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Microreactor Plant for the Large-scale Production of a Fine Chemical Intermediate: a Technical Case Study

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10.1
Introduction

The fine chemical industry is often characterized by small-scale plants producing a variety of chemicals using frequently hazardous starting materials and extreme conditions. Products are commonly manufactured in a batchwise, multi-product plant provided with a substantial amount of multi-purpose equipment. Typically, the production volume is not large, say less than 10 kt p.a., although this is not a scientific boundary.

Although a multi-product plant is often based on a certain key technology, many reactions and chemistries are carried out in one plant. Hazardous chemicals have to be handled, often in relatively large quantities, for a short time. Reactions with high heat effects need to be carried out, for example hydrogenations and oxidations, obtaining unstable and toxic products or waste. In many cases the conventional way to deal with different systems is to use the stirred tank concept, sometimes modularly provided with additional heating or cooling capacity.

As an alternative to the batch stirred tank, a versatile continuous reactor would be needed. Microreactors, which have seen developments in the last few years, might become this alternative. Already a wide variety of reactors can be obtained constructed with different internals. Currently, a diverse range of construction materials is also available, from simple stainless steel, through Hastelloy to several types of glass and silicon carbide. It should be noted, however, that the choice of construction material often requires a certain manufacturing method for the microreactors. For example, metals can be used in combination with etching technology; sandblasting can be used for glass; and routing, drilling and milling for silicon carbide. The chosen material–technology combination will have an impact on application in manufacturing fine chemicals. For example, etching is a well-established technology nowadays for creating microstructures ("open reaction space") in a metal, but one may safely assume that corrosion resistance in the application, the fine chemical manufacturing process, will be limited. If the material is too resistant to corrosion, one needs to

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sandblast, mill or drill to create the reactor and the smallest dimensions are limited while the costs of equipment manufacturing increase.

The producers of microreaction equipment are to date generally small in turnover and number of employees. These companies are frequently a spin-off from academic institutions and consequently there is little experience with implementing the reactors in an industrial environment. The focus is stronger on the manufacturing of a microreactor and less on the application. Moreover, gaining insight into scale-up is still an on-going process.

A clear hurdle for the application of a microstructured reactor in a multi-product or multi-purpose environment is that a relatively large part of the fine chemical processes contain solids. Some newer reactor concepts seem to be able to handle solids better than the early microreactors but this still needs to be developed further.

DSM is a leader in fine chemical production and several multi-product sites exist where combinations of batch and continuous operation is possible from the kilogram to the multi-tonne scale. In the technology portfolio, oxidations and hydrogenations are important, and also chiral technologies. However, there is strength in hazardous chemistry and combinations of enzymatic and chemical steps and there is also a continuous drive to make processes more efficient and safer by improving control of temperature, reaction conditions and reducing the inventory of reactors. Speed of process implementation, including process adjustment and development, is a key factor.

Some of the DSM products have been produced in campaigns for many years and therefore need a limited amount of special equipment. These products are often characterized by hazardous chemistry. A few years ago, microreactors were evaluated for such a manufacturing process in the DSM fine chemical plant at Linz.

10.2
Problem Description

For several years, a fine chemical intermediate has been made from two highly toxic starting materials and concentrated sulfuric acid at a scale of ~500 t p.a. The reaction is fast and highly exothermic; the viscosities of the two liquid starting materials are very different and the viscosity of the mixture increases rapidly during the reaction. For manufacturing, a 10-m^3 stirred vessel was applied as a batchwise chemical reactor and productivity was kept at a low rate to avoid hot spots and uncontrolled temperature excursions. Wall cooling by external cooling loops was provided for heat removal, but tubular reactors also had been tested.

The corrosive nature of the reaction mixture led to operational problems using the cooling loops, and the choice of this reactor type led to serious back-mixing of the reactants, thus keeping the selectivity of the reaction low. Typically 35% of toxic waste products were obtained from the starting materials.

Although the process operated within the DSM boundary conditions on safety and economy, the development of microreactor systems made major improvements possible. In process development, several boundary conditions have been set:

- The process heat should be removed as quickly as possible to improve temperature control, that is, to avoid hot spots and temperature excursions.
- Back-mixing should be avoided and therefore a continuous plug-flow type of reactor would be ideal.
- The internal reactor volume should be small to avoid safety risks as the starting materials and (waste) products are toxic.
- The reactor should be inserted in the current process as a retrofit of the existing stirred tank to avoid the need for a completely new plant.

It was decided that a new technology, based on microreactors, would be the best approach to accommodate the above conditions.

10.3 Solution Methodology

The development of the microreactor system started with the notion that at that time standard solutions were not commercially available. Therefore, cooperation with the Institut für Mikroverfahrenstechnik (IMVT), part of the Forschungszentrum Karlsruhe (FZK) in Germany, was set up. IMVT was able to provide the detailed design knowledge needed and it was able to manufacture small-scale units. DSM provided the engineering knowledge in the field.

In January 2003, a PhD student at DSM in Linz started to develop a small model reactor. Scale-up by numbering-up was assumed to be the way forward for large-scale application.

10.4 Experimental

A small-scale reactor of the IMVT design was used (Figure 10.1). The reactor set-up consists of a micro-mixing section and a separate micro-heat exchange section separated by a small gap. The laboratory-scale reactor was designed for a capacity of $\sim 1\,\mathrm{L\,h^{-1}}$ ($1\,\mathrm{kg\,h^{-1}}$) product flow rate at a maximum pressure of 20 bar and a maximum temperature of 180 °C. Hastelloy C22 was chosen as a corrosion-proof construction material. The mixing section was made in such a way that it could be replaced quickly for optimization of the mixing performance. Three pumps, virtually pulsation free, from HNP Mikrosysteme, type MZR-2905, were used for the main product flows. A particle filter was applied to prevent particles larger than 10 μm from entering the reactor to prevent blockage of the internal structure.

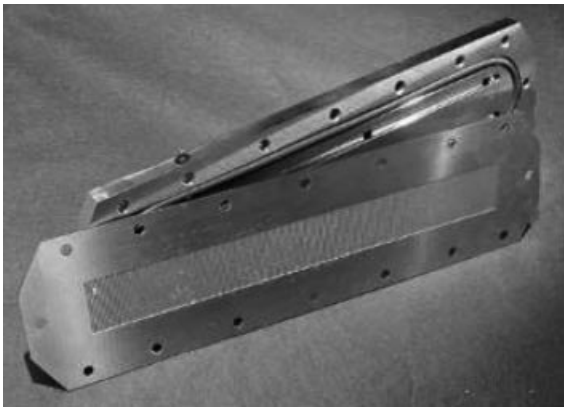

Figure 10.1 Internal view of the IMVT laboratory-scale microreactor used for experimental determination of optimal reaction conditions and residence time.

The reactor set-up was first characterized and great attention was paid to start-up of the reactor. Mainly, the difference in the viscosities of the starting materials and the viscosity increase during reaction made adjustments during the procedures necessary.

10.5 Results of Laboratory-scale Development

Experiments were carried out first to characterize the microreactor set-up performance. The reaction was optimized first towards maximum yield in the microreactor. This was done by varying the residence time, temperature and the proportions of the three reactants. A typical normalized behavior is shown in Figure 10.2. These experiments made it clear that the heat evolved could be removed by the microreactor in such a way that temperature control was possible. More importantly, it was found that the reaction yield showed a maximum with a residence time of a few minutes and that the exact optimal time is dependent on the conditions chosen.

The reaction time turned out to be too short to obtain a satisfactory yield and therefore the set-up was modified and a stirred-tank reactor was added after the microreactor. The total yield increased to values which made the reactor combination attractive for application.

10.6 Design

Based on the experimental data obtained from the laboratory-scale tests, a large-scale microreactor was designed with cooperation between DSM Linz and IMVT.

The design capacity would be 2 kt p.a. if continuous operation were used, but in reality the product is made in campaigns of a few months per year. Furthermore, only

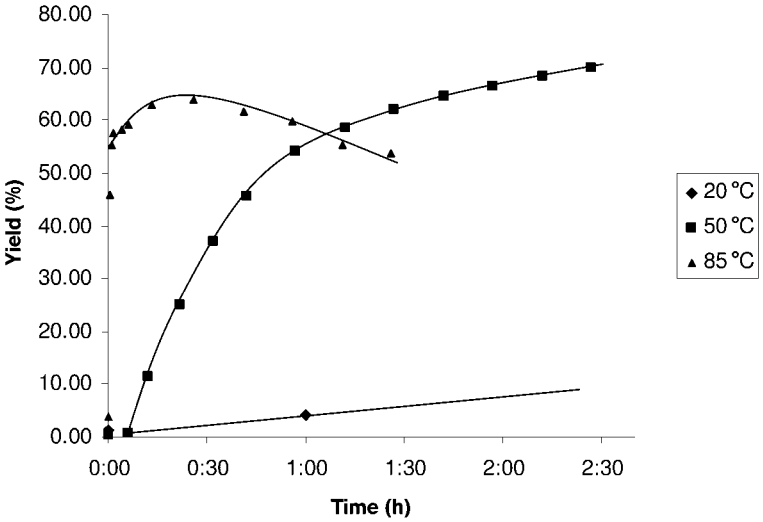

Figure 10.2 Representative kinetic data for the reaction applied, showing that higher reaction temperature reduces substantially the reaction time required.

the first part of the reaction is carried out in the microreactor with a residence time of less than 10 s; the final part of the conversion is still carried out in conventional equipment (a recirculation loop and a stirred tank). Clearly, all the important safety issues and the waste generation are greatly reduced. The design of the microreactor was done simply by numbering-up or "equaling-up" of the 1 L min^{-1} element, tested in the laboratory, to the 2 kt p.a. capacity (Figure 10.3).

For material choice, several aspects were considered and Hastelloy C22 was chosen in accordance with the laboratory-scale equipment.

Figure 10.3 The microreactor before the conventionally used 10-m^3 stirred vessel in the plant, just prior to installation.

10.7 Operation

The reactor was meant to be a retrofit into the current plant. In practice, it has become an additional reactor with very well-controlled process parameters and small inventory prior to the "old" reactor. The microreactor has been installed and the start-up was in mid-2005.

First indications showed that the reactor performed as designed and that the numbering-up concept worked satisfactorily.

In the period after this start-up, several modifications were proposed and made to improve performance further. It turned out that on the production scale and with the length of a production run, some fouling occurred which was not observed in the laboratory, where quantities were very small, and the production runs were much longer than the laboratory-scale tests. The fouling led to blocking of the heat exchanger. The solution was that in a new design the mixer and heat exchanger needed to be closer together than in the initial design, and this solved the problem.

Another unknown issue was the corrosion resistance of the production-scale reactor. The thickness of the metal sheets used is so small that even a 0.1 mm p.a. corrosion rate is relatively large. Inspection of the reactor showed that the corrosion rate was indeed potentially large, meaning that the reactor needed replacement too quickly. Therefore, methods were found to improve the corrosion resistance.

As the reactor is small and the cooperation with FZK–IMVT is strong, we were able to make small changes to the reactor quickly. Such cooperation strongly facilitated the development, optimization and application of the microreactor in our fine chemical process at DSM Linz.

10.8 Conclusion and Outlook

The development of a microreactor for a retrofit of a fine chemical production at DSM Linz was described. Its success was strongly dependent on the good cooperation between DSM Linz and FZK–IMVT, which initially led to the first microreactor design and subsequently facilitated design modifications. Also, application of the numbering-up concept for direct scale-up of laboratory-scale experiments facilitated application on the production-scale tremendously.

The reactor at DSM has shown that microreactors can play a significant role in the transformation from batch to continuous processes while increasing safety, flexibility and process output. Microreactors are now starting to break through in other chemical production processes.