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Study of the PP Pyrolysis Kinetics

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A kinetic study of Polypropylene was performed in order to analyse, if the direct conversion of this plastic waste into gaseous, liquid and solid products was favoured, or if parallel reactions and/or reversible elementary steps should be considered. Based on the experimental results obtained at different temperatures and reaction times, a possible reaction pathway was proposed. The fitting of a kinetic model to the experimental data was performed. The models fitted reasonably well the results and gave a satisfactory explanation of several experimental data obtained during the thermal degradation of PP. The kinetic parameters were estimated and it was observed a temperature dependence of the activation energy and of the pre-exponential factor. This fact probably indicates that temperature affects reaction mechanism.

1. Introduction

Modern societies are over dependent on petroleum for fuels and for raw material in many industries. In the world, this raw material is the most consumed to produce energy. Hence, efforts have to be undertaken to implement a better management of the petroleum resources and to optimize the energy efficiency technologies finding alternative means for obtaining fuels, as for example by recycling and reutilization of the products obtained from petroleum. Furthermore the fraction of plastics in municipal solid wastes (MSW) is continuously rising, hence becaming one of the main concerns of the European Union.

The need of finding viable solutions quickly for the mentioned problems, had led to the idea of applying pyrolysis technology to plastic waste to allow the recovery of its energy content.. In pyrolysis both industrial plastic waste mixtures that can not be incorporated in the industrial process, and the plastic mixtures present in municipal solid wastes could be used. Pyrolysis is a thermochemical process which has the inherent advantages of high flexibility with respect to feedstock characteristics, so it can be applied to plastic mixtures even if they are contaminated. This is the main advantage of this process.

The majority of the kinetics studies on PP thermal degradation have been based on Thermal Gravimetric Analysis (TGA). TGA measurements have major limitations, because they are only able to describe the steps which are normally associated with weight loss (Agrado and Serrano, 1999). Also by using TGA in kinetic studies, it is only determined the evaporation rate of products and not the intrinsic chemical reaction rate, once only product fragments which are small enough will evaporate and lead to a decrease of the polymer mass (Westerhout et al., 1997).

Several thermogravimetric analyses were performed on samples of Polypropylene. Westerhout et al. (1997) studied the kinetics of pyrolysis plastic waste using TGA at temperatures below 450 ºC. Aguado et al. (2002) performed a kinetic study on a conical spouted bed reactor and compared the results with those obtained by thermogravimetry and by using a high-heating-rate micro-reactor.

2. Experimental Part

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

X-ray Fluorescence Spectrometry analysis of the PP used showed that the elements detected in higher amounts were calcium and chlorine. Lead, zinc, titanium sulphur, potassium, silicon, aluminium and iron were also detected but in very low amounts. The plastic samples used were also characterized by elemental analysis to carbon, hydrogen and nitrogen (CHN), and always presented a C:H ratio of 6.30 (85.0% C, 13.5% H, <0.2% N).

A system involving five 160 ml microautoclaves was used in the present study. The autoclaves were placed inside a stirred heated oven one by one. When the desired temperature was reached, each autoclave was left in the oven for the reaction time previously pre-set. All gaseous hydrocarbons were measured and collected in a sampling bag for direct analysis by GC. The liquid hydrocarbons were distilled and three fractions were obtained: the light oil, with a distillation point lower than 150 ºC, the heavy oil that distillates between 150 ºC and 270 ºC and the liquid residue. The solid fraction and the liquid residue were extracted, first with dicloromethane and then with tetrahydrofuran. The first two fractions of distillation, the extracted light oil and the extracted heavy oil were analysed using a GC-MS to identify their main compounds, which were quantifyed by GC.

3. Results and discussion

Half of the carbon atoms that constitute the polymeric chain of the PP are tertiary, therefore, the thermal degradation of the PP occurred at lower temperatures than those observed for the PE pyrolysis. Based on the experimental results obtained at four different temperatures (380ºC, 400ºC, 420ºC and 440ºC) and at reaction times between 8 and 1200s, it was proposed a reaction pathway that is presented in Figure 1. Several reaction pathways (Ramdoss et al., 1998) were tested but they did not validate the experimental results obtained in this study. The reaction pathway shown in Figure 1 was the one that best fitted the experimental results. In this reaction pathway, it is assumed that the PP is converted into solid (P1), gas (G), light oil (L) and heavy oil (H). This division was made based on the solubility of the products in organic solvents. The compounds soluble in dicloromethane (included the distilled fractions which were verified to be soluble in dichloromethane) were called light oil, the ones soluble in tetra-hydrofuran were named heavy oil. The fraction not soluble in either of these solvents was called solid and could correspond to a polymer of lower molecular weight because it was detected at very short reaction times and lower temperatures.

The following assumptions were made for 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 are described by the Arrhenius equation.

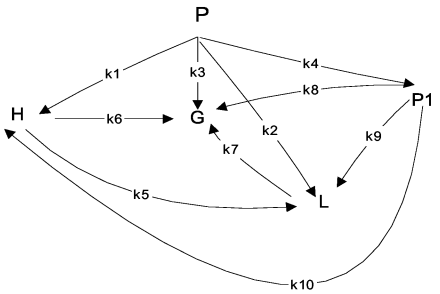

Figure 1. Reaction pathway for Polypropylene pyrolysis.

The model is described by the following differential rate equations, concerning the reactant P and all the products considered:

$$dP/dt = -k_1P - k_2P - k_3P - k_4P \quad (1)$$

$$dP1/dt = k_4P - k_8P1 - k_9P1 - k_{10}P1 \quad (2)$$

$$dH/dt = k_1P - k_6H - k_5H + k_{10}P1 \quad (3)$$

$$dL/dt = k_2P + k_5H + k_9P1 - k_7L \quad (4)$$

$$dG/dt = k_3P + k_6H + k_7L + k_8P1 \quad (5)$$

The ten rate constants present in this model were estimated based on the experimental results obtained at four different temperatures (380°C, 400°C, 420°C and 440°C). These parameters were calculated by the resolution of the differential equation system, equations (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 made using the Stineman method with least squares analysis.

The application of the model for the temperature of 440°C produced the worse agreement with the experimental results, and this might be explained by a significant change in the reaction mechanism. At this temperature the solid yield rose with the increase of the reaction time, which can mean that this solid fraction is different from the one formed at the other temperatures tested. This solid (R) appears to have been formed only after by the combination of the lighter molecules initially formed. So, another reaction pathway for the pyrolysis of PP at 440°C was proposed and it is presented in Figure 2.

The values obtained for the rate constants indicated that some of the steps considered in the reaction pathways proposed do not seem to have occurred, as their values were approximately zero for some of the temperatures tested. For the lowest temperatures used (380 and 400°C), the reaction pathways were similar. At 420°C, the heavy oil seems to have been converted into light oil and at 440°C, the light oil fraction seems to have only been formed by the direct conversion of PP. Also, at this temperature the gas fraction seems to be formed by the conversion of PP and of the light oil.

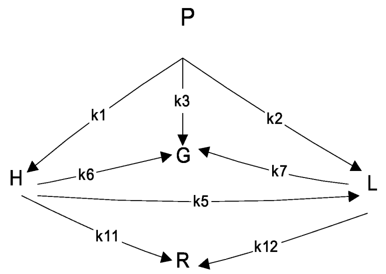

Figure 2. Reaction pathway for Polypropylene pyrolysis at 440 °C.

The comparison of the experimental results with those predicted by the models is shown in Figures 3 to 6. The adjustments of the models agree well with the experimental results and provide a reasonable understanding of the mechanism prevailing during the thermal degradation of PP.

The experimental results obtained in the pyrolysis of PP, showed that the selectivity for the production of light oil rose from 48% to 91% (%w/w), whilst the heavy oil decreased considerably for a temperature range of 380 to 440°C. The solid product also decreased with the temperature, from 36% to 2.5% (%w/w). Furthermore, the reaction time at which the maximum conversion of light oil was obtained decreased with the increase of reaction temperature. At higher temperatures, a high value for the light oil yield at very low reaction times was obtained. This product yield was 91.8% (w/w) for a reaction time of 8s and a reaction temperature of 440°C.

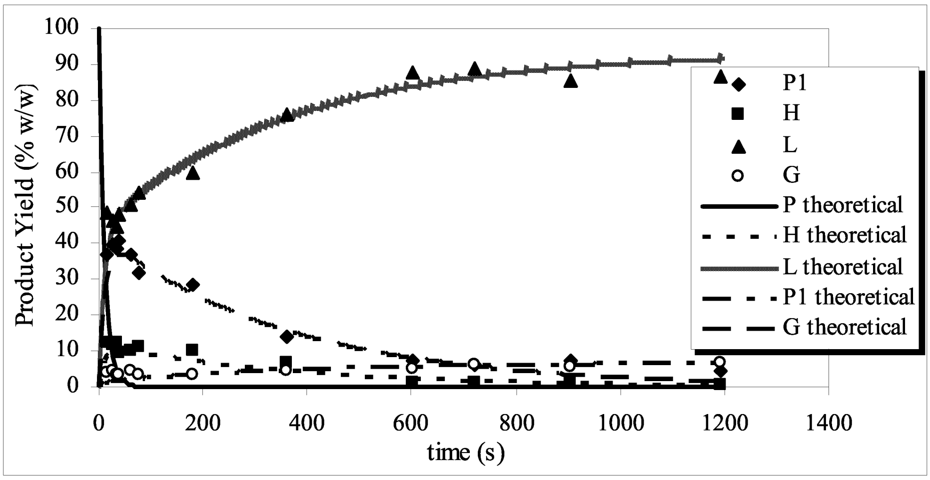

Figure 3. Model validation. Comparison between the model and experimental data at 380 °C.

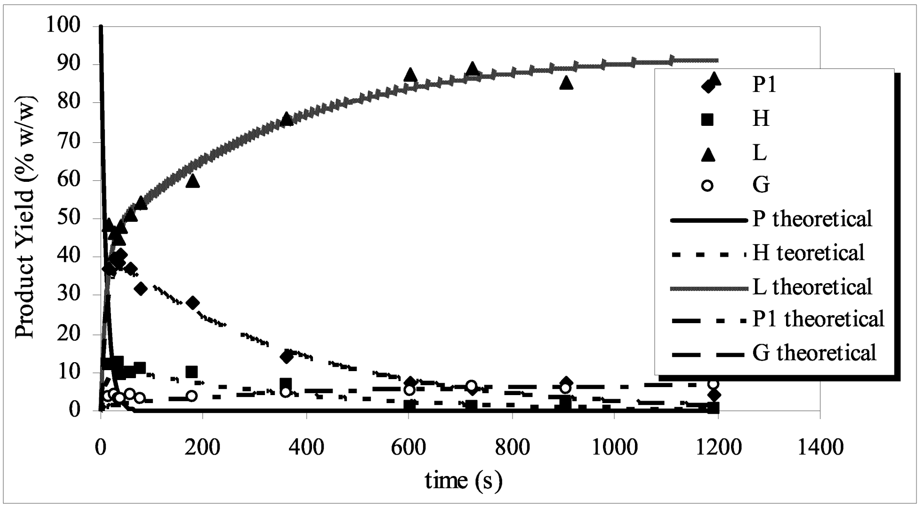

Figure 4. Model validation. Comparison between the model and experimental data at 400 ºC.

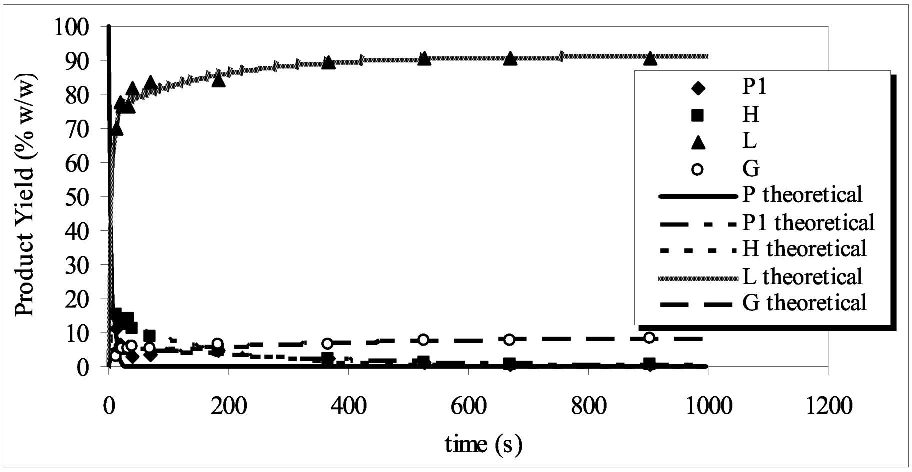

Figure 5. Model validation. Comparison between the model and experimental data at 420 ºC.

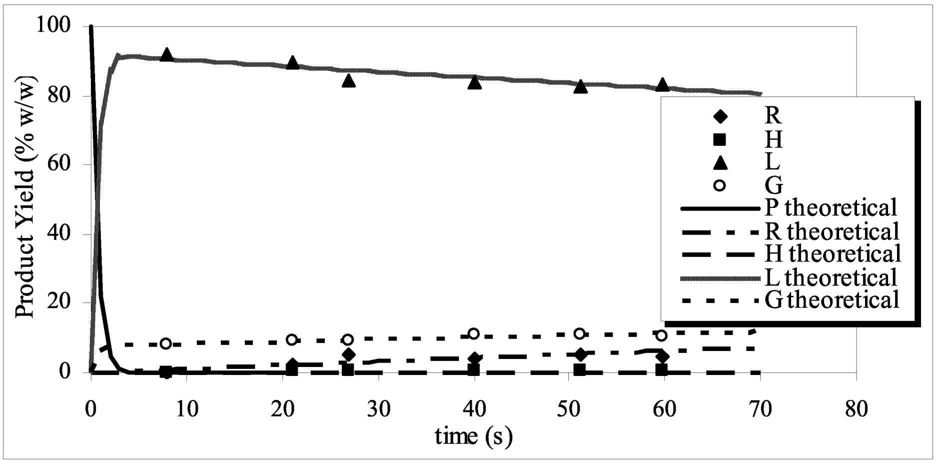

Figure 6. Model validation. Comparison between the model and experimental data at 440 °C.

4. Conclusions

The experimental results were compared with those obtained using a kinetic model. It was verified that the model adjusts to the experimental results sufficiently well permitting to explain satisfactorily the mechanism of PP pyrolysis. The rate constants of the first order elementary reactions were calculated.

From the experimental results it was verified an increase in the light oil and gas yield and a reduction in the heavy oil and solid. It was also observed that the reaction time at which the maximum conversion of light oil was obtained decreased with the rise of the reaction temperature. The reduction of the solid and of the heavy oil was, probably, due to the conversion of the polymer of lower molecular weight initially formed and of the heavy oil in light oil. When the temperature of 440ºC was used, it seems to occur a significant alteration of the reaction mechanism. At this temperature, it was detected the formation of a solid fraction whose yield increased with the rise of the reaction time, and by the decrease of the light oil yield. This fraction seems to have been formed through reactions between molecules of lower molecular weight initially formed, which originated compounds of higher molecular weight (solid in the PTN conditions). Thus, during the PP pyrolysis, the reactions between lighter molecules initially formed, appeared to originate heavier molecules that subsequently seem to have been favored at higher reaction temperatures and times.

5. References

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