CATALYTIC DEGRADATION OF HIGH DENSITY POLYETHYLENE AND ASSOCIATED MODEL

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Abstract: Catalytic degradation of high density polyethylene (HDPE) using silica-alumina has been investigated in a thermogravimetric analyser, and the degradation kinetics determined using a population balance model recently published by our laboratory. An earlier model used [1]considered only a single catalytic mechanism, and consequently under predicted the amount of gaseous products at high temperatures. The new model accounts for both thermal and catalytic modes of degradation acting in parallel, with the latter influenced by molecular size-dependent surface adsorption, yielding activation energies of about 256 kJ/mol and 174 kJ/mol respectively. This new model agrees better with experimental data than single mechanism models. Whilst catalytic cracking was predominant for most polymer chain sizes, this model shows that thermal cracking is responsible for the over cracking of molecules after desorption from the catalyst, leading to the formation of excessive gaseous products.

This model can predict product distributions while varying temperature and catalytic loading.

1. Introduction

The knowledge of the kinetics of catalytic degradation of high density polyethylene is important in many applications, including recycling. The breaking of the β bond, known as β-scission, is the most common method of cracking [2,3]. This paper reports the experiments performed, and new model developed, to determine the kinetic parameters.

2. Experimental Methods

The thermogravimetric (TGA) experiments were performed on a NETZSCH STA 409C, using silica-alumina (Si/Al ratio of 4.9) from Sigma Aldrich as the catalyst, and HDPE supplied by Qenos (polyethylene fluff). Experimental runs at loadings of 0% (thermal), 0.25%, 0.5%, 0.75%, 1%, 1.5% and 2% were performed using a heating rates of 1, 14 and 20 K/min until a constant temperature of 748 K was attained.

3. Model

Our model uses population balances to track the mass loss by evaporation as the cracking proceeds. The derivation of the model is beyond the scope of this short note, further details are provided in Sarathy et al[4].

There were two specific models used: the first assumed a single catalytic mechanism, while the second accounted for thermal and catalytic mechanisms occurring in parallel (Eq. (1). The former occurs by setting $A_{thermal} = 0$. Both are developed from that proposed by Wallis and Bhatia[5], but are improved with the incorporation of a term accounting for size dependent multisite adsorption of the molecules on the catalyst.

$$\frac{\partial N(x,t)}{\partial t}_{total} = \int_{y_{\min}}^{\infty} \frac{2}{y} A_{thermal} e^{\frac{-E_{thermal}}{RT}} y^{p} N(y,t)dy - A_{thermal} e^{\frac{-E_{thermal}}{RT}} x^{p} N(x,t)$$

$$+ \int_{y_{\min}}^{\infty} \frac{2z^{v-1}(1-z)^{v-1}}{yB(v,v)} A_{cat} e^{\frac{-E_{cat}}{RT}} \left(y - \frac{72-\tilde{x}_{\min}}{\tilde{x}_{avg}} \right) \frac{\theta(y,t)}{\upsilon(y)} dy - A_{cat} e^{\frac{-E_{cat}}{RT}} \left(x - \frac{72-\tilde{x}_{\min}}{\tilde{x}_{avg}} \right) \frac{\theta(x,t)}{\upsilon(x)} \quad \textbf{(1)}$$

where $x \geq \frac{72-\tilde{x}_{\min}}{\tilde{x}_{avg}}$ and y_{min} refers to the smallest molecule still in liquid form which is found from the following correlation derived by using a cubic line of best fit of the boiling points of n-paraffins[6].

$$x = 1.0673 \times 10^{-7} T^{3} - 6.1439 \times 10^{-5} T^{2} + 0.0339T - 2.5855 \quad \textbf{(2)}$$

The terms are defined as follows: $N(x,t)$ is the number density of the polymer at any dimensionless size x where x is defined as:

$$x = \frac{\tilde{x} - \tilde{x}_{min}}{\tilde{x}_{avg}} \quad \textbf{(3)}$$

The mass of the molecules in g/mol is defined by $\tilde{x}$, $\tilde{x}_{min}$ is the mass of the smallest carbon chain (methane at 16 g/mol), whilst $\tilde{x}_{avg}$ is the number average molecular weight of the polymer chains (5218.46 g/mol). $A_{thermal}$, A_{cat}, $E_{thermal}$, and E_{cat} refer to the pre exponential factors and activation energies of the thermal and catalytic portions, R is the universal gas constant and $B(v,v)$ is the beta function[7]. The parameter v[8,9] determines the width of the product distribution and was fixed at 4.54 which produced the best fit to experimental data in previous experiments[10].The value p was fixed equal 1, which assumes that breakage is linearly proportional to size. The number of catalytic sites a molecule of size x occupies is given by:

$$\upsilon(x) = N_{C}^{\kappa} \quad \textbf{(4)}$$

where N_C is the number of carbons, and κ was set equal to 2/3 – reflecting the relation between the molecular surface area and volume. A further assumption made is that after a size of 100 carbons, all molecules occupy the same number of sites

$\theta(x,t)$ is calculated from the following implicit equation

$$(N_c - 5)K_0 e^{-\frac{\Delta H^0}{RT(t)}} = \frac{\theta(x,t)}{\left(1 - \int_0^\infty \theta(x',t)dx'\right)^{N_c^K} X(x,t)} \tag{5}$$

$X(x,t)$ is the mole fraction of molecules of size x, K_0 and ΔH^0 represent the equilibrium parameters of adsorption, the factor $(N_C - 5)$ represents the number of carbon numbers adsorbed.

To solve the above population balance model we discretise using the fixed pivot method[11] to obtain a set of ordinary differential equations which are solved using MATLAB.

For the single catalytic mechanism, $A_{thermal}$ was set to 0, and Eq. (1) was fitted to data. For both methods simultaneously, it was necessary to find the thermal parameters, $A_{thermal}$, and $E_{thermal}$. This was done by fitting Eq. (1), with A_{cat} set to 0, to thermal experiments. Once known, they were substituted into Eq. (1) and fitted onto experimental data. The fitting parameters for both ways were A_{cat}, E_{cat}, K_0 and ΔH^0.

4. Results and Discussion

Fig. 1 depicts the experimental data and model fits at 20 K/min, showing excellent agreement between the model and experimental values for all cases. The quality of fit between the model and the experimental data was quantitively measured by the sum of squared residuals. The total sum of squared errors was 0.7381 (single catalytic mechanism) and 0.5408 (thermal and catalytic). Whilst it is clear that the separation of thermal and catalytic rates is more successful, both methods show considerable improvement over our recent model[1] which yielded a total sum of squared error of 1.3457 for data obtained here.

Fig. 2 compares a typical fit with the current model (thermal and catalytic rates separated) and the previous model (0.25% catalyst, 20 K/min). It can be seen that the previous model underestimated the rate of cracking at large time, causing it to have a larger error than the current model. The values of parameters are shown in Tab. 1.

Tab. 1 Parameters for catalytic kinetics used in model fit

parameter	Catalytic parameters and mechanism considering catalytic and thermal rates	Mechanism assumed purely catalytic
E (kJ/mol)	173.95	185.95
$-\Delta H^0$ (kJ/mol)	7.884	7.873
K_0 (-)	2.089×10^{-4}	2.089×10^{-4}

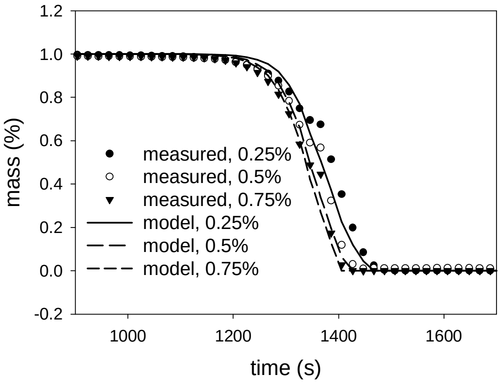

Fig. 1. Experimental data and model fits, for a model [1]Heat in rate of 20 K/min and catalyst loadings of 0.25%.

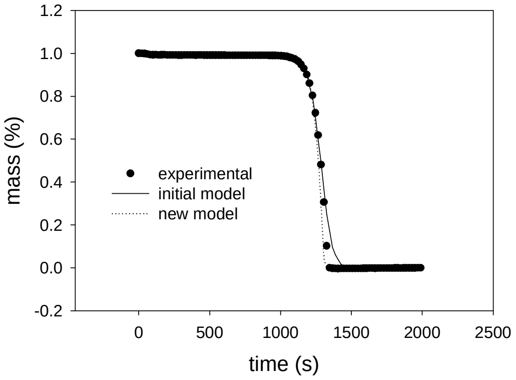

Fig. 2. Comparison between previous and new model. Heating rate = 20 K/min.

Thus the novel consideration of the multisite adsorption in the current model yields considerable improvement over the conventional homogenous model such as that adopted earlier[1].

The overall activation energy with the kinetics represented by a mechanism with a single rate constant, was found to be 185.95 kJ/mol, comparing favourably with Hara et al[12] who calculated 188 kJ/mole for β scission (catalytic cracking). The thermal activation energy was found to be 256.44 kJ/mole, in excellent agreement with published data by Lin et al[13] of 256.11 kJ/mole when calculated by the Ozawa[14] method. When subsequently isolating the catalytic rate constant while considering both the thermal and catalytic mechanisms as simultaneously operative, it was found that the activation energy of the catalytic reaction is 173.95 kJ/mol.

The ratio of the thermal rate to the overall rate was plotted against conversion for a range of molecular sizes and catalytic loadings. Fig. (3) shows that C_5 is predominately formed by thermal cracking, half the C_{12} is formed thermally, and a large portion of C_{16} forms catalytically. Hence it is surmised that a two step process naturally occurs: initially the catalyst cracks the polymer, producing mainly liquid products which then desorb; then these products crack further, by a thermal process, into lighter liquids and gaseous products. This finding has major implications for reactor and process design if a specific size range (i.e. petrol, diesel) is to be created.

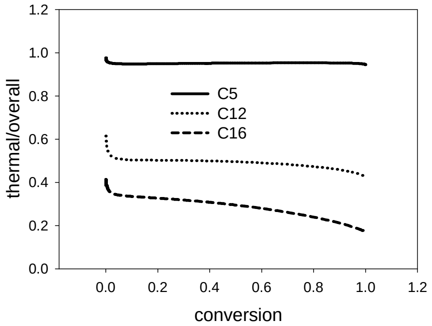

Fig. 3 Ratio of thermal rate / overall rate for 2% catalytic loading

5. Conclusion

Our strategy of incorporating multisite adsorption in the model greatly enhanced the fit and was successful in determining the kinetic parameters, with the activation energy values determined (E_{single} = 185.95 kJ/mol) being more consistent with published data than a previous model that overlooks adsorption-desorption effects. Further, the strategy of separating the thermal and catalytic contributions led to a better fit than the traditional method of assuming a single catalytic mechanism. It is proposed that a two step process occurs with the initial catalytic cracking to liquid (E_{cat} = 173.95 kJ/mol) followed by thermal cracking ($E_{thermal}$ = 256.44 kJ/mol) to a gas.

Acknowledgments

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