

Review

Chemical Recycling of Polymer Materials

By Frank Sasse and Gerhard Emig*

Dedicated to Prof. Dr. Ulrich Hoffmann on the occasion of his 60th birthday

After the first life cycle of plastics various recycling processes are available for further utilization of these valuable materials. For an ecologically and economically satisfying solution the most suitable process has to be chosen.

In chemical recycling polymers are degraded to basic chemical substances which can be reused in the petrochemical industry. For soiled waste plastics or waste plastics which could not be recycled until now, chemical recycling plays a key role.

The pyrolysis of acrylic polymers provides a good example for comparing a fluidized-bed reactor and a tubular reactor on the basis of reactor modelling evaluations. The used tubular reactor with internal mass transport is a simplified model for a rotary kiln. Relevant parameters for reactor design and scale-up are presented.

1 Problem of Polymer Wastes

The problems of used polymers do not derive from the necessity of saving natural resources, because only approx. 4–8 % of crude oil is used for polymer production. The predominant portion of crude oil (86 %) is still worldwide used as a source of energy [1]. Therefore, it would be more reasonable to save natural resources by reducing energy consumption.

The necessity of polymer recycling is a result of the increasing quantity of polymer wastes with landfilling areas decreasing at the same time, and of the understanding that a used polymer is a valuable raw material.

1.1 Legal Guidelines in Germany

The further utilization of used polymers in Germany is regulated by several legal standards, e.g., by acts, decrees and administrative instructions.

In Germany, mainly three different laws regulate the field of environmental care:

- the Recycling and Waste Act (Kreislaufwirtschafts- und Abfallgesetz, KrW-/AbfG),
- the Immission Act (Bundesimmissionsschutzgesetz, BImSchG),
- the Chemicals Act (Chemikaliengesetz, ChemG).

Further rules that directly or indirectly influence the recycling of polymers are the acts, decrees and technical rules for packaging materials, municipal waste, air pollution, water and risk materials.

1.2 Quantity of Polymers Used

In Germany, a total of 11 million tons of polymers were produced in 1995, which is about 10 % of the world production. In the same year, 3 million tons of polymer waste material were obtained, as depicted in Fig. 1. As polymer materials are usually very longlived, the amounts of waste obtained clearly delay behind polymer production and product consumption. For this reason, an overproportional increase in polymer wastes has to be expected accordingly in the next years. Polymers have been applied as materials on a larger scale only for 30 years, and the present waste has its origin mainly in short- and medium-term applications. In Germany, a total of 1.3 million tons of polymer wastes were recycled in 1995, which is roughly one half of all wastes obtained in an amount of 3 million tons. With 1.4 million tons packaging holds the largest share of the total amount of polymer wastes. The remaining 1.6 million tons of wastes have their origin in the fields of automobiles (120.000 tons), electronics (370.000 tons), building (200.000 tons), polymer processing and manufacturing (660.000 tons) and others (210.000 tons). In the fields of building, electronics and automobile approx. 80.000 tons of polymer wastes could be recycled (material recycling!). Related to the quantity of municipal waste and commercial waste similar to municipal waste of about 35.6 million tons [2], the share of polymers is approx. 8 wt.-% or 20 vol.-%. The polymer wastes which are recycled come from production and manufacturing wastes (55 %) and from used products (45 %). Among the last, 490.000 tons result from collections of the 'Dual System Germany' (DSD).

Fig. 1 presents the ratios of production, consumption and waste. Additionally, Fig. 1 also clearly shows that the bulk quantities of recycled polymer wastes come from the packaging sector, which is controlled by legal standards, and from processed manufacturing wastes, which can be recycled

[*] Dipl.-Ing. F. Sasse, Prof. Dr. G. Emig, Department of Industrial Chemistry I, Friedrich-Alexander-University of Erlangen-Nürnberg, Egerlandstraße 3, D-91058 Erlangen, Germany. Fax: 09131/857421

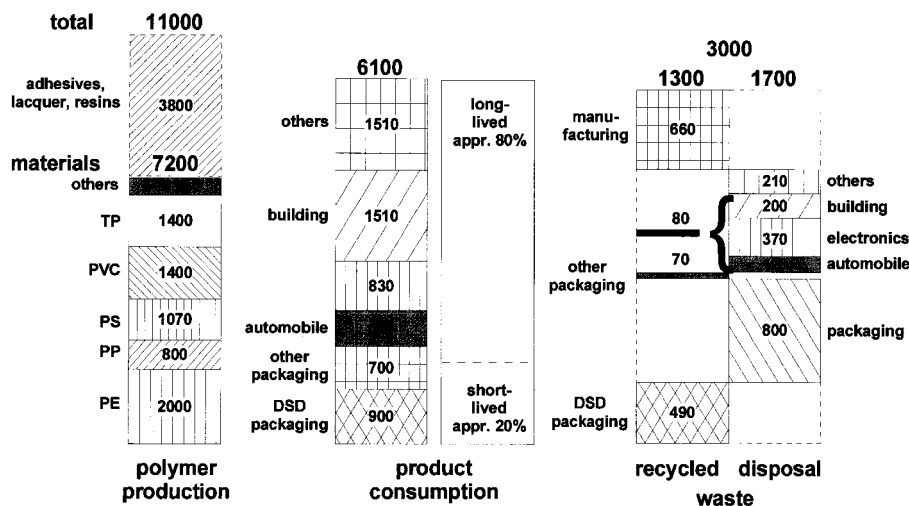


Figure 1. Polymer production, consumption and waste in Germany in 1995 (kt/a)

without economical or technological problems. Here is obviously a potential of used polymers which has not been exploited so far.

1.3 Quantities of Acrylic Polymers

Acrylic polymers, polymethylmethacrylates (PMMA) and their copolymers, are not bulk polymers. Because of their high quality and optical properties, they are applied mainly in fields where high transparency and colorfast properties are required. Examples are light coverings and automobile rear lights. In 1993, the world production totalled 1 million tons, divided in roughly one third on Europe, Japan and the USA [3]. Acrylic polymers are fabricated mainly as long-lived consumer goods. One-way articles of PMMA are used at most for hygienic reasons, e.g., in the health care application. Acrylic polymers will not be used as packaging materials or appear in domestic wastes.

2 Chemical Recycling Processes

At the end of the first life cycle of polymer material various processes for the recycling of used polymers are available. From an ecological point of view a convincing optimal solution for the recycling problem cannot be found as all recycling processes use up energy and raw materials. The choice of the most suitable process has to be made by considering ecological and economical criteria. Yet, each special waste problem has to be solved for its own. In the following, the usual recycling terminology will be explained in more detail.

'Material recycling' can be described as the reprocessing of used plastics as polymer raw materials in a physical process (remolding or regrinding processes). The chemical structure of the polymers is not changed. For this purpose, above all classified and clean polymer wastes obtained during polymer production and processing are well suited. In

the case of postconsumer wastes, materials as collected within the German DSD system, above all bottles and sheets can be used.

'Chemical recycling' is understood as the conversion of plastic materials into low-molecular products which can be reused as raw materials for the production of high-quality chemical products. Here the slogan 'oil – polymer – oil/gases – polymer' gets a real meaning. The advantage of chemical recycling is the possibility of using mixed and/or soiled waste materials. Here, processes which convert certain polymer classes into monomer fractions are of special interest.

In a wider sense, the use of polymers as reduction agent (reduction process) in a blast furnace for steel production can also be regarded as a recycling process.

For badly soiled small-sized and mixed polymer wastes the energetical usage may be a useful alternative. In this case the high energy content of the polymer material is exploited (e.g., in the cement production).

In the following, the material recycling as well as the energetical usage will not be discussed. Processes of chemical recycling usually need an integrated flow of material and energy within the framework of chemical industry because of their appreciable complexity. Therefore, the processes known today are all integrated into larger chemical complexes. Often, these larger plant sites also guarantee the further utilization of all products and residuals generated. Only in this way an economical operation is possible. A further requirement for an economical operation of a process is the guaranteed supply of feed material. The further extension of the BASF pyrolysis process had to be stopped, because the amount of polymer waste of 150.000 t/a needed as a minimum feed rate could not be guaranteed by the DSD organization [4]. Meanwhile, a real competition for the available polymer materials can be observed in this market sector. The most important processes for the chemical recycling of polymer materials, which above all are processing polymer wastes from the DSD-system, are – in the order of the quantities utilized in 1995 [5] –

1. gasification processes,
2. hydrogenation in the coal/oil plant Bottrop,

3. BASF pyrolysis,
4. blast furnace process of Bremer Stahlwerke.

2.1 Gasification Processes

The main purpose of gasification processes in the processing of polymer wastes is the generation of synthesis gas (CO, H₂). Possible byproducts in these processes are CO₂, H₂O, CH₄ and soot. The gasification can be described as a partial oxidation of hydrocarbons with an oxygen quantity which is understoichiometrical with respect to total combustion. The reaction temperatures range up to 1600 °C at a pressure of up to 150 bar. After the total conversion of the hydrocarbons CO₂ and H₂O can be formed. As gasification agents mainly oxygen, air, flue gas, steam and carbon dioxide are used. In special cases the application of hydrogen is also possible. Depending on the process applied, these agents can be used separately or in combination.

The technical processes of partial oxidation have been developed mainly on the basis of coal and heavy oil gasification processes. Technically reliable processes of coal gasification are the 'high-temperature Winkler process' (5) in the autothermal fluidized bed, the 'Koppers-Totzek process' in the flue dust cloud and the 'Lurgi pressure gasification' in the rotary-head generator (countercurrent) [6]. Common processes of heavy oil gasification are the Shell and Texaco processes and the submerged flame process of BASF [7]. From these basic processes many new and advanced processes have been developed which can also process polymer wastes as a cofeed. Here, two of these processes will be explained in more detail.

2.1.1 The Fixed-Bed Pressure Gasification of SVZ Schwarze Pumpe GmbH

The feedstock of brown coal briquet is mixed with plastic wastes (max. 50 %). This mixture is charged into a reactor where it is gasified with an oxygen-steam mixture at temperatures up to 1000 °C and at a pressure of 25 bar. The reactor operates in a countercurrent flow. The generated synthesis gas is converted into electricity by a gas engine or it is used as raw material for further petrochemical processes.

2.1.2 The High-Temperature Winkler Process of Rheinbraun AG

The gasification is performed with air and steam in an autothermal fluidized-bed reactor at 1000 °C. After purification the synthesis gas is used in the methanol synthesis. The quality of the product can be improved within certain limits by changing the feed ratios of the reactants, by suitable choice of temperature and pressure and by subsequent product purification.

The correct choice of the gasification process itself may be decisive, too. The most valuable product is a hydrogen-rich synthesis gas with a high portion of reactive components (no inerts) and only minor impurities. This product is a valuable feedstock for the methanol synthesis. Fuel gas which can be classified by different caloric values is the product of the lowest value. It can be used for the generation of heat and electricity. With regard to the recycling concept, of course, the route via synthesis gas to methanol should be preferred. A good overview of the different processes for polymer gasification is given by Gebauer and Stannard [8].

2.2 Reduction in the Blast Furnace

At the company site of 'Bremer Stahlwerke' a waste polymer agglomerate is substituted for the heavy oil normally necessary for the operation of the blast furnace. In the blast furnace steel production process iron ore as feedstock must be reduced. Possible reducing agents are carbon, carbon monoxide or hydrogen. The gases necessary for reduction are formed as soon as the polymer material is blown into the 2000 °C hot melt at the bottom of the blast furnace. At these temperatures the polymer is gasified instantly. As the chemical nature of waste polymer and heavy oil is very similar, one kilogram of waste polymer can be substituted for one kilogram of oil. During the passage of the hot gases through the long blast-furnace moving bed more than 80 % of the reduction potential of the gases generated from the waste polymer are utilized. At the top of the blast furnace a mixture of carbon dioxide, carbon monoxide and steam is obtained. This mixture – after separation of water also known as furnace gas – has a low caloric value and is used internally in the iron works [9]. Different metals and above all chlorine are undesired components because of their strong influence. Therefore, the chlorine content has to be kept below a value of 2 % during the partial substitution. For this reason a degradative extrusion with a view to dehydrochlorination and viscosity breaking can be introduced as pretreatment [10].

2.3 Pyrolysis Processes

The pyrolysis is very well suited for the further processing of polymer wastes. By thermal treatment under usually inert conditions a high-quality product can be obtained from a vast number of different polymers. The pyrolytical breakdown into chemical feedstocks allows a reuse in the original markets. The pyrolysis can be looked upon as a degradation of macromolecules into smaller fragments. Depending on the polymer used, a product similar to crude oil or even the monomer can be generated. The working temperatures of pyrolysis processes aimed at obtaining a high-quality product are within the range of 350–600 °C and therefore have to be classified as low-temperature pyrolysis. Besides the choice of temperature, above all the choice of a suitable reactor type is decisive for the

product selectivities. Obviously, reactor concepts should be preferred which show a behavior of optimal mass and heat exchange. From these points of view the following process concepts must be assessed:

2.3.1 The BP Chemicals Pyrolysis Process

The BP Chemicals pyrolysis process is presently in operation in a pilot plant in Grangemouth (GB) [11]. It is run by a group of the companies BP, Fina, DSM, Enichem and Atochem in cooperation with the University of Hamburg. The process makes use of the basic work of the research group of Sinn and Kaminsky [12–15] who developed the so-called ‘Hamburg process’. Here, an indirectly or directly heated fluidized bed of sand is used as a pyrolysis reactor. At low pressure and at modest reaction temperatures of about 500 °C mixed plastic wastes can be used as feedstocks. The product purification is performed in a hot gas cyclone, a bed of CaO for chlorine separation and a fractionating condensation. The main product is a paraffin wax obtained as top product of the fractionation.

2.3.2 The BASF Thermolysis Process

The BASF thermolysis plant has a capacity of 15.000 t/a of polymer wastes. This process is a good example for the integration of product and energy cycles into a larger company plant site (Fig. 2). Here, the selection of the plant location inside the Ludwigshafen plant area is of big advantage. In the first process step, the liquefaction in a cascade of stirred-tank reactors at 350 °C, a nearly complete dehalogenation is achieved at the same time. The main product from the next step in a tubular cracking reactor (450 °C) has, after fractionation, nearly the same composition as the common naphtha. It can therefore be used as feedstock for a steam cracker.

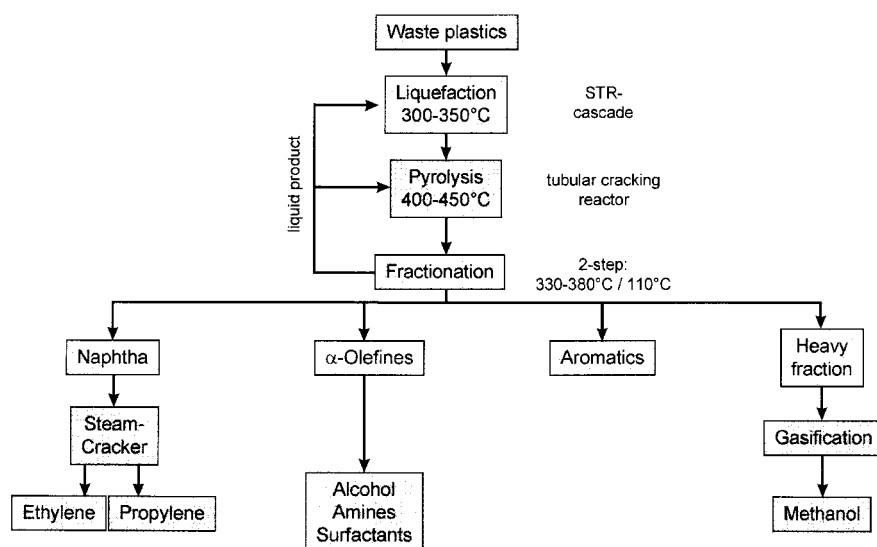


Figure 2. BASF-Thermolysis – process integration.

2.3.3 The Fuji Process

In Japan, Fuji Recycle Industries KK run two plants for the production of fuels from polymers with capacities of 400 and 5000 t/a, respectively [16,17]. This process has the special feature that the primary gaseous products from the cracker are converted into oil fractions by applying ZSM5 zeolites in a catalytic reactor. Altogether, more than 80 % of products can be obtained as liquid petrochemical products.

Besides the pyrolysis processes mentioned a vast number of differing concepts are known which so far have only partly been realized in a laboratory or bench scale. Examples are the pyrolysis in a circulating fluidized bed [18], the mid-range temperature pyrolysis in a rotary kiln [19], the stepwise pyrolysis according to Bockhorn [20,21] as well as the thermal degradation of polymers in an extruder. The product of the latter process is utilized as blending material for high-boiling paraffin-rich feedstocks in the steam cracker [22–25]. A promising extension of pyrolysis is the use of catalysts in the process to produce better-quality products already in the primary step [26–29].

2.4 Polymer Hydrogenation

The polymer hydrogenation process is derived from coal refining processes and the processing of heavy crude oil residues. The process of the coal/oil plant in Bottrop (KAB) (Fig. 3), developed by Veba-Oel AG, is mainly based on the ‘Veba Combi-Cracking process’ (VCC) [30]. After visbreaking in a depolymerization reactor at temperatures of about 420 °C (with the polymer alone or in a mixture with heavy crude oil components), the real hydrocracking follows in a bubble-column-type reactor. Molecular hydrogen is used for this hydrogenation at approx. 200 bar and 480 °C. Less aggressive conditions can be applied when polymers are used exclusively as feedstocks. Hydro-bitumen and a syncrude as products can be further converted to chemical raw materials.

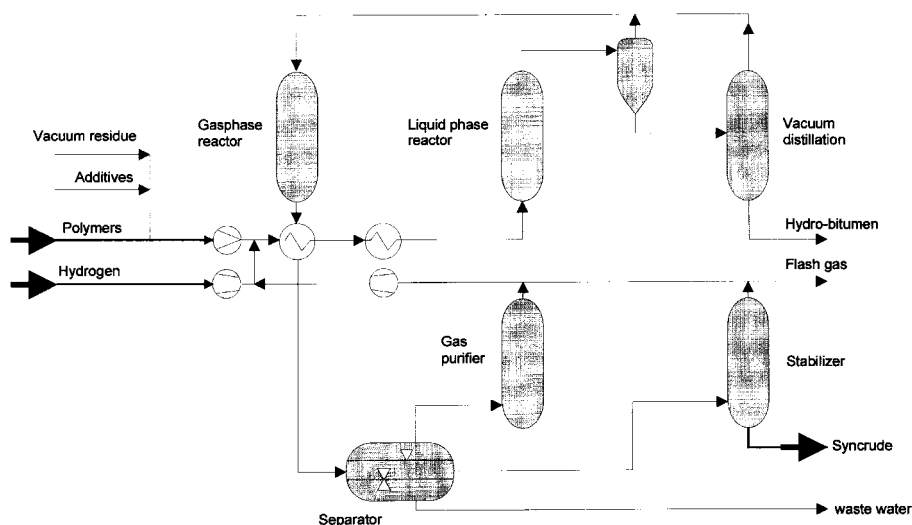


Figure 3. Flowchart of the polymer hydrogenation process (coal/oil plant Bottrop).

However, restrictions with respect to heteroatoms in the polymers (chlorine, nitrogen) have to be considered, as HCl and NH_3 are formed under conditions of hydrogenation.

2.5 Solvolysis of Polymers

For a number of polymers, such as PU, POM and PET, processes have been developed which take into consideration the specific decomposition properties of certain classes of polymers. In this context, above all processes must be mentioned which are designed to reproduce the original monomers or starting substances from the polymer material. In this case the term 'depolymerization' is used. An overview of the recycling opportunities of these polymers is given by different authors in Brandrup et. al. [31]. Solvolysis is a general expression comprising processes like glycolysis, methanolysis, hydrolysis, acidolysis and alcoholysis. Preferentially, these processes are utilized when the polymers are classified and precleaned manufacturing wastes. As an example, Hoechst AG started with a recycling plant for polyacetal production wastes in her Ticona plant

site. They use an acidolysis process with a capacity of 3000 t/a [32].

All the processes discussed so far are depicted in Tab. 1 which gives an overview of the present possibilities of the chemical recycling of polymer wastes. Only the basic process characteristics are described. Additionally, many modifications have been developed to meet different feedstock properties and plant location conditions.

2.6 Chemical Recycling of Acrylic Polymers

The basic principle of the chemical recycling of acrylic polymers is the thermal decomposition of the polymer chains. The aim of this decomposition is the production of the pure monomers. The depolymerization of PMMA, which is the reversal of the polymerization, generates stable MMA monomers under pyrolytic conditions, as a further degradation of MMA does not occur because of the stabilizing mesomeric effects.

Basically, all pyrolysis processes should be applicable for the chemical recycling of acrylic polymers. Already early it

Table 1. Chemical recycling processes

Process	Reactor	Reaction conditions	Products	Note
pyrolysis	fluidized bed, rotary kiln, tubular crackers	400°C - 900°C	wax, oil, gas, energy	mainly pilot plants
gasification	fluidized bed, fixed bed, pneumatic transport reactor	- 150 bar, - 1600°C	synthesis gas, el. energy	co-gasification with municipal waste, coal, heavy oil
hydrogenation	bubble column	- 200 bar, 500°C	hydrogenation bitumen, syncrude	KAB: -25% mixture with vacuum residuals, capacity appr. 40000 t/a
reduction in a blast furnace	blast furnace	- 2000°C	pig iron, furnace gas	Stahlwerke Bremen: 40.000 t/a projected
solvolysis	extruder, STR	depends on reactants -200°C and higher pressure	mainly monomers	small plants at producer or manufacturer sites

was demanded to reuse the manufacturing wastes of acrylic polymers as it was observed that the valuable material could be recycled by depolymerization. The processes first known used discontinuous retorts with sand as a heat transfer medium [33]. As soon as it was realized that heat transfer was the decisive factor for pyrolytic depolymerization, other heat transfer media like superheated steam or phenol were used, too [34,35]. Further investigations either to improve heat transfer during depolymerization or to reduce the residence time of the material in the reactor, led to processes like dry distillation and flash distillation [36] or degradative extrusion [37]. All these processes either showed an undesired formation of byproducts or led to deposits on the reactor walls. For these reasons, only two different pyrolysis processes could be successfully applied in this area so far.

2.6.1 Fluidized-Bed Pyrolysis

Kaminsky and co-workers [12–15] were the first to investigate the pyrolysis of polymers in a pyrolytic fluidized-bed reactor. The process developed therefore is known as the ‘Hamburg process’. The general feasibility of this process could be demonstrated also for the pyrolysis of acrylic polymers which could be reprocessed with a high yield of monomer.

2.6.2 Molten Metal Bath Process

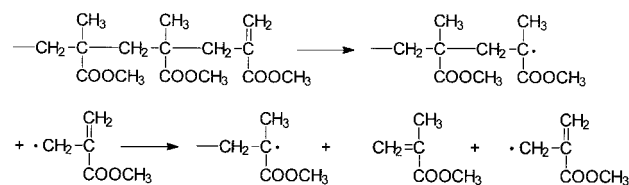
Smaller recycling plants for the recycling of acrylic polymers according to the metal bath process are operated by Degussa AG. A heated metal bath with a stirring device is used as depolymerization reactor. Metals used are preferentially tin (m.p. 232 °C) and lead (m.p. 327 °C). With suitable dosing devices the crushed granulate is fed directly into the hot metal melt. The stirrer provides a thorough mixing and thereby guarantees a good heat transfer from metal to polymer. Under these conditions PMMA depolymerizes spontaneously and the gaseous product leaves the reactor. Depending on the reaction temperature, high yields of monomer can be obtained. As byproducts higher- as well as low-boiling components are generated. Usually, the operator has to determine individually the optimal state of operation [38]. There are some inherent disadvantages of the molten metal process to be considered:

- Pigments and attached dust and dirt particles have to be separated from the metal melt.
- The raw condensate of MMA may be contaminated by the metal.
- The raw condensate produced has a yellowish color. It contains further undesired byproducts which either have to be separated completely or which reduce the product quality.

3 Mechanism of the Thermal Decomposition of PMMA

Resulting from the radical polymerization of MMA, two different types of polymer chains are generated with respect to the disproportionation as terminal reaction. Either chains with unsaturated chain ends or completely saturated chains are formed. The mechanism of the thermal decomposition can be described by an endothermic radical chain reaction with two different initiation reactions (radical formation) to occur at the different polymer chains mentioned above (Fig. 4 according to [39]). The intrinsic mechanism of the primary radical formation by bond rupture of the saturated chains randomly in the backbone is still not finally enlightened [40,41], because also a bond rupture of the carboxylic group is under discussion [42]. The primary radical formation is followed by an unzipping mechanism which releases monomers (propagation reaction) until a termination reaction (mostly disproportionation) occurs which again generates unsaturated polymer chains. It should be noted that the unsaturated polymer chains are less stable than saturated ones, so that unsaturated polymer chains are further decomposed already at lower temperatures.

Initiation at unsaturated chain ends:



Initiation by random scission:

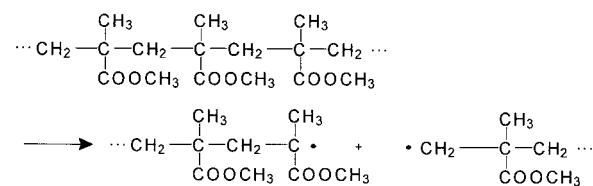


Figure 4. Initiation at unsaturated and saturated polymer chains.

During the production process, the polymers can be thermally stabilized by the addition of mercaptanes which saturate thermally unstable double bonds. Furthermore, suitable comonomers can act as stabilizer in the polymer chain. McNeill [43] as well as Grassie and Torrance [44] demonstrated that methylacrylate (MA) as comonomer has a great influence on the depolymerization behavior of acrylic polymers. An increasing portion of MA in the polymer diminishes the portion of MMA released by reaction on terminal double bonds. Additionally, a blocking effect of the MA units on the depolymerization reaction in the chain backbone is postulated. The main factors of influence on the

thermal depolymerization are the molecular weight of the polymer, the portion and type of the comonomer and the addition of mercaptane. Further subordinate influencing factors are, for example, cross-linking, pigments and dyeing of the polymer.

4 Decomposition Kinetics

The determination of the temperature- and time-dependent degradation of the polymer to the monomer is a presupposition for the design of a technical-scale reactor for the recycling of acrylic polymers. However, a precise kinetic description of the intrinsic processes in the complex radical reaction is not necessary. Simplifying, the respective initiation reaction (radical formation) can be assumed as the rate-determining step. It is then not considered that high-molecular polymer chains are not decomposed by one single initiation reaction followed by the consecutive degradation, but that termination reaction occurs before the total decomposition of one polymer chain and generates partially degraded polymer chains. These polymer chains cannot be further decomposed to monomers until a renewed initiation reaction occurs. Therefore, the following kinetic model must be looked upon as a lumped reaction system. The kinetic parameters estimated on this basis only give a lumped kinetic expression of the polymer degradation.

4.1 Specification of Testing Materials

The acrylic polymer samples were provided by Röhm GmbH Chemical Company. These samples can be subdivided into low-molecular molding materials and high-molecular casting materials, both specified in Tab. 2. The acrylic polymers were produced by radical polymerization. The casting material was obtained by bulk polymerization.

4.2 Modelling of the Reaction Paths

The reaction paths during the pyrolytic decomposition under inert atmosphere were detected by thermogravimetric measurements (Fig. 5) and by the method of differential scanning calorimetry (Fig. 6). The thermogravimetric inves-

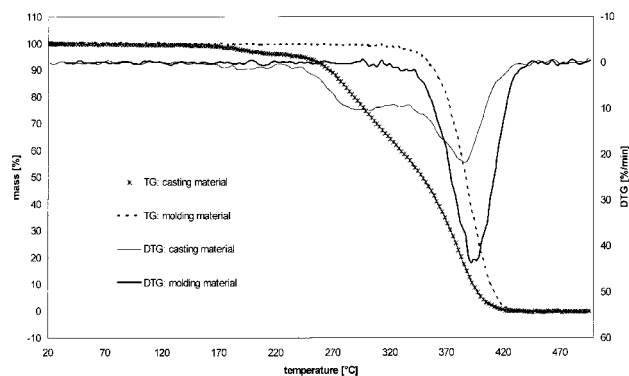


Figure 5. Thermogravimetry: Comparison of mass losses and reaction rates of molding and casting materials of acrylic polymers.

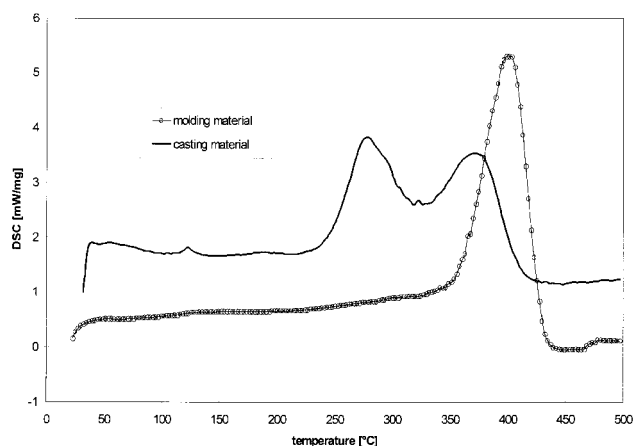


Figure 6. Dynamic Differential Calorimetry: Comparison of the endothermic reaction paths of molding and casting materials.

tigations showed the temperature-dependent mass loss of the acrylic polymers. Kinetic parameters for suitable reaction models could be determined by nonlinear regression techniques. For the choice of the most probable reaction model statistical methods were applied.

4.2.1 Molding Materials

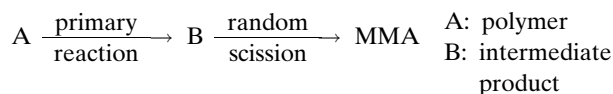
The results of the thermal analysis showed that the decomposition can be described mainly by a reaction step

Table 2. Specification of testing materials

Molding materials	Casting materials
trade mark Plexiglas ®: 7N, 7H, 7H (TiO ₂), 8N, 8N (red transparently colored)	trade mark Plexiglas ®: GS 233, Creanit, GS 2399 (sanitary material)
molecular weight: 100.000- 200000 g/mol	molecular weight up to 2000000 g/mol
pigments, coloring materials, mercaptane	pigments and filling material (Al(OH) ₃)
comonomer < 6% MA	partly cross-linked

initiated by random chain scission (Figs. 5, 6). However, before this step a reaction with a minor mass loss occurs which can be explained by a depolymerization of the main chain up to blocking comonomer units. Due to the presence of polymerization regulators hardly any unsaturated chain ends can be found in the polymer. Therefore, the molding materials depolymerize at temperatures not below 350 °C.

The reaction system can be described as:



4.2.2 Casting Materials

As no polymerization regulators were added to the casting materials, these polymers depolymerized already at temperatures of about 250 °C due to reactions at the unsaturated chain ends. The saturated chains reacted from approx. 350 °C onward by random chain scission (Figs. 5 and 6). Therefore, one can assume that there are two different reactants which depolymerize at different temperatures. The reaction system, therefore, is:

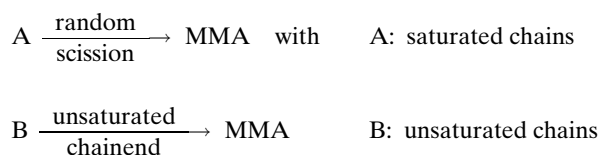


Fig. 7 demonstrates the good fit of the reaction model with the experimental data for the example of a high-molecular casting material with a high filler content (Creanit®).

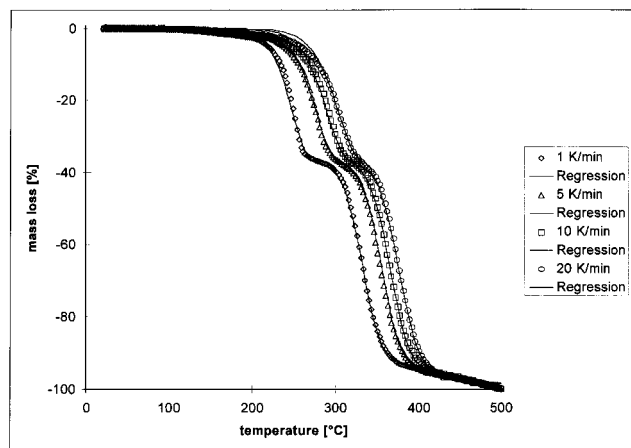


Figure 7. Comparison of the thermogravimetric measurement with the regression of the kinetic model (casting material Creanit®)

The determination of kinetic parameters for the reaction models makes it possible to predict the temperature-dependant reaction times for the total decomposition of the polymers (i.e. conversion > 99 %). The reaction times

necessary for the total conversion to gaseous products of molding materials.

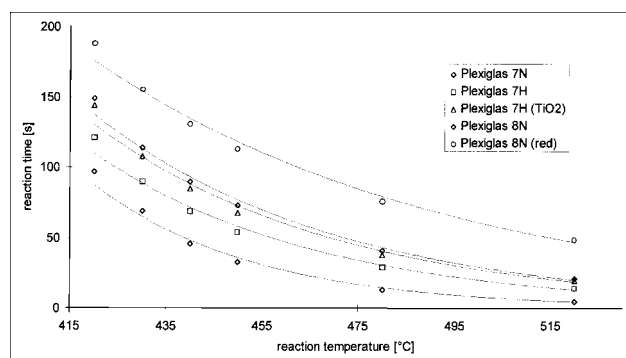


Figure 8. Reaction times for total conversion to gaseous products of molding materials.

5 Pyrolysis in the Fluidized Bed and the Tubular Reactor

The reaction engineering experiments were carried out in a laboratory-scale device. Fig. 9 shows the laboratory fluidized-bed reactor with externally heated reactor, dosage of solid and fluidizing gas, product processing and product analysis. Quartz sand of different grain size served as fluidization medium and reaction surface at the same time.

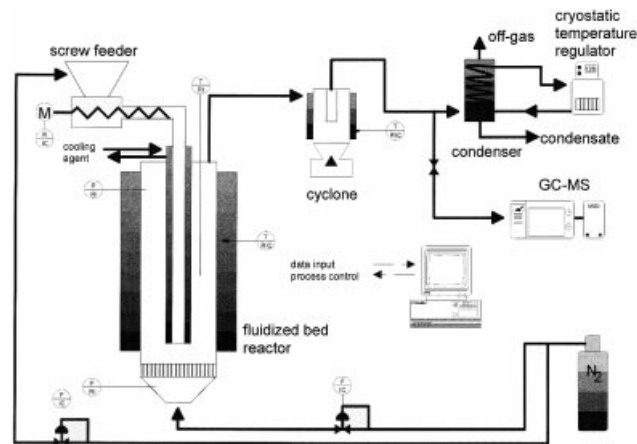


Figure 9. Laboratory fluidized-bed reactor.

The externally heated tube reactor was equipped with an internally operating transport spindle (Fig. 10). Thus it was possible to transport a polymer-sand mixture with variable residence times through the horizontal reactor. The reactor is comparable to a simplified rotary kiln. The feeding of the reactor was achieved by a screw feeder and a double lock system. The hot sand together with unreacted polymer was quenched in a water bath after a second double lock system. As can be seen from Fig. 10, the apparatus was flushed with N₂ and the product gases were analyzed by a gas chromatograph.

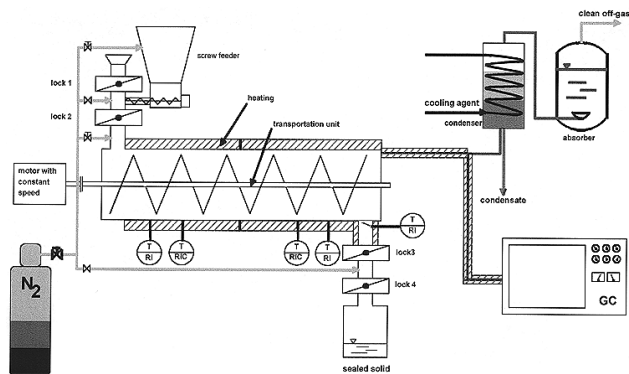


Figure 10. Laboratory tube reactor with internal mass transport.

Tab. 3 summarizes the important technical data of both laboratory reactors.

The fluidized-bed reactor was operated in continuous mode, the tubular reactor was operated in continuous mode as well as in batch mode.

5.1 Product Selectivities

In the fluidized-bed reactor the product selectivities were determined in dependence of the acrylic polymer feed rate, the reaction temperature and the N_2 flow. With respect to these variables the product selectivities remained almost constant. Small changes in the course of selectivities mainly result from thermal degradation of the MMA formed. However, in the tubular reactor a strong increase of the byproduct selectivities can be observed especially when the mean reaction temperature is increased (Fig. 11). This can be explained by the strongly polytropic behavior of the tubular reactor showing axial as well as radial temperature profiles. In this respect, the almost ideal mass- and heat-transfer behavior of the fluidized-bed reactor promotes an optimal reaction

control. Tab. 4 shows typical product selectivities (depending on the polymer type) which can be observed under optimal reaction conditions.

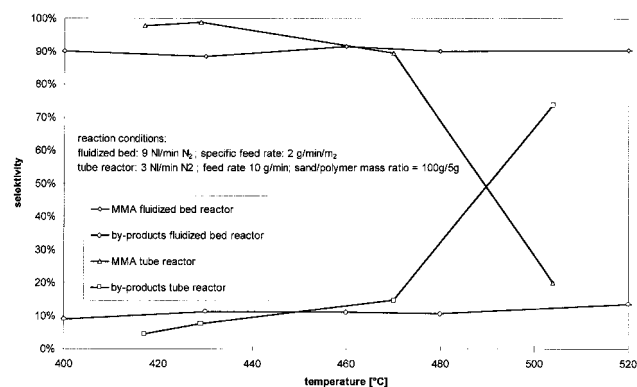


Figure 11. Comparison of temperature-dependent product selectivities of fluidized-bed reactor and tube reactor.

Table 4. Product selectivities at 430 °C and high N_2 -flow.

Products	Selectivity (appr.)
MMA	80–95%
MA	2–4%
total by products individual portions:	2–20%
i-Butene	60%
Propane/Propene	20%
others	Ethane/Ethene, Methane, IBME, PME
furthermore	CO, CO ₂ , high-boiling products

Table 3. Technical data of the laboratory reactors.

Technical data	Fluidized bed reactor	Tube reactor	
height [m]:	0,40	length [m]:	0,71
inner diameter [m]:	0,07		0,12
bottom plate:	sintered metal 50 µm	locks:	2 double-locks
fluidized agent:	quartz sand 50-400 g; diff. grain	mixing and transport agent:	quartz sand 500-1000 g; grain 400 µm mass ratio sand/polymer 20/1-8/1
pressure drop measurement:	0-100 mbar differential	solid trans- port:	rotor shaft with const. speed but alternating direction of rotation
cyclone:	separation limit appr. 10µm		
dosing apparatus:	screw feeder 0-50 g/min acrylic polymer		
indirect heating:	electrical max. 900°C		
gas input:	N_2 heated 0-30 NL/min	N_2 0-10 NL/min	
flush gas feeder:	N_2 0-0,5 NL/min		
temperature of piping:	> 200°C		
off-gas condensation:	2 multiple coil condensers	off-gas cleaning:	multiple coil condenser + quenching with water

5.2 Scale-up Procedures

5.2.1 Fluidized Bed

For the chemical engineering design of the pyrolysis process, the maximum loading of the reactor during the stationary operation is of decisive importance. For the fluidized-bed process this is the maximum possible feed rate of acrylic polymer for given reaction conditions. As standard temperature 430 °C was chosen with an N₂ volumetric flow rate corresponding to the triple minimum fluidizing velocity. Under these conditions an increase of the pressure drop above the fluidized bed due to the increase of the feed rate of acrylic polymer was observed. This increase of the pressure drop is equivalent to an increase of the total mass of reactant in the reactor. Beyond a certain limit of the specific feed rate, which is dependant on the decomposition rate of the polymer, the reactor exhibited a strongly instationary behavior. This caused a more than proportional pressure drop increase in the case of the low-molecular molding materials. Investigations under variation of mass of sand and particle diameter showed that the limits of specific feed rate determined in this way are directly proportional to the available sand surface. From this it can be derived that the polymer in the reactor is evenly distributed as melt on the sand surface. In the course of transition to the instationary reactor behavior the mass of polymer fed into the reactor can no longer be decomposed completely to gaseous products because of transport limitations. Thus, an accumulation of mass in the reactor occurs. Using a mass balance equation for the mass stream fed and the necessary reaction time for total conversion (kinetics), the actual amount of molten acrylic polymer in the reactor and thus a film thickness on the sand particle can be calculated. As the pressure drop increase is directly proportional to the mass increase in the reactor, a film thickness can also be given for the instationary case.

Fig. 12 clearly demonstrates that inspite of different limits of specific feed rates (related to the available sand surface) a

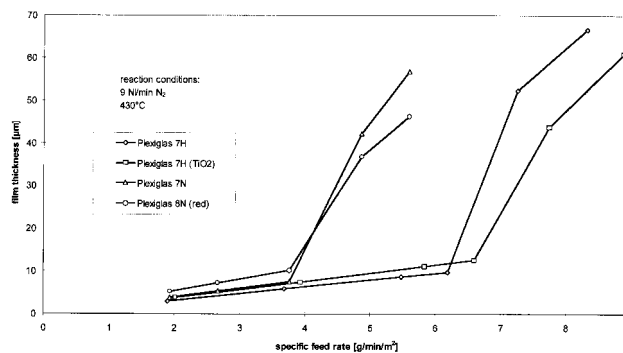


Figure 12. Maximum feed rate (related to the sand surface) of the molding materials.

uniform limiting film thickness of 10 µm as an average will be found. High-molecular casting materials do not exhibit such a behavior determined by transport limitations. Here, the sand particles stick together as soon as the maximum feed rate is reached and thus lead to an irreversible breakdown of fluidization.

The maximum feed rates and the necessary reaction surfaces (see Tab. 5) are suitable scale-up parameters for a fluidized-bed process, mainly for a reaction temperature of about 430 °C.

5.2.2 Tubular Reactor

Because of its mixing and transport characteristics, the modelling of the pyrolysis process in the tubular reactor with internal mass transport is much more difficult. In a first step, the mixing and transport behavior of the reactor was elucidated by instationary residence time experiments with a pulse technique. The variables mass of sand and relative speed of the transportation unit were varied. This relative transportation speed is the ratio of time in forward motion to the sum of times in forward and reverse motion of the spindle, which

Table 5. Scale-up parameters for a fluidized bed process of pyrolysis of acrylic polymers.

Acrylic polymer	τ_R (430 °C, conversion = 99%) [s]	d_{Gr} [µm]	$O_{spez.,min}$ [m ² /kg/h]	$M_{spez.,max}$ [g/min/m ²]
Plexiglas 7H	90	9.8	2.7	6.2
Plexiglas 7H (TiO ₂)	108	12.6	2.5	6.6
Plexiglas 7N	114	7.6	4.4	3.8
Plexiglas 8N (red)	155	10.3	4.4	3.8
Plexiglas GS 233	98	6.4	4.5	3.7
Plexiglas GS 2399	31	10.6	0.9	19.5
Creanit	22	2.3	2.8	5.7

τ_R [s]: Reaction time for total conversion (=99%) at 430 °C
 d_{Gr} [µm]: Maximum film thickness
 $O_{spez.,min}$ [m²/kg/h]: Minimal sand surface with a feed rate of 1 kg/h acrylic polymer
 $M_{spez.,max}$ [g/min/m²]: Maximum feed rate related to 1 m² of sand surface

means that for a relative speed of 1 the transportation spindle moves the solids only towards the reactor exit with the maximum transportation velocity. Mean residence times between 60 s and 200 s could be realized. Bodenstein numbers, Bo, which represent the ratio of convective to dispersive transport, varied between Bo = 2.3 and Bo = 6.5.¹⁾

Therefore, the following model can be applied for the conversion of acrylic polymers in a tubular reactor with internal mass transport unit:

$$\frac{\partial x_i}{\partial t} = -u_K \frac{\partial x_i}{\partial z} + D_{ax} \frac{\partial^2 x_i}{\partial z^2} + \sum_j v_{ij} r_j \quad i, j = 1, 2 \quad (1)$$

The agreement of the model with the experimental data was checked by instationary pyrolysis experiments. For this, the instationary mass balance equation (Eq. 1) had to be solved numerically. The heat balance could be neglected in the case of this laboratory reactor, as only negligible temperature gradients were observed because of the small reactor load in these experiments. It must be considered that for a sand-to-polymer ratio smaller than 8:1 the conversions predicted theoretically can no longer be obtained. This can be explained by the formation of agglomerates when sand and polymer particles stick together. These agglomerates leave the reactor after a much shorter time and therefore do not react to the extent that was expected.

With this knowledge the stationary process of acrylic polymer pyrolysis can be simulated. But it is a precondition that for a comparison with a technical-scale rotary kiln a similar transport and mixing behavior can be assumed [45,46]. In Figs. 13 and 14 the conversion versus residence time for different types of acrylic polymers is depicted for the Bodenstein numbers Bo = 4.2 and Bo = 100. The simulation in Fig. 13 demonstrates that a very long residence time is necessary for the total conversion of the polymers. In a simulation as plug-flow reactor, i.e. Bo = 100, the residence time necessary can be significantly reduced, as Fig. 14 shows. This means, however, that the product of transport velocity times and reactor length must be very large. This is met, for example, by very long rotary kilns. An alternative could be reactors without solid entrainment, e.g., ball-mill-type reactors. Ball mills which still use sand as mixing medium and reaction surface show a mixing characteristic comparable to a continuously stirred tank reactor. Consequently, larger dead spaces which occur unavoidably in a usual rotary kiln, can be avoided.

5.2.3 Heat Input

A quantity of heat up to 800 kJ/kg is necessary for the endothermic pyrolysis reaction. With an increase of plant capacity, it is more and more difficult to transfer this quantities of heat through the jacket area of the reactor alone. As, generally, the fluidized-bed reactor in comparison to a rotary kiln shows a better heat transfer characteristic, smaller

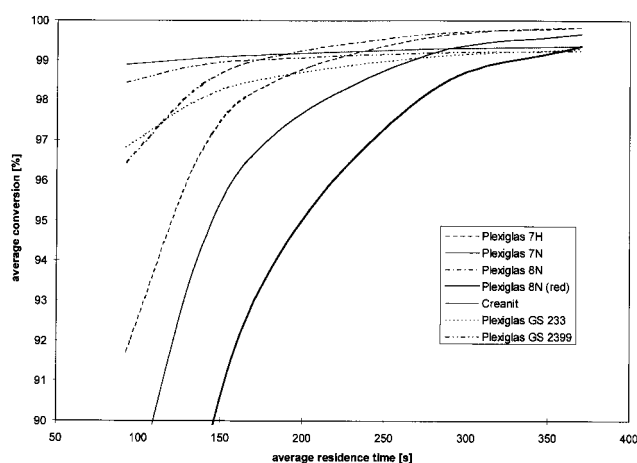


Figure 13. Bo=4.2: conversion/residence time behavior in a tube reactor (430 °C)

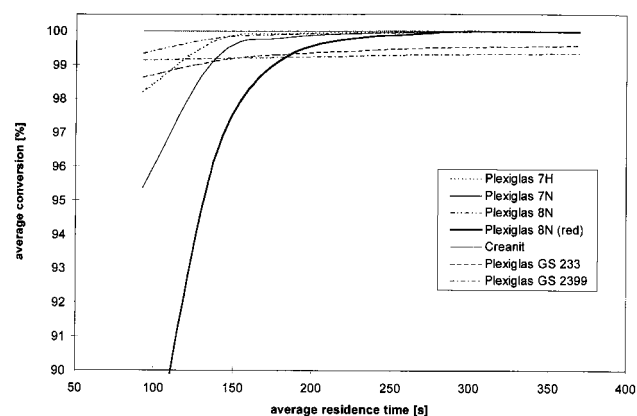


Figure 14. Bo=100: Conversion/residence time behavior in a tube reactor (430 °C)

temperature gradients are needed for the heat transfer, which results in a positive effect on the product selectivities. Also in this respect, a reactor with an intensive mixing should be preferred, so that the concept of the ball-mill-type reactor will offer advantages compared to a conventional rotary kiln.

5.3 Reactor Design for the Pyrolysis of Acrylic Polymers

Both, a fluidized-bed reactor and a rotary kiln were designed approximately on the basis of an estimated future capacity demand of 15000 t/a. It was assumed that a mixture of acrylic polymers was converted with a maximum of 6 g (min/m²) at a reaction temperature of 430 °C. A safety factor of 2 was chosen for the design, i.e., the reactor operates normally with only 50 % of its maximum capacity. As the large dead space of a long rotary kiln has a negative effect on the byproduct selectivities, an apparatus comparable to a ball mill was chosen. It is a drum reactor with a diameter-to-length-ratio of approx. 1/1. In Tab. 6 a survey of the technical data and the reactor dimensions of both reactor types is given.

1) List of symbols at the end of the paper.

Table 6. Technical data and reactor dimensions of a pyrolysis plant.

Reactor data	Fluidized bed reactor	Drum reactor
feed PMMA	15000 t/a (e.g. molding material)	
time on stream	8000 h/a	
reaction temperature	430 °C	
heat of reaction	max. 800 kJ/kg acrylic polymer	
sand density	2650 kg/m ³	
particle diameter	230 μm	400 μm
sand mass	1.1 t ⇒ 10500 m ² surface	1.0 t ⇒ 0.63 m ³ bulk volume (ε=0.4)
reactor dimensions	diameter: 0.8 m to 1 m height: 4 m	reactor volume: 2.1 m ³ (φ=0.3)
reactor heating surface	11 m ²	7.9 m ²
needed heating power	appr. 420 kW	
combustion of byproducts	appr. 540 kW (5 mol% combustible by products)	
needed heating surface (ΔT=50 °C, α _w =500 W/(m ² K))	17 m ²	

During the operation of the fluidized-bed reactor the problem arises that an entrainment of solids caused by the product gas streams generated must be prevented by means of suitable equipment. The biggest problem before technical realization arises with the necessary energy input into the reacting system. For the determination of the necessary heat transfer area it is assumed that a maximum temperature difference ΔT of 50 °C exists between the reactor jacket and the reacting medium. From Fig. 11 it can be derived that the fluidized-bed process is not so sensitive against higher temperatures, whereas in the rotary-kiln process an increased formation of byproducts must be expected at elevated temperatures. Therefore, for the construction of a technical-scale rotary kiln above all the problem of appropriate energy input has to be solved. The gaseous byproducts formed may be used for the heating of the reactors.

6 Summary

On the basis of the present practice for the recycling of polymers, different types of pyrolysis reactors for the chemical recycling of acrylic polymers have been discussed applying reaction engineering techniques. The knowledge of the reaction kinetics of the depolymerization and the use of a suitable reactor model is the basis for the modelling and simulation of the pyrolysis in the fluidized-bed reactor and in a tube reactor with internal solid transport. For the scale-up of the pyrolysis process in the fluidized bed, the maximum feed rate related to the reaction surface is decisive.

The simulation of a rotary kiln process demonstrates that for a total decomposition of acrylic polymers very long tubes are necessary. Because of large dead spaces in the tube, an increase of byproduct formation cannot be avoided. Therefore, it is proposed to look closer on the concept of a reactor without solid entrainment similar to a ball mill. In this case an

isothermal operation could be achieved more easily because of intensive mixing of the solid.

Besides MMA, the condensed liquid raw product contains further byproducts which demand an expensive purification of the condensate. Investigations of the raw condensate show that the fluidized-bed reactor generates less difficult byproducts to be separated because of its more selective reaction operation.

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Symbols used

Bo	[-]	Bodenstein number $Bo = (u_K * L) / D_{ax}$
u_K	[m/s]	Velocity of convection
L	[m]	Length of reactor
D_{ax}	[m ² /s]	Axial dispersion coefficient
x_i	[-]	Mass of component i relative to initial mass
t	[s]	Time
z	[m]	Axial coordinate
v_{ij}	[-]	Stoichiometrical coefficient of component i in reaction j
r_j	[1/s]	Rate of reaction j
ε	[-]	Volume porosity of the sand
φ	[-]	Drum reactor filling
ΔT	[°C]	Temperature gradient between reactor wall and reaction media

α_w [W/(m²K)] Heat transfer coefficient in an agitated bulk material

Abbreviations

DSC	Differential Scanning Calorimetry
DSD	Duales System Deutschland ('Dual System Germany')
IBME	Isobutyric acid methylester
KAB	Coal/oil plant Bottrop
MA	Methylacrylate
MMA	Methylmethacrylate
PET	Polyethyleneterephthalate
PME	Propionic acid methylester
PMMA	Polymethylmethacrylate
POM	Polyoxymethylene
PU	Polyurethane
TG	Thermogravimetry

References

- [1] N. N., Asse im Recyclingpoker, *Chem. Ind.* 10 (1992) p. 19 f.
- [2] Umweltbundesamt, Federal Republic of Germany.
- [3] N. N., Marketing Research Report: Acrylic Resins and Plastics, *Chemical Economic Handbook*, SRI International, Zürich 1994.
- [4] N. N., *Europa Chemie* 33 (1996).
- [5] DSD GmbH, Wandlungen – Kunststoffrecycling heute, 2nd ed.
- [6] Weissermel, K.; Arpe, H.-J., *Industrielle organische Chemie*, 2nd ed., Verlag Chemie, Weinheim 1978.
- [7] Supp, E., Gaserzeugung aus Schweröl, in: *Ullmann's Encyclopädie der technischen Chemie*, Verlag Chemie, Weinheim 1977.
- [8] Gebauer, M.; Stannard, D., Vergasung von Altkunststoffen, in: [31] p. 463 ff.
- [9] Niemöller, B., Reduktion im Hochofen, in: [31] p. 490 ff.
- [10] Menges, G.; Lackner, V., Degradative Extrusion von Kunststoffreststoffen, in: [31] p. 416 ff.
- [11] Svalander, J., A Polymer Cracking Concept, REC 1993, Genf 1993.
- [12] Kaminsky, W.; Menzel, J.; Sinn, H., Recycling of Plastics, Conservation & Recycling, Vol. 1 (1976) p. 91 ff.
- [13] Kaminsky, W., Possibilities and Limits of Pyrolysis, *Makromol. Chem., Macromol. Symp.* 57 (1992) p. 145 ff.
- [14] Kastner, H.; Kaminsky, W., Recycle Plastics into Feedstocks, Hydrocarbon Processing (May 1995) p. 109 ff.
- [15] Franck, J., Pyrolyse ausgewählter Kunststoffe in einer indirekt beheizten Wirbelschicht, Ph. D. Thesis, Hamburg 1993.
- [16] Ehrig, R. J., *Plastics Recycling – Products and Processes*, Hanser Verlag, Munich 1992.
- [17] N. N., Useful Oil Reclaimed from Waste Plastics (Polyolefins), *Jap. Chem. Week* (31.05.90) p. 6.
- [18] Paisley, M. A.; Litt, R. D., Monomer Recovery from Polymeric Materials, U. S. Pat. 5326919 (5.7.94).
- [19] Hamm, M., Stoffliches Recycling von Shredderleichtgut durch Pyrolyse im Drehrohrofen, Ph. D. Thesis, Essen 1993.
- [20] Bockhorn, H.; Hornung, A.; Hornung, U., Gestufte Pyrolyse als Verfahrensprinzip zur chemischen Auftrennung von Kunststoffgemischen, DECHEMA Ann. Conf., Wiesbaden 1995, Vol. 2, p. 270.
- [21] Bockhorn, H.; Knümann, R., Pyrolyse von PVC und Kunststoffgemischen bei milden Bedingungen als Möglichkeit zur Auftrennung von Kunststoffabfällen, *VDI-Berichte Nr. 1090* (1993) p. 423 ff.
- [22] Ondruschka, B.; Struppe, H. G.; Hofmann, J.; Luther, U.; Ahlheim, J.; Gebauer, M.; Timm, D., Konversion von Gemischen aus Pyrolyse-Feedstocks und thermochemisch vorbehandelten Altkunststoffen: Eine Alternative des rohstofflichen Kunststoffrecyclings, *Chem. Tech.* 47 (1995) 4, p. 171 ff.
- [23] Struppe, H. G.; Ahlheim, J.; Luther, U.; Ondruschka, B., Konversion von Gemischen aus Pyrolyse-Feedstocks und thermochemisch vorbehandelten Altkunststoffen: Vereinfachte Bilanzierung von Laborversuchen aus GC-Analysen unter Einsatz verschleißbarer Probennahmesäulen, *Chem. Tech.* 47 (1995) 4, p. 179 ff.
- [24] Tille, A.; Dardulla, H.-J.; Knebel, H.; Richter, M., Untersuchungen zur Depolymerisation von Kunststoff-Modellgemischen unter vermindertem Druck, *Chem. Tech.* 47 (1995) 4, p. 190 ff.
- [25] Gebauer, M.; Schermaul, D.; Timm, D., Olefine aus Altkunststoffen, *Chem. Tech.* 47 (1995) 4, p. 195 ff.
- [26] Nakamura, I.; Fujimoto K., Development of New Disposable Catalyst for Waste Plastics Treatment for High Quality Transportation Fuel, *Cat. Today* 29 (1996) p. 175 ff.
- [27] Zhibo, Z.; Nishio, S.; Morioka, Y.; Ueno, A.; Ohkita, H.; Tochiara, Y.; Mizushima, T.; Kakuta, N., Thermal and Chemical Recycle of Waste Polymers, *Cat. Today* 29 (1996) p. 303 ff.
- [28] Zhibo, Z.; Hirose, T.; Nishio, S.; Morioka, Y.; Azuma, N.; Ueno, A.; Ohkita, H.; Okada, M., Chemical Recycling of Waste Polystyrene into Styrene over Solid Acids and Bases, *Ind. Eng. Chem. Res.* 34 (1995) p. 4514 ff.
- [29] Hirota, T.; Fagan, F. N., Liquefaction of Plastics, *Makromol. Chem., Macromol. Symp.* 57 (1992) p. 161 ff.
- [30] Niemann, K., Hydrierung, in: [31] p. 451 ff.
- [31] Brandrup, J.; Bittner, M.; Michaeli, W.; Menges, G. (ed.), *Die Wiederverwertung von Kunststoffen*, Hanser Verlag, München 1995.
- [32] N. N., Polyacetal – Hoechst startet Recycling-Anlage; *Europa-Chemie* 31 (1996) p. 4.
- [33] Weisent, P., Fortschritte in der Teerfarbenfabrikation, Vol. 23/2, p. 1621.
- [34] Kautter C. T.; Leitenberger, W., *Deutsche Reichspatente aus der organischen Chemie*, Vol. 6.1, p. 1211.
- [35] DRP 698643.
- [36] Strain, D. E., U. S. Pat. 2030901 (1935).
- [37] Michaeli, W.; Breyer, K., Chemisches Recycling von PMMA – Depolymerisation durch Extrusion, *ACHEMA Magazine* 97 (1997) p. 53 ff.
- [38] Brand, N., Depolymerisation von Polymethylmethacrylat (PMMA), in: [31] p. 497 ff.
- [39] Morrow, G. R.; Rae, I. D., Thermal Degradation of Polymers and Polymer Models, *Aust. J. Chem.* 40 (1987) p. 1477 ff.
- [40] Kashiwagi, T.; Inabi, A., Behavior of Primary Radicals during Thermal Degradation of Poly(methylmethacrylate), *Polym. Degrad. and Stab.* 26 (1989) p. 161 ff.
- [41] Chiantore, O.; Luda di Cortemiglia, M. P.; Guaita, M., Changes of Degree of Polymerisation in the Thermal Degradation of Poly(methylmethacrylate), *Polym. Degrad. and Stab.* 24 (1989) p. 113 ff.
- [42] Manring, L. E., Thermal Degradation of Poly(methylmethacrylate), 4. Random Side-Group Scission, *Macromolecules* 24 (1991) p. 3304 ff.
- [43] McNeill, I. C., A Study of the Thermal Degradation of Methylmethacrylate Polymers and Copolymers by Thermal Volatilization Analysis, *Eur. Polym. J.* 4 (1968) p. 21 ff.
- [44] Grassie, N.; Torrance, B. J. D., Thermal Degradation of Copolymers of Methylmethacrylate and Methylacrylate 1 and 2, *J. Polym. Sci.* (1968) Part A-1 (6), p. 3303 ff.
- [45] Merz, A., Untersuchungen zur Axialvermischung in einem kontinuierlich betriebenen Drehrohr mit Isotopenmarkierung, Ph. D. Thesis, Karlsruhe 1973.
- [46] Roth, G., Transport in Drehrohren und Kugelmöhlen, Ph. D. Thesis, Karlsruhe 1982.

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