Summary

In the recent years, microreactors have been recognized as a potent technology for enhancing reaction rates at low energy input and simplified scale up issues. The aim of this thesis was to develop and apply microreactors for biocatalytic reactions. In this context, the potential advantages of microreactors were explored for both forms of biocatalysts, isolated enzymes and whole cells.

Fast inactivation of the respective enzyme was a key problem when applying it in aqueous-organic segmented flow microreactors. The large aqueous-organic interfacial area and the strong fluidic forces within the segments mostly accounted for enzyme inactivation. Enzyme immobilization and addition of surfactant to the aqueous phase were explored as possible solutions to overcome fast enzyme inactivation. At an optimal concentration of surfactant (Tween 20), the direct contact of enzymes with the interface was prevented, resulting in almost 100 % recovered enzyme activity as compared to 45% without any medium modification. After stabilizing enzyme activity, the enzymatic performance was evaluated in the segmented flow reactor for 1-heptanol synthesis by using thermostable alcohol dehydrogenase (TADH) and formate dehydrogenase (FDH). An average volumetric productivity of 10.4 $g_{product}\ L_{org}^{-1}\ hr^{-1}$ (90 mM h^{-1}) was obtained in the 0.5 mm (i.d.) capillary microreactor. The study performed revealed that the capillary diameter, flow velocity, and enzyme as well as substrate concentrations were important parameters regarding reactor performance. These parameters govern the interplay between reaction rates and mass transfer rates and for the systematic optimization of the enzymatic microreactor an operational window approach was proposed.

The concept of segmented flow was expanded to whole-cell catalysis by utilizing biofilms as biocatalysts in the microreactor system. The development and maintenance of a stable biofilm without clogging the capillary was achieved by following a three step procedure: i) Development of a first-stage biofilm during single phase flow. ii) Introduction of air segments which leads to a significant detachment of the biofilm. iii) Development of an adapted second-stage biofilm under segmented flow conditions. Based on this concept, two reactor set-ups (aqueous-air) segmented flow biofilm membrane reactor (SFBMR) and (aqueous-air-organic) segmented flow biofilm reactor (SFBR) were developed, and their applicability were investigated for several reactions. For styrene epoxidation to (*S*)-styrene oxide oxygen availability was identified as key limiting parameter in the SFBMR, and by enhancing the air flow rates the volumetric productivity was improved by 4-fold (11 to 46 $g_{sty.\ oxid.}\ L_{tube}^{-1}\ day^{-1}$).

In summary, this thesis shows the development of the segmented flow microreactor technology for enzyme and biofilm catalysed reactions, and emphasizes the potential of this technology for biocatalytic reactions.