Kinetic studies of the polystyrene pyrolysis reactional pathways

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This paper aims to develop a reaction pathway for the pyrolysis of PS (polystyrene) based on the experimental results obtained in a six-micro-autoclave system using different temperatures and reaction times. In the model used, the PS was assumed to form gas, light oil, heavy oil and solid. Kinetic studies of PS were performed in order to determine whether, if the direct conversion of plastic wastes into gaseous, liquid and solid products was favoured, or parallel reactions and/or reversible elementary steps should be considered. The fitting of a kinetic model to the experimental data was performed. The adjustment of the model fitted reasonably the results and gave a satisfactory explanation for several experimental data of the thermal degradation of PS. The kinetic parameters were estimated. The product composition was also analysed

1. Introduction

Kinetic studies of pyrolysis reaction is a very important issue to predict products yields and composition and to optimise overall process conversion. Some work has already been done in kinetic studies of PS pyrolysis, but mostly using termogravimetric analysis (TGA). However, the use of TGA measurements has the limitation of only being able to describe the weight loss steps (Agrado and Serrano, 1999). On the other hand, the transformations that take place through a random scission mechanism, producing intermediate species (heavy waxes and tars), which are not volatilized at relatively low temperatures are not detected in the TGA measurements (Agrado and Serrano, 1999). Also the use of TGA in kinetic studies only allows the determination of the evaporation rate of products, but not the intrinsic chemical reaction rate (Westerhout et al., 1997).

Some authors developed PS degradation models based on TGA measurements. Faravelli et al. (2001), developed a detailed kinetic model for the pyrolysis of PS. The authors compared three types of experimental data (isothermal data, TGA curves, and gas product distributions) with the model predictions. Faravelli et al. (2001) also compared the predictions of overall rates of degradation and volatile product distribution with experimental results obtained by different authors at different pressure and temperature conditions.

2. Experimental Part

The type of plastic used was Polystyrene collected from households and than mechanically recycled, presented in small pellets with a diameter of 0.5 cm.

The plastic samples used were characterized by elemental analysis of carbon, hydrogen and nitrogen (CHN), and were found to always present a C:H ratio of 12,34 (86.4% C, 7.0% H, 6,4% N). X-ray Fluorescence Spectrometry analysis showed that the elements detected in higher amounts were sulphur, iron, siliceous, aluminium, magnesium and sodium. Titanium, zinc and chlorine were also detected but in very low amounts.

The pyrolysis experiments were carried out in a six micro autoclaves system using different temperatures and reaction times. Authors previous work, Pinto et al. (1999) indicated that the pyrolysis reaction rate was very high, what can mean that this process had a fast kinetic, so, in this work, very low reaction times were used. Higher reaction times were also tested to verify the length of time before achieving the stabilization point of the product yield and composition Hence, the following conditions for the pyrolysis of PS were chosen: reaction temperature — 350 to 420 °C, reaction time — 10 to 900 seconds, initial pressure — 0.41 MPa. All gaseous hydrocarbons produced were measured and collected for direct analysis by gas chromatography (GC), whilst liquid hydrocarbons were distilled and solids were extracted first with dichloromethane and then with tetra-hydrofuran. Liquid fractions were analysed using a GC-MS (gas chromatograph – mass spectrometer) to quantify their main compounds, which were quantified by GC.

The products obtained were divided in four fractions: solid, gas, heavy oil and light oil under NPT (normal pressure and temperature) conditions. The approach was to group the compounds produced based on their solubility in solvents. It was observed that the distilled fractions were soluble in dichloromethane. So, the light oil were the compounds soluble in dichloromethane and the heavy oil were the compounds soluble in tetra-hydrofuran. The compounds not soluble in these two solvents were called solid.

3. Results and discussion

Based on the experimental results obtained at different reaction temperatures and times, it was proposed a reaction pathway for the pyrolysis of PS. The reaction pathway proposed which best fitted the experimental results is shown in Figure 1. Several reaction pathways such as the one proposed by Ramdoss et al. (1998) were tested but they did not validate the experimental results obtained in this study.
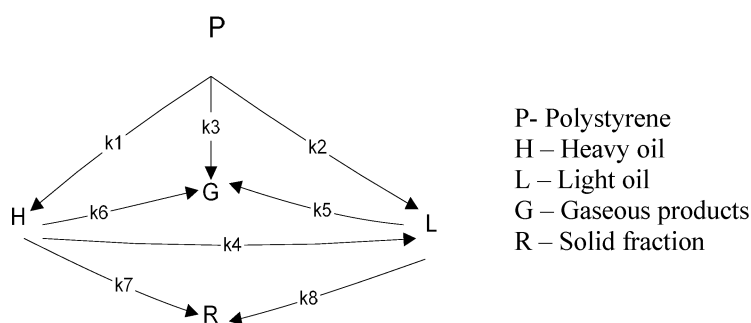

P- Polystyrene
H – Heavy oil
L – Light oil
G – Gaseous products
R – Solid fraction

Figure 1. Reaction pathway for Polystyrene pyrolysis.

The following assumptions were made in the development of the reaction pathway:

1) all the reactions are first order;
2) all the reactions are irreversible;
3) there are no mass transfer resistances;
4) the temperature dependence of the rate constants is described by the Arrhenius equation.

$$dP/dt = -k_1P - k_2P - k_3P \qquad (1)$$

$$dR/dt = k_7H + k_8L \qquad (2)$$

$$dH/dt = k_1P - k_6H - k_4H - k_7H \qquad (3)$$

$$dL/dt = k_2P + k_4H - k_5L - k_8L \qquad (4)$$

$$dG/dt = k_3P + k_6H + k_5L \qquad (5)$$

Based on the above assumptions, a theoretical kinetic model was developed. The parameters estimated in this model involved eight constants, which were determined at four different temperatures (350°C, 380°C, 400°C, and 420°C). These parameters were calculated by the resolution of the differential equation system (1) to (5), by using the program Micromath® Scientist® for Windows™ and the Runge-kutta method based on the Taylor theorem. The numerical adjustment interactions were undertaken using the Stineman method with the least squares analysis.

Following the calculation of the rate constants, it was verified that some of the steps considered in reaction pathway proposed, might not have occurred, because the values of the rate constants of these reactions was zero or very close to zero. These steps varied, depending on the temperature used, thus, the reaction pathway initially proposed becoming more simplified at higher temperatures. Hence, at the lower temperature tested, the initial polymer seems to be converted directly into light oil, heavy oil and gases. The light oil appears to have been also formed by the cracking of the C-C bond of the heavier compounds initially produced. The gaseous compounds might also have been formed by the cracking of the bonds C-C present in the compounds of the light oil. At 380°C and 400°C, the PS seems to have been converted exclusively into light oil and gases because the heavy oil was not formed. However, at 400°C and 420°C a solid fraction was also detected. This fraction was only formed at higher reaction temperatures and times and was, probably, produced by reactions between the compounds present in the light oil, which lead to higher molecular mass compounds, which were solid under NPT conditions.

The comparison of the experimental results with those predicted by the models is shown in Figures 2 to 5. The models agree well with the experimental results and provide a reasonable understanding of the mechanism prevailing during the thermal degradation of PS.
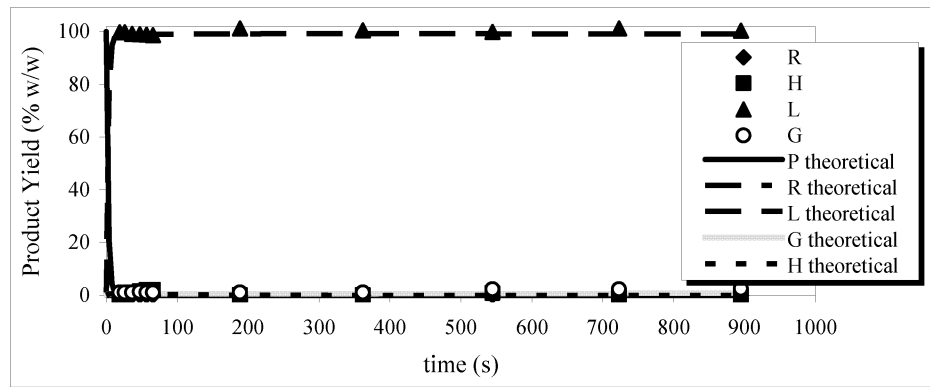
Figure 2. Model validation. Comparison between the model and experimental data at 350 °C.
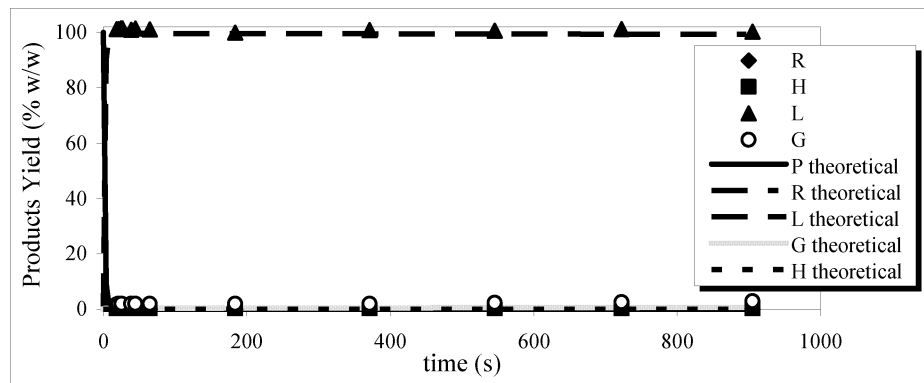

Figure 3. Model validation. Comparison between the model and experimental data at 380 °C.
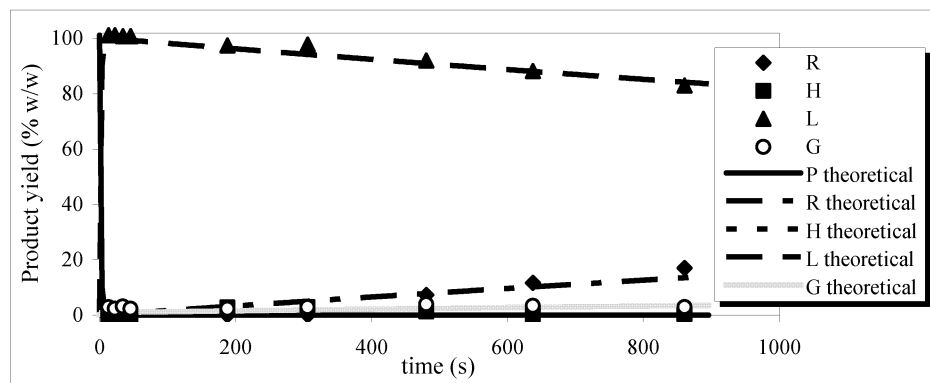

Figure 4. Model validation. Comparison between the model and experimental data at 400 °C.
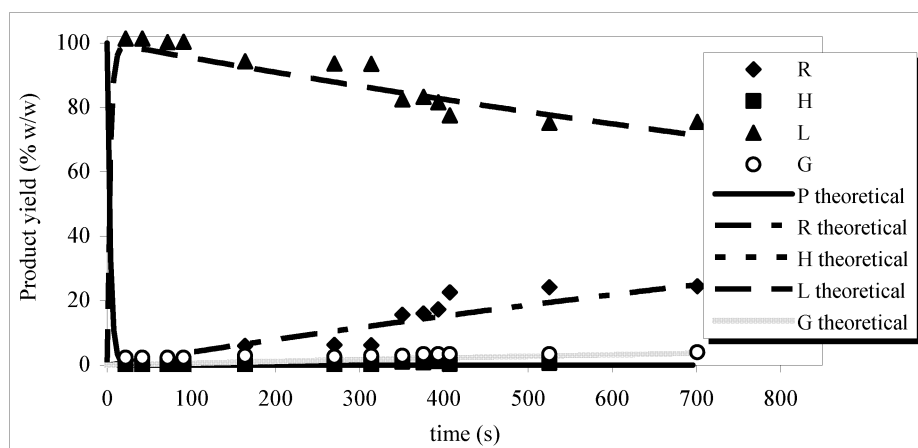
Figure 5. Model validation. Comparison between the model and experimental data at 420 °C.

From the experimental results obtained, it can be observed that the formation of light oil was always very high, about 100%, for all the temperatures tested and for very low reaction times. The experimental results obtained at 350°C and 380°C were similar. When these two temperatures were tested there was no formation of solid and the heavy oil only appeared at 350°C and in very low concentrations (less than 2.1% w/w). For the other two temperatures used, 400°C and 420°C, the formation of light oil decreased and those of heavy oil and solid increased with the rise of the reaction time. This decrease in the light oil was more significant (24.8%) at the higher temperature tested. this occurred over a time range initiating at 90.85s and most likely ending at about 525s. At 400°C, this decrease in the light oil yield was 17.7% and took place after 65s. The solid fraction was detected at higher reaction times and temperatures. When the temperature of 400°C was tested its value rose from 0% at 306s to 7.3% at 481s, achieving 17% after 861s of reaction time. When the temperature of 420°C was used, the same fraction was detected at a lower reaction time (164s), increasing its value from 6.0% for 24.5% (w/w). This means that the higher is the temperature used, the larger is the increase of the solid yield and smallest the reaction time during which it was detected. These results seem to indicate that the reactions between the lighter molecules initially formed was favored at higher reaction times and temperatures, originating compounds with higher molecular weight (solid under NPT conditions). The reactions were observed to be endothermic because it was tested a significant reduction of the temperature in the interior of the reactors, even with the oven switched on. This fact suggests that the energy necessary for this reaction to occur was very high and it could only happen at greater reaction temperatures. The heavy oil was always detected in very low amounts (less than 3% w/w).

For all the temperatures tested, the gas yield increased, almost linearly, with the reaction time. However, the cracking of the C-C bond of the molecules initially formed in order to originate even more lighter compounds (gases), does not seem to have been favored, because the gases yield was always lower than 4% (w/w). This low value of the gas yield, can, perhaps, be explained by the aromatic structure of this plastic, which, during the cracking of the polymeric chain in the PS pyrolysis, led to the formation of intermediate radicals with more steady links and so with lower trend to be broken and to form compounds of smaller molecular weight.

With the aim of calculating the activation energy and the pre-exponential factor of the different steps presented in the reaction pathway considered for the pyrolysis of PS, it was represented the temperature dependence of the rate constants assuming the Arrhenius law. However, the constants rate in the logarithmic form do not show a linear dependence on the temperature, and for reactions 1, 4 and 8 the rate constant was calculated to be almost zero for some of the tested reaction temperatures. Thus the activation energy and the pre-exponential factor could not be calculated. This fact probably indicates that temperature affects reaction mechanism and diffusion limitations started to become rate controlling.

The product composition was determined. In the gaseous fraction alkanes and alkenes were detected involving methane and other compounds with up to five carbon atoms. It was found that there was same hydrogen but only when the temperature of 420°C was used and its percentage did not exceed 4.5% (v/v). The liquid fraction was, mainly, constituted by aromatic compounds, namely, styrene, α-methylstyrene, toluene, ethylbenzene and cumene. It was observed a higher concentration of styrene and α-methylstyrene when lower reaction temperatures and times were used. The decrease of the concentration of these two compounds was accompanied by an increase in ethylbenzene and cumene concentration. This evolution seems to indicate that α-methylstyrene initially formed, which was subsequently converted in ethylbenzene and cumene, could only be present by supplying more heat to the reaction system.

4. Conclusions

A kinetic model involving eight elemental first order reactions was proposed. The model fits reasonably well with the experimental results. It was observed the presence of a solid product which was detected at higher reaction temperatures and times during experimental runs. This fraction has been, probably formed by reactions between the lighter molecules initially formed, subsequently giving rise to products with larger molecular weight. These reactions seem to have been favoured at higher reaction times and temperatures. For lower temperatures (350 and 380°C), the presence of the solid fraction was not detected and the heavy oil yield was very low. The level of the light oil yield was very high (approximately 100%), and this was obtained at very low reaction times. This fraction seems to have been formed through the direct conversion of PS, for all temperatures tested. The gas yield was always very low, however, its value increased with the rise of the reaction temperature. The formation of gases directly from the polymeric chain of PS seems to have been favoured for the temperatures up to 400°C; however, when the highest reaction temperature was tested this fraction appeared to have been formed only from cracking of the C-C bonds of the light oil compounds.

5. References

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