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TECHNICAL PAPER

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Polymeric Cracking of Waste Polyethylene Terephthalate to Chemicals and Energy

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ABSTRACT

Polyethylene terephthalate (PET) is a widely used thermoplastic. PET residues represent on average 7.6 wt% of the different polymer wastes in Europe. Pyrolysis of these wastes is attracting increasing interest, and PET is a potential candidate for this thermal process. The paper measures and discusses the kinetics of the pyrolysis reaction in terms of the reaction rate constants as determined by dynamic thermogravimetric analysis, with special emphasis on the required heating rate to obtain relevant results. The product yields and compositions are also determined. Gaseous products represent 16–18 wt%. The amounts of condensables and carbonaceous residue are a function of the operating mode, with slow pyrolysis producing up to 24 wt% of carbonaceous residue. Major condensable components are benzoic acid, monovinyl terephthalate, divinyl terephthalate, vinyl benzoate, and benzene. The present paper complements previous literature findings by (1) the study of the influence of the heating rate on the reaction kinetics in dynamic pyrolysis tests, (2) the isothermal investigation in a fluidized bed reactor to pyrolyze PET, and (3) the assessment of upgrading and recovery of the products. The paper concludes with a proposed reactor recommendation for PET pyrolysis, in either the bubbling or circulating fluidized bed operating mode.

IMPLICATIONS

Plastic solid waste (PSW) represents up to 8% by wt and 20% by volume of household waste. Landfill disposal wastes valuable energy and chemical feedstock. Incineration for energetic valorization (waste-to-energy) is applied for ~50% of PSW. To date, research focuses increasingly on pyrolysis, which has the advantage over incineration of producing value-added chemicals, even from commingled or mixed feedstock. The process gains in efficiency and yield if PSW fractions are collected separately or presegregated. The cost of separate collection is easily overcome by the value of the pyrolysis products. The pyrolysis of polyethylene terephthalate is developed as an example of the above.

INTRODUCTION

In 1996, the total plastic consumption in Western Europe was 33.4 million tons, whereas in 2008 it was estimated to be 52 million tons, an increase by almost 4% per year. These synthetic polymers include mostly high , medium, linear low, and low-density polyethylene, polypropylene, polyvinyl chloride, polystyrene, and polyethylene terephthalate (PET). Postconsumer plastic solid waste (PSW) finds its way into household solid waste (HSW) representing 7–8 wt% of the HSW or up to 20 vol%. Polymer-derived thermoplastics are widely applied in industrial and commercial products and usually contain stabilizers and additives.[1]

One of the major thermoplastics used in our daily life is PET, almost solely accounting for the production of containers, bottles, fibers, and so on. PET residues represent on average ~7.6 wt% of the different polymer residues in Europe.

The disposal of postconsumer plastics has become an important environmental concern. Current treatment and disposal options include recovery and recycling, landfilling, and (co-)incineration. Because of increasing landfilling constraints and the difficulties encountered in attempts to recycle mixed and/or partly presegregated plastic wastes, incineration is often applied.[2,3] The research focus has recently shifted toward a different thermal treatment process, pyrolysis. Pyrolysis takes place in the absence of oxygen and is capable of recycling PSW

Table 1. Heat requirements for pyrolysis of PET and other PSW.

PSW	C (J/g)	c_p (J/g · °C)
PET	214.35	1.44
PS	678.55	1.30
PE	257.65	2.30
PP	361.80	1.70
PC	148.00	1.20
ABS	473.85	1.42
PMMA	472.00	1.47
Nylon	364.15	1.70

Notes: C = endothermic heat required for pyrolysis, c_p = specific heat at 20°C, PET = polyethylene terephthalate, PS = polystyrene, PE = polyethylene, PP = polypropylene, PC = polyvinyl chloride, ABS = acrylonitrile butadiene styrene, PMMA = poly(methyl methacrylate).

into chemicals and/or fuel. Pyrolysis can overcome certain disadvantages of incineration and recycling by producing value-added products such as liquid and gaseous fuel, polymer monomers, and a carbonaceous residue (char) as a candidate for possible upgrading to activated carbon or carbon black.

Mixed PSW is difficult to treat or recycle because of its complex nature and composition, the structural deterioration of the polymeric components, and the contamination with various organic, inorganic, or biological residues. High temperature incineration might cause hazardous emissions,[4] and co-incineration is controlled by strict emission standards as, for example, those set by the European Union Hazardous Waste Incineration Directive.[5]

Pyrolysis is one of the most promising methods for recovering material and energy from PSW, because only ~5% of the PSW energy content is used in the endothermic cracking process, as shown in Table 1: the heat required for PET pyrolysis is 214 kJ kg^{-1} only, ~5% of the calorific value of PET. Contrary to mechanical and/or chemical reprocessing, pyrolysis can treat almost all types of plastics, commingled or mixed with other materials such as wood, paper, ink, and paint. It does not produce large volumes of flue gases and toxic emissions as incineration does.

Pyrolysis involves thermal decomposition at moderate temperature and in the total absence or the presence of low amounts of oxygen. The polymer structure is broken down into smaller intermediate products, which can be used as fuel or as raw material for the petrochemical industry. Pigments, inorganic fillers and supports, and other additives possibly present in minor concentrations in the polymers mostly remain in the solid residue.

Thermal degradation of polymer mixtures is more complex than degradation of single polymers because of possible interactions during decomposition in the polymer bulk and interactions between the components of the mixture and the low molecular weight products and free radicals formed by the scission of the polymeric chains.[6,7] These can affect the quality of pyrolysis products and are hence of importance when the pyrolysis products need to meet high quality standards for use as feedstock or fuels.[2,3]

The present paper is focused on a single polymer, PET, representing 7–8 wt% of the PSW, that generally is collected as preselected waste in the European Union.

PET and Its Pyrolysis

PET is the dominant aromatic polyester produced, polybutylene terephthalate, polypentene terephthalate, and polyhexene terephthalate being of minor, albeit growing, importance. The polymer structure of PET is shown in Figure 1, together with its most likely thermal cleavage mechanisms. Among the thermally weak linkages, that is, the C–O bonds along the polymer chains, those located at

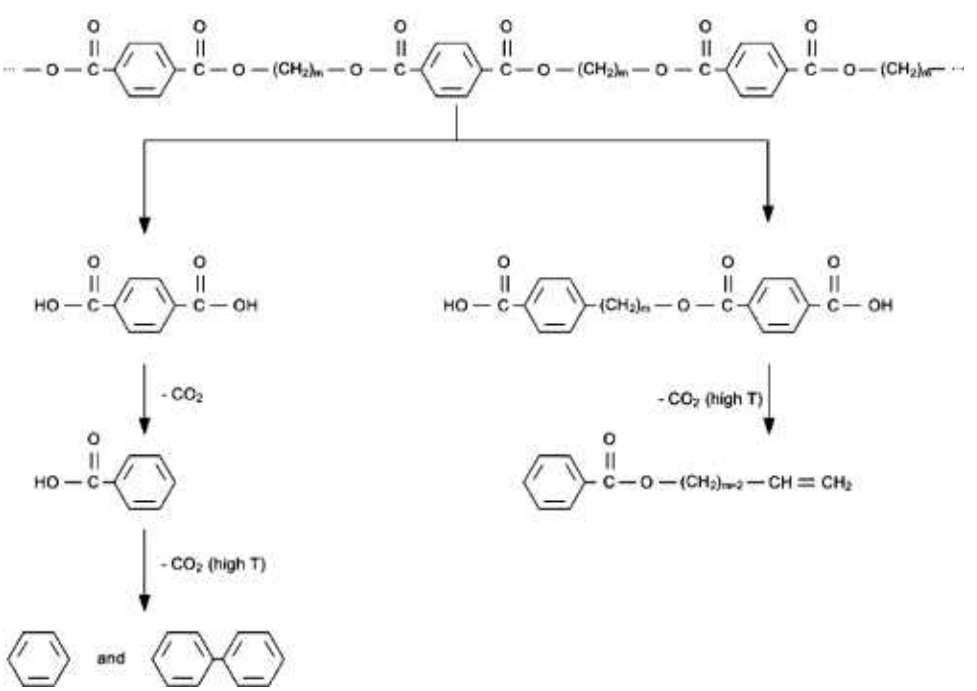

Figure 1. PET and its most likely thermal cleavage mechanisms to various products (m = 2).

the adjacent position of C=O bonds are most likely subject to thermal cleavage with further degradation to phthalic and benzoic acid and possibly to benzene with CO_2 release.

PET is a thermoplastic polymer best known for its application in plastic bottles and containers. Other applications include synthetic fibers, thermoforming materials, and tire cords.

Ethylene terephthalate (the PET monomer) is the esterification product of terephthalic acid and ethylene glycol. Polymerization occurs through polycondensation of the monomers, immediately after esterification, with ethylene glycol being subtracted and directly recycled in the production. PET recycling processes can be based on the reversibility of this condensation reaction (chemical recycling by hydrolysis or solvolysis[8]), which results in total recycling. Numerous papers deal with this reversible reaction for PET recycling and potential techniques include different methods of hydrolysis,[9–12] glycolysis,[13–17,] and methanolysis.[18–20] However, these processes demand intensive bottle cleaning: polyethylene caps, paper, binder, and residual content have to be thoroughly removed.

As world prices of crude oil increase and resources are depleted, new recycling processes (either physical, chemical, or thermal) are being developed. In physical processing, clean waste PET is molten and processed to fibers.[8] Additional direct PET valorization routes include the use in cement concrete[21] and in feeding packaging-derived fuels from PET sources in fluidized beds combustors[22] and development of high-density polyethylene/PET composites for commercial use.[23] The study of the pyrolytic cracking of PET to produce gases, condensable vapors, and a carbonaceous residue has received increasing attention.[24–31] The pyrolytic degradation mechanisms for PET (and its polyester homologs) into chemical building blocks have been determined previously,[28–30] albeit for low heating rates in dynamic thermogravimetry and/or for operating temperatures beyond the common range of pyrolysis temperatures but with a specific target such as maximizing the production of pyrolysis gas and a carbonaceous residue.[31,32]

From this literature survey on previous research for pyrolysis at moderate temperatures emerges the fact that generally a mixture of organic acids (i.e., benzoic and terephthalic acid with a ratio of ~10:1) and a solid carbonaceous residue are produced, together with a gas ($<C_4$). Whereas the gas fraction is limited to 5–10 wt% of the PET feed, the acids and carbonaceous residue vary in wt% as a function of the pyrolysis temperature and the mode of operation (fast, slow, or intermediate): whereas fast pyrolysis (a few seconds) produces mostly acids (up to 70 wt%), slow pyrolysis (minutes) favors the formation of a higher fraction of solid residue (up to 25 wt%).

Objectives of the Present Research

To assess (1) design parameters of a potential PET pyrolysis reactor, (2) composition and quantities of products produced, and (3) possible commercial valorization of the pyrolysis products, the present research covered several items. The fundamental kinetic and thermodynamic properties were determined using the traditional dynamic thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), both with a preset temperature ramp. Because these dynamic studies do not necessarily provide appropriate chemical information regarding the products formed in the isothermal environment of a common reactor, pyrolysis was repeated under isothermal conditions in a bubbling fluidized bed (BFB) reactor. To establish a mass balance, vapors were condensed and subsequently analyzed after dissolution, and the carbonaceous residue was separately collected. Finally, the upgrading of the main products, that is, condensate and carbonaceous residue, was examined. The research presented thereby completes previous findings by (1) studying the influence of the heating rate on the reaction kinetics as determined from dynamic experiments; (2) using an isothermal reactor in a slow or fast heat transfer mode to evaluate the product distribution; and (3) assessing the possible upgrading and recovery of the products.

EXPERIMENTAL PROCEDURES

Experimental Conditions: General

This paper investigates the thermal pyrolysis kinetics and products of PET from waste soft drink bottles of Coca-Cola and Pepsi. These bottles were crushed and milled to thin PET chips of ~0.3- to 0.5-mm length and less than 0.1-mm thick, thus avoiding heat and mass transfer limitations during subsequent thermal cracking investigations as shown below. Essential for the fast decomposition and high liquid yields is the fast heating of the particles. Slow pyrolysis is suspected to decrease the liquid yield in favor of gas and char, because long residence times favor secondary cracking.

This fast heating of the whole particle to a uniform temperature requires high heat transfer. If the heat supply is insufficient, important thermal gradients would occur, leading to slow pyrolysis and/or incomplete reactions in the core of the particle. Smaller particles have a larger specific surface and are more mobile within the reactor mass, which enhances the heat transfer. In addition, temperature gradients in small particles are expected to be negligible, as will be shown below.

When the experimental and large scale parameters are chosen, the thermal characteristics of the particles, the reaction kinetics, and the heat transfer will have to be jointly considered. Some basic principles of the reaction kinetics and the conversion of solid particles, of heat transfer in powder reactors and of heat penetration inside a particle allow the determination of these conditions in anticipation, which makes it possible to program the experiments in a relevant and effective way. At the same time, this analysis allows to critically evaluate the literature data: research has not always been performed under these optimum conditions, with results that could lead to wrong conclusions.

To meet these targets, avoidance of thermal gradients in and around the particle is very important. Application of the basic principles of both heat transfer to the particle and of heat conduction within the particle allows determination of the required working conditions. The temperature uniformity throughout the particles can be determined by the heat conduction law of Fourier, here

applied in a nonstationary regimen and for the simple case of a spherical particle:

$$\frac{\partial T}{\partial t} = \frac{k_p}{\rho_p c_p}\left(\frac{\partial^2 T}{\partial r^2} + \frac{2\partial T}{r\partial r}\right) \quad (1)$$

where k_p is heat conductivity of the particle at temperature T (W m^{-1} K^{-1}), c_p is the specific heat capacity of the particle at temperature T (J kg^{-1} K^{-1}), and ρ_p is density of the particle (kg m^{-3}).

When heated at rate β (K sec^{-1}):

$$\frac{\partial T}{\partial t} = \beta \text{ for } r = 0 \text{ to } R = \frac{d_p}{2} \text{ and } \frac{\partial T}{\partial r} = 0 \text{ for } r$$

$$= 0 \text{ (in the core)}$$

The solution is given by Carslaw and Jaeger[33] as

$$\Delta T_{max} = (T_R - T_C) = \beta\frac{d_p^2}{24a} \quad (2)$$

where T_R is T at the surface of the particle (at $r = R$) (K), T_C is T in the core of the particle (at $r = 0$) (K), β is the heating rate (K sec^{-1}), and a is thermal diffusivity = $(k_p/c_p\rho_p)$.

Equation 2 can be applied for various values of β and with, for example, the characteristic properties of the particle at 773 K; that is, k_p = 0.15 W m^{-1} K^{-1}, c_p = 1500 J kg^{-1} K^{-1}, and ρ_p = 1100 kg m^{-3}. The results are a set of curves in function of the diameter as shown in Figure 2.

These calculations show that the temperature differences between the particle surface and core are very limited, certainly when considering that the surrounding temperature is ~773 K and that the heating rate will vary between minimally 0.1 K sec^{-1} in a TGA experiment to a few hundred K sec^{-1} in a BFB or circulating fluidized bed (CFB). To minimize ΔT_{max} (<10 K) even at high heating rates, it is appropriate to use small particles (e.g. <300 μm for PET). No significant thermal gradient will thus occur in these small particles or when working at slow heating rates: the core and the surface of the particle will behave both thermally and kinetically in a similar way.

The high heat transfer is conditioned by the degree of gas and solid turbulence achieved in the reactor.[34–36] The heat transfer coefficient depends on the gas-solid contacting mode. It ranges from 10 W m^{-2} K^{-1} for a static bed to 50–100 W m^{-2} K^{-1} in a fixed bed with forced gas circulation (as in TGA), and several hundreds of W m^{-2} K^{-1} for BFBs and CFBs. This explains why the fluidized beds are specifically considered as top technologies for pyrolysis conversions. The heat transfer coefficient in a CFB can be estimated from the results of Kobro and Brereton.[37] In a CFB operating with 100 μm sand as bed material at a recommended gas velocity of 5 m sec^{-1} and a solids circulation rate of 200 kg m^{-2} sec^{-1}, the convective heat transfer coefficient is 620 W m^{-2} K^{-1}.

Because not only external convection but also internal conduction is important, the overall picture is expressed by the Biot number:

$$\text{Bi} = \frac{d_p/k_p}{1/h}$$

= internal resistance to heat penetration/external resistance to heat transfer

For the 100 μm bed particle at 773 K, the values are as follows:

h = 300 W m^{-2} K^{-1} → Bi = 100 × 10^{-6} × 300/0.15 = 0.2

h = 500 W m^{-2} K^{-1} → Bi = 100 × 10^{-6} × 500/0.15 = 0.33

h = 700 W m^{-2} K^{-1} → Bi = 100 × 10^{-6} × 700/0.15 = 0.47

The Biot number is <1 in all cases, implying that the external resistance associated with convectional heat transfer largely dominates. Biot is only >1 for coarse

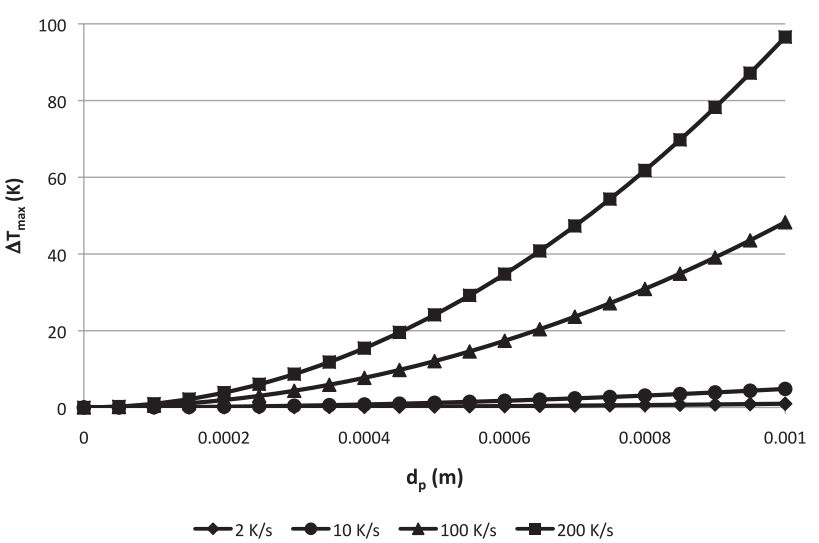

Figure 2. Maximum temperature difference (ΔT_{max}) between the surface and the core of the particle in function of the particle diameter at different heating rates (β).

particles. This result confirms Figure 2, for which increasing ΔT_{max} values are noticed with increasing β values (achieved at high convection heat transfer rates).

Kinetic and Thermodynamic Parameters

The thermal behavior of polymers is usually investigated by TGA and DSC, two methods that provide useful information about the thermal characteristics of materials: glass transition temperature, heat of crystallization, melting point, weight loss during thermal degradation, and others. These parameters can provide a kinetic model, necessary to predict reactor behavior and tentative product distribution.

In the literature, very different experimental TGA conditions are used: broad ranges of sample amount, of heating rates, of temperatures, and of reaction atmospheres. Thermal decomposition is often described by a power law equation, and most authors perform dynamic experiments. Although depending on the atmosphere, sample size, heating rate, and other parameters, the reaction order can be assumed to be close to 1. This first-order will be confirmed by the experimental results. Values for the kinetic parameters found in literature show a significant variation, which can be associated with different causes: the existence of temperature profiles inside the sample, the thermal gap between system and sample temperatures, the influence of the heating rate on the reactions taking place during decomposition, and the existence of a more complex reaction mechanism.[28]

For the TGA, a Hi-Res TGA 2950 thermogravimetric analyzer was used at atmospheric pressure with a nitrogen flow of 50 ml min^{-1}. The TGA scale was made of platinum, and the weight was registered every 0.5 sec. The different temperature rampings in time, or heating rates ($\Delta T/\Delta t$), enable us to determine the weight loss as a function of the temperature, shown by the TGA profiles. The dynamic thermogravimetry was conducted on the polymer samples using five constant temperature rampings or heating rates β; that is, β = 3, 15, 50, 100, and 120 K min^{-1}. The runs were conducted twice, and average results are reported hereafter.

To measure the heat requirement of the pyrolysis reaction of PET, a DSC with a refrigerated cooling system was used, operating in a temperature range from 183 to 823 K at a constant heating rate of 10 K min^{-1}. The experiments were performed at atmospheric pressure, with nitrogen (supplied at 50 ml min^{-1}). The DSC scales were made of aluminum, and the DSC was calibrated regularly with indium as reference material. The DSC curves obtained give the heat flux (W g^{-1}) as a function of the temperature.

Gas chromatography (GC) and mass spectrometry (MS) are used to obtain information on pyrolysis products and degradation mechanisms. These additional techniques were used in conjunction with the isothermal experiments.

PET pyrolysis has been shown to be a single-step mechanism of first-order, with gas, condensables, and char residue being formed.[24–31] As shown below, the char residue will further decompose at temperatures in excess of ~600 °C, far above the optimum temperatures commonly applied in pyrolysis.

Isothermal Experiments and Product Characterization

The slow to moderate temperature ramp used in a TGA or DSC is not fully representative of the operating conditions in a commercial reactor, in which isothermal conditions are maintained and heat transfer to the particles is very rapid, especially when fluidized bed reactors are used. This difference may influence the reaction mechanisms and product distribution. To obtain more representative results toward product yields and composition, batches of PET (~50 g) were injected into a BFB operated at a preset temperature (between 420 and 450 °C, corresponding with the optimum pyrolysis conditions of PET in TGA experiments). The fluidized bed of 0.1-m i.d. used Ballotini glass beads (147–208 μm) as the bulk bed material. The N_2 velocity was varied from 2 to 5 times the minimum fluidization velocity, U_{mf}. All equipment parts are electrically traced up to the condenser. The isothermal setup is shown in Figure 3. To collect the products, char was sieved from the bed material after reaction, vapors were condensed and dissolved using 25% tetramethyl ammonium hydroxide (TMAH) in methanol (because some products seem to desublimate rather than condense). Gases were exhausted to the atmosphere. Dissolved components and liquids were analyzed by GC-MS (Voyager 8000, Fisons Instruments). Carbonaceous residues were weighed and further upgraded using a steam autoclave at pressures up to 30 bar, as described in a later section of the paper.

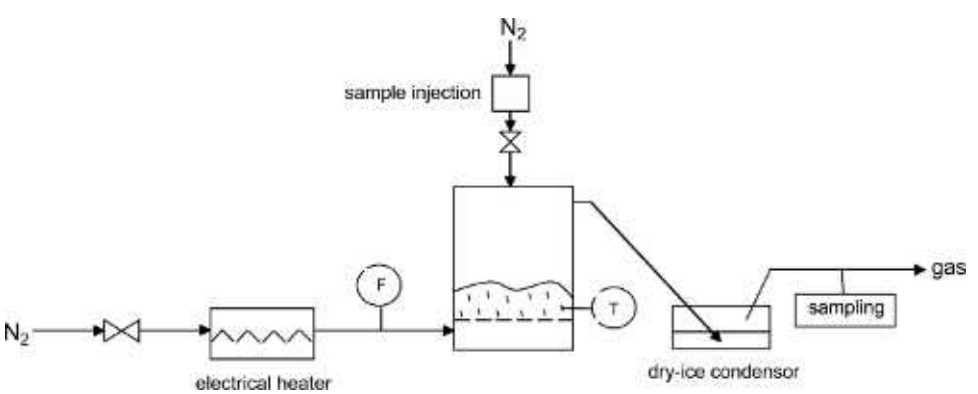

Figure 3. Set-up of isothermal tests in a bubbling fluidized bed.

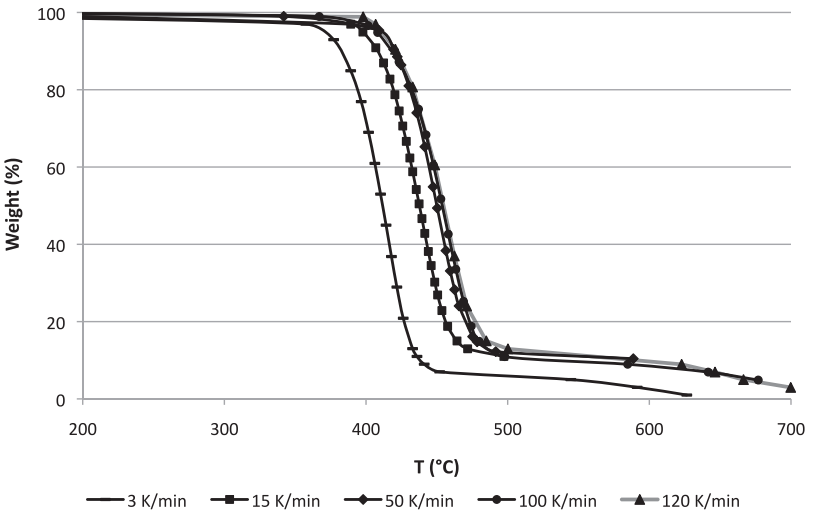

Figure 4. TGA plot for PET: results at different temperature ramps, β.

EXPERIMENTAL RESULTS

Dynamic TGA Experiments

TGA plots at different temperature ramps are illustrated in Figure 4. The results show that pyrolysis occurs within a narrow temperature range of 410 to 470 °C. Similar thermogravimetric curves are found in literature data, although most of these results were determined at lower values of β (~10 K min^{-1}). Pyrolysis occurs within a 410–460 °C temperature range.[24,28–30] Results of Girija et al.[30] are also in line with the TGA graphs obtained, but pyrolysis starts at 390 °C and is complete at 450 °C.

The pyrolysis reaction produces a solid carbonaceous residue or char, indicated in the TGA plot by a final constant weight. This char consists of the organic coking residue of PET and represents up to 10 wt% of the PET loading. At higher temperature (>600 °C), a further decomposition of the char occurs, as already suggested in the literature.

From the dynamic TGA experiments, the reaction rate constant k can be determined by eqs 3–5, as used by, for example, Van de Velden et al.[38,39] and assuming a first-order reaction rate:

$$\frac{dX(t)}{dt} = k(X_p - X(t)) \quad (3)$$

$$X(t) = \frac{(m_0 - m(t))}{m_0} \quad (4)$$

$$X_p = \frac{(m_0 - m_\infty)}{m_0} \quad (5)$$

where m_0 is the initial weight of PET (at $t = 0$) (mg), m_∞ is the residual weight of PET after the reaction (mg), $m(t)$ is the weight of PET at time t during the experiment (mg), and k is the reaction rate constant, by the Arrhenius equation $k = Ae^{(-E_a/RT)}$ E_a is the activation energy (J/mol) and A is the pre-exponential factor (sec^{-1}).

Because the weight of the sample is continuously registered, X and X_p are defined, and the reaction rate constant can be derived from eq 3 at every moment, because of the known temperature ramp of the TGA (known $\Delta T/\Delta t$). The Arrhenius equation can be applied after data transformation and plotting of the results as ln(k) versus $1/T$. The activation energy and the pre-exponential factor are given by the slope and the intersection of the straight line obtained with the ln(k)-axis, respectively.

Transformed TGA results for the pyrolysis of PET at different values of β are illustrated in Figure 5. The heating rate β clearly affects the pyrolysis reaction and the associated reaction rate constant. The slope of the ln(k) versus $1/T$ dependence is, moreover, lower for results obtained at low β. The activation energy E_a, determined from the slope, is hence different from that obtained at higher β (where E_a can be considered constant). At low β values, a linearization of ln(k) versus $1/T$ is tentative only and valid within a narrow temperature range. At higher β values (≥50 K min/min) the linear dependence is more obvious throughout the measured temperature range. The Arrhenius factor A increases, as β increases, and a nearly constant A value is obtained for $\beta > 50$ K/min. Values of E_a, A, and k will be further discussed, together with the effect of β on the results and alternative methods to derive the reaction rate parameters.

Thermodynamic Properties

The thermal parameters are necessary to formulate the heat balance of the pyrolysis reaction. Because pyrolysis, is an endothermic reaction, as is every cracking reaction, the reaction heat is supplied indirectly (heat exchangers) or directly (e.g., by preheating the bed material or the fluidization gas). Usually the combustion of pyrolysis gas supplies the required heat (C, J g^{-1}) and the combustion gases form the oxygen-free carrier gas.[39] The heat required to pyrolyze PET contains three components: the heat of PET fusion (ΔH_f), the heat required to heat the PET to the temperature at which pyrolysis occurs, and the heat required for the endothermic pyrolysis as such (ΔH_p). Hence the required heat can be written as follows:

$$C = mc_p(T_p - T_0) + m\Delta H_p + m\Delta H_f \quad (6)$$

The heat of fusion, ΔH_f, is given in the DSC results of Figure 6 at 240 °C.

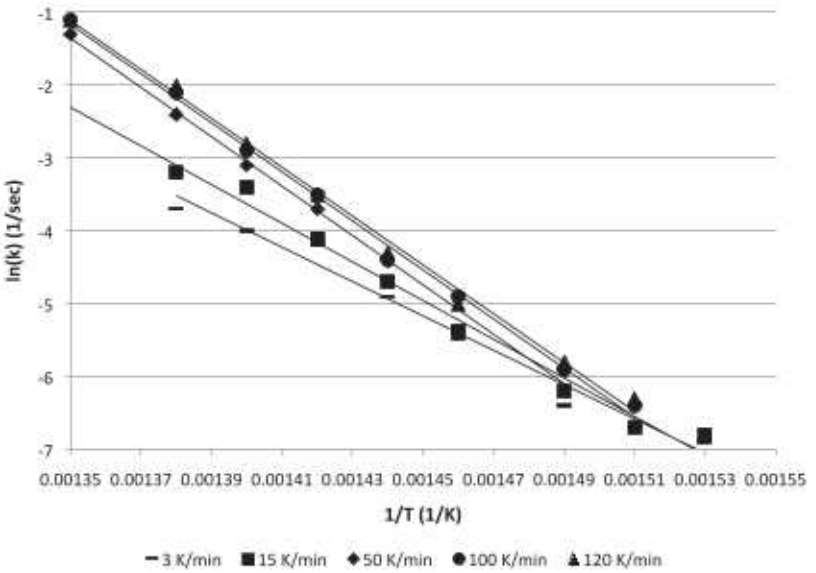

Figure 5. Kinetic analysis of PET.

The temperature at which pyrolysis occurs and the reaction heat ΔH_p (J g^{-1}) required for the pyrolysis itself were experimentally determined from the DSC curves and will be discussed later.

The specific heat capacity c_p (J g^{-1} K^{-1}) of the PET sample was determined in a Leybold-Hereaus calorimeter between 15 and 97 °C and found to be 1.44 kJ kg^{-1} K^{-1}. Because c_p values increase slightly with increasing temperature, the value at 450 °C will be ~10% higher than the experimental value at 20 °C.

The average DSC curves obtained from three repeated experiments as a function of the temperature (or as a function of the time, considering the constant $\Delta T/\Delta t = 10$ K min^{-1}) are shown in Figure 6. The DSC curves show that the heating process is clearly in the domain of heat requirement, which confirms the endothermic character of fusion and pyrolysis. The first valley corresponds to the melting point of PET, representing the heat of phase transition. Integration of these heat fluxes over time (eq 7) gives the total heat requirement C (J g^{-1}) as a function of the temperature. The endothermic valley at 240 °C was eliminated before integration. When the pyrolysis is completed, the heat requirement decreases. Declining values before the end of the reaction and beyond the normal temperature range of pyrolysis can be explained by the occurrence of secondary reactions (e.g., the aggregation or further decomposition of the char).

$$\frac{dC}{dt} = c_p \frac{dT}{dt} + \Delta H_r \rightarrow C = \int_0^t \left(c_p \frac{dT}{dt} + \Delta H_r \right) dt = \Delta H_p \quad (7)$$

The calculated heat requirements for pyrolysis of the tested PET sample, and other PSW as basis of comparison, are presented in Table 1. These values are the average of three experiments, with a maximum deviation of 6%. The end temperature of pyrolysis corresponds with values obtained in the authors' own TGA experiments and literature.

For all of the PSW tested, the reaction is moderately endothermic. For PET, heat requirements represent ~5% of its heat content. Data for C and c_p will be used to assess the kinetic results in the discussion.

Isothermal Experiments

Isothermal experiments were performed at 450 °C, but in two operating modes, that is, at a lower and at a higher

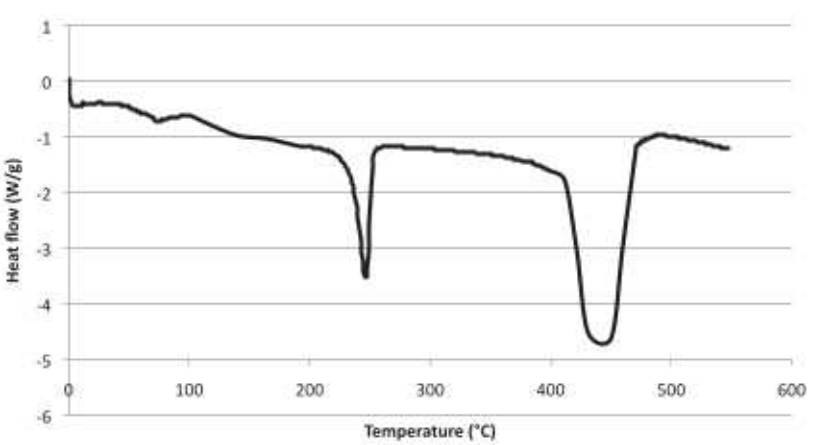

Figure 6. DSC results for PET at β = 10 K/min.

heating rate, the former when the bed is fluidized at low velocities (~2 U_{mf}) and the latter at the velocity of optimum heat transfer (~5 U_{mf}). The heat transfer rate differs in both cases by a factor of ~3 and is on the order of 100 W m^{-2} K^{-1} at 5 U_{mf}.[34–36] The amount of gaseous products formed remains about constant at 16–18 wt%. The slow or fast heating mode has moderate consequences for the condensable compounds formed, ranging, respectively, from 58 to 66 wt% in the fast mode to 55 to 65 wt% in the slow mode. The average balance of, respectively, 24 wt% (slow mode) and 16 wt% (fast mode) consists of the carbonaceous residue. It is thus clear that the operating mode of the reactor can be used to shift product ratios as a function of the target product.

Characterization of Condensables

The condensables were dissolved using 25 wt% TMAH in methanol and further diluted with acetone. GC-MS results demonstrated that the monomers of PET are not present as such, but that benzoic acid and monovinyl terephthalate are major components and that divinyl terephthalate and vinyl benzoate occur in lesser amounts along with traces of benzene. Further research is required and will be performed by both pyrolysis and GC techniques and possibly also by reactive pyrolysis in the presence of TMAH during the pyrolysis reaction and by additional isothermal runs in the fluidized bed reactor.

Upgrading of the Carbonaceous Residue

After the thermal decomposition, a black glossy carbon residue, of equal size to the milled PET feed, remains in the fluidized bed. This carbon is very light with a specific weight as low as 510 kg m^{-3}, has a porous structure, and is brittle but very hard. Results of analyses of input raw PET and carbon residue are shown in Table 2. Carbon, hydrogen, sulfur, and nitrogen were determined using a laboratory elemental analyser (CE440, Exeter Analytical Inc.). Oxygen was estimated as the difference.

To study a potential use of the carbon residue, as an alternative to using it as a carburizer in the steel industry,[40] samples of the residue were steam-activated at different pressures and for different times. BET (Brunauer, Emmett and Teller) (TriStar II 3020, Micromeretics) and pore volume (AutoPore IV, Micromeretics) were measured. The activation pressure was maintained at 30 bar for the tests at different durations. For additional tests, pressures of 10 and 20 bar were used during 30 min. Results are given in Table 3.

The density of the steam-activated carbon was 410–440 kg m^{-3}. It is clear that the carbon residue can potentially be upgraded to commercial value activated carbon (>700 m^2 g^{-1}), provided that the activation pressure and duration are appropriately selected. Similar results were reported in literature.[41,42] In further tests, the adsorption properties will be tested by using the PET-derived activated carbon in adsorbing various organic pollutants from an aqueous solution. Results in Table 3 predict that increasing either pressure or duration of the activation could further increase the specific surface and pore volume.

Table 2. Elemental analysis of PET and carbon residue on a dry basis.

Parameter	PET (wt%)	Carbon (wt%)
S	<0.01	0.27
C	62.5	97.3
H	3.8	<0.1
N	<0.01	<0.01
O	23.5	2.3
VOC	91.0	<1

Table 3. Results of the char activation.

	Specific Area (m^2/g)	Pore Volume (cm^3/g)
PET char (not activated)	286	0.178
PET char activated at ~10 bar (30 min)	418	0.255
PET char activated at ~20 bar (30 min)	533	0.317
PET char activated at ~30 bar (30 min)	612	0.250
PET char activated at ~30 bar (60 min)	718	0.300
PET char activated at ~30 bar (90 min)	1012	0.360
Commercial activated carbon	700–900	0.400–0.500

DISCUSSION

Reaction Kinetics

Experimental results have demonstrated that kinetic constants are a function of the heating rate of PET. This observation is generally accepted and implicitly included in methods to derive the kinetic constants from dynamic TGA experiments. From the data of Figure 5, E_a was determined to be 237,000 J mol^{-1}, whereas A varied from 10^{16} sec^{-1} at β = 3 °C min^{-1} to 2.5 × 10^{16} sec^{-1} at β > 100 °C min^{-1}.

Alternative Data Treatment

Alternative methods were summarized by Al-Salem et al.,[2,3,43] stressing the dependence of the kinetics on factors such as reaction atmosphere; sample weight, shape, and type; and heating rate and purge gas flow rate and also on the mathematical treatment used to evaluate certain parameters.

If the temperature rises with a constant heating rate β and the kinetic parameters at any weight loss fraction are approximately equal to those of neighboring weight loss fractions, eq 5, expressed in terms of any polymer conversion order, n, can be differentiated with respect to the temperature T to obtain the second derivative, as described by Oh et al.[44]:

$$\frac{-E}{RT} = \ln\left[\left(\frac{dx_s}{dT}\right)\frac{1}{A_0\sqrt{T(1-x_s)^n}}\right] \quad (8)$$

where E is the apparent activation energy (J mol^{-1}), x_s is the polymer solid conversion fraction, T is the temperature (K) at time t (sec), n is the polymer conversion order (equal to 1 for pyrolysis of PET), and A_0 is the collision theory dependent variable (sec^{-1} $T^{-1/2}$). Equation 8 gives the estimate of the activation energy at each date point. The average activation energy can be determined using the Coats and Redfern approximation[45]:

$$\bar{E} = \frac{\sum_{i=1}^{n} E_i(\alpha_i - \alpha_{i-1})}{\alpha_f} \quad (9)$$

where E_i is the activation energy corresponding to point i and time t, α_i is the weight loss fraction at point i, and α_f is the weight loss fraction at the final status of maximum degradation.

A valid approximation at maximum degradation is also presented by Oh et al.,[44] combining the heating rate β and the first-order Arrhenius fitting equation:

$$\ln(\beta) = \ln(A_0) + \frac{3}{2}\ln(T_m) - \ln\left(\frac{E_m}{RT_m} + \frac{1}{2}\right) - \frac{E_m}{RT_m} \quad (10)$$

where E_m is the activation energy at maximum degradation conditions (J mol^{-1}) and T_m is the final temperature or maximum degradation temperature (K).

Alternatively, the Ozawa-Flynn-Wall (OFW) method remains widely applied and used, especially at high heating rates. Ceamanos et al.[46] expressed the OFW equation in terms of the heating rate β and the solid conversion x_s as follows:

$$\ln(\beta) + 5.33 + \ln(1 - x_s) = \ln\left(\frac{k_0 E}{R}\right) - 1.05\left(\frac{E}{RT}\right) \quad (11)$$

E and k_0 can thus be calculated for sets of β and x_s.

Application of eq 11 yields an activation energy of between 229,000 and 245,000 J mol^{-1} for β = 100–120 K min^{-1}, corresponding with 237,000 J/mol derived from the present experimental results. Both the approaches of Oh et al.[44] and OFW[46] confirm that β affects the values of the kinetic parameters as was also previously shown in Figure 5. It was therefore essential to elucidate this phenomenon.

Considerations of Heating Rate and Reaction Progress

The external heating rate β (K min^{-1}) can be programmed in TGA experiments, and the above data are available for β values between 2 and 100 K min^{-1}. Values of k vary significantly, even for a single PSW. The influence of the heating rate is of paramount importance because the heat transferred must be sufficient to supply the total endothermal heat of reaction (C, J kg^{-1}). A heating rate that is too low (low value of β) will retard the pyrolysis reaction and will yield an apparently lower value of the reaction rate constant. The anticipated definition of the required minimum β value can prevent faulty experiments and derived experimental data.[38]

During TGA pyrolysis, reactions take place at an average of 723 K. The relationship between sufficient heat supply and reaction yield can be expressed in terms of kinetic and thermal data, as determined below. The first-order kinetics relate conversion (X), reaction rate constant (k), and time (t), according to a first-order reaction rate expression. Because the heat supplied should at any time and for any conversion exceed the heat consumed, a heat balance can be made. The heat supplied during the reaction equals $m_0 \cdot c_p \cdot \beta \cdot t$ (J), where m_0 is the initial amount of PET (kg). Heat requirements (C) were measured by DSC. The required heat of reaction is hence $C \cdot m_0$ (J). The heat balance then results in eq 12a:

$$m_0 c_p \beta t \geq m_0 C \quad (12a)$$

For a first-order reaction,

$$\ln(1 - \eta) = -kt \quad (12b)$$

where η is the fractional conversion at time t.

Inserting the value of t from eq 12b, the general eqs 12c and 12d are obtained:

$$\frac{-c_p \beta \ln(1 - \eta)}{k} \geq \eta C \quad (12c)$$

or

$$k \leq \frac{-c_p \beta \ln(1 - \eta)}{C} \quad (12d)$$

This equation can thus be applied to any values of fractional conversion (η). In the present research, overall values of k are measured, that is, at nearly complete conversion of the PET (Figure 5). Equation 12d is hence applied using these experimental k values. At 450 °C the TGA curves demonstrate a fractional conversion of ~70%. Equation 12d is then reduced to

$$k \leq \frac{1.2 c_p \beta}{C} \quad (12e)$$

It should be noted that for very low conversions ($X \rightarrow 0$) a more restrictive condition on k is obtained because the initial reaction rate is highest. This condition of very small conversions will, however, not be applied in the present treatment because only overall k values are known.

This approach was tested using the TGA results obtained at the different heat supply rates and given for PET in Figure 5, which clearly indicates that relevant k values can only be obtained if β exceeds 50 K min^{-1}. Application of eq 12e at an average of 723 K, with a c_p of 1.58 kJ kg^{-1} K^{-1} (at 723 K), with k equal to 0.25 sec^{-1}, and with the experimentally determined C values (Table 1), demonstrates that the theoretical value of β should exceed 30 K min^{-1} to meet the equality of reaction and heat transfer rate, in line with the experimental findings.

The theory demonstrates that only for β > 30 K min^{-1} are correct values of E_a and A obtained. These values should be used in the design of the pyrolysis reaction. As illustrated in the heat transfer calculations of the Experimental Procedure section, heating rates in excess of 30 K min^{-1} can only be reached in fluidized bed reactors, as used in the batch isothermal experiments of the present research.

Product Yield, Composition, and Possible Upgrading

It has been demonstrated that the carbonaceous residue (char) can be upgraded to a substitute for commercially available activated carbon. This is certainly a value-added approach, as the market value is more than €700 per ton, compared with €100–150 per ton if the char is used as a carburizer.[40]

The valorization of the condensables is less obvious, because of the acid or esterified nature of these products, although the deleted vinyl esters of terephthalic acid are formed by reaction with TMAH and methanol. PET monomers are absent. The upgrading by separation is not obvious, because of their high boiling points (terephthalic acid even desublimates at temperatures of 400 °C when exposed to air). Further research is needed and will be performed when larger pilot scale bubbling and circulating fluidized pyrolyzers are in operation (from July 2010 onward). If upgrading fails, these products can be used as fuel.

The gas produced ($<C_4$ hydrocarbons) can be combusted for supplying the pyrolysis reaction heat. In addition, Its combustion products can be used as a nearly inert carrier gas in the reactor, as proposed previously by Van de Velden et al.[39]

In consideration of the current market value of mechanically recovered PET (approximately €30–50 per ton), the sole valorization of the char and the extra benefit of the organic fuel equivalents certainly indicate the commercial potential of the pyrolysis process.

Selected Reactor Configurations

According to the results of the present investigations, the use of a fluidized bed reactor seems indicated, thus confirming its previous use in research on, for example, PET,[32] poly(methyl methacrylate),[47] and end-of-life tires[43,48]. The advantages of a fluidized bed reactor include (1) its isothermal operating mode, both at low and high fluidization velocities, (2) its operability at low fluidization velocities with a low heat transfer coefficient, thus favoring slow pyrolysis and char formation, (3) its operability at high fluidization velocities to enhance the liquid production, and (4) its isothermal operability at high temperatures to reduce the production of the liquid fraction.[32]

Although sufficient design data for fluidized bed reactors are available,[34–39] both in the bubbling and circulating mode, a desk design appears premature and the authors are currently investigating the use of a 0.2-m i.d. BFB and a 0.1-m i.d. CFB, both operating at temperatures up to 600 °C. Results and design recommendations will be included in a follow-up paper.

CONCLUSIONS

The paper described and discussed the kinetics and thermodynamics of the pyrolysis reaction of PET, as obtained from both dynamic and isothermal experiments. Activation energy, pre-exponential factor, heat of reaction, and reaction rate constant were determined. It was shown that a fairly high temperature ramp is required during dynamic experiments to obtain correct values of the kinetic parameters. Product yields and compositions were examined. The upgrading and recovery of these products were investigated, resulting in the confirmation of the PET pyrolysis potential through its production of both a carbonaceous residue with adsorbing characteristics and a mixture of organic acids and esters that can possibly be used as chemical feedstock or as fuel. The paper concluded by proposing the use of a BFB or CFB as the most appropriate pyrolysis reactor. Research on a pilot BFB and CFB is ongoing.

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