HELIX REACTOR: GREAT POTENTIAL FOR FLOW CHEMISTRY

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ABSTRACT

The Helix reactor is highly suited for precise reaction control based on good hydrodynamics. The hydrodynamics are controlled by the Dean vortices, which create excellent heat transfer properties, approach plug flow and avoid turbulence. The flexibility of this reactor has been demonstrated using a very exothermic, temperature sensitive alkylation reaction, a mechanically delicate emulsion polymerisation reaction and a precipitation reaction. The reactor proved to be able to control the highly exothermic reaction leading to no side reactions. In the case of the emulsion polymerisation reaction the gentle mixing conditions of the Helix reactor were used to control particle size and size distribution in contrast to the same reaction performed in a straight tube reactor. This holds through also for the precipitation reaction. It is demonstrated that the helix reactor is a worthwhile tool transforming batch wise processes to continuous processing reducing costs while improving safety and quality.

Keywords: Helix reactor, Dean vortices, flow chemistry, process intensification, alkylation, emulsion polymerisation, precipitation, exothermic reaction, hazardous reaction

1. PROCESS INTENSIFICATION

Significant amount of running industrial processes are based on process designs that date back decades. Often generating significant amount of waste material and consuming large amounts of energy. Therefore, there is a need for improving processes. The general concept of process intensification can be an interesting route for the processes of the 21st century. One of driving forces is the desire to transform inefficient batch process towards continuous processes, leading to molecular and energy efficient processes. Especially, in potentially dangerous reaction can benefit from this paradigm shift leading to intrinsically safe processes. Microreactors are one of the tools which are attracting considerable attention. One of the reasons for this is the high surface area versus volume ratio which enables a good temperature control. Another reason is the relatively small volume of the reactor which, in case of leakage, leads to the loss of only very small amounts of potentially harmful components. However, drawbacks are that the throughput per micro reactor is relatively low, scaling up by numbering up is sometimes not economically attractive and that the presence of solids can lead to malfunction of the equipment. In this work the Helix reactor is presented as a reactor type, where efficient energy and mass transfer can occur.

2. INTRODUCTION TO THE HELIX REACTOR

A number of years ago TNO developed a heat exchanger with the shape of a twisted tube (Walpot, 2003), which has excellent heat transfer characteristics, which was named the Helix heat exchanger. This device was further improved and adjusted to suit continuous reactions, which it could host because of its heat exchanging properties (Naphon and Wongwises, 2006), mixing characteristic and plug flow nature (Nauman, 1976). The Helix is a continuous tubular reactor with very good heat transfer characteristics compared to straight tubular reactors (see Figure 1).
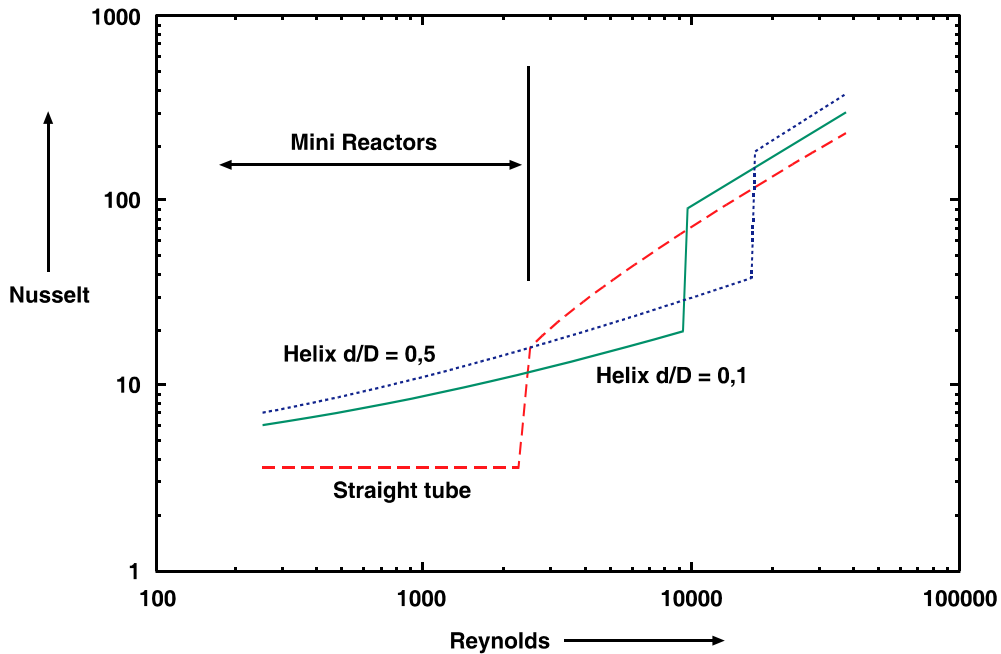
Figure 1: The Nusselt number as function of the Reynolds number comparing the difference between the Helix reactor and a normal tubular reactor

The increased heat transfer is caused by Dean vortices as illustrated in Figure 2. These vortices are secondary flows in radial direction at laminar flow speeds. These vortices stabilise the flow so that turbulent properties are formed at higher Reynolds (Hüttl and Friedich, 2000). This results in a flow characteristic that approaches plug flow and a low pressure drop in the tube. It is clear that because of the increased mixing properties of the Helix, this equipment can be suited for continuous reactions.

Figure 2. Dean vortices moving from the wall to the centre of the tube and vise versa

Process intensification using the Helix reactions.
Due to the plug flow nature of the Helix reactor, distribution of the retention time of the reactor is narrow, resulting is a high quality product. This reactor type is especially suited for highly exothermic reactions and reactions concerning harmful components. In this article the potential of the Helix reactor is exemplified using three different cases. Namely, a highly exothermic alkylation reaction, emulsion polymerisation and reactive crystallisation.

3   CASE 1: SOLVENT FREE CONTINUOUS ALKYLATION REACTION

The synthesis of 1-Ethyl-3-methyl-imidazolium bromide ([EMIM] [Br]) is from an industrial perspective an interesting model reaction. [EMIM] [Br] is the ionic liquid produced from 1-Methylimidazole (MIM) and Ethylbromide (EtBr). The reaction between MIM and EtBr is a highly exothermic and hazardous reaction, with an estimated adiabatic temperature rise of 345 °C. Traditional method of production involves dissolving both reactants 20 times, reaction in a stirred tank and distillation after the reaction is completed.
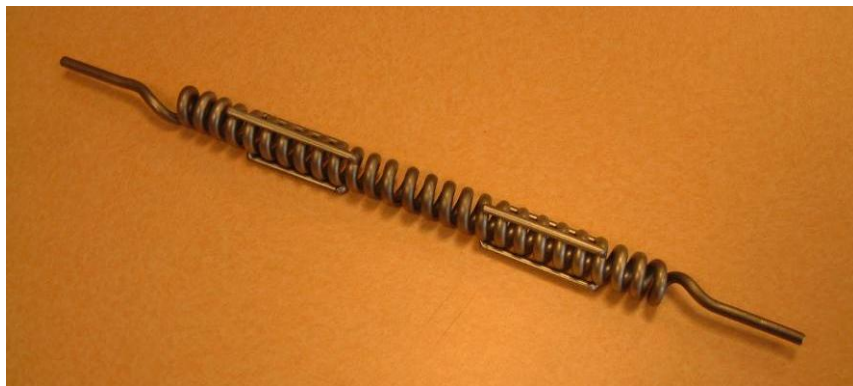

Figure 3. Helix module, which can be inserted in a shell

Two separate pressurised vessels, one containing Ethylbromide, the other containing Methylimidazol were pressurised to approximately 6 bars, to assist the pumps to achieve the desired pressure and flow conditions to enter the Helix. The process was employed starting with The helices had an inner diameter of 2.4 mm and a pitch of 12 mm and were made of stainless steel (Figure 3). The Helix reactor was inserted in a shell to optimise the contact with the heat exchanging fluid. 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 bars to keep Ethylbromide 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 corriolis flow metres were used to control the flow.

It was found that optimal process conditions were 87°C and 5 bar pressure in a helix reactor with a total length of 21 m and a flow of 7.8 kg/hr, resulting in a retention 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. In Figure 4 the final product is displayed showing all product is completely converted within the desired temperature range resulting in a white crystalline product.
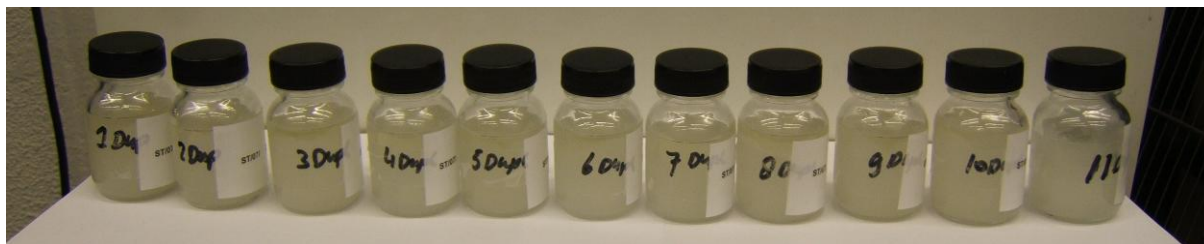

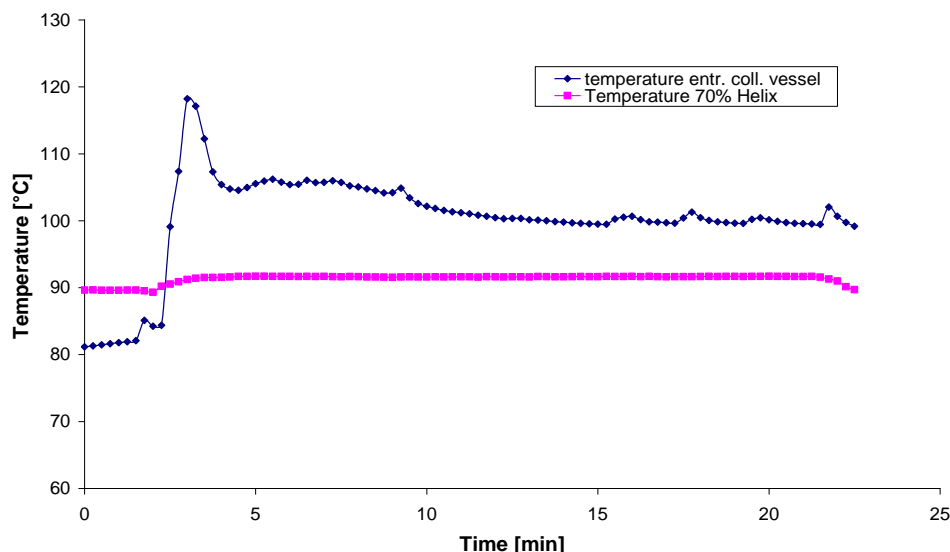Figure 4. White crystalline [EMIM][Br], produced with the Helix reactor

Figure 5. Results of a typical experiment with the Helix reactor to produce [EMIM][Br]. Temperature was measured both at 70% of the helix reactor and at the entrance of the collection vessel

The temperature at the entrance of the collection vessel is of key importance using the Helix reactor. Because of the absence of cooling capabilities in the tubing from the Helix reactor to the collection vessel, an incomplete reaction will result in thermal runaway in this part of the reactor and created a yellow to brown colour. In the experiment of which the results are displayed in Figure 5 this temperature stays well below 120 °C indicating the reaction is completed within the Helix reactor. In fact, besides the start up, the temperature stays very stable during the full length of this experiment, between 99°C and 105°C. The experiment proved to be reproducible. The obtained product started to crystallise minutes after a sample was taken at high temperature. This indicated a high purity of the product. After crystallisation, there was a fraction in each vessel that did not crystallise. This fraction made out less then 10% of the total volume of the sample. HPLC analyses showed a conversion in all samples of 90% or more using a residence time of 113 s.

The temperature inside the reactor could be fully controlled and colourless liquid product could be obtained which solidified into a white product upon standing. Using this cheap and simple piece of equipment a production of up to 100 tonnes per year can be reached.

4. CASE 2:EMULSION POLYMERISATION USING THE ALTERNATING HELIX REACTOR

A typical emulsion polymerisation process consists of two steps. The first step is the formation of a monomer emulsion and the second one the reaction from monomer droplet to polymer particle retaining the size of the dispersed phase. The challenges in the second step are avoidance of particle growth and the avoidance of blockage due to polymer deposits. The transition from monomer to polymer runs via a very sticky intermediate which causes adhesion to the wall and particle growth when collisions are sufficiently intense. Prevention of particle growth is performed in the Helix reactor by reducing the difference in speed between particles. Dean vortices result in a plug flow that moves particles both at the wall as in the middle of the tube at the same speed. The absence of internals prevent adhesion of particles at the reactor itself and Dean vortices keep the fluid at the wall moving and in this way prevent adhesion of particles to the wall.

This is illustrated with the following reaction. Poly methylmethacrylate (p-MMA) was produced from 35% methylmethacrylate (MMA), 4 % hexadecane, 5 % emulsifier (SDS) reg. to monomer and 1 % initiator azo iso-butyronitril (AIBN) reg. to monomer. After an emulsion of the monomer was created using ultrasound, the initiator was added and the mixture was introduced into the Helix reactor. The helices had an inner diameter of 2.4 mm and a pitch of 12 mm and were made of glass. 15 meters of helix reactor was set up as a U-shape, of which only the bottom was filled with liquid. Subsequently the fluid was alternating moved

back and forth through the reactor using an overpressure. The fluid could move in one direction during 20 seconds before the flow direction was reversed. The optimal liquid velocity in this system proved to be 25 cm/s. After 20 minutes at 75°C conversion was completed and the reaction was quenched.
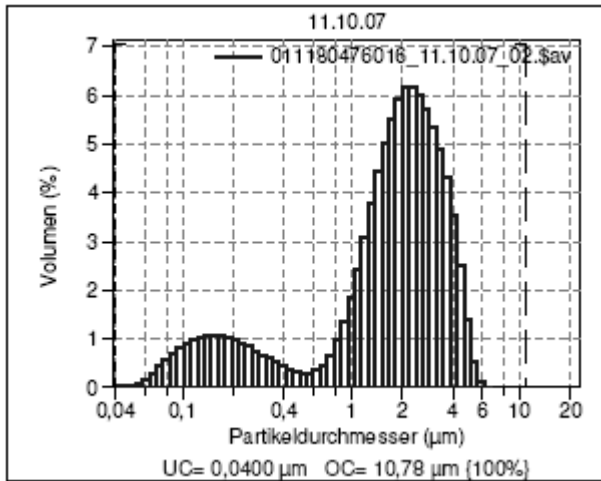

Figure 6. Wide particle size distribution after polymerisation in a straight tube

Figure 6 displays the particle size of the polymerised particles produced in a straight tube reactor using the same flow conditions. The graph shows particle size distribution is large and the particle size is on average >2μm. 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 in the end of the polymerisation results in an agglomerate since the emulsion droplets are becoming more viscous.

In Figure 7 the particle size distribution is displayed (vol. %) after polymerisation of the emulsion was performed in the alternating Helix reactor. The conversion was complete (<1% monomer left in the product) and the particle size distribution was greatly improved compared to the same reaction, performed in a straight tube reactor (figure 6). The average particle size was approximately 70 nm.
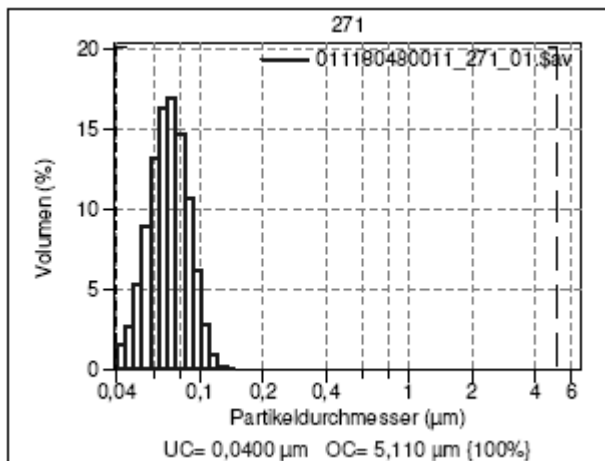

Figure 7. Narrow particle size distribution after polymerisation in the alternating Helix reactor

5. CASE 3: PRECIPITATION

In the field of particle engineering good control of particle size and size distribution is a sine qua non. Continuous stirred reactors can lead to a wide distribution of particle sizes that may negatively 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 reactor a more precise control of particle size distribution was obtained based on the precipitation of calcium carbonate. Figure 8 displays how flow conditions can influence crystal size and shape.
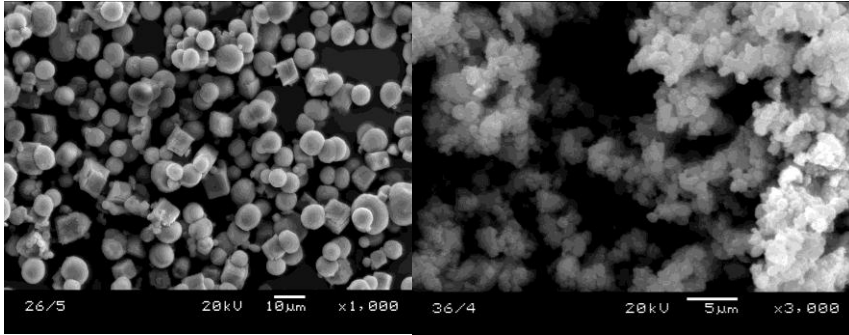

Figure 8. Influence of flow on crystal size and shape; left reaction in a straight tube, right a Helix reactor

The Helix reactor has been tested for its ability to control size and morphology of precipitated $CaCO_3$. Before entering either the Helix reactor or the straight tube reactor a solution of $CaCl_2$ was mixed with Na_2CO_3 in a premixer (Y or T-shaped) followed by further reaction in the reactor. Crystals were obtained and analyzed by FBRM and SEM. A large variety of experimental conditions have been tested. The general conclusions regarding the particle size and particle size distribution are summarized in table 1. Due to good mixing behavior of the Helix reactor combined with a minimum back mixing, it can be concluded that this type of reactor are suitable for liquid/solid reactions.

Table 1. influence of flow on particle size and size distribution using a Helix reactor and a straight tube

Parameter		Helix versus 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

6. CONCLUSIONS

The Helix reactor proves to be a multi-purpose tool that can be designed to suit various continuous processes. It is able to transport vast amounts of heat to suit highly exothermic reactions while its plug flow characteristic ensures continuous high product quality and low byproduct formation. The Helix reactor possesses a gentle mixing characteristic that allows delicate emulsion polymerization reactions to be performed while preventing particle growth by collision or particle adhesion at the wall. Because the Helix reactor prevents back mixing, it is a suitable tool for liquid/solid reactions such as precipitation, which requires a small particle size and a narrow particle size distribution. By changing the size of the channel of the Helix reactor, the production rate can be adjusted to fit a desired amount.

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