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Polymerisation Technology in Continuous Static Tube Reactors

Static CSE-X® mixers and CSE-XR® heat exchangers made by Fluitec are ideally suited for free-radical, cationic or anionic continuous polymerisations and have been used in the plastics industry for many years. Various polymerisation concepts are described in this document. The optimal reaction concept depends on the heat effect of the polymerisation and the characteristics of the polymer. Initial information is gathered in the laboratory and with the reaction calorimeter. A small-scale continuous pilot plant and successful testing are then followed by the scale-up to real production.



Fig. 1 Fluitec CSE-XR mixer/heat exchanger (DN50 / PN320) for isothermal polymerisations

Introduction

Static mixers and mixer/heat exchangers are ideally suited for free-radical, cationic or anionic continuous polymerisations and have been used in the plastics industry for more than twenty years. They generally make impeccable tube reactors with excellent mixing properties even at laminar flow.

Once they get going, continuous polymerisations offer several crucial benefits, such as:

- Improved reaction control and safety
- High space/time yield
- No dead spots
- Stable operating parameters
- No time needed for filling or cleaning
- Minimal space requirement
- Improved product quality, etc.

Static tube reactors are characterised by their lack of moving parts, which means that virtually no maintenance is needed.

The most important advantage, however, is that static tube reactors are predictable and scalable. They combine low energy consumption with high mixing efficiency and minimal back-mixing (high Bodenstein numbers). The heat balance for the ideal continuous flow reactor provides a perfect starting point for calculating the CSE-XR mixer/heat exchanger.

The equation is as follows:

$$\frac{\partial Q}{\partial t} = -\bar{c}_p \cdot m \cdot \frac{\partial [u_z \cdot T]}{\partial z} + (-\Delta H_R) \cdot V \cdot r_v + \alpha \cdot A \cdot (T_{gr} - T)$$

Equation 1: Heat balance for the ideal continuous flow reactor

Principles of polymerisation reactions

Continuous polymerisations with static tube reactors are mainly operated as mass, emulsion, precipitation or solvent processes.

The high heat effect and the simultaneous sharp increase in the viscosity of the reaction mixture are the main process parameters that need to be considered.

Since polymerisations are usually carried out until full conversion is achieved, the high final temperatures must be monitored by means of an additional solvent and/or technical measures.

A radically triggered reaction consists of two coupled, temperature sensitive chemical reactions: first the decomposition reaction of the initiator and then the polymerisation itself. It is important to remember that the decreasing quantity of initiator over time, the increasing viscosity and the decreasing monomer concentration, especially in continuous processes with no back-mixing, result in incomplete conversions even if a long residence time is offered.

All this leads to a clash of conflicting process requirements: on the one hand, the aim is to complete the conversion as quickly as possible, in other words at the highest possible temperature, in order to make optimum use of the available reactor volume (high space/time yield). On the other hand, the conversion must never be allowed to get out of control, nor must the product be exposed to excessive heat, because this would encourage depolymerisation and side reactions. Another problem associated with localised superheating is what is referred to as speck formation (fish eyes). An inhomogeneous product may need to be pigmented or filled and can no longer be used as transparent mass.

Characterisation in the laboratory

A new form of polymerisation can be approximately characterised with very simple means. Semi-quantitative preliminary tests are extremely important for the development of the process and can in most cases be performed in a simple beaker. In particular, the following parameters must be measured:

- Reaction rate
- Reaction enthalpy
- Thermodynamic equilibrium
- Product stability as a function of temperature and time
- Formation of by-products, precipitations, etc.
- Viscosity curve
- Influence of mixing intensity
- Opportunities for control

Reaction control if the viscosity increases abruptly and analysing both the products themselves and any by-products can be especially difficult challenges.

These preliminary findings should normally be followed by a more detailed characterisation, preferably using a high-precision reaction calorimeter. To facilitate this full characterisation and analysis, Fluitec offers all customers a chance to collaborate with the nearby Zurich University of Applied Sciences Winterthur, which has access to modern equipment and qualified personnel.



Fig. 2 Fluitec CSE-X polymer reactors, throughput 2 - 10 kg/h, $\varnothing 8 - \varnothing 27$, rated pressure PN700

From batch to conti

Once it has been sufficiently characterised in the lab, the reaction can be transferred to the tube reactor taking account of all relevant variables. Fluitec can draw on extensive industrial experience in this area. In addition to the reaction process, the design of a pilot plant is also influenced by physical parameters - not only pressure and temperature but also the dosing technology, choice of materials, explosion protection, level of automation, etc. The aim is to verify and flexibly optimise the recommended operating parameters and to acquire all data necessary for the scale-up. The customer's production requirements are invariably accorded top priority.



Figure 3 shows an isothermal loop reactor for a free-radical polymerisation. This Fluitec pilot plant has a capacity of 1500 tons a year.