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Kinetic study of the catalytic cracking of polypropylene in a semibatch stirred reactor

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Abstract

A lumped kinetic model including both thermal and catalytic cracking and catalyst decay has been developed for the cracking of polypropylene in a semibatch stirred reactor. Two decay equations in where the catalyst decay is either a function of time on stream or function of coke on catalyst have been tested. The kinetic model fits very well the experimental results and is able to simulate the process in a wide range of operating conditions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Polypropylene; Catalytic cracking; Thermal cracking; USY zeolite; FCC equilibrium catalyst; Deactivation; Kinetics

1. Introduction

Nowadays, tertiary recycling is growing in importance as a feasible solution for the treatment of plastic wastes. Within the different options, catalytic cracking of plastic wastes by direct contact with a cracking catalyst seems to be an attractive alternative. Therefore, work has been done on the direct catalytic cracking of different type of plastics, using a large variety of catalysts and reaction systems [1–10]. Nevertheless, the economical feasibility of the process is enormously affected by the cost of the catalyst. We have proved in the laboratory that the catalytic cracking of plastic wastes of polypropylene (PP) and low density polyethylene (LDPE) by direct contact with a spent equilibrium FCC catalyst, with practically zero catalyst cost, is technically feasible [9,10]. However, the scale-up of such a process requires the development of a kinetic model that will help in the design of an industrial reactor, and/or in the simulation of the process under different operating conditions.

Much work has been done on the kinetics of the thermal cracking of plastic wastes [11–14], but little on the catalytic cracking, and this has been mainly done by using thermogravimetric techniques (TGT) [2,8,15]. TGT implies the use of reduced amounts of polymer and catalyst (in the order of milligrams) and the results are affected by mass transfer problems, with the corresponding limitations when a realistic model for the design or simulation of reactors for the catalytic cracking of plastic wastes has to be developed. The most realistic kinetic study of the catalytic cracking of plastics is that of Lin et al. [5], based on a lumping reaction scheme for the products which takes into account the catalyst deactivation. However, this was obtained using a laboratory fluidized bed reactor, and the results cannot be extrapolated to other reaction options that can also be realistic. For instance in the case of a process using a semibatch stirred reactor, this will use much lower nitrogen flows and catalyst to plastic ratios than the fluidized bed reactor, with longer catalyst/plastic contact times.

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Nomenclature

a	degree of polymerization of the largest molecule that can evaporate from the reactor
E	activation energy (kJ mol^{-1})
k_d	decay parameter (min^{-1})
k_{ic}	kinetic rate constant for the *i*th product in catalytic cracking (g min^{-1} gcat^{-1})
k_{it}	kinetic rate constant for the *i*th product in thermal cracking (min^{-1})
m_0	initial mass of plastic loaded in the reactor (g)
$m_P(t)$	remaining mass of plastic at time t (g)
P_0	initial degree of polymerization of the plastic
$P(t)$	degree of polymerization of the plastic at time t
R_{ic}	extensive reaction rate of *i*th product in catalytic cracking (g min^{-1})
R_{it}	extensive reaction rate of *i*th product in thermal cracking (g min^{-1})
SSR	sum of the squares of the residuals
t	time (min)
W	catalyst mass (g)
X(%)	conversion (%)
Y_i(%)	yield to product i (%)

Greek letters

α	decay parameter (min^{-1})
$\phi(t)$	catalyst decay function

In this work, we have developed a kinetic model for the cracking of plastic wastes in a semibatch stirred reactor. The model takes into account both thermal and catalytic cracking, including catalyst decay, and consequently allow us to simulate the process under different operating conditions.

2. Experimental

2.1. Materials

The PP was provided by Repsol (PP-050, $M_n = 69\,800$) in the form of pellets and it was used without additional treatment. The catalysts studied were a USY zeolite (CBV 712) and an equilibrium FCC commercial catalyst (Resoc-g), provided by Cepsa. The catalysts were pelletized, crushed and sieved and particles with sizes 0.25–0.42 mm were used. The catalyst characterization is given elsewhere [9].

2.2. Reactor and experimental procedure

The catalytic tests were performed in a stainless steel semibatch stirred reactor, at atmospheric pressure under a nitrogen flow, whose detailed description and experimental procedure is given elsewhere [9]. In each catalytic experiment, 24.5–35.0 g of PP were loaded into the reactor and 0.7–1.5 g of catalyst were stored into the catalyst tank. The reactor was continuously purged with a nitrogen flow (21 ml/min) and heated by an electric furnace. Stirring (960 rpm) was started after the polymer melted. When the temperature inside the reactor reached the reaction temperature (340–380 °C), the catalyst was introduced into the reactor and this was considered as the zero reaction time. At different time intervals, liquid and gaseous products were collected in several glass receivers and their associated gas burettes, respectively. The total reaction time was variable, depending on the operating conditions. At the end of the experiment, the reactor was cooled at room temperature. Thermal cracking tests were carried out in a similar way but without catalyst.

2.3. Products analysis

The reaction products were classified from an analytical point of view into gases, liquid hydrocarbons and residue (waxy compounds + coke deposited on the catalyst), and from a kinetic point of view into gases, gasoline and diesel + gasoil. The gaseous products were analyzed using a HP-5890 GC equipped with two capillary columns connected in series with TCD and FID detectors. The first column separates H_2, N_2 and CH_4 (molecular sieve 15 m × 0.53 mm i.d.), while the second column separates hydrocarbons C_2–C_6 (alumina 50 m × 0.53 mm i.d.). The liquid products were analyzed by simulated distillation (ASTM-D 2887) in a Varian 3400 GC equipped with FID and a DB5 capillary column, fused silica 15 m × 0.53 mm i.d. Fractions used for processing the results of simulated distillation were: gasoline boiling point (BP) $\leq$ 235.4 °C, and diesel + gasoil BP>235.4 °C.

2.4. Mass balance

The mass balance was calculated as the ratio between the sum of weights of gas, liquid and residue and the weight of the feed, so that only those experiments giving mass balances above 95% were considered as valid. Hydrogen and C_1–C_4 were taken as gases, while C_5–C_6 analyzed in the gas stream were added to the liquid composition.

The yield to one product for a determined reaction time, Y_i, was the ratio between the weight of that product accumulated during that period of time and the weight of the feed. The conversion, X, was the sum of the yields to all the products and the selectivity to one product was the ratio between yield and conversion.

3. Results and discussion

3.1. Kinetic model

The lumped kinetic model proposed here is based on the reaction pathway shown in Fig. 1, where $k_{i\mathrm{t}}$ and $k_{i\mathrm{c}}$ are the kinetic rate constants for thermal and catalytic cracking, respectively. We suppose that thermal and catalytic cracking of plastic occur simultaneously when the catalyst is introduced into the reactor, both take place only in the liquid phase and are competitive (parallel) reactions. Catalytic cracking occurs on the acid sites of the catalyst (carbocation mechanism), while thermal cracking occurs in the bulk of the melted plastic (radical mechanism).

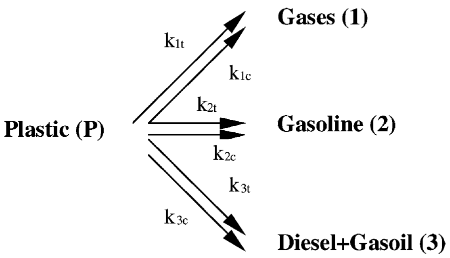

Fig. 1. Reaction pathway for the kinetic model of thermal and catalytic cracking of plastics in a semibatch stirred reactor. Subscript “c” refers to catalytic cracking, while “t” refers to thermal cracking.

Taking into account our reaction system, we have assumed that all the reaction lumped products formed in the liquid phase evaporate immediately after being formed and are collected outside the reactor. In agreement with this we have then considered that no accumulation of reaction products in the liquid phase occur and consequently recracking of products does not need to be considered. One could reach a similar conclusion on recracking just by considering that the melted plastic has a much higher adsorption enthalpy than the cracked products and, consequently, recracking could only compete when the remaining melted plastic will be very low. This, together with the fact that in our reaction system the products are really removed from the reaction media, should make the recracking of primary products negligible. Indeed, when the yield to diesel + gasoil is plotted versus total conversion (Fig. 2), there is not a decrease in the slope of the line that will indicate an unstability by recracking.

Based on the above assumption, the reaction scheme from Fig. 1 and the reactor used (Fig. 3), the following can be elaborated. In Eq. (1), the kinetic rate expression for thermal cracking is given as taken from [12,14]:

$$R_{i\mathrm{t}}\,(\mathrm{g\,min^{-1}}) = k_{i\mathrm{t}}\frac{m_{\mathrm{P}}(t)}{P(t)}(a+1)a \tag{1}$$

where

$$P(t) = (a+1) + \frac{1}{(\exp((k_{1t}+k_{2t}+k_{3t})t)/C) - 1} \tag{2}$$

$$C = \frac{P_0 - a - 1}{P_0 - a} \tag{3}$$

and m_{P} is the remaining mass of plastic (g) at time t, $k_{i\mathrm{t}}$ the kinetic rate constant ($\mathrm{min^{-1}}$) for the ith product in thermal cracking, while P_0 the initial degree of polymerization of the plastic (calculated from M_n), and a the degree of polymerization of the largest molecule than can evaporate from the reactor (determined experimentally).

For catalytic cracking, we propose the following kinetic expression:

$$R_{i\mathrm{c}}\,(\mathrm{g\,min^{-1}}) = Wk_{i\mathrm{c}}\frac{m_{\mathrm{P}}(t)}{m_0}\phi(t) \tag{4}$$

where W is the mass of catalyst (g), m_0 the initial mass of plastic (g) loaded, $k_{i\mathrm{c}}$ the kinetic rate constant

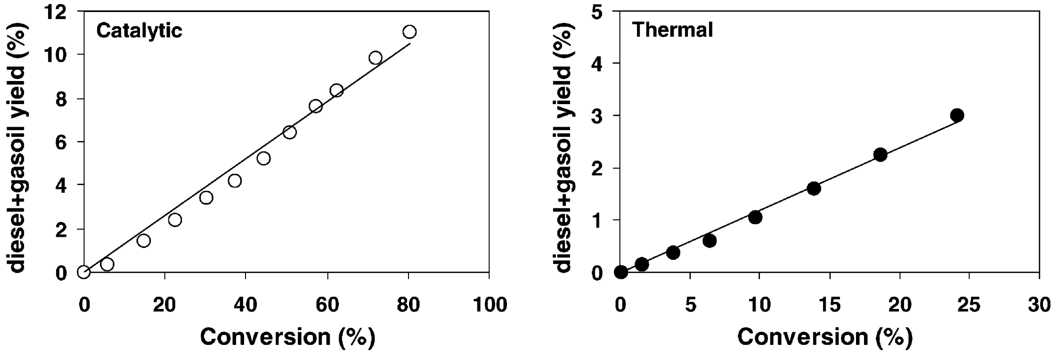

Fig. 2. Yield to diesel + gasoil versus conversion for thermal (●) and catalytic cracking (○) of PP. Reaction conditions for catalytic cracking with Resoc-g (0.25–0.42 mm) are $T = 380\,^{\circ}\mathrm{C}$ and catalyst/plastic = 1.5/35.0 (w/w), while for thermal cracking, $T = 380\,^{\circ}\mathrm{C}$ and 35.0 g of plastic.

($\mathrm{g\,min^{-1}\,gcat^{-1}}$) for the ith product in catalytic cracking and $\phi(t)$ the catalyst decay function. A first reaction order with respect to plastic has been adopted with the aim of reducing the number of adjustable parameters, and the same catalyst decay function has been considered for all the parallel cracking reactions.

As catalyst decay functions, we have tested two equations used for catalytic cracking of hydrocarbons, where the catalyst decay is either a function of time on stream [16]:

$$\phi(t) = \exp(-\alpha t) \tag{5}$$

or a function of coke on catalyst [17]:

$$\frac{\mathrm{d}\phi}{\mathrm{d}t} = -k_{\mathrm{d}}\phi^2\frac{X(\%)}{100} \tag{6}$$

which is derived from

$$\phi = \exp(-\beta C_{\mathrm{C}}) \tag{7}$$

where C_{C} is the concentration of coke formed over the catalyst and β an adjustable parameter. The decay parameters for Eqs. (5) and (6) are α and k_{d} ($\mathrm{min^{-1}}$), respectively.

Applying a non-steady state mass balance on the volume of control depicted in Fig. 3 over each lumped product, considering the rate of thermal and catalytic cracking described above, and introducing the definitions of conversion and yields to products, the following dynamic model is obtained:

$$\left(\frac{k_{i\mathrm{t}}}{P(t)}(a+1)a+\frac{W}{m_0}k_{i\mathrm{c}}\phi(t)\right)(100-Y_1(\%)-Y_2(\%)-Y_3(\%))=\frac{\mathrm{d}Y_i(\%)}{\mathrm{d}t}\quad i=1,2,3 \tag{8}$$

Combination of Eqs. (8) and (5) constitutes Model 1, while (8) and (6) define Model 2. If we set

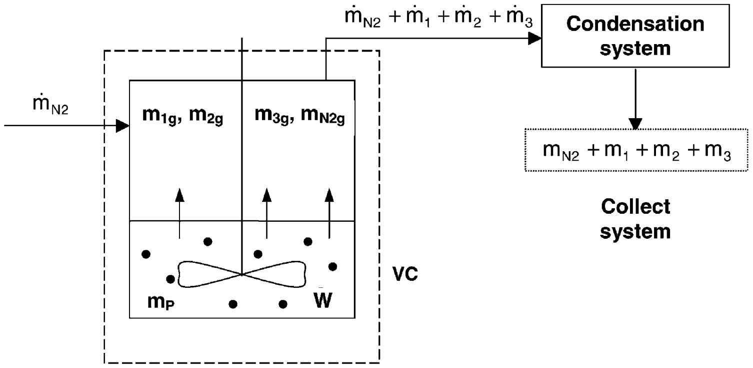

Fig. 3. Schematic drawing for the semibatch stirred reactor.

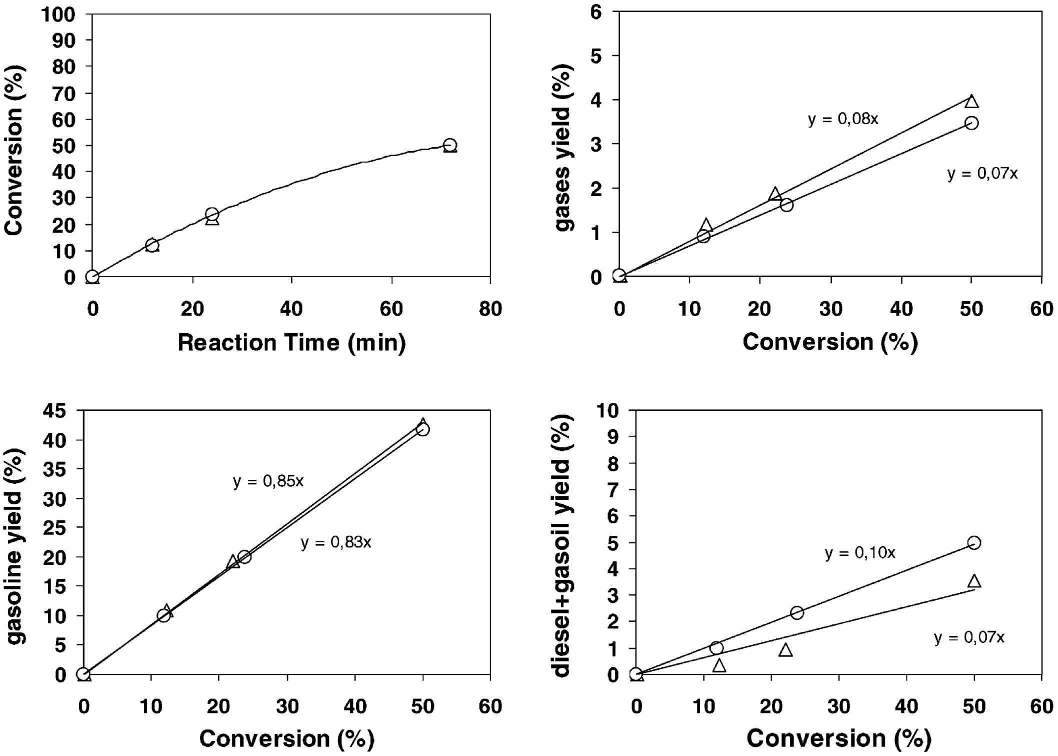

Fig. 4. Effect of W/m_0 ratio in catalytic cracking of PP at 380 °C, using H-USY 712 (0.42–0.59 mm) as catalyst: $W/m_0 = 1.0/35.0$ (w/w) (○) and $W/m_0 = 0.7/24.5$ (w/w) (△).

$W = 0$ in both models, only thermal cracking can be simulated.

Fitting of the experimental results to the models was carried out by minimizing the sum of the squares of the residuals (SSRs) by means of the Levenberg–Marquardt's algorithm:

$$\mathrm{SSR} = \sum_{j=1}^{N\,\mathrm{exp}} [(Y_1(\%)_j^{\mathrm{exp}} - Y_1(\%)_j^{\mathrm{cal}})^2 + (Y_2(\%)_j^{\mathrm{exp}} - Y_2(\%)_j^{\mathrm{cal}})^2 + (Y_3(\%)_j^{\mathrm{exp}} - Y_3(\%)_j^{\mathrm{cal}})^2] \quad (9)$$

3.2. Kinetic results

Since the kinetic model does not contemplate mass transfer steps, the experiments were carried out using sufficiently small catalyst particle size and high stirring velocity for which was seen that reaction was not mass transfer-limited. Since W/m_0 ratio appears as a control variable in the kinetic model, we have proved that modifications in the amounts of W and m_0 does not affect as far as W/m_0 ratio remains constant (Fig. 4).

Fig. 5 shows the experimental results obtained at different reaction temperatures for thermal and catalytic cracking of PP when using an equilibrium FCC catalyst. It has been found that the experimental results fit very well the proposed models, and the best fitted parameters for thermal and catalytic cracking are given in Tables 1 and 2, respectively. It can be seen that the kinetic rate constants for thermal cracking are considerably lower than those for catalytic cracking. We can also see that, regardless of the model used, the decay constant decreases when increasing temperature. This agrees with the fact that exothermic bimolecular hydrogen transfer reactions leading to coke become relatively less important when increasing the reaction temperature [18]. The SSR for Model 1 are

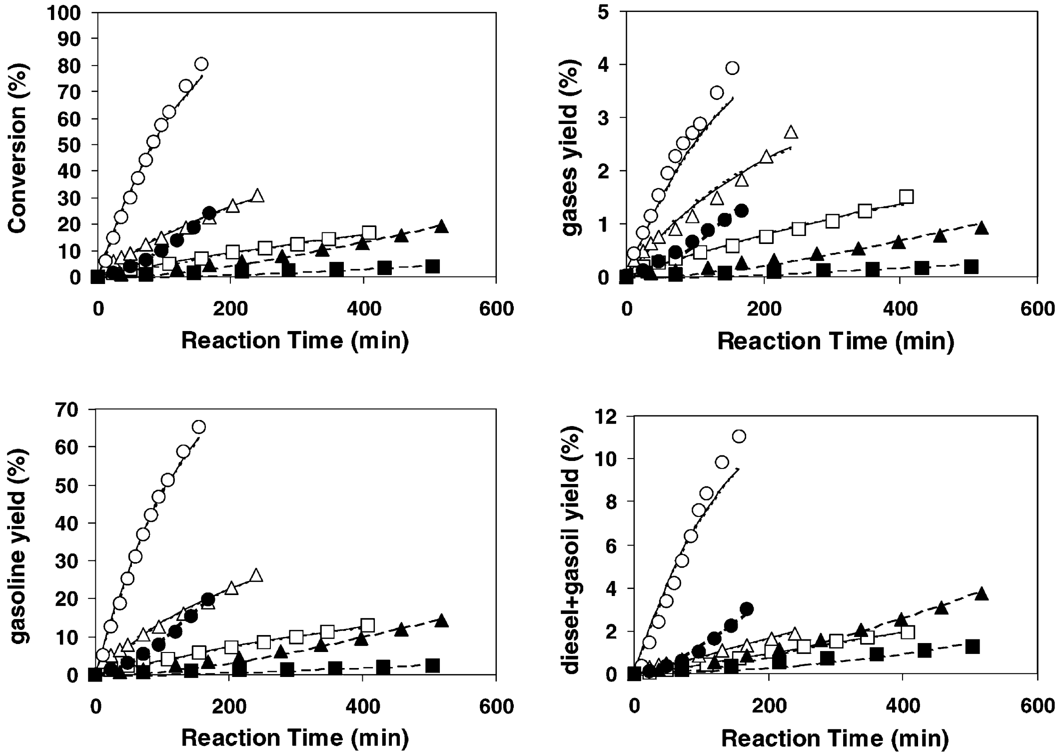

Fig. 5. Experimental results for thermal ((■): 340 °C, (▲): 360 °C, (●): 380 °C) and catalytic cracking ((□): 340 °C, (△): 360 °C, (○): 380 °C) of PP. Reaction conditions for catalytic cracking with Resoc-g (0.25–0.42 mm) are catalyst/plastic = 1.5/35.0 (w/w), while for thermal cracking are 35.0 g of plastic. Lines correspond to calculated values: Model 1 (——), Model 2 (. . .) and thermal model (– –).

slightly lower than that for Model 2, although small differences in the values of the kinetic rate constants were obtained.

The selectivity towards the gasoline fraction is higher than that of gases and diesel + gasoil in the range of temperatures studied. Although the selectivity towards the gas fraction decreases when increasing the temperature, the gasoline fraction shows a maximum at 360 °C and decreases at higher temperatures, while the diesel + gasoil fraction increases. This behavior can be explained taking into account the competing effects between cracking and evaporation of the reaction products, whose relation varies with temperature. At the range of temperatures studied here and higher, the reaction products of higher boiling point leave the reactor avoiding recracking and consequently increasing the diesel + gasoil fraction [10]. It should also be taken into account for selecting the best reaction temperature that at higher temperatures than the ones studied here the relative contribution of thermal cracking increases, increasing therefore the selectivity to diesel + gasoil.

Table 1
Best fitted parameters for thermal cracking ($P_0 = 4986, a = 30$)

T (°C)	$k_t = \Sigma k_{it}$ (min^{-1})	k_{1t} (min^{-1})	k_{2t} (min^{-1})	k_{3t} (min^{-1})	SSR (%)
340	2.17×10^{-5}	$1.16 \times 10^{-6} \pm 1.78 \times 10^{-6}$	$1.36 \times 10^{-5} \pm 1.49 \times 10^{-6}$	$6.87 \times 10^{-6} \pm 1.60 \times 10^{-6}$	1.51
360	5.14×10^{-5}	$2.68 \times 10^{-6} \pm 1.34 \times 10^{-6}$	$3.86 \times 10^{-5} \pm 1.12 \times 10^{-6}$	$1.01 \times 10^{-5} \pm 1.28 \times 10^{-6}$	5.21
380	1.80×10^{-4}	$1.02 \times 10^{-5} \pm 2.68 \times 10^{-6}$	$1.48 \times 10^{-4} \pm 2.25 \times 10^{-6}$	$2.14 \times 10^{-5} \pm 2.63 \times 10^{-6}$	1.43

Table 2
Best fitted parameters for catalytic cracking with Model 1 and Model 2 ($P_0 = 4986, a = 30$)

T (°C)	$k_c = \Sigma k_{ic}$ ($\mathrm{g\,min^{-1}\,gcat^{-1}}$)	α ($\mathrm{min^{-1}}$)	k_{1c} ($\mathrm{g\,min^{-1}\,gcat^{-1}}$)	k_{2c} ($\mathrm{g\,min^{-1}\,gcat^{-1}}$)	k_{3c} ($\mathrm{g\,min^{-1}\,gcat^{-1}}$)	SSR (%)	k_{1c}/k_c (%)	k_{2c}/k_c (%)	k_{3c}/k_c (%)
Model 1									
340	1.21×10^{-2}	$1.99 \times 10^{-3} \pm 3.18 \times 10^{-4}$	$1.11 \times 10^{-3} \pm 1.26 \times 10^{-4}$	$9.96 \times 10^{-3} \pm 4.36 \times 10^{-4}$	$9.95 \times 10^{-4} \pm 1.25 \times 10^{-4}$	0.46	9.2	82.5	8.3
360	4.63×10^{-2}	$4.37 \times 10^{-3} \pm 1.06 \times 10^{-3}$	$4.05 \times 10^{-3} \pm 9.69 \times 10^{-4}$	$4.04 \times 10^{-2} \pm 3.24 \times 10^{-3}$	$1.94 \times 10^{-3} \pm 9.35 \times 10^{-4}$	6.56	8.7	87.1	4.2
380	1.74×10^{-1}	0.0	$7.36 \times 10^{-3} \pm 2.64 \times 10^{-3}$	$1.45 \times 10^{-1} \pm 4.33 \times 10^{-3}$	$2.22 \times 10^{-2} \pm 2.78 \times 10^{-3}$	35.31	4.2	83.0	12.8
E ($\mathrm{kJ\,mol^{-1}}$)			157.9	222.7	256.8				
T (°C)	$k_c = \Sigma k_{ic}$ ($\mathrm{g\,min^{-1}\,gcat^{-1}}$)	k_d ($\mathrm{min^{-1}}$)	k_{1c} ($\mathrm{g\,min^{-1}\,gcat^{-1}}$)	k_{2c} ($\mathrm{g\,min^{-1}\,gcat^{-1}}$)	k_{3c} ($\mathrm{g\,min^{-1}\,gcat^{-1}}$)	SSR (%)	k_{1c}/k_c (%)	k_{2c}/k_c (%)	k_{3c}/k_c (%)
Model 2									
340	1.10×10^{-2}	$3.47 \times 10^{-2} \pm 8.96 \times 10^{-3}$	$1.02 \times 10^{-3} \pm 1.38 \times 10^{-4}$	$9.11 \times 10^{-3} \pm 3.96 \times 10^{-4}$	$9.11 \times 10^{-4} \pm 1.38 \times 10^{-4}$	0.69	9.2	82.5	8.3
360	4.24×10^{-2}	$4.47 \times 10^{-2} \pm 1.69 \times 10^{-2}$	$3.71 \times 10^{-3} \pm 1.00 \times 10^{-3}$	$3.70 \times 10^{-2} \pm 2.94 \times 10^{-3}$	$1.78 \times 10^{-3} \pm 9.74 \times 10^{-4}$	8.52	8.7	87.1	4.2
380	1.74×10^{-1}	0.0	$7.36 \times 10^{-3} \pm 2.64 \times 10^{-3}$	$1.45 \times 10^{-1} \pm 4.33 \times 10^{-3}$	$2.22 \times 10^{-2} \pm 2.78 \times 10^{-3}$	35.31	4.2	83.0	12.8

4. Conclusions

A semibatch reaction system has been found adequate to carry out in the laboratory the catalytic cracking of PP and PE and to produce kinetic results. A kinetic model that includes both thermal and catalytic cracking has been developed which fits very well the experimental results. The model and kinetic parameters obtained allow the simulation of the process and catalyst behavior in a wide range of reaction conditions.

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