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# Stepwise Pyrolysis for Recycling of Plastic Mixtures

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Abstract: For chemical recycling of plastic refuses a cascade of cycled-spheres reactors has been developed combining separation and decomposition of polymer mixtures by stepwise pyrolysis at moderate temperatures. In low-temperature pyrolysis, mixtures of poly(vinyl chloride), polystyrene and polyethylene or polystyrene, polyamide 6 and polyethylene have been separated into hydrogen chloride, styrene and polyamide 6 and aliphatic compounds from polyethylene decomposition. Compared with the low-temperature pyrolysis of the single components, some interactions between the polymers are found when pyrolyzing mixtures. Some mechanistic aspects of these interactions are discussed.

## INTRODUCTION

High costs of pollution control for incinerators, the high energy content of plastics as well as the chemical composition of plastics require an alternative treatment of plastic refuses where plastic waste is considered as an alternative source of energy and as chemical raw material (Refs. 1-5). Pyrolysis of plastic wastes is discussed as an alternative procedure for incineration and pyrolysis is suggested to serve as pretreatment of polymer mixtures by which clean products, e.g. fuels or steam-cracker feed, can be obtained.

The kinetic data of low-temperature pyrolysis of plastics (some results from isothermal and dynamic measurements are given in Refs. 6-12) reveal that different chemical structures of commodity plastics cause different reaction mechanisms of decomposition, different reaction rates and, particularly, different temperature dependences of decomposition rates. Hence, a stepwise pyrolysis of plastic mixtures in which different components of a plastic mixture are subsequently pyrolyzed at different temperatures seems to be reasonable.

In this work, experimental results for thermal decomposition of mixtures of commodity plastics by stepwise pyrolysis on laboratory scale are presented. Some examples of pyrolysis of plastics at moderate temperatures up to 440 °C are given, by which chemical separation of plastic mixtures (polystyrene, polyethylene and poly(vinyl chloride) or polyamide 6) into by-products (e.g., hydrogen chloride), monomers or aliphatic compounds and raw materials is performed.

Furthermore, a mechanistic discussion of interactions of the different polymers in the liquid polymer mixture is given. Chemical interactions of single components in the liquid polymer mixture provide an additional tool to control thermal decomposition. For instance, the amount of ethylbenzene from polystyrene degradation increases and the amount of styrene dimer and trimer decreases in the presence of polyethylene in the liquid polymer mixture, whereas the amount of olefinic compounds in the pyrolysis products of polyethylene increases. For polyamide 6 in a mixture of polystyrene and polyethylene, the amount of [illegible]-caprolactam increases as well as the amount of styrene dimer and trimer, whereas the amount of ethylbenzene decreases drastically.

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## EXPERIMENTAL

The pyrolysis experiments were carried in a cascade of three well stirred reactors filled with spheres (Fig. 1), the details of which are given in Refs. 12-16. The advantages of the cycled spheres are good heat transfer to the liquid, short residence times for products and the pyrolysis reactions taking place in thin films around the spheres to prevent secondary reactions. Gaseous products are collected in several cold traps and analyzed off-line with GC-MS (Ref. 12). Chlorine was measured by the Wickbold procedure (Ref. 12).

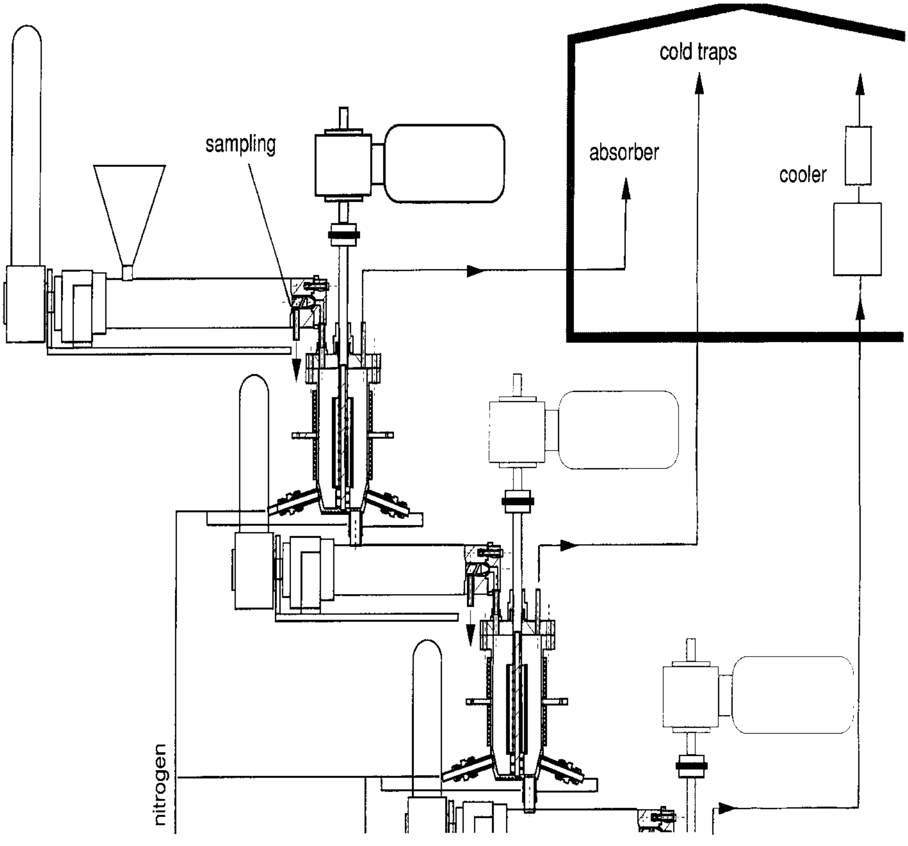

Figure 1: Schematic diagram of the reactor cascade

## RESULTS

The stepwise low-temperature pyrolysis on laboratory scale (maximum feed 3 kg/h) can be well predicted by means of the rate data from isothermal and dynamic measurements (Refs. 11,15). The following examples of low-temperature pyrolysis of plastic mixtures refer to a run where the first reactor is at 330 °C, the second at 380 °C and the third at 440 °C. The temperature has to be controlled; a temperature variation of about 20° causes failure of the separation. The results given below are obtained for mixtures of pure polymers without stabilizers, fillers and dyes. The polymers are trademarks of the BASF (Ludwigshafen, Germany): polyamide 6 (Ultramid

B3™), polystyrene (Polystyrol 143 B™), polyethylene (Lupolen 5261™), poly(vinyl chloride) (Vinoflex S 5715™).

Pyrolysis products

Dynamic and isothermal experiments (Refs. 6,7,11) show that the dehydrochlorination of poly(vinyl chloride) at about 330 °C is almost quantitative. On laboratory scale in the first reactor of the cascade, a degree of dehydrochlorination of 99.6 % was attained at 330 °C. Figure 2 shows the chlorine balance and the main products in pyrolysis of a mixture of PVC, PS and PE in the cascade of cycled-spheres reactors throughout the three reactors.

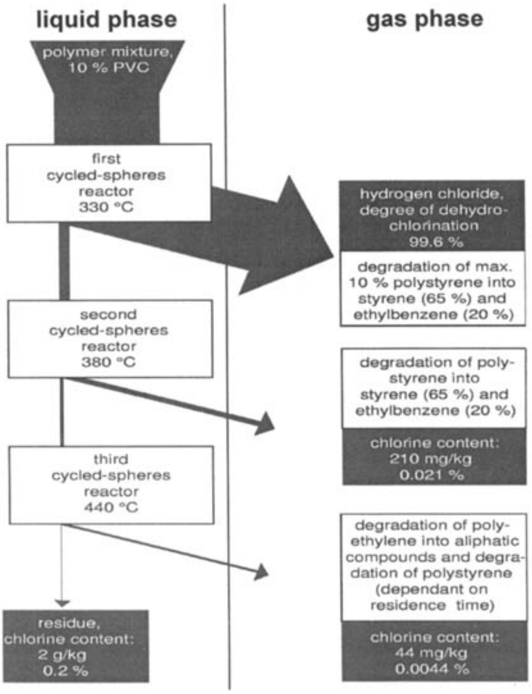

Figure 2: Chlorine balance and main pyrolysis products for the stationary operation of the cascade of three cycled-spheres reactors. Feed: poly(vinyl chloride), polystyrene, polyethylene, 1:6:3 by weight, 0.5 kg/h

The amount of chlorine in the residue from the third reactor is about 0.2 wt.-%. A small amount of chlorine has been detected in the pyrolysis gas from the second and third reactor of the cascade. For a feed containing 10 wt.-% of poly(vinyl chloride) (without fillers), the amount of chlorine in the pyrolysis gas of the second reactor, containing the monomer fraction as well, is about 0.021 wt.-% and the amount of chlorine in the pyrolysis gas of the third reactor of the cascade, containing aliphatic compounds, is about 0.0044 wt.-%. An increase in the poly(vinyl chloride) content (15 wt.-%) in the feed does not increase the chlorine content in the gaseous phase and in residues from the second and third reactor.

In the second reactor of the cascade, polystyrene and polyamide 6 decompose into the monomers in the absence of poly(vinyl chloride). A precise temperature control is important to prevent the formation of gaseous pyrolysis products from polyethylene. Figures 3 and 4 show characteristic pyrolysis products from the thermal degradation of two mixtures - a mixture of poly(vinyl chloride), polystyrene and polyethylene (weight ratio 1:6:3, mixture 1) and a mixture of polystyrene, polyamide 6 and polyethylene (weight ratio 3:1:1, mixture 2). The obtained products are significantly different in both cases. The degradation of mixture 1 leads to styrene, styrene dimer, styrene trimer as well as 2-phenylpropene and ethylbenzene (cf. Fig. 3). After three hours, the operation is stationary and the distribution of the products is constant. The molar fraction of styrene in the second reactor is about 58 % and that of ethylbenzene about 35 %. Styrene dimer, trimer and 2-phenylpropene appear in smaller amounts. The stationary operation with a constant feed and outlet is marked in Figs 3 and 4.

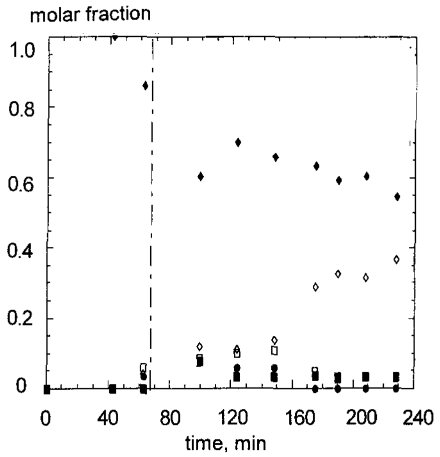

Figure 3: Products of stationary low-temperature pyrolysis of a mixture of PVC, PS and PE (weight ratio 1:6:3) in the second reactor of the cascade at 380 °C (feed 0.5 kg/h)

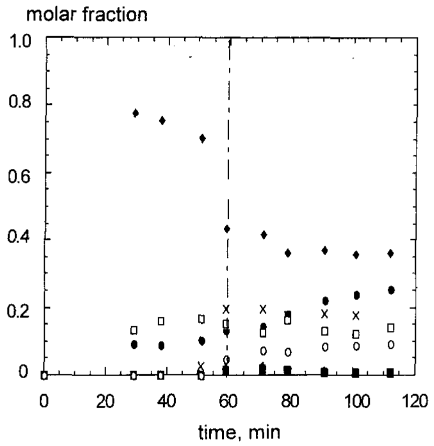

Figure 4: Products of stationary low-temperature pyrolysis of a mixture of PS, PA 6 and PE (weight ratio 3:1:1) in the second reactor of the cascade at 380 °C (feed: 0.5 kg/h)

◆ styrene monomer, ● styrene dimer, □ styrene trimer, ◊ ethylbenzene, ■ 2-phenylpropene, O 1,3-diphenylpropane, X ε-caprolactam

During the run, no gaseous pyrolysis products from the decomposition of polyethylene are detected in the second reactor. This result is consistent with the calculated rate of conversion for the decomposition of polyethylene on the basis of kinetic data from isothermal measurements (Refs. 11,15).

Different products are obtained during the thermal degradation of mixture 2 (Fig. 4). The conversion of polyamide 6 into caprolactam is about 95 %, resulting in 18 vol. % of caprolactam in the pyrolysis gases. 18 vol.-% of styrene is obtained along with a small amount of ethylbenzene. The content of styrene dimers and trimer increase up to 25 and 15 vol.-%, respectively. Apart from that, 10 vol.-% of 1,3-diphenylpropane is formed. The yield of styrene decreases in the presence of polyamide 6 in the mixture and higher yields of styrene dimer and trimer are obtained. A mechanistic discussion of the interactions of the polymers in the liquid polymer mixture is given in the next section. During the pyrolysis of mixture 2, no gaseous pyrolysis products from the decomposition of polyethylene are observed in the second reactor, even after an operation time of four hours. The decomposition takes place only in the third reactor at 440 °C giving paraffins and olefins.

## Polymer interactions in pyrolysis of plastic mixtures

Figures 5-7 show the distribution of main products and by-products for the batch pyrolysis of neat polystyrene and a mixture of polystyrene and polyethylene at 380 °C. For neat polystyrene, about 65 mol-% of styrene and about 22 mol-% of styrene dimer and trimer are obtained (Fig. 5). The results are in good agreement with those of Refs. 17 and 18. The pyrolysis products contain less than 1 mol-% of by-products (0.1 mol-% 2-phenylpropane, 0.8 mol-% 1,3-diphenylpropane).

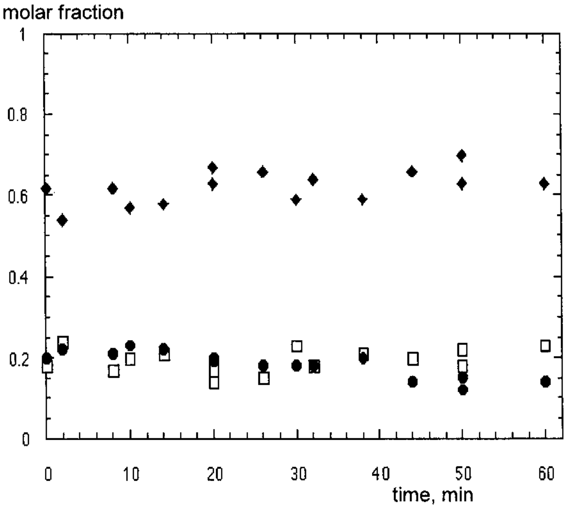

Figure 5: Products of low-temperature batch pyrolysis of polystyrene at 380 °C

♦ styrene monomer
● styrene dime r
□ styrene trimer

For a mixture of polystyrene and polyethylene (weight ratio 4:1), the distribution of main products and by-products of pyrolysis changes. While the amount of styrene (50 mol-%), styrene dimer (12 mol-%) and trimer (12 mol-%) decreases (Fig. 6), the amounts of ethylbenzene and 1,3-diphenylpropane increase up to 10-15 mol-% (Fig. 7).

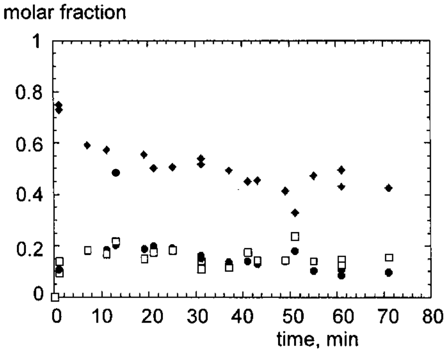

Figure 6: Main products of low-temperature batch pyrolysis of a mixture of PS and PE (weight ratio 4:1) at 380 °C (for symbols, see Fig. 5)

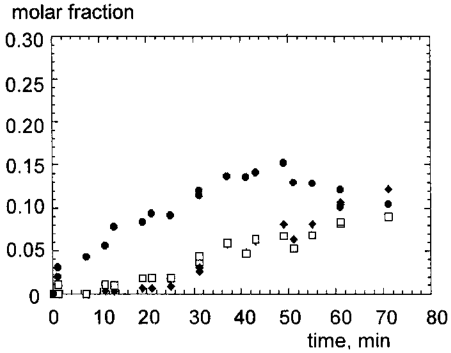

Figure 7: By-products of low-temperature batch pyrolysis of a mixture of PS and PE (weight ratio 4:1), at 380 °C (♦ ethylbenzene, ● 1,3-diphenyl-propane, □ 2-phenylpropene)

The high amount of ethylbenzene in the products of pyrolysis of polystyrene in the presence of polyethylene can be explained by hydrogen transfer from the polyethylene chain to the styrene monomer during pyrolysis.

Figure 8 shows the results of on-line mass spectrometry during the pyrolysis of neat polyethylene and a mixture of polyethylene and polystyrene (weight ratio 1:1) in an isothermal microreactor at 430 °C (Ref. 11).

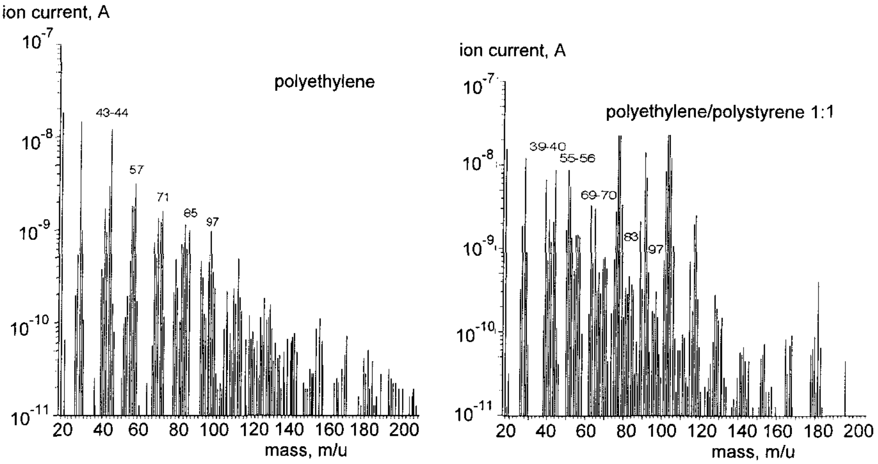

Figure 8: On-line mass spectrometric data for isothermal (430 °C) pyrolysis of polyethylene and a mixture of polyethylene and polystyrene (weight ratio 1:1) in a microreactor

Polyethylene chain scission takes place statistically and characteristic aliphatic mass fragments are detected. The mass fragments are multiples of the $CH_2$ group with one or two additional H atoms (Fig. 8). In the pyrolysis products from a mixture of polyethylene and polystyrene, a shift to characteristic olefin mass fragments is observed. The molecular weight of the products is by 1-3 units lower (Fig. 8) indicating that the hydrogen transfer is associated with higher concentrations of olefin components.

The interactions of single polymers in the liquid polymer mixture provide an additional means of controlling the products of polystyrene pyrolysis. High amounts of monocyclic aromatic compounds like styrene monomer and ethylbenzene can be obtained.

## CONCLUSION

The 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.-% of poly(vinyl chloride), no 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 corresponds 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.-% of chlorine. The second reactor of the cascade is used to decompose polystyrene and polyamide-6 yielding the monomers in high yields. Neither hydrogen chloride nor gaseous pyrolysis products of polyethylene decomposition are detected in the second reactor. Polyethylene is decomposed in the third reactor of the cascade into paraffins and olefins. Their molecular weight distribution can be controlled by the residence time.

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, pyrolysis products of polystyrene can be shifted to monocyclic aromatic compounds.

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