

Reactor Performance and Design Concept in Additively Manufactured Milli-Scale Reactors

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Abstract

Millireactor or minireactor technology in small scale production has gained increasing attention in microreactor technology research because high pressure drops, unequal flow distribution into micrometer scale channels, and channel blocking can be reduced in larger scale. In this work, additive manufacturing suitability for reactors has been studied based on reactor surface properties. Mixing and heat transfer have vital role in reactor design when exothermic and fast or relatively fast reactions are considered. Here, mixing efficiencies of Hartridge-Roughton reactor and its modifications have been evaluated. The surface roughness and surface rugosity had influence in experimentally determined mixing efficiencies which made a clear difference when comparing simulation results. Reactor temperature fields were experimentally measured with IR camera technology as well as the heat flows were simulated for instantaneous acid-base neutralization reaction. The milli-scale mixer design cycle consisting Computational Fluid dynamics (CFD), additive manufacturing and experimentation is proposed. The proposed methodology is geometry independent and millireactor design steps here are discussed in detail. The design tasks are introduced for illustrating the proposed design concept for reactor geometry optimization.

Keywords: 3D printing; Additive manufacturing; Millireactor; IR camera; Computational fluid dynamics

Introduction

The applications of microreactor technology have attracted a growing number of interest over the last decade for process intensification, for increasing process safety and especially for running very fast exothermic reactions [1]. Microreactors present unique properties and novel process windows especially for very fast reactions of high risk thermal runaway that are usually difficult to control under typical conventional reactors [2]. Typically fast kinetics (reaction times <1 s) are involved in organometallic and acid chloride reactions, but also reactions having highly hazardous reactants or products like halobenzenes, phosgene, diazomethane or peracetic acid [3-5] have their place in microreactor technology as reaction times are within 10 s to a couple minutes. Microreactors are characterized as reactors with at least one of its dimensions smaller than 1000 μm scale. The smaller dimensions in the micro scale reactors offer substantially high surface area to volume ratio and they significantly increase the mass and heat transfer rates by more than 3 orders of magnitudes [6]. Elvira et al. [7] found out that heat transfer characteristics in 500 μm and 1 mm can be similar, but radical change occurs in 5 mm scale. Industrial production is difficult due to the small reactor volumes. Scale-up using numbering up of reactor units can cause difficulties due to unequal flow distribution into channels and due to high pressure drops in units. Additionally, the danger of microchannel clogging is present because of micrometer scale dimensions in flow channels. Channel blocking, high reactor pressure drops and uneven flow rates in channels can be prevented in mini/millireactor scale [8].

The combination of small scale reactor technology and additive manufacturing techniques is a novel concept in the design of micro/millireactors which can be used for reactor performance studies [9-13]. The degree of design freedom, cost effectiveness, time savings and ability to manufacture almost all types of complex geometry have increased the prospect of AM. The advantage is clearly rapid prototyping for experimentation. Combination of CAD tools, computational fluid dynamics (CFD) and the additive manufacturing offers a design platform where common geometry files (e.g., IGES, STP, STL, DWG types) can

be used. Nowadays a large variety of materials (plastics, metals, alloys) and different manufacturing techniques have been used for small scale reactors production: Fused Deposition Modeling (FDM), Selective Laser Sintering (SLS), Selective Laser Melting (SLM) and Stereolithography (SLA). Poor chemical and thermal stabilities have been reported in FDM, SLS and SLA techniques, while SLM reactors were found resistant to high temperatures and suitable for a wide range of chemicals. On the other hand poor surface smoothness and build orientation should be considered in the selection of additive manufacturing technique. Typically, channel roughness increases with decreasing diameter.

Hartridge-Roughton (HM) mixers are well-known rapid mixers which are efficient even at low Reynolds numbers [14,15]. Patrizio et al. [16] studied different HM mixer geometries and their mixing efficiencies using Villermaux-Duschman model reaction and CFD for homogenous phase flow simulations in turbulent flow conditions. The mixing efficiency was studied using RNG k-epsilon model and species transport equation. The mixer with conical narrowing had better mixing efficiency performance compared to the case without narrowing. Lindenberg and Mazzotti [17] studied the mixing efficiency comparison of Y-mixer and HM-mixer both experimentally and using CFD in low to medium viscosity solutions. The mixing times were much shorter with HM-mixer compared to Y-mixer. They also used RNG k-epsilon model in simulation because turbulent Reynolds number was a little bit over 20 at flow velocity 10.5 m/s.

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Heat transfer coefficients higher than 1000 W/m²K in micro- and millireactors are typically high due to the high surface area to reactor volume [18,19]. The temperature measurements, however, in small scale are difficult to arrange and therefore surface measurements using IR camera technology has been used [20-23] in the heat releasing systems such as exothermic reaction studies.

The micro- and millireactor design has lately gained attention as the reactor concept has been studied in more detail. Rodriguez-Guerra et al. [24] presented reactor performance parameters, such as product quality, safety, costs, environmental impact, operability, reaction conversion and selectivity. The reactor consists of feed pumps, quenching zone for stopping the reactor, and in the core the reactor zone. Syringe pumps or high-performance liquid chromatography pumps are used which provide high fluid pressures and steady flows. Mixing time determination, flow dynamics, and heat transfer are key factors in homogenous flow reactors. Additionally, mass transfer is considered in multiphase systems. The general design methodology is an iterative process where initial data is collected containing fluid properties, reaction data and capacity information. The selection consists of pumps, quenching process, controls (temperature, pressure), analysis and the selection of reactor. Mixing, mass transfer, heat transfer, reaction yields and scale-up are in the center of evaluation. The iterations are between the selection and evaluation phases [25]. However, Zhang et al. [25] do not explain how the reaction zone can be modified in detail. Rodriguez-Guerra et al. [24] presented the micro/millichannel sizing selection for preventing reaction hot-spots based on maximum heat generation (reaction enthalpy) and based on overall heat release related to the reaction rate. Their method was restricted to the pipe channels.

In this work, milli-scale mixer design using the cycle consisting CFD, additive manufacturing and experimentation is proposed. The design tasks are introduced for illustrating the proposed design concept for reactor geometry optimization. The Roughton mixer geometry modification has been selected for the design basis.

Materials and Methods

Design and fabrication of milli scale reactors

The milli-scale Roughton-Hartridge (R1) reactor and two different

reactor modifications (B1 and K1) were designed using Solid works. A laser melted layer-by-layer deposition of AISI 316L stainless steel powder was used for fabricating reactors with an EOS M-series system (EOS M2703D) (Figures 1-3). The surface profiles of the reactors were measured using a diamond tip profilometer to determine the roughness of the reactors. The equivalent roughness of the surfaces was determined based on [26]:

$$R=R_{pm}+F_p \quad (1)$$

where R is the equivalent roughness of the surfaces, RPM is the mean leveling length and Fp is the floor distance to the mean line. The reactor B1 was cut from the upper part (18 mm diameter mixer) horizontally for evaluating the surface roughness and stereomicroscopic image was taken from the inside of the surface, see Figure 4. Average values of 0.015 mm and 0.076 mm for Fp and Rpm respectively were determined using diamond profilometer. The surface roughness equivalent R was determined 0.09 mm from Eq. (1). It equals roughness value of stainless steel pipe upper limit (0.02 - 0.10 mm) [27]. The geometry shape evaluation was evaluated using Shadowgraph imaging from pipe cross sections. Images were acquired using backlight in digital single-lens reflex camera, and using post-processing with the GNU Image Manipulation Program GIMP for threshold image generation, see Figure 5 some rugosity and irregularity can be observed due to the build orientation in horizontal oriented pipe fabrications.

Step response analysis

Several methods for the mixing performance evaluation in micro-milli channels have been proposed. This work focuses on the tracer step response experiment for the evaluation of mixing performance in the milli channel. Analytical grade sodium hydroxide pellet and ultrapure Millipore water were used for the experiment. The experiment was conducted in a continuous flow mode as shown in Figure 6. The mixer was supplied with two ultrapure Millipore water streams with the third stream containing 0.1 M tracer (sodium hydroxide). A tracer solution was introduced by closing one of the water feed stream while simultaneously opening the tracer solution feed stream using syringe pumps from World Precision instrument (model number AL-1000).

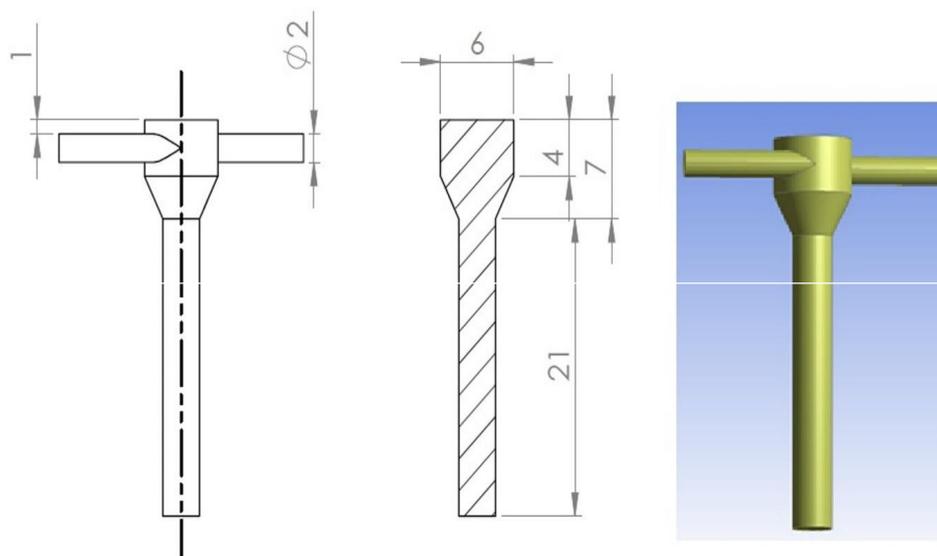


Figure 1: Hartridge-Roughton (Lindenberg et al.) wetted wall R1 mixer geometry. Outlet pipe diameter is 4 mm.

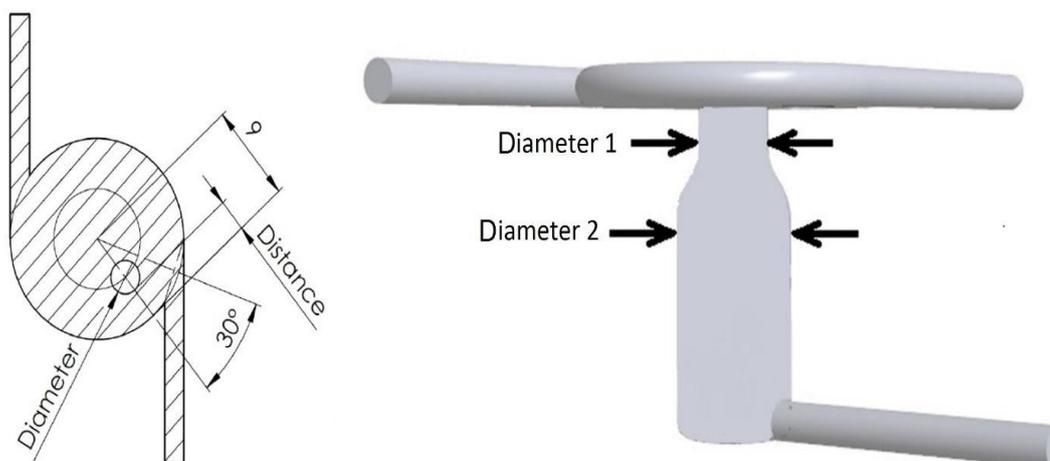


Figure 2: B1 and K1 wetted wall reactor modifications. Baffle diameter in the upper part=3 mm, Baffle Distance from wall=1.5 mm, upper part diameter=18 mm, Diameter 2=6.5 mm, B1 Diameter 1=4 mm, K1 Diameter 1=2.5 mm, inlet and outlet pipe diameters 2 mm, outlet pipe length 16 mm.

The analysis of the samples was conducted using C3010 multi parameter pH analyzer (De Bruyne instruments). The pH values of the tracer at the outlet were recorded every second which were converted to H^+ concentrations. The one second time mark of the instrument is the smallest time scale and was also set as a basis for the recorded 4.3 Thermal IR analysis The surface temperature of the reactor was measured using FLIR infrared thermometry model A655 series with the following camera specifications: Spatial resolution from 7° : 0.19 mrad to 80° : 2.62 mrad, temporal resolution of 50 Hz, uncooled microbolometer focal array detector type (7.5-14 μm), IR resolution 640×480 pixels and operating temperature range from $-20^\circ C$ to $2000^\circ C$. The FLIR research IR software was used for temperature data acquisition. The temperature associated to the infrared radiation off the surface of the reactor at any given point was collected by the camera and processed by the software to get readable numbers. The measurement accuracy of the camera is $\pm 2\%$ of the reading with thermal sensitivity of less than $0.05^\circ C$. The accuracy of the camera can be affected by a number of factors namely emissivity of the object, reflected apparent temperature, distance between the object to the camera, relative atmospheric humidity and temperature. However, the FLIR camera is provided with compensation for these parameters to maximize degree of accuracy. The experiment was also conducted in an environment where possible apparent reflection and humidity were minimized. The heat source for this experiment was neutralization reaction between equimolar sodium hydroxide and nitric acid solutions. Analytical grade sodium hydroxide pellet and nitric acid solution (65%) were used for the experiment. The feed streams of sodium hydroxide solution and nitric acid solution were supplied to the reactor by syringe pumps World Precision instruments (model number AL-1000) as shown in Figure 6.



The neutralization reaction is instantaneous reaction. The first order irreversible elementary reaction rate constant $K=1.3 \times 10^8 \text{ m}^3/(\text{mol}\cdot\text{s})$ was used here to describe this instantaneous reaction [28]. This extremely fast exothermic reaction generates heat of reaction 57.3 kJ/mol. The infrared camera captures the heat radiated through the surface of the reactor. The mixing of NaOH and HNO_3 solutions was continued for several minutes before starting measurements for assuring steady-state conditions.

CFD modeling

In this work, the multiphysics problems of fluid flow, transport of diluted species, chemical reaction and heat transfer problems were coupled into a single model. The discretization of the partial differential equations (PDEs) from different multiphysics involved in the process, were solved using finite element method (FEM). Numerical solutions were carried out using COMSOL v5.1, where 3D unstructured triangular mesh was used in this work ($8.2E+5$ elements). The mesh size was refined at walls, and at corners of the geometries. In this study, all discretization of the convective terms were performed using higher order discretization scheme to suppress artifacts from numerical diffusion. Two different flow rates were considered namely; 10 ml/min (0.053 m/s) and 15 ml/min (0.08 m/s). The velocities at the inlets and the zero pressure at the outlet were set as a boundary conditions. No slip boundary condition was assumed for fluid flow. In the species transport, normalized concentrations were set to 0 and 1 at the velocity inlets. The solution strategy was to solve the laminar flow model and heat transfer as steady-state mode, and then the species transport as transient state model. The fluid flow modeling follows the methods described by Woldemariam et al. [10]. The mixing efficiency (η) of the model reactors were quantified at the outlet cross section defined by equation (3) in step response test simulations.

$$\eta = \left(\frac{1}{c} \sqrt{\frac{1}{N} \sum_{i=1}^N (c_i - \bar{c})^2} \right) \quad (3)$$

where \bar{c} is the mean concentration field, i^{th} is the concentration for i^{th} cell in the outlet cross sectional area of the reactor, N is the number of nodes inside the cross sectional area. To ensure the high accuracy of the method, more than 400 sampling nodes were considered at the outlet cross section of the reactor. The Eq. (3) is calculated transiently, and thus it is used to describe normalized concentration in the reactor outlet.

The temperatures at the inlets and zero flux at the outlet and nonzero heat flux elsewhere were considered as a heat transfer boundary



Figure 3: R1 reactor and modified type B1.



Figure 4: Stereomicroscopic image inside the B1 reactor wall.

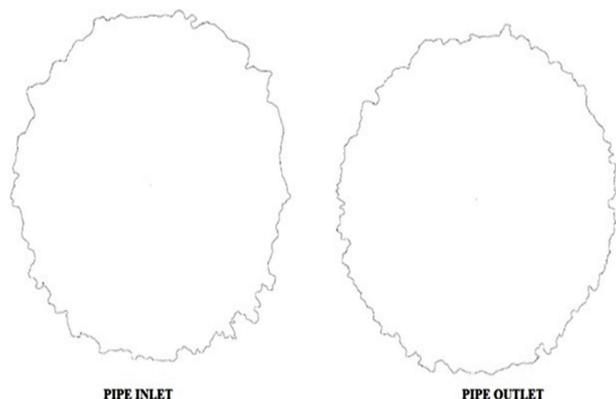


Figure 5: Shadowgraph images from B1 reactor inlet and outlet pipes cross sections.

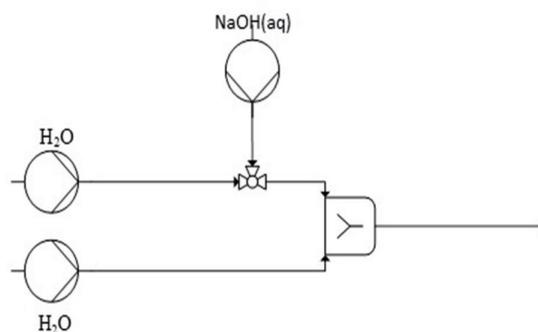


Figure 6: Experimental set-up for step response test.

conditions. The reaction rate constant for the reaction equation (2) was set to $1.3 \times 10^8 \text{ m}^3/(\text{mol s})$. NaOH and HNO_3 concentrations in the inlets were 0.025 mol/L , and the reaction enthalpy was set to 57.3 kJ/mol . The fluid side was used in the reactor modeling and heat losses were not included in simulations due to the near ambient conditions.

Results

Mixing efficiency

The measured step response curves from 0.1 M NaOH-water solution for reactors R1, B1 and K1 are plotted in Figure 7. The H^+ concentrations have been normalized $[\text{H}^+]/[\text{H}^+]_{\text{max}}$ and step response time is converted to space-time normalized t/tR where tR is reactor residence time for generalized presentation of different reactor volumes. B1 and K1 type reactors are more efficient mixers than Roughton-Hartridge based on experimental comparison. The step response comparison of K1 and B1 types experimentally and using CFD simulation are presented in Figures 8 and 9. Maximum Reynolds numbers (outlet pipe) were 106 and 159.

The mixing performances of B1 and K1 reactors based on CFD simulations and experiments were very similar due to the geometric similarity of the reactors which was as expected because of small geometrical changes. The rugosity and surface roughness observed due to slower mixing as simulated and experimental step response curves were compared. The faster mixing in CFD simulations was obtained compared to experiments because of smooth surface models used at reactor walls.

Reactor heat transfer

The surface temperature measurements of reactors B1 and K1 were performed at Reynolds numbers 53 (10 ml/min), 112 (15 ml/min) and 159 (20 ml/min). The thermal image differences could be obtained only at outlet flow 20 ml/min with FLIR infrared thermometry model A655, see Figure 10. The corresponding CFD simulation results were presented in Figure 11. The hot spots due to the instantaneous neutralization were of similar shape and simulated temperature fields correspond the measurements. Interestingly, the temperature in K1 is a little higher and temperature gradients sharper than in B1 mixer which has bigger outlet after the first mixing chamber. The baffle in the first mixing chamber influences in homogenizing acid and basic solutions see B1 reactor case in Figure 11.

Process design concept

We found out based on the previous results, that milliscale reactor design is really an iterative process which is a combination of

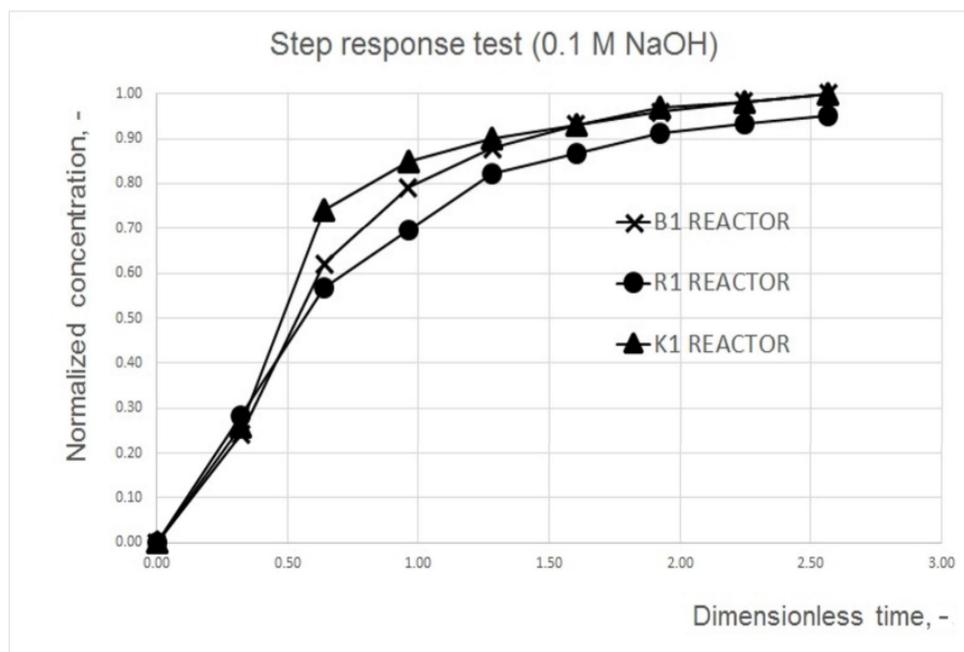


Figure 7: Step response test results for Roughon-Hartridge type (R1) reactor and its modifications B1 and K1. Dimensionless time determined from reactor space-times. Inlet flow rate 10 ml/min.

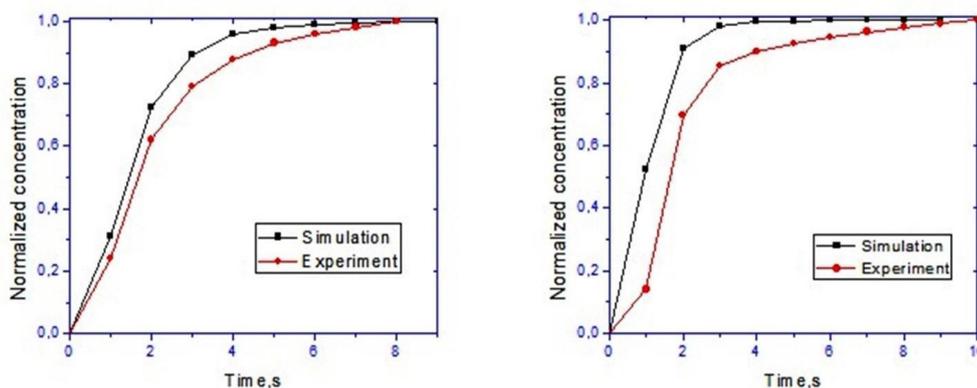


Figure 8: Measured and simulated step response test for B1 reactor. Re-number 106 (left) and Re-number 159 (right).

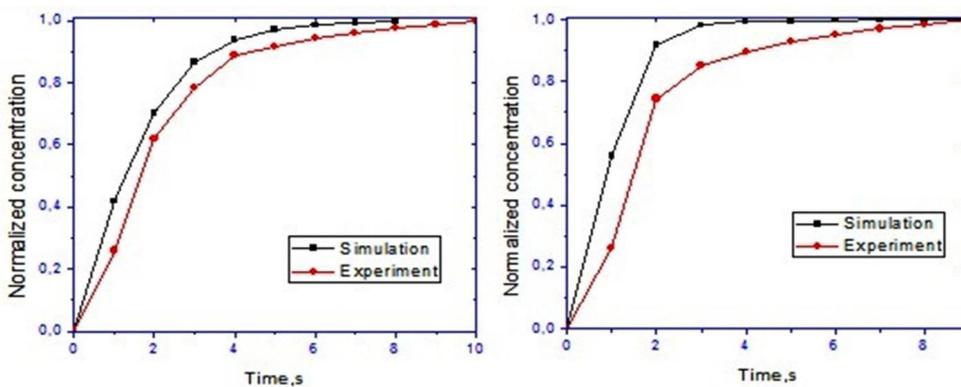


Figure 9: Measured and simulated step response test for K1 reactor. Re-number 106 (left) and Re-number 159 (right).

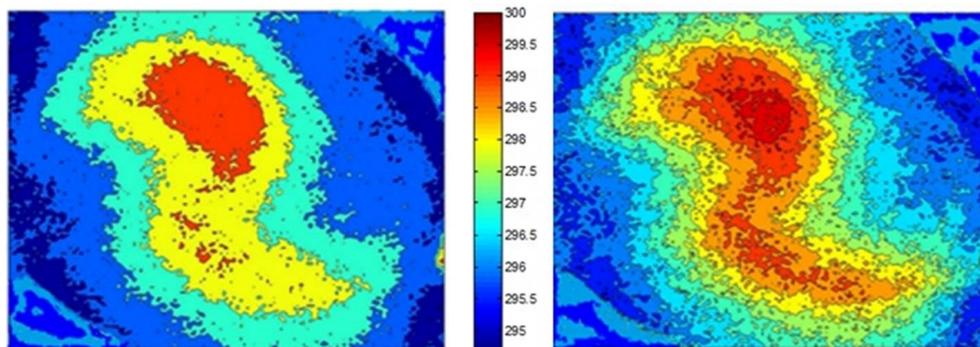


Figure 10: Surface temperature profiles of B1 (left) and K1 (right) reactors from the top with FLIR A655, 640 × 480 pixel resolution, 2% accuracy of the reading scale, the actual image size about 7 × 9 mm.

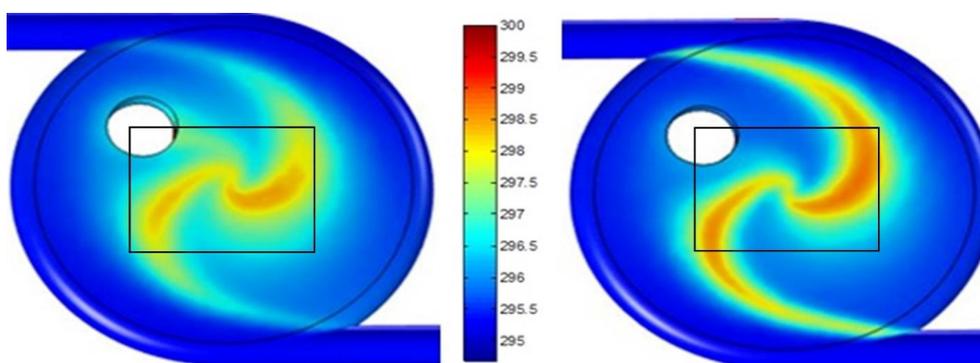


Figure 11: Simulated surface temperatures from the mixer top part using COMSOL Multiphysics v. 5.1. B1 reactor (left) and K1 reactor (right), laminar flow, heat conduction and convection, and first order reaction kinetics with exothermic heat generation. Thermograph image range marked as squares.

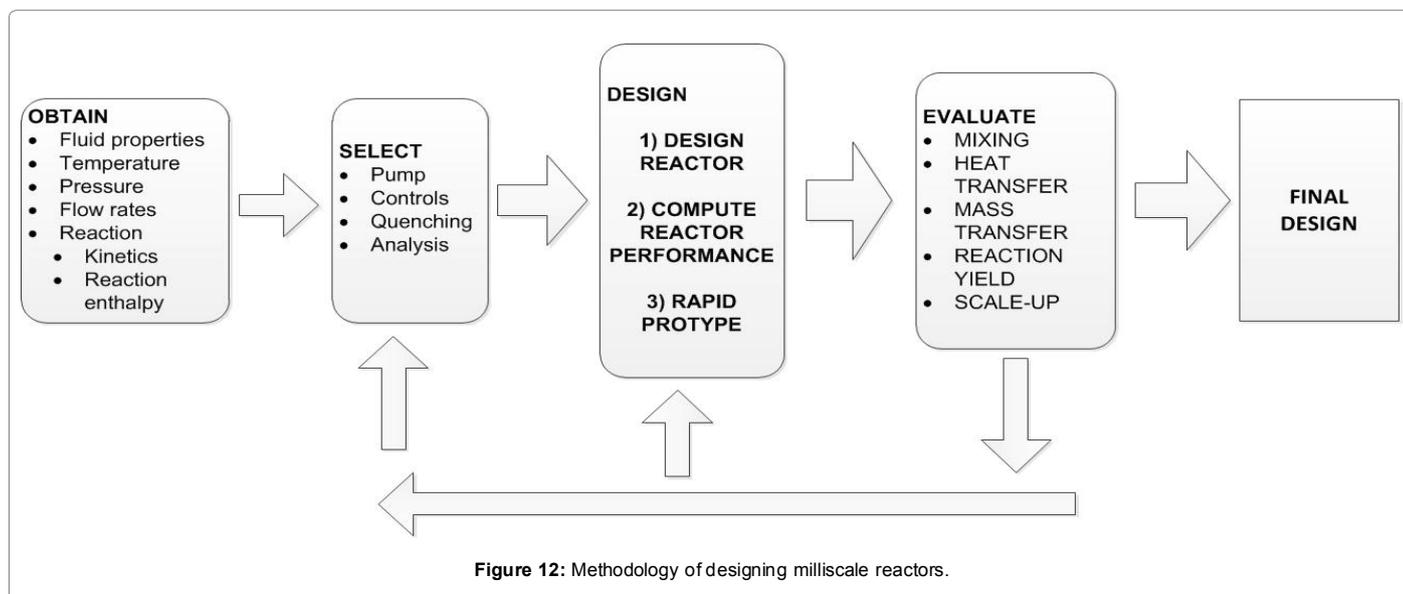


Figure 12: Methodology of designing milliscale reactors.

experimentation and virtual design in novel environments consisting of CFD, additive manufacturing tools and selected experimentation. This enables fast design cycle from scratch to so called mock-up experiments where reactor geometry and process performance (mixing efficiency, heat transfer) can be optimized without necessarily running actual

reactions especially when hazardous or expensive compounds are involved. We propose the milliscale reactor design concept based on the modification of Zhang et al. [25], the methodology of microchemical systems design as described in Figure 12. The iterations after reactor evaluation turn back into design phase or in some cases for selecting

other millireactor parts. The modifications in reactor geometry, like changing the outlet diameter after the first mixing chamber from K1 type to B1 type can be simulated before evaluating experimentally. The additive manufacturing fabrication from drawing to experimental reactor evaluation is relatively fast compared to traditional methods, but it depends on fabrication equipment. The CFD simulation allows to study the phenomena in more detail, and it is a good tool for supporting measurement results.

Conclusion

Additive manufacturing suitability for reactors has been studied based on reactor surface properties. Mixing efficiencies of Hartridge-Roughton reactor and its modifications have been evaluated. Laminar flow model in CFD was used here due to very low flow velocities in narrow channels. The effect of surface roughness and surface rugosity in experimentally determined mixing efficiencies made a clear difference when comparing with the simulation results under the similar reaction conditions. Very likely, the fabricated mixer having a rough and irregular surface acts as a porous wall for liquid solution bleeding during the step response, as also indicated by Woldemariam et al. [10]. Reactor temperature fields were experimentally measured with FLIR A655S IR camera. The heat flow simulations for instantaneous acid-base neutralization reaction matched well with experimentally determined temperature fields. The temperature gradients were sharper and reactor temperature was a bit higher with K1 compared to B1 reactor type. Finally, milli-scale mixer design cycle consisting Computational Fluid dynamics (CFD), additive manufacturing and experimentation was proposed based on the microchemical systems design methodology by Zhang et al. [25].

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