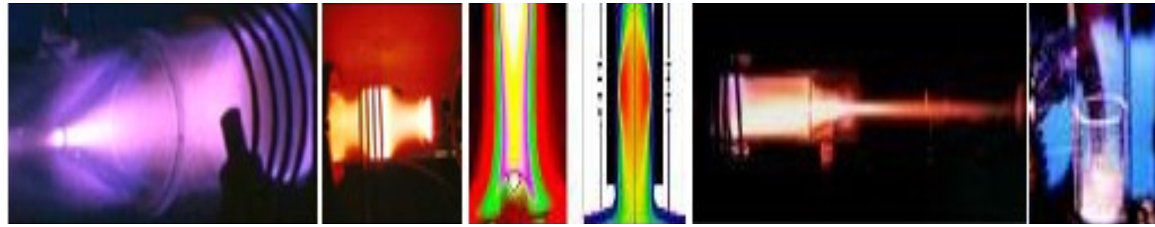
Chimie ParisTech

PSL Research University Paris

IRCP Institut de Recherche de Chimie Paris



Microfluidique et procédés plasmas pour la synthèse chimique

S. Ognier[1], M. Zhang[1], S. Cavadias[1], M. Tatoulian[1]

Collaborations :

Prof. Xavier Duten – LSPM- Univ. Sorbonne Paris Nord (Plasma physics)

C. Ollivier, L. Fensterbank - IPCM-Sorbonne U - (Organic chemistry)

PSL Université Paris

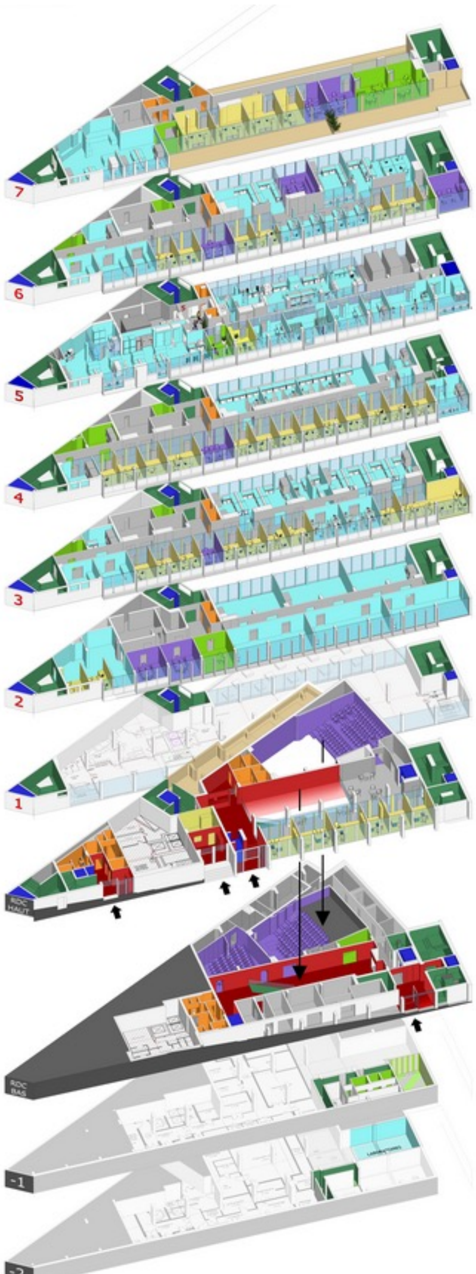
Our group is specialised in plasma technology and chemical engineering

Our group is part of the National excellence laboratory IPGG

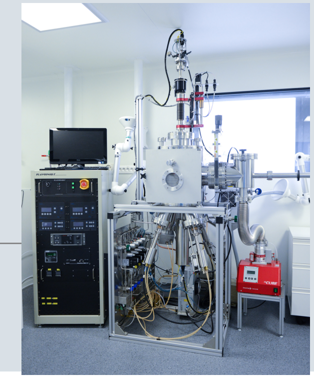
Pierre Gilles de Gennes Institute for microfluidics

IPGG: 5000 m^2 dedicated to microfluidic and its applications…

7th floor: « Plasma, Processes, Microsystems » group



Technological platform IPGG



Clean room (110 m^2)

Grey room
(140 m^2/ISO 9)

Microscopy room
(1 Confocal, 2 Videomicroscopes,
1 Spinning-disk)

Possibility to engineer/fabricate our own continous flow reactors
Analytocal tools for in line analysis

Outline

Organic synthesis in gas/liquid plasma micro-reactor

Challenges and opportunities?

Generation of radical species by Dielectric Barrier Discharge

Starting from simple ***gases***, it is possible to generate a wide variety of radicals at ambient pressure and temperature by only applying high electric field in the gas

$O_{2gas} + e^- \rightarrow O^{\bullet}_{gas} + O^{\bullet}_{gas} + e^-$

$H_{2gas} + e^- \rightarrow H^{\bullet}_{gas} + H^{\bullet}_{gas} + e^-$

$Cl_{2gas} + e^- \rightarrow Cl^{\bullet}_{gas} + Cl^{\bullet}_{gas} + e^-$

$HCF_{3gas} + e^- \rightarrow CF_3{}^{\bullet}_{gas} + H^{\bullet}_{gas} + e^-$

$H_2O_{gas} + e^- \rightarrow H^{\bullet}_{gas} + HO^{\bullet}_{gas} + e^-$

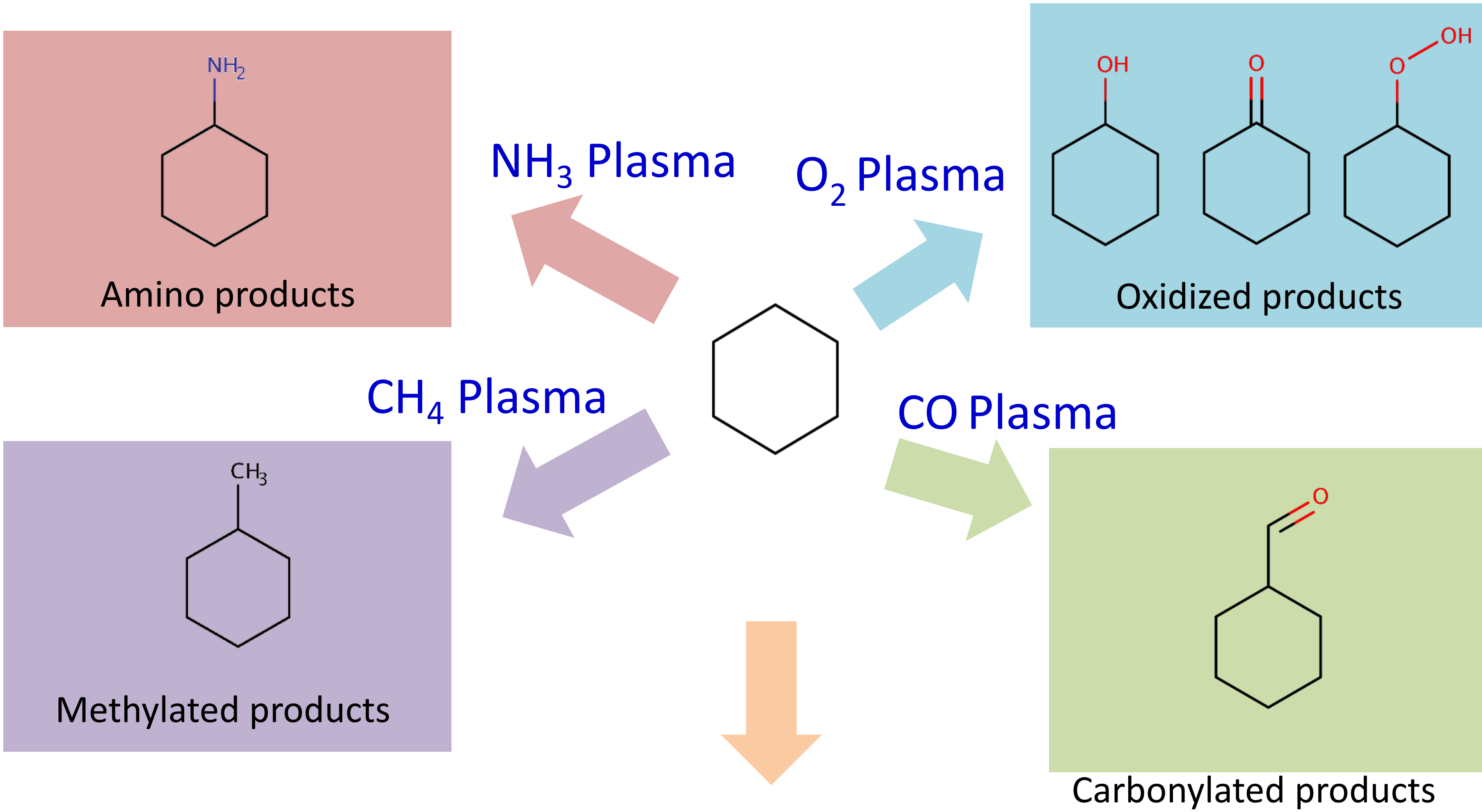
$NH_{3gas} + e^- \rightarrow NH_2{}^{\bullet}_{gas} + H^{\bullet}_{gas}$

$C_2H_{6gas} + e^- \rightarrow {}^{\bullet}CH_{3gas} + {}^{\bullet}CH_{3gas} + e^-$

Lifetime of gaseous radicals: ~ ms

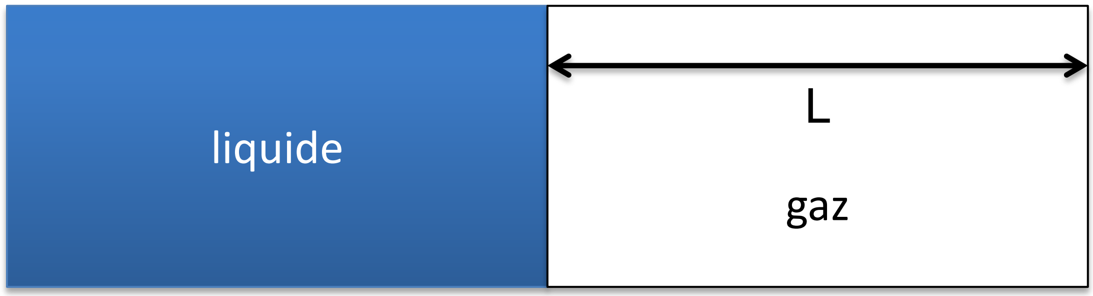
Going small for the better use of short-lived radicals

Toward gas/liquid plasma reactor for chemical synthesis



Objective: to functionnalize organic molecules using plasma-generated gaseous radicals

Temps de diffusion



L (mm)	$t_{diffusion}$ (seconds)
10	10
1	0.1
0.1	0.001
0.01	10^{-5}

$$t_{diffusion} = \frac{L^2}{D}$$

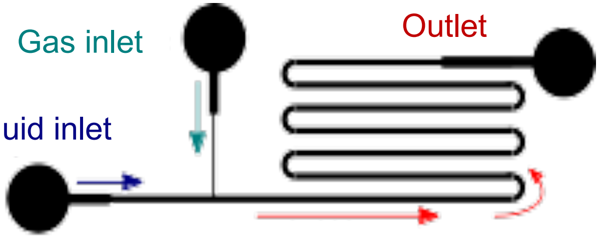
D: molar diffusion coefficient ($m^2.s^{-1}$)

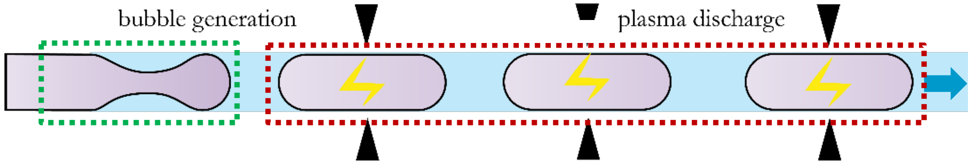
The width L of the plasma zone should not be too large so that the radical species diffuse rapidly in the liquid phase!

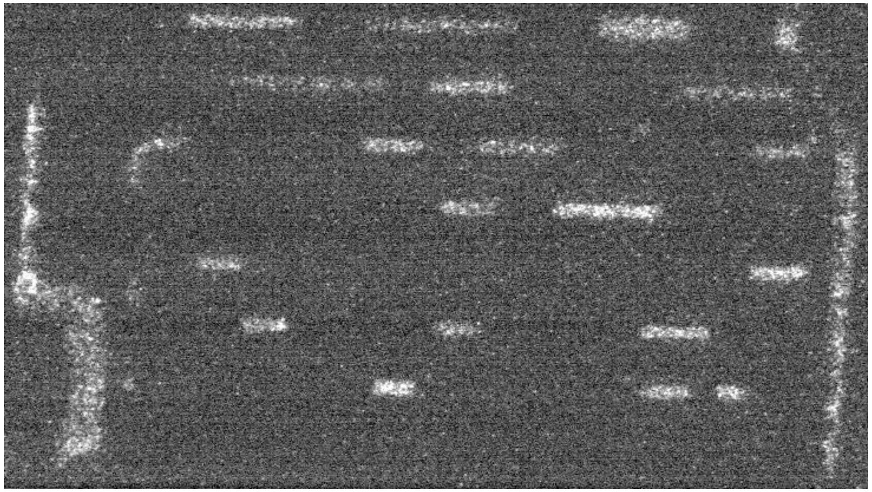
Toward High efficiency chemical process:
→ **smaller reactor with high S/V ratio**
→ **by optimizing G/L transfer thanks to miniaturised systems…**

1st PhD student
2013 – 2016

A bubbling plasma/liquid microreactor

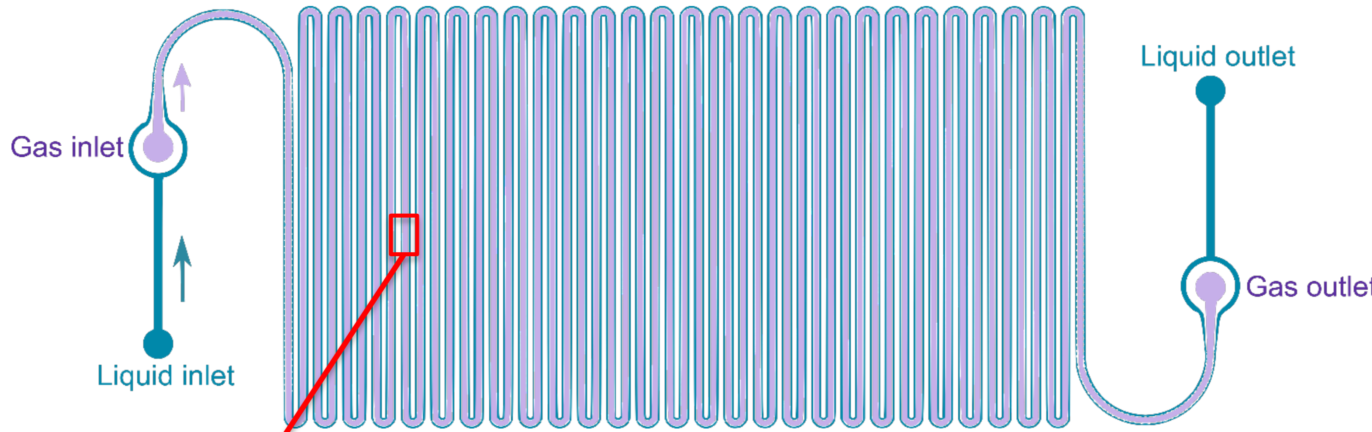






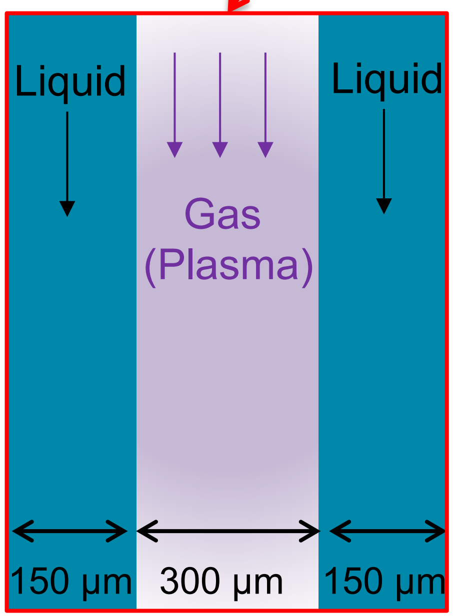
European Patent: « Diphasic gas/liquid plasma reactor » M. TATOULIAN, S. OGNIER, M. ZHANG, 2015. PCT/EP2016/080475.
Zhang, M. et al. *Green Processing and Synthesis* 6, nº 1 (2017): 63-72.

Second step: to increase the residence time…
The latest “Biflow” geometry

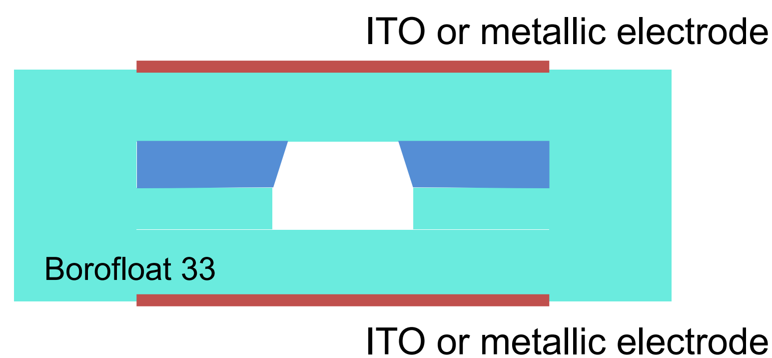


Top view

Julien Wengler
PhD :2015 – 2018



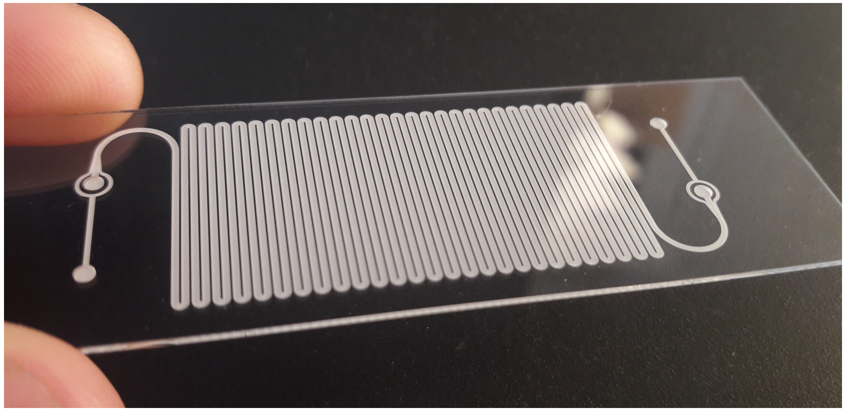
Top view (zoom)

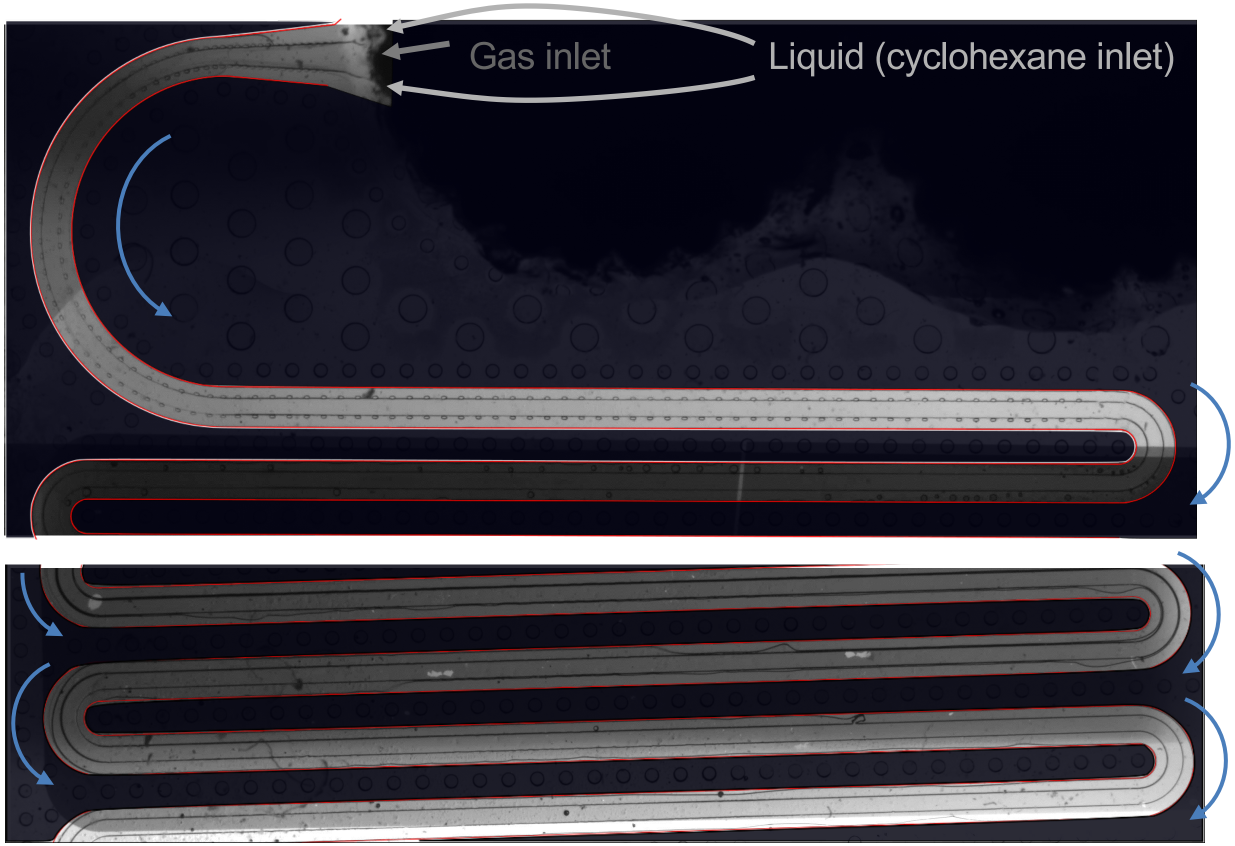


Cut view

Patent pending: (EP 18305214.1)
J. Wengler, S. Ognier, S. Al Ayoubi, M. Tatoulian

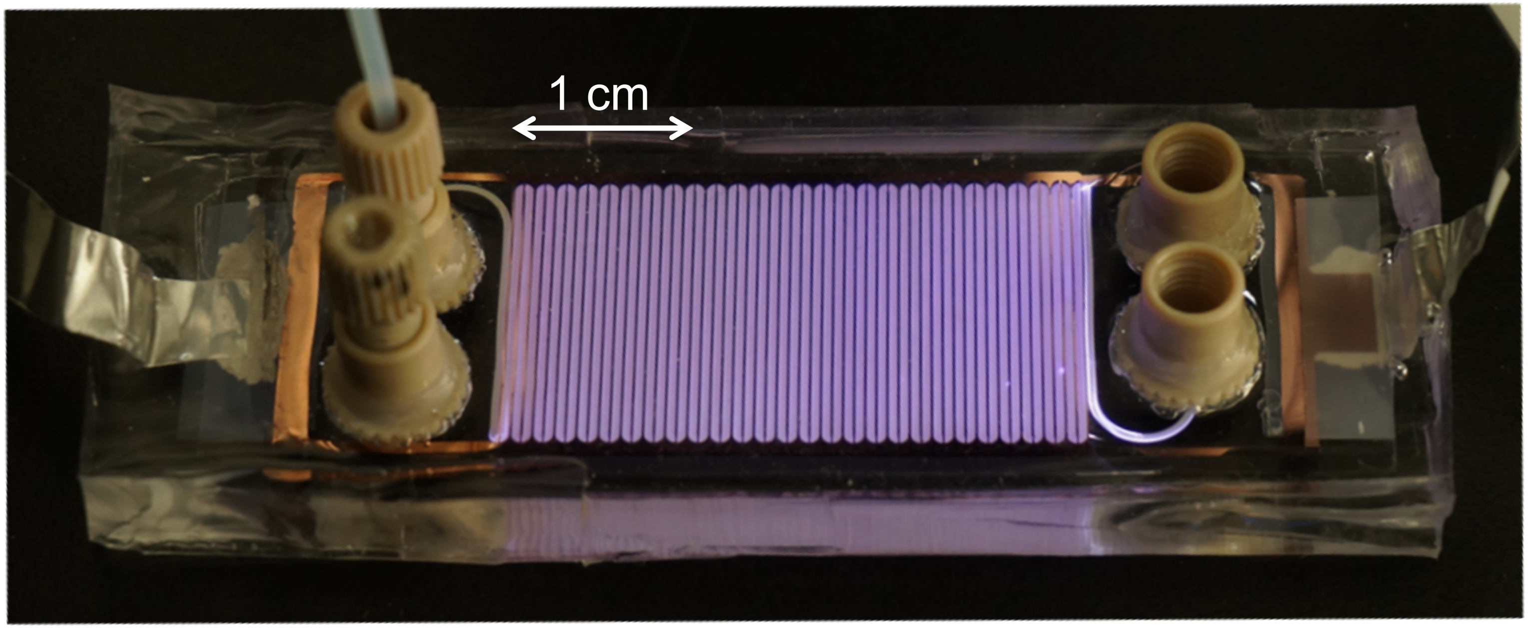
A biflow plasma/liquid microreactor





Stable G/L flow along a 1-3 m channel !

A biflow plasma/liquid microreactor



Channel Length ~ 1 m-3 m

Liquid residence time ~ 1-2 min

Typical flow rate values:

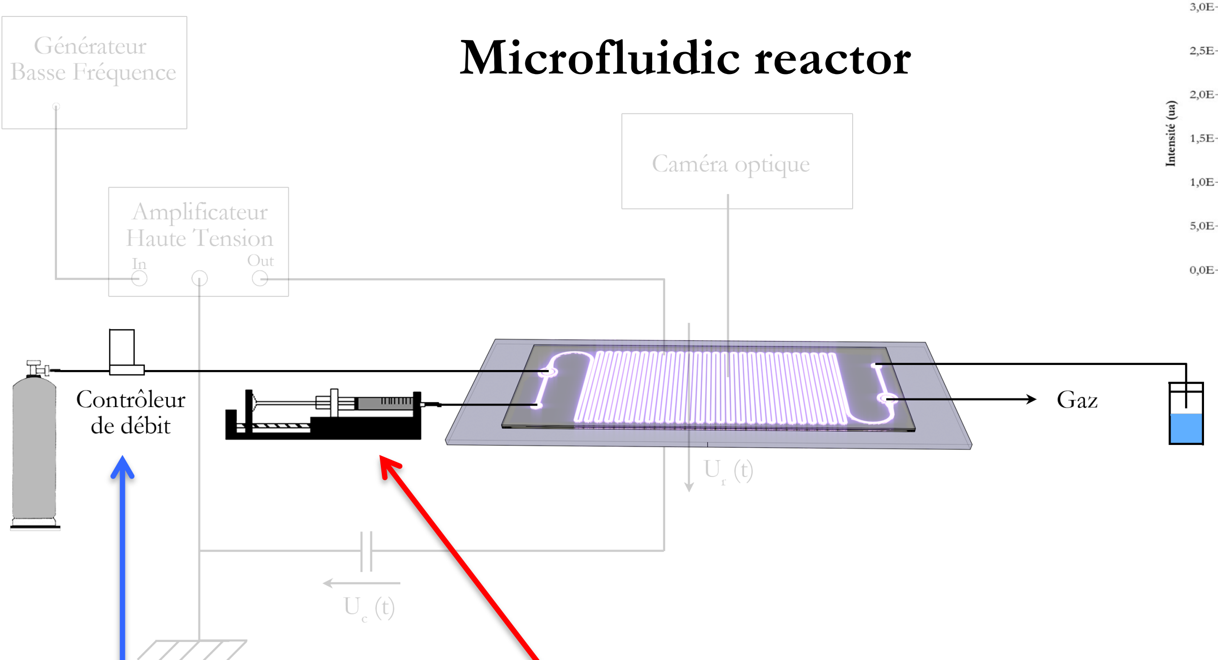
- Gas: 1 mL/min
- Liquid: 10-50 µL/min

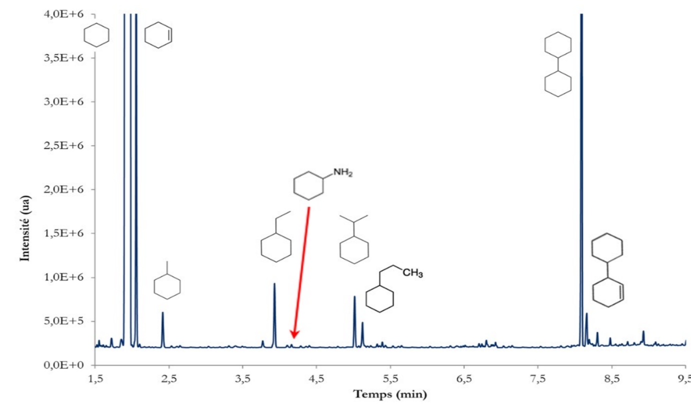
European Patent pending (EP 18305214.1) J. Wengler, S. Ognier, S. Al Ayoubi, M. Tatoulian

Organic synthesis in gas/liquid plasma micro-reactor

Experimental set-up for organic synthesis in a biflow plasma/liquid microreactor

Microfluidic reactor





Analysis of liquid phase
(GC-MS, LC/MS, NMR, GC-FID)

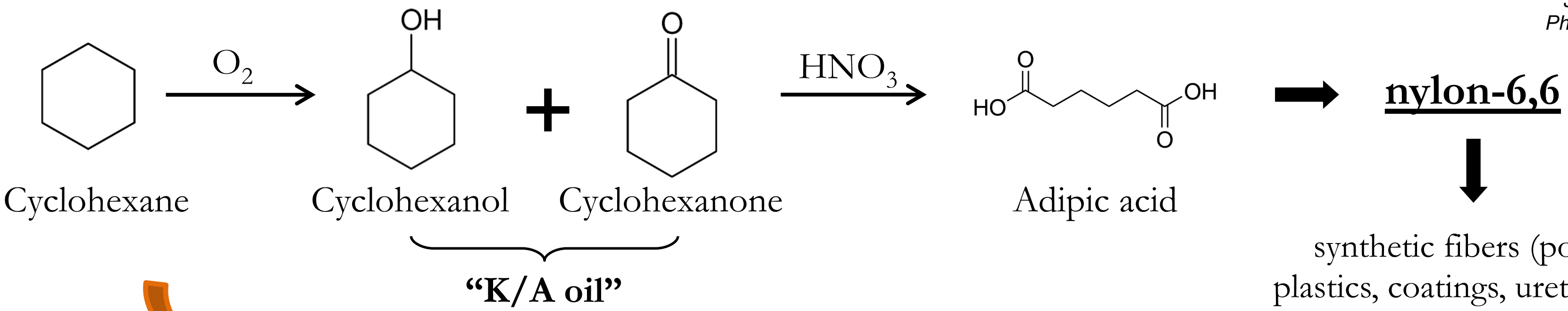
Injection of gas reactants
(O_2, NH_3, CO, CH_4….)
Q_{gaz}: 1 - 5 ml/min

Injection ol liquids
(cylohexane
or benzene)
$Q_{liquide}$: 3 à 40 µL/min

Prof. L. Fensterbank
Dr. C. Ollivier

A biflow plasma/liquid microreactor: Oxidation of Cyclohexane

Julien Wengler
PhD :2015 – 2018



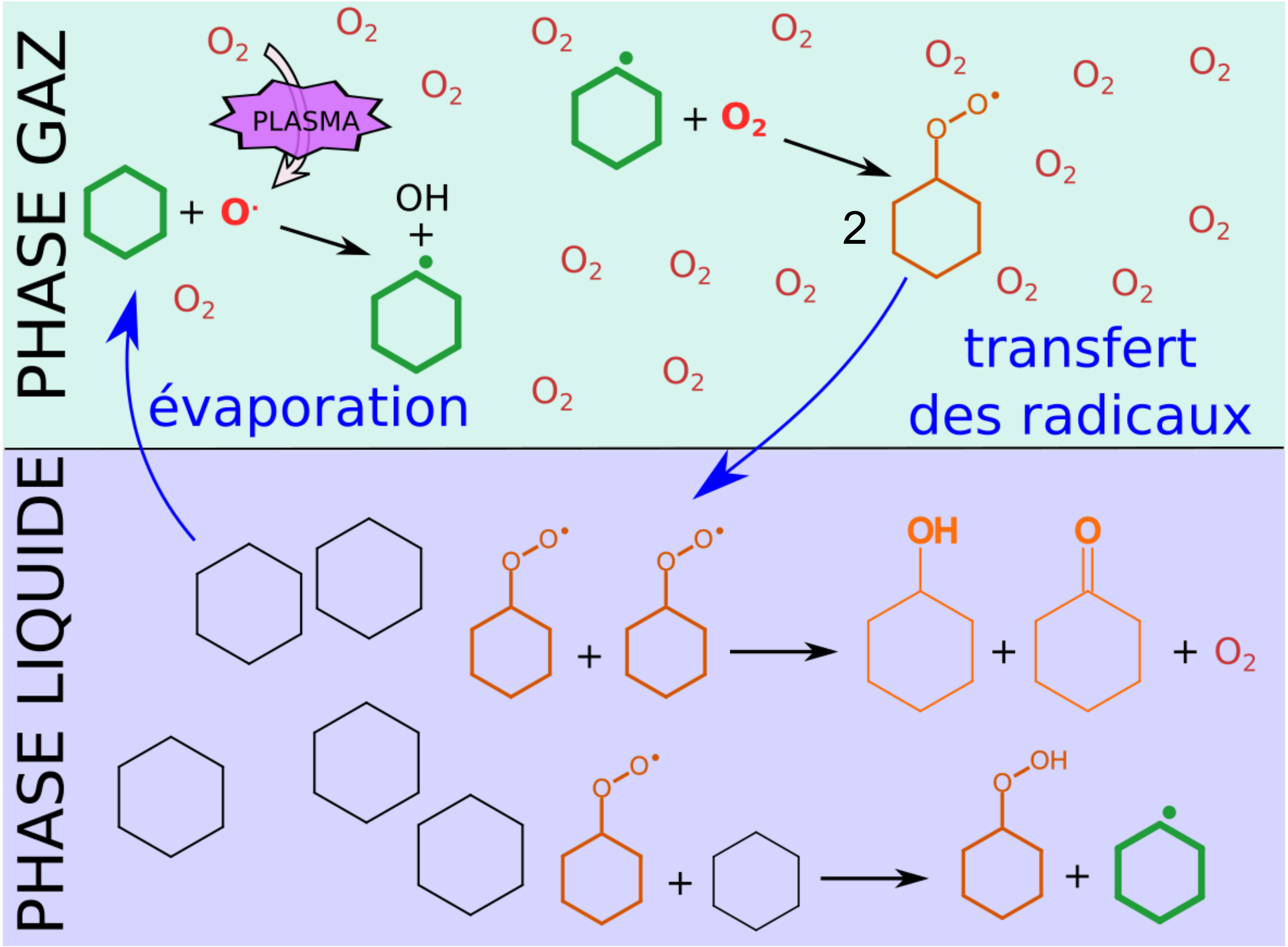
synthetic fibers (polyesters), plastics, coatings, urethane foams, elastomers, and synthetic lubricants...

Current industrial process (BASF Industrial Process)	125 – 175°C ; 8 – 15 bar **Several hours** ; Co based catalysis	**Poor conversion 5-15%** **Selectivity : 85-90 %**
Our plasma process:	O_2 plasma Ambiant T, atmospheric P No catalyst Residence time : 1-2 min	**Conversion : up to 30%** **Selectivity: 70 - 80%** **(To be improved)**

Improved conversion under milder conditions !

J. Wengler, S. Ognier, M. Zhang, E. Levernier, C. Guyon, C. Ollivier, L. Fensterbank, et M. Tatoulian , Reaction Chemistry & Engineering, Issue 6, 2018 DOI: 10.1039/C8RE00122G

A biflow plasma/liquid microreactor: Mechanism of Cyclohexane oxidation



Cyclohexanol and cyclohexanone are produced by the recombination of $C_6H_{11}OO°$ radicals in liquid phase

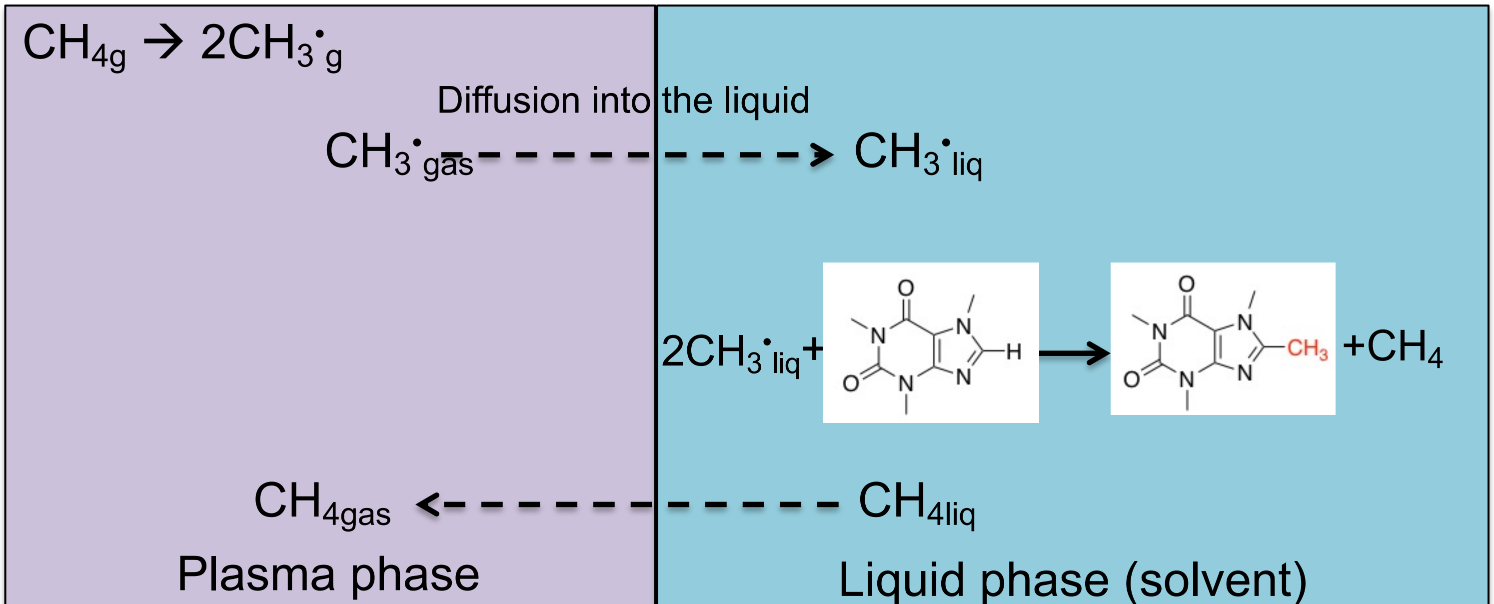
Cylohexanol and cyclohexanone are prevented from overreaction

Perspectives

Perspectives

Functionalization of non volatile complex molecules dissolved in an organic solvent

Example: methylation of cafeine



Challenges

Generating plasma in the presence of various organic solvents

Radicals need now to be transferred from gas to liquid

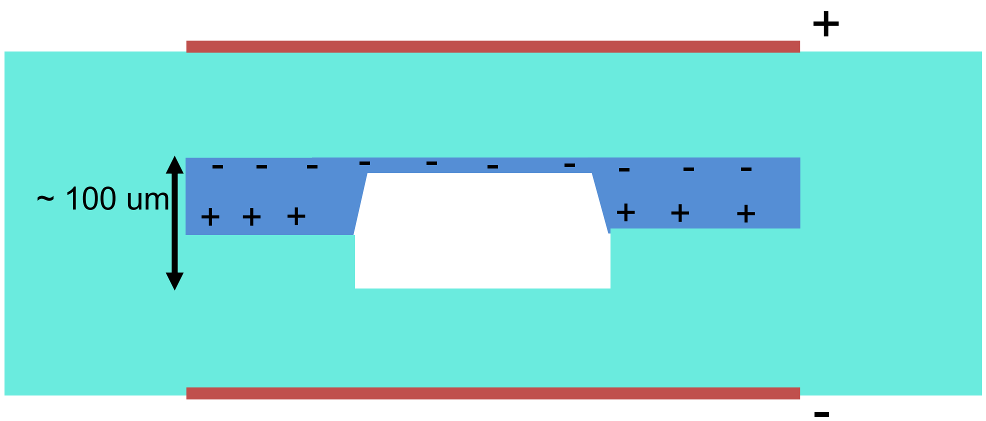
Challenges associated with the plasma functionalization of molecules in liquid phase

Plasma ignition in gas-liquid microreactors with various organic solvents

Solvant	ε	µ (mPa.s)	P_{vsat} 20°C (hPa)	ΔU Ar (kV) (1 kHz)	ΔU CH_4 (kV) (1 kHz)	ΔU O_2 (kV) (1 kHz)
Cyclohexane	2	0,89	104	11	13	9
1,4-dioxane	2	1,18	41	5 ?	10	9
THF	1,63	0,46	200	10	11	9
EtOAc	6	0,43	97	10	15	14
Pipéridine	5,9	1,6	3,9	6 ?	-	11
DCM	1,84	0,42	475	16 – 18 ?	25	-
CH_3COOH	6,2	15,3	1,12	14	-	?
$CHCl_3$	4,8	0,54	210	7	13	-
Acétonitrile (CH_3CN)	37,5	0,34	97			
Eau	80	0,89	17,5			-
DMF	37	0,8	3,5			-
DMSO	46,7	2	0,61			-
MeOH	33	0,54	200			-
Acétone	21	0,3	240			-

Challenges associated with the plasma functionalization of molecules in liquid phase

Ion mobility in liquid water influences the electric field?

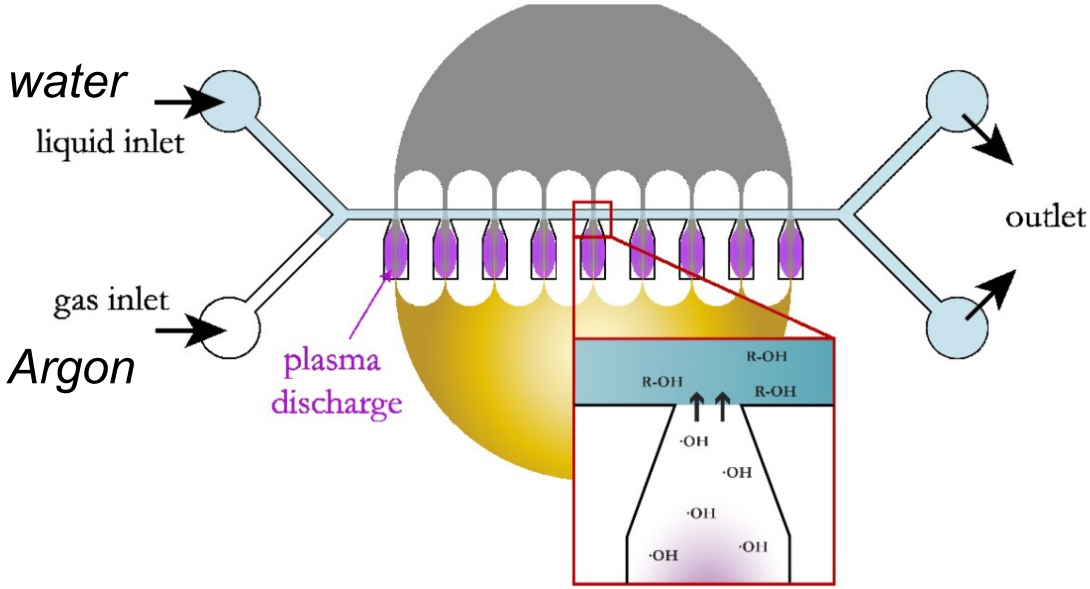


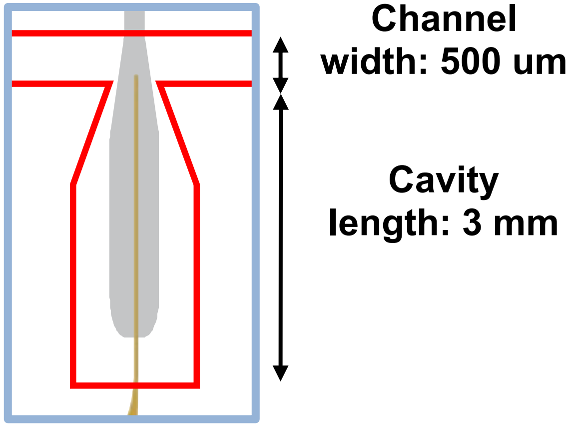
H^+ mobility in water : ~10^{-6} $m^2/V/s$
For an electric field of 10^7 V/m, the H^+ drift velocity: 10^2 m/s
For a gap of 100 um, it takes : **0.1 ms** for the proton to travel

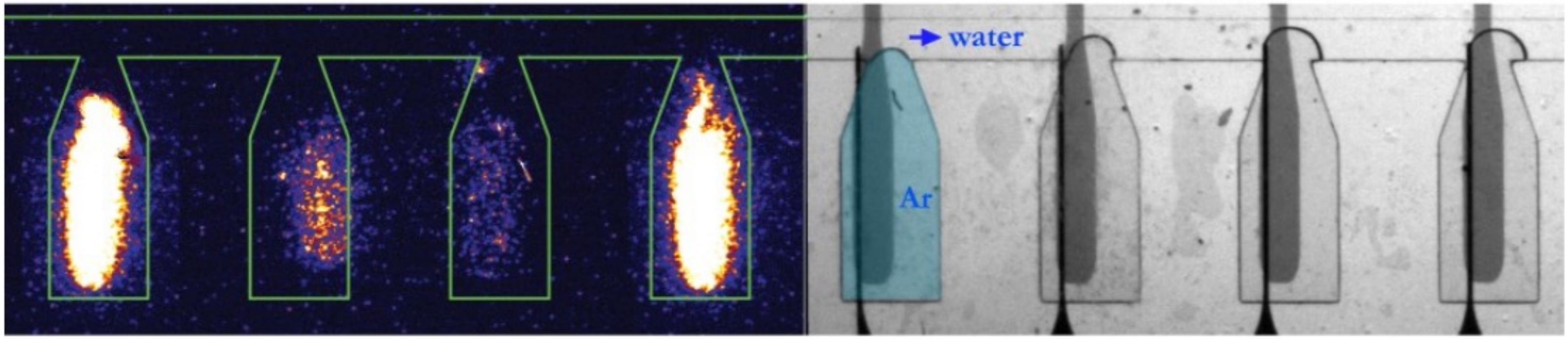
Use higher frequency of nano-pulsed sources?

Experimental study of mass transfer in the two-phase plasma/liquid reactor

Thèse Mengxue Zhang
2013-2016



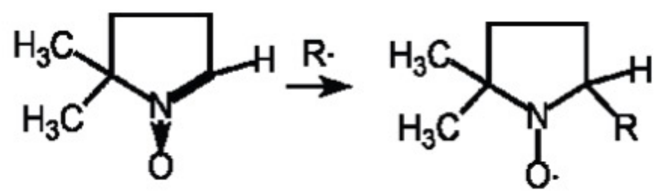


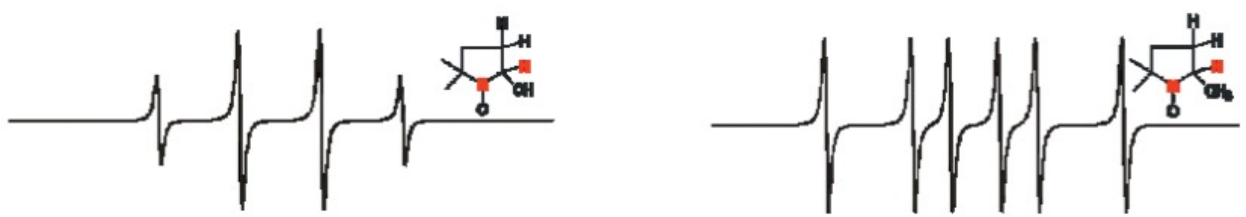


Experimental study of mass transfer in the two-phase plasma/liquid reactor

EPR measurements

> **DMPO**, 5,5-dimcthylpyrrolinc N-oxidc





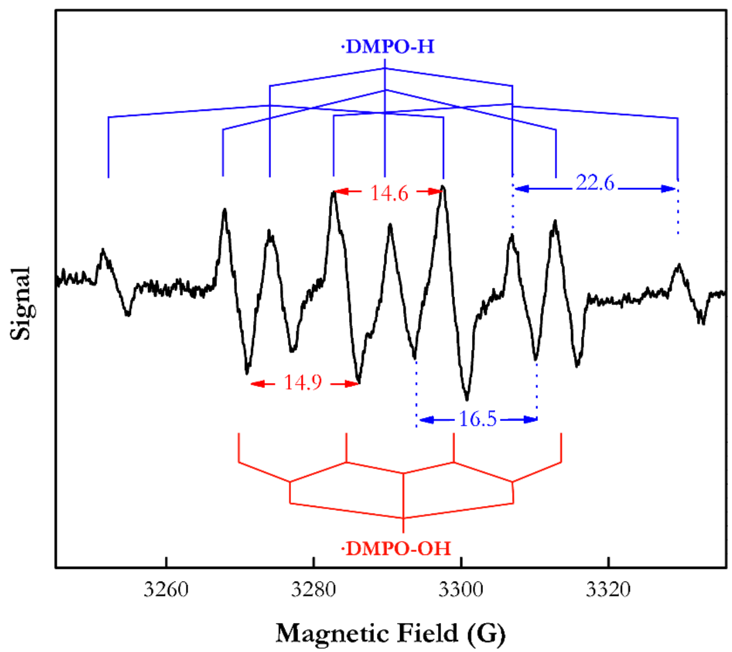
EPR signal of the spin adduct

La DMPO est ajoutée dans l’eau avec une concentration de 0,4 mol/L.
Il est nécessaire d’avoir une concentration en DMPO élevée afin d’être toujours en excès de DMPO à l’interface gaz/liquide

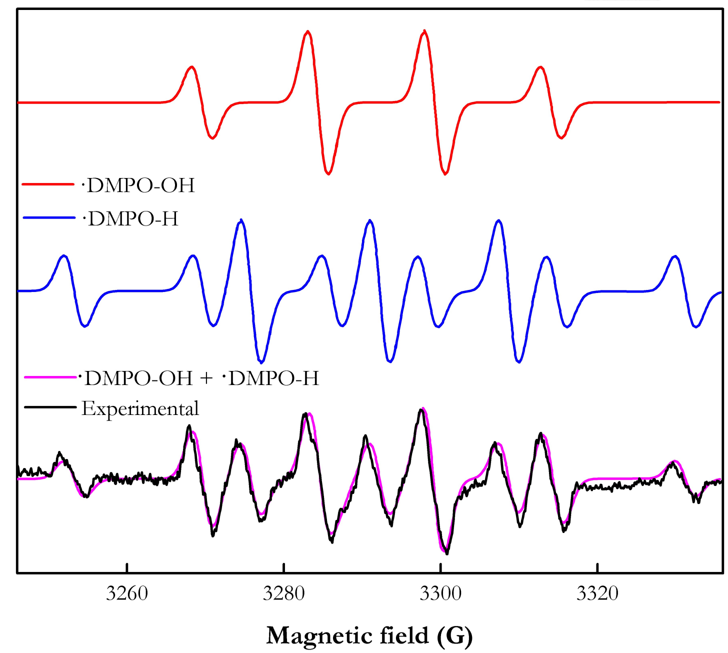
M. Zhang S. Ognier N. Touati, I. Hauner, C. Guyon, L. Binet , M. Tatoulian Plasma Processes and Polymers, 2018, vol 15

Experimental study of mass transfer in the two-phase plasma/liquid reactor

Spectre expérimental



Expérience vs Simulation

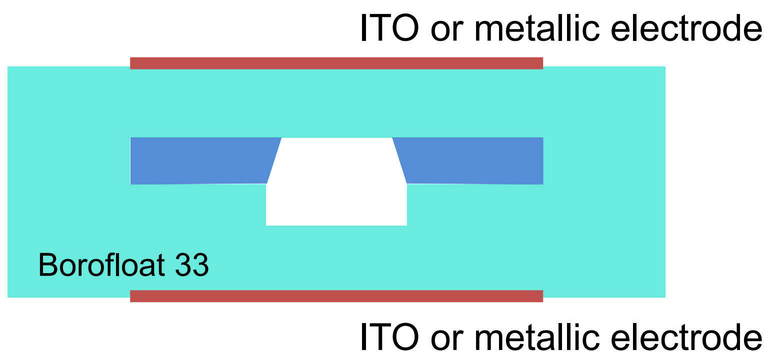


Piégeage de •H et de • OH en phase liquide

[DMPO-OH] ~ [DMPO-H] ~ 10^{-6} mol/L

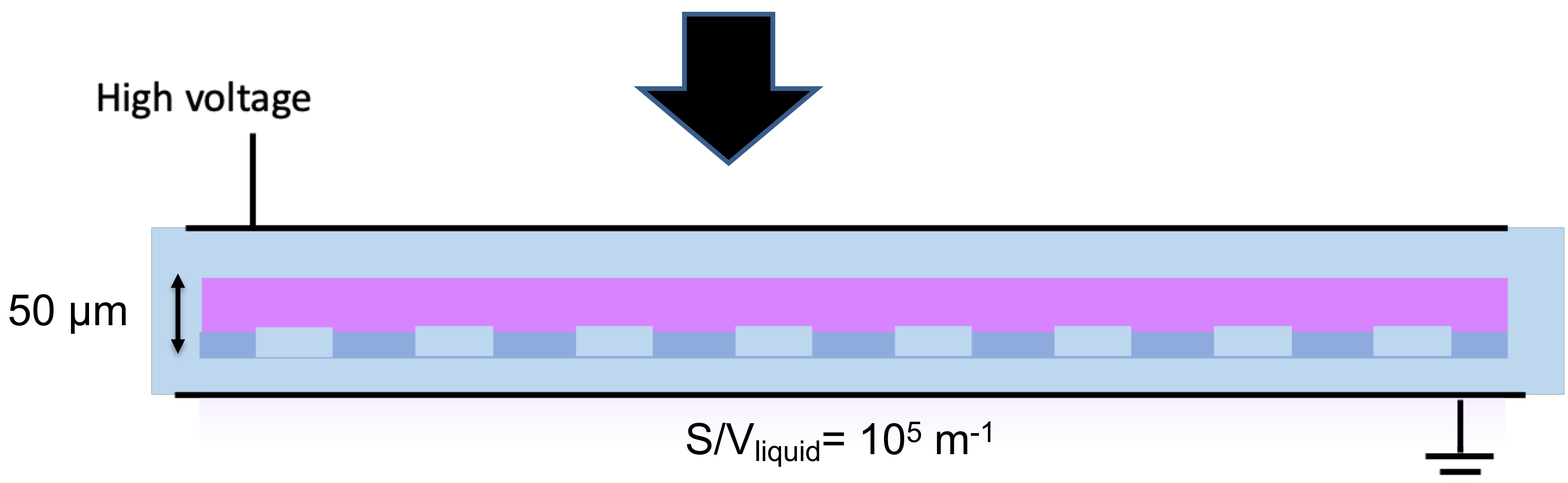
Le flux interfacial de OH° et H° est faible, aux environs de 10^{-5} mol.m^{-2}.s^{-1}, en raison des réactions de recombinaison très rapides en phase gaz

Challenges associated with the plasma functionnalization of molecules in liquid phase



$S/V_{liquid} = 10^4\ m^{-1}$

$T_{diffusion\ gas} = 2\ ms$



$T_{diffusion\ gas} = 0.2\ ms$

Conclusion

Plasma/liquid continuous microreactors can be a tool to functionnalize organic compounds in the absence of catalyst

Improving the selectivities of the reactions needs a fine tuning of the operating conditions, what is compatible with microfluidics

The functionalization of low volatile compounds in liquid phase is still a challenge

Acknowledgements

Partnership &Collaborators

Prof. L. Fensterbank
Dr. C. Ollivier

Equipe MACO, Sorbonne Université

Prof. Xavier Duten
– LSPM- Univ. Sorbonne Paris Nord

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Sanofi

Merci