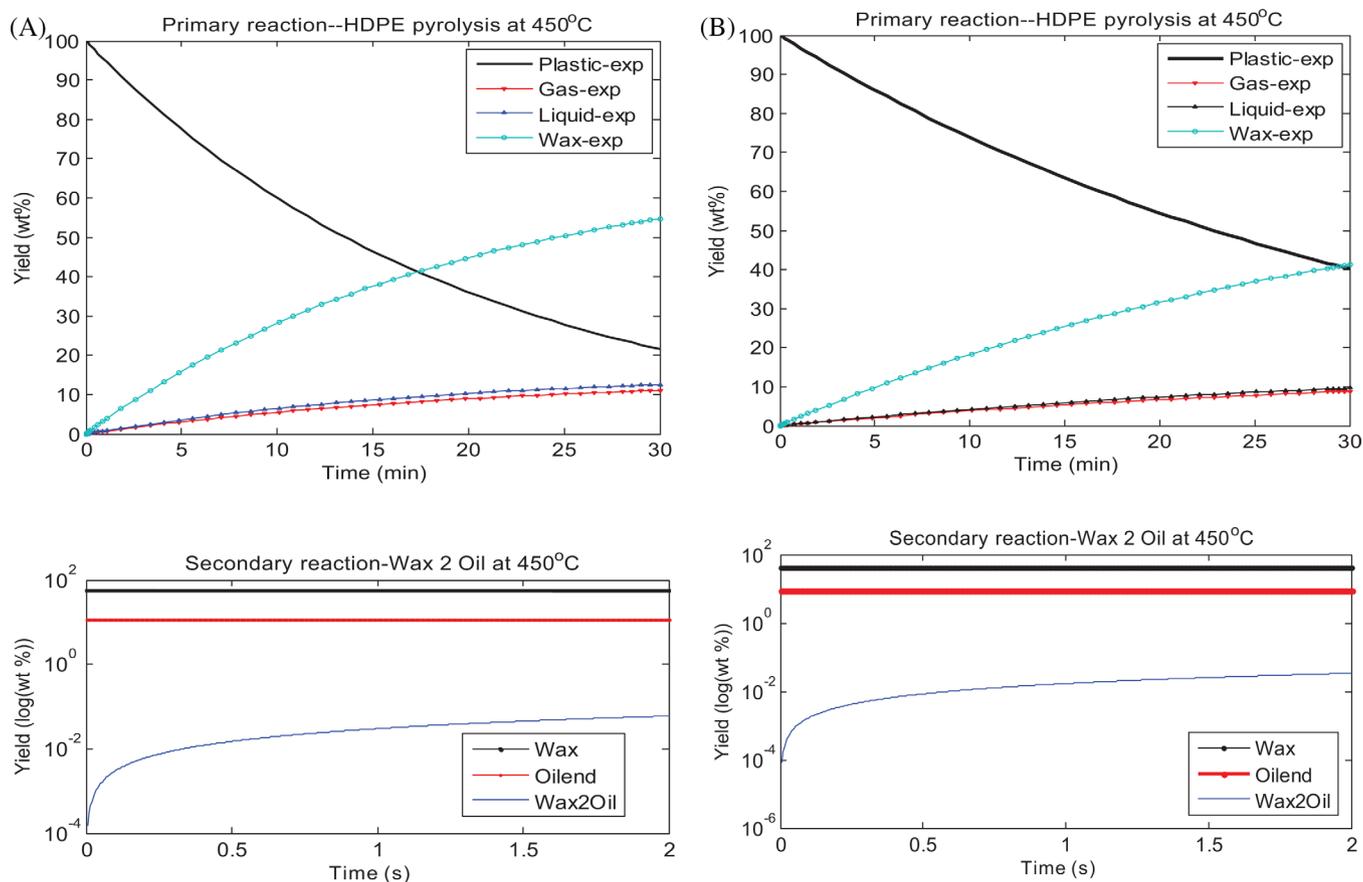
**FIGURE 7**    Model prediction of high-density polyethylene (HDPE) primary pyrolysis and secondary reaction at 450°C in (A) thin bed and (B) thick bed
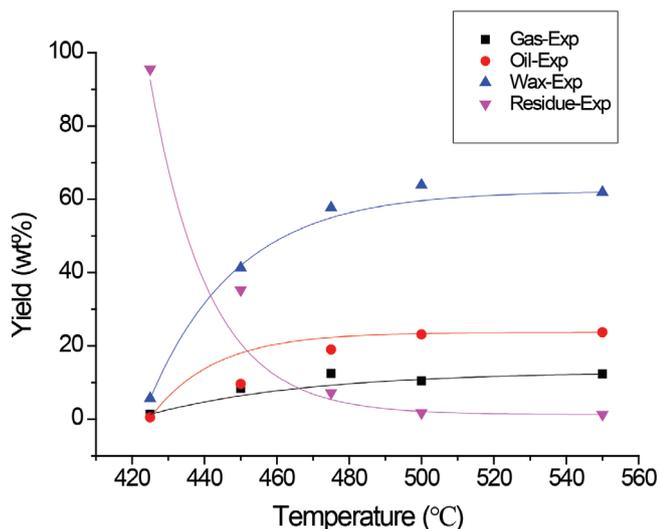


**FIGURE 8**    Model validation based on high-density polyethylene (HDPE) pyrolysis

Figure 7 shows that the model result fits well with the experimental data. A prediction of wax cracking within 1 s residence time was simulated for the cracking process (this is hypothetical time because it is difficult to control

the residence time of volatiles in the high-temperature zone in the reactor). The logarithmic yield of oil generated from wax cracking from $10^{-4}$–$10^{-2}$ occurred within 0.3 s in thin bed and 0.4 s in thick bed. This indicates that the cracking reactions occur in a very short time at reaction temperature. It can be concluded that thinner bed thickness has more effect on wax cracking.

Figure 8 compares the experimental results and the predictions of the kinetic model. The predicted data curves from the model agree well with the experimental data, and the model provides a reasonable result for HDPE pyrolysis.

### 3.5.1 | Estimation of activation energy and pre-exponential factor

Using the results obtained at 450, 500, and 550°C, the Arrhenius plots for the kinetic rate constants are shown in Figures 9–11 and Table 4. The slopes and intercepts of plots were used to calculate the activation energies and pre-exponential factors via linear regression. The overall activation energy of the HDPE thermal decomposition

process via TGA and FRPR with thin bed and thick bed were estimated to be 197.35, 177.58, and 196.78 kJ mol$^{-1}$, respectively. This result indicates that bed thickness can

cause the variation of kinetics estimation. Nevertheless, the values are in accordance with data in the literature (160–320 kJ mol$^{-1}$ estimated by Gao et al.[43]; 207–220 kJ mol$^{-1}$ estimated by Westerhout et al.[16]; 185–271 kJ mol$^{-1}$ estimated by Conesa et al.[44]; and 147.3 kJ mol$^{-1}$ estimated by Al-Salem and Lettieri[4]). The activation energies and pre-exponential factors for HDPE decomposition into gas, oil, and wax, and wax cracking into oil are summarized in Table 4 obtained from Figures 10 and 11.

The variation of the activation energy with conversion is possibly due to multiple competing reactions (steps) in HDPE degradation. The evaluation of activation energy represents the kinetics of the steps estimated which dominate the kinetic process.[45] Nevertheless, the presence of heteroatom groups and their uncertain content may influence the decomposition mechanism of HDPE to increase the variation of activation energy of HDPE decomposition.
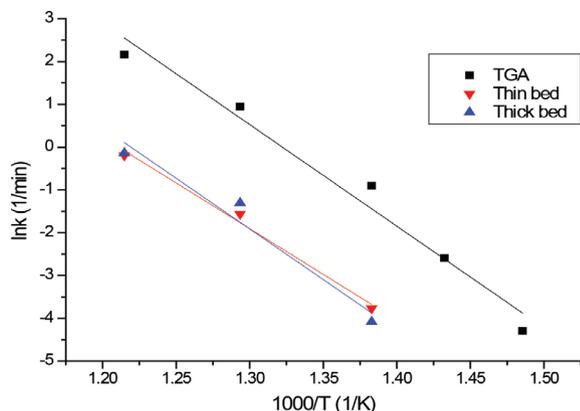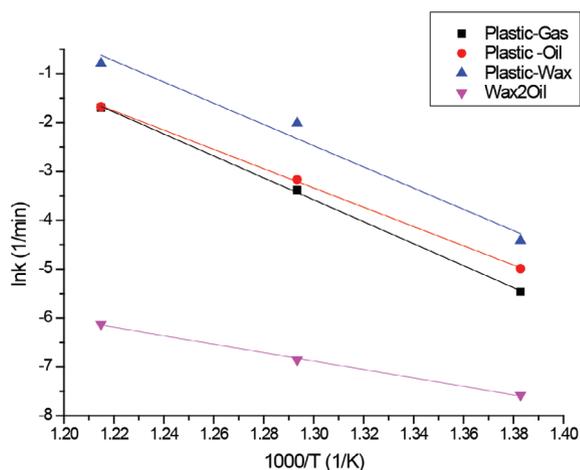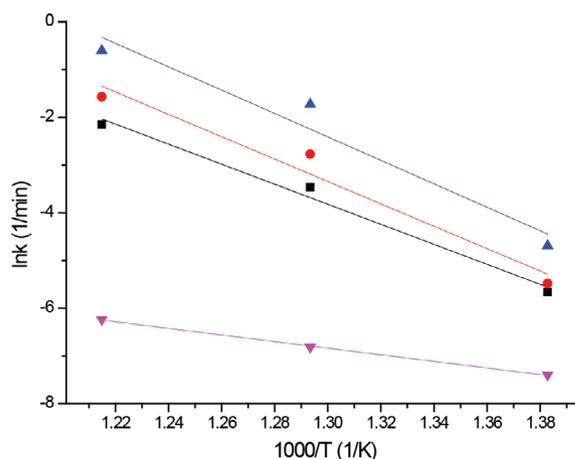


**FIGURE 9** Arrhenius plot of high-density polyethylene (HDPE) pyrolysis



**FIGURE 10** Arrhenius plot of high-density polyethylene (HDPE) pyrolysis into gas, oil, and wax from thin bed reactor



**FIGURE 11** Arrhenius plot of high-density polyethylene (HDPE) pyrolysis into gas, oil, and wax from thick bed reactor

| Reactor bed | Reaction pathways | E (kJ mol$^{-1}$) | A (min$^{-1}$) | R$^2$ |
|---|---|---|---|---|
| Thin bed | HDPE-gas, oil, and wax | 177.58 | 1.7E+11 | 0.9814 |
| | HDPE-gas | 174.40 | 1.52E+10 | 0.9989 |
| | HDPE-oil | 194.84 | 6E+11 | 0.9992 |
| | HDPE-wax | 203.92 | 6.31E+12 | 0.9564 |
| | Wax-oil | 57.45 | 8.54 | 0.9972 |
| Thick bed | HDPE-gas, oil, and wax | 196.77 | 3.4E+12 | 0.9254 |
| | HDPE-gas | 186.76 | 1.34E+11 | 0.9776 |
| | HDPE-oil | 164.09 | 4.92E+09 | 0.9347 |
| | HDPE-wax | 180.57 | 1.54E+11 | 0.9278 |
| | Wax-oil | 71.80 | 77.09 | 0.9975 |
| TGA | HDPE-volatile | 197.35 | 4.26E+13 | 0.9667 |

**TABLE 4** Kinetic parameters of reaction pathways of high-density polyethylene (HDPE) pyrolysis from different bed thickness and thermogravimetric analysis (TGA)

# 4 | CONCLUSIONS

The kinetic degradation behaviour of HDPE has been examined via TGA at different temperatures and for two different bed thicknesses in FBPR. Bed thickness presented a significant influence on product yield distribution at different temperatures. Higher yields of wax fractions were obtained in the FBPR with the thin bed at the lower temperature of 425°C. With increased temperature, higher wax yields in the thick bed of the FBPR were found in the temperature range of 450–550°C; also, more oil was generated in the thick bed of the FBPR in the whole temperature range investigated. Better heat transfer in thin bed may influence this difference. This result can also be helpful to inform the possible scale-up for pyrolysis processes from lab to pilot-scale, and then to commercial scale. The validation study of the first-order four lump kinetic model developed demonstrated a good agreement with experimental data from HDPE pyrolysis. The estimated overall apparent activation energy ($E_a$) and pre-exponential factor ($A_0$) of HDPE pyrolysis between 450–550°C via TGA and FBPR for thin bed and thick bed are in accordance with the results in the literature. Nevertheless, the estimated kinetics present some differences for different bed thickness. Following this model development, and its validation with experimental data, the proposed kinetic scheme is capable of predicting the thermal conversion of HDPE in practical applications.

## PEER REVIEW

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