The Helix Reactor in Flow Chemistry

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The Helix reactor in flow chemistry

Ir. Peter Geerdink and **Dr Jean-Marie Bassett** of **TNO Science & Industry** examine three cases of the use of the TNO Helix reactor*

In the fine chemicals industry, the batch reactor has been the established workhorse for carrying out reactions. Its main advantage here is being multi-purpose.

The chemistry that fits with this kind of equipment is, however, limited to relatively slow and mild reactions because of the limited wall surface area available for cooling. This limitation hinders the implementation of more demanding exothermic and hazardous reactions in the industry, creating a need to intensify the existing processes.

Continuous reactors have the advantage that a relatively large surface area is available for cooling, allowing better control over temperature and hence the reaction conditions, while also suppressing undesired side reactions and ultimately resulting in a higher selectivity. This translates to a potentially higher yield from raw materials, less demanding separations and less waste.

Another potential benefit of flow chemistry is the possibility of reducing the number of processing steps, especially in downstream processing. This makes continuous reactors especially suitable for highly exothermic and hazardous reactions.

Microreactors have been introduced in recent years for laboratory-scale processes but 'numbering up' by massive parallelisation remains a major challenge. Furthermore, solids cannot be processed in them because of clogging problems.

Micro-structured reactors are now being developed for production-scale processes. In this type of equipment, intensified mixing and efficient heat transfer are created by secondary flow structures. This paper looks at the Helix reactor as an example of such an intensified reactor for flow chemistry, where efficient energy and mass transfer can occur.[1]

The Helix reactor

A number of years ago TNO developed a heat exchanger in the shape of a twisted tube with excellent heat transfer characteristics, which was named the Helix heat exchanger.[2] This device was further improved and adjusted to suit continuous reactions, which it could host because of its heat exchanging properties, mixing characteristic and plug flow nature.[3,4]

The Helix is a continuous tubular reactor with very good heat transfer characteristics compared to straight tubular reactors. Figure 1 compares the Helix with a straight tubular reactor by showing their respective Nusselt numbers, a dimensionless number indicating the heat transfer properties of a system, as function of their Reynolds numbers.

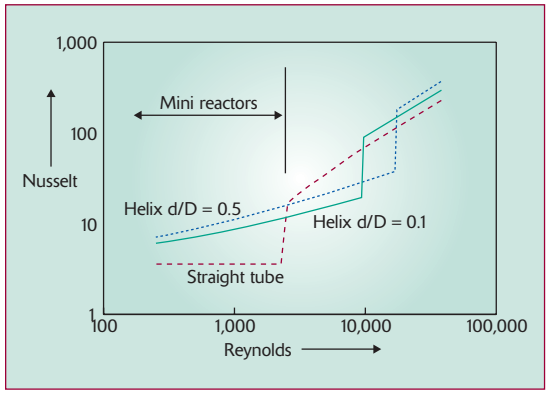


Figure 1 - Comparative heat transfer characteristics of reactors

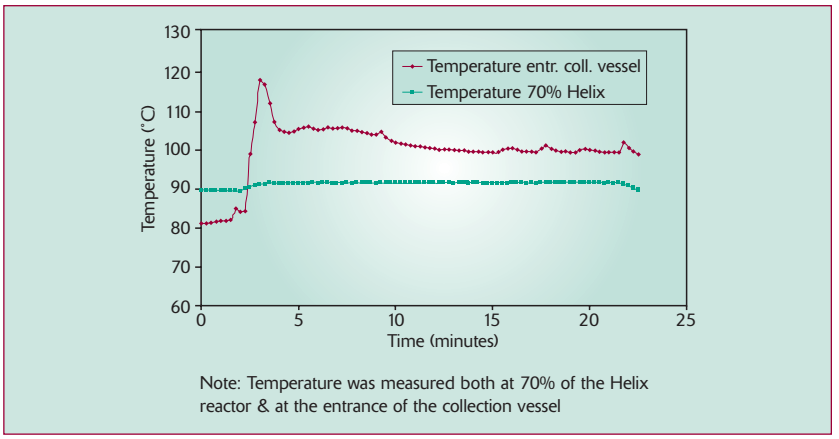
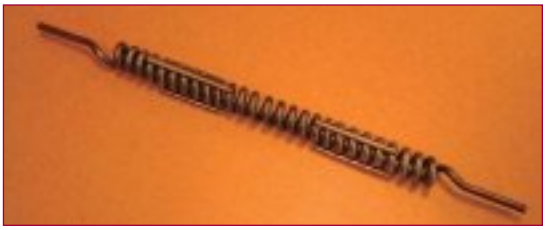


Figure 2 - (above) **Results of a typical experiment with the Helix reactor to produce [EMIM][Br]**

(right) **Helix module, which can be inserted into a shell**



The increased heat transfer in the Helix is caused by Dean vortices, secondary flows in radial direction at laminar flow speeds.[5] This results in a flow characteristic that approaches plug flow but with a low pressure drop over the tube. The vortices stabilise the flow so that turbulence is created at higher Reynolds number compared to flow in a straight tube.[6]

It is clear therefore that, because of the increased mixing properties of the Helix, this equipment can be suited for continuous reactions. Due to its plug flow nature, the distribution of the residence time in the reactor is narrow, resulting in a high quality product.

This reactor type is especially suited for highly exothermic reactions and those with harmful components. Below, we examine three different cases: a highly exothermic liquid-phase alkylation reaction and two multi-phase reactions, i.e. emulsion polymerisation and reactive crystallisation.

Solvent free continuous alkylation reaction

The synthesis of 1-ethyl 3-methyl imidazolium bromide ([EMIM][Br]) is an interesting model reaction from an industrial perspective. [EMIM][Br] is the ionic liquid produced from 1-methyl imidazole (MIM) and ethyl bromide (EtBr).

The reaction between MIM and EtBr is highly exothermic and hazardous, with an estimated adiabatic temperature rise of 345°C. Traditionally, the method of production involved diluting both reactants 20 times to obtain a 5% solution, followed by reaction in a stirred tank and distillation after the reaction is completed.

Two separate pressurised vessels, one containing ethyl bromide, the other methyl imidazol, were pressurised to approximately 6

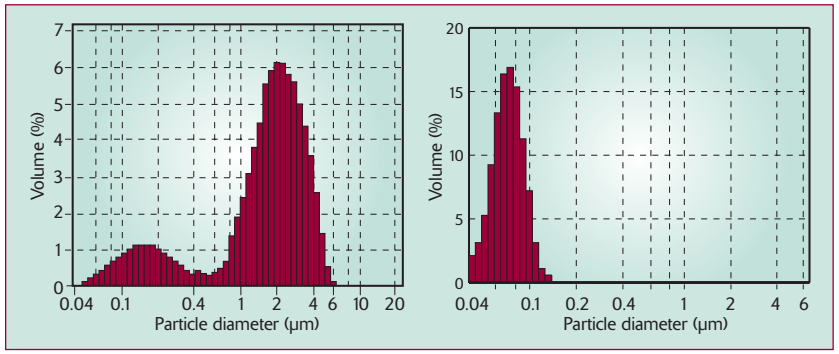


Figure 3 - Influence of flow on particle size distribution after polymerisation in a straight tube (a) & a Helix reactor (b)

bar, to assist the pumps to achieve the desired pressure and flow conditions to enter the Helix. The reactor employed had as starting configuration helices with an inner diameter of 2.4 mm and a pitch of 12 mm and was made of stainless steel (*pictured*).

The Helix was inserted into a shell to optimise the contact with the heat exchanging fluid. The temperature of the reaction medium was measured at 70% of the total length of the Helix and before the collection vessel.

The collection vessel was kept at 5.5 bar to prevent the ethyl bromide from boiling. The tubing from the final Helix to the collection vessel was insulated and heated using tracing to keep the product from crystallising inside the tube. Gear pumps and Coriolis flow meters were used to control the flow.

It was found that the optimal process conditions were 87°C and 5 bar pressure in a Helix reactor with a total length of 21 metres and a flow of 7.8 kg/hour, resulting in a residence time of approximately 113 seconds.

A temperature above 120°C in the reactor will result in side reactions, colouring the product yellow to brown and making it impossible to sell. Using the optimal process conditions, the final product was completely converted within the desired temperature range, resulting in a colourless crystalline product.

The temperature at the entrance to the collection vessel is of key importance when using the Helix. Because of the absence of cooling capabilities in the tubing from it to the collection vessel, an incomplete reaction will result in a thermal runaway in this part of the reactor.

In the experiment (Figure 4), this temperature remained well below 120°C, indicating that the reaction was completed within the Helix. In fact, other than during start up, the temperature stayed very stable in the range of 99-105°C for the full length of this experiment.

The experiment also proved to be reproducible. After crystallisation, there was a fraction in each vessel that did not crystallise but this represents less then 10% of the total volume of the sample. HPLC analysis showed a conversion in all samples of 90% or more using a residence time of 113 seconds.

The temperature inside the reactor could be fully controlled and colourless liquid product could be obtained which solidified into a colourless product upon standing. Using this relatively cheap and simple piece of equipment, production at up to 100 tonnes/year scale can be achieved.

Emulsion polymerisation

A typical emulsion polymerisation process consists of two steps: the formation of a monomer emulsion and the reaction from monomer droplet to polymer particle, retaining the size of the dispersed phase.

The challenges in the second step are to avoid both particle growth and blockage due to polymer deposits. The transition from monomer to polymer runs via a very sticky intermediate, which causes adhesion to the wall and also particle growth when collisions are sufficiently intense.

In the Helix, particle growth is inhibited by reducing the difference in speed between particles. Dean vortices create plug flow-like conditions, resulting in particles at the wall and in the middle of the tube moving at the same speed. The absence of internals prevents the adhesion of particles at the reactor itself, while Dean vortices keep the fluid at the wall moving and prevent the adhesion of particles to the wall.

This is illustrated by a reaction in which polymethyl methacrylate was produced from 35% methyl methacrylate, 4% hexadecane, 5% emulsifier (sodium dodecyl sulphate) to monomer and 1% azo iso-butyronitrile as the initiator to monomer.

After an emulsion of the monomer was created using ultrasound, the initiator was added and the mixture was introduced into the Helix. The helices had an inner diameter of 2.4 mm and a pitch of 12 mm and were made of glass. 15 metres of Helix reactor were set up as a U-shape, of which only the bottom was filled with liquid.

The fluid was moved back and forth alternately for 20 seconds through the reactor using an overpressure, before the flow direction was reversed. The optimal liquid velocity in this system proved to be 0.25 metres/second. After 20 minutes at 75°C, conversion was completed and the reaction was quenched.

By contrast, polymerisation in a straight tube reactor using the same flow conditions resulted in particle growth. Microscopic observation of the product produced in a straight tube reactor indicated that besides agglomerates, the individual particles were also large.

An explanation for this is that collision takes place during the entire reaction and the particles that collide in an early stage of the polymerisation result in larger particles, because the monomer is still a liquid, while collision at the end of the polymerisation results in an agglomerate because the emulsion droplets are becoming more viscous.

Figure 3 shows the particle size distribution after the polymerisation of the emulsion was performed in the alternating Helix reactor and in a straight tube. The conversion in both cases was complete (<1% monomer left in the product) and the particle size distribution was greatly decreased compared to the same reaction performed in a straight tube reactor. The average particle size was approximately 70 nm.

Reactive crystallisation

Good control of particle size and size distribution is a *sine qua non* in the field of particle engineering. Continuous stirred reactors can lead to a wide distribution of particle sizes that may negatively

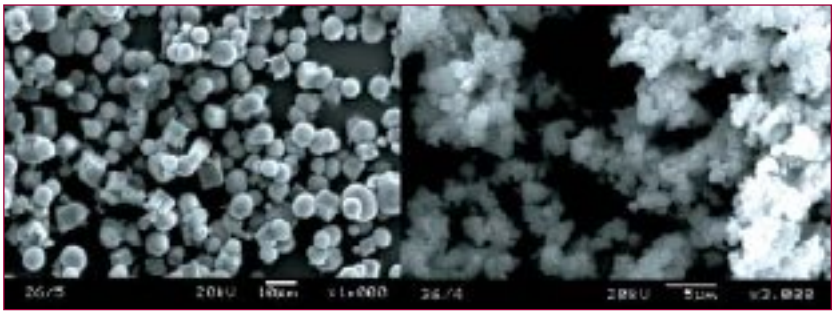


Figure 4 - Influence of flow on crystal size and shape in a straight tube (a) & a Helix reactor (b)

Table 1 - Influence of flow on particle size & size distribution using a Helix reactor & a straight tube

Parameter		Helix v. straight tube	
Flow	Concentration	Particle size	Particle size distribution
Low	Low	Smaller	Much narrower
	High	Smaller	0
High	Low	0	0
	High	Much smaller	Smaller

affect product quality. Reactors which resemble more the ideal plug flow conditions can be a beneficial tool for obtaining monodisperse and/or sub-micron particles.

Using the Helix, a more precise control of particle size distribution was obtained for the reactive crystallisation of calcium carbonate.[7] Figure 4 displays how flow conditions can influence crystal size and shape.

The Helix has been tested for its ability to control the size and morphology of precipitated $CaCO_3$. Before entering either the Helix or the straight tube reactor, a solution of $CaCl_2$ was mixed with Na_2CO_3 in a pre-mixer (Y- or T-shaped) followed by further reaction in the reactor. Crystals were obtained and analysed by FBRM and SEM.

Many different experimental conditions have been tested. Table 1 summarises the general conclusions about particle size and particle size distribution. Due to the good mixing behaviour of the Helix, combined with a minimum back mixing, it can be concluded that this type of reactor is suitable for liquid/solid reactions.

Conclusion & prospects

The Helix reactor has proven to be a multi-purpose tool for process intensification that can be designed to suit various reactions. Its improved heat transfer capability allows for highly exothermic reactions, while its near plug flow characteristic ensures low by-product formation due to improved selectivity.

The Helix possesses a gentle mixing characteristic that allows delicate emulsion polymerisation reactions to be performed while preventing particle agglomeration by collision or particle adhesion at the wall. Because it prevents back mixing, it is a suitable tool for liquid/solid reactions such as reactive crystallisation, which requires a narrow particle size distribution.

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The production rate can be scaled up either by increasing the number of Helix reactors or also, to a certain extent, by changing the diameter. The Helix is therefore a useful tool for the introduction of flow chemistry in the fine chemicals industry.

TNO has initiated a programme of research into flow chemistry in the fine chemicals industry, for which it is seeking potential partners. The further development of the Helix reactor will be one special aspect of this, but the work will range much wider.

In this project a test rig is being set up to facilitate benchmarking studies for different reactions, both liquid-phase and multiple-phase and to overcome the associated challenges of product separation, recovery and purification. In short, TNO is addressing the potential of flow chemistry technology as an integrated processing system.

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References:

1. D.M. Roberge, L. Ducry, N. Bieler, P. Cretton & B. Zimmermann, Microreactor Technology: A Revolution for the Fine Chemical and Pharmaceutical Industries?, *Chemical Engineering & Technology* **2005**, *28*, 318-323

2. J.I. Walpot, TNO's Work on Intensification: Practical Examples, *Journal of Chemical Technology & Biotechnology* **2003**, *78*, 236-240

3. P. Naphon & S. Wongwises, A Review of Flow & Heat Transfer Characteristics in Curved Tubes, *Renewable & Sustainable Energy Reviews* **2004**, *10*, 463-490

4. E.B. Nauman, The Residence Time Distribution for Laminar Flow in Helically Coiled Tubes, *Chemical Engineering Science* **1976**, *32*, 287-293

5. W.L. Koot, Spiral Heat Exchanger. EP 0553238 (B1) **1992**, WO 92/07226

6. T.J. Hüttl & R. Friedrich, Influence of Curvature & Torsion on Turbulent Flow in Helically Coiled Pipes, *Int. Journal of Heat & Fluid Flow* **2000**, *21*, 345-353

7. D. Verdoes, E.L.V. Goetheer, Z. Hornstra-Xu & J.I. Walpot, Process & Apparatus for Carrying out Crystallization, EP 1807163 (A2), WO 2005NL00636, 20050902, **2005**