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Design and Simulation of a New Reactor for the Production of High-Viscosity Polymer Melts

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Summary: Innovative reactor internals consisting of a number of vertically stacked perforated plates have been proposed to increase mass transfer rates of volatiles from highly viscous polymer melts. A mathematical model comprising mass and enthalpy balances for the polycondensation of polyamide 6 has been used to evaluate the new reactor design. According to the simulation, the alternating arrangement of devolatilization and residence zones leads to an effective removal of reaction water from the polymer melt. Compared to the VK-tube reactor, which is most commonly used to produce high quality PA-6, the new reactor design produces high quality polymer with a high degree of polymerization within a considerably shorter residence time. The application of the proposed reactor internals is not limited to PA-6 production, since the removal of volatiles is of the same major importance during all reversible polycondensation reactions, e.g. the production of PET.

Keywords: devolatilization; falling strand; mass transfer; modelling; PA 6; reactor design; viscous polymer melts; water removal

Introduction

During the polycondensation of polymers such as PA or PET small molecules are generated which have to be evaporated efficiently in order to drive the equilibrium reaction into high reaction rate and high conversion.

The VK-tube reactor, which is most commonly used for PA-6 production,[1] does not provide sufficient surface between the gas phase and the polymer melt for high reaction rates. Conventional surface generating installations for gas-liquid reactions such as bubble columns or pneumatic agitators can only be applied during the low viscous prepolymerization stages at the beginning of the reaction. Hence, a solution for surface generation in a highly viscous polymer melt is needed, which does not require any moving internals and could preferably be integrated in an existing reactor.

A number of mass transfer models are available for every kind of devolatilization units such as bubble columns, packed columns and structured packing. The viscosities of the involved fluids limit the application of these models. In case of the VK-tube reactor, the fluid viscosity is not available as a function of the position within the reactor. Furthermore, the mass transfer correlations found in literature are limited to a specific viscosity range, too. A viscosity above 30 Pas, which is reached early in the polymerization process, is usually not covered by available mass transfer models.

Gupta and Kumar[2] proposed segmentation of the VK-tube reactor into three or more segments, assuming that the basic operations prepolymerization (ring-opening), polycondensation / water removal and polyaddition are restricted to the respective segment of the tube. Due to the lack of important information regarding melt viscosity (important for bubble formation) or specific surface area (important for every mass transfer model), the mass transfer

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coefficients are chosen arbitrarily, returning a number of results with significant difference. The results of Gupta and Kumar[2] yield a degree of polymerization between 80 (simulation with no removal of water) and 240 (simulation with instantaneous removal of water), which underlines the significance of a consistent model for water removal.

Reactor Design

The prepolymerization stage, which is located in the first section of the reactor, is pressurized in order to prevent water evaporation. The main reaction taking place in this stage is the ring opening of ε-caprolactam. This section is followed by a bubble column section, where most of the water is removed and the viscosity increases up to approximately 10 Pas. The subsequent stages of the reactor comprise the proposed new reactor internals consisting of a number of vertically stacked perforated plates (multi-tray arrangement, Figure 1). The polymer melt enters this section on the topmost plate forming a layer with a certain residence time on this plate. During this residence time, the polymer melt undergoes polycondensation reactions. The polymer melt flows continuously through holes in the plate downwards to the next plate. The number and size of the holes control the layer thickness and the residence time of the melt on the plate and the thickness of the falling polymer strands. The falling polymer strands provide a high surface area to volume ratio and facilitate the devolatilization of water formed during the polycondensation. The distance between the plates influences the time during which increased devolatilization occurs and the thickness of the polymer strands controls the mass transfer rate.

This multi-tray arrangement results in an alternating sequence of devolatilization and reaction zones. A further advantage of the multi-tray concept is the narrowed residence time distribution, since the melt cannot flow backwards to preceding trays. The residence time in each segment can be optimized according to simulation results and adjusted by the configuration of the plates.

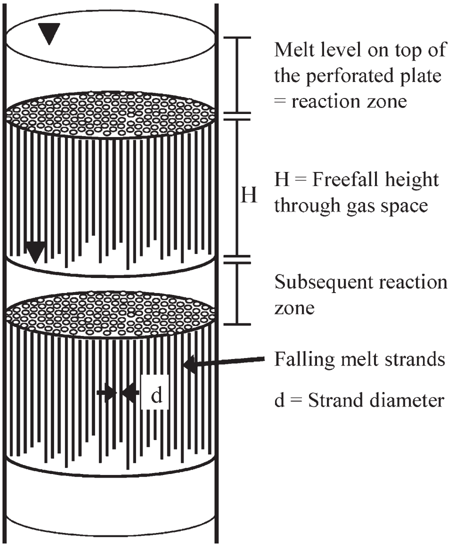

Figure 1.
Layout of the new reactor design with two alternating devolatilization / reaction zones.

Experimental Part

At first, a number of different standard reactor internals has been tested for their applicability in the new reactor design. A vertically arranged piece of sheet metal was the simplest among the tested internals. Different types of random packing, commercially available expanded metal and two different types of structured packing (Sulzer Mellapack) have been tested as well. All reactor internals were effectively degreased using ethanolic KOH solution and acetone prior to the experiments. For the experiments, glucose syrup adjusted to a viscosity of 40 Pas as a model fluid was distributed evenly on top of the respective reactor internal. A viscosity of 40 Pas represents the lower end of the typical viscosity range of polymerization processes and was chosen as a starting point. The behaviour of the model fluid flowing

Table 1.
Results of the experiments on flow behaviour and surface generation of a highly viscous model fluid for different standard reactor internals.

Type of Structure	Result, Observation
Sheet metal	Steady and even film formation, thickness > 5mm, no surface renewal
Expanded metal	Formation of film which closes the lattice structure. Film thickness equals sheet metal structure
Random packing	local stagnation at horizontal parts of the packing, uneven fluid distribution and insufficient wetting
Structured packing	Retention and formation of fluid reservoirs within the structure, no sufficient surface generation and or renewal

through the different reactor internals was investigated by observing film formation, surface renewal, and steadiness of flow together with measuring the film thickness. In all experiments, the film thickness exceeded 5mm and neither significant surface generation nor considerable surface renewal could be observed. In case of the structured packing, even blockage of the flow occurred. The results of these experiments are summarized in Table 1.

Neither of the primarily tested reactor internals was applicable for the new reactor design even at comparably low fluid viscosities. Therefore, a design with perforated plates as reactor internals was devised. The flow of the highly viscous model fluid through a vertically arranged perforated plate proved to be homogeneous and sufficient surface generation was provided by the formation of falling strands. A number of experiments has been performed to evaluate the flow behaviour and to provide modelling parameters regarding the liquid throughput in dependency on primary pressure, viscosity of the liquid and geometry of the perforated plate. The correlation between the liquid throughput and the liquid column height (corresponds to the primary pressure) has been determined using model fluids with a viscosity of 40 Pas, 150 Pas, and 400 Pas, respectively. Perforated plates with different void fractions and hole diameters of 5 mm, 7.5 mm, and 10 mm, respectively, have been employed.

Figure 2 shows the results for the correlation of throughput with liquid column height for plates with different hole diameters and a viscosity of the model fluid of 400 Pas. For all three hole diameters, the correlation was linear in the complete range

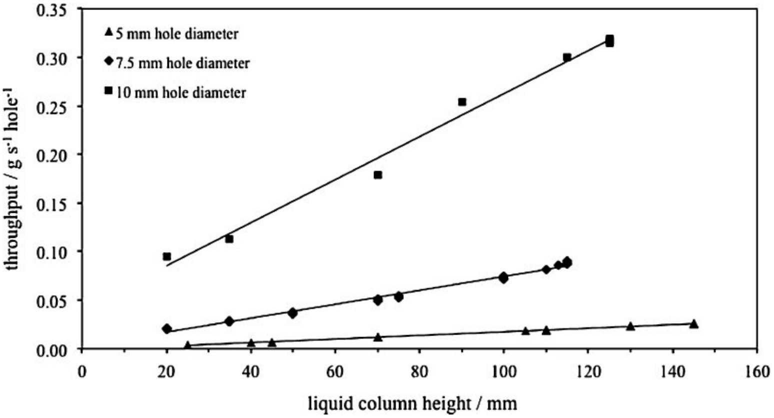

Figure 2.
Correlation between throughput and liquid column height (corresponds to primary pressure) for different hole diameters (viscosity of the model fluid: 400 Pas).

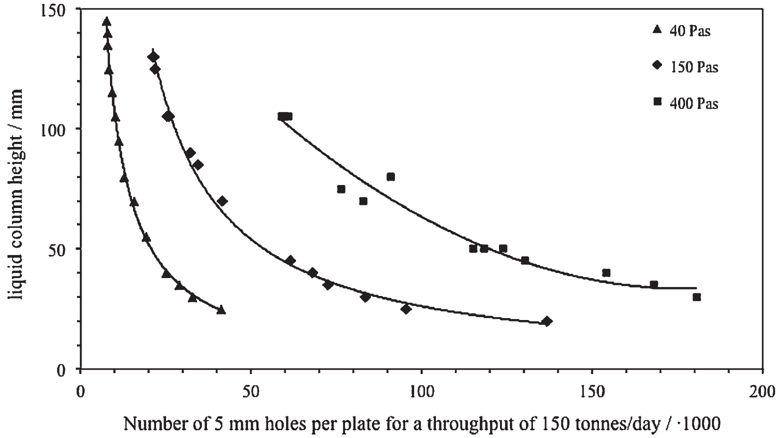

Figure 3.
Correlation between number of 5 mm holes per plate required for a full-scale throughput of 150 tonnes/day and liquid column height for different liquid viscosities.

of tested liquid column heights. The model fluids with viscosities of 150 Pas and 40 Pas, respectively, exhibited equal behaviour.

Figure 3 demonstrates the number of holes with a diameter of 5 mm which would be required in a plate to allow a full-scale throughput of 150 tonnes per day in dependency of the liquid column height for different liquid viscosities. As expected, the required number of holes increases with lower liquid column height and rising liquid viscosity. The required number of holes per plate can exceed 150,000 for a liquid viscosity of 400 Pas. Therefore, not only the number of holes per plate but also their diameter has to be optimized for each plate depending on the actual liquid viscosity in the respective reactor section. The design of the plate not only influences the throughput but can also be used to adjust the residence time (= reaction time) of the polymer on the tray and the total surface area of the falling strands (= mass transfer area).

Simulation

A comprehensive literature research has been carried out before selecting a state of the art model of PA-6 polymerization, which also considers the side reactions. A recent approach by Seavey and co-workers[3,4] resulted in a well-described system of reaction equations with a consistent set of kinetic data. Equilibrium and kinetic constants were taken from older but well established and widely recognized sources.[5] The proposed reactor design has been considered in the parameter set of the simulation, since each zone can possess individual parameters such as specific surface areas and residence times. The reaction system comprises 15 parallel reactions with a total of 11 species involved. The modelling of a cascade of CSTRs allows the simulation of different reactor characteristics. The program MATLAB has been applied for the numerical solution of the mathematical equations.

The mass balance equation has been solved for each finite element of the CSTR cascade. The reaction rates of the respective species have been calculated using the Arrhenius equation to account for the temperature dependency.

$$\begin{aligned} \frac{dc_A}{dt} &= \frac{c_{A0}-c_A}{\tau} + r_A \\ r_A &= k \cdot c_A = k_0 \cdot \exp\left(\frac{-E_A}{R \cdot T}\right) \cdot c_A \end{aligned} \tag{1}$$

The enthalpy balance equation has been calculated for each species in each finite element. The temperature change results from the addition of the enthalpy balances of all species.

$$\frac{dT}{dt} = \frac{T_0 - T}{\tau} + \frac{-\Delta_R H}{c_P} \cdot r_A - \frac{\Delta_V H \cdot kl_W \cdot a \cdot c_A}{c_P} + \frac{k_{HEAT} \cdot A_{HEAT} \cdot (T_{HTM} - T)}{V \cdot c_P \cdot \rho} \tag{2}$$

The enthalpy balance takes the evaporation of water into account. The evaporation of ε-caprolactam does not contribute significantly to the overall temperature change, since its mass transfer rate is negligible due to the low diffusion coefficient which is some 3 orders of magnitude lower than D_W. A heat transfer term has also been included in the enthalpy balance. The process temperature in each zone can individually be adjusted by changing the temperature of the heat transfer oil. The heat transfer area (A_{HEAT}) matches the dimensions of the reactor jacket together with some additional heat transfer installations.

Mass Transfer

The proposed reactor design aims at the reduction of the uncertainties regarding the specific mass transfer area and the residence time in the individual zones of the reactor. The diffusion path has been identified as the decisive parameter for the rate and the extent of mass transfer and therefore has to be shortened by providing a high specific surface area and a continuous surface renewal.

The prepolymerization zone is modelled as a CSTR reactor with suppressed mass transfer.

The subsequent bubble column zone is modelled as a series of 12 CSTR reactors in order to approximate plug flow characteristics. The mass transfer coefficient has been calculated using the following correlation[9] (d_B = bubble diameter, ν = kinematic viscosity).

$$\frac{k \cdot d_B}{D} = 0.31 \cdot \left(\frac{d_B^3 \cdot g \cdot \Delta\rho/\rho}{\nu^2} \right)^{1/3} \cdot \left(\frac{\nu}{D} \right)^{1/3} \tag{3}$$

The bubble column is a simple and convenient reactor with high gas-liquid mass transfer rates, but its applicability is limited to liquids with a rather low viscosity. In liquids with high viscosities, bubble formation is retarded and the bubbles are retained in the liquid. Both factors lead to a decline of the overall mass transfer coefficient. The viscosity limit where mass transport in the bubble column becomes less effective than in a falling strand has yet to be determined. For the simulation, this viscosity limit has arbitrarily been set to 10 Pas.

The surface renewal theory has been used to model the devolatilization zone. This theory has previously been applied in a number of mathematical models dealing with mass transfer in high viscosity polycondensation reactors such as rotating disc finishers and wiped surface evaporators.[6] The surface renewal theory accounts only for the mass transfer coefficient in the liquid phase. To allow for the approximation $k_{OVERALL} = k_W$, the gas flow rate has to be higher than 0.9 m/min (0.015 m/s) to ensure a negligible mass transfer resistance at the gas side.

$$k_W = \sqrt{\frac{D_W}{\theta}} \tag{4}$$

The contact time (θ) of the falling polymer strand is the key parameter in this theory and allows the computation of mass transfer in this zone. The diffusion coefficients for water (D_W) and ε-caprolactam (D_{CL}) have been calculated using a correlation from[3] which includes a temperature correction term. The activation energy for the diffusion of ε-caprolactam is significantly higher than that for the diffusion of water. Therefore, the diffusion coefficient of ε-caprolactam is 3 orders of magnitude smaller then the diffusion coefficient of water at typical process temperatures around 265 °C.

$$D_W = 2.21 \cdot 10^{-8} \cdot \exp\left(\frac{-3010}{R \cdot T} \right) \tag{5}$$

$$D_{CL} = 1.41 \cdot 10^{-8} \cdot \exp\left(\frac{-33457}{R \cdot T} \right) \tag{6}$$

The proposed reactor design leads to a calculable contact time θ. The lifetime of the surface of the falling polymer strand equals the time needed by the polymer strand to travel from the upper perforated plate to the melt layer on the downstream plate. (H = freefall distance of the strand, u_{STRAND} = strand flow rate, N = total number of holes)

$$\theta = \frac{H}{u_{STRAND}} \tag{7}$$

$$u_{STRAND} = \frac{F}{N\,\frac{\pi}{4}\,d^2} \tag{8}$$

Specific Surface Area

The specific surface area in the proposed reactor design can be calculated straight forward. The specific surface area of the polymer strand increases linearly with decreasing cylinder diameter according to (9). Therefore, this design is most effective with a maximum number of individual strands.

$$a = \frac{4}{d} \tag{9}$$

Assuming a strand diameter of 2 mm, the surface area to volume ratio is calculated to be 2000 m^2/m^3. Our experiments with the model fluid showed that a minimum strand diameter of about 1 mm can be achieved resulting in a surface area to volume ratio of 4000 m^2/m^3.

The specific surface area of the residence zones equals the reactor cross-sectional area but has not been considered in the calculation, because the mass transfer coefficient in the residence zone has been set to zero.

Melt Viscosity

Equation (10) introduces the Mark-Houwink constants for PA-6 according to,[7] valid for a melt temperature of 250 °C.

$$\eta_0 = \left(9.5 \cdot 10^{-14} \cdot M_W{}^{3.4}\right) \tag{10}$$

The index 0 indicates zero shear tension which approximates the situation in the reactor. The shear stress generated by gravity flow through a perforated plate is not high enough to cause a considerable shear thinning effect. The temperature dependency of the melt viscosity has been quantified by[8] using the Arrhenius equation with an activation energy of 60 kJ/mol. Equation (10) allows the computation of the temperature-correlated melt viscosity directly from the molecular weight.

$$\eta_T = \left[9.5 \cdot 10^{-14} \cdot M_W{}^{3.4}\right] \cdot \exp\left[\frac{60000}{R} \cdot \left(\frac{1}{250 + 273} - \frac{1}{T_0}\right)\right] \tag{11}$$

Results

Simulations have been performed varying the number of trays and the total residence time in the tray reactor. The simulation runs (Table 2) have been carried out with a rather conservative set of parameters. The mass transfer coefficient for the residence zones has been set to zero, although the volatiles might evaporate from the liquid surface of these zones.

The simulation with 8 trays creates a considerably higher degree of polymerization (dP_N) in shorter overall residence times compared to the simulation with 6 trays. The concentrations of cyclic dimer and total volatiles in the polymer are less affected by the number of trays whereas the water concentration is considerably lowered by using more trays. Reaction kinetics reveals that low water concentrations are crucial for the development of high relative viscosities. Therefore, effective devolatili-

Table 2.
Parameter sets and results of simulation runs.

number of run		1	2	3	4
number of trays	[-]	6	6	8	8
overall residence time	[b]	10	12	10	12
Process temperature	[°C]	265	265	265	265
dPn	[-]	191	20S	240	270
relative viscosity	[dL/g]	2.04	2.19	2.47	2.72
cyclic dimer cone.	[%]	0.77	0.79	0.77	0.78
total volatile cone.	[%]	8.6	8.6	8.5	8.5
water cone.	[%]	0.071	0.071	0.026	0.025

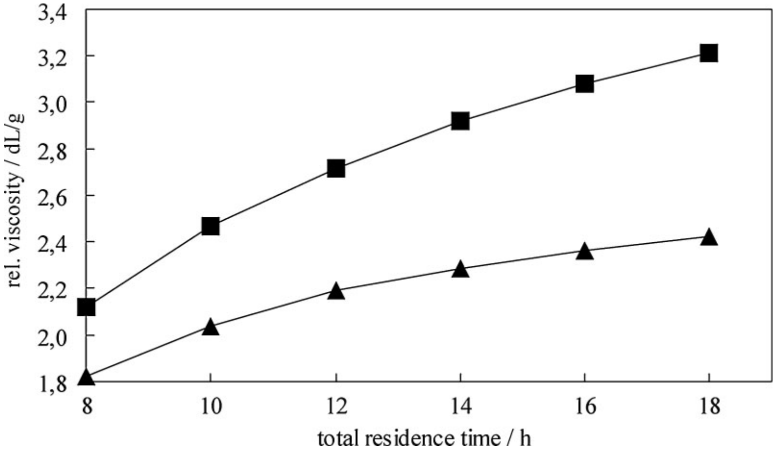

Figure 4.
Simulated η_{REL} as function of total residence time, (▲) = 6 trays, (■) = 8 trays.

zation of water during the course of reaction is of particular importance.

Figure 4 shows the relative viscosity of the polymer obtained after different residence times in a reactor with either 6 (▲) or 8 (■) trays. The results clearly indicate the advantage of an increased number of trays and respective devolatilization zones in the reactor. The relative viscosity of the polymer generally increases with higher residence time but considerable differences are observed between the 6-tray and the 8-tray reactor. In the 6-tray reactor, a relative viscosity of 2.49 dL/g is obtained after a residence time of 18 hours. In the 8-tray reactor, the relative viscosity after a residence time of only 12 hours is already higher with 2.72 dL/g achieving 3.26 dL/g after a residence time of 16 hours. Typical residence times in the common VK reactor lie between 10 and 12 hours for a relative viscosity of the polymer of 2.2–2.4 dL/g which is comparable to the 6-tray reactor.

Conclusion

A number of different reactor designs have been tested towards their suitability for surface generation and continuous surface renewal of high-viscosity polymer melts. Experiments showed that a model fluid with corresponding viscosity formed films of considerable thickness on every tested surface, even though the surfaces had been thoroughly cleaned. The required extent of devolatilization of water from such films may not be accomplished within a reasonable period of time.

It has been found that the model fluid forms narrowing falling strands when flowing through circular holes with a diameter of 5–10 mm. Strand diameters of about 1 mm can be achieved, providing a large surface area to volume ratio according to (9) and short diffusion paths. Measurements of the flow rate through circular holes with fluids in the viscosity range of 40–400 Pas confirm the necessity of a structure providing a large number of holes, designating the perforated plate as the most adequate and cost-efficient alternative. Correlations between the throughput and the liquid column height (corresponds to the primary pressure) have been determined experimentally, varying the hole diameter, the viscosity of the model fluid, and the void fraction of the tray.

The extent of the reaction can generally be increased by increasing the overall residence time. The installation of more devolatilization zones has been proven even more efficient, and a dP_N of 270 can be generated in a typical total residence time of 12 hours (simulation run no. 4) using a reactor with 8 trays.

The residual amount of water in the polymer is one of the key parameters in the reaction system. In the proposed tray reactor, the final water concentration is significantly lowered with each additional tray and therefore a considerably higher degree of polymerization and a higher relative viscosity of the polymer will be obtained. The polymerization has to take place as far away from the reaction equilibrium as possible to achieve high reaction rates together with high degrees of polymerization. This can only be obtained by allocating sufficient reaction volumes for the step-growth reactions in alternating combination with the efficient devolatilization of water, which is guaranteed by the new reactor design.

The application of the proposed tray-reactor design is not limited to PA-6, but can be transferred to other step growth polymers like PET or PC where the removal of volatiles is of comparable importance to shift the equilibrium reactions.

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