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Kinetics of polystyrene pyrolysis in a conical spouted bed reactor

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Abstract

A conical spouted bed reactor (CSBR) has been used for the kinetic study of polystyrene pyrolysis in the 723–823 K range and the results have been compared with those obtained by thermogravimetry (TGA) and in a microreactor (MR) of very high sample heating rate. The comparison proves the advantages of the gas–solid contact of this new reactor for the kinetic study of pyrolysis of plastics at high temperature, which stem from the high heat transfer rate between gas and solid and from the fact that particle agglomeration is avoided. It has been proven that, in the temperature range required for maximizing the yield of styrene, heat and mass transfer limitations within the particle are important when polystyrene particles of 1 mm are fed into the reactor. A high yield of styrene is obtained (64.5 wt.%) in the 723–773 K range.

Keywords: Polystyrene pyrolysis; Waste plastics; Thermal degradation

1. Introduction

Obtaining feedstock and fuels by pyrolysis of waste plastics is one of the methods for upgrading these materials with best perspectives for its implementation at large scale. Although the fluidized bed, either bubbling [1–8] or circulating [9,10], has been successfully used, the debate on the more suitable technology is open. In the pyrolysis of polystyrene, high yields of the monomer, styrene, have been reported in the literature. Scott et al. [2] obtained 75% of styrene in a fluidized bed reactor in the 805–1081 K range. Continuous operation in this reactor allows for controlling the residence time of the products and, consequently, the yield is higher than in the batch operation. Thus, following this latter strategy, Koo et al. [11] have obtained 55 wt.% at 973 K.

In the literature [12–15], new reactors have been proposed in order to reduce the limitations inherent to the handling of plastics (low density, irregular texture) and to improve the gas–solid contact. The aim of these reactors is to allow for operation at uniform temperature with the minimum energy requirement (pyrolysis of these materials is highly endothermic) and to obtain a higher production than in the bubbling fluidized bed. In fact, a high volume reactor with a large amount of inert solid (sand) is required in this latter technology in order to facilitate fluidization and to avoid particle agglomeration provoked by the sticky nature of the melted plastic [16,17].

The first step for a suitable design of any pyrolysis reactor is a knowledge of kinetics. Nevertheless, appropriate information on this requirement is rather difficult to find for the pyrolysis of plastics, which is due to the fact that the kinetic studies have been carried out under different conditions (especially concerning temperature range) to those of the industrial process to be designed and under possible gas–solid contact limitations in the technology used for the kinetic study (generally thermogravimetry (TGA)).

The mechanism of thermal degradation of polystyrene is very complex and includes, amongst others, the following reactions: chain fission, radical recombination, carbon–hydrogen bond fission, hydrogen abstraction, mild-chain β-scission, radical addition, end-chain β-scission, 1,5-hydrogen transfer and disproportionation [18]. Nevertheless, few mechanistic kinetic models have been developed for this pyrolysis. Westerhout et al. [19] have reviewed (up to 1997) the kinetic results of polystyrene pyrolysis at low temperature, which have been usually fitted in the literature to a potential kinetic model of *n*th order.

$$-\frac{\mathrm{d}W}{\mathrm{d}t} = kW^n = k_o \exp\left(-\frac{E}{RT}\right) W^n \qquad (1)$$

In most of the kinetic studies [19–26], the degradation of polystyrene is fitted to a first order kinetics. Nevertheless, as happens in the pyrolysis of polyolefins, certain authors determined a zero order for low conversion [27–29] and other authors have an order between 0 and 1 [30,31], and an order between 1 and 1.1 [32–34] for complete pyrolysis. The important differences in the kinetic results of the literature

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Nomenclature

Dc, Do, Di	diameter of the cylindrical section, of the bed bottom, and of the gas inlet, respectively (m)
E	Activation energy (kJ mol^{-1})
H_c, H_T	height of the conical section and total height of the reactor (m)
k	kinetic constant (s^{-1})
k_o	frequency factor (s^{-1})
n	reaction order
R	gas constant (kJ mol^{-1} K^{-1})
T	temperature (K)
t	time (s)
W, W_0	plastic mass at t time and at zero time (kg)
X	conversion, defined in Eq. (3)
Greek letters	
β	heating rate in thermobalance (K s^{-1})
γ	contactor angle (°)

are attributed by Carrasco and Pagés [35] and by Conesa et al. [36] to differences in both the experimental equipment and the methodology followed for obtaining and analysing the kinetic data.

In this paper, the kinetic study of polystyrene pyrolysis has been carried out in the new reactor, i.e. a conical spouted bed reactor (CSBR), which has considerable advantages for this process due to the vigorous gas–solid contact and the reduced segregation obtained as a consequence of the cyclic circulation characteristic to spouted beds, where all the solids rise through the spout and descend along the annular zone [37]. The conical spouted bed has been successfully used in other processes that require handling of solids that have particle size distribution, irregular texture and/or are sticky, as is the case of catalytic polymerizaton [38,39], thermal pyrolysis [40] and catalytic pyrolysis of vegetable biomass [41].

The kinetic results obtained in this reactor have been compared with those obtained by TGA and in a MR of very high sample heating rate. The comparison of the results enables to evaluate the capacity of this new reactor for kinetic studies of pyrolysis of polystyrene and of other plastics. This comparison will also permit us to contemplate this technology for its use in continuous operation in order to obtain high yields of feedstock (in the case of polystyrene) and fuels, as an alternative to the fluidized bed reactor or to the other reactors proposed in the literature.

2. Experimental

The polystyrene is supplied by Dow Chemical (Tarragona, Spain) and it has the following properties: MW = 311600, polydispersity (ratio of weight-to number-average molecular weights) = 2.39, density = 1030 kg m^{-3}, heat value = 49 MJ kg^{-1}.

The thermogravimetric equipment used is a Setaram TAG 24 symmetrical thermobalance, connected to a vacuum system (10^{-1} Pa). In this equipment, two sets of runs have been carried out, one series at constant temperature in the 613–663 K range and the second one following temperature–time sequences at heating rates 3.33×10^{-2}, 8.03×10^{-2} and 1.67×10^{-1} K s^{-1}. This latter set allows for obtaining kinetic parameters at higher temperatures than those corresponding to constant temperature runs.

The microreactor (MR) is a commercial piece of equipment, Pyroprobe 1000, in which the analysis of the gaseous products is carried out on line by means of a Hewlett-Packard 6890 chromatograph. The sample of plastic material is placed in a quartz tube surrounded by a platinum filament. The runs have been carried out at 773, 823 and 873 K. The temperature is attained at a heating rate of 10^4 K s^{-1}. As the maximum run duration allowed for the equipment is 100 s, the runs of longer duration have been carried out by repeating reaction cycles of 100 s. Subsequent to each run, the tube containing the sample is weighed.

Fig. 1 shows a scheme of the laboratory set-up. The plastic is fed by placing the inlet tube over the annular zone of the bed. The vigorous cyclic movement of the particles, Fig. 2b, enables their individual circulation without problems of agglomeration.

Fig. 2a shows a scheme of the reactor where its characteristic dimensions are defined: $H_T = 0.340$ m; $H_c = 0.205$ m, $\gamma = 28°$; $D_c = 0.123$ m; $D_i = 0.02$ m; $D_o = 0.01$ m. These dimensions have been established from previous hydrodynamic studies carried out on the spouted bed regime in conical contactors [42–44] and bearing in mind the versatility of the equipment. When the inert gas flow rate is

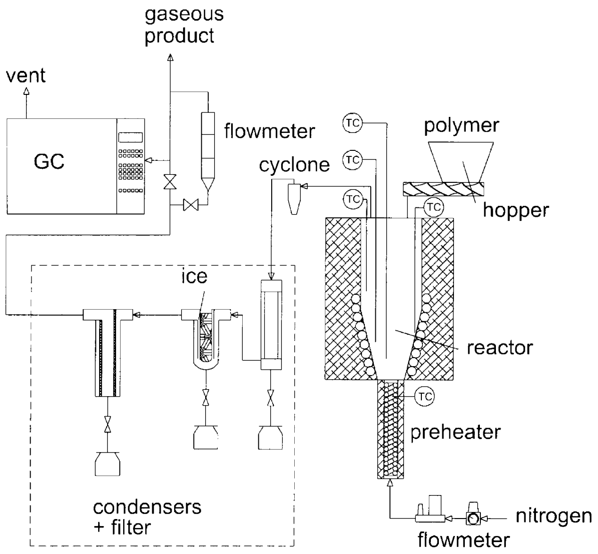

Fig. 1. Diagram of the pyrolysis equipment.

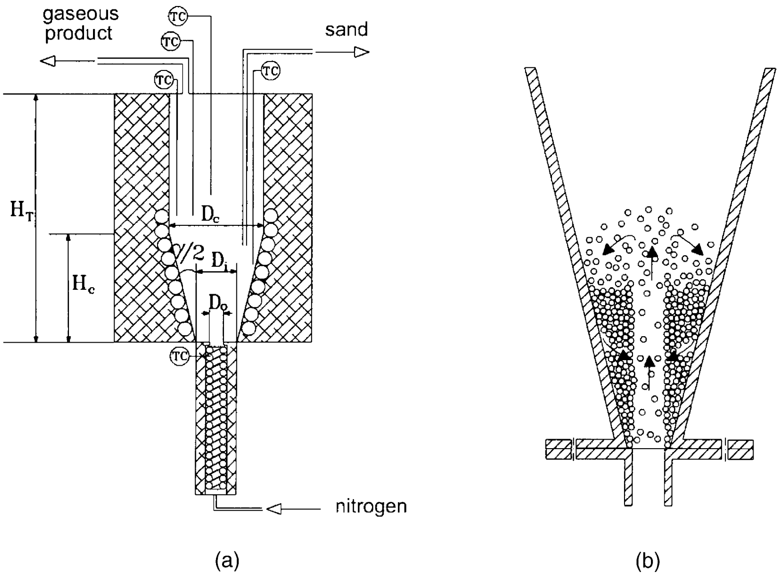

Fig. 2. Scheme and design parameters of the CSBR.

increased, the gas–solid contact regime evolves from the conventional spouted bed to a diluted spouted bed and the gas residence time decreases from a few seconds to approximately 2×10^{-2} s. The gas flow pattern is described by a disperse plug flow model, with coefficients that are calculated as a function of the geometric factors of the reactor–particle system and process conditions [45].

Temperature is measured by means of three thermocouples placed at different radial positions in the reactor and provided with free vertical movement, which allow for temperature measurement at any position in the reactor. Bed isothermicity is noteworthy and is attained through vigorous particle circulation. The results used in the kinetic study are those corresponding to the runs in which the maximum temperature difference between the different bed positions was lower than 2 K.

Reaction temperature is attained by means of two electric resistances surrounded by ceramic material, Fig. 2. One resistance is located within the tube for heating the inert gas before entering the reactor and the second one surrounds the conical section of the reactor. Temperature in these two positions is measured by two thermocouples. The two heating zones are thermally insulated.

The pyrolysis product stream is transported by the inert gas towards a condensing system made up of a cooling device, a trap with salt-water ice and a 25 μm filter made of sintered steel. The non-condensable gases of the product stream are analysed by gas chromatography (Hewlett-Packard 6890) using a BPX5 capillary column of 50 m.

The runs for the kinetic study have been carried out by feeding 10^{-3} kg of plastic material (with a particle size of approximately 10^{-3} m) and using 3×10^{-2} kg of sand (with a size between 6.3×10^{-4} and 1.0×10^{-3} m). The temperatures studied are 723, 773 and 823 K and the reaction times are between 1 and 1080 s (sufficient time for reaction to be completed at 723 K).

3. Results

3.1. Thermogravimetry

In Fig. 3 (each line corresponds to a temperature) the results of conversion obtained at constant temperature are fitted to linearized Eq. (1), which expressed in terms of

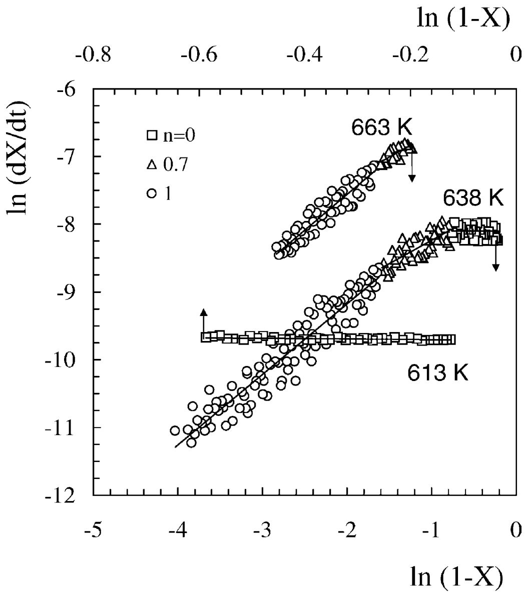

Fig. 3. Results of $\ln(dX/dt)$ vs. $\ln(1\text{-}X)$ obtained in thermobalance.

conversion is:

$$\frac{dX}{dt} = k(1 - X)^n \tag{2}$$

The results in Fig. 3 are evidence that the reaction order changes with conversion. These results are fitted to three successive straight lines whose slopes (orders) are 0, 0.7 and 1. Conversion has been determined as:

$$X = \frac{W_0 - W}{W_0} \tag{3}$$

Table 1 shows the values of the reaction order that best fit the experimental results for the different conversion ranges, and the corresponding values of frequency factor and activation energy (between 207 and 223 kJ mol^{-1}). These results are given with a 95% confidence interval.

TGA carried out following temperature ramps reduces the limitations of constant temperature experimentation, where the solid is partially converted when the set temperature is reached. Furthermore, one run is enough to calculate the kinetic constant (for $n = 1$) as a function of temperature:

$$k = \frac{dX/dT}{1 - X} \tag{4}$$

Fig. 4 shows the Arrhenius plot of $\ln k$ versus $1/T$ corresponding to the results for the three temperature ramps of 3.33×10^{-2}, 8.03×10^{-2} and 1.67×10^{-1} K s^{-1}. The values of k obtained in the runs at constant temperature are also plotted in this figure.

As is shown in Fig. 4, the activation energy calculated increases slightly as the temperature ramp is decreased, which is a consequence of heat transfer limitation within the sample. The results corresponding to the ramp of 3.33×10^{-2} K s^{-1} are $E = 221$ kJ mol^{-1} and $k_o = 7.05 \times 10^{14}$ s^{-1}. These almost coincide with those corresponding to constant temperature runs. These results are close to those obtained in the literature [19,20,24,30,31,46].

3.2. Microreactor

A microreactor (MR) similar to that employed in the present study has been used by different authors [47,48] for the kinetic study of pyrolysis of several materials and it allows for the experimentation to be carried out at high temperature, which is attained by a very high heating rate of the material fed, as happens in continuously operated large-scale reactors. Furthermore, the gas–solid contact is more efficient than in thermobalance.

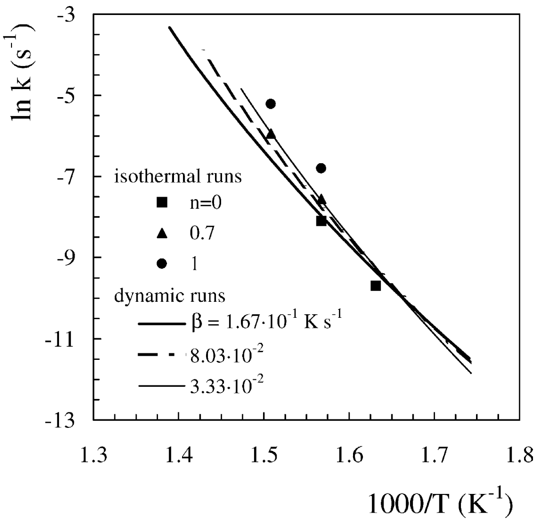

Fig. 4. Fitting to Arrhenius equation of the experimental results obtained for HDPE pyrolysis in thermobalance. Lines, results obtained following ramps of 2, 5 and 10 K min^{-1}. Points, results obtained in runs at constant temperature.

Pyrolysis has been carried out at 773, 823 and 873 K. Fig. 5 shows the results of evolution of conversion with time. The lines correspond to the best fitting to a potential equation.

Fig. 6 shows the fitting of the experimental results (points correspond to the X vesus t curve obtained experimentally) to the integrated equation of first order:

$$\ln(1 - X) = -kt \tag{5}$$

From the kinetic constants calculated by the fitting of Fig. 6, the values of the kinetic parameters are determined: $E = 83$ kJ mol^{-1}, $k_o = 1.82 \times 10^4$ s^{-1}, with a 95% confidence interval. These values are appreciably different to

Table 1
Kinetic parameters for polystyrene pyrolysis determined by TG at constant temperature

T (K)	X	n	k, s^{-1}	E, kJ mol^{-1}	k_o, s^{-1}
613	0.05–0.45	0	6.19×10^{-5}		
	–	0.7	–		
	–	1	–		
638	0.15–0.53	0	3.04×10^{-4}	207 (±10)[a]	$2.69\ (\pm 0.13) \times 10^{13}$
	0.53–0.8	0.7	5.24×10^{-4}	227 (±12)[b]	$1.99\ (\pm 0.12) \times 10^{15}$
	0.8–0.98	1	1.11×10^{-3}	223 (±11)[b]	$2.25\ (\pm 0.11) \cdot \times 10^{15}$
663	–	0	–		
	0.7–0.8	0.7	2.63×10^{-3}		
	0–0.99	1	5.44×10^{-3}		

[a] 613–638 K.
[b] 638–663 K.

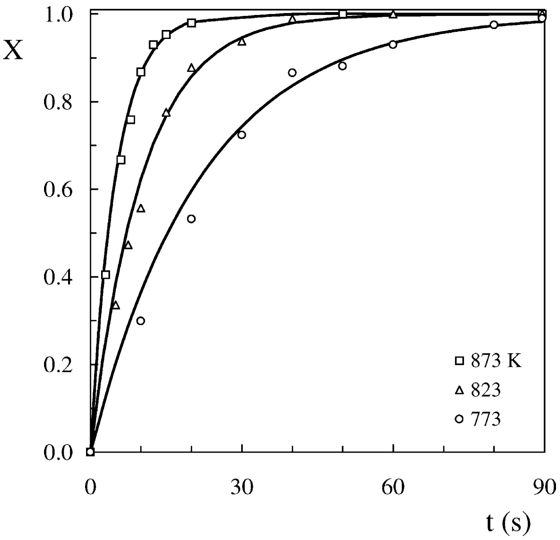

Fig. 5. Results of evolution of conversion with time obtained in MR at different temperatures.

those obtained by thermobalance and they will be analyzed subsequently.

3.3. Spouted bed reactor

The bubbling fluidized bed reactor [1–8] performs well with respect to heat transfer which allows for reaching isothermal regime in the reactor. Furthermore, pyrolysis occurs with a random movement of the melted plastic coating the sand particles. The residence time of the gas is relatively low, which minimizes the secondary reactions of the primary pyrolysis products. These properties provide important advantages over other previously studied technologies, such as rotary beds [49,50] and stirred tanks containing dissolved plastic [51].

Nevertheless, the fluidized bed reactor presents defluidization problems due to the stickiness of the sand particles coated with melted plastic [16,17]. In order to minimize these problems, measures must be taken, which consist of reducing the particle size fed and increasing the amount of sand in the reactor (in order to reduce the plastic layer coating the sand). These measures imply a considerable increase in energy requirements (especially for heating the sand) and a great reactor volume and, unfortunately, defluidization problems are not totally avoided. It must be taken into account that particle stickiness is a consequence of their insufficient momentum, which causes particle fusion and subsequent defluidization. Unfortunately, the momentum of sand particles in the fluidization regime hardly increases as gas velocity is increased, which is because most of the gas in excess of that corresponding to minimum fluidization passes through the bed as bubbles.

These difficulties have furthered the proposal of alternative reactors to the bubbling fluidized bed reactor, as are the internally circulating fluidized bed [9,10], the rotating cone reactor [12,13] the circulated-spheres reactor [14] and a reactor with stirred heat medium particles [15].

The kinetic study in the plant provided with the CSBR described in Fig. 1 has been carried out under the following conditions: temperature, 723, 773 and 823 K; polystyrene weight fed, 1 g; particle size, 1 mm, sand weight, 30 g; nitrogen flow rate, $4.0 \times 10^{-4}\,\mathrm{m^3\,s^{-1}}$, which corresponds to 20% in excess of that for minimum spouting [41,43].

Fig. 7 shows the fitting of the results of X versus time to the integrated kinetic equation of first order, Eq. (5). From the kinetic constants, the values of kinetic parameters have

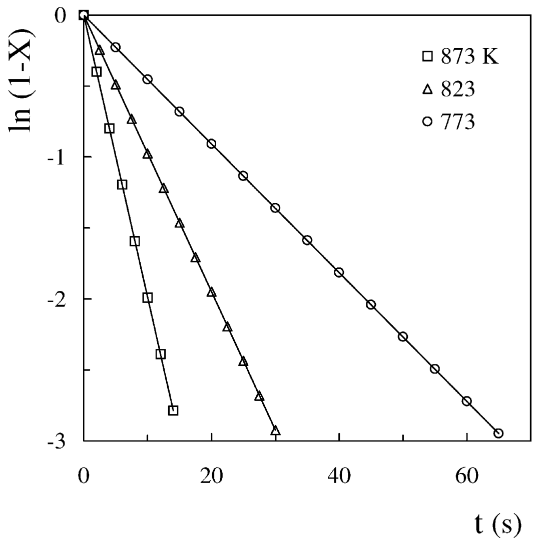

Fig. 6. Fitting of conversion results in MR to the integrated kinetic equation for first order. Lines, calculated by using the kinetic constant of best fitting. Points, corresponding to X vs. t.

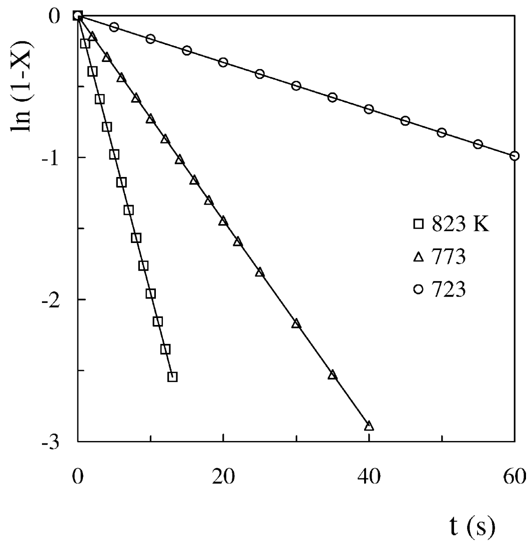

Fig. 7. Fitting of conversion results in the CSBR to the integrated kinetic equation for first order. Lines, calculated by using the kinetic constant of best fitting. Points, corresponding to X vs. t.

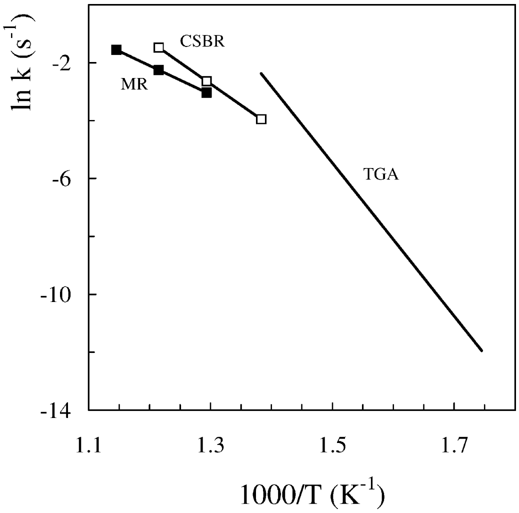

Fig. 8. Results of kinetic constants for polystyrene pyrolysis obtained with the three experimental techniques: TGA, MR and CSBR.

been calculated: $E = 123\,\mathrm{kJ\,mol^{-1}}$, $k_o = 1.27 \times 10^7\,\mathrm{s^{-1}}$, with a 95% confidence interval.

With the aim of evaluating the kinetic results, Fig. 8 shows the comparison (in an Arrhenius plot) of the kinetic constants determined in this paper for pyrolysis of polystyrene by means of the three experimental techniques used. It is appreciated that the results obtained in the MR and in the CSBR correspond to higher temperatures, which cannot be reached by TGA. The values of the kinetic constants corresponding to the CSBR are higher than those of the MR but lower than those obtained by extrapolation of thermogravimetric data (straight line of Fig. 8) to higher temperatures.

This comparison of the kinetic constants clearly shows that the CSBR avoids certain limitations of the gas–solid contact, which are unavoidable in the MR, as is the fact that the solid particles are stagnant and, consequently, when the plastic is melted they agglomerate. This result is evidence of the good performance of the spouted bed reactor for the kinetic study of pyrolysis of plastics at high temperature.

The activation energy corresponding to experimentation in the spouted bed reactor is lower than that obtained by TGA, which is due to the unavoidable mass and heat transfer limitations that occur in the individual particles of polystyrene + sand at high temperatures. Polystyrene is not a crystalline material and after the glass transition it does not coat the sand particles uniformly with a thin layer, as happens in the case of polyolefins [52] and, consequently, higher transfer limitations are expected.

The kinetic results obtained in a conical spouted bed regime are an indication of the maximum rate of polystyrene pyrolysis in this temperature range, when this solid plastic is fed. It must be taken into account that a small plastic/sand ratio (1/30 in weight) has been used and that any fluidized or spouted bed reactor operating at larger scale, in order to increase productivity, would require decreasing this ratio. The conical spouted bed ratio is very versatile for this productivity increase, but at the expense of reaction rate, due to the fact that an increase in the plastic layer coating the sand increases heat and mass transfer limitations. In any case, these aspects should be quantified in future papers by carrying out the operation at larger scale and with continuous plastic feed.

Table 2
Yields (wt.%) of the products obtained by polystyrene pyrolysis in the CSBR at different temperatures

Compound	723 K	748 K	773 K	823 K
Methane	7.0	8.3	8.3	7.3
C_2–C_4	4.8	5.1	7.7	19.8
C_5–C_8	15.0	11.3	10.2	10.4
Benzene	5.4	3.8	4.6	5.9
Toluene	6.7	7.0	7.1	6.5
Styrene	61.1	64.5	62.1	50.1

Under the operating conditions studied, all the products of polystyrene pyrolysis are present in the gaseous stream. Gas chromatography identifies 25 peaks, of which 15 account for 98.4 wt.% of the polystyrene fed. The yields of individual products and of the lumps are set out in Table 2.

Noteworthy is the high yield of styrene, whose maximum value is 64.5 wt.% in the 723–773 K range. As temperature is increased to 823 K the yield of styrene decreases to 50.1 wt.% as a consequence of the increase in the formation of light olefins (by cracking the aromatic ring), which are those which mostly make up the C_2–C_4 lump.

Although the maximum yield of styrene obtained in the CSBR is 10 wt.% lower than that obtained by Scott et al. [2] in a fluidized bed reactor, it is noteworthy that the temperature in our reactor is lower and that, in the type of experimentation carried out (batch operation for polystyrene), the optimization of the residence time of the gaseous products was not the aim of this study. In fact, the temperature corresponding to the maximum yield of styrene (723–773 K) is lower than the range studied by Scott et al. [2], 805–1018 K, which is a consequence of the excellent gas–solid contact in the CSBR.

The evolution of the individual yields has been calculated by measuring the concentrations throughout time of the different products and lumps in the outlet stream. These yields are shown in Fig. 9, where each graph corresponds to one temperature.

Table 3
Kinetic parameters of individual product formation for polystyrene pyrolysis in a CSBR

Compound	E, kJ mol^{-1}	k_o, s^{-1}
Methane	126 (±6)	$2.10\ (\pm 0.10) \times 10^7$
C_2–C_4	129 (±6)	$3.53\ (\pm 0.18) \times 10^7$
C_5–C_8	103 (±5)	$6.12\ (\pm 0.31) \times 10^5$
Benzene	123 (±6)	$1.47\ (\pm 0.07) \times 10^7$
Toluene	122 (±6)	$1.19\ (\pm 0.06) \times 10^7$
Styrene	132 (±7)	$5.08\ (\pm 0.25) \times 10^7$

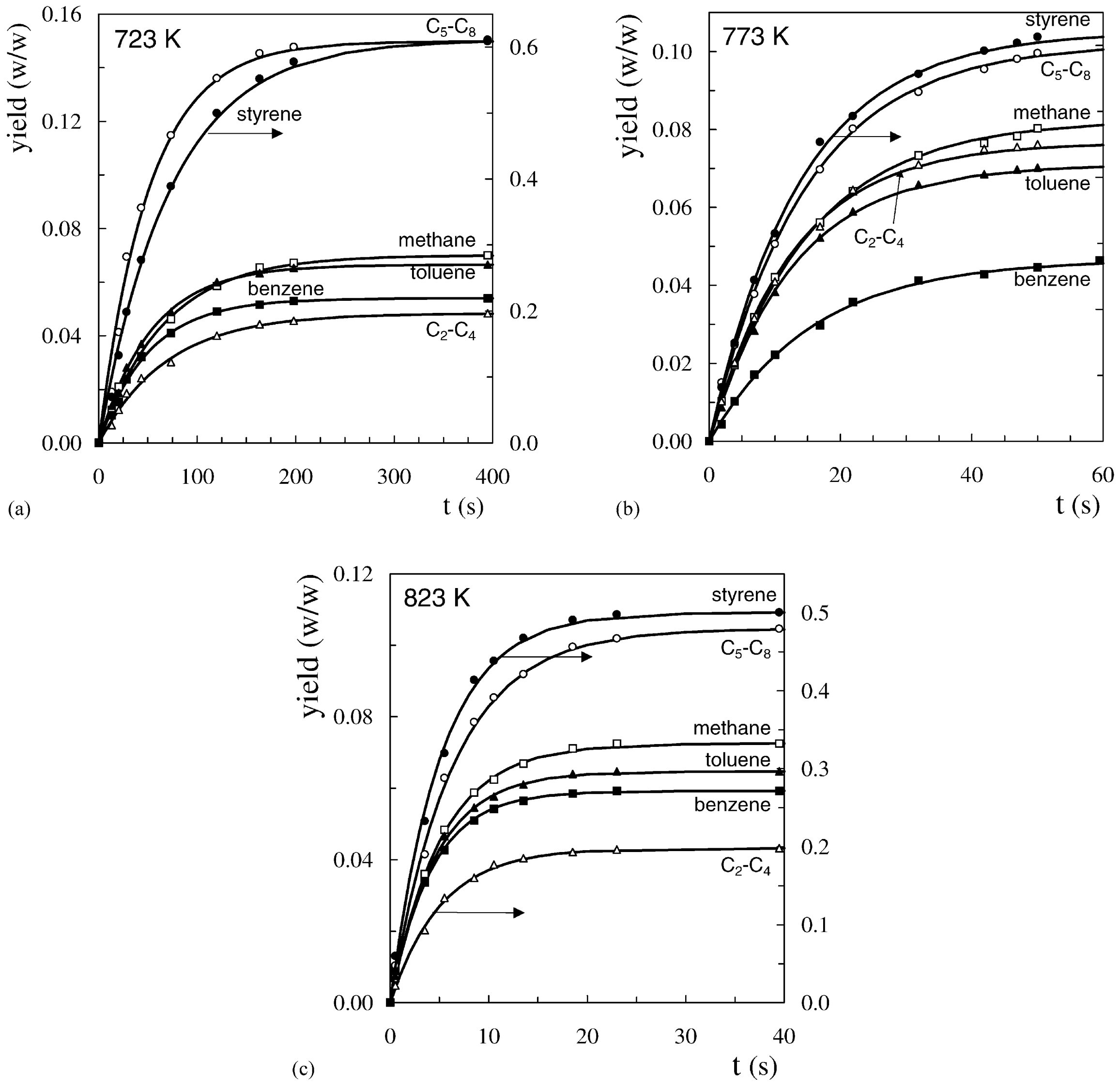

Fig. 9. Results of evolution with time of yields of the different products obtained in the CSBR at different temperatures. Graph (a), 723 K; (b), 773 K; and (c), 823 K.

The results of Fig. 9 suitably fit a first order kinetics. The values of activation energy and of frequency factor corresponding to the individual products are set out in Table 3. It is noteworthy that the different products are formed following individual steps whose activation energy is very similar.

4. Conclusions

The CSBR has highly suitable characteristics for the kinetic study of pyrolysis of plastics: bed isothermicity, operation versatility with different particle sizes, excellent contact between phases, vigorous movement of the solid (which avoids particle agglomeration), small segregation and reduced residence time of the primary products of pyrolysis.

The kinetic results obtained in the pyrolysis of polystyrene are evidence of the benefits of the CSBR over TGA and the MR for obtaining kinetic data under conditions similar to those foreseen for pyrolysis of plastics at large scale, at high temperature and continuous operation. Although the reactor minimizes the limitations of heat and mass transfer between the gas and the solid, it is clearly seen that the kinetics of pyrolysis is affected by heat transfer restrictions within the particle above 723 K. In view of the difficulty for obtaining and handling very small plastic particles at large scale, the kinetic results obtained in this paper for a particle diameter of 1 mm are useful for ascertaining the performance of pyrolysis at this scale.

Furthermore, the conical spouted bed may be an alternative to the fluidized bed, although this is a conclusion that requires subsequent studies in continuous operation for the solid. Nevertheless, certain facts are noteworthy, on the one hand, the simplicity of the spouted bed design because it does not require a distributor plate and, on the other, the absence of scaling limitations, as it does not have maximum spoutable bed height.

The versatility of the CSBR allows for increasing the plastic/sand ratio (by increasing the inert gas flow rate), minimizing the amount of sand but still maintaining the properties characteristic to the spouted bed regime. Although the experimentation for the kinetic study was carried out with a plastic/sand mass ratio of 1/30 at the beginning of the batch operation (in order to ensure bed isothermicity and individual movement of polystyrene + sand particles), the capacity for treating plastic is very low under these conditions. In order to increase the capacity for treating polystyrene, the plastic/sand mass ratio may be increased up to 1/10, which in volume is approximately 1/4, much higher than that corresponding to the fluidized bed reactor. This volume of sand suffices for ensuring the cyclic movement of the bed.

Acknowledgements

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