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Examination and Evaluation of the Use of Screen Heaters for the Measurement of the High Temperature Pyrolysis Kinetics of Polyethene and Polypropene

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A screen heater with a gas sweep was developed and applied to study the pyrolysis kinetics of low density polyethene (LDPE) and polypropene (PP) at temperatures ranging from 450 to 530 °C. The aim of this study was to examine the applicability of screen heaters to measure these kinetics. On-line measurement of the rate of volatiles formation using a hydrocarbon analyzer was applied to enable the determination of the conversion rate over the entire conversion range on the basis of a single experiment. Another important feature of the screen heater used in this study is the possibility to measure pyrolysis kinetics under nearly isothermal conditions. The influence of the mixing process in the gas phase on the measured hydrocarbon concentration versus time curve was assessed and it was demonstrated that the residence time distribution of the gas phase, which has to be accounted for to correctly interpret the experiments, becomes the limiting factor when measuring pyrolysis kinetics at high temperatures and not the heat transfer rate. With this type of apparatus, pyrolysis reactions with a first order rate constant lower than 2 s^{-1} can be studied, which implies that the pyrolysis kinetics of the forementioned polymers could be determined at temperatures below 530 °C. The kinetic constants for LDPE and PP pyrolysis were determined, using a first order model to describe the conversion rate in the 70–90% conversion range and the random chain dissociation model for the entire conversion range. Our experiments revealed that both LDPE and PP possess the same conversion rate, which is unexpected behavior since PP should be more sensitive to thermal degradation than LDPE. A comparison of the thermo gravimetric analyzer results with those obtained with the screen heater indicates an enhancement of the pyrolysis kinetics in the latter equipment. Several hypotheses were tested to explain this phenomenon and led to the suspicion that the discrepancy is possibly due to the effect of the electrical current passing through the screen on the pyrolysis reaction, although most of the evidence for this hypothesis is indirect. Screen heaters can therefore not be used in this configuration to measure the pyrolysis kinetics, if this hypothesis is correct. In addition to the experimental work two single particle models have been developed which both incorporate a mass and a (coupled) enthalpy balance, which were used to assess the influence of internal and external heat transfer processes on the pyrolysis process. The first model assumes a variable density and constant volume during the pyrolysis process, whereas the second model assumes a constant density and a variable volume. An important feature of these models is that they can accommodate kinetic models for which no analytical representation of the pyrolysis kinetics is available. Model calculations revealed that heat transfer limitations were not important during the pyrolysis experiments performed in the screen heater and could not explain the forementioned results.

1. Introduction

In the Netherlands some 780 kton of mixed plastic waste (MPW) is produced every year (Rijkema *et al.*, 1992), whereby households account for approximately 580 kton MPW. The MPW consists mainly of polyethene (PE) and polypropene (PP, together 70 wt %), polystyrene (PS, 14 wt %), and poly(vinylchloride) (PVC, 11 wt %). Until recently the MPW was dumped or incinerated together with household waste, but countries like Germany and the Netherlands have or will probably forbid these disposal methods in the near future. It is believed that many other countries in Europe and the U.S.A. and Japan will follow.

As a result much research is being conducted on alternative disposal methods like recycling. One of the most promising recycling methods is the pyrolysis of MPW at high temperatures. Using this method valuable chemicals like ethene, propene, benzene, and styrene can be produced, which subsequently can be used to produce new polymers. Some high temperature

pyrolysis processes were already developed in the early 1970's (Sinn *et al.*, 1974, 1976; Batelle Memorial Institute, 1992; BP, 1992; Union Carbide, 1975), but none of these processes ever reached a commercial status. Due to the absence of economical, environmental, and political incentives at that time, there was no further development of these processes.

To enable design, evaluation, and optimization of high temperature pyrolysis reactors, data on pyrolysis kinetics at elevated temperatures have to be available. Therefore the aim of this article is the examination and evaluation of the use of a screen heater to measure the pyrolysis kinetics of polymers or other substances. To achieve this goal the kinetic parameters for PE and PP were measured at elevated temperatures (450–600 °C) using a screen heater with novel features, which was developed for this study.

Darivakis *et al.* (1990) and Sawaguchi *et al.* (1980, 1981) investigated the high temperature pyrolysis kinetics of some polymers (respectively PE/PS and PE/

PP), whereby the first authors used a screen heater for this purpose. The polymer samples were rapidly pyrolyzed in a helium atmosphere by using heating rates of typically 1000 K/s from room temperature to a prescribed final (peak) temperature ranging between 400 and 800 °C. To extract the kinetic parameters from the experimental data a model assuming a large number of independent parallel first order reactions was used, whereby corrections had to be made to account for the temperature history experienced by the polymer sample.

Kinetic studies can roughly be divided into two classes depending on the fact whether isothermal or nonisothermal conditions are employed. Isothermal conditions are preferred because interpretation of the experimental data is simpler, since only one parameter, namely, the conversion, changes during an experiment, instead of two parameters (conversion and temperature) in the case of nonisothermal methods. Another advantage of isothermal methods is the fact that a change in the reaction mechanism due to a temperature change cannot occur. The design of the screen heater used in the present study enables operation under nearly isothermal conditions, which is a major improvement in comparison with previous designs.

In previous studies screen heaters have often been used to study the pyrolysis of coal and wood (for instance Hamilton *et al.*, 1980, Hajaligol *et al.*, 1982), where the screen heater was typically operated in the nonisothermal mode, with heating rates which varied between 1 and 10 000 K/s. Conversions were determined by weighing the screen before and after each experiment. Curie point pyrolysis, a technique similar to the one used in the screen heater, was also used in the past to study the pyrolysis of plastics (Sodero *et al.*, 1996).

Summarizing the main features of our screen heater:

- application of a gas sweep for rapid removal of the pyrolysis products.
- real-time measurement of the total hydrocarbon concentration in the gas phase enabling measurement of the conversion rate over the entire conversion range during one experiment.
- operation under isothermal and nonisothermal conditions is possible.

2. Description of Pyrolysis Kinetics

In this paper two models will be used, which have been applied to describe and study the pyrolysis kinetics of PE, PP, and PS. A detailed description of these models is given elsewhere (Westerhout *et al.*, 1997). A first order kinetic equation was used to describe the pyrolysis kinetics for high conversions (70–90% conversion):

$$\frac{\partial \xi}{\partial t} = k_0 e^{(-E_{act}/R_g T)} (1 - \xi) \quad (1)$$

The first order kinetic model was applied, because it has frequently been used in the literature to describe the pyrolysis kinetics of PE, PP, and PS (Westerhout *et al.*, 1996). The use of this model enables comparison between literature data and our experiments. Another reason, why this model was applied, is that it can be implemented without any difficulty in the single particle models (see section 6).

By using an apparatus like a screen heater or a thermo gravimetric analyzer (TGA) in a kinetic study, in fact the rate of evaporation of pyrolysis products is measured and not the chemical reaction rate (breaking

of bonds) itself. Breaking of bonds does not necessarily lead to product evaporation: only polymer chains which are small enough to evaporate under the prevailing conditions will actually leave the polymer sample. This phenomenon is the main reason for the complex kinetic pyrolysis behavior of the polymers.

A new model termed the random chain dissociation (RCD) model, recognizes and accounts for the forementioned effect. It considers the pyrolysis process as a random process, where each bond of the same type has an equal probability for cleavage, with a rate description according to a first order model. Because of the differences in stability of chains bonds, caused by attached functional groups or radicals, a separate kinetic constant k_i is introduced for each type of bond:

$$\frac{\partial N_i}{\partial t} = -k_i e^{(-E_{act,i}/R_g T)} N_i \quad (2)$$

In this model the mass of the polymer sample decreases due to evaporation of chains shorter than a certain "evaporizable" chain length L_c . This parameter is a function of temperature and its value can be estimated from the boiling temperatures of n -alkanes and n -alkenes. This approach implies that cleavage of the first bonds will not immediately result in evaporation of the degraded chains and thus this model predicts an initiation period with a comparatively low conversion rate. Following this initiation period the conversion rate first increases until it reaches a maximum, after which the conversion rate decreases due to a decrease of the available number of bonds.

Due to the complex nature of this kinetic description it is not possible to derive an analytical representation for the pyrolysis kinetics. Only by computer simulations the conversion can be obtained as a function of time for a given set of (kinetic and physical) parameters.

Resuming, the incorporation of the influence of different types of chemical bonds and the correction for the difference between bond cleavage and evaporation of volatile fragments constitute the main features of the RCD model. Furthermore the RCD model can be used to predict the primary product spectra and the influence of the molar weight on the reaction kinetics. The only fit parameters required are the kinetic constants for the different types of bond cleavage. In the standard situation the number of fit parameters is the same as in the first order model (namely, two). Only if β -scission or side chains have an significant influence on the conversion rate, the number of fit parameters increases to four, due to the fact that two reactions have to be accounted for.

3. Equipment and Experimental Procedures

3.1. Equipment. The screen heater can be divided into three parts: the reactor section (including the piping), the temperature control section, and the analysis section.

The screen heater has a rectangular shape (dimensions: width 90 mm, height 22 mm, and length 530 mm; see Figure 2) and is equipped with a removable cover section containing the screen clamps and the thermocouple connections. Between the two clamps a 65 × 55 mm folded stainless steel (RVS 310) wire mesh screen (with 40- μ m wires and 62- μ m holes) can be positioned in which a polymer sample can be sandwiched (see Figure 3). Two 50 μ m chromel/alumel K-type thermocouples were used to measure the screen temperature.

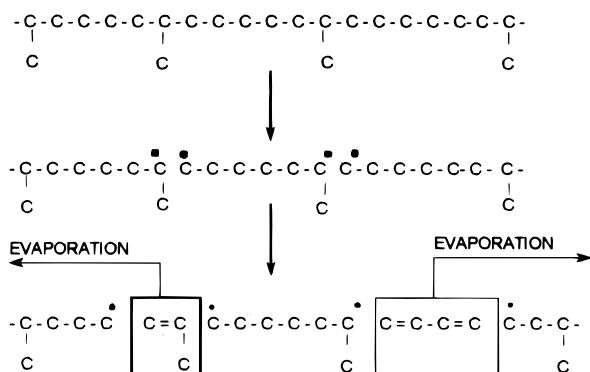


Figure 1. Schematic representation of processes incorporated in the RCD model.

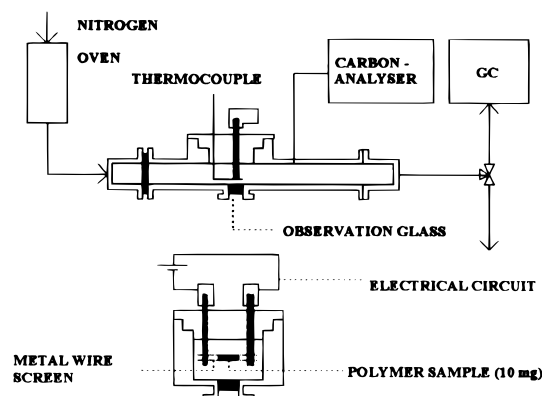


Figure 2. Side and front view of the screen heater.

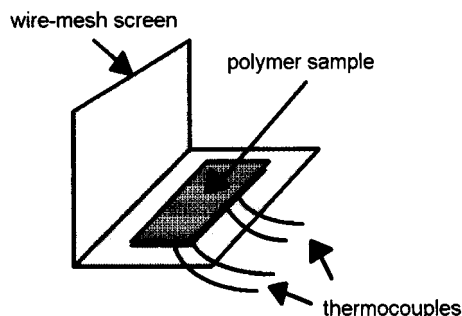


Figure 3. Screen with polymer sample and thermocouples.

The thermocouple wires were welded on one side into the wire mesh screen, while the other ends were attached to the thermocouples connections, which were connected to the temperature control section. One thermocouple was used to control the screen temperature, while the other was used to detect temperature differences over the screen. The reactor also contains an in- and outlet for the gas stream passing along the screen. To suppress secondary gas phase reactions, the volatile products of the primary pyrolysis reactions were removed from the screen area and rapidly quenched by the cold gas stream. However, to avoid any possible condensation of products in the reactor, the nitrogen fed to the reactor and the reactor itself were preheated to 150 °C. Our screen heater operates under atmospheric pressure.

By suddenly passing a strong electric current ("pulse") through the screen, a screen heating rate of approximately 10^4 K/s could be achieved, whereby the final temperature could be set by choosing the pulse duration. The required heating power was supplied by three conventional 12-V batteries connected in series to produce a maximum possible current of approximately

200 A. After this initial heating period, which typically had a duration of 20–40 ms, the temperature control system maintained the screen temperature at the desired final value (within a tolerance of ± 2 °C) by appropriately changing the current passing through the screen. To avoid influences of the electrical current passing through the screen on the temperature measurements the DC current was alternately switched on and off with a frequency of 1 kHz. During one cycle the current was on during 0.7 ms and off during 0.3 ms, whereby the screen temperatures were measured halfway the off period. Based on the temperature measurement of the first thermocouple the temperature control system adjusted the current fed through the screen to maintain the preset temperature.

A JUM 3–300 hydrocarbon analyzer was used to continuously sample the exiting gas flow. To reduce radial concentration gradients a turbulent gas flow (10.6 Nm³/h) was used. By varying the radial position of the sample inlet it could be established that radial concentration gradients were virtually absent. The actual hydrocarbon concentrations were measured with a flame ionization detector (FID) in the hydrocarbon analyzer.

A personal computer was used for data acquisition and postprocessing of the temperature and hydrocarbon concentration measurements.

3.2. Experimental Procedure. A stainless steel wire-mesh screen was used as sample holder as shown in Figure 3. Two thermocouples were welded into the mesh at a certain distance (typically 10–20 mm) from each other. Subsequently the screen was weighed and with the aid of a rectangular mould approximately 5–10 mg of polymer was spread equally on the screen to produce a monolayer of particles, after which the screen was folded. After reweighing, the screen was positioned between the screen clamps (connected to the removable reactor screen section) and the thermocouple wires were connected to the thermocouple connections. The reactor was closed with the cover section and with a rotameter the desired gas flow rate was set. After setting the initial pulse duration and the desired final temperature, the experiment was started and the temperatures and hydrocarbon concentrations were registered with the personal computer as a function of time.

The actual instantaneous hydrocarbon concentration (x_{hc}) can be related to conversion rate of the polymer sample by use of the following mass balance:

$$\frac{\partial m}{\partial t} = -\Phi_{m, hc} = -x_{hc} \Phi_m \quad (3)$$

The actual mass fraction of hydrocarbons in the gas phase (x_{hc}) can be related to the voltage signal of the hydrocarbon analyzer ($y(t)$) by a calibration factor a . By assuming that the product composition remains constant in time, the equation above can be written in terms of the conversion ξ and the hydrocarbon analyzer voltage signal $y(t)$:

$$\xi(t) = a \Phi_m \int_0^{t_{end}} y(t) dt \quad (4)$$

in which a can be calculated from the initial mass of the polymer sample and the hydrocarbon analyzer voltage signal $y(t)$.

In case the gas flow through the reactor and downstream equipment (i.e., analyzer including tubes etc.) exhibits plug flow behavior, the actual hydrocarbon

concentration close to the screen will be the same as the hydrocarbon concentration detected by the analyzer (except for a time lag) and consequently the response of the analyzer can directly be used to calculate the kinetic constants after correction for the time lag. However, due to mixing in the gas phase the hydrocarbon concentration detected by the analyzer differs from the concentration close to the screen. In order to evaluate and correct for the effect of gas phase mixing, the residence time distribution (RTD) of the screen heater was studied in more detail.

3.3. Residence Time Distribution of the Screen Heater Setup. In our RTD studies propane was injected at various locations in the system to determine the relative contributions of the various sections (i.e., the reactor, tubes, hydrocarbon analyzer) to the overall RTD of the system.

The measurements showed that the most important contribution to the RTD of the system is by the hydrocarbon analyzer itself, while the reactor and the sampling sections exhibited the desired plug flow behavior. By removing an internal filter the RTD caused by the hydrocarbon analyzer could significantly be reduced.

Measurements and calculations showed that the analyzer hampers the application of this apparatus (even after the modifications) for very fast reactions (i.e., in the case where the first order reaction constant exceeds 2 s^{-1}). For a first order reaction with a rate constant exceeding 2 s^{-1} , calculations showed that the conversion rate is so high that the shape of the measured concentration versus time curve is almost completely determined by the RTD and not the intrinsic chemical kinetics. The calculations also showed that for experimentally observed k values below 2 s^{-1} the experiments did not have to be corrected for the RTD in the system to obtain the intrinsic kinetic constants.

4. Experimental Results

4.1. Screen Heater Experiments. In this study low density polyethylene (LDPE1) with a density of 917 kg/m^3 and an average initial molar weight of $350\,000 \text{ g/mol}$ and polypropylene (PP) with a density of 905 kg/m^3 and an unknown molar weight were investigated. Both polymers were powders with a particle diameter ranging from 65 to $125 \mu\text{m}$. Despite the complexity of the experiments, reproducible kinetic constants could be obtained from the experiments. The main source of inaccuracy could be attributed to small temperature differences across the screen. Several experiments did not meet the requirement set for this temperature difference and were not considered for interpretation.

The screen heater experiments had to be conducted in the temperature range from 450 to 600°C , since pyrolysis experiments conducted at lower temperatures produced very low hydrocarbon concentrations ($<10 \text{ ppm}$), which could not be measured accurately, whereas experiments conducted at temperatures higher than 600°C were clearly not influenced by the temperature, which indicated that the conversion rate was not determined by the intrinsic chemical kinetics during these experiments but by the RTD or heat transfer processes.

As described in section 4 the experiments were fitted with a first order kinetic model for the 70–90% conversion range and with the RCD model for the entire conversion range. An example of an experimental curve and the obtained model fits is shown Figure 4.

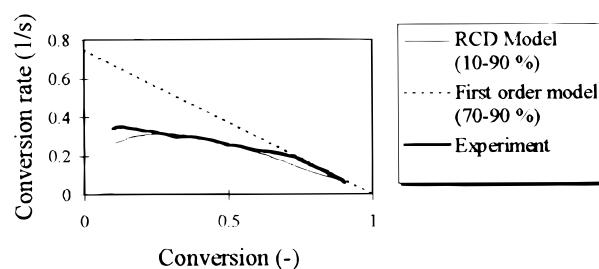


Figure 4. Example of measured conversion curve and model fits (LDPE1, 503°C).

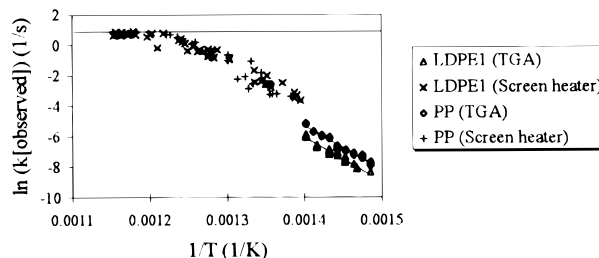


Figure 5. Arrhenius plot for the first order rate constants of LDPE1 and PP obtained from screen heater and TGA experiments.

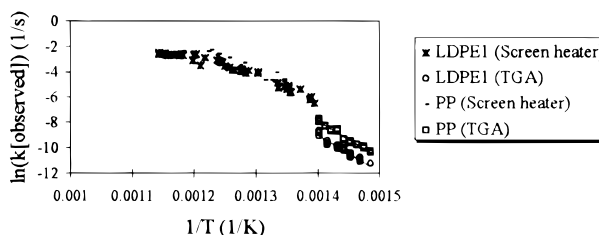


Figure 6. Arrhenius plot of the RCD model rate constant for LDPE1 and PP obtained from screen heater and TGA experiments.

In Figures 5 and 6 the rate constants for the pyrolysis of LDPE1 and PP for respectively the first order model and the RCD model are shown. Rate constants measured with a Seteram TG-85 TGA in the temperature range from 400 to 450°C are also shown in these figures. The TGA equipment used and the experimental procedure, which was followed, are described in more detail elsewhere (Westerhout *et al.*, 1997).

The kinetic constants obtained on the basis of screen heater experiments show no significant temperature dependence at temperatures exceeding 530°C , for which the following two reasons can be given:

- Internal or external heat transfer processes limit the conversion rate. Because of the very large external heat transfer coefficient in the screen heater possible heat transfer resistances will be situated inside the polymer particle. The pyrolysis number Py (Pyle *et al.*, 1984) represents the ratio of the time constant for a first order pyrolysis reaction and the time constant for unsteady internal heat conduction for spheres and is given by

$$Py = \frac{\lambda_p}{k_1 \rho_p c_{pp} x_p^2} \quad (5)$$

The physical significance of Py implies that the internal heat transfer resistance can be neglected if $Py \gg 1$, which means that the reaction is slow compared to the heat penetration. In the case $Py \ll 1$ internal heat transfer limitations become important. From the kinetic parameters listed in Table 1 and the thermophysical data of the polymers used, it could be established that the internal heat transfer resistance influenced the

Table 1. First Order Kinetic Parameters for LDPE1 and PP Pyrolysis Obtained from Screen Heater and TGA Experiments

polymer type	$\ln(k_0)$, s ⁻¹	E_{act} , kJ/mol	k_{773K} , s ⁻¹	r^2 ^b
LDPE1 (screen heater)	31.2 ± 1.6	207 ± 10	0.36 ± 0.02	0.95
PP (screen heater)	34.7 ± 2.4	230 ± 15	0.34 ± 0.02	0.91
LDPE1 (TGA)	34.6 ± 1.7	241 ± 10	0.05 ^a ± 0.009	0.96
PP (TGA)	35.7 ± 1.3	244 ± 8	0.10 ^a ± 0.006	0.94

^a Extrapolated. ^b Only gives indication of experimental uncertainty.

Table 2. Kinetic Parameters of RCD Model for LDPE1 and PP Pyrolysis Obtained from TGA and Screen Heater Experiments

polymer type	$\ln(k_0)$, s ⁻¹	E_{act} , kJ/mol	k_{773K} , s ⁻¹	r^2 ^b
LDPE1 (screen heater)	19.4 ± 0.9	152 ± 6	0.014 ± 0.0005	0.94
PP (screen heater)	24.9 ± 1.7	185 ± 11	0.021 ± 0.0002	0.92
LDPE1 (TGA)	32.2 ± 2.1	244 ± 12	0.003 ^a ± 0.0008	0.94
PP (TGA)	32.1 ± 1.3	237 ± 7	0.008 ^a ± 0.0019	0.95

^a Extrapolated. ^b Only gives indication of experimental uncertainty.

measured conversion rate only at temperatures exceeding 620 °C. It can thus be concluded that heat transfer limitations did not cause the apparent insensitivity of the kinetic parameters to the temperature at temperatures above 530 °C. This conclusion was confirmed by calculations performed on the basis of the single particle models described in section 5.

• The RTD has a dominant influence on the measured conversion versus time curve at temperatures higher than 530 °C. This is most likely to be the case, because the experimentally determined value of k is approximately 2 s⁻¹ in this temperature range. As stated before, for these k values the RTD determines the shape of the measured concentration curve and not the intrinsic kinetics of the pyrolysis process. The RTD therefore largely determines the experimentally observed k value at temperatures exceeding 530 °C.

The kinetic parameters corresponding to the first order model and the RCD model, which were calculated from the experimental data in the temperature range from 460 to 530 °C, are summarized in Tables 1 and 2. The values for the TGA experiments in the range from 400 to 450 °C are also given in these tables.

The kinetic parameters for LDPE1 and PP pyrolysis obtained from screen heater experiments differ substantially, but the resulting k values for both polymers are virtually the same as can be seen in Figures 5 and 6. The reason for the difference in the kinetic parameters is the large mutual influence of k_0 and E_{act} . The fact that the k values do not differ substantially is remarkable since our previous study and literature data have shown that side chains have a significant influence on the conversion rate of polymers during pyrolysis (Westerhout *et al.*, 1997).

Another remarkable result is that, especially for LDPE, the (extrapolated) kinetic constants measured with the screen heater and the TGA show a large discrepancy. If the kinetic constants measured with the TGA are extrapolated to higher temperatures, lower rate constants are found than can be expected on the basis of the screen heater experiments.

This fact and the fact that no influence is found of the type of polymer lead to the suspicion that another phenomenon besides thermal degradation reactions may have occurred during the pyrolysis experiments con-

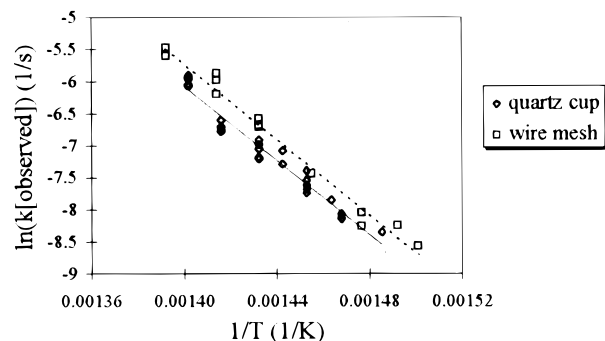
Table 3. Influence of Type of Carrier Material in TGA Experiments on Kinetic Data

carrier material	$\ln(k_0)$, s ⁻¹	E_{act} , kJ/mol	k_{703K} , s ⁻¹	r^2 ^a
quartz	34.6 ± 1.7	241 ± 10	0.0012 ± 0.00001	0.96
stainless steel 316	35.1 ± 2.2	243 ± 13	0.0016 ± 0.00008	0.98
wire-mesh				

^a Only gives indication of experimental uncertainty.

Table 4. Measured First Order Rate Constants for Different Heating Rates

heating rate, 1/K	end temp, K	k , s ⁻¹
16	766	0.257
45	762	0.264
580	760	0.245
10000	764	0.246

**Figure 7.** Arrhenius plot for first order kinetics for TGA experiments with different crucible materials.

ducted in the screen heater. In the next section the results of the experiments performed to test possible causes for the observed discrepancy between the TGA and screen heater results will be reported.

4.2. Comparison between Screen Heater and TGA Experiments. To provide a reasonable explanation for the discrepancy between the rate constants obtained from the screen heater and TGA experiments, three hypotheses were proposed. Some of these hypotheses were investigated experimentally.

4.2.1. Influence of Type of Carrier Material. In the screen heater a stainless steel screen was used as the sample carrier material, while for TGA measurements a small quartz crucible or cup was used. The influence of the type of carrier material was investigated by using a crucible for TGA measurements which was made of the same material as the screens used in the screen heater. The results are shown in Table 3 in terms of k_0 and E_{act} .

While the kinetic constants, especially the k_0 values, differ for the different experimental setups, the actual k values do not differ substantially from each other as is shown in Figure 7. The polymer degrades somewhat faster in the crucible made from the screen material, but this effect is probably due to more efficient heating of the sample or better product removal. The difference, however, is small and cannot explain the large discrepancy observed between the TGA and screen heater experiments.

4.2.2. Influence of the Heating Rate in the Screen Heater. The wire-mesh screen in the screen heater is heated to the final temperature with a heating rate of approximately 10⁴ K/s. Because of the large external heat transfer coefficient, the polymer sample between the screen has approximately the same heating rate. However, the heating rate in the TGA is significantly smaller (~1 K/s).

The effect of heating rates between 1 and 1000 K/s on coal pyrolysis has been examined by Gibbins-Matham *et al.* (1988). A significant increase in total volatile yield was found for most of the coals tested if the heating rate was increased from 1 to 1000 K/s. An effect of the heating rate was also reported by some authors for polymers (see, for instance, Cascaval *et al.*, 1970).

To study the influence of the heating rate, the first order rate constants for LDPE1 pyrolysis were determined by applying various heating rates in the screen heater. The results are shown in the table below in which also the first order fit of the "normal" LDPE1 pyrolysis experiments (carried out at a heating rate of approximately 10^4 K/s) is given.

These results indicate that there is no dependence of the heating rate in the screen heater on the first order kinetic constants.

4.2.3. Influence of Electrical Current. A major difference between the TGA and the screen heater is the way in which heat is supplied to the polymer sample. In the TGA equipment a gas flow heats the quartz crucible which contains the polymer sample. However, the sample in the screen heater is heated by passing a large electrical current through the folded screen, which is in close contact with the polymer sample.

The large electrical current results in an abundance of free electrons which may activate the metal atoms or directly interact with the polymer. This may lead to a change in the reaction mechanism by which the polymer is degraded. For instance the mechanism may change from a radical to a catalyzed ionic mechanism.

A change of the reaction mechanism by the electrical current is a possible explanation for the difference found between the kinetic constants measured with a TGA and a screen heater, as this is the major difference between the two apparatuses. However, most proof for this hypothesis is indirect, as the effect of the electrical current could not be determined experimentally with the existing equipment. Some indications for this hypothesis are discussed in the next section.

4.2.4. Comparison between LDPE and PP Screen Heater Experiments and Literature. If a comparison is made between LDPE and PP pyrolysis experiments conducted in the screen heater, the kinetic constants are close to each other (see Figures 5 and 6). The differences between the two types of polymer are smaller than can be expected on the basis of their molecular structure. The presence of the side chains on the main chain as is the case for PP should influence the thermal degradation rate significantly, because more stable ternary and secondary radicals can be formed instead of unstable secondary and primary radicals in the case of LDPE pyrolysis. This is expected to result in a higher conversion rate and therefore larger rate constants for PP compared to LDPE at the same temperature. TGA experiments showed this effect clearly (Westerhout *et al.*, 1996), but this effect is hardly noticeable in the results obtained from the screen heater experiments. Figure 8 summarizes our own and the literature first order rate constants for high temperature polymer pyrolysis.

The stability of the radicals formed during polymer pyrolysis can be arranged in order of increasing stability: HDPE < LLDPE < LDPE < PP < PS. As a result the conversion rate (and also the rate constant) should increase from left to right in this series.

The screen heater experiments, however, do not show a significant difference in rate constants for LDPE and

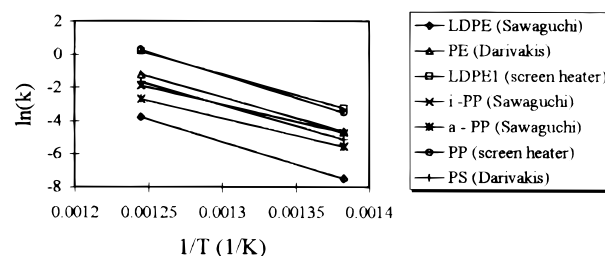


Figure 8. Arrhenius plot for first order kinetic constants for high temperature pyrolysis of various polymers reported in literature together with our data.

PP. The small differences are mainly caused by experimental errors and should not be attributed to differences in polymer type. A similar effect was found by Darivakis *et al.* (1990) for PE and PS, who also measured their kinetic parameters with a screen heater. Only the results of Sawaguchi *et al.* (1980, 1981) show the trend which is consistent with the TGA experiments and the expected trend in the conversion rates on the basis of the stability of the radicals produced during the pyrolysis process.

The fact that different polymers do not exhibit different conversion rates in screen heater experiments supports the hypothesis that the mechanism and its rate are influenced by the electrical current. This hypothesis is also supported by a study of Shevchenko *et al.* (1993), who investigated the effect of the electrical current frequency on the activation energy of the reaction of water vapor with raw charcoal. Shevchenko *et al.* found that the rate constant for the reaction of carbon with water vapor is dependent on the frequency of the current flowing through the sample. Shevchenko *et al.* concluded that an alternating current should be considered as physical activator, enhancing the kinetics of the process studied. However, the reaction studied by Shevchenko *et al.* differs significantly from the pyrolysis reaction of polymers and therefore the conclusions made by Shevchenko may but do not have to apply to the pyrolysis reaction of polymers.

5. Modeling of the Influence of Heat Transfer on the Pyrolysis Process

During the pyrolysis process both heat and mass transfer processes can limit the chemical conversion rate. These processes may have to be considered during the evaluation of pyrolysis experiments and for this purpose single particle models were developed. These models will be discussed below in more detail. Similar models with more or different assumptions describing the volatilization of a solid were published by, for instance, Villermaux *et al.* (1986) and Pyle *et al.* (1984).

5.1. Model Assumptions. Due to the pyrolysis process the mass m of the polymer decreases and this decrease can be related to density and volume as follows:

$$\frac{\partial m}{\partial t} = V \frac{\partial \rho}{\partial t} + \rho \frac{\partial V}{\partial t} \quad (6)$$

Both density and volume will probably change simultaneously during an actual pyrolysis process, but for our modeling purposes the following two limiting cases have been considered: 1. The density (ρ) is variable and the volume (V) remains constant. 2. The density (ρ) remains constant and the volume (V) changes.

The cases labeled 1 and 2 correspond to model 1 and model 2, respectively. For both models the following general assumptions were made:

- The heat penetration is considered to be one dimensional.
- The thermophysical polymer properties (λ_p , c_{pp}) in the solid and the molten state are identical, for which data of Bandrup *et al.* (1989) has been used.
- The heat transfer coefficient λ_p is independent of temperature.
- The heat capacity c_{pp} only depends on the temperature (Bandrup *et al.*, 1989)
- Mass transfer limitations are absent. This assumption may not be valid for large particles.

By introduction of the geometrical factor γ , different geometrical shapes can be represented in the model: infinite plate ($\gamma = 0$), infinite cylinder ($\gamma = 1$) and sphere ($\gamma = 2$).

5.2. Model 1: Variable Density and Constant Volume. The enthalpy balance is given by

$$\rho_p c_{pp} \frac{\partial T_p}{\partial t} = \lambda_p \frac{1}{x'} \frac{\partial \left(x' \frac{\partial T_p}{\partial x} \right)}{\partial x} - \frac{\partial \xi}{\partial t} \rho_{p0} \Delta H_r \quad (7)$$

whereas the mass balance can be formulated as

$$\frac{\partial \xi}{\partial t} = f(T_p, \xi) \quad (8)$$

The following initial and boundary conditions are used for the mass and enthalpy balance:

$$t = 0, \quad \forall x \rightarrow T_p = T_{p,0} \wedge \xi = 0$$

$$x = 0, \quad \forall t \rightarrow \frac{\partial T_p}{\partial x} = 0$$

$$x = r_p, \quad \forall t \rightarrow \lambda_p \frac{\partial T_p}{\partial x} = \alpha (T_s - T_{p,x=r_p}) + \epsilon \sigma (T_s^4 - T_{p,x=r_p}^4) \quad (9)$$

In the case of the first order pyrolysis kinetics model, eq 8 can be written as

$$\frac{\partial \xi}{\partial t} = k_0 e^{(-E_{act}/R_g T_p)} (1 - \xi) \quad (10)$$

5.3. Model 2: Variable Volume and Constant Density. Because the density is assumed to remain constant, shrinkage of the particle due to the pyrolysis process occurs and a pseudoconvection term appears in the balance equations. For this model the enthalpy balance can be written as

$$\rho_p c_{pp} \frac{\partial T_p}{\partial t} = \lambda_p \frac{1}{x'} \frac{\partial \left(x' \frac{\partial T_p}{\partial x} \right)}{\partial x} - \rho_{p0} \frac{1}{x'} \frac{\partial (x' v c_{pp} T_p)}{\partial x} - \frac{\partial \xi}{\partial t} \rho_{p0} \Delta H_r \quad (11)$$

whereas the mass balance is given by

$$0 = \frac{1}{x'} \frac{\partial (x' v)}{\partial x} - \frac{1}{(1 - \xi)} \frac{\partial \xi}{\partial t} \quad (12)$$

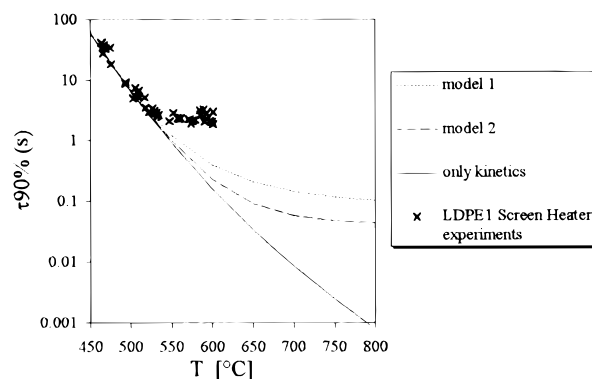


Figure 9. Time for 90% conversion as a function of temperature.

Most of the initial and boundary conditions for the enthalpy balance are given by eq 9, except the initial condition for the shrinkage velocity v , which equals zero for $t = 0$ for all values of x . The initial and boundary conditions for the mass balance are given by

$$\begin{aligned} t = 0, \quad \forall x \rightarrow v = 0 \wedge x_p = x_{p0} \wedge \xi = 0 \\ x = 0, \quad \forall t \rightarrow v = 0 \end{aligned} \quad (13)$$

In case of the first order kinetics, model eq 10 can be used to calculate the conversion rate.

Both models were solved numerically using the discretization scheme of Baker and Oliphant (for the first time step the backward Euler method was used). Both models were programmed in Pascal and were validated by using well-known analytical solutions of limiting cases such as instationary heat penetration without reaction and reaction without external and internal heat transfer limitations.

5.4. Incorporation of the Random Chain Dissociation Model in Pyrolysis Process Models. To enable incorporation of highly complex and more realistic kinetic models, such as the RCD model, prior to the solution of the single particle models, a two dimensional matrix was generated containing the values of the conversion rate at certain, discrete values of the temperature T and conversion ξ . An appropriate interpolation method was used to calculate the conversion rate at intermediate values of temperature and conversion. Using the matrix and the interpolation method, the conversion rates necessary to solve the single particle model were calculated.

6. Model Results

The single particle models, described in section 6, were used to simulate the effect of heat transfer limitations on the experiments and the pyrolysis processes.

In Figure 9 the time required to obtain 90% conversion of the LDPE particles, $\tau_{90\%}$, is shown as a function of the temperature for the two single particle models assuming first order kinetics for the entire conversion range. To enable comparison, the experimental data are included in the figure together with the model results obtained in case no internal or external heat transfer limitations were taken into account.

As Figure 9 shows, heat transfer limitations during the kinetic experiments played a minor role in the temperature range from 450 to 530 °C. Both models predict therefore the same $\tau_{90\%}$ for this temperature range. When heat transfer limitations occur, the predicted $\tau_{90\%}$ differs, because the influence of the decrease of the mass of the polymer sample on the heat transfer

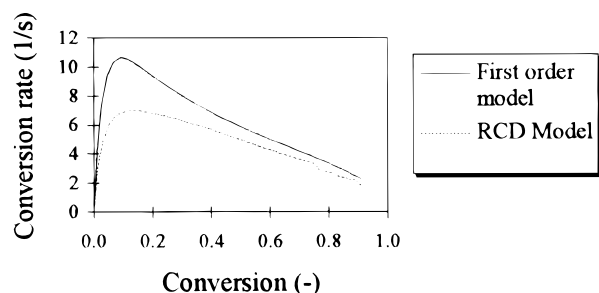


Figure 10. Conversion rate as a function of conversion at 650 °C as predicted by model 1 for different kinetic models.

processes in the models is different because of different assumptions.

At high temperatures the experimentally determined $\tau_{90\%}$ values exceed the theoretical values. This is, however, not a result of heat transfer limitations but is due to the large influence of the RTD of the system, as stated before.

For model 2 the heat transfer resistance decreases during the pyrolysis process, because the diameter of the particle decreases, which is not the case in model 1. Due to this inherent better heat transfer characteristic, model 2 predicts smaller $\tau_{90\%}$ values compared to model 1. At temperatures exceeding 700–750 °C this difference does not increase, because at these temperatures the time required for heating to the final temperature is long compared to $\tau_{90\%}$.

When heat transfer limitations are absent, an increase of temperature will lead to higher conversion rates and thus to smaller $\tau_{90\%}$ values. However, the $\tau_{90\%}$ values predicted by both models show no temperature dependence for temperatures exceeding 700–750 °C. Clearly, at these temperatures the conversion rate is mainly determined by heat transfer limitations instead of the chemical kinetics. At a temperature of 650 °C both kinetics and heat transfer processes will play a role. In Figure 10 the computed conversion rate for both the first order model and the RCD model are plotted as a function of the conversion. The conditions were chosen to represent those of typical screen heater experiments (very high external heat transfer coefficient, small particles). Compared with Figure 4, where both models are plotted for conditions where only chemical kinetics play a role, the difference in Figure 10 between the two kinetic models is smaller. This is a result of the increased influence of heat transfer limitations on the conversion rate. At still higher temperatures both kinetic models will predict the same curve because the pyrolysis process will then be completely limited by heat transfer. The use of a more realistic but complex kinetic model becomes then less important, so that the use of a simple first order model will be sufficiently accurate.

7. Conclusions

The use of a screen heater to measure the pyrolysis kinetics of polymers or other substances was examined and evaluated. For this study a screen heater with a gas sweep was developed to determine the pyrolysis kinetics of PE and PP. Novel features of this new screen heater are the on-line measurement of the gas phase pyrolysis product concentration with the aid of a hydrocarbon analyzer to enable the determination of the conversion rate over the entire conversion range on the basis of a single experiment and the possibility to

perform nearly isothermal experiments over the entire conversion range on the basis of a single experiment.

On the basis of tracer experiments with propane the effect of gas phase mixing on the measured hydrocarbon concentration versus time curve could be calculated. This made it possible to evaluate the effect of gas phase mixing on the apparent kinetic parameters. It was proven that the required correction for the residence time distribution (RTD) and not the heat transfer rate was the limiting factor to accurately determine the intrinsic pyrolysis kinetics at high temperatures. With this type of apparatus, reactions can be studied with first order rate constants lower than 2 s^{-1} . For the present study this implied that the pyrolysis reaction could be studied at temperatures up to 530 °C.

The kinetic parameters for LDPE and PP were determined in the temperature range from 460 to 530 °C and were interpreted with both a simple first order model for the 70–90% conversion range and the random chain dissociation model for the entire conversion range. The kinetic constants for LDPE and PP pyrolysis obtained from screen heater experiments were the same for both polymers at a certain temperature. This finding indicates that another mechanism than purely thermal degradation occurs during the pyrolysis process in the screen heater, as PP should degrade more rapidly compared to LDPE, because of the influence of the side chains on the thermal degradation process. Comparison with TGA experiments also showed a large discrepancy between the results of the screen heater and the TGA. Several hypothesis were put forward and tested. The cause of aforementioned effects is possibly due to the influence of the electrical current, which influences the mechanism and the rate at which the polymer is degraded, although most of the evidence for this hypothesis is indirect. It can be concluded from the experimental evidence, that screen heaters cannot be used to measure the pyrolysis kinetics of polymers in this configuration.

Two single particle models were developed to evaluate the effect of heat transfer limitations during the pyrolysis process. A “matrix” method was developed and implemented to enable the use of any type of kinetics in the model, even if no analytical conversion rate equation for the model is available but only values of the conversion rate are known at discrete values of temperature and conversion. It was demonstrated with these models that heat transfer processes play no role of importance in the screen heater experiments at temperatures below 530 °C. It was also shown that the difference between the two models under conditions encountered in the screen heater are limited.

The models were also used to evaluate the error made in case a simple first order model, which is only accurate for 70–90% conversion, is used instead of the more complex and harder to use RCD model. It was shown that under conditions where both kinetics and heat transfer play a role, the use of the more complex RCD model is necessary to obtain an accurate description of the pyrolysis process. However, a first order model can be used to obtain a relatively good first estimation of the conversion rate.

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List of Symbols

a = calibration factor (1/kg V)
 c_p = heat capacity (J/kg K)
 $E(t)$ = differential residence time distribution (1/s)
 E_{act} = activation energy (kJ/mol)
 $F(t)$ = cumulative residence time distribution
 ΔH_r = reaction enthalpy (J/kg)
 k = first order reaction constant (1/s)
 L_c = vaporizable chain length
 m = mass (mg)
 N_i = actual number of i -type bonds
 R_g = gas constant (J/mol K)
 Py = dimensionless pyrolysis number
 t = time (s)
 T = temperature ($^{\circ}$ C)
 v = shrinkage velocity (m/s)
 V = volume (m^3)
 x = radial coordinate in particle (m)
 x = total mass fraction hydrocarbons (mg/kg)
 $y(t)$ = voltage signal from hydrocarbon analyzer (V)

Greek Symbols

α = external heat transfer coefficient (W/m^2 K)
 γ = geometrical factor
 ϵ = radiation emission coefficient
 λ = heat conduction coefficient (W/m K)
 ρ = density (kg/m^3)
 σ = Stefan– Boltzmann constant (W/m^2 K 4)
 τ = characteristic time (s)
 Φ_m = mass flow (kg/s)
 ξ = conversion $(m_0 - m)/m_0$

Subscripts

β = β scission
 hc = hydrocarbon
 m = mass
 p = particle or polymer
 s = surrounding
 0 = initial
 90% = 90% conversion

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