Product distribution modelling in the thermal pyrolysis of high density polyethylene

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Abstract

The thermal fast pyrolysis of high density polyethylene (HDPE) has been carried out in a conical spouted bed reactor in the 450–715 °C range, and individual products have been monitored with the aim of obtaining kinetic data for the design and simulation of this process at large scale. Kinetic schemes have been proposed in order to explain both the results obtained in the laboratory plant and those obtained in the literature by other authors operating at laboratory and larger scale. Discrimination has been carried out based on the contribution of the variance of model parameters (stepwise regression) to the total variance explained by the model. The models based on that of Westerhout et al. [R.W.J. Westerhout, J. Waanders, W.P.M. Van Swaaij, Recycling of polyethene and polypropene in a novel bench-scale rotating cone reactor by high-temperature pyrolysis. Ind. Eng. Chem. Res. 37 (6) (1998) 2293–2300] do not adequately predict the experimental results, especially those corresponding to aromatics and char, which is probably due to the very short residence times attained in the conical spouted bed and, consequently, to the lower yields of aromatics and char. The model of best fit is the one where polyethylene degrades to give gas, liquid (oil) and wax fractions. Furthermore, the latter undergoes secondary reactions to give liquid and aromatics, which in turn produce more char.
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1. Introduction

In today's society, plastics provide a fundamental contribution to all major daily activities and consequently, their production and use are increasing sharply. Thus, 32 million tonnes were produced in Western Europe in 2004 [2], of which 21 million tonnes were polyolefins and 5 million tonnes of these were high density polyethylene. The disposal of used plastics has become a serious problem. Today, only a small percentage (approximately 10%) of plastic waste is recycled and disposal is mainly by landfill or incineration, both associated with environmental problems. An alternative process to convert and upgrade plastic wastes is through the application of fast pyrolysis technology.

Pyrolysis is a very versatile process, given that it allows for the simultaneous feed of a variety of wastes of polymeric nature (tyres, biomass, plastics and so forth) in order to upgrade them together. Furthermore, different operating strategies may be established in order for the products obtained to be used in different applications. Thus, there are two interesting variables in these strategies: operating temperature (thermal pyrolysis) and the use of catalysts (catalytic pyrolysis).

Kinetic knowledge is essential for the determination of the optimum conditions for maximization of a given product [3] and for the design and simulation of commercial reactors [4]. In this sense, although polyethylene and polypropylene pyrolysis have been widely studied, the kinetic studies published in the literature are not suitable for reactor design, given that they are mostly studies carried out in a microreactor [5,6], under very different operating conditions to those of industrial reactors. Furthermore, the studies published up until now are simple approaches that exclusively describe the weight loss of the feed [7] and, in the few studies that follow product formation, secondary reactions are not taken into account (although they are essential for a proper explanation of the experimental results), or a kinetic mechanism is proposed but no kinetic parameters are determined.

Amongst the models in the literature, the one based on lumps is more suitable for reactor design, given that it allows for ascertaining the conditions for optimization of a given product or group of products. According to Westerhout et al. [1], polyolefin thermal decomposition takes place following a random degradation mechanism, Fig. 1. Based on this fact, they are able to relate temperature to product formation.

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Nomenclature

Φ, Φ_t, Φ_x overall objective function

ω_t, ω_x weight factors for final reaction time and yield objective functions

dX_i/dt formation rate of i reactant (s^{-1})

E_a activation energy (kJ mol^{-1})

F value of F statistics (ratio of mean square sums)

F_c critical value of Fischer distribution

k_0 frequency factor

k_{AC} kinetic constant for the formation of char from aromatics

k_{PG} kinetic constant for the formation of gas from the plastic (s^{-1})

k_{PL} kinetic constant for the formation of liquid from the plastic (s^{-1})

k_{PW} kinetic constant for the formation of waxes from the plastic (s^{-1})

k_{WA} kinetic constant for the formation of aromatics from waxes

k_{WL} kinetic constant for the formation of liquid from waxes

$\dot{m}_i$ mass flow rate of each i component (kg s^{-1})

M_0 total mass of plastic in the feed (kg)

M_i mass of lump i formed up to a given time (kg)

n_l number of lumps of each scheme

n_T number of temperature values

T temperature (°C)

t_i, $t_{i(calc)}$ experimental and calculated values of time required for degrading the sample at each i temperature (s)

X_i, $X_{i(calc)}$ experimental and calculated yields of each lump (kg$_{lump}$ kg$_{feed}$$^{-1}$)
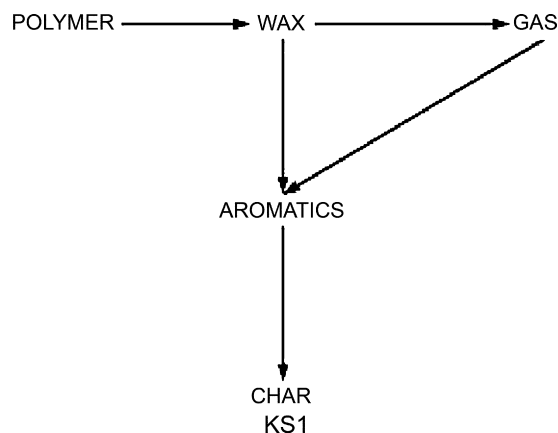

Fig. 1. The kinetic scheme proposed by Westerhout et al. [1].

2. Experimental

In this study, a conical spouted bed reactor has been used, Fig. 2, with the aim of obtaining flash pyrolysis data under conditions similar to industrial units. This reactor is especially suitable for flash pyrolysis [8–12], given that the gas residence time is very short. Runs have been carried out in the 450–715 °C range. The reactor bed consists of 15 g of sand (d$_p$ < 1 mm), and batches of 2 g of plastic (2 mm particle size) are fed into the reactor for product monitoring. The nitrogen flow rate is 20% in excess of that required for minimum spouting velocity (6.5 L min^{-1}).

Product analysis has been carried out by means of an Agilent 6890 gas chromatograph provided with thermal conductivity (TCD) and flame ionization (FID) detectors, being connected on-line to the reactor by means of a thermostated line. Furthermore, product identification has been carried out by means of a mass spectrometer (Shimadzu GC-MS-QP2010S).
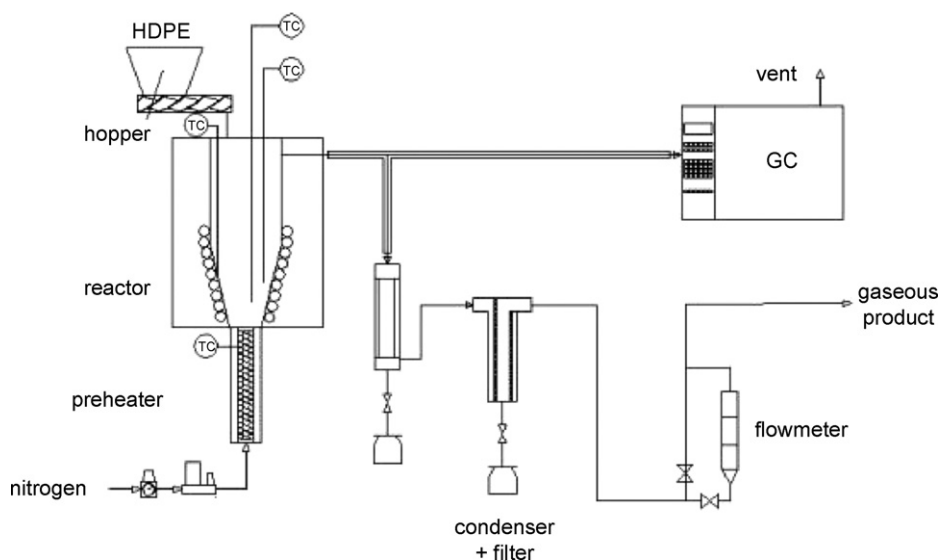

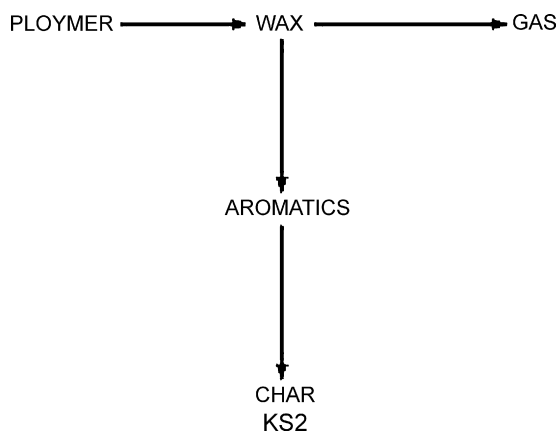Fig. 2. Schematic representation of the pyrolysis unit.

Fig. 3. Kinetic scheme of Westerhout et al. [1] without the step of aromatics to gases.
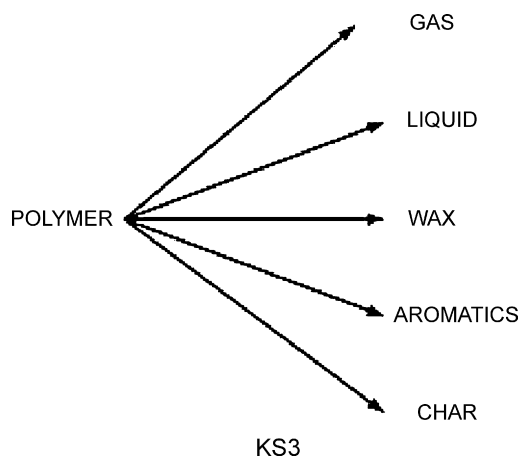

Fig. 4. Kinetic scheme of parallel reactions.

3. Proposal of kinetic mechanisms

Several kinetic schemes are proposed in order to model the thermal pyrolysis of HDPE in a conical spouted bed reactor. The fitting of the experimental data (Section 5) to a model based on the kinetic model of Westerhout et al. [1] (KS1), Fig. 1, clearly

shows that the step of aromatic formation from gases is not significant in this case. Moreover, the experimental results poorly fit the kinetic scheme forthcoming by removing this step (KS2), Fig. 3, which means that the scheme proposed by Westerhout et al. [1] needs modification in order to explain the experimental trend observed for the different lumps.
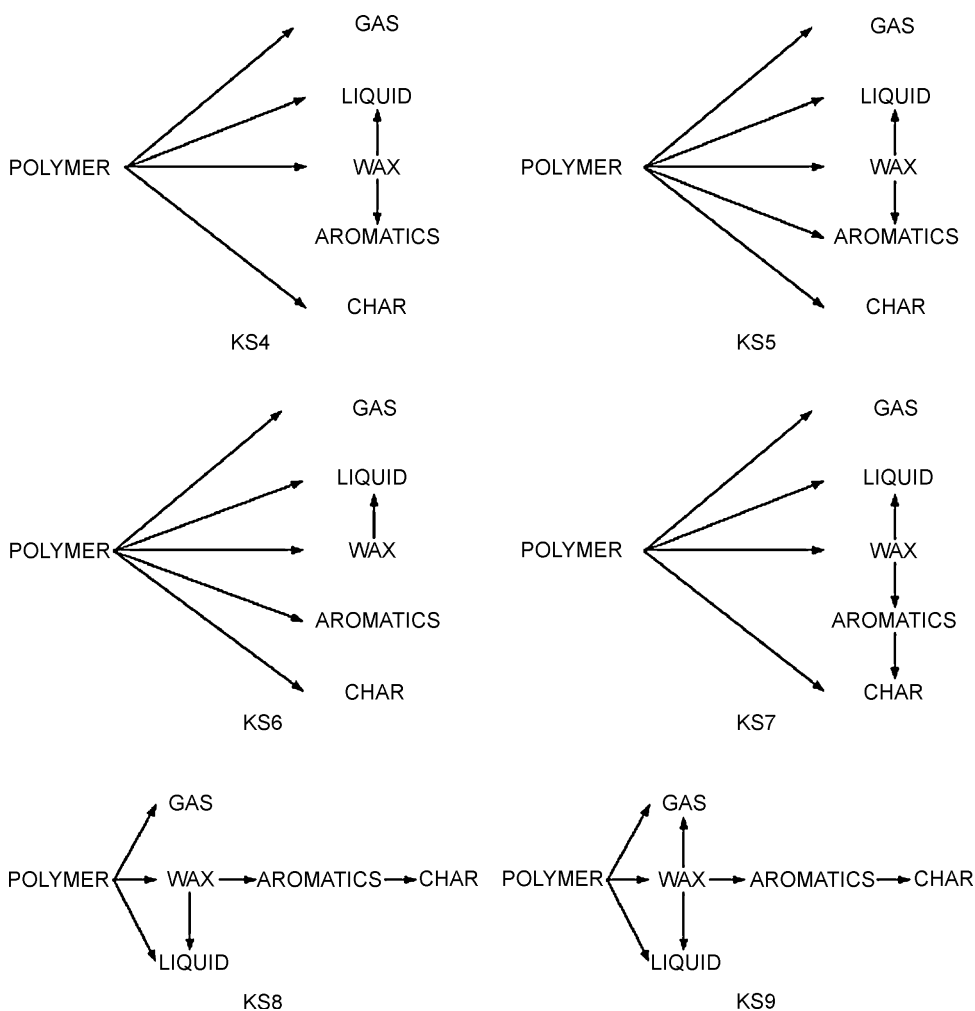

Fig. 5. Kinetic schemes that consider secondary reactions.

Westerhout et al. [1] proposed that waxes were the only primary product, but other authors [13] also propose gases and liquid as primary products at low temperatures (around 400 °C) at which pyrolysis begins to take place. The lump named liquid contains non-aromatic components. Accordingly, several kinetic schemes not based on that by Westerhout et al. [1], but that have gases, liquid, waxes, aromatics and char as primary products, have been proposed. As an initial scheme, the one shown in Fig. 4 (KS3) has been proposed. In this kinetic scheme, all the lumps are obtained from the plastic.

Concerning the liquid fraction, the experimental data obtained in this study shows that the formation of this fraction decreases as temperature is increased from low temperatures to intermediate ones, and then it increases at higher temperatures. Consequently, the liquid fraction is formed following two steps, as a primary product at low temperatures, as was also observed by Horvat and Ng [13], and as a secondary product from the cracking of waxes. This is reflected in the kinetic scheme KS4 shown in Fig. 5.

The other kinetic schemes proposed, shown in Fig. 5, contemplate that aromatics are also formed from waxes, as was also considered by Westerhout et al. [1], or that they are only formed from waxes and not from the plastic.

It is well known that char is formed from aromatics [14], which have prompted the proposal of kinetic scheme KS7 in Fig. 5, but char may also be formed only from aromatics, which is the case in kinetic scheme KS8 in Fig. 5. Finally, a new step has been introduced for the formation of gases from waxes, kinetic scheme KS9 in Fig. 5.

4. Modelling of the different kinetic schemes

The modelling of the discontinuous pyrolysis process implies writing the kinetic equations for the formation of the different lumps and the consideration that at the end of the process the total amount of plastic has been degraded (conversion 1) to give the different products.

The amount of each lump formed up to a given time is calculated by integrating the mass evolution of this lump with time. Given that total conversion of the plastic is attained, the sum of all the lump masses at the end of the reaction must be the total mass of plastic in the feed:

$$M_0 = \sum_{i=1}^{n} \int_{t=0}^{t_f} \dot{m}_i \, \mathrm{d}t \qquad (1)$$

The mass flow rate and yield of each lump are given by

$$\dot{m}_i = M_0 \frac{\mathrm{d}X_i}{\mathrm{d}t} \qquad (2)$$

$$X_i = \frac{M_i}{M_0} \qquad (3)$$

Given that the reaction time in the conical spouted bed is very short (an average of 60–100 ms), the kinetic equations will not be written as a function of reactant concentrations within the reactor, but as a function of reactant formation rate corresponding to this step. Thus, the formation of a given lump is

proportional to the formation rate of the reactant lump in this step. As an example, for the development of the model for the kinetic scheme of Westerhout et al. [1], the kinetic equations for each lump are as follows:

- Wax:

$$\dot{m}_W = \frac{\mathrm{d}X_W}{\mathrm{d}t} M_0 = k_{PW}(1 - X_P)M_0 - (k_{WG} + k_{WA})\frac{\mathrm{d}X_W}{\mathrm{d}t} M_0 \qquad (4)$$

- Gas:

$$\dot{m}_G = \frac{\mathrm{d}X_G}{\mathrm{d}t} M_0 = k_{WG}\frac{\mathrm{d}X_W}{\mathrm{d}t} M_0 - k_{GA}\frac{\mathrm{d}X_G}{\mathrm{d}t} M_0 \qquad (5)$$

- Aromatics:

$$\dot{m}_A = \frac{\mathrm{d}X_A}{\mathrm{d}t} M_0 = k_{WA}\frac{\mathrm{d}X_W}{\mathrm{d}t} M_0 + k_{GA}\frac{\mathrm{d}X_G}{\mathrm{d}t} M_0 - k_{AC}\frac{\mathrm{d}X_A}{\mathrm{d}t} M_0 \qquad (6)$$

- Char:

$$\dot{m}_C = \frac{\mathrm{d}X_C}{\mathrm{d}t} M_0 = k_{AC}\frac{\mathrm{d}X_A}{\mathrm{d}t} M_0 \qquad (7)$$

By reordering this set of equations, the following set of differential equations is obtained:

$$\frac{\mathrm{d}X_W}{\mathrm{d}t} = \frac{k_{PW}}{1 + k_{WG} + k_{WA}}(1 - X_P) \qquad (8)$$

$$\frac{\mathrm{d}X_G}{\mathrm{d}t} = \frac{k_{PW}k_{WG}}{(1 + k_{WG} + k_{WA})(1 + k_{GA})}(1 - X_P) \qquad (9)$$

$$\frac{\mathrm{d}X_A}{\mathrm{d}t} = \frac{k_{PW}[k_{WA}(1 + k_{GA}) + k_{WG}k_{GA}]}{(1 + k_{WG} + k_{WA})(1 + k_{GA})(1 + k_{AC})}(1 - X_P) \qquad (10)$$

$$\frac{\mathrm{d}X_C}{\mathrm{d}t} = \frac{k_{PW}k_{AC}[k_{WA}(1 + k_{GA}) + k_{WG}k_{GA}]}{(1 + k_{WG} + k_{WA})(1 + k_{GA})(1 + k_{AC})}(1 - X_P) \qquad (11)$$

A similar procedure is followed for the other kinetic schemes.

The discrimination of models and the calculation of kinetic parameters have been carried out by fitting the experimental values of yield of each lump and reaction end time to the mass conservation equations obtained for the kinetic schemes, Eqs. (8)–(11), which have been solved by a program written in Matlab, using a numerical procedure based on finite differences.

The kinetic parameters of best fit have been determined by multivariable non-linear regression, using the Complex [15] algorithm.

The objective function, Φ, takes into account the deviations between the experimental and calculated yields and reaction end times. As the error in the estimation of the end time is much greater than that of yield, the objective function takes this into account by means of weight factors:

$$\Phi = \omega_x \Phi_x + \omega_t \Phi_t \qquad (12)$$

The objective function for the yields, Φ_x, is the sum of square residuals corresponding to the differences between the

Table 1
Yields of the different lumps and reaction times required for 99.5% degradation of the sample at the different temperatures studied

T (°C)	t (s)	X_W	X_G	X_L	X_A	X_C
450	650	8.00×10^{-1}	5.90×10^{-2}	1.35×10^{-1}	6.00×10^{-3}	0.00
500	250	6.58×10^{-1}	2.02×10^{-1}	1.32×10^{-1}	8.00×10^{-3}	0.00
550	120	5.82×10^{-1}	3.28×10^{-1}	8.00×10^{-2}	1.00×10^{-2}	0.00
600	36	4.41×10^{-1}	4.37×10^{-1}	1.10×10^{-1}	1.20×10^{-2}	0.00
650	24	2.54×10^{-1}	5.52×10^{-1}	1.57×10^{-1}	3.70×10^{-2}	0.00
700	11	4.80×10^{-2}	6.45×10^{-1}	2.23×10^{-1}	4.50×10^{-2}	3.90×10^{-2}
715	9	6.00×10^{-3}	6.62×10^{-1}	2.42×10^{-1}	4.60×10^{-2}	4.40×10^{-2}

experimental values and those calculated for the different lumps:

$$\Phi_x = \frac{\sum_{i=1}^{n_1}\sum_{j=1}^{n_T}(X_{i,j} - X_{i(calc),j})^2}{n_1 n_T} \tag{13}$$

The objective function for the end times, Φ_t, is the sum of square residuals corresponding to the differences between the experimental and calculated values for the different temperatures:

$$\Phi_t = \frac{\sum_{i=1}^{n_T}((t_i - t_{i(calc)})/t_i)^2}{n_T} \tag{14}$$

The weight factors have been obtained by taking into account the experimental error involved in the calculation of the yield and in the estimation of the time needed for reaching almost total degradation of the waste plastic in the feed at each temperature. The real time needed for total degradation at any temperature is infinite, but we have decided to take a more realistic value corresponding to 99.5% degradation of the initial sample. The standard deviations of the errors introduced in the estimation of the reaction end time and yield have been calculated from runs repeated under the same conditions. The error in the estimation of the reaction end time is approximately two orders of magnitude greater than that of the yield. Consequently, the weight factor estimation for the yield objective function is 0.99, whereas that for the end time is 0.01. The kinetic constants have been reparameterized [16,17] in order to reduce the correlation between the estimations of frequency factor and activation energy. Consequently, the parameters calculated are the kinetic constants for a reference temperature (550 °C) and the corresponding activation energies.

The discrimination of the kinetic schemes has been carried out on the basis of the statistics calculated for the Fischer distribution. The procedure used is stepwise regression, which is based on introducing new parameters one by one and testing the significance not only of the new one but also of the other ones in the model. This procedure continues until a parameter introduced in the model is not significant, which means that the variance explained by this last parameter is comparable to the experimental error and, consequently, does not make a significant contribution to improving the model.

5. Results

Batch runs have been carried out in the conical spouted bed in the 450–715 °C range for the development of the model. Table 1 shows the experimental values obtained for the yields of the

Table 2
Significance of aromatic formation from gases in the model by Westerhout et al. [1]

Kinetic scheme	Φ	F	F_c	Chosen model
KS2	3.12×10^{-3}	0.05	3.39	KS2
KS1	3.10×10^{-3}			

different lumps and the time required for 99.5% degradation of the sample at each temperature.

The kinetic scheme proposed by Westerhout et al. [1] does not distinguish between the gas and liquid fractions, but both are included in the lump termed gas. Nevertheless, operation in the conical spouted bed allows for distinguishing these lumps and it seems reasonable to take them separately. In order to start model building, the significance of the parameters in the scheme by Westerhout et al. [1] has been checked. The result is that the step of gases to aromatics is not significant. Table 2 shows the Fisher test with and without this step. The value of the F statistics obtained is much lower than the critical one and, consequently, this step is not significant.

Nevertheless, when a test is carried out on the variance corresponding to the lack of fitting, this is significant compared to the true experimental error. Consequently, both models leave too much unexplained variance and need to be improved. In fact, the lump of liquid is one that should be considered. For this purpose, a kinetic scheme with five parallel reactions has been taken and the significance of this model has been compared with that based on kinetic scheme KS2. This kinetic scheme made up of five parallel reactions, KS3, is clearly more significant than that obtained by modifying the kinetic scheme of Westerhout et al. [1]. Nevertheless, aromatics, char and liquid obtained based on KS3 are poorly fitted to the experimental data, Fig. 6.

Following the procedure for building the model, the next stage is to check the significance of a secondary step. Testing all the possible secondary reactions, the more significant one is the formation of liquid from waxes and all the other reaction steps continue to be significant, Table 3. Consequently, this step is introduced in the kinetic scheme (KS4 in Fig. 5).

Kinetic scheme KS4 again leaves too much unexplained variance (on the basis of the lack of fitting test), which is due to the fact that the model based on this scheme is unable to predict the experimental trend observed for the lump of aromatics. Accordingly, a secondary reaction that gives way to the formation of aromatic has been considered. Testing
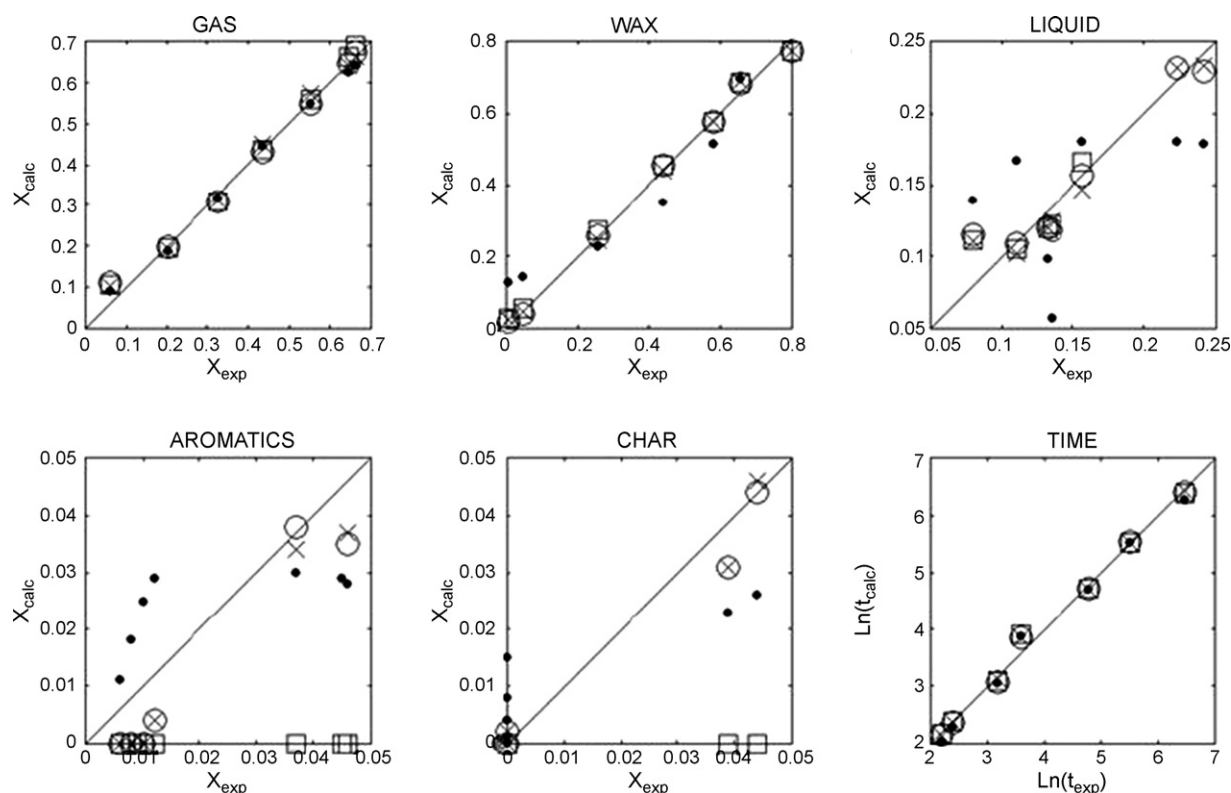
Fig. 6. Fittings of different kinetic schemes tested. Kinetic schemes: (●) KS3; (□) KS4; (○) KS8; (×) KS9.

Table 3
Comparison of F statistics values for the different kinetic schemes tested

	Models compared					
	KS3-KS4	KS4-KS5	KS5-KS6	KS6-KS7	KS7-KS8	KS8-KS9
F	67.15	5.41	1.12	6.42	0.57	0.91
F_c	3.42	3.47	3.47	3.47	3.47	3.47
	Chosen model					
	KS4	KS5	KS6	KS7	KS8	KS8
Φ (chosen model)	8.91×10^{-4}	5.88×10^{-4}	6.50×10^{-4}	4.04×10^{-4}	4.25×10^{-4}	4.25×10^{-4}

the significance of all possible secondary reactions to give aromatics, the formation from waxes is the more significant one, kinetic scheme KS5 in Fig. 5, but the introduction of this step diminishes the significance of the formation of aromatics from the plastic, kinetic scheme KS6 in Fig. 5. Continuing the same procedure with a third secondary reaction step, the result is that char formation from aromatics is significant, kinetic scheme KS7 in Fig. 5, but not from the plastic, kinetic scheme KS8 in Fig. 5. This step is a usual one in a heterogeneous catalyst, given that char is formed from the polymerization of aromatics [14].

The model corresponding to the kinetic scheme KS8 provides a good fit for the experimental data corresponding to all the lumps, Fig. 6. In fact, the lack of fitting is not significant in this case.

Finally, the introduction of another secondary reaction was tested. The one that provided the higher value of statistics F was the formation of gas from waxes, kinetic scheme KS9 in Fig. 5, but it is not significant. Consequently the model of best fit is that corresponding to the kinetic scheme KS8 shown in Fig. 5. This is also observed in Fig. 6, where no improvement is appreciated by introducing the formation of gases from waxes (kinetic scheme

Table 4
Parameters obtained for model corresponding to the kinetic scheme KS8 shown

	k_{PW} (s^{-1})	k_{PG} (s^{-1})	k_{PL} (s^{-1})	k_{WL}	k_{WA}	k_{AC}
E_a (kJ mol^{-1})	71.2	137	84.3	411	392	382
k_0	9.77×10^2	7.31×10^6	1.30×10^3	4.72×10^{22}	2.39×10^{21}	2.01×10^{20}

KS9) The values of activation energy and frequency factor for the optimum model (the one based on the kinetic scheme KS8) are set out in Table 4.

6. Conclusions

Kinetic models based on that of Westerhout et al. [1] do not adequately predict the experimental results, especially those corresponding to aromatics and char. This lack of fit is probably due to the residence time and to the fact that the step of gases to aromatics is not significant. Thus, the conical spouted bed operates with very short residence times (of the order of 50 ms), whereas the device of Westerhout et al. [1] operates in the range between 0.1 and 1 s. In fact, we obtain lower yields of aromatics and char. The optimum model (the one that does not leave unexplained variance with the minimum number of parameters) is the one listed as KS8 in Fig. 5. According to this model, polyethylene degrades to give gas, liquid (oil) and wax fractions. The latter undergoes secondary reactions to give liquid and aromatics, which in turn produce char.

Acknowledgements

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