Chemistry in Single and Double Emulsion Droplets

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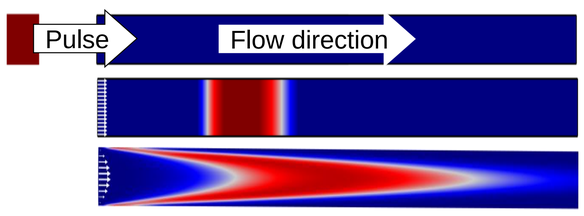
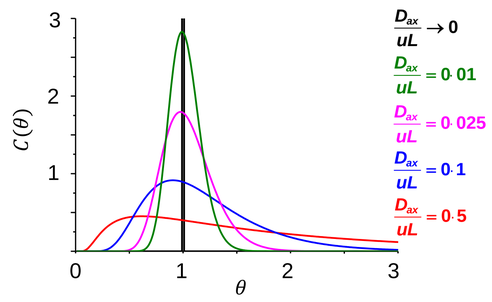
Introduction

The main advantages of chemical processing under micro-flow conditions are well known. Mass transfer problems are commonly solved by the use of micro mixers, which allow mixing faster than the chemical reaction proceeds. Micro heat exchangers ensure e.g. safe processing of chemical reactions with high heat release, or for fast quenching of temperature-sensitive products. In addition, the application of unusual T, p process regimes are advantageous. However, the broadening of the residence time distribution in homogeneous flow due to the developed Poiseuille profile inside micro channels or capillaries should be taken into account. With segmented-based microfluidics, e.g. formed as single or double emulsion droplets, a well-defined and reproducible residence time distribution could be achieved. Good examples for the influence of mixing and flow regime are the selective mono-Wittig reaction on a symmetrical, bifunctional dicarbonyl compound (benzene-1,4-dicarbaldehyde), and the phase-transfer-catalysis (PTC) performed in double emulsion segments with an inert core droplet moves along the phase boundary of the shell segment and continuous phase and acts as an “internal mixer” by shaking or jiggling the reactor..

Residence Time Distribution: Laminar Flow Tube Reactor

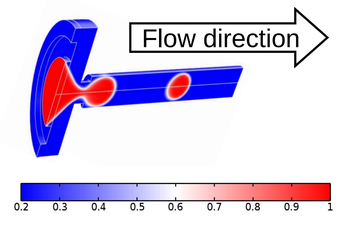


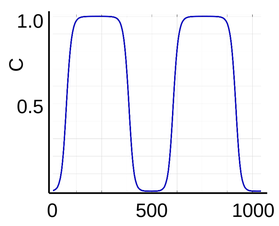
Dispersion becomes dominant for laminar flow in a tube reactors with a small diameter!

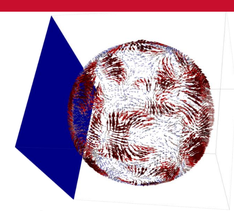


Dispersion number = Mass transport by axial diffusion / Mass transport by convection

Residence Time Distribution: Segmented Flow



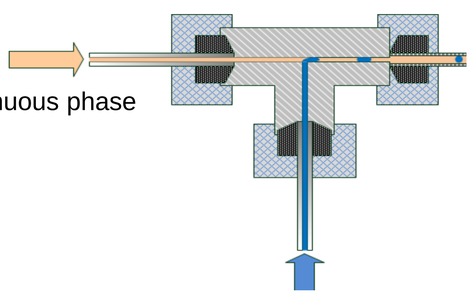




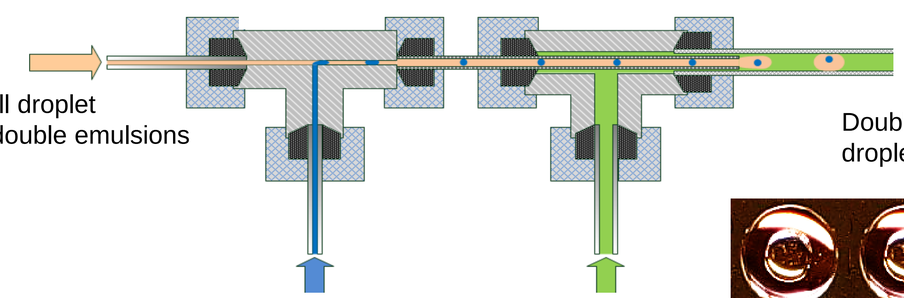
For example:
Droplet diameter: D = 500 µm
Volume: V = 6.54 × 10^{-11} m^3 = 0.0654 µl
Surface area: A = 7.85 × 10^{-7} m^2
Specific surface area: A_s = 12,000 m^2 m^{-3}

Droplet and continuous phase are immiscible.
Droplet acts a an isolated chemical (micro) reactor

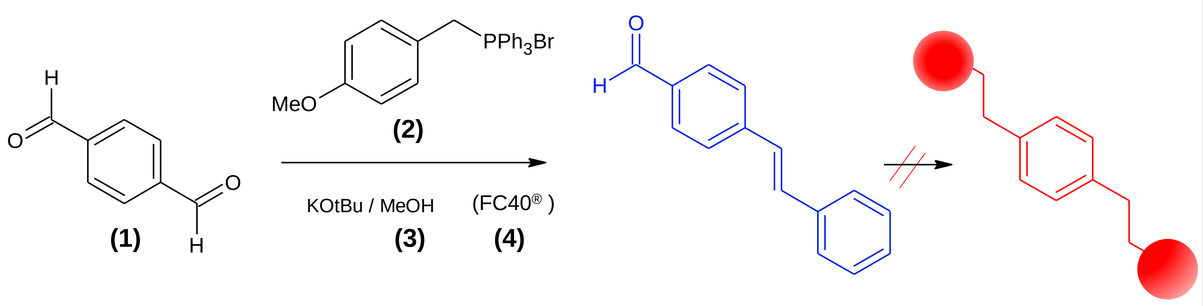
Single Doplet Formation

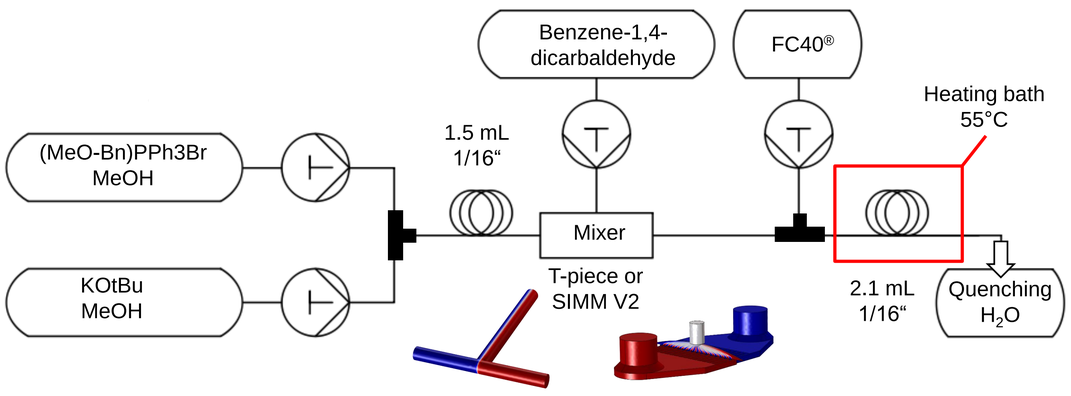


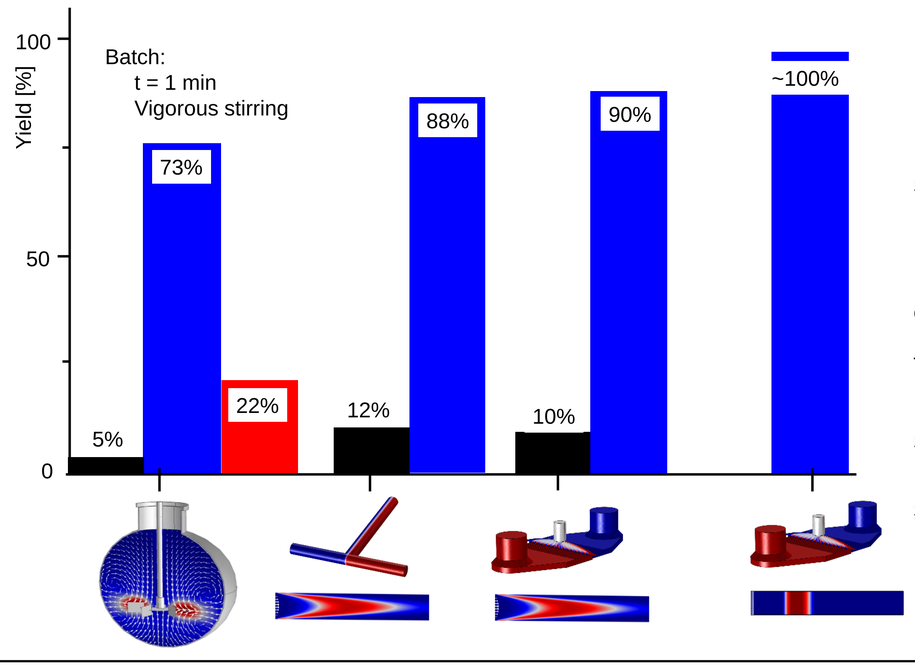
Single and Double Emulsion Doplet Formation



Selective Olefination: WITTIG-Reaction







Stock solutions:
$c_{(1,2)}$ = 50 mMol
$c_{(3)}$ = 100 mMol

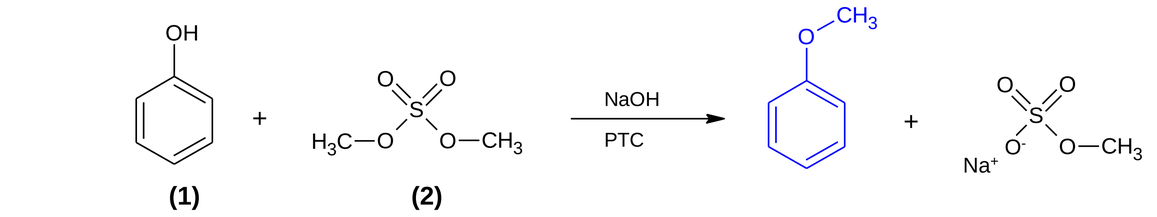
Conti-flow

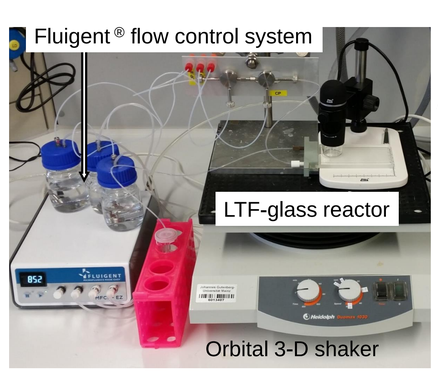
T-piece:
$Q_{(1,2,3)}$ = 330 µl min^{-1}

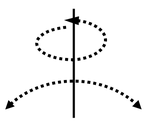
SIMM V2, homogeneous
$Q_{(1,2,3)}$ = 330 µl min^{-1}

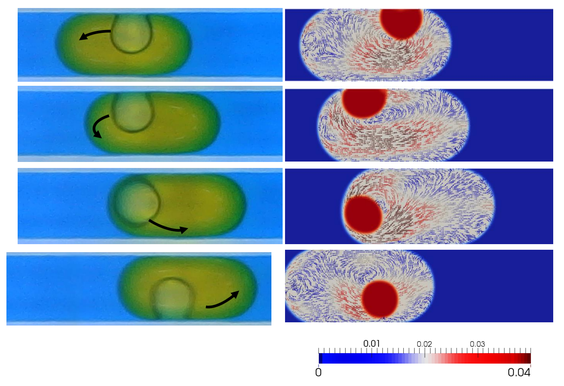
SIMM V2, segmented flow
$Q_{(1,2,3,\ 4)}$ = 250 µl min^{-1}

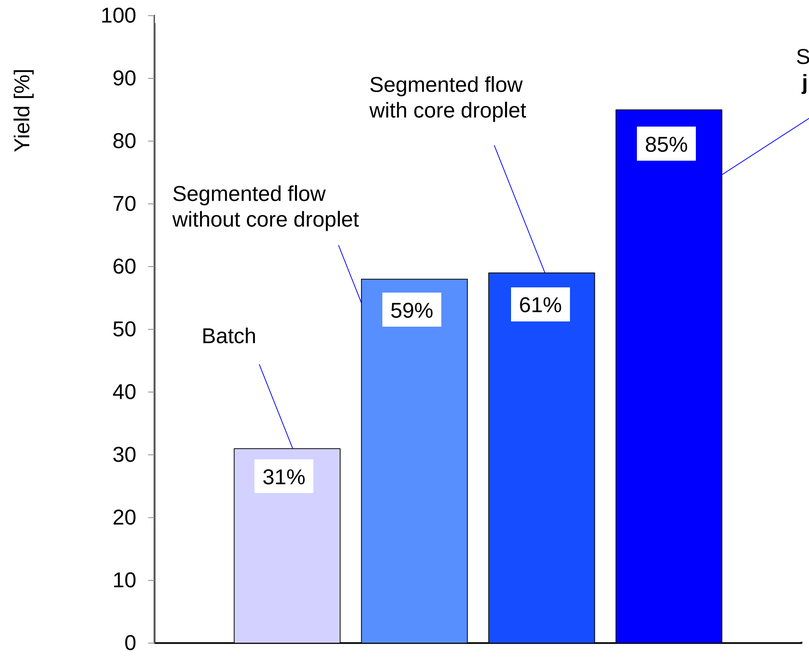
Phase-Transfer-Catalysis (PTC): Etherification











Conti-flow:

Q_{CP} = 50 µl min^{-1}

Q_{DP} = 10 µl min^{-1}

c = 0,2 mol l^{-1}

τ = 21 min

Batch:

c = 0,2 mol l^{-1} each

t = 21 min

Vigorous stirring

Summary

- Dispersion becomes dominant for laminar flow in tube reactors with a diameter in the µm or mm range! Laminar flow in tube reactors with small diameters (mm to µm) increases residence time distribution Residence time is no longer valid!
- Mass transfer can be enhanced by forced mixing within segment by jiggling an internal droplet, e.g. for PTC reactions
- Selective Wittig olefination can only be realized by segmented flow conditions successfully

Solution : Performing chemical reactions in segments or droplets in continuous flow

References

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