



Design and application of a millistructured heat exchanger reactor for an energy-efficient process



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ABSTRACT

Flow chemistry in milli- and microstructured reactors exhibits great potential for process intensification. In the present work, this potential has been demonstrated through the process development for a solvent-free production process including a Michael addition and following product purification. Process simulation was used to maximize the material and energy efficiency of the overall process by recycling unconverted reactants and a catalyst (water) and by utilizing heat from the exothermic reaction to substitute external energy supply in the heat demanding process steps. As a proof-of-concept experiment, millistructured equipment was designed, manufactured and tested at a laboratory scale. A three-stream counter-current heat exchanger for reactant preheating and a plate heat exchanger reactor with zigzag reaction channels were investigated regarding the maximum transfer of reaction heat available for further process steps via a heat carrier cycle. The experiments showed stable reactor control in steady state operation and efficient heat transfer with a small driving temperature difference at the outlet of the heat exchanger reactor.

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1. Introduction

In pharmaceutical and fine-chemical production, fast and exothermic reactions can bring batch reactors to their technical limits and reduce productivity due to the need for safe and controlled reactor operation. Heat transfer limitation in vessels requires time-consuming semi-batch operation or low reactant concentrations. Thus, high potential exists for process intensification via flow chemistry, which can provide safer operating conditions, reduced waste, higher productivity, and higher energy efficiency. The transfer of batch processes to continuous production enables new chemical paths, and process conditions far from conventional practices can be considered. Often referred to as Novel Process Windows [8,19], these possibilities offer numerous benefits associated with process intensification [7]. Contrary to the optimization of an existing traditional process, the approach of process intensification [17,18] involves the utilization of entirely new equipment and process designs. The present paper focuses on a heat transfer limited process with an exothermic reaction; thus,

two major aspects of heat exchange intensification are emphasized: (1) process intensification by miniaturization [4] (milli/micro process technology) and (2) the combination of a reactor and heat exchanger as one multi-functional piece of equipment (Heat exchanger (HEX) reactors) [1].

Using millistructured flow reactors for a small-scale production considerably improves mass and heat transfer. The large surface-to-volume ratio and small length scales for heat transfer reduce the risk involved by handling fast and exothermic reactions. Better control of temperature and residence time distribution often results in higher yields and selectivity. Instead of the reaction time being determined by slow reactant dosing in semi-batch mode, the required residence time in the continuous reactor depends mostly on reaction kinetics. Furthermore, increased reactant concentrations or even solvent-free syntheses are possible. As a consequence, not only reaction time is reduced but also solvent waste and energy consumption for later solvent removal. Although miniaturization itself enhances heat removal, a further step for intensifying heat exchange is to utilize HEX reactors. Their design has to meet the requirements for both heat exchange and reaction control (e.g., residence time distribution) and is often based on the design of compact heat exchangers, i.e., plate heat exchangers.

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Nomenclature

| | |
|---------------|--|
| a_V | Surface-to-volume ratio (m^{-1}) |
| A_w | Wetted surface area (m^2) |
| $c_{EA,0}$ | Theoretical, initial concentration of ethyl acrylate in the reaction mixture (mol m^{-3}) |
| c_p | Heat capacity of the fluid ($\text{J kg}^{-1} \text{K}^{-1}$) |
| d_h | Hydraulic channel diameter (m) |
| $E_{A,obs,i}$ | Observed activation energy of reaction i (J mol^{-1}) |
| h | Channel height (m) |
| ΔH_R | Enthalpy of reaction (J mol^{-1}) |
| k | Overall heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$) |
| $k_{obs,i}$ | Observed rate constant of reaction i , n -th order ($\text{L}^{n-1} \text{mol}^{1-n} \text{s}^{-1}$) |
| L | Reactor length (m) |
| N | Time ratio of reaction and cooling (dimensionless) |
| Nu | Nusselt number (dimensionless) |
| Q | Volumetric flow rate ($\text{m}^3 \text{s}^{-1}$) |
| r_{EA} | Rate of disappearance of ethyl acrylate due to reaction ($\text{mol m}^{-3} \text{s}^{-1}$) |
| $r_{EA,0}$ | Initial rate of disappearance of ethyl acrylate due to reaction ($\text{mol m}^{-3} \text{s}^{-1}$) |
| R_{th} | Thermal resistance (K W^{-1}) |
| Re | Reynolds number (dimensionless) |
| t_h | Characteristic time scale of heat transfer (s) |
| t_r | Characteristic time scale of reaction (s) |
| T | Temperature (K) |
| T_c | Heat carrier temperature (K) |
| u | Axial flow velocity (m s^{-1}) |
| w | Channel width (m) |
| X_{EA} | Conversion of ethyl acrylate (dimensionless) |
| z | Axial distance from the reactor inlet (m) |

Greek Symbols

| | |
|-----------|--|
| α | Heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$) |
| λ | Heat conductivity of the fluid ($\text{W m}^{-1} \text{K}^{-1}$) |
| ρ | Density of the fluid (kg m^{-3}) |

Contrary to batch processes, continuous production in a HEX reactor enable the steady removal of reaction heat, almost as rapidly as it is generated by the reaction. Thus, the exothermic reaction can be considered as a potential heat source in the overall process. Consequently, continuous production processes with millistructured reactors enable new options for energy savings via heat recovery. Systematic approaches to heat integration, such as pinch analysis [9,11], are state-of-the-art in the continuous production of petrochemicals and bulk chemicals, where energy savings is a main target for process design. For the small scale production of pharmaceuticals or fine chemicals, the dominating aspect is the aim for higher material yield. However, direct energy savings (heat recovery) or indirect energy savings (less solvent to remove, higher raw material yield) can also decrease costs and significantly improve eco-efficiency (green processing) [6,7].

In the first part of this paper, the full potential for process intensification in a continuous production process is examined with respect to the addition of piperidine to ethyl acrylate (Michael addition). The overall process, including purification via distillation, is investigated and optimized via process simulation. To maximize heat recovery, the basic principles of pinch analysis are applied. In the second part of the paper, we present an integrated millistructured HEX reactor for controlling a fast and exothermic reaction while transferring the heat of the reaction to a heat carrier stream. Reaction conditions close to the simulated process are

chosen for a proof-of-concept laboratory experiment. With an additional capillary heat exchanger, reactant streams are heated to reaction temperature using the hot product stream in counter-current operation.

2. Materials and methods

The process was modeled using the SIMSCI Pro/II process simulator, version 9.3 (Invensys Systems Inc.). Steady-state temperature and conversion profiles in the HEX reactor were calculated by solving the following mass and heat balances for an ideal plug flow reactor.

$$\frac{dX_{EA}}{dz} = \frac{r_{EA}}{c_{A,0}u} \quad (1)$$

$$\frac{dT}{dz} = \frac{r_{EA}(-\Delta H_R)}{u\rho c_p} - \frac{4k(T - T_c)}{d_h u \rho c_p} \quad (2)$$

Herein, r_{EA} is the rate of disappearance of ethyl acrylate and is defined by the kinetic model of the Michael addition with two parallel reactions, as described in Section 3.1. Calculation of the distillation column is based on the theory of separation stages.

Experimental investigations were performed with a setup for continuous reactor operation, using a laboratory automation system (LabBox and LabVision Software, HiTec Zang GmbH, Germany) for control and permanent data logging. The feed and quench streams were supplied by three continuous syringe pumps (Syrdos 2, HiTec Zang GmbH) with 10 mL glass syringes. The heat carrier cycle was realized using a thermostat (Ministat 230, Huber GmbH, Germany) and silicon oil (M20.195/235.20, Huber GmbH). For measurement of the heat carrier flow rate, an ultrasonic flow sensor (Sonoflow IL.52, Sonotec Ultraschallsensorik Halle GmbH, Germany) was employed.

A plate reactor designed for flow rates in the range between 10 and 30 mL/min was used for the continuous production experiment. Mixer, reactor channels and heat carrier channels were milled into an aluminum plate on opposite sides. Design criteria and channel dimensions are described in Section 4. Both channels were covered with additional aluminum plates, which were evenly pressed onto the reactor plate to avoid significant bypass flow. Five Pt100 sensors were inserted through the side of the reactor directly into the flow channel to measure the temperature of all inlet and outlet streams. The reactant preheater was manufactured by soldering three stainless steel capillaries (1/16 in. outer diameter, 1 mm inner diameter) of 1.2 m in length in direct contact. On the cold side of the heat exchanger, three further Pt100 sensors were used for temperature measurement. Both the reactor and reactant preheater were covered with Armaflex insulation.

The synthesis of 3-piperidinopropionic acid ethyl was realized without any solvent. However, water was used as a catalyst and was premixed with piperidine. For the proof-of-concept experiments, the molar ratio of reactants was 1.1 (piperidine/ethyl acrylate) and the molar ratio of water was 0.5 (water/ethyl acrylate). To determine the reaction conversion, the reaction mixture at the reactor outlet was effectively quenched via continuous mixing with a solution of acetic acid in methanol (11 vol.%). Product samples were analyzed using an Agilent 7820 gas chromatograph equipped with a HP-5 column (30 m × 0.32 mm × 0.25 μm, Agilent) and a flame ionization detector. The inlet temperature was 275 °C, the inlet pressure, 50 kPa, and the split ratio, 100:1. An injection volume of 0.5 μL was used in the automatic liquid sampler. The oven temperature (60 °C) was kept constant for 2 min and then increased to 200 °C with a ramp of 20 K/min.

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