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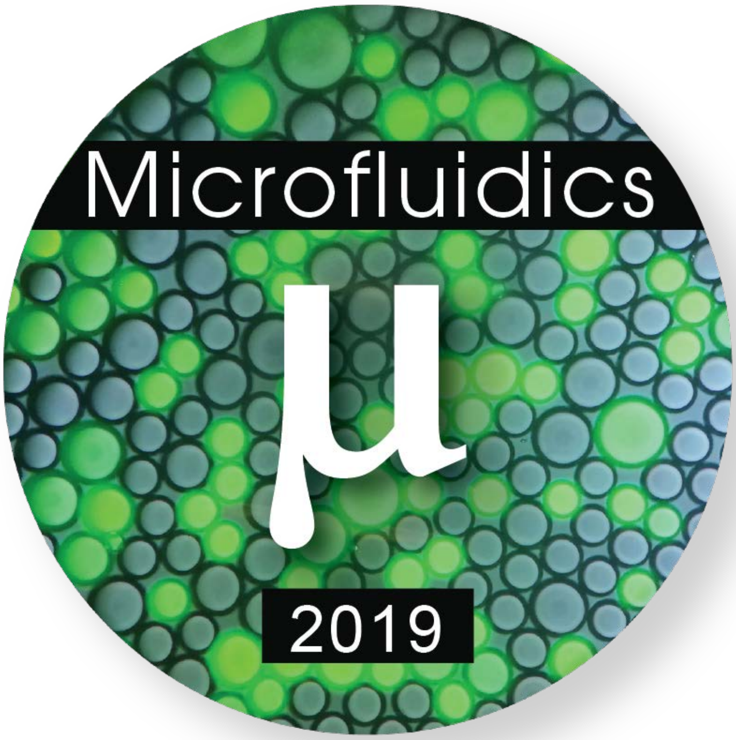
# Abstract volume

## From laboratory tools to process development



Rueil-Malmaison ■ France
13 - 15 November 2019

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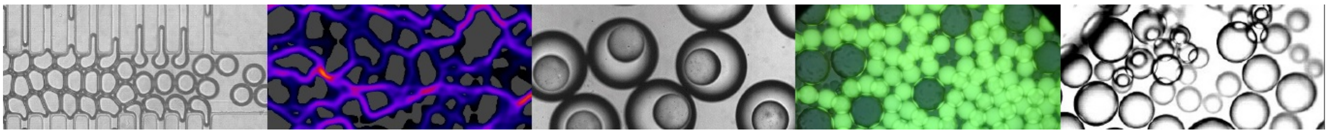
## Context and objectives

After two decades of development, microfluidics is now pushing back the boundaries to tackle a range of industrial challenges, including high-throughput experimentation, on-chip analysis, extreme conditions (pressure, temperature, etc.) and environmental footprint limitation.

Microfluidics 2019 will examine these topics in detail.

The sessions will focus on:
>> Fluids and flow characterization
>> Fluid separation and on-chip analysis
>> Synthesis and performance monitoring
>> New technologies for the environment and alternative energies



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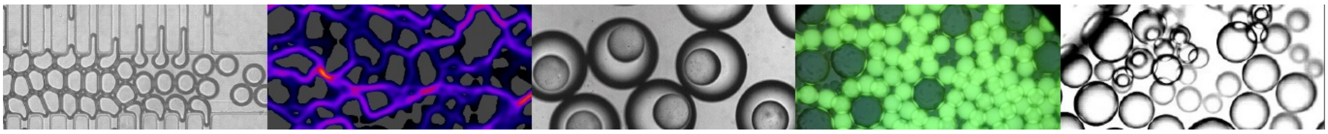


# PROGRAM

## Wednesday 13 November

9:00 *Registration and welcome coffee*

9:30 **Opening of the conference**
M. Marsiglia and C. Marlière (Microfluidics 2019 scientific correspondents, IFP Energies nouvelles, France)

## 9:30 - 12:30 TUTORIALS

9:30 **Miniaturized on-line analysis**
N. Caillol (Axel'One, France)

10:30 **Novel microfluidic devices for fluid and material characterization**
A. Lindner (ESPCI Paris, France)

11:30 **Microfabrication for extreme conditions**
S. Marre (ICMCB, France)

12:30 *Lunch*

14:00 **Welcome address**
X. Longaygue (IFPEN Scientific Division, France)

## 14:05 - 17:00 SESSION 1: FLUID SEPARATION AND ON-CHIP ANALYSIS

14:05 **Keynote address**
R. Lammertink (Univ. of Twente, Netherlands)

14:50 **An unconventional microfluidic strategy for the separation of chiral amino-acids**
A. Perro[1], S. Assavapanumat[1,2] N. Sojic[1], P. Garrigue[1], B. Goudeau[1], T. Yutthalekha[2], C. Wattanakit[2], A. Kuhn[1] (1 Univ. of Bordeaux, CNRS, ISM, Bordeaux INP, France; 2 Vidyasirimedhi Institute of Science and Technology, Thailand)

15:15 *Coffee break*

15:45 **Towards microfluidic measurements of colloidal dispersions equations of states**
C. Keita, J.-B. Salmon (CNRS, Solvay-LoF, Univ. of Bordeaux, France)

16:10 **Two-phase microfluidic flow in hydrodynamic filtration for continuous particle sorting**
K. Yoon[1,2], H. W. Jung[2], M.-S. Chun[1] (1 Korea Institute of Science and Technology ,2 Korea Univ., Republic of Korea)

16:35 **Dynamics and mass transfer of bubbles in microchannels**
J. Rivero-Rodrigues, B. Scheid (Univ. libre de Bruxelles, Belgium)

## 17:00 - 19:30 POSTER SESSION

*Pitch, poster presentation and networking refreshment break*

19:30 *End of the poster session*

## Thursday 14 November

## 9:00 - 12:00 SESSION 2: FLUIDS AND FLOW CHARACTERIZATION

9:00 **Influence of the inlet flow profile on the channel flow stability after a sudden expansion**
R. Debuysschère, B. Rimez, L. Siconolfi, F. Gallaire, B. Scheid (Univ. libre de Bruxelles, Belgium)

9:25 **Surfactant effects on droplet formation in microfluidic systems**
M. Kalli, E. Roumpea, S. H. (B.) Hue, P. Angeli (UCL, UK)

9:50 **Characterisation of viscoelastic properties using particle migration in confined Poiseuille flows**
A. Naillon, X. Salas-Barzola, W. Chèvremont, C. De Loubens, H. Bodiguel (Univ. Grenoble Alpes, CNRS, Grenoble INP, LRP, France)

10:15 *Coffee break*

10:45 **Experimental microfluidics to improve mechanistic understanding of multiphase and reactive flow in porous media**
S. Roman[1], C. Soulaine[2] (1 Univ. of Orléans, CNRS, BRGM, 2 BRGM, France)

11:10 **A microfluidic investigation of oil mobilization during improved oil recovery**
M. Saadat[1], M. Dudek[1], T. Ho[2], P. A. Tsai[2], G. Øye[1] (1 Norwegian Univ. of Science and Technology, Norway; 2 Univ. of Alberta, Canada)

11:35 **Low salinity water flooding in a PDMS micro-model**
N. K. Karadimitriou[1], H. Mahani[2], H. Steeb[1], V. Joekar-Niasar[3] (1 Stuttgart Univ., Germany; 2 Shell Global Solutions International B.V., Netherlands; 3 Univ. of Manchester, UK)

12:00 *Lunch*

## 13:30 - 17:50 SESSION 3: SYNTHESIS AND PERFORMANCE MONITORING

13:30 **Keynote address: Microchannel reactors for energy related applications – Fuel synthesis, fuel processing and power-to-gas**
G. Kolb (Eindhoven Univ. of Technology, Netherlands)

14:15 **Process intensification for the synthesis of fluorescent organic nanocrystals by microfluidics supercritical antisolvent**
T. Jaouhari[1], G. Aubert[1], O. Nguyen[1], T. Tassaing[2], S. Fery-Forgues[3], A. Erriguible[1,4], C. Aymonier[1], S. Marre[1] (1 CNRS, Univ.of Bordeaux, Bordeaux INP, ICMCB, 2 CNRS, Univ. of Bordeaux, Bordeaux INP, ISM, 3 SPCMIB, Univ. Paul Sabatier, 4 CNRS, Univ. of Bordeaux, Bordeaux INP, I2M, France)

14:40 **A tubular nucleation process device for continuous crystallization with polymorph selection of small organic molecules**
B. Rimez (Univ. libre de Bruxelles, Belgium)

15:05 *Coffee break*

15:30 **Gas-liquid flow characterisation and mass transfer study in a microreactor for oligomerization catalyst testing**
M. Kamaleddine[1], C. Bonnin[1], T. Michel[1], L. Brunet-Errard[1], J. Aubin[2], L. Prat[2] (1 IFP Energies nouvelles, 2 Univ. of Toulouse, CNRS, France)

15:55 **Effect of flocculants on on-chip coalescence of crude oil droplets in produced water**
M. Dudek[1], A. Wehrle[2], G. Øye[1] (1 Norwegian Univ. of Science and Technology, Norway; 2 ESICAEN, France)

16:20 **Development of a commercially-viable system for the automatic generation of high-throughput monodisperse microdroplets**
R. Vasiliauskas[1], A. Vigne[1], G. V. Casquillas[1] (1 Elvesys innovation center, France)

16:45 *Coffee break*

17:00 **Microfluidics applied to the detection of insoluble hydrocarbons for the oxidation monitoring of fuels and biofuels**
E. Bordes, C. Dalmazzone, L. Starck, D. Frot, M. Alves-Fortunato
(IFP Energies nouvelles, France)

17:25 **Development of plasma-activated reactions in a liquid-gas micro-reactor**
P.-A. Royoux, S. Ognier, M. Zhang, C. Thomas, M. Tatoulian (Chimie ParisTech, PSL University, CNRS, Institut de Recherche de Chimie de Paris, France)

17:50 ***End of the presentations***

18:00 *Departure to the cocktail party*

18:30 ***Cocktail party at the Domaine de Vert-Mont***

21:00 ***Bus transfer*** *from the Domaine de Vert-Mont to the hotels in Rueil then to Place Charles de Gaulle-Étoile in Paris*

## Friday 15 November

### 9:00 - 12:05 SESSION 4: NEW TECHNOLOGIES FOR THE ENVIRONMENT AND ALTERNATIVE ENERGIES

9:00 **Keynote address**
D. Sinton (Univ. of Toronto, Canada)

9:45 **Emergence of microflow based photocatalytic reactors for selective oxidation of benzyl alcohol to benzaldehyde**
J. C. Colmenares, V. Nair, S. Rashmi Pradhan (Polish Academy of Sciences, Poland)

10:10 *Coffee break*

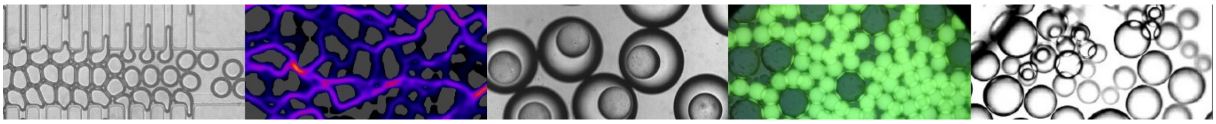
10:30 **Optimizing energy production in an osmotic engine: adjustment of hydrogel-particles size by microfluidic glass capillary device**
A. Jangizehi, L. Arens, C. Fengler, M. Wilhelm (Karlsruhe Institute of Technology, Germany)

10:55 **High-pressure microfluidic approaches to study $CO_2$ bioconversion within deep saline aquifers**
A. Cario, M. Perroux, C. Fauveau, O. Nguyen, C. Lecoutre, Y. Garrabos, S. Marre (CNRS, Univ. Bordeaux, ICMCB, France)

11:20 **Keynote address**
D. Weitz (Harvard Univ., USA)

12:05 *Lunch*

| | |
|---|---|
| 13:30 | START-UPPERS SHARINGS<br>L. Bocquet (ENS, France), L. Boitard (MilliDrop, France), F. Hamber (Fluigent, France) |
| 14:30 | BRING HOME LEARNINGS<br>By A. Lindner (ESPCI Paris, France) and P. Maestro (Solvay, France) |
| 14:50 | ***Closing address** by the Organization Committee* |
| 15:00 | *End of the conference* |



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# ABSTRACTS
# OF THE ORAL
# PRESENTATIONS

Abstracts are listed following the order of the program

The abstracts are published in their original format, i.e. the format in which they were sent to the Scientific Committee.

# An unconventional microfluidic strategy for the separation of chiral amino-acids

**Adeline Perro[1], Sunpet Assavapanumat[1,2], Neso Sojic[1], Patrick Garrigue[1], Bertrand Goudeau[1], Thittaya Yutthalekha[2], Chularat Wattanakit[2] and Alexander Kuhn[1]**

1. Univ. de Bordeaux, CNRS, ISM, UMR 5255, Bordeaux INP, Pessac, France.
2. Department of Chemical and Biomolecular Engineering, School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong, Thailand

## ABSTRACT

Chiral separation is of crucial importance in the pharmaceutical industry to obtain a single enantiomer because the undesirable chiral compound exhibits a different biological activity in the human body. For example, L-tryptophan (L-Trp) is well-known as natural essential amino acid, involved in protein synthesis and as precursor of the neurotransmitter serotonin, whereas the mirror enantiomer, D-tryptophan (D-Trp), is used in pharmaceutical applications as an intermediate in the synthesis of peptide antibiotics. Recently, chiral imprinted mesoporous platinum films have been successfully prepared and employed as working electrodes for chiral electroanalysis[1]. In addition, the chiral-imprinted mesoporous metal matrix has been used for chiral electrosynthesis leading to very high enantiomeric excess of over 90%[2]. Here, we propose the integration of these high surface area electrodes as chiral stationary phases in a hyphenated device for the separation of enantiomers under electrochemical potential control.[3] The device, constituted of a tryptophan-encoded platinum film is coupled with UV spectroscopic characterization, allowing to analyse in situ the base-line separation efficiency of the injected racemate. This approach constitutes a promising strategy in the frame of chiral discrimination technologies.

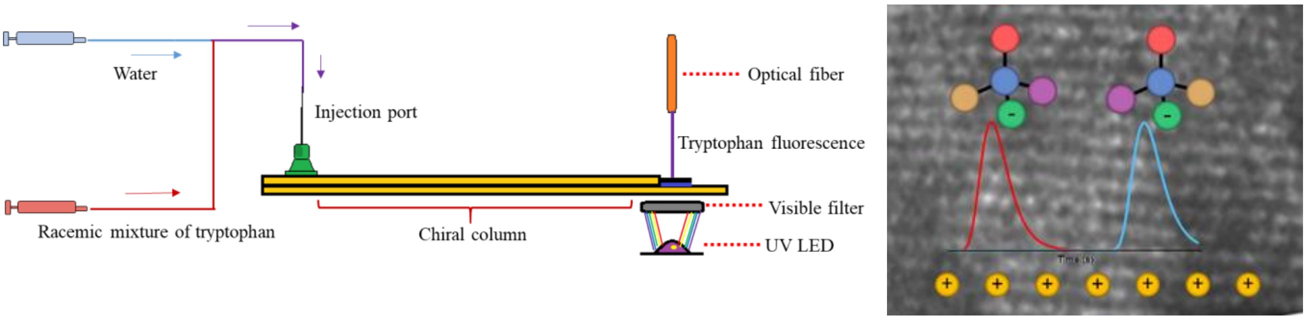


Figure 1. A) Separation and detection scheme of a racemic tryptophan mixture in the microfluidic device integrating a tryptophan-encoded mesoporous platinum film as stationary phase in the microchannel. B) Schematic representation of the racemate separation exploiting a mesoporous platinum phase.

## References:

1. Wattanakit, C.; Come, Y. B.; Lapeyre, V.; Bopp, P. A.; Heim, M.; Yadnum, S.; Nokbin, S.; Warakulwit, C.; Limtrakul, J. and Kuhn A. (2014) Enantioselective recognition at mesoporous chiral metal surfaces. *Nat Commun*, 5, 3325.
2. Wattanakit, C.; Yutthalekha, T.; Asssavapanumat, S.; Lapeyre V. and Kuhn, A. (2017) Pulsed electroconversion for highly selective enantiomer synthesis, *Nat Commun*, 8, 2087.
3. Assavapanumat, S.; Yutthalekha, T.; Garrigue, P.; Goudeau, B.; Lapeyre, V.; Perro, A.; Sojic, N.; Wattanakit C. and Kuhn, A. (2019) Potential-Induced Fine-Tuning of the Enantioaffinity of Chiral Metal Phases, *Angew Chem Int Ed*, 58 (11), 3471.

# TOWARDS MICROFLUIDIC MEASUREMENTS OF COLLOIDAL DISPERSIONS EQUATIONS OF STATES

**Camille KEITA[1], Jean-Baptiste SALMON[1]**

[1]CNRS, Solvay-LoF, UMR 5258, University of Bordeaux F-33600 Pessac, France

We first report the fabrication of poly(ethylene glycol) diacrylate (PEGDA)-based microfluidic chips, integrating highly permeable nano-porous membranes inside microchannels for the investigation of ultra-filtration processes at the nanoliter scale.

More precisely, after fast prototyping of PEGDA chips, a maskless UV projection device is used to photo-pattern PEGDA-based hydrogel solutions within the channels. This set-up makes possible the polymerization of in-situ membranes with a spatial resolution of a few microns. These membranes withstand transmembrane pressure drops up to several bars owing to their strong anchoring on the chip walls. We also perform in-situ Darcy permeability measurements of these membranes. Permeability can be tuned by adjusting the deposited exposure energy and/or the hydrogel formulation (namely PEG chains playing the role of porogen agents). This methodology [1] allows us to integrate strongly anchored membranes with permeabilities ranging from $K = 10$ to 50 nm$^2$, corresponding to typical porosities $l \sim K^{1/2}$ in the 3 to 7 nm range, in line with ultra-filtration processes.

We are currently using these chips to measure the equation of states of charged colloidal dispersions (e.g. nano-latexes or nano-silica), i.e. the relation between osmotic pressure and colloids concentration. We are indeed able to compress micro-dialysis sacks containing colloids within a micro-channel ended by the nano-porous membrane, see Figure 1. A tangential flow downstream the membrane also imposes the chemical potentials, as the macroscopic tank of usual osmotic compression experiments making use of milliliter dialysis sacks immersed in larger baths. We expect that the small volumes involved in such experiments (typically 0.1 to 5 nL), combined with the possibility of in-situ observations and high throughput screening, will open the way to fast and accurate microfluidic measurements of equations of states of complex fluids, a highly tedious task at macroscopic scale.

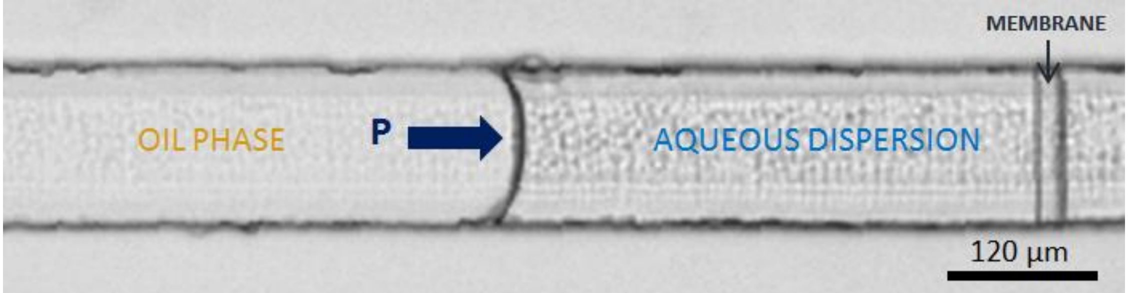


Figure 1: Ludox silica nanoparticles dispersion (AS40) within a micro-dialysis sack compressed at a pressure P against a nano-porous membrane. The width of the channel is 120 µm and its height is 45 µm. The thickness of the membrane is 20 µm.

**References:**

[1] J. Decock, M. Schlenk, J.-B. Salmon (2018). In-situ photo-patterning of pressure resistant hydrogel membranes with controlled permeabilities in PEGDA microfluidic channels. *Lab on a Chip 18*, 1075.

# TWO-PHASE MICROFLUIDIC FLOW IN HYDRODYNAMIC FILTRATION FOR CONTINUOUS PARTICLE SORTING

**Kyu YOON[1,2], Hyun Wook JUNG[2], Myung-Suk CHUN[1,*]**

[1]National Agenda Research Division, Korea Institute of Science and Technology (KIST),

Seoul 02792, Republic of Korea

[2]Department of Chemical and Biological Engineering, Korea University, Seoul 02841,
Republic of Korea

## Introduction

Based on the benefits of microfluidics, various sorting methods of suspended rigid or deformable particles have been developed. As one of the flow-based passive sorting techniques, the hydrodynamic filtration (HDF) has shown to effectively and continuously separate into different sized subpopulations from particle dispersions [1,2].

## Problem Formulation

We have investigated HDF with two-phase flow of either Newtonian or non-Newtonian fluid by extending our previous works [3], due to its importance in both fundamental researches and various industrial applications. The model framework was examined for the rational design of particle sorting, by considering the complete analysis of laminar flow and complicated networks of main and multiple branch channels. The flow fraction, which is relevant to the hydrodynamic focusing, can be defined as a ratio between main and side flows. As the objective parameters for optimum design, both the number of branch channels and each length of individual branches were decided for different viscosity ratios between main and side flows.

## Results

As the viscosity ratio increases, the interfacial position extends towards the side stream and the flow fraction into the branch becomes decreasing. As a result, the number of branches increases distinctly so that a channel with the individual length results in efficient design of microfluidic-chip being operated under the same throughput condition. Pursuing its justification, pressure drop, average fluid velocity, and the ratio of flow fraction at each branch point were quantified, and validated with particle tracing simulations [Fig.1]. The flow fraction of Carreau type non-Newtonian solution is further examined with variations of power-law index and relative zero-shear viscosity. Our model framework can serve as a useful basis for practical design and enhancement of sorting efficiency.

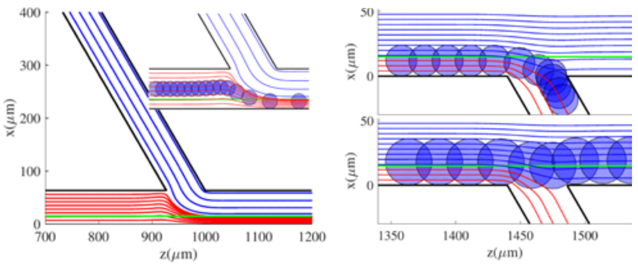


Fig. 1. Streamlines and particle trajectory in main/side channel node (left) and first branch region (right) with H/W = 2.5. Side flow, main flow, and $W_C$ (= 15 μm) are represented by blue, red, and green lines. Small particle with radius 12 μm and large particle of 18 μm are shown separately.

## References:

1) Yamada, M. and M. Seki (2005). Hydrodynamic filtration for on-chip particle concentration and classification utilizing microfluidics. *Lab Chip 5*, 1233.
2) Fouet, M. et al. (2016). Filter-less submicron hydrodynamic size sorting. *Lab Chip 16*, 720.
3) Jung, H., M.-S. Chun and M.-S. Chang (2015). Sorting of human mesenchymal stem cells by applying optimally designed microfluidic chip filtration. *Analyst 140*, 1265.

# DYNAMICS AND MASS TRANSFER OF BUBBLES IN MICROCHANNELS

**Javier RIVERO-RODRIGUES and Benoit SCHEID**

*TIPS C.P.165/67, Université Libre de Bruxelles, Av. F. Roosevelt 50, 1050 Brussels, Belgium*

This talk will discuss the dynamics of a train of unconfined droplets or bubbles flowing in microchannels. We show how inertial and deformation-induced migration forces both play a crucial role in determining the transverse equilibrium position of the bubbles. In addition, we show how the bubble velocity is affected by surface rigidification due to the presence of surfactants. All these effects can influence the surrounding flow structure, which is in turn determinant for the mass or heat transfer process in case of dissolution. Therefore, by varying the Péclet number over eight decades, we identify five different mass or heat transfer regimes, as illustrated in the figure below.

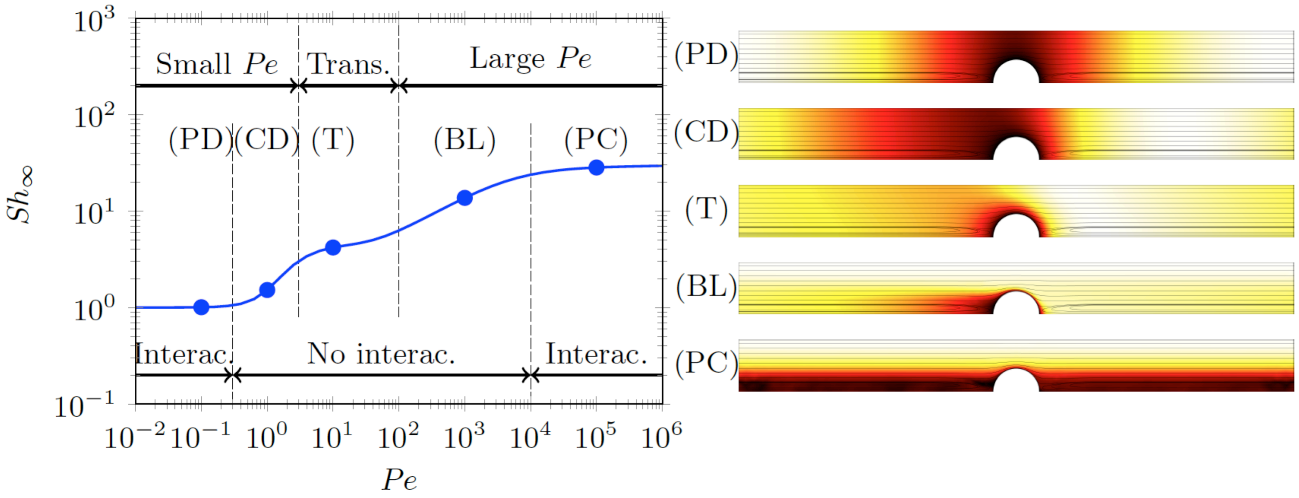


Figure 1: Influence of the Péclet number (Pe) on the Sherwood number (Sh) for bubbles with stress-free interfaces. Regimes are classified depending on the Pe number and the interaction between bubbles. Colormaps represent the dissolved gas concentration in the liquid (dark red corresponds to saturation) for given Pe number denoted by in the different regimes: (PD) pure dffusion, (CD) convection-diffusion, (T) transition, (BL) boundary layer and (PC) pure convection. The flow field is represented by the streamlines.

## References:

Rivero-Rodrigues, J. and Scheid, B. (2018). Bubble dynamics in microchannels: inertial and capillary migration forces. *Journal of Fluid Mechanics 842*, 215-247.
Rivero-Rodrigues, J. and Scheid, B. (2019). Mass transfer around flowing bubbles in cylindrical microchannels. *Journal of Fluid Mechanics (In Press)*.

# Influence of the inlet flow profile on the channel flow stability after a sudden expansion

**DEBUYSSCHERE Robin, RIMEZ Bart, SICONOLFI Lorenzo, GALLAIRE François, SCHEID Benoit**

Université Libre de Bruxelles , Belgium

In the context of continuous crystallisation process, it has been experimentally shown that introducing a flow restriction in tabular micro-channel influences the nucleation rate, hence the production of crystals such as pharmaceutical ingredients [1]. In order to fully comprehend those restriction effects, such systems were modelled.

In a channel flow with a sudden-expansion, as for 3D tubular flow [2,3] than for 2D planar flow [4,5,6,7], it is known that increasing the Reynolds number beyond a critical value $Re_c$ induces a symmetry breaking between the recirculation zones (pitchfork bifurcation). The linear stability of the symmetric steady solution enables to determine efficiently the $\mathrm{Re}_c$ and thus explore the influence of the expansion ratio (*ER*).

In this study, we investigate the behaviour of the flow after 2D sudden expansions while varying the ER and the inlet flow profile. Indeed, it is known for straight channel that flow profiles deviating from the Poiseuille induces an increase of the critical Reynolds number for the appearance of instabilities [8]. As far as our knowledge, the influence of such deviating profiles at the inlet of a sudden expansion has never been studied. In this work we focus on the transition profiles between the plug and the Poiseuille flow, such transitions could be reached for flow after sudden constriction [9] such as those used in our previous researches [1].

The modelling shows that an increase of the ER induces a decrease of the $\mathrm{Re}_c$ as for a Poiseuille flow than for other transition profiles. It also shows that imposing a plug flow at the inlet gives the highest $\mathrm{Re}_c$ and the flow the recirculation zones are the shortest, whatever the value of ER. We show that theses results can be rationalized using simple convection-diffusion arguments.

**References:**

[1] Bart Rimez, Robin Debuysschère, Jennifer Conté, Edith Lecomte-Norrant, Christophe Gourdon, Patrick Cognet, and Benoit Scheid (2018) Continuous-Flow Tubular Crystallization To Discriminate between Two Competing Crystal Polymorphs. 1. Cooling Crystallization. *Crystal Growth & Design*, 18(11):6431–6439.

[2] T. Mullin, J. R. T. Seddon, M. D. Mantle, and A. J. Sederman (2009) Bifurcation phenomena in the flow through a sudden expansion in a circular pipe. *Physics of Fluids*, 21(1):014110.

[3] E. Sanmiguel-Rojas and T. Mullin (2012) Finite-amplitude solutions in the flow through a sudden expansion in a circular pipe. *Journal of Fluid Mechanics*, 691:201–213.

[4] Andrea Fani, Simone Camarri, and Maria Vittoria Salvetti (2012) Stability analysis and control of the flow in a symmetric channel with a sudden expansion. *Physics of Fluids*, 24(8):084102.

[5] Francine Battaglia, Simon J. Tavener, Anil K. Kulkarni, and Charles L. Merkle (1997) Bifurcation of Low Reynolds Number Flows in Symmetric Channels. *AIAA Journal*, 35(1):99–105.

[6] Francine Battaglia and George Papadopoulos (2005) Bifurcation Characteristics of Flows in Rectangular Sudden Expansion Channels. *J. Fluids Eng,* 128(4), 671-679

[7] D. Drikakis. (1997) Bifurcation phenomena in incompressible sudden expansion flows, Physics of Fluids, 9(1):76–87.

[8] Merle C. Potter. (1971) Linear Stability of Turbulent Flow Profiles. *Physics of Fluids*, 14(7):1323.

[9] F. Durst and T. Loy. (1985) Investigations of laminar flow in a pipe with sudden contraction of cross sectional area. *Computers & Fluids*, 13(1):15–36.

# SURFACTANT EFFECTS ON DROPLET FORMATION IN MICROFLUIDIC SYSTEMS

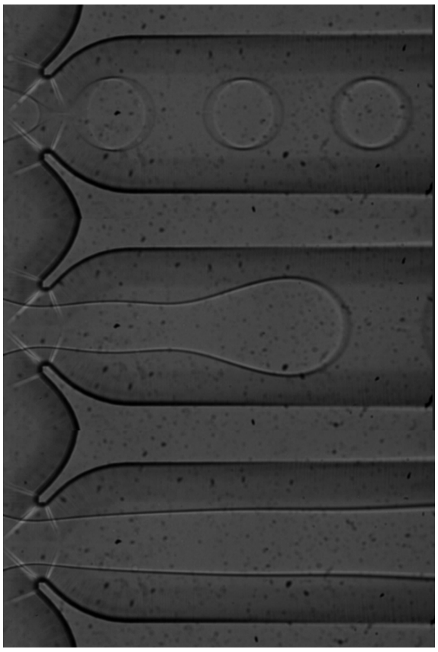
**Maria Kalli, Evangelia Roumpea, Seng Hoe (Billy) Hue, Panagiota Angeli***

ThAMeS Multiphase, Department of Chemical Engineering, UCL
Torrington Place, London WC1E 7JE, UK

## Abstract

Multiphase flows in microscale channels allow manipulation of the flow patterns and offer high heat and mass transfer rates. Surfactants are commonly used in a wide variety of applications from emulsification to DNA extraction and inkjet printing, and their effects on droplet formation is of great importance. In this study, the formation of aqueous droplets in an organic continuous phase was studied experimentally using a flow-focusing microchannel in the presence of a range of surfactants. A two-colour PiV system was used to identify changes in the interface during the drop formation and to obtain velocity fields in both phases. A low viscosity silicone oil (0.0046 Pa s) was used as the continuous phase and a mixture of 48% w/w water and 52% w/w glycerol was the dispersed phase. Two cationic surfactants, $C_{12}TAB$ (50 mM) and $C_{16}TAB$ (5 mM) were added in the aqueous phase, at concentrations above the CMC values. An ionic surfactant, SDS (1 mM) was also used to compare the effects on the drop formation. Four regimes of drop formation were identified, namely squeezing, dripping, jetting and threading, whose boundaries changed when the surfactants were present. For all solutions studied, three distinct drop formation stages were identified, expansion, necking and pinch-off. Smaller drops were observed at higher concentrations of surfactant, as expected. The dynamics of surfactant adsorption can play a vital role in the drop formation process and were studied. The effect of dynamic interfacial tension at the characteristic time scale of drop formation becomes more significant at for surfactants with low CMC values, which suggests increased surfactant activity. Using this information, the differences between surfactant systems during the transitions between drop formation stages could be explained.

* Corresponding author.
E-mail address: p.angeli@ucl.ac.uk (P. Angeli).



**References:**

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# Characterisation of viscoelastic properties using particle migration in confined Poiseuille flows

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Flows of particles in viscoelastic liquids are involved in geological, biological or industrial applications. Recently, studies have revealed that the particle motion is affected by fluid elasticity. In particular, transverse migration of particles, i.e. a motion across streamlines, is reported due to a gradient of shear rate around particles [1]. The fine comprehension of this phenomena should allow us to manipulate and control the particle motion in confined flows, and reciprocally to characterize the viscoelastic properties of the carrying solution.

To this goal, we have developed a technic to recover the 3D trajectories of particles using a standard optical microscope. It is based on a 2-dimension particle tracking velocimetry, coupled with the detection of the particle distance to the focal plane. Thus, we have managed to measure the transverse particle migration kinetics in confined Poiseuille flows of dilute polymer solutions [2]. The migration velocity is correlated with direct measurements of rheological properties (e.g. viscosity, relaxation time). The fluid being weakly elastic, measurements with standard rotational rheometer are not efficient and we have used the slow retraction method of CaBER experiment which allows us to measure fluid relaxation time smaller than 1 ms.

Experimental data are compared with theoretical prediction developed by Ho et Leal [3] and Brunn [4] for solutions with constant viscosity. Same scaling law has been found but with a migration velocity 30% slower than the predicted one. Then, we are expanding our measurement in shear-thinning solution, for which it appears that the dynamics of particle migration is very much affected by the non-linear rheology.

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# Experimental Microfluidics to Improve Mechanistic Understanding of Multiphase and Reactive Flow in Porous Media

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There is strong interest in imaging and numerical modeling of multiphase and reactive flow at the pore scale with application to reservoir engineering, subsurface hydrology, CO2 sequestration. The hydro-geochemical dynamics at the pore scale, however, remain relatively unknown but influence macroscale behaviors considerably. Accordingly, this work focuses on pore-scale mechanisms using micromodels. Such micromodels have the pore network pattern and pore sizes of a real rock or idealized medium. Importantly, these micromodels permit direct, high-magnification, time-lapse observations of fluid movement through pores, as well as visualization of the evolution of the pore space due to dissolution or precipitation. Data analysis include particle image velocimetry, fluid-fluid interface tracking, water film thickness measurements, and quantification of mineral dissolution. In this work, we discuss the recent progress we made in the understanding of immiscible two-phase flows and of coupled hydro-geochemical processes at the pore-scale.

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# A MICROFLUIDIC INVESTIGATION OF OIL MOBILIZATION DURING IMPROVED OIL RECOVERY

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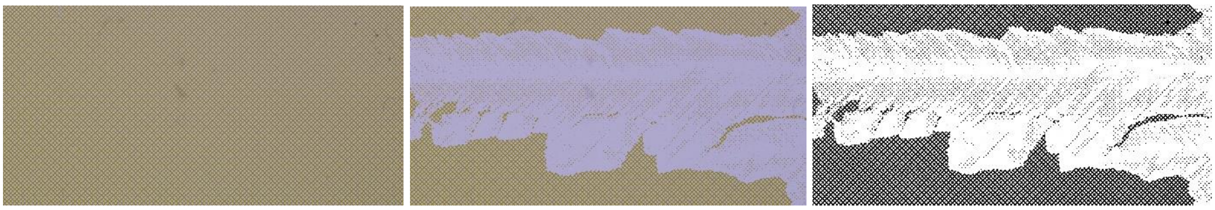
Even slight improvements in oil recovery methods translate to additional value and decreased environmental impact. To recover additional oil beyond natural drives, sea water is injected into the reservoirs as a common practice at the Norwegian Continental Shelf. The interactions between crude oil, brine, and reservoir rocks determine the efficiency of improved oil recovery (IOR), governed by the interfacial phenomena at the pore level. Therefore, microfluidics is an effective tool for visualization and fundamental studies of the phenomena governing oil mobilization and displacement at length scales where the capillary forces dominate.
In this study, the IOR process is simulated by injecting high-salinity water into oil-filled micromodels. The chip is a hydrophilic, uniform interconnected network, representing the throats and pores of a reservoir rock. Through direct optical visualization (Figure 1), the effects of oil type, oil adsorption on the rock surface, injection rate, and flood volume are investigated based on the overall recovery and direct observation of mechanisms and phenomena at the pore level. Wide field-of-view and high-resolution features are critically useful for the image analysis of the experiments. In an attempt to re-create actual oil recovery, a few different types of crude oil from the Norwegian Continental Shelf with different compositions are used. This will allow us to explore a broad range of capillary numbers, viscosity ratios and wetting conditions. The experiment results have also shown to be reproducible. The microfluidic data provides not only oleic and aqueous phase saturations and volumes, but also fluid-fluid displacement dynamics. The analysis results consist of overall oil recovery, flow pattern, displacement stability, breakthrough information, and propagation rate. Other characterization and measurement methods such as pressure recording, rheometry and tensiometry will also be used as auxiliary means of correlation/justification.



a b c

Figure1. Images of a microfluidic experiment showing: a) initial oil-saturated chip, b) after high salinity flooding (10 µL of 0.6 mM NaCl at 0.5 µL/min), and c) processed image of b.

# LOW SALINITY WATER FLOODING IN A PDMS MICRO-MODEL

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## Abstract

In an attempt to increase the oil production, the concept of Low Salinity Water Flooding (LSWF) has been under investigation for the last years, with controversial results. The basic principle of the method relies on the injection of water into the reservoir, with a salinity usually lower than this of the existing water in the reservoir.

In the literature one can find a number of contributions dealing with potential reasons behind the effectiveness (or not) of the method, with the most notable one being this of the wettability alteration, leading to an increased oil recovery. Despite the existence of the substantial volume of contributions where LSWF is under investigation, there is no investigation studying the effect of the salinity concentration on the time scale of the recovery process and the dynamics of two-phase flow, while offering a direct visualization of the on-going events, on the pore scale.

In this fundamental research work, a PDMS micro-model is used as a representation of a porous medium, consisting of a number of pore bodies and throats, forming a closed network of capillaries. Under different primary drainage conditions, water dyed with ink carrying various concentrations of NaCl is displacing Fluorinert in a hydrophobic porous medium, and the resulting breakthrough saturations and total recovery times are compared against brine concentration.

The experimental results clearly indicate an optimal range for the ionic strength where the breakthrough saturations get maximized, and the total recover times become shorter. It is also shown that there is an adverse effect of the ionic strength belonging in this range on the evolution of two-phase flow. To our knowledge, this is the first reported REV-scale experiment with pore-scale, real-time observations in which the effect of LSWF is studied.

# Microchannel Reactors for Energy Related Applications – Fuel Synthesis, Fuel Processing and Power-to-Gas

**Gunther KOLB**

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Microchannel reactors have been developed for more than 25 years at Fraunhofer IMM for a variety of applications such as de-centralised production of fine chemicals, nano-particle synthesis and in the field of renewable energy. The reactors, which are built from stainless steel in most cases, carry ten thousands of channels coated with durable and robust catalysts tailor-made for the intensified reactions. The microchannels are introduced into stainless steel sheets by wet chemical etching for rapid prototyping while embossing is used to reduce future fabrication cost. A unique screen printing technology was developed which allows the low-cost coating of the catalysts into the microchannels. The catalyst coated steel sheets are stacked then and sealed by laser welding. Inlet and outlet connections are fabricated by additive manufacturing technology and connected to the plate stacks by laser-welding as well. Fluidic simulations ensure the even distribution of fluid flows and temperature in the reactors, which allows the scale-up from catalyst testing to full reactor size by a factor of ten thousand and more.

Applications of the reactors are manifold. The de-centralised and intensified synthesis of biodiesel from used cooking oil (Schuerer et al., 2014) and the transformation of pyrolysis oil to synthetic gasoline in a containerized environment (Sunadaram et al., 2017) are examples from the field of fuel synthesis. The provision of hydrogen for fuel cell applications from a large variety of fuels is another prominent application. Fuel processors for methanol. bio-ethanol, poly-alcohols, natural gas, LPG and diesel have been realised successfully in a power range up to 50 $kW_{el}$ of the fuel cell connected (Kolb, 2008, 2013). Novel concepts for the utilisation of an excess of electric energy from renewable sources such as wind and solar are required. The transformation of carbon dioxide from biogas or other industrial sources is on possible solution for this, while electrochemical and photochemical reactions are others. Examples of reactors and complete systems will be presented.

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# PROCESS INTENSIFICATION FOR THE SYNTHESIS OF FLUORESCENT ORGANIC NANOCRYSTALS BY MICROFLUIDICS SUPERCRITICAL ANTISOLVENT

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**Suzanne FERY-FORGUES,[3] Arnaud ERRIGUIBLE,[1,4] Cyril AYMONIER,[1]**
**Samuel MARRE[1]**

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Precipitation and nucleation processes are key steps in many industrial applications, in particular in the pharmaceutical industry for drugs and organic fluorescent probes for bio-imaging processing (Fluorescent Organic Nanocrystals - FONs). FONs have been investigated in recent years for sensors in the biological field. Specifically, AIE (Aggregation Induced Emission) nanomaterials can exhibit a fluorescent emission increase when they are crystallized. These nanomaterials present promising properties as low cytotoxicity, long fluorescence lifetime, and high quantum yield. Besides conventional evaporation-induced crystallization, antisolvent processes have been largely considered. However, such processes generally required several purification and drying steps to remove the remaining solvent molecules contained within the organic crystals.

We adopt an innovative strategy to overcome the limitation of classical precipitation process by first focusing on microfluidic approaches. Microreactors exhibit characteristics allowing for getting insights and better understanding of fluid hydrodynamic, including mixing []. Besides, microfluidic reactors (μ) are solution of choice towards improved control of crystallization mechanisms: nucleation and growth, size, morphology, etc. Second, we used supercritical $CO_2$ as an antisolvent (supercritical antisolvent process - SAS), both for inducing the nucleation on chip and for drying the obtained powders [1]. Here, we propose a continuous process based on high pressure microfluidic supercritical antisolvent (μSAS) [1] for the processing of Fluorescent Organic Nanocrystals.

A model AIE molecule was chosen for this study, namely: the TPE (Tetra Phenyl Ethylene). We performed solubility experiments of TPE in the mixture [solvent (THF) + antisolvent ($CO_2$)] with FTIR spectrometry to determine the best thermodynamic conditions for the controlled nucleation of the particles. Then, we demonstrate the process of TPE nanoparticles using μSAS and we finally compare the results with conventional processing approaches using liquid antisolvent and supercritical fluids.

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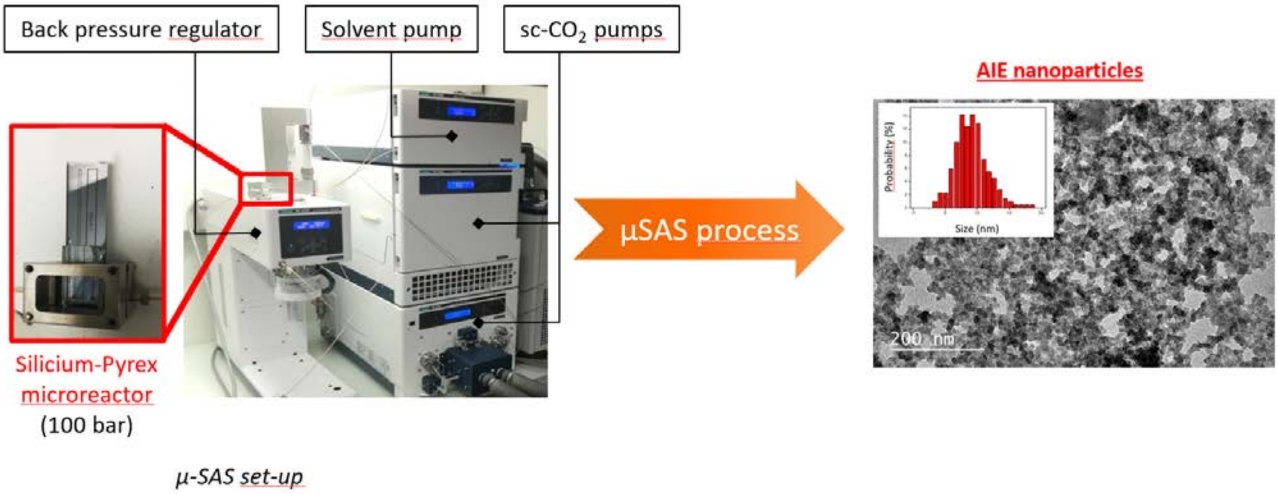
Back pressure regulator
Solvent pump
sc-CO$_2$ pumps
Silicium-Pyrex microreactor
(100 bar)
μ-SAS set-up
μSAS process
AIE nanoparticles
Probability (%)
Size (nm)
200 nm

# A TUBULAR NUCLEATION PROCESS DEVICE FOR CONTINUOUS CRYSTALLIZATION WITH POLYMORPH SELECTION OF SMALL ORGANIC MOLECULES

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More than 80% of all production lines of Active Pharmaceutical Ingredients (API) contain at least one crystallization step. Therefore, the crystallization process is an interesting case to be reconverted into a more intensified process step, like today: separate generation of nuclei; addition of nuclei in large batch systems to let them grow by slowly cooling and addition of liquids at different stages. After filtration, typically a micronization step is required to achieve the desired crystal size and distribution[1].

A simplified tubular reactor device is proposed to perform a controlled spontaneous nucleation by rapidly cooling to a highly supersaturated state. The combination of a rapid temperature decrease to a preset nucleation temperature and used initial concentrations allows polymorph selection, even for molecules possessing an enantiotropic behavior between two competing polymorphs[2]. A typical crystallization scenario is shown in figure.

Next to the dependence on temperature and concentration, also shear rates and inertial migration of nuclei away from the tube wall have an identified influence on the nucleation rate. By altering the hydrodynamics inside the tubular device, an increase in nucleation rate over two orders of magnitude has been reached for the API Brivaracetam[2] .

High nucleation rates result in crystal growth times reduced to 60s in benefit of smaller crystal size. For instance, the average crystal size obtained after filtration of a slurry that was set to grow until saturated conditions can go down to 3 µm as was experimentally obtained for the crystallization of aspirin using acetic acid as solvent[3].

With the control over nucleation rate and hence the obtained crystal sizes for different crystallization setups based on spontaneous nucleation, it is possible to avoid seeding and micronization steps. Hence, the classic three steps used for crystallization are reduced to one single step with obvious advantages regarding the yield.

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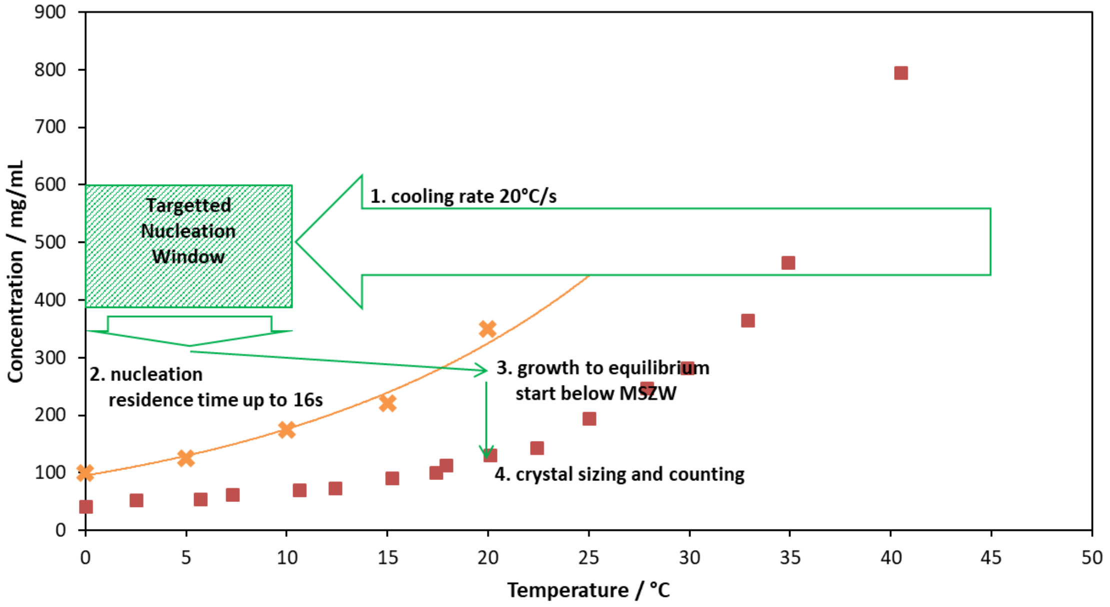

Figure: Typical crystallization protocol applied inside the tubular crystallizer setup to achieve fast spontaneous nucleation behavior of small organic molecules. Example: the crystallization of Brivaracetam Phase I crystals in isopropyl acetate. Red: solubility; orange: metastable zonewidth, green: applied temperature evolution of the solution[2].

# Gas-liquid flow characterisation and mass transfer study in a microreactor for oligomerization catalyst testing

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Among the industrial applications of olefin conversions, the oligomerization of light olefins by homogeneous catalysts is of utmost importance. However, process optimization, as well as new catalyst development still face numerous issues. In particular, a large number of catalysts and operating conditions need to be tested during the development phase and this is time consuming in stirred tank reactors. The use of microreactors, which minimizes liquid hold-up, is expected to drastically reduce the duration of experiments. Such a transposition has been rarely addressed in the literature, and hence, involves a complete hydrodynamic and mass transfer characterization.

The reaction of interest is the two-phase dimerization of ethylene into butene and hexene, employing a homogeneous catalytic system. Experiments were conducted in a tubular microreactor (ID: 530 µm) under the operating conditions of oligomerization (typically 45°C and 20 barg).

Taylor flow was generated by introducing nitrogen (instead of ethylene) and cyclohexane in a T-junction. The injection of the catalyst stream was mimicked by introducing cyclohexane in a second T-junction, downstream of the gas-liquid flow generation. Bubble velocity was found to be constant over time, which demonstrated the possibility of generating a stable Taylor flow under the reaction conditions. The possibility of injecting a liquid into the bubble train without affecting this stability has been demonstrated as well. It has also been shown that the bubble length and the slug length varied linearly with the superficial velocity ratio, in agreement with Van Steijn [1] and Völkel [2].

The second part of the work was dedicated to ethylene mass transfer in cyclohexane by monitoring the evolution of bubble length over time. The measured mass transfer coefficients are compared with reaction kinetics for a wide range of working conditions to determine whether the reaction is controlled by kinetics or by mass transfer.

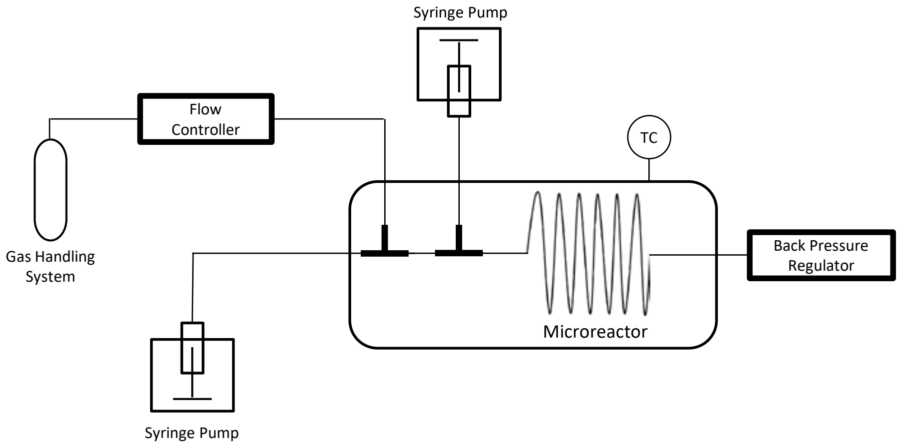

**Figure 1 – Experimental set-up**

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# Effect of flocculants on on-chip coalescence of crude oil droplets in produced water

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[2]ESICAEN, Caen, France

With this paper we present a microfluidic method to study the effect of flocculants on the coalescence of crude oil-in-water emulsions. Moreover, we analyse the influence of the oil and water composition on the coalescence process in the presence of various flocculating agents.

## Introduction

Produced water is a by-product of petroleum production. Before disposal (e.g. discharge or re-injection), it must be treated, as most environmental regulations set the acceptable range of dispersed oil between 30 and 40 ppm. Flocculating agents are often added during the water treatment in order to assist the droplet growth process and improve separation [1]. A microfluidics-based method can be a useful tool for quick assessment of the stability of oil droplets in water upon addition of flocculants. In addition, it can provide more fundamental insight and help improve the produced water treatment processes.

## Methods and Results

Previously we have reported a method for studying coalescence of crude oil droplets in various water phases [2]. Here we modify that technique to study the effect of flocculating agents on the coalescence of oil droplets and enable to control the concentration of the additive during analysis. A glass microfluidic chip was used to simultaneously generate monodisperse droplets (ca. 50 µm) and follow the outcome of coalescence with high-speed imaging (Fig. 1). A series of images, recorded at the beginning and end of the channel, are processed with ImageJ, where the size and number of droplets are obtained, and used to determine the coalescence frequency. A different microfluidic chip is used to measure the effect of flocculants on the coalescence time of drops.

In addition to studying the coalescence frequency and time of droplets in different conditions, we also introduce the possibility of controlling the concentration of flocculant during the analysis to further decrease the experimental time.

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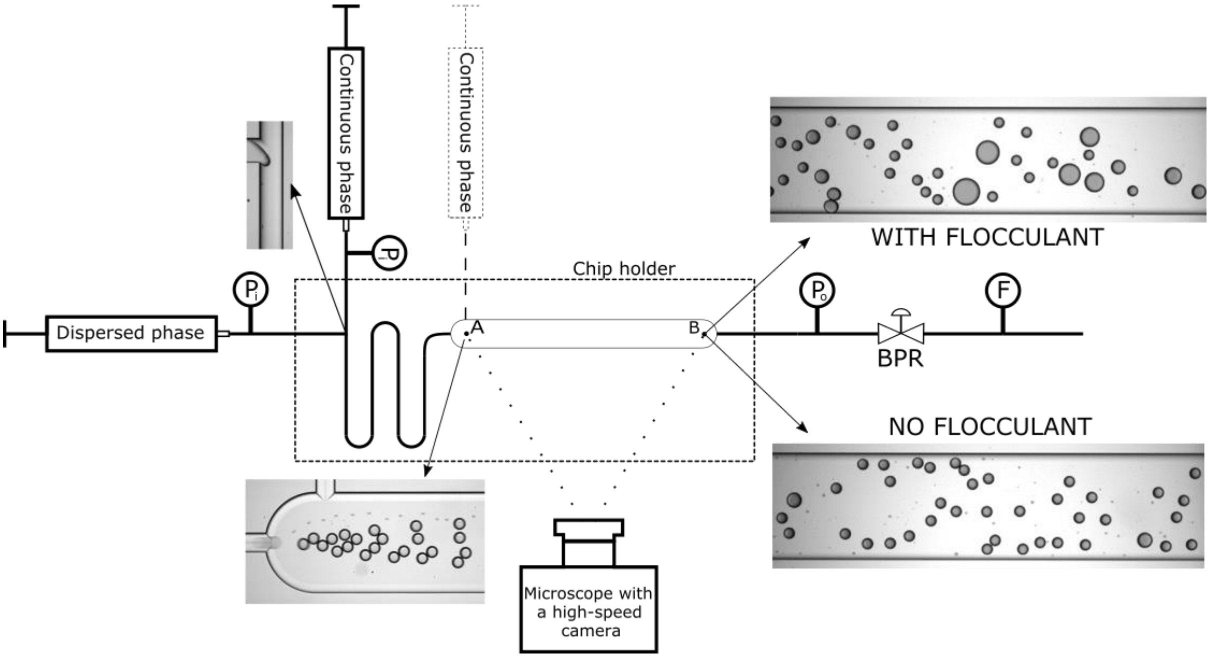

**Figure 1 Microfluidic method used for studying the effect of flocculant on coalescence of crude oil drops in produced water.**

# DEVELOPMENT OF A COMMERCIALLY-VIABLE SYSTEM FOR THE AUTOMATIC GENERATION OF HIGH-THROUGHPUT MONODISPERSE MICRODROPLETS

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## Introduction.

Using conventional techniques, it is difficult to control the size distribution of the produced droplets in an emulsion, which may affect the rate of the droplet degradation, the kinetics of encapsulant release, and decrease the stability of the emulsion. This is particularly problematic in the pharmaceutical industry, where irregular drug quantities encapsulated in polydisperse drug-loaded droplets and particles can cause an initial burst of drug release in vivo, which eventually can lead to undesirable cytotoxic effects[1,2].

## Novelty.

In this paper we report development of fully automated droplet production system (fig. 1), which can monitor droplet size, adjust flow rates and pressures of the liquids to compensate for any changes in the droplet production system and to maintain very high droplet uniformity with coefficient of variation (C.V.) below 0.2% for long periods of time at high production rates.

## Details.

The feasibility of such a system was demonstrated by D.F. Crawford et al.[3] where very uniform droplets were produced using microfluidics chip and Elvesys pressure driven flow controller OB1. Authors were using image analysis system to detect and measure the droplet size. This approach is functional, however it is vary compute-intense and limits the detection rate at 250 Hz. On the other hand our system, does not utilize image analysis, but instead uses fluorescence or reflected light from the droplets directly to detect and measure the size of the droplets, which is much faster process not limited by the processing power. In this way droplets are detected very rapidly at speeds higher than 10000 Hz at the same time regulating their size with the feedback loop and keeping very high droplet size uniformity (C.V. > 0.2% achieved). Thus opening gates to use microfluidics in the industry, where high throughput for long periods of time, without human interaction is very important.

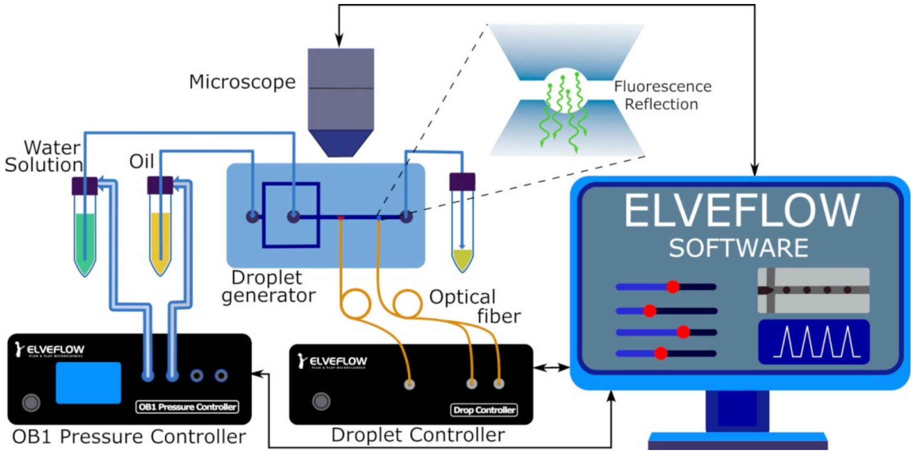

Fig.1. Schematic view of the droplet detection and regulation system. It consists of pressure controller, droplet generator chip, optical droplet controller, microscope to observe droplets, processing software with a feedback loop.

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# Microfluidics applied to the detection of insoluble hydrocarbons for the oxidation monitoring of fuels and biofuels.

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The fuels and biofuels oxidation is a major concern to the transport industry. [1-2] Fuels can react with atmospheric oxygen and depending of their relative susceptibility to degradation, insoluble hydrocarbons deposits can be formed. Failure of engine or components can be caused by the deposit formation. To prevent this kind of issues, we develop a system able to detect the formation of deposits and to monitor oxidation of fuels online. Actual fuels are complex mixtures of hundreds of chemical components from multiple chemical classes and their degradations generate other hundreds of oxidation products. [3] The main challenge of this study is to identify these oxidation products and/or physical chemical changes early in the process to prevent insoluble issues for all types of fuels.

A microfluidic system compatible with fuels and biofuels flow was developed in order to identify the different levels of oxidation and the presence of deposit. An autoclave was used to perform intense controlled accelerated thermal oxidations. Model fuels (mixtures of pure compounds) and real fuels have been studied. The main oxidized compounds have been identified by GC-MS in different mixtures in order to find tracers to monitor fuel degradation.
Preliminary studies have investigated physical chemical properties, such as viscosity, density and heat capacity. Infrared and fluorescence spectroscopies have been identified to follow the level of oxidation of compounds. Depending on the composition of the fuels, changes on these physicochemical and optical properties were significant enough to be easily detected, before and after the oxidation step.

The result of this study is the design of a microfluidic system able to monitor the fuel oxidation stage and to detect the formation of deposits online. This system follows with time and online the variations of the heat capacity reflecting the presence of liquid deposits, as the emitted fluorescence intensity which is proportional to the quantity of oxidized fuel. It works with a low fuel volume and in a compact and lightweight equipment. This innovative approach using a microfluidic system should improve the online detection of oxidation of new alternative biofuels.

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# Development of plasma-activated reactions in a liquid-gas micro-reactor

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## *Abstract*

Intensified processes are keys to energy, cost and material savings. The following liquid-gas microreactor was developed in this spirit. Indeed, plasma-activation can be considered as a green and cost effective process for chemical synthesis, since it does not require catalyst, activator, hard temperature or pressure conditions, and even neat reactions can be realised. Indeed, plasma discharge generates radical species, which are able to easily functionalize the targeted molecule.

Combined with microfluidics, which allows a precise control of the reactivity of radical species thanks to extremely fast mass and heat transfers, these plasma-activated reactions can be used to realise different kind of chemical reactions: functionalization, coupling, polymerization… Our plasma-activated liquid-gas microreactor is the result of this idea, through several years of development [1]. It is a patented device [2] which already proved its efficiency in oxidative processes [3].

In order to investigate new reactivities and to reach a better understanding of plasma chemistry inside this reactor, an unsaturated model molecule has been chosen: 1-hexen. Starting from this molecule, two types of reaction were studied: oligomerization using an Argon plasma and functionalization by an oxygen group using an O2 plasma. For these two different studies, the aim is to understand and distinguish the influence of plasma parameters – frequency, voltage and consequently power – and the one of other processes parameters – flowrate and residence time, nature of the plasma gas, temperature.

The results in argon have shown a controlled and repeatable synthesis of an oligomer constituted of 4-5 monomer units. Using an Oxygen plasma, we succeeded to obtain several functions synthesis. Mainly aldehyde and epoxyde, these functions are specifically located on the alkene - more precisely on terminal carbon – a promising result.

Now, our goal is to understand how we could reach a better control on oxygen functionalization, in order, for instance, to favor one of those functions over the others. We also are willing to test the chemoselectivity of those reactions, starting from a more complex molecule e.g. 6-Chloro-1-hexene or 1-hexene-6-ol.

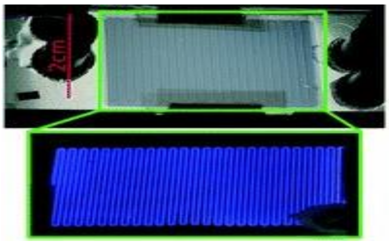

**Figure 1 - Picture of a homogeneous plasma in the plasma microreactor**

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# Emergence of Microflow based Photocatalytic Reactors for Selective Oxidation of Benzyl Alcohol to Benzaldehyde

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## Abstract

Lignocellulosic biomass is a valuable raw material for biorefineries and other chemical industries which is stated to increase the usage of renewable resources for energy applications and reduce the consumption of fossil fuels. However, lignin, a major component of lignocellulosic biomass, is a major byproduct produced in vast scale in these industries and finds minimal application.[1] Recent studies on depolymerisation of this complex polyphenolic polymer have shown to generate chemical compounds which are of great value to the pharmaceutical and fine chemical industries.[2]

The development of a heterogeneous photocatalytic system based on microflow system for lignin depolymerization is an innovative but challenging approach due to the limited number of research works being carried out in this field.[3] Recent studies on photocatalytic reactions in a microfluidic reactor system have shown better performance when compared to the conventional batch processes. The superior performance can be stated to the increase of contact surface area between the reagents and the catalyst, shorter molecular diffusion distance, improved mass transfers, and a facile control of reaction parameters, all this together leading to high catalytic activity in a microflow system.[3,4]

The current work focusses on developing photocatalytic microreactor which involves ultrasound based deposition of commercial $TiO_2$ and ZnO photocatalysts in the internal walls of fluoropolymers like Perfluoroalkoxy alkane (PFA) and Polyfluoroethylenepropylene (FEP) microtubes. The photocatalytic activity of the semiconductor coated fluoropolymer based microcapillary was evaluated for selective photocatalytic oxidation of the simplest model aromatic compound of lignin-benzyl alcohol to benzaldehyde. Later the photocatalytic studies in batch reactors were also performed and showed lower conversion rate and product selectivity compared to the reaction carried out in photomicroreactor. It is observed that during the ultrasonication process, changes in the polymer surface in form of rough patches are seen. The rough patches form sites for catalyst deposition resulting in the formation of thin layer of photocatalyst nanoparticles in the inner walls of the microtube.[5] The photocatalyst coated microreactor also showed higher stability during multiple repetition of the photocatalytic reaction.

**Acknowledgements**

This work was supported by the National Science Centre (NCN) in Poland within research project Sonata Bis 5 Nr. 2015/18/E/ST5/00306. More information on this project at http://photo-catalysis.org

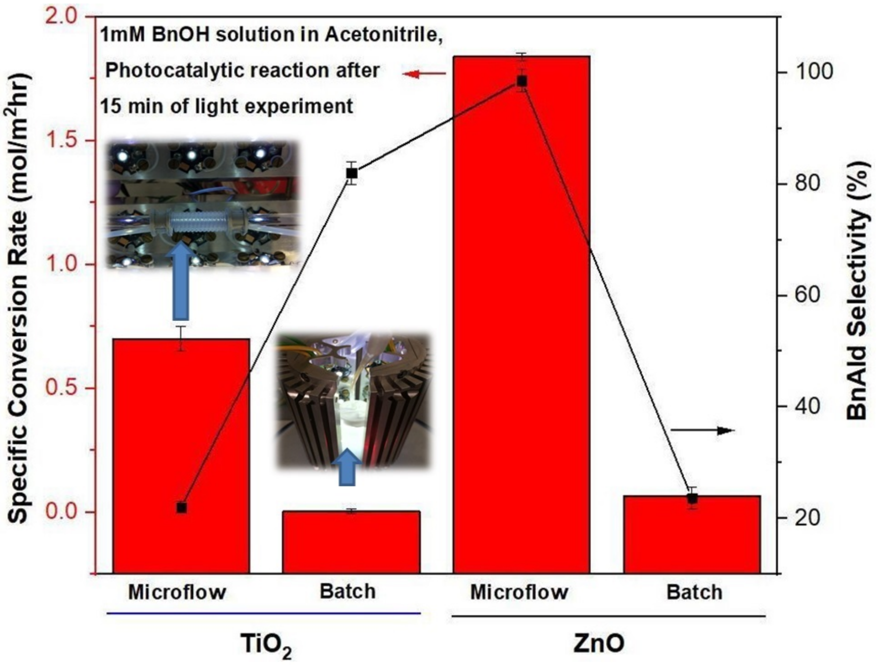

**Fig. 1.** Selective photocatalytic oxidation of benzyl alcohol to benzaldehyde in microflow and batch reactor

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# Optimizing Energy Production in an Osmotic Engine: Adjustment of Hydrogel-Particles Size by Microfluidic Glass Capillary Device

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## Abstract

Superabsorbers are charged polymeric networks, with a high swelling capacity of up to 10-1000 times of their own weight in water. These hydrogels are commercially utilized e.g. in hygiene applications .[1] The swelling capacity of superabsorbers in saline water is 2-12 times lower than that in desalinated one due to the screening of the charged groups by a reduced osmosis.[2] This variable change in volume expansion as a function of salinity can be used to design an osmotic motor to convert the chemical potential differences between fresh and seawater at deltas into the mechanical force as a renewable energy source. This osmotic motor has a superabsorber-filled chamber, attached to a piston. The hydrogels are exposed alternatively to fresh and saline water, which makes swelling-shrinking cycles and leads to the reciprocation motion of the piston.[3]

The power production in the described engine depends on parameters like monomer type, degree of crosslinking, degree of neutralization, particle size and particle shape. In a series of poly (acrylic acid-*co*-sodium acrylate) networks with undefined shape and large size distribution, a maximum power of 0.23 W/kg dry hydrogel has been obtained by using 370-670 µm large hydrogels.[3] Anisotropic particles with a broad size distribution lead to a lower power production due to the gel-blocking effect, which prevents water flow to the inner particles. Gel-blocking can be reduced if the voids between hydrogels are maximized by using spherical particles with a narrow size distribution. In this work, we use a microfluidic glass capillary device to fabricate such hydrogels. The diameters of particles are 105, 234, and 624 µm, which are examined further in an osmotic engine to investigate the dependency of the power production on the particle size. We found that the maximum power of 0.54 W/kg is currently obtained when the smallest particles are utilized in the engine (Figure 1). This result shows that the microfluidic setup is an effective method to fabricate hydrogels for new applications like power production in osmotic engines.

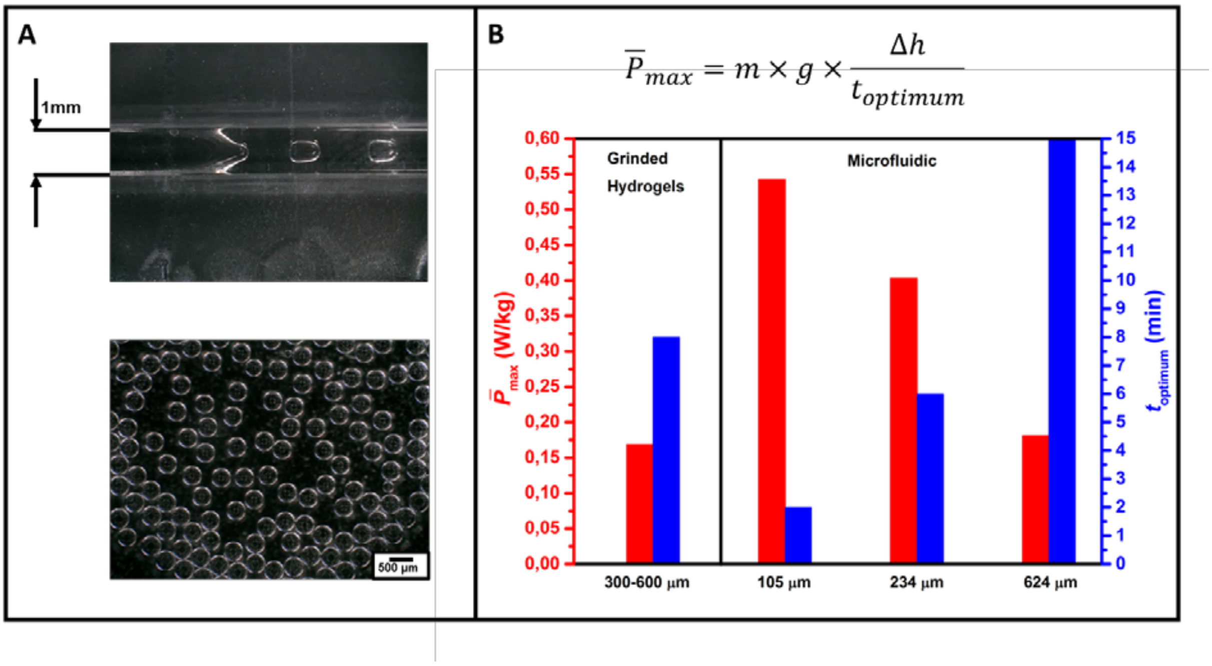

Figure 1. (A) Fabrication of hydrogels by microfluidic glass capillary device. The hydrogels have a narrow size distribution. (B) The dependency of the maximum power production in the osmotic engine on the particle size. In contrast to the hydrogels fabricated by microfluidic, grinded hydrogels have an undefined shape and a larger size distribution.

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# High-pressure microfluidic approaches to study $CO_2$ bioconversion within deep saline aquifers

**Anaïs CARIO[1*], Maxence PERROUX[1], Cyrielle FAUVEAU[1], Olivier NGUYEN[1], Carole LECOUTRE[1], Yves GARRABOS[1] and Samuel MARRE[1*]**

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## Abstract:

Among the various Carbon Capture Utilization and Storage (CCUS) strategies, $CO_2$ geological storage (CGS) in deep saline aquifers represents a sustainable solution for reducing the anthropogenic $CO_2$ emissions. So far, little is known about the $CO_2$ storage impact on both the underground geochemistry and on the indigenous microbial diversity. Consequently, this kind of storage requires adequate scientific knowledge and tools at the pore scale to evaluate injection scenarios or to estimate reservoir capacity. In this context, research projects gathering interdisciplinary partners are highly desired to address part of these limitations.

This talk will present first the experimental tools developed in the lab for investigating the coupled mechanisms (thermodynamics, hydrodynamics, chemistry and biology) involved in such storage processes. These new devices are high pressure / high temperature porous microfluidic reactors (geological labs on chip – GloCs [1]) designed to investigate the different mechanisms associated with CGS within deep saline aquifers [2]. We will highlight some results concerning the application of the GLoCs to study the invasion processes of $CO_2$ in water and brine saturated GLoCs. In particular, direct optical visualization and *in situ* characterization techniques allow following the evolution of the $CO_2$/brine phase distribution within the pores, including displacement mechanisms, pore saturation levels [3] and reactive transport. Eventually, as part of the ERC project “Big Mac” [4], we will introduce the use of GLoCs as a significant tool to mimic the *in situ* reservoir conditions (*i.e.* porous media, high pressure and high temperature) to study $CO_2$ bioconversion (Fig. 1). Indeed, beyond CGS investigations, the GLoCs could provide new insights into bioremediation mechanisms to restore $CO_2$ as a valuable energy resource (*i.e.* $CH_4$ via methanogenesis process). These tools could also find wider applications in geological-related studies such as Enhanced Oil Recovery, shale gas recovery or geothermal energy.

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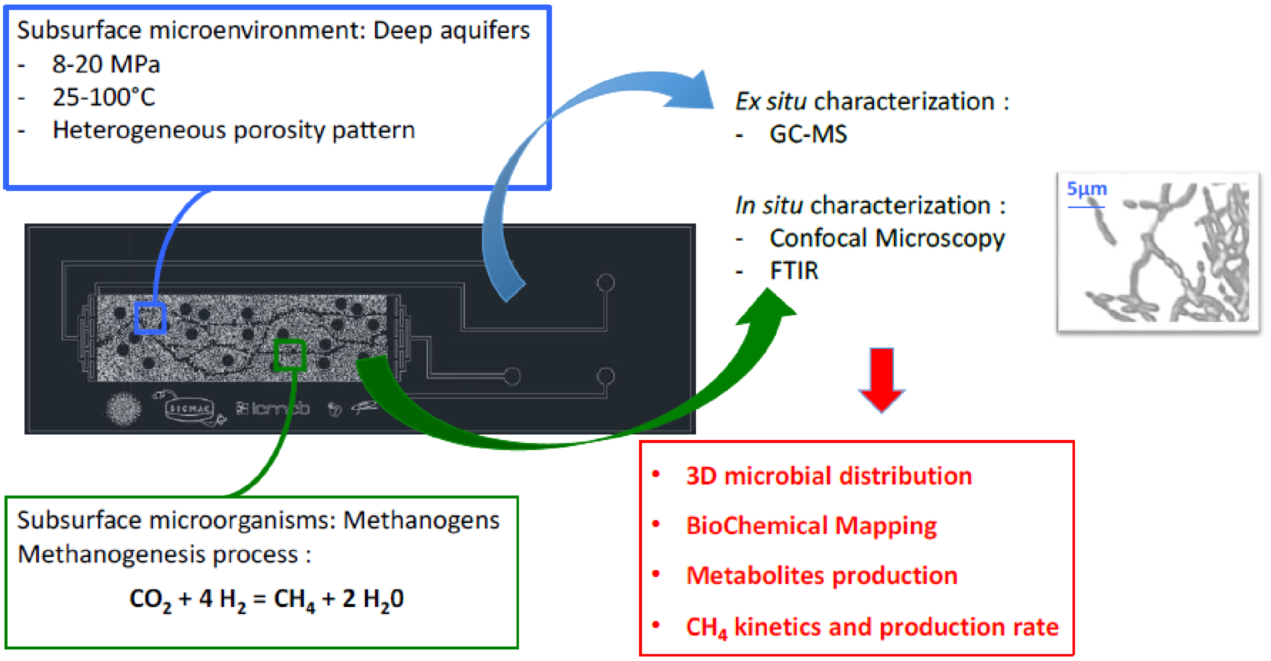

**Figure 1.** Example of a high-pressure GLoC for investigating $CO_2$ bioconversion into $CH_4$ by subsurface microorganisms (*i.e.* methanogens) inhabiting deep saline aquifers.

# ABSTRACTS
# OF THE POSTERS

The abstracts are listed in their reference order

The abstracts are published in their original format, i.e. the format in which they were sent to the Scientific Committee.

# Radial distribution function of Lennard-Jones fluids in shear flows from intermediate asymptotics

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The microstructure of a suspension of particles is determined by the probability of finding a reference particle at a certain position with respect to a target particle, namely the pair correlation function [1]. Its description under shear flow conditions has been a challenge for theoretical and computational methods due to the singularly-perturbed boundary-layer nature of the problem [2]. Previous approaches have been limited to the case of hard-sphere systems and suffer from various limitations in their applicability [1]. Here, we present a new analytic scheme based on intermediate asymptotics [3] which solves the Smoluchowski diffusion-convection equation formulated in spherical coordinates including both intermolecular and hydrodynamic interactions. Our ultimate goal is the description of the pair correlation function or radial distribution function (rdf) for realistically interacting particles in shear flows as a function of interparticle interaction and Peclet number. First, the method has been validated through a comparison with the microstructure of a hard-sphere fluid under strongly sheared conditions [4]. Afterwards, we have analysed the trend of the rdf at different shear rates for the same test suspension to check the reliability of the method. Finally, we have been capable of predicting for the first time the microstructure of a complex interacting fluid such as the Lennard-Jones (LJ) one which has been shown in Figure 1 at varying values of the attraction strength λ.

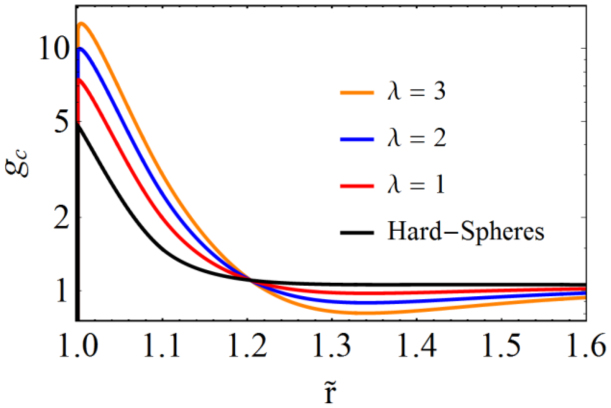

**Figure 1:** Rdf of a complex interacting fluid under simple shear flow adopting the 12-6 Lennard-Jones interaction potential; λ is normalized by $\beta = k_b T$.

In particular, a new depletion effect is predicted in the microstructure of the LJ fluid under shear, a feature to our knowledge never discovered before. This method will be further used for the theoretical modelling and understanding of other real fluids in shear flow, with applications ranging from microfluidics, shear aggregation of colloids [5], rheology of complex plasmas and atmospherical science.

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# DESIGN AND CHARACTERIZATION OF A CONTINUOUS ON-CHIP MICRO-DISTILLATION TOOL.

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Distillation is a key step for the chemical industry, being an efficient process for recovering pure compounds from complex mixtures. However, from a chemical engineering point of view, traditional distillation columns are limited to a minimum diameter and a certain range of flow rates, both for design and efficiency constraints. Such classical distillation columns are not always adapted to multiple-step continuous synthesis processes or research purposes, for which the fluid's quantity is small. Therefore, there is an increasing need for micro-distillation units able to operate with lower fluid volumes at few $mL.h^{-1}$.

The main challenge associated with micro-distillation process development is that it cannot be based on gravity forces, which is the gas-liquid separation's principle in conventional distillation column. Indeed, at the microscale, the effect of gravity fades in favor of surface forces. Thus, new designs of vapor-liquid contactors have to be considered. Capillary forces[1] and many others[2] are gravity alternative forces for driving the liquid phase and establishing the gas-liquid interface. Up to now, several works reported the interesting performances of on-chip microdistillation; nonetheless there is no in-depth study describing the hydrodynamics inside the micro-column and identifying the parameters on which capacity and separation efficiency depend. It is therefore needed to characterize the two-phase flow within the micro-column.

In this presentation, a silicon-based microchip distillation integrated with micropillars guiding the liquid flow is used to investigate the hydrodynamic behavior. Various techniques, such as micro-particle image velocimetry, are employed to characterize the flow profile inside the micro-distillation column along with the axial dispersion in the liquid phase and the mass transfer between the phases. These measurements will relate the hydrodynamic parameters to the micro-distillation performance. Moreover, these results are supported by a simulation using proprietary software.

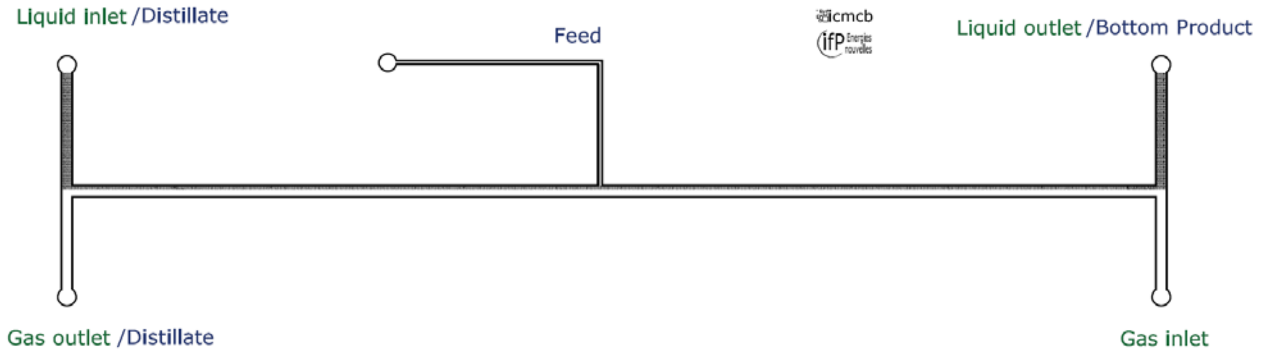

Figure 1: Design of the microchip device developed in the frame of this work, dedicated to both hydrodynamic (green) and distillation (blue) studies.

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# Development of an optical measurement method for “sampled” micro-volumes and nano-flow rates

**Florestan OGHEARD**

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Radiopharmaceuticals used in nuclear medicine for therapy or diagnosis (molecular imaging, PETscan, scintigraphy) are characterized in terms of volume activity before injection to patients. The current measurement process relies on dose calibrators which have to be calibrated by transfer standards, traceable to primary standards. For very short half-life radionuclides (few minutes), the metrological traceability can only be assured through an on-site calibration with primary standards. However, until now, there is no primary system for the direct measurement of such high activity radioactive solutions. In the scope of the development of on-site primary measurement system allowing the direct measurement of highly active radiopharmaceuticals, this study presents the sub-system under development for the measurement of a sampled volume in the order of one microliter with an associated relative target standard uncertainty of 1 %.

In practice, the method chosen for the measurement of the activity per unit of volume of a radiopharmaceutical solution includes four main steps: sampling, volume measurement, activity measurement, and sample ejection.

This article focuses on the volume measurement method development and its validation by comparison to the gravimetric method.

The paper, in a first part, describes the developed method and the associated hardware and software. The authors have chosen a non-contact, optical method implemented by a microscope camera and associated optics in front of a transparent capillary.

The second part of the paper describes the measurement model. Several corrections are described and the traceability to both dimensional unit and mass are presented. In particular, the article discusses the optical distortion and evaporation corrections.

Finally, the paper presents some validation results by comparison to a gravimetric measurement, including repeatability and reproducibility tests. Further development and improvements, necessary for the finalization of the prototype are discussed.

# HIGH-PRESSURE MULTIPHASE MICROFLUIDICS FOR GREENER MANUFACTURING OF ACTIVE PHARMACEUTICAL INGREDIENTS

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## Abstract

This paper reports the behaviour of multiphase microfluidic streams of carbon dioxide in its gaseous, liquid and supercritical state and conventional solvents (e.g. ethanol). The fluidics at high pressures plays a major role in process intensification of small-batch manufacturing of active pharmaceutical ingredients (APIs), which is the ultimate objective of this study. Priest et al.[1] have adapted stream-based microfluidic extraction to the refining of platinum and rare earth elements at relatively high throughputs (pilot-scale) at < 3 bar. Foster et al.[2] have demonstrated improved bulk-scale efficiency, micronization and sorting of pharmaceutical particles (up to 40 °C and 76 bar). Here, we investigate stream and droplet-based fluidics that have potential for reengineering of APIs.

High-pressure microfluidics offers unique opportunities for greener extraction and precipitation using subcritical carbon dioxide as an antisolvent or subcritical water dissolution of lipophilic drugs. Our microfluidic setup incorporates a thermally bonded borosilicate glass chip, which can withstand up to 100 bar. A custom-made provides a reliable interface to the high pressure pumps (ISCO 260D). We have investigated stream and droplet-based flows at up to 70 bar as platforms for multiphase synthetic chemistry.

Multiphase flow of nitrogen or $CO_2$ with ethanol at low (1-5 bar) and high (40-60 bar) pressures was quantified by the liquid stream width versus the pressure ratio (Figure 1). The dependence is linear, steeper than the liquid-liquid co-flow and shifting upwards with the pressure of the gas. At higher pressure, ethanol and subcritical carbon dioxide co-flow as streams or bubbles and a gas-expanded state is gradually achieved. The bubbly flow was used to study the kinetics of dissolution. We have demonstrated synthesis of copper indomethacin on a bulk scale by spraying ethanol solutions into subcritical $CO_2$[2]. Current results suggest that high pressure microfluidics would be a suitable green platform for the synthesis of APIs.

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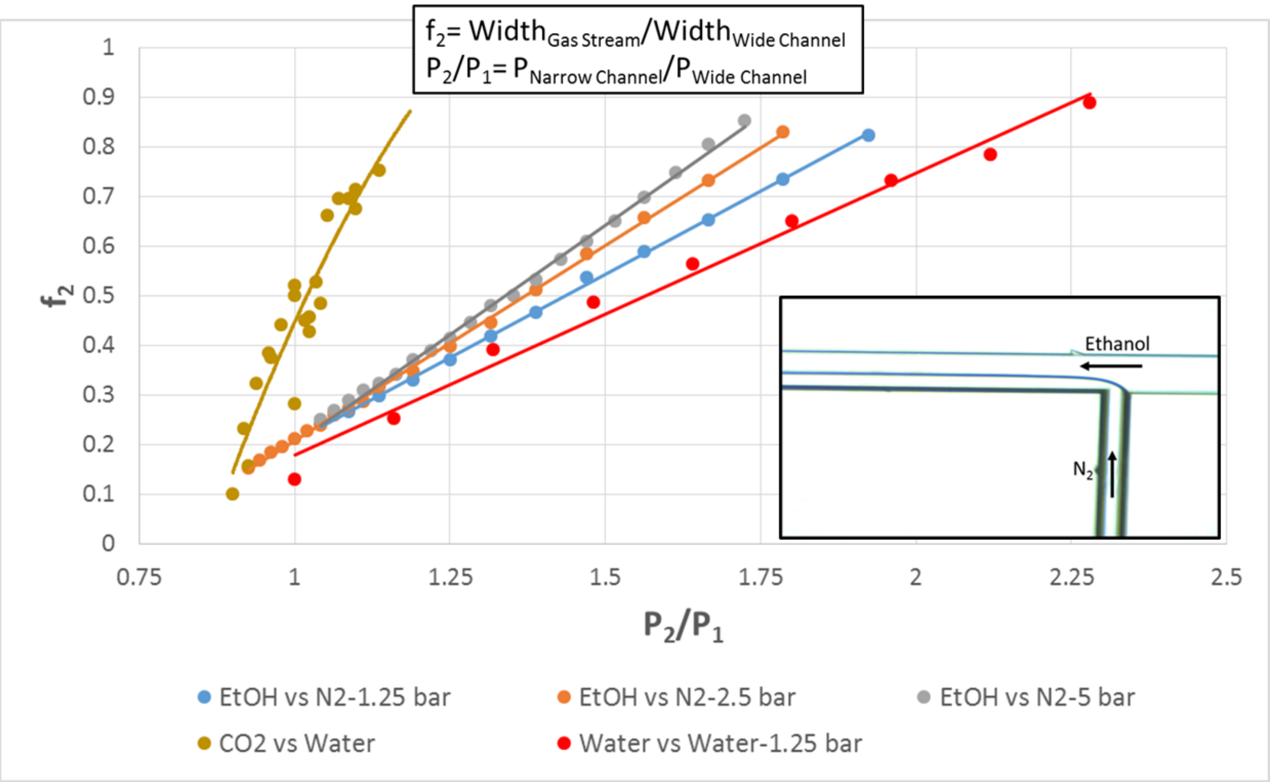


Figure 1: Stream-based two-phase flow: comparison of gas/liquid and liquid/liquid co-flow.

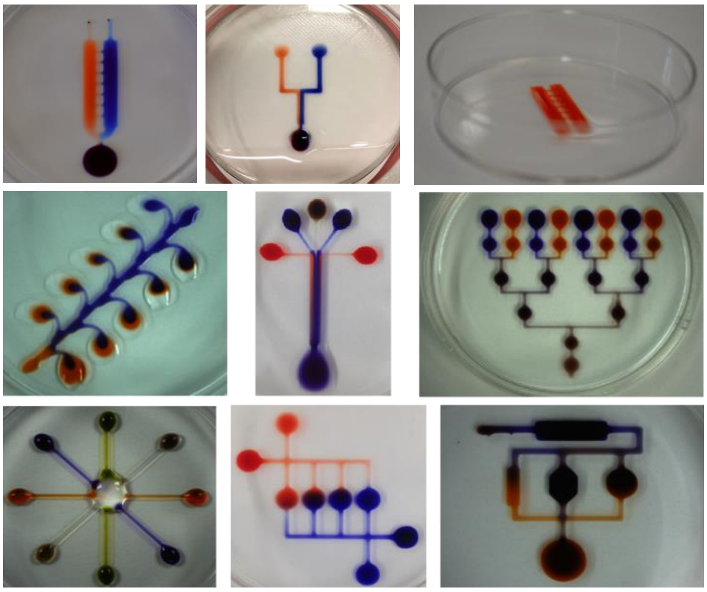
# MICROFLUIDICS WITH FLUID WALLS FOR CELL MIGRATION ASSAYS

**Cyril Deroy**

University of Oxford, UK

## Abstract

Over the past couple of decades, microfluidics has offered experimental methods for the study of cell migration. Despite their wide range of applications, versatility and flexibility, the adoption of such devices within the lab has remained challenging. Some of the main reasons cited for this lack of uptake include technical complexity, high failure rate due to gas-bubbles, as well as questionable bio-compatibility of polydimethylsiloxane (PDMS). Our lab has developed an open fluid-walled microfluidic system which searches to answer such problems by utilizing only the materials familiar to biologists, cell culture media and tissue culture dishes [1]. By handling microscale amounts of fluid, interfacial forces allow us to shape the media directly onto a petri dish. The fluidic, hence open, nature of the devices imply that cells may be added and retrieved anywhere within the system. To demonstrate the versatility of this method, we show that flow can be driven from any point by passive or active means to establish chemical gradients, and performed cell migration based assays of immune cells using real time imaging.



***Microfluidics with Fluid Walls***

*Caption: Circuits were stained with various dyes (red, blue or green), in order to visualise flow patterns and circuit geometries.*

## References:

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# In situ photo-patterning of hydrogel membrane in PDMS microfluidic channels

**Hoang Thanh NGUYEN, Camille KEITA, Jean-Baptiste Salmon***

Laboratory of the future, Bordeaux, France

## Abstract

For the past decades, hydrogel membranes were integrated in microfluidic chips thus opening a variety of applications including pre-purification/concentration, separation of samples required in analytical chemistry[1] and bioanalytical purposes[2], and membrane microreactors[3]. Recently, hydrogel nanoporous membranes have been fabricated *in situ* in acrylate-based microfluidic devices[4]. This method is based on the UV-induced spatially-resolved polymerization of a mixture containing functional monomers, cross-linkers, photo-initiators, and porogens injected within the microchannel. However, *in situ* fabrication of pressure-resistant hydrogel membranes in PDMS channels still remains a challenge due to the solubility of oxygen in PDMS inhibiting free-radical polymerization, and the lack of chemical bonding between the hydrogel network and the PDMS channel surface. In this work, we report *in situ* fabrication of hydrogel membranes in PDMS chips which are then used for separation of macromolecules and for protein crystallization. To overcome the difficulties mentioned above, oxygen was depleted from the channel walls by nitrogen flowing in a channel placed on top of the main fluidic channel (multilayer soft lithography). An anchoring layer on the PDMS channel surface was also obtained by UV-initiated graft polymerization of poly-acrylic acid within the PDMS prior to the polymerization of the PEG-based hydrogel membrane. Both the Darcy permeability and molecular weight cut-offs (MWCOs) of the hydrogel membranes were measured as the function of the deposited UV dose during the photo-polymerization of these membranes. Application potential will be illustrated by the separation of different macromolecules by size, and by the real time monitoring of crystallization of model proteins.

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# NUMERICAL SIMULATION OF SPREADING LIQUID FILM SUBJECT TO INTERACTION WITH TWO SPHERICAL PARTICLES ON HORIZONTAL SMOOTH SUBSTRATE

**Hayate NAKAMURA[1], Victor DELAFOSSE[2], Georg DIETZE[3], Harunori N. YOSHIKAWA[4], Farzam ZOUESHTIAGH[2], Lizhong Mu[5], Takahiro TSUKAHARA[1] and Ichiro UENO[1]**

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## Abstract

Acceleration of the spreading liquid film in the vicinity of the macroscopic contact line (M-CL) after interaction with spherical particles on the horizontal smooth substrate has been indicated in the experiments (Mu et al., 2017). By arranging multiple structures in a row, an acceleration phenomenon is caused successively, and the liquid film can be driven in a direction parallel to the particles row (Mu et al., 2018). We carried out numerical analysis to investigate how the distance between two particles on the substrate affects the liquid film behaviour. The results showed that the smaller the inter-particle distance, the larger the maximum M-CL velocity after that liquid film interact with the second particle (Fig. 1). It was also found that after the interaction between the liquid film and each particle, a meniscus is formed around the particles, and that the M-CL is driven by the pressure difference between upstream and downstream sides of the particles. Focusing on the second particle, it was clarified that the smaller the inter-particle distance, the larger the pressure difference around the particle, and this increases the M-CL maximum velocity. From the above, we concluded that the linear array of particles can successively cause the meniscus formation around each particle, that is, the change of the pressure distribution inside an amount of liquid, and as a result, the liquid film is driven in the direction parallel to the particles row.

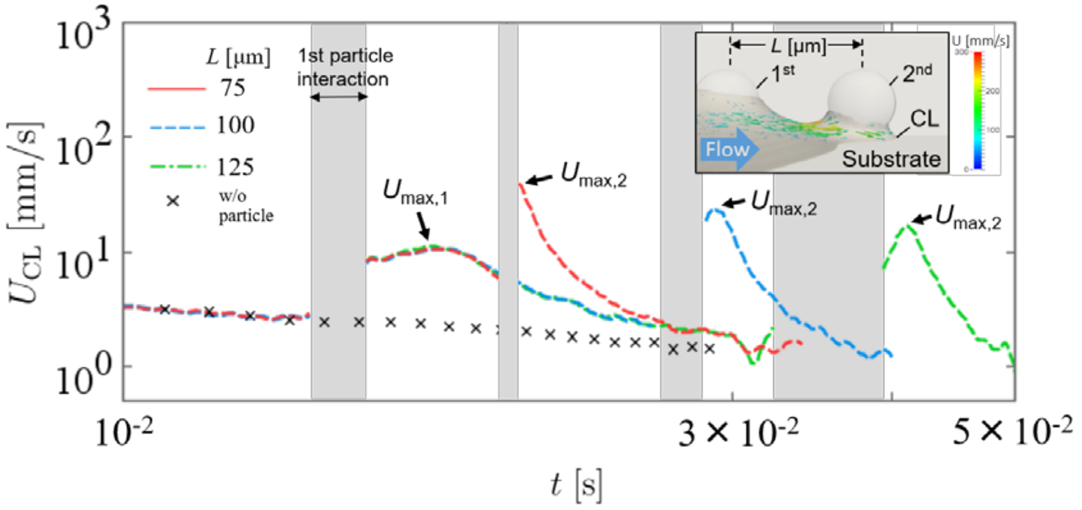

Figure 1: Temporal variations of CL velocity $U_{CL}$. The distances between two particles $L$ are varied as 75,100 and 125 µm. Inset shows meniscus formation around particles in side view ($L$ = 100 µm). Vector indicates the liquid velocity on the film surface.

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Mu, L., Yoshikawa, H. N., Kondo, D., Ogawa, T., Kiriki, M., Zoueshtiagh, F., Motosuke, M., Kaneko, T., Ueno, I. (2018). Control of local wetting by microscopic particles. *Colloids and Surfaces A 555*, 615–620.

# SUCCESSIVE ACCELERATION OF MACROSCOPIC CONTACT LINE OF DROPLET INDUCED BY INTERACTION WITH MULTIPLE PILLARS

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## Abstract

It has been observed experimentally that the macroscopic contact line (MCL) of a droplet spreading on a substrate is locally accelerated by the interaction with tiny obstacle(s) installed on the substrate (Mu et al., 2017; Mu et al., 2018). The purpose of the present study is to examine the effect of the height of the obstacle(s) on the local acceleration of MCL. We first examine the effect in the case of a single pillar. When the pillar has a sufficient height, the wetting height of the liquid film does not reach the top of the pillar before MCL reaches the maximum velocity. Thus the fully developed meniscus is formed around the pillar in the acceleration process. When the pillar height is insufficient, on the other hand, the liquid film reaches the apex of the pillar before the MCL reaches the maximum velocity, then the maximum velocity of MCL becomes smaller than the previous case. We then examine the case of multiple pillars aligned normal to MCL. Figure 1 indicates a typical example of successive acceleration of MCL by the interaction with three pillars with sufficient height. We find that menisci around the foot of the pillars play a role of pump to supply amount of liquid in downstream direction. We will illustrate correlations the pillar height and successive local accelerations.

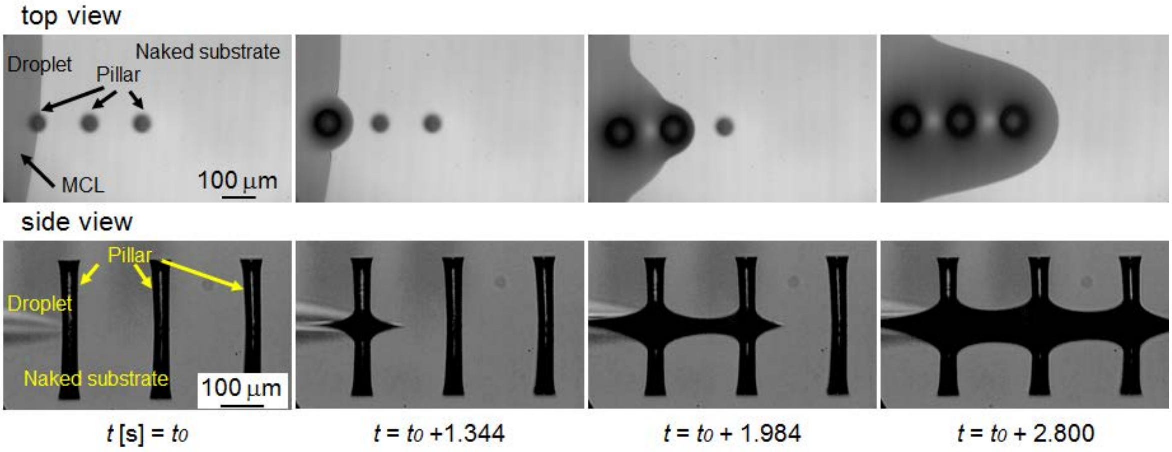

Figure 1: Top and side views of successive interaction of droplets with pillars. The height of pillars is 200 μm.

**References:**

Mu, L., Kondo, D., Inoue, M., Kaneko, T., Yoshikawa, H. N., Zoueshtiagh, F. and Ueno, I. (2017) Sharp acceleration of a macroscopic contact line induced by particle, *Journal of Fluid Mechanics*, *Vol. 830*, 1-12.

Mu, L., Yoshikawa, H. N., Kondo, D., Ogawa, T., Kiriki, M., Zoueshtiagh, F., Motosuke, M., Kaneko, T. and Ueno, I. (2018). Control of local wetting by microscopic particles, *Colloids and surfaces A, Vol. 555*, 615-620.

# GENERATION OF NANOPARTICLE SUPERLATTICES BY USING AN OFF-THE-SHELF MICROFLUIDIC DEVICE

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Commonly fabricated by soft lithography and more recently by micromachining of metals, plastics (e.g. PMMA) and glass, microfluidic devices are powerful tools to produce and or reproduce processes in many domains.

Our goal is to generate an oil in water emulsion by flow focusing using a device [1] that combines commercial capillaries and commercial tees as connectors, as shown in Figure a. The device is composed of two face-to-face thinned circular capillaries, inserted in a square capillary. The two orifices, one for injection of the inner fluid phase and one for the focusing of the flow, are created by flaming the ends of the glass capillaries. The droplet size is controlled by the oil and the aqueous surfactant solution flows, the orifice diameters and the distance between the two cylindrical capillaries.

When the oil is doped with hydrophobically coated gold nanoparticles (NPs), the emulsion droplets can be used as confined medium containing the gold nanoparticles. After collection, the oil droplets evolves either through Ostwald ripening or oil evaporation. This evolution induces the slow nanoparticle self-assembly and the formation of superlattices [2] inside the droplets (Figure b).

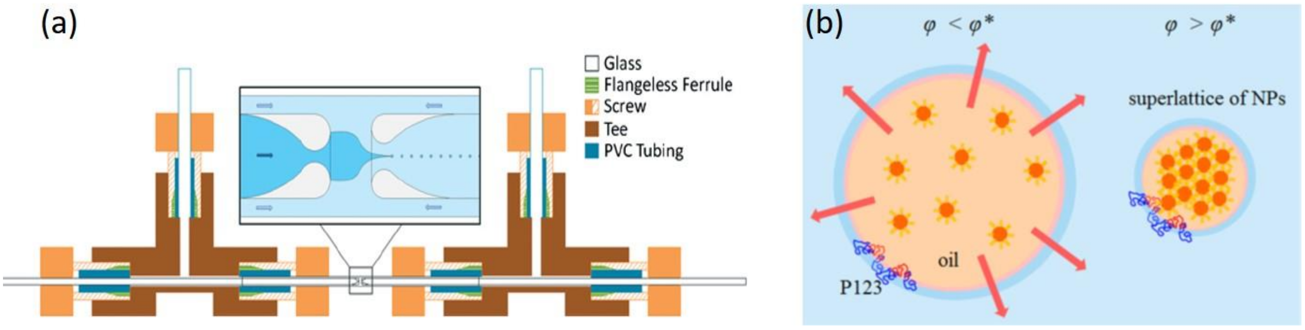

**Figure (a) Schematic of the capillary device, the zoom represents the focus of the flow. (b) Illustration of the formation of a superlattice of Nps. Adapted from [1] and [2].**

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# Methodology to Study Microgel Behavior for IOR projects

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## Abstract

Nano and microgels are pre-gelled polymers used to improve oil recovery on mature fields.
This technology can be applied for deep conformance control in heterogeneous reservoir with high permeability channels. The nano and micro gel size can be “tailor-made” based on the reservoir permeability, temperature and salinity.
This paper presents the methodology to characterize and understand the mechanism of commercial microgel using microfluidic devices.
The salinity, temperature and oil viscosity were selected based on “Argentina Mendoza Norte” Fields conditions.
The study began with the main properties evaluation of commercial product in two brines (47.7 and 73 G/l) at 3 concentrations (0.2-0.5 and 1%). The gel size evolution, density, viscosity and interfacial tension were measured under 3 temperature conditions (room, 65°C and 95°C). Note that due to the slow swelling kinetics of this microgels, they were preswelled before use. These characterizations aimed at selecting the appropriate temperature and salinity for microfluidic study.
The objective of these experiments was to understand the behaviour of microgels in confined channels under flow and to assess their capacity to modify the flow capacity and remobilize trapped oil.
In this purpose, microgels behaviours (jamming, adsorption, bridging mechanism, etc.) were observed in monophasic flow thanks to a simplified microfluidic device with different size restrictions. Then, a microfluidic 2D porous media device designed from a rock picture was used to evaluate the microgel performance on oil recovery.

# MEASURING OIL RECOVERY USING OPTICAL MICROSCOPY WITH PACKED BEDS IN MICROFLUIDIC CHANNELS

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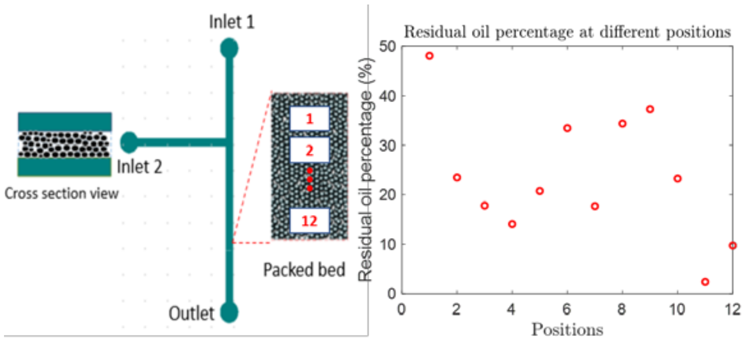
## OBJECTIVE

We have developed a microfluidic platform as a complementary tool for core flooding procedures concerning enhanced oil recovery (EOR). Assessing the effects of water compositions on oil recovery using core rock is time and cost intensive. By mimicking the structure and process on a microfluidic scale and by visualization of in situ oil and water distributions, almost immediate results and mechanistic insights can be obtained. With this motivation, we introduce a microfluidic platform for 'rock-on-chip' experiments and related data analyses procedures concerning oil recovery.

## METHOD

The chip design consists of a polydimethylsiloxane channel sealed with a glass coverslip. Synthetic calcite particles are assembled into a packed bed by using a barrier within the channel. The packed bed is first aged with formation water and then with oil. Next water flooding process is mimicked by injecting distinct brines at controlled flow rate (c.q. capillary number). Confocal fluorescence microscopy is used to visualize the spatial distributions of calcite, brine and oil, up to a depth of 5 µm. To quantify mineral, water and oil distributions, three-dimensional image data are collected and an automated image analysis is applied to convert grayscale images to residual oil percentages.

## RESULTS



(a) (b)

Figure (a) illustrates the calcite packed bed within the microfluidic channel and data acquisition performed at different positions. From image post-processing, figure (b) shows residual oil percentage at 12 positions along the packed bed after water-flooding.

## NOVEL/ADDITIVE INFORMATION

Experimental simulation of EOR processes by microfluidic platforms is currently in infancy. Few visualization studies using packed beds were done using an artificial chemistry/quasi-monolayer [1, 2, 3]. We focus on the in situ chemical aspects by using packed mineral particles and process relevant fluid compositions. Our microfluidic platform should produce similar trends as for 3D rock system, will be extended to elevated temperatures and real rock material.

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# Use of micromodels for understanding the mechanisms of capillary trapping in porous medium

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## Abstract in 300 words (maximum)

In oil production context, most of the studies show that primary and secondary recovery methods fail to yield above 20 %–40 % of original oil in place. By using modern enhanced oil recovery (EOR) techniques, recovery can reach up 60 to 65 %. These techniques of EOR are essentially designed to recover the residual oil. Recently, a renewal of interest in those techniques restarts the research dedicated to those methodologies. In this work, we focus on chemical EOR when surfactants are injected in water wet oil reservoirs. In this situation, the capillary trapping is important and can lead to a high level of residual saturation. At the end of the secondary recovery, the residual oil is trapped in the pore structure in a discontinous way and it becomes very difficult to mobilize the oil ganglia due to capillary trapping. A better understanding of the phenomena causing physical retention and mobilization of oil in porous media is essential to predict the volume and distribution of recoverable oil, and thus optimize the use of recovery processes.

In this work, we study the conditions of trapping and untrapping of an oil phase after water flooding in a microsystem initially saturated with oil. We use 2D transparent porous medium (micromodel) with a fixed geometry. The first step of the experiment is to set a reproducible disconnected non-wetting phase saturation. The following sequence is then applied: initial saturation of the micromodel with the wetting phase and drainage by injecting the non-wetting phase at fixed rate. Then, spontaneous and forced imbibition of the wetting phase is performed at different flow rates. All the sequences are recorded and treated by image processing and the non-wetting phase saturation and distribution is measured through time. We focus particularly on the study of the role of interfacial tension (IFT) on the level of residual saturation in connection with the mechanisms of breakage of oil continuity. We also determine and compare the capillary desaturation curves obtained with different pairs of model fluids with different IFT in the same geometry, which allow to separate capillary effects from geometric effects.

# NOVEL THERMOPLASTIC FLUOROELASTOMER FOR RAPID FABRICATION OF CHEMICALLY COMPATIBLE MICRODEVICES

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Here we present a novel soft thermoplastic fluoroelastomer that can be rapidly patterned with microchannels through hot embossing and self-sealed to make microfluidic chips. The polymer, called “Fluoroflex,” exhibits resistance to a range of commonly used organic solvents that are incompatible with devices made from polydimethylsiloxane and other common polymeric materials [1-2].

Our current work focuses on determining the suitability of Fluoroflex as a chemically compatible microfluidic material with a facile fabrication process. Its compatibility with a variety of organic solvents was evaluated by determining the degree of swelling, if any, when exposed to a solvent. The swelling behavior is correlated with the solubility parameters of each solvent, a good predictor of swelling behavior in polymer-solvent interactions [3]. The resulting swelling behavior for a range of organic solvents, along with their solubility parameters, is summarized in Table 1 (Annex 1). An estimation of the three-component, Hansen solubility parameter of Fluoroflex was made based on the swelling data gathered and could be used to predict whether or not an untested solvent would have an unfavorable interaction with Fluoroflex.

Fluoroflex was also characterized to determine its potential as microfluidic chip material. The polymer is optically transparent – critical for visualization and in photochemical applications – through the visible and near ultraviolet ranges, and profilometer measurements on micropatterned Fluoroflex showed good molding resolution and mold-chip fidelity.

Ongoing evaluation includes the characterization of Fluoroflex chip assembly and sealing behavior (the material has been shown to be reversibly self-sealing) and bulk mechanical characterization. Through the existing and ongoing characterization we have demonstrated Fluoroflex to be a material largely suitable for use with organic solvents while being rapid and facile to fabricate, giving way to the potential for low-cost, high throughput flow chemistry devices as well as the feasibility of microreactor rapid prototyping.

# Annex 1

| Solvent | $\delta_T$ | $\delta_D$ | $\delta_P$ | $\delta_H$ | $S_{Fluoroflex}$ | $S_{PDMS}$ |
|---|---|---|---|---|---|---|
| Pentane | 14.5 | 14.5 | 0.0 | 0.0 | 1.00 | 1.44 |
| Hexane | 14.9 | 14.9 | 0.0 | 0.0 | 1.00 | 1.35 |
| n-heptane | 15.3 | 15.3 | 0.0 | 0.0 | 1.01 | 1.34 |
| Diisopropylamine | 15.3 | 14.8 | 1.7 | 3.5 | 1.00 | 2.13 |
| Cyclohexane | 16.8 | 16.8 | 0.0 | 0.2 | 1.00 | 1.33 |
| 1,2-dimethoxyethane | 17.6 | 15.4 | 6.0 | 6.0 | 1.27 | 1.32 |
| Triethylamine | 17.8 | 17.8 | 0.4 | 1.0 | 1.00 | 1.58 |
| Xylenes | 18.1 | 17.8 | 1.0 | 3.1 | 1.00 | 1.41 |
| Toluene | 18.2 | 18.0 | 1.4 | 2.0 | 1.02 | 1.31 |
| Benzene | 18.5 | 18.4 | 0.0 | 2.0 | 1.00 | 1.28 |
| Dimethylcarbonate | 18.7 | 15.5 | 3.9 | 9.7 | 1.18 | 1.03 |
| Chloroform | 18.9 | 17.8 | 3.1 | 5.7 | 1.01 | 1.39 |
| 2-butanone | 19.1 | 16.0 | 9.0 | 5.1 | 1.43 | 1.21 |
| Tetrahydrofuran | 19.5 | 16.8 | 5.7 | 8.0 | 1.43 | 1.38 |
| Chlorobenzene | 19.6 | 19.0 | 4.3 | 2.0 | 1.00 | 1.22 |
| Acetone | 19.9 | 15.5 | 10.4 | 7.0 | 1.43 | 1.06 |
| Dichloromethane | 20.2 | 18.2 | 6.3 | 6.1 | 1.03 | 1.22 |
| 1,4-dioxane | 20.5 | 19.0 | 1.8 | 7.4 | 1.13 | 1.16 |
| Pyridine | 21.8 | 19.0 | 8.8 | 5.9 | 1.08 | 1.06 |
| N-methylpyrrolidone | 23.0 | 18 | 12.3 | 7.2 | 1.27 | 1.03 |
| Acetonitrile | 24.4 | 15.3 | 18.0 | 6.1 | 1.08 | 1.01 |
| 1-Propanol | 24.6 | 16 | 6.8 | 17.4 | 1.00 | 1.09 |
| Dimethylformamide | 24.9 | 17.4 | 13.7 | 11.3 | 1.22 | 1.02 |
| Nitromethane | 25.1 | 15.8 | 18.8 | 5.1 | 1.03 | 1.00 |
| Ethanol | 26.5 | 15.8 | 8.8 | 19.4 | 1.00 | 1.04 |
| Methanol | 29.6 | 15.1 | 12.3 | 22.3 | 1.01 | 1.02 |
| Water | 47.8 | 15.6 | 16.0 | 42.3 | 1.00 | 1.00 |

*Table 1: The swelling ratios of Fluoroflex ($S_{Fluoroflex}$) and PDMS ($S_{PDMS}$) (where, for example, a swelling ratio of S=2 would indicate the material swelling to twice its original size when exposed to the solvent) for a selection of common organic solvents along with their three-component, Hansen solubility parameters, describing different molecular interactions that contribute to the cohesive energy, and thus the solubility, of a compound, where $\delta_D$ is the dispersion parameter, $\delta_P$ is the polar parameter, and $\delta_H$ is the hydrogen bonding parameter. $\delta_T$ is the total, or Hildebrand, solubility parameter, found through the relationship $\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$. Solubility parameters in [joule$^{1/2}$ cm$^{-3/2}$]. Swelling ratios in red indicate those that are above the threshold (S>1.20) that has been considered unusable in PDMS devices. This level of swelling in Fluoroflex is observed in very few of the solvents tested. PDMS swelling ratios from [1].*

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# Characterization of extensional properties of polymer solutions with a dedicated microfluidic device: applications to drag reducers and water treatment

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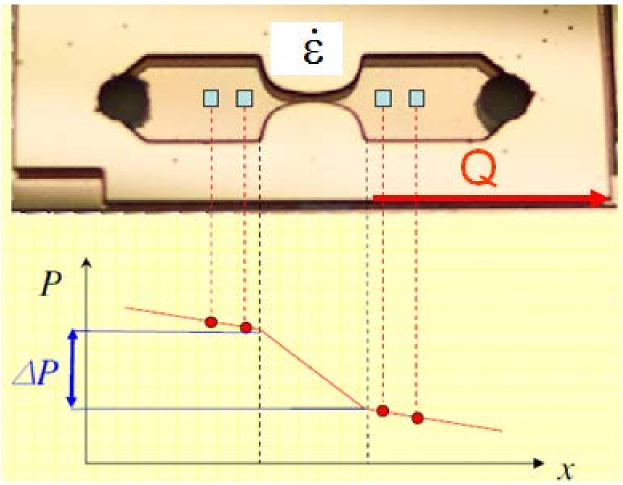
IFPEN, France

## Abstract

Flow properties of polymer solutions are basically related to their rheological properties. They are usually measured with rotational rheometers in shear conditions. Anyhow for specific processes, extensional properties may also be useful to determine [1, 2]. This can be particularly achieved with the Evroc microfluidic device that displays an hyperbolic contraction instrumented with pressure gauges. From the relationship between imposed flow rates and resulting pressures drops, extensional properties of fluids can be characterized. For a Newtonian fluid, it has been checked that expected Trouton Number is well measured. This number is the ratio between extensional and shear viscosities. It equals either 3, 6 or 4 respectively for uniaxial, biaxial or planar extensions [3] . For non-Newtonian fluids, these values are only expected at small strains. With higher deformation, imposed extensional flows will induce the maximum stretching of macromolecules and higher values are obtained. They help comparing extensional properties of fluids. This ability has been successfully applied to study drag reducing agents. These organic or aqueous additives are high molecular weight polymers that are able to eliminate bursts in turbulent flows [4]. They are implemented in many applications such as crude oil transports, medicals, irrigation, fire-fighting operations etc. Thanks to the microfluidic apparatus, it has been shown that the most efficient drag reducers are the ones with higher extensional properties. The comparison of extensional properties has also been done for two polymers: a biopolymer and a synthetic one. Despite the similarity of their shear viscosity, they display different extensional properties. These differences explain their opposite responses in the flotation of their respective oily effluents. Actually when the fluids display extensional properties, drainage films are significantly slow down and the related water treatment is less efficient to remove oil [5].



Hyperbolic contration of Evroc device

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# Breast tumor-on-chip

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**Back ground and Aim**: Breast cancer is the most common invasive cancer among women. There are several chemotherapeutic and radiotherapeutics approaches are available but they have certain limitations. Over the past few years, improved understanding of the microenvironment heterogeneity of breast cancer has allowed the development of more effective treatment strategy. However, researchers have still not been able to recapitulate the entire tumor microenvironment to study the tumor progression and invasion. In this way, more complex 3D *in vitro* cancer models have been developed. These 3D tumor models still lack the cell-cell, cell-tissue interactions, and more balanced interstitial fluidic flow that are present within living system. Furthermore, mimicking of different physiological condition and collection of samples from tumor microenvironment is also difficult. In this direction, breast tumor-on-chip model has emerged as an alternative system to study the tumor microenvironment and deciphering its role in metastasis. In this work microfluidics system is integrated to 3D breast tumor to bridge the gap between 2D and animal model effectively, to evaluate the efficacy of anti-cancerous drug. These microfluidic systems contain small chambers for cell culture, enabling control over local gradients and maintain the interstitial fluidic flow of the local breast tumor microenvironment.

**Experimental Procedure:** In this work the multi-compartment microfluidics platform is generated by designing a specific PDMS chip with three channels which are separated by specific barriers (50 µm). The cancerous and fibroblast cells (cocultures) are suspended with collagen hydrogel and loaded into central channel, one of the side channels are used to grow the endothelial cells to make this system vascularized. The barriers inside the chips will allow to exchange the signaling molecules.

**Results:** The cancer cells in presence of fibroblast cells are growing very well into these microchannels and this result is confirmed with live/dead assay. At this stage we got the preliminary data, we are still working in this area.

**Conclusion:** Integration of microfluidics system into breast tumor will add as another toolset that can make a more efficient testing platform in the current therapeutic development pipeline.

# ONLINE OIL-IN-WATER EMULSION CHARACTERIZATION FOR ENHANCED OIL RECOVERY APPLICATIONS

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Enhanced Oil Recovery (EOR) is one of the methods used to meet the growing demand for oil. Generally, EOR formulation are evaluated through a "coreflood test" which is carried out on a rock sample under conditions very close to those of the reservoir. The performance of a coreflood experiment is evaluated by determining the amount of oil recovered and the amount of surfactants retained in the reservoir.

Currently, coreflood effluents are analyzed offline. The quantity of oil recovered is measured by volumetry or RMN. Surfactants are dosed by hyamine assay or by HPLC. It is noteworthy that these analyses are difficult to carry out since the effluents may contain emulsions that are difficult to separate. Moreover, it is unclear whether all surfactants are well in the aqueous phase, or whether they are partly trapped in the oil phase.

To overcome these difficulties and quantify the two important parameters, we have developed an integrated online measurement technique based on microfluidic tools. The experimental setup includes: a dilution and mixing chip, an observation chamber, a membrane-based separation device, and an on-line UV-visible spectrometer. This experimental setup was validated with model fluid mixtures, and was evaluated on real systems. Finally, it was tested under representative conditions of coreflood experiments.

The obtained results proved the effectiveness of the experimental setup and showed a clear improvement compared to the quantification protocols currently applied.

# METHODOLOGIES FOR THERMODYNAMIC PROPERTIES CHARACTERIZATION IN MICROFLUIDIC SYSTEMS

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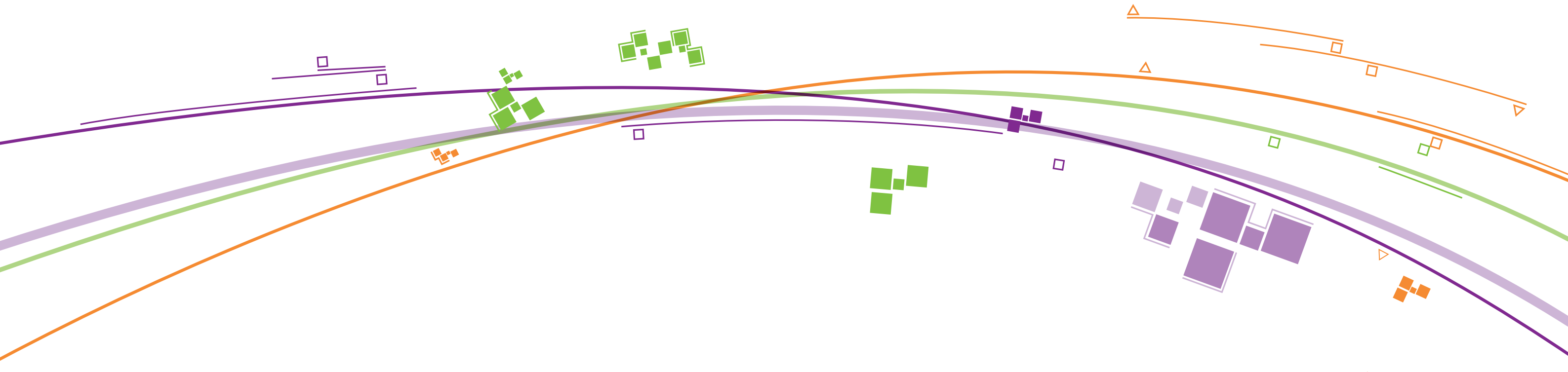
Today, knowledge and access to experimental thermodynamic data under high pressure and high temperature conditions is a major challenge in the industry. Being aware of and anticipating the behavior of a fluid regarding its state, viscosity or density is crucial in the oil extraction sector or in substance transformation processes (refining, separation, conversion, ...), for example.

This work is part of this problematic with the desire to develop tools for high throughput experimentation allowing the rapid acquisition of experimental data in order to improve the accuracy, operator safety and environmental impact by using small quantities of products.

In this context, the development of a microfluidic experimental set-up was carried out. Approaches were developed for the construction of phase diagrams of fluid mixtures, based on the optical detection of bubble point and dew point under high pressure and high temperature conditions (up to 100 bar and 350 °C). We also present the results obtained with silicon-Pyrex microfluidic chips, on ideal systems (CO2 + pentane, CO2 + MEG) and not ideal systems (water + n-propanol). The results obtained highlighted the current advantages and limitations of microfluidic approaches for characterizing phase equilibria. In comparison with experimental data from the literature and data from thermodynamic models, this thesis work is a first step towards the development of methodologies adapted to more complex systems for applications in the field of energy, in particular.



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