Environmental engineering: Stepwise pyrolysis of plastic waste

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Abstract

Kinetic data obtained from micro thermogravimetry and gradient free reactor experiments confirm that different molecular structures of commodity plastics bring about different reaction mechanisms of thermal decomposition, different reaction rates, and different temperature dependencies of the decomposition rates. From that, stepwise pyrolysis of mixtures of plastics seems to be reasonable where the different components of the mixture are pyrolysed at different temperatures.

To perform a stepwise pyrolysis in laboratory scale a cascade of well stirred reactors has been developed where mixing of the reactor contents occurs by circulating of stainless steel spheres. Examples for the separation of single plastics by stepwise thermal decomposition of mixtures of poly(vinyl chloride), polystyrene and polyethylene are presented. In the first step hydrogen chloride from poly(vinyl chloride) is released, in the second step styrene from polysytrene is formed and in the third step aliphatic compounds from polyethylene decompositon are trapped.

Differences in the thermal degradation of single polymers and mixtures of polymers, e.g. in the apparent activation energies and preexponential factors, are investigated using mixtures and blends of polyethylene and polystyrene. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Incineration of plastic refuses is a widely used method in waste management. The polymer fraction in domestic refuses comes to 7–8% by weight and encompasses about 77% polyolefines such as polyethylene or polypropylene, 12% polystyrene, 5% poly(vinyl chloride) and 6% other polymers. Particularly, this small amount of chlorine containing polymers causes the most serious problems in incineration, fires or recycling procedures. Poly(vinyl chloride) is a source of hydrogen chloride and under circumstances dioxines and chlorinated aromatic and aliphatic compounds may be formed at higher temperatures (Kaminsky, 1992). Therefore, chlorine has to be eliminated before processing plastic waste in incinerators or in processes for utilizing plastic wastes.

High costs of pollution control for incinerators, the high energy content of polymers as well as the chemical composition of plastics are demanding for alternative treatment of plastic refuses where plastic waste is considered as an additional resource of energy and as chemical raw material (Kaminsky, 1992; Plaßmann and Schock, 1996). Pyrolysis of plastic wastes is discussed as one alternative procedure compared against incineration (Kaminsky, 1992; Leidner, 1981; Albright et al., 1983; Ferrero et al., 1989; Thomé-Kozmiensky, 1985; Sinn et al., 1976; Matsumoto et al., 1975; Kobe Steel, 1974; Piskorz et al., 1986; Jones and Radding, 1980).

For designing pyrolysis procedures, the behaviour of polymers during thermal decomposition with regard to the decomposition products and the kinetics of decomposition must be known. Furthermore, changes in the kinetics of decomposition of polymers due to interactions of the polymers during thermal degradation have to be quantified and explained. The kinetics of decomposition of various plastics and plastic mixtures have been investigated by isothermal and dynamic measurements (e.g. Bockhorn et al., 1996; Knümann and Bockhorn, 1994; Paabo and Levin, 1987; Guyot, 1986; Lüderwald et al., 1978; Hornung, A., 1997). Data for the overall rate of

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thermal decomposition for different plastics is given in Table 1. The data in Table 1 refers to a rate expression for the thermal decomposition as given by $d\alpha/dt = k_0 e^{-E_a/RT}(1-\alpha)^n$, where α is the conversion $(m_0 - m)/(m_0 - m_\infty)$, m_0 being the initial mass, m the actual mass and m_∞ the final mass. E_a means the apparent activation energy and n the apparent reaction order. The data in Table 1 refer to pure plastics without fillers, stabilizers and colours (BASF, Ludwigshafen, Germany, compare

Section 3) as well as mixtures and blends of polyethylene and polystyrene.

The kinetic data confirms that different molecular structures of commodity plastics bring about different reaction mechanisms of thermal decomposition, different reaction rates and, particularly, different temperature dependencies of the decomposition rates. Futhermore, the data reveals that the decomposition rate of plastics is strongly affected by interactions of different plastics in

Table 1
Rate coefficients and apparent activation energies for the thermal decomposition of different plastics according to a rate expression $d\alpha/dt = k_0 e^{-E_a/RT}(1-\alpha)^n$

Polymer	$E_a/\text{kJ} \cdot \text{mol}^{-1}$	$\log(k_0/\text{min}^{-1})$	n	Reference
PVC dehydrochlorination				
Poly(vinyl chloride), isothermal[a]	136 ± 5	11.48 ± 0.09	1.54	U. Hornung (1997)
Poly(vinyl chloride), dynamic	143.5 ± 2.9	12.5 ± 0.18	1.54	Knümann and Bockhorn (1994)
Polystyrene, isothermal[a]	172 ± 4	12.47 ± 0.02	1.04	U. Hornung (1997)
Polystyrene, dynamic	322.8 ± 2.4	24.61 ± 0.19	1.09	Knümann and Bockhorn (1994)
Polyethylene, isothermal[a]	268 ± 3	17.78 ± 0.01	0.8–1.4	U. Hornung (1997)
Polyethylene, dynamic	262.1 ± 1.9	18.00 ± 0.14	0.83	Knümann and Bockhorn (1994)
PVC 2nd degradation step				
Poly(vinyl chloride), isothermal[a]	217 ± 5	14.9 ± 0.02	1–1.8	U. Hornung (1997)
Poly(vinyl chloride), dynamic	234.1 ± 2.1	16.35 ± 0.15	1.64	Knümann and Bockhorn (1994)
Polyamide 6, isothermal	211.0 ± 3	14.9 ± 0.05	1–1.29	U. Hornung (1997)
ε-Caprolactame, isothermal	205.0 ± 1	14.5 ± 0.03	0.98	U. Hornung (1997)
Polyamide 6, dynamic	210.8	15.01	0.82	U. Hornung (1997)
Polypropylene, isothermal	220 ± 5	15.06 ± 0.06	1.1	Bockhorn et al. (1998)
Polypropylene, dynamic	223.7 ± 1.6	15.9 ± 0.2	0.77	Knümann and Bockhorn (1994)
Polyethylene therephthalate, isothermal	214 ± 2	15.2 ± 0.04	1.15	Bockhorn et al. (1998)
Polyethylene therephthalate, dynamic	238.7	18.00	1.15	Bockhorn et al. (1998)
Polyethylene in mixture or blended with polystyrene (1 : 1), isothermal[a]	166 ± 12	10.8 ± 1.9	1–1.6	

Note: The data is obtained from isothermal and dynamic measurements. As far as there are differences in the rate coefficients from isothermal and dynamic measurements, two values are given.

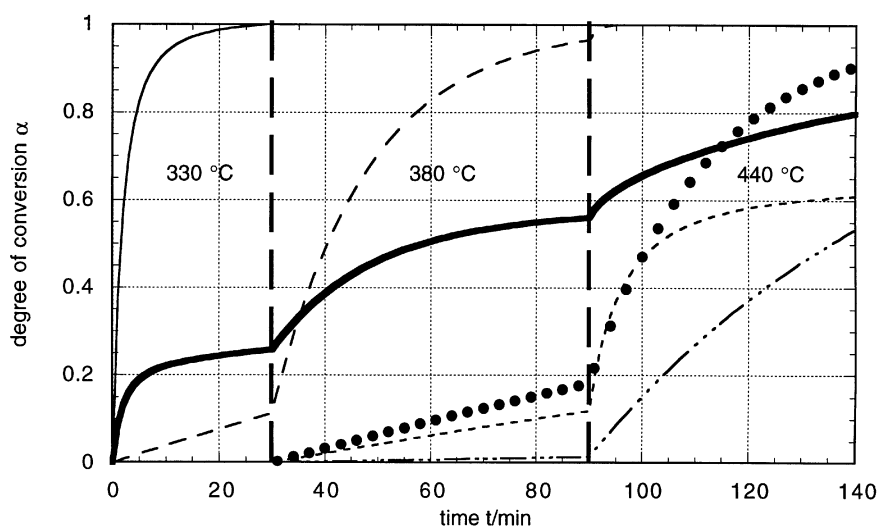[a] Data used for calculation of conversion displayed in Fig. 1.

Fig. 1. Calculated degree of conversion for batch wise decomposition of a mixture of PVC, PS and PE (1 : 1 : 1 by weight) at various temperatures in stepwise low temperature pyrolysis (data from isothermal measurements, compare Table 1); (▬) total degree of conversion, (— —) polystyrene, (—···) polyethylene, (– –) PVC (dehydrochlorination), (···) PVC (2nd. step), (●) PE in mixture or blended with PS.

a mixture. E.g. for the thermal decomposition of PE in a mixture of PS/PE the apparent activation energy is shifted by about $100 \, \text{kJ} \, \text{mol}^{-1}$ to lower values.

The temperature dependency of the rates for thermal decomposition of different plastics varies widely, so that single polymers in a mixture decompose at different temperatures. This is demonstrated in Fig. 1, where the degree of conversion α for the batchwise decomposition of a mixture of PVC, PS and PE (1:1:1 by weight) in a stepwise pyrolysis procedure at different temperatures is given, without considering interactions. Additionally, the degree of conversion $\alpha(\bullet)$ for PE in mixture or blended with PS is given including the experimentally determined interactions. The conversion has been calculated on the basis of the data in Table 1 and with the corresponding rate expression.

At 330°C dehydrochlorination of poly(vinyl chloride) occurs and about 10% of the polystyrene are decomposed (reaction time 30 min). At 380°C depolymerization of the major part of polystyrene into its monomer takes place and about 10% of the residue from dehydrochlorination of PVC are decomposed (reaction time 60 min). A small amount of polyethylene is pyrolysed at that temperature (about 1%, reaction time 60 min). At higher temperature (440°C) the decomposition of polyethylene and of the major part of the residue from dehydrochlorination of PVC occurs.

Considering the interactions of polyethylene and polystyrene the conversion of PE in the second step is up to 18% at a reaction time of 60 min. To supress PE pyrolysis in the second step a reaction time of about 25 min is reasonable leading to a conversion of 80% for PS and 8% for PE. The formal kinetic parameters for the thermal decomposition of PS in a mixture or blended with PE remain unaffected.

In the following the experimental set-up and results for the thermal decomposition of mixtures of commodity plastics by a stepwise pyrolysis at different temperature levels are presented. Some examples of pyrolysis of plastics at moderate temperatures up to 440°C are given, by which a chemical separation of plastic mixtures (polystyrene, polyethylene and poly(vinyl chloride)) into monomers or aliphatic compounds and raw materials is performed.

Finally, a discussion of the changes in mechanism and products of thermal degradation of polymer mixtures, e.g. the interaction of polyethylene and polystyrene, is presented.

2. Experimental set-up

The circulated-spheres reactor (Bockhorn et al., 1998; Hornung, A., et al., 1998, Hornung, A., et al., 1997), see Fig. 2, is used to perform chemical reactions in viscous and high viscous media. The circulated-spheres reactor
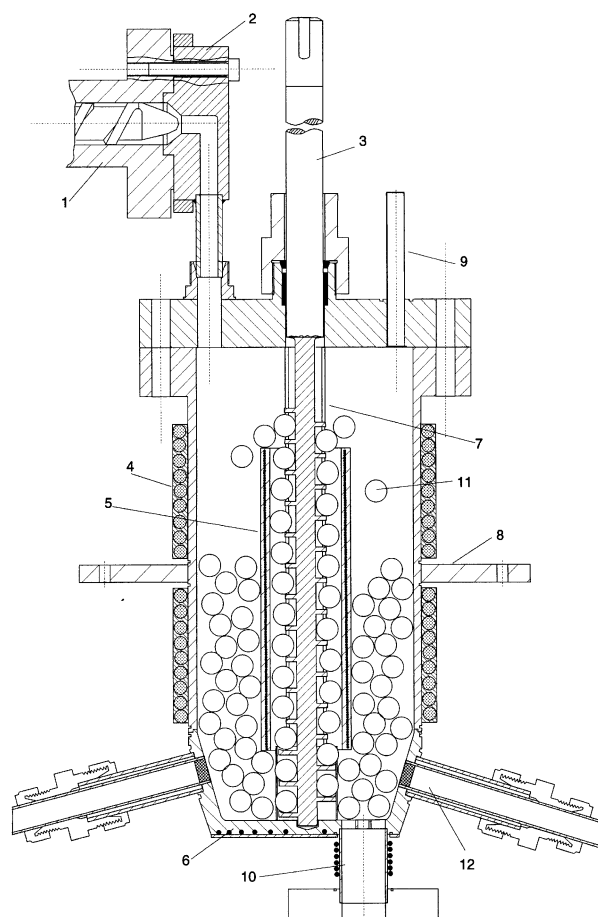

Fig. 2. Section of the reactor unit; (1) extruder, (2) connection, (3) conveyor screw, (4) outer heating, (5) inner heating (heating and reaction zone), (6) heating, (7) screw guide, (8) mounting, (9) gas outlet, (10) outlet, (11) spheres, (12) gas inlet.

with an inner diameter of 100 mm and a height of 220 mm is made of stainless steel (1.4571). The reactor is filled with about 500 spheres ($d = 10$ mm, stainless steel 1.4034) and equipped with a conveyor screw (stainless steel 1.6358) to circulate the spheres, Fig. 3. Chemical reactions take place within a thin film of the liquid medium around the spheres. Due to the circulated spheres well mixing of the reactor contents, i.e. spheres and liquid, is achieved. The conveying rate of the screw is up to 90 spheres min^{-1}. The spheres are circulated through a heated pipe (1), which serves as reaction zone, Fig. 3.

The conveyor screw (2) consists of a feed zone (4) for spheres and viscous liquid at the bottom and a heating and reaction zone (3) above, see Fig. 3. The spheres enter the pipe in the feed zone through slits (9) at the bottom and are transported to the top. In the feed zone the spheres are kept in the conveyor screw by a small rim (5). In the reaction zone the conveyor screw has a smaller diameter and the spheres are kept in an upward motion by means of a rim on the inner wall of the pipe. Within the pipe there is sufficient free volume to enable gaseous
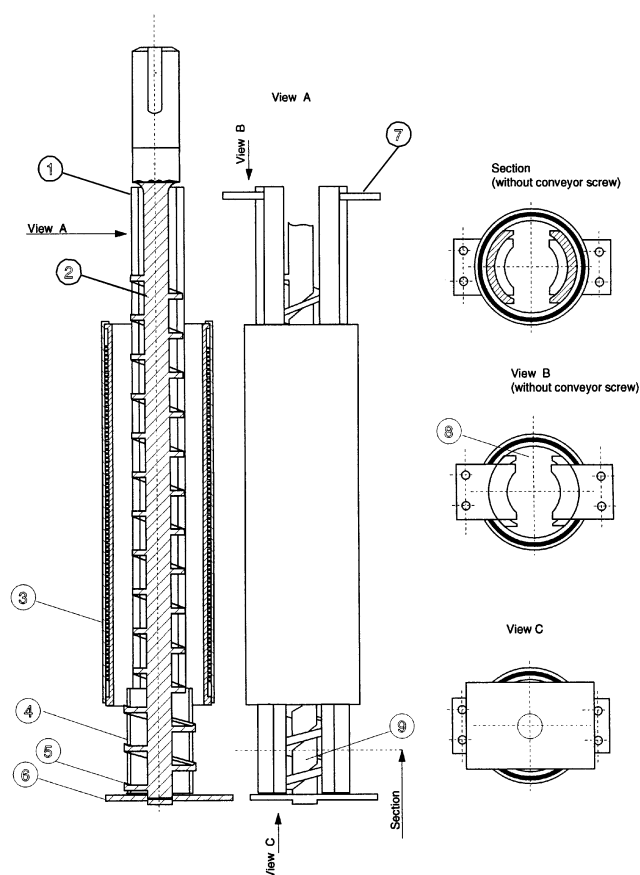
Fig. 3. Section of the conveyor unit.

Fig. 4. Schematic of the cascade of well-stirred reactors.

reaction products to escape from the reaction zone. By this, consecutive reactions are avoided.

At the bottom of the screw an eccentric plate (6) is fixed to keep the spheres in motion and to prevent blocking of the transport.

The reactor is purged with preheated inert gases. The purge gas flow is controlled via mass- and pressure controllers (Brooks), see Fig. 4. The advantages of this design are good heat transfer to the liquid and short residence times for products in the reactor to prevent secondary reactions. The reactor, the reaction zone and the purge gases are heated with electrical heaters. Each heating unit is controlled by Eurotherm-controllers equipped with thermocouples (Ni–Cr/Ni).

For application of this reactor concept for thermal decomposition of plastics these are liquified in an extruder (19/25 D, max. feed 3 kg h^{-1}, Brabender OHG (Duisburg, Germany)) and conveyed into the reactor. Liquified polymer mixtures with a viscosity of 5–200 000 mPa can be processed. The extruder is used to control feed and to keep off gaseous products from the feed system, see Figs. 2 and 4.

The pyrolysis experiments were carried out with a cascade of three well-stirred reactors. Fig. 4 shows the set-up of three well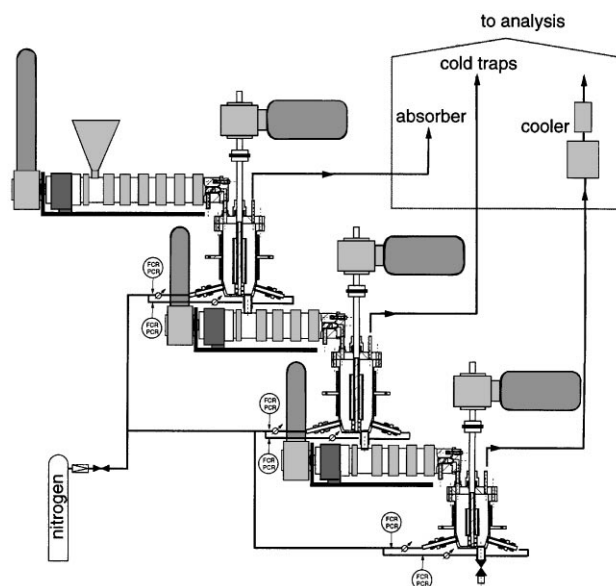-stirred reactors linked with extruders to control feed (max. 3 kg h^{-1}), residence time (26 min in each unit) and pressure (0.1 MPa). The different reactor units are sealed by means of the extruders.

3. Results

The following results are obtained in a stepwise low temperature pyrolysis in laboratory scale (max. feed: 3 kg h^{-1}). The operating conditions have been estimated by means of the rate data from isothermal measurements, see Table 1. The examples presented below refer to a run where the first reactor is kept at 330°C, the second at 380°C and the third at 440°C. The mean residence time in each reactor amounted to 26 min. The temperature control in the single reactors was better than $\pm 5°C$, which is essential because temperature variation of about 20°C causes failure of the separation. The results are obtained for mixtures of pure polymers without stabilizers, fillers and colors. The polymers are trademarks of BASF (Ludwigshafen, Germany); polystyrene (Polystyrol 143 B^{TM}), polyethylene (Lupolen 5261^{TM}), poly(vinyl chloride) (Vinoflex S 5715^{TM}).

3.1. Dehydrochlorination

As is known from dynamic and isothermal experiments an approximate quantitative dehydrochlorination of poly(vinyl chloride) is possible at temperatures of about 300–350°C (Bockhorn et al., 1996; Knümann and Bockhorn, 1994; Hornung, U., 1997). In laboratory scale in the first reactor of the cascade a degree of dehydrochlorination of 99.6% is achieved for the above given operating conditions, see Fig. 5. In case of

dehydrochlorination of a polymer mixture (PE-HD, PE-LD, PE-LLD, PP, PVC, 1:1:1:1:1 by weight) by degradative extrusion (Menges and Lackner, 1991; Menges and Lackner, 1992) a chlorine content in the residue of 0.2 wt% (Menges, 1994) is obtained. This corresponds to a degree of dehydrochlorination of 98%. Other commercial recycling procedures or procedures in laboratory scale (Kaminsky, 1992; Setzer and Hedden, 1996; Niemann, 1996; Schneider et al., 1996; Janz, 1996) use heavy oil to reduce the viscosity of the polymer mixture. In that case a dehydrochlorination of only 50% to 70% is obtained due to secondary reactions with the oil (Setzer and Hedden, 1996).

Fig. 5 shows the chlorine balance during pyrolysis of a mixture of PVC, PS and PE (1:6:3 by weight) through-

out the three reactors. The residue from the first and second reactor is transported within the molten polymer into the third reactor. The amount of chlorine in the residue from the third reactor is about 0.2 wt% (all given Cl-values are calculated on the basis of the weight of the corresponding fraction). A small amount of chlorine has been detected in the pyrolysis gas from the second and third step of the cascade. For a feed containing 10 wt% poly(vinyl chloride) (pure poly(vinyl chloride) without fillers) the amount of chlorine in the pyrolysis gas from the second reactor – containing the monomer fraction as well – is about 0.021wt% and the amount of chlorine in the pyrolysis gas of the third step of the cascade – containing the aliphatic compounds – is about 0.0044 wt%. An increase of the poly(vinyl chloride) content (15%) does not change the chlorine balance at all. Apart from the degradative extrusion, the other mentioned procedures as well as the hydrogenation require feeds containing less than 5 wt% poly(vinyl chloride) (Kaminsky, 1992; Niemann, 1996).

3.2. Monomer yield – second reactor of the cascade

In the second reactor of the cascade at 380°C polystyrene decomposes into its monomer. An exact temperature control is important to prevent the formation of gaseous pyrolysis products from polyethylene. Fig. 6 shows the characteristic pyrolysis products from the thermal degradation of a ternary mixture of poly(vinyl chloride), polystyrene and polyethylene (1:6:3 by weight).

The degradation of the mixture leads to styrene, styrene dimer, styrene trimer as well as 2-phenylpropene and ethylbenzene, compare Fig. 6. After three hours – during stationary operation – the concentration of the products in the gaseous phase is stationary. The amount of styrene in the pyrolysis gases from the second reactor is about 58% by volume and that of ethylbenzene about
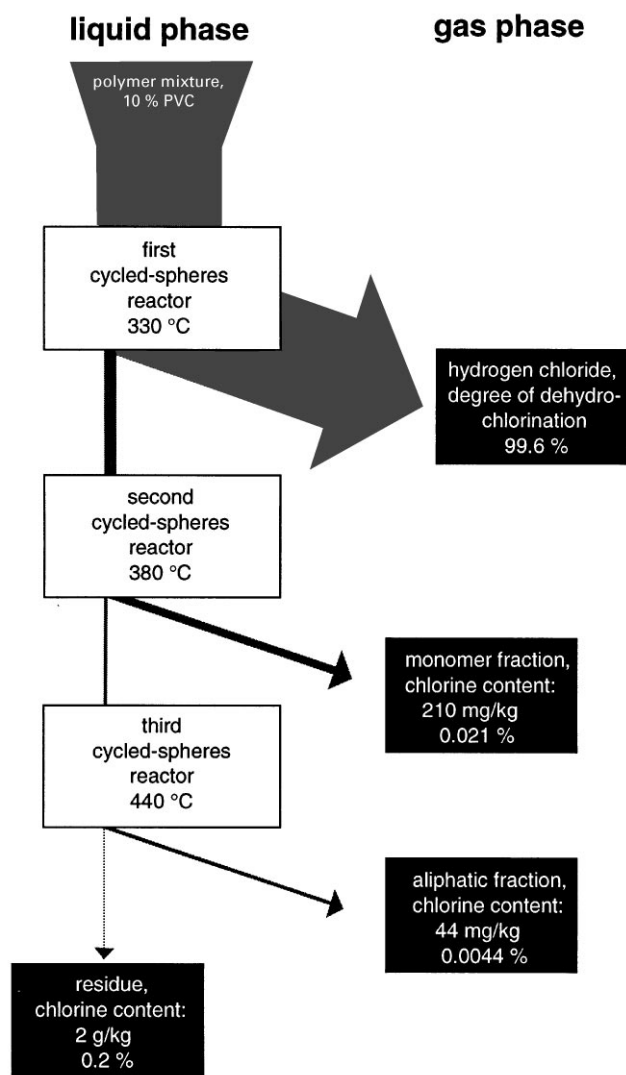
Fig. 5. Chlorine balance for the stationary operation of the cascade of three well stirred reactors; mixture: poly(vinyl chloride), polystyrene, polyethylene (1:6:3 by weight), feed: 0.5 kg h^{-1}; Cl-values are calculated on the weight of the respective fraction; mean residence time 26 min in each unit.
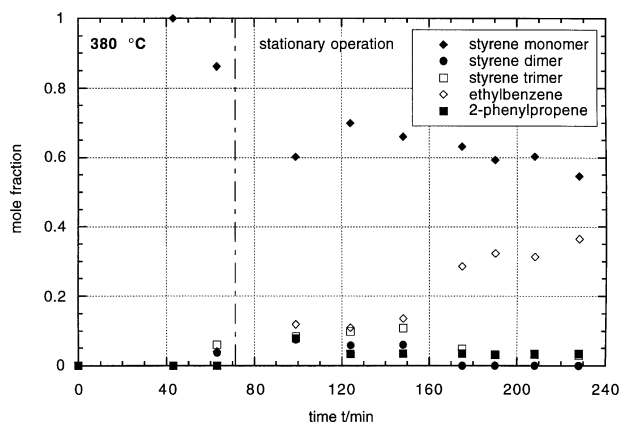
Fig. 6. Products from low temperature pyrolysis of a mixture of PVC, PS and PE (1:6:3 by weight)-second reactor of the cascade, 380°C, feed: 0.5 kg h^{-1}, abs. error in mole fractions ±3 mol%.

35%. Styrene dimer, -trimer and 2-phenylpropene appear in smaller amounts. Stationary operation as indicated in Fig. 6 means constant feed and outflow.

As indicated in Fig. 1 products from the degradation of the dehydrochlorinated residue of poly(vinyl chloride) should be detected in small amounts in the pyrolysis products from the second reactor. At a residence time of about 26 min the degree of conversion is less than 5% (see Fig. 1). One of the major pyrolysis product from the dehydrochlorinated PVC is styrene itself. The other aromatic compounds formed during decomposition of dehydrochlorinated poly(vinyl chloride) (Knümann and Bockhorn, 1994; Hornung, U., 1997) are below the detection limits of the used analytical procedure because of their low concentrations due to the low degree of conversion and the large variety of compounds.

Negligible amounts of gaseous pyrolysis products from the decomposition of polyethylene are detected in the second reactor. An indication for interactions between PS and PE is the high amount of ethylbenzene (Fig. 6), which is not formed during thermal degradation of pure PS. Referring to Fig. 1 for batch wise operation about 8% pyrolysis products of PE should be obtained in the second step at a residence time of 26 min. In batch mode the concentration of PE in the molten polymer increases with time due to the degradation of PS. This is different in continuous mode, where the concentrations of not converted polymers are constant. Therefore, conclusions about interactions between PS and PE during pyrolysis are difficult to draw.

However, the high amount of ethylbenzene from polystyrene in presence of poly(vinyl chloride)/polyethylene as well as in presence of polyethylene hints to interactions, which can be explained by a hydrogen transfer from the polyethylene chain to the polystyrene chain during pyrolysis (Hornung, A., 1997; Bockhorn et al., 1999, in press). The hydrogen transfer from polyethylene to polystyrene yields monocyclic aromatic compounds (ethylbenzene and styrene) from polystyrene up to 93% (Fig. 6). This is discussed in more detail in the next section.

The formation of ethylbenzene in the second step is then accompanied by the formation of a higher amount of olefinic compounds during pyrolysis of polyethylene in the third reactor.

In the third reactor of the cascade the polyethylene fraction of the polymer mixture, the major part of the residue from poly(vinyl chloride) dehydrochlorination and the minor part of polystyrene are decomposed at a temperature level of 440°C. Polyethylene is degraded into paraffines and olefines.

3.3. Interactions of PE and PS during thermal degradation

To elucidate interactions of single polymers during pyrolysis of mixtures the thermal degradation of mix-

tures of polyethylene and polystyrene are investigated under isothermal conditions with the help of a gradient free reactor with on-line mass spectrometry (Hornung, U., 1997; Hornung, U., et al., 1998). With the help of the mass spectrometric data the overall formal kinetic parameters (apparent energy of activation, preexponential factor and apparent order of reaction) are determined. Samples of about 30 mg of mixtures and blends of PE and PS have been investigated under inert atmosphere at 0.1 MPa. Mixtures and blends of weight ratios $50:50$, $80:20$ and $20:80$ were used.

The kinetic parameters of decomposition of polystyrene were found not to be influenced during thermal degradation in presence of polyethylene. Neither the apparent activation energy and the preexponential factor nor the apparent order of reaction change. Isothermal pyrolysis followed by GC-MS-analysis reveal an increase of hydrogenated pyrolysis products such as ethylbenzene.

In Fig. 7 the rate coefficients for the thermal degradation of pure polyethylene as well as degradation of polyethylene in presence of polystyrene are given in an Arrhenius plot. The apparent activation energy of the thermal decomposition of polyethylene decreases by about 90 kJ mol^{-1} in presence of polystyrene, compare Table 1 and Fig. 7. The order of reaction is not affected in the presence of polystyrene. A variation of the apparent reaction order with temperature from 0.8 to 1.5 is detected in the temperature range from 410°C to 480°C (Bockhorn, 1998b). The increasing order of reaction is correlated with the intermolecular hydrogen transfer during alkane formation at higher temperatures (Bockhorn, 1998b).

The production of volatile products from polyethylene is accelerated especially during the initial phase of pyrolysis. Fig. 8 shows the ion current of $57u$ from on-line mass spectrometric analysis for isothermal degradation
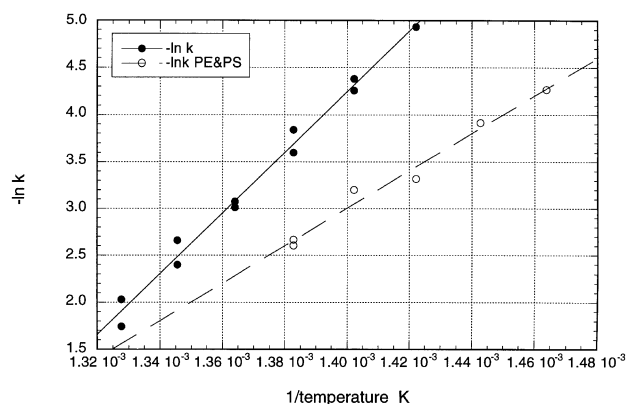

Fig. 7. Arrhenius plot for the thermal degradation of pure polyethylene ($E_a = 268 \pm 3$ kJ mol^{-1}, log(k_0/min^{-1} = 17.78 ± 3) and polyethylene in presence of polystyrene (PE:PS, 1:1 by weight: $E_a = 166 \pm 12$ kJ mol^{-1}, log(k_0/min^{-1} = 10.8 ± 1.9).
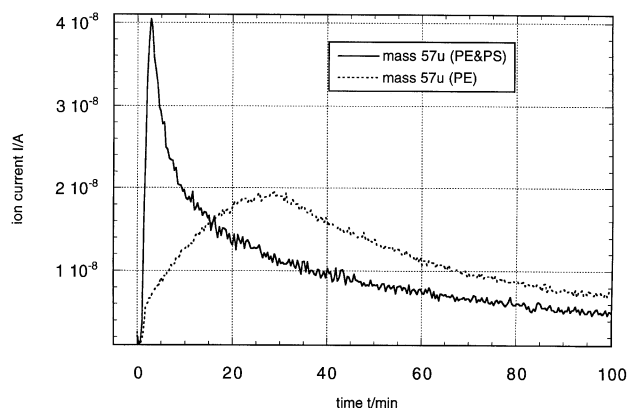
Fig. 8. Initiation of the decomposition of polyethylene in absence and presence of polystyrene elucidated by the main ion current of 57*u* from on-line mass spectrometric analysis.
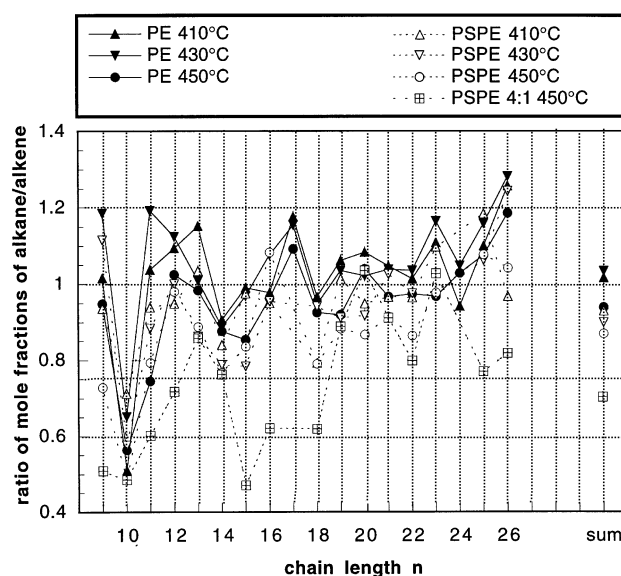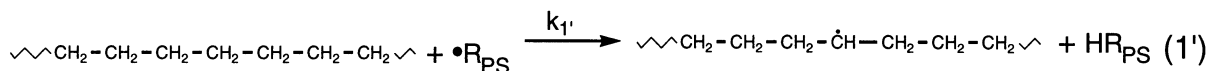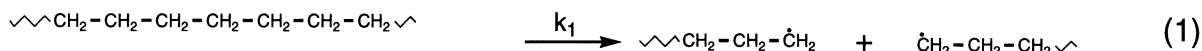

Fig. 9. Ratio of mole fractions of alkanes to that of alkenes in dependence on chain length for different pyrolysis temperatures and the total ratio of mole fractions of alkanes to that of alkenes for mixtures of PE and PS and pure PE.

of pure polyethylene and polyethylene degradation in presence of polystyrene in the gradient free reactor. The ion current 57*u* is characteristic for the C_4-fragment formed during ionization of olefines and paraffines in mass spectrometric analysis. High initial rates of decomposition of PE are detected in presence of PS. Main products were *n*-alkanes and *n*-alkenes, *n*-alkadienes occurred in negligible quantities, concentrations of other products as products of cross-repolymerisation were below the detection limit of the applied method. Fig. 9 shows the ratio of mole fractions of alkanes to that of alkenes in dependence on chain length and the total ratio of mole fractions of alkanes to that of alkenes for isothermal pyrolysis at different temperatures followed by GC-MS. All mixtures except one (PS:PE 8:2) are mixtures of PS and PE 1:1 by weight. The more polystyrene is added the more unsaturated products were detected (Fig. 9). The formation of higher amounts of unsaturated products from PE is accompanied by formation of higher amounts of hydrogenated products from PS, so that a hydrogen transfer from PE to PS seems to be reasonable. These results are consistent with the over-all picture from Fig. 6. Similar results have been found by McCaffrey (McCaffery et al., 1996).

The degradation mechanism of PS and PE are radical chain mechanisms (Guyot, 1986; Lehrle et al., 1982). The rate determining step of the thermal degradation of polystyrene is the initiation reaction, i.e. the homolytic chain scission to a chain carrier, which is the secondary radical $\cdot$R$_{PS}$. The apparent activation energy of that reaction is relatively low because these are relative stable radicals. This reaction is not affected by the degradation of polyethylene, which proceeds very slow. The propagation of the reaction chain has only minor influence on the over-all activation energy. Therefore, no changes of the apparent activation energy are found under the addition of polyethylene despite the shift of products towards saturated products (e.g. ethylbenzene). The initiating step

of the decomposition of polyethylene is also the homolytic chain scission with a high apparent activation energy of 356 kJ mol^{-1} (1), which is also rate determining. The thermal degradation of polystyrene starts at relatively low temperatures compared to that of polyethylene. The decomposition of PS provides polyethylene with radicals ($\cdot$R$_{PS}$). After H-abstraction from the polyethylene and a beta-scission similar to (4) and (4'), respectively, the reaction path of the decomposition of pure polyethylene is taken. Therefore chain transfer reactions with $\cdot$R$_{PS}$ can bypass the initiation reaction of PE degradation – the homolytic chain scission with its high apparent activation energy (Scheme 1) – resulting in a decreased overall activation energy. The change in the initiation reactions with higher initial rates of conversion can be observed from the on-line mass spectrometric data, see Fig. 8. For the assumed mechanism the following kinetic expression can be derived under quasistationary conditions for the primary and secondary radical (Bockhorn, 1998b):

$$\frac{\mathrm{d}[P]}{\mathrm{d}t} = k_2\left(\frac{k_1}{k_6}\right)^{0.5}[P]^{0.5} + \frac{k_4 k_3}{k_4 + k_4'}\left(\frac{k_1}{k_6}\right)^{0.5}[P]^{0.5}$$

$$+ \cdots \frac{k_4 k_5}{k_4 + k_4'}\left(\frac{k_1}{k_6}\right)^{0.5}[P]^{1.5} + k_5\left(\frac{k_1}{k_6}\right)^{0.5}[P]^{1.5}.$$

The contribution of the inititation step to the apparent activation energy is $E_{a_{(1)}}/2$. Assuming that the changed initiation step is controlled by the radical forming decomposition of polystyrene, the apparent activation energy of the polystyrene decomposition (172 kJ mol^{-1}) is

initiation

$$\wedge\!\!\wedge\!\!CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2 \wedge\!\!\wedge \quad \xrightarrow{k_1} \quad \wedge\!\!\wedge CH_2-CH_2-\overset{\cdot}{C}H_2 \quad + \quad \overset{\cdot}{C}H_2-CH_2-CH_2 \wedge\!\!\wedge \qquad (1)$$

$$\wedge\!\!\wedge CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2 \wedge\!\!\wedge + \bullet R_{PS} \quad \xrightarrow{k_{1'}} \quad \wedge\!\!\wedge CH_2-CH_2-CH_2-\overset{\cdot}{C}H-CH_2-CH_2-CH_2 \wedge\!\!\wedge + HR_{PS} \quad (1')$$

propagation

$$\wedge\!\!\wedge CH_2-CH_2-CH_2-CH_2-\overset{\cdot}{C}H_2 \quad \xrightarrow{k_2} \quad \wedge\!\!\wedge CH_2-CH_2-\overset{\cdot}{C}H_2 \quad + \quad H_2C\!=\!CH_2 \qquad (2)$$

$$\wedge\!\!\wedge CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\overset{\cdot}{C}H_2 \quad \xrightarrow{k_3} \quad \wedge\!\!\wedge CH_2-CH_2-\overset{\cdot}{C}H-CH_2-CH_2-CH_2-CH_3 \qquad (3)$$

$$\wedge\!\!\wedge CH_2-CH_2-\overset{\cdot}{C}H-CH_2-CH_2-CH_2-CH_3 \quad \overset{k_4}{\nearrow} \quad \wedge\!\!\wedge\overset{\cdot}{C}H_2 \quad + \quad CH_2\!=\!CH-CH_2-CH_2-CH_2-CH_3 \qquad (4)$$

$$\overset{k_{4'}}{\searrow} \quad \wedge\!\!\wedge CH_2-CH_2-CH\!=\!CH_2 \quad + \quad \overset{\cdot}{C}H_2-CH_2-CH_3 \qquad (4')$$

$$CH_3-(CH_2)_n-CH_2-\overset{\cdot}{C}H_2 + \wedge\!\!\wedge CH_2-CH_2-CH_2 \wedge\!\!\wedge \quad \xrightarrow{k_5} \quad CH_3-(CH_2)_n-CH_2-CH_3 + \wedge\!\!\wedge CH_2-\overset{\cdot}{C}H_2-CH_2 \wedge\!\!\wedge \qquad (5)$$

termination

$$\wedge\!\!\wedge \overset{\cdot}{C}H_2 \quad + \quad \overset{\cdot}{C}H_2 \wedge\!\!\wedge \quad \xrightarrow{k_6} \quad \wedge\!\!\wedge CH_2-CH_2 \wedge\!\!\wedge \qquad (6)$$
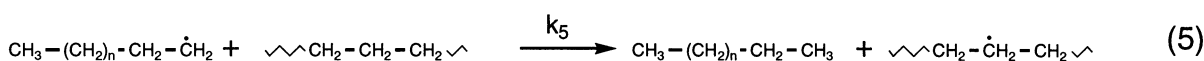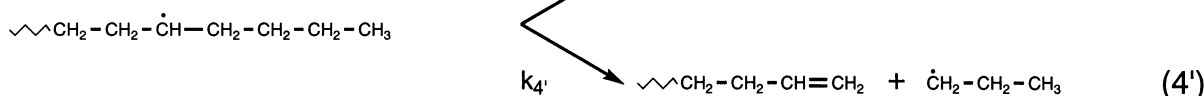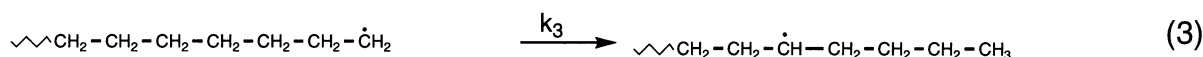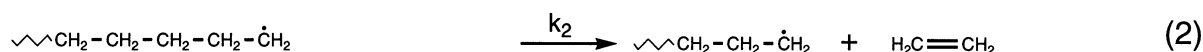
Scheme 1. Radical chain mechanism of the thermal degradation of polyethylene in presence of polystyrene.

relevant. This is about $184 \, kJ \, mol^{-1}$ less than the value of chain scission of the polyethylene chain. Taking into account, that the initiation step contributes one half to the overall activation energy (Bockhorn, 1998b), the apparent energy of activation should be decreased about $184/2 = 92 \, kJ \, mol^{-1}$. The decrease found in the experiments is close to this value ($88 \, kJ \, mol^{-1}$).

4. Conclusions

The above reported results confirm that the stepwise decomposition of polymers for gasification and separation of plastic mixtures in a cascade of cycled-spheres reactors is an alternative pyrolysis procedure.

For processing mixtures containing up to 15 wt% poly(vinyl chloride) no further pretreatment of the mixture is necessary. The dehydrochlorination takes place

quantitatively in the first reactor of the cascade. The chlorine balance gives a rate of conversion of about 99.6%. This result is corresponding to those of isothermal measurements. In spite of the high chlorine amount in the feed the product gases from the third reactor of the cascade contain only 0.0044 wt% chlorine.

The second reactor of the cascade is used to decompose polystyrene. The monomer is obtained in high yield. Neither hydrogen chloride nor gaseous pyrolysis products of the decomposition of polyethylene are detected in the second reactor.

Polyethylene is decomposed in the third reactor of the cascade into paraffines and olefines.

The interactions of single polymers in the liquid polymer mixture provide an additional means to control the products from polystyrene pyrolysis. In dependence on the composition of the mixture the pyrolysis products of polystyrene can be shifted to monocyclic aromatic

compounds with a yield up to 93% and the amount of styrene dimer an trimer decreases.

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