



HAL
open science

Strong multiphysics coupling towards simulation of edible oil hydrogenation in monolith type reactor

Pierre Albrand, Anne-Marie Billet, Carine Julcour

► To cite this version:

Pierre Albrand, Anne-Marie Billet, Carine Julcour. Strong multiphysics coupling towards simulation of edible oil hydrogenation in monolith type reactor. COMSOL conference 2020, COMSOL, Oct 2020, Toulouse (FR), France. <hal-04750040>

HAL Id: hal-04750040

<https://hal.science/hal-04750040v1>

Submitted on 23 Oct 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Strong multiphysics coupling towards simulation of edible oil hydrogenation in monolith type reactor

Pierre ALBRAND, Anne-Marie BILLET & Carine JULCOUR

**COMSOL
CONFERENCE**
2020 EUROPE

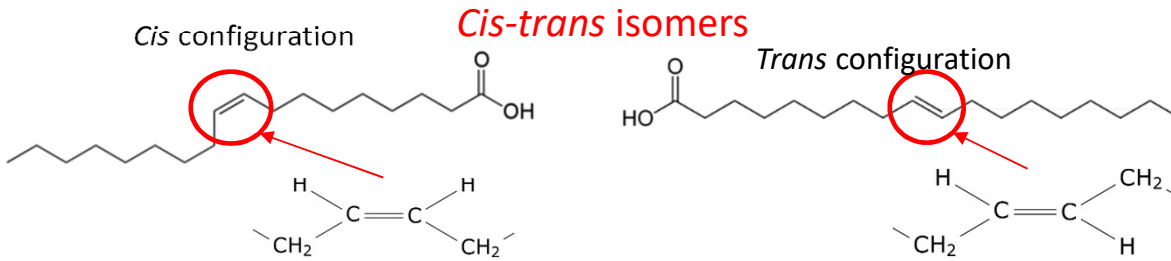


Université
de Toulouse

Vegetable oils & Hydrogenation

- What are vegetable oils made of?
 - Various fatty acid = carboxylic acids with 12 to 22 carbons
 - ... with carbon-carbon double bonds or *unsaturations*

Two possible configurations:

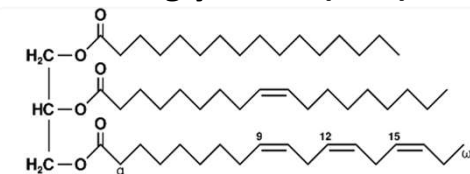


Rapeseed



Sunflower

Fatty acids are esterified to glycerol molecule → *triglycerids (TAG)*:



TAG represent 97% to 99%-mass of refined vegetable

Edible oil hydrogenation reaction

- Reaction in presence of solid catalysis :
 - $-HC=CH- + H_2 \rightarrow -CH_2-CH_2-$
- Objectives :
 - Reduce oil rancidity
 - Increase melting point temperature and oil viscosity
 - Produce *cis* monounsaturated FA (MUFA)

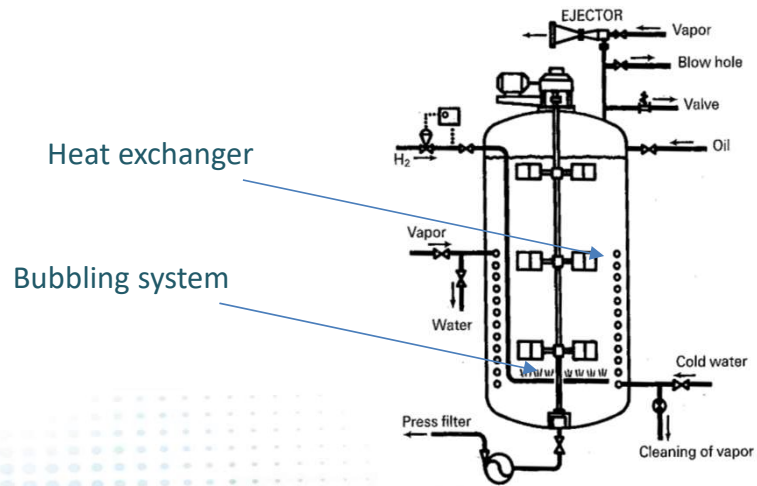
Problem → Trans and totally saturated fatty acids (SFA and TFA) produced as well (isomerisation)



Soy oil before and after hydrogenation

Hydrogenation technologies

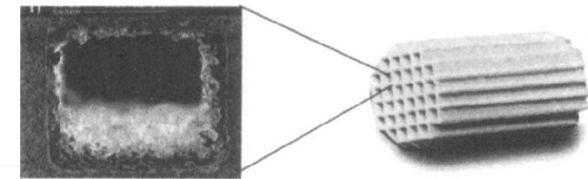
- **Current technology:** Batch reactor with with nickel powder (slurry) [FAUR, 1992].



Batch reactor for industrial edible oil hydrogenation [FAUR, 1992]

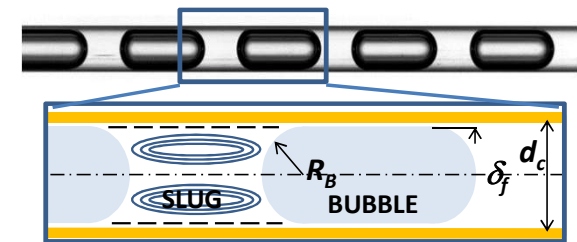
- **Advantages:**
 - Simple & flexible,
 - Low internal mass transfer resistance ($d_p \sim 10 \mu\text{m}$),
- **Drawbacks:**
 - Nickel catalysis not really selective
 - Operating conditions favor trans fat production [VELDSINK et coll.,1997],
 - Limited temperature control
 - Limited G-L transfer

- **Innovative technology:** Monolithe type reactor?
 - Reactor made of millimetric canals whose section is rectangle or circular
 - Catalysis layer at the wall (*washcoat*)



Monolith type reactor for GL reaction [FARRUSSENG et coll., 2002]

- **Application extended to three phase reaction in Taylor flow condition**



TAYLOR flow

- **Advantages:**
 - Low pressure drop
 - Enhanced GL mass transfer thanks to lubrication film and slug recirculation
 - Short diffusion length (also in the washcoat)
 - Near plug flow condition

This work goal

Are monolith type reactors suitable for edible oil hydrogenation i.e. (production of *cis* MUFA)?

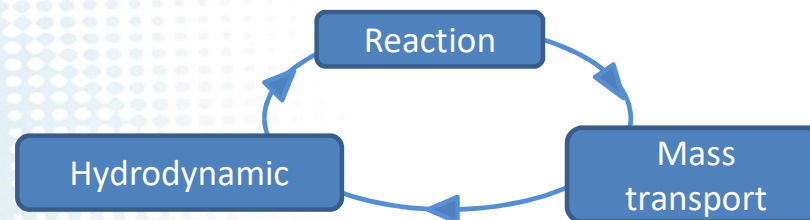
- **Why?**

- Existing technology produces SFA and TFA linked to cardiovascular diseases (CVD)
- Monolith type reactors in Taylor flow good candidate for three phase reaction:
 - Good GL mass transfer
 - Plug flow behavior

- **This case specificity:**

→ Viscosity depends of the oil's saturation degree

Strong multiphysic coupling expected between the different transport phenomena



Strong multiphysics coupling in edible oil hydrogenation

- **Viscosity model**

- By introducing p'_{ref} , the average number of unsaturation per FA, semi predictive group contribution model has been developed:

$$\ln \mu_L = K_0 + K_1 X + K_2 X^2 \text{ where } X = \frac{p'_{ref} - p'}{p'_{ref}}$$

$$A_{i,k} + \frac{B_{i,k}}{T} - C_{i,k} \ln(T) - D_{i,k} T$$

- **Diffusivity model**

$$D_{H_2-oil} = \frac{1,858 \times 10^{-15} (\Theta M_{oil})^{0.5} T}{\mu_L^{0.4} V_A^{0.6}}$$

$$D_{H_2-oil} \approx 10^{-8} \text{ m}^2/\text{s}$$

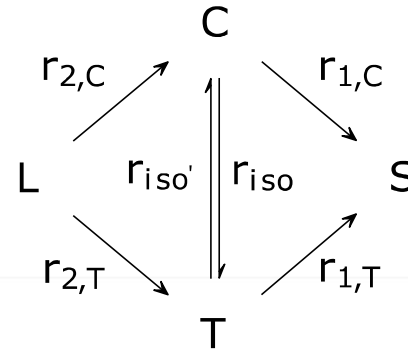
$$D_{TAG-oil} = \frac{AT}{\mu_L^{1.2}}$$

$$D_{TAG-oil} \approx 10^{-10} \text{ m}^2/\text{s}$$

Kinetic modelisation

- **Experiments show :**

- High temperatures tend to:
 - Favor MUFA production
 - ... but TFA as well
- High H₂ pressures tend to:
 - Favor saturation reaction
 - ... and limit isomerization reaction



Sunflower

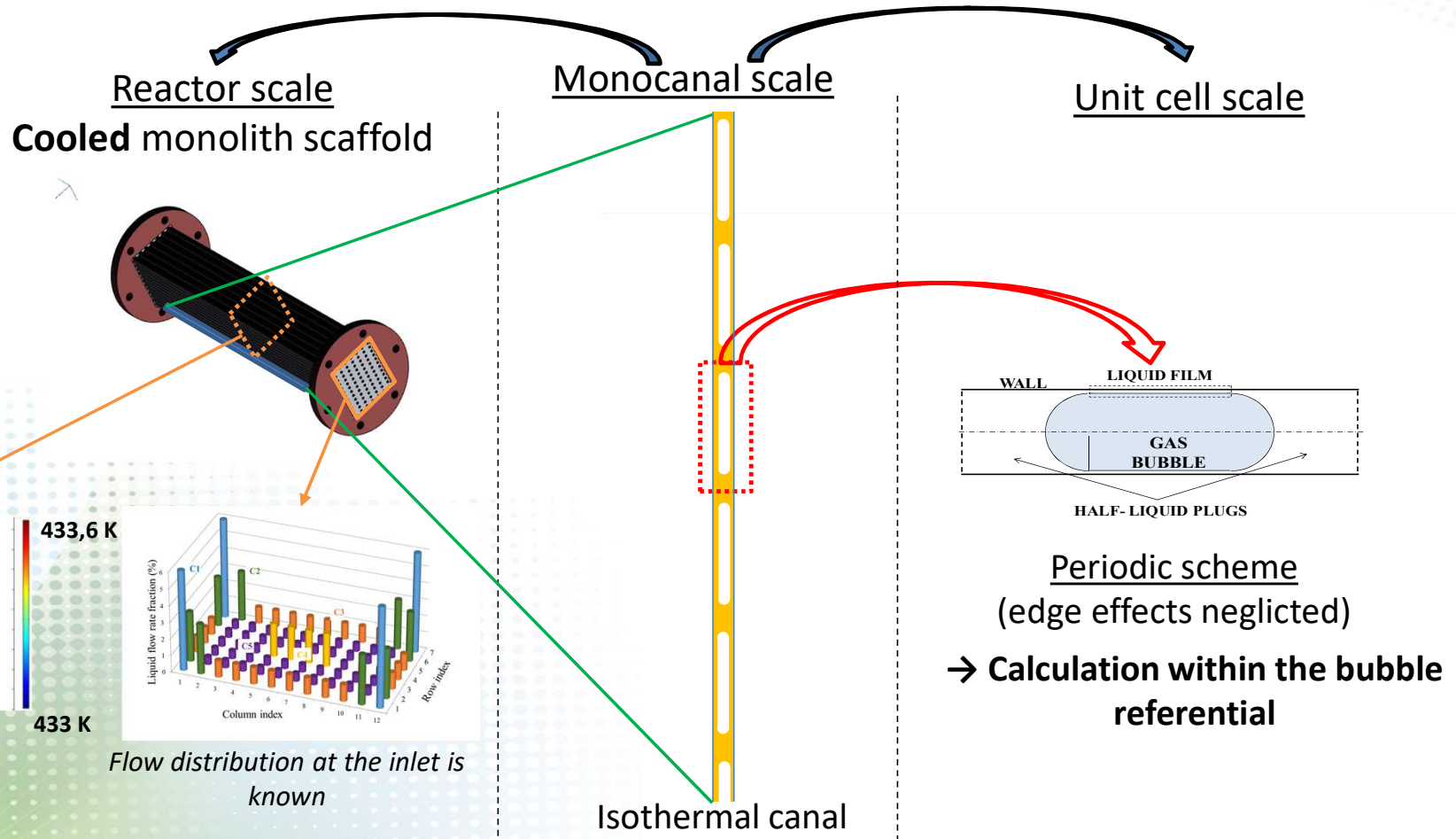
L: C18:2 (PUFA)
 C: C18:2 (MUFA *cis*)
 T: C18:2 (MUFA *trans* or TFA)
 S: C18:0 (SFA)

Kinetic model for sunflower oil

Saturation reactions	Isomerisation reactions
$r_{2,C} = \kappa_{2,C} \theta_L \theta_H$	$r_{iso} = \kappa_{iso} \theta_C (1 - \theta_H)$
$r_{2,T} = \kappa_{2,T} \theta_L \theta_H$	$r_{iso'} = \frac{\kappa_{iso}}{K_{iso}} \theta_T (1 - \theta_H)$
$r_{1,C} = \kappa_1 \theta_C \theta_H$	
$r_{1,T} = \kappa_1 \theta_T \theta_H$	

Monolith reactor modeling

Unit Cell (UC) approach

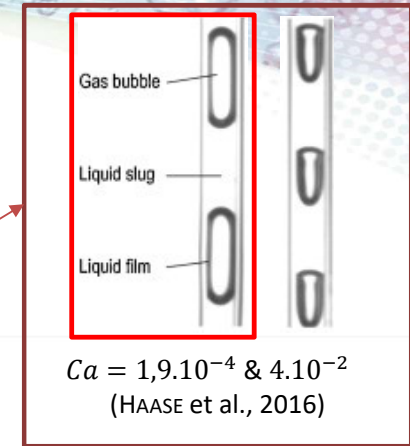


Simplification hypotheses

- Laminar flow ($Re < 1000$)
- Cylindrical and vertical canal \rightarrow 2D-axisymmetric geometry
- Low capillar number:

$$Ca = \frac{\mu_L U_B}{\sigma} \sim 10^{-3}$$

\rightarrow Ideal shaped bubble : cylindrical body with two hemispheres



- Pur gas \rightarrow resolution only for the liquid phase

- UC geometry unchanged during resolution

Gas consumption taking into account
by updating bubble velocity

Mathematical modeling

- Continuity and momentum equations (NAVIER-STOKES), **spf** :

$$\nabla \cdot (\rho_L \mathbf{u}) = 0$$

$$\frac{\partial \rho_L \mathbf{u}}{\partial t} + \rho_L (\mathbf{u} \cdot \nabla) \mathbf{u} = -\nabla P + \nabla \cdot [\mu_L (\nabla \mathbf{u} + \nabla \mathbf{u}^T)] + \rho_L \mathbf{g}$$

- Mass transport equation, **tds**:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_{i-oil} \nabla c_i) + \mathbf{u} \cdot \nabla c_i = 0$$

where i is a fatty acids (linked to a TAG) or H_2

→ ρ_L constant (TOPOLLAR, 1995)

→ μ_L and D_{i-oil} fonction of the local saturation degree

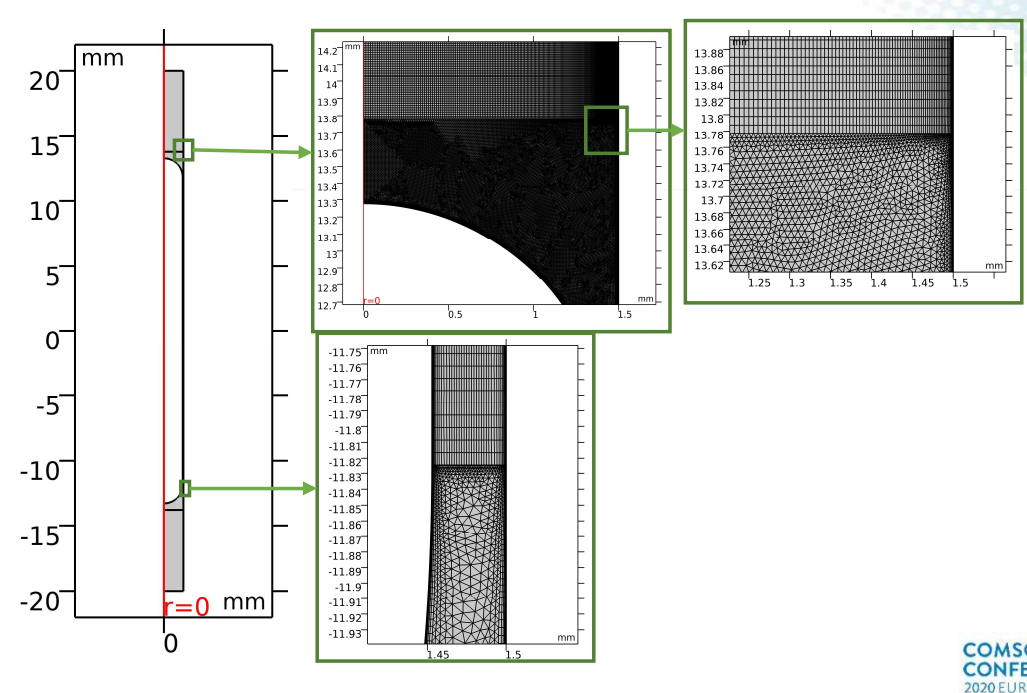
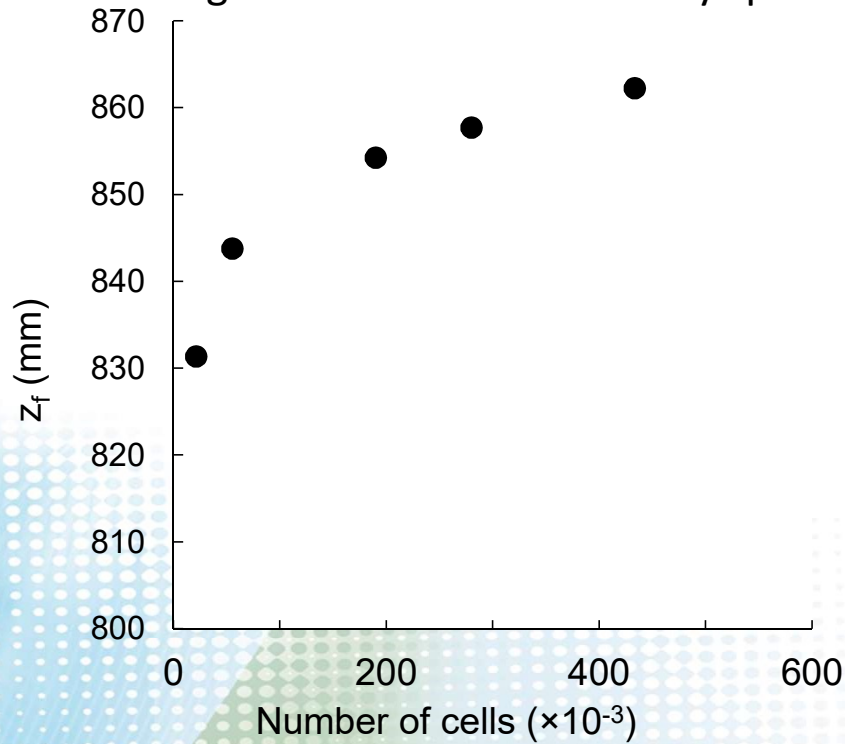
Numerical resolution

CFD software : COMSOL MULTIPHYSICS™ (v5.4 et v5.5)



Meshing convergence criteria:

Canal length to reach a theoretically sphere bubble (prelimary cases)

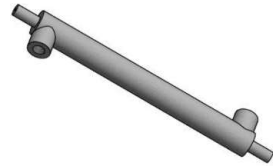


Meshing used: 266 000 cells
 → 3 to 4 days to compute (Intel Xeon @ 3,6 GHz, 128 Go RAM)

Monocanal reactor

- **Reactor made of monotubes**

- 2 mm diameter
- 20 cm long

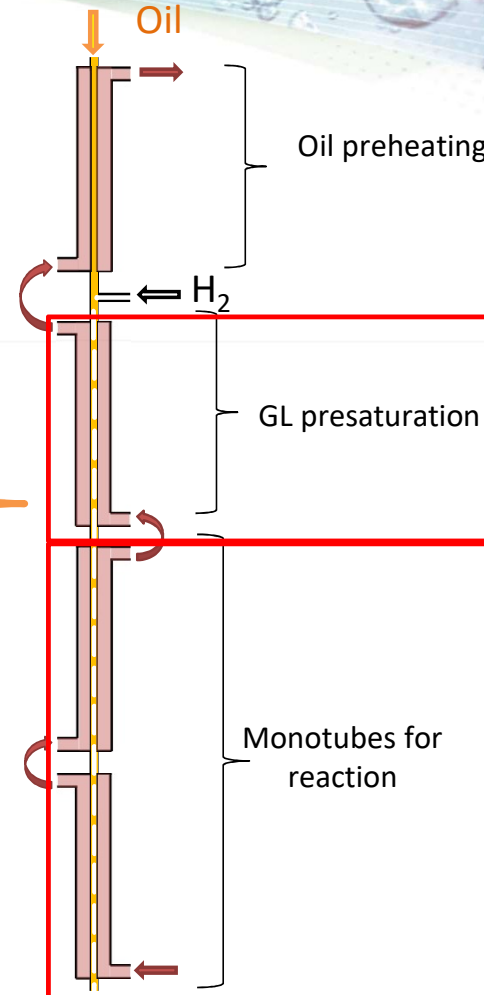


- **Monotubes set up**

- First monotube: oil heating
- Second monotube: G-L pre-saturation
- ... followed by one monotube pair for sunflower hydrogenation:



- Total length: 40 cm
- 10 μm thick washcoat (0,7% mass-Pd)

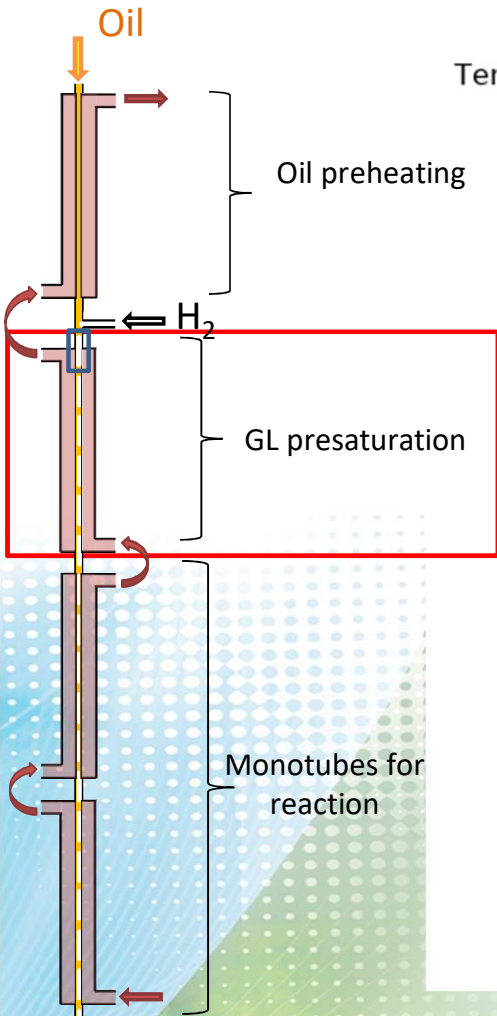


First simulation:
GL transfer only

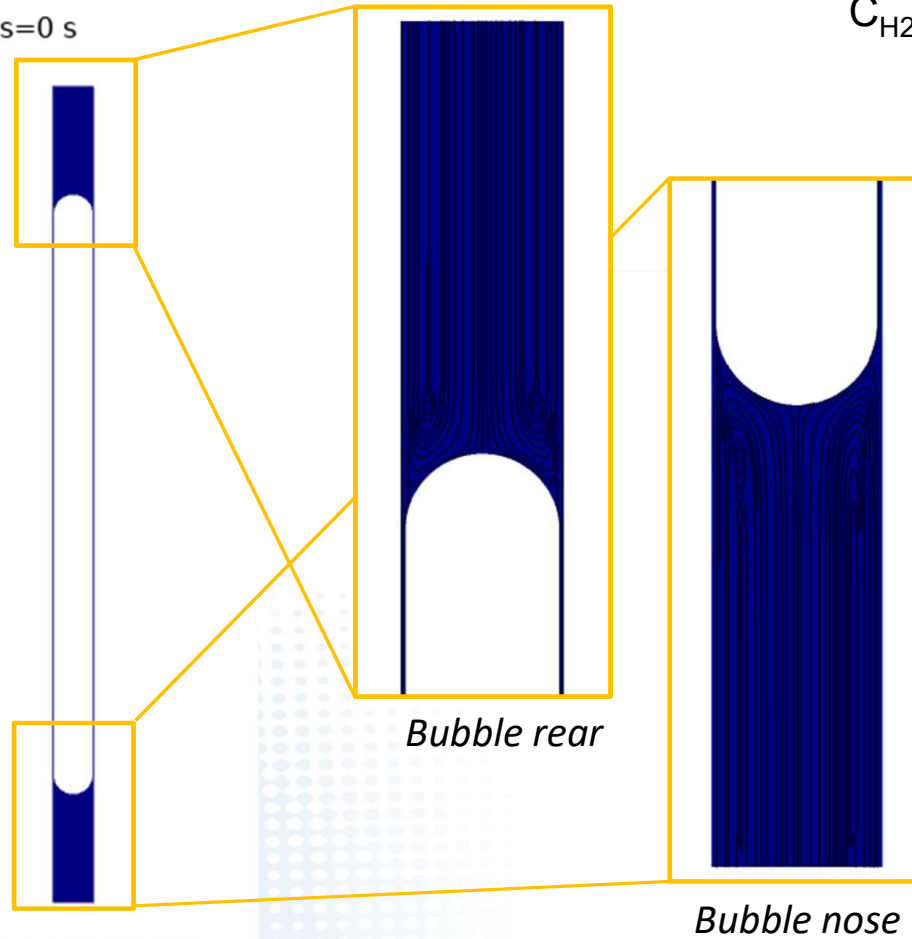
Second simulation:
Reaction and coupling considered

Pre-saturation GL section

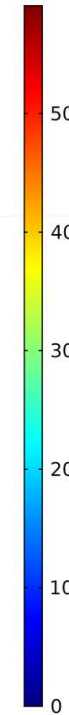
Case 160°C – 21 bar



Temps=0 s



C_{H₂} (mol.m⁻³)



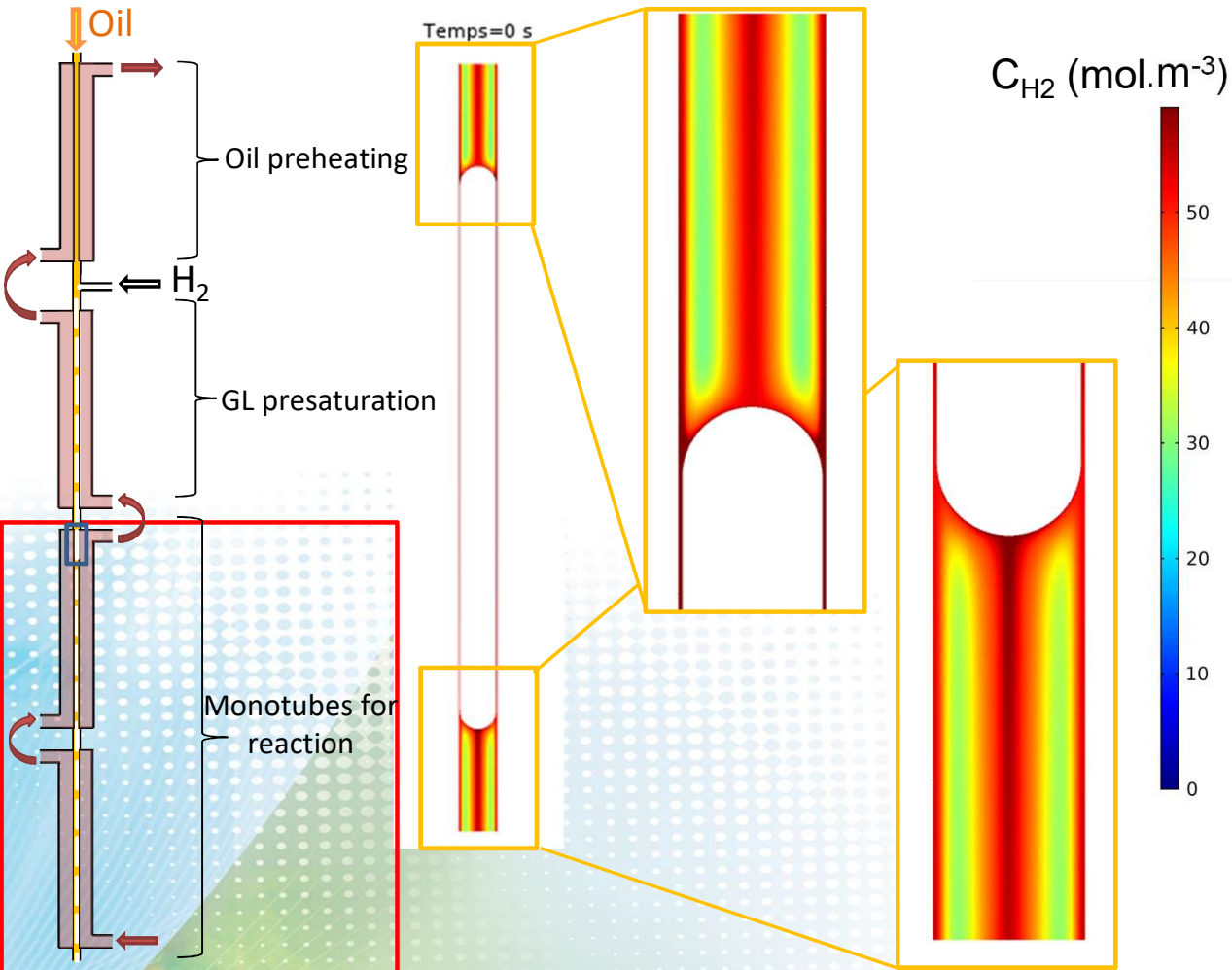
Gaz-liquid transfer without reaction at the wall

- Quick saturation of the lubrication film
- Quick saturation of the canal's center through convective transport
- Diffusive transport to vortex center

At the outlet: $c_{H_2}/c_{H_2}^* = 76\%$

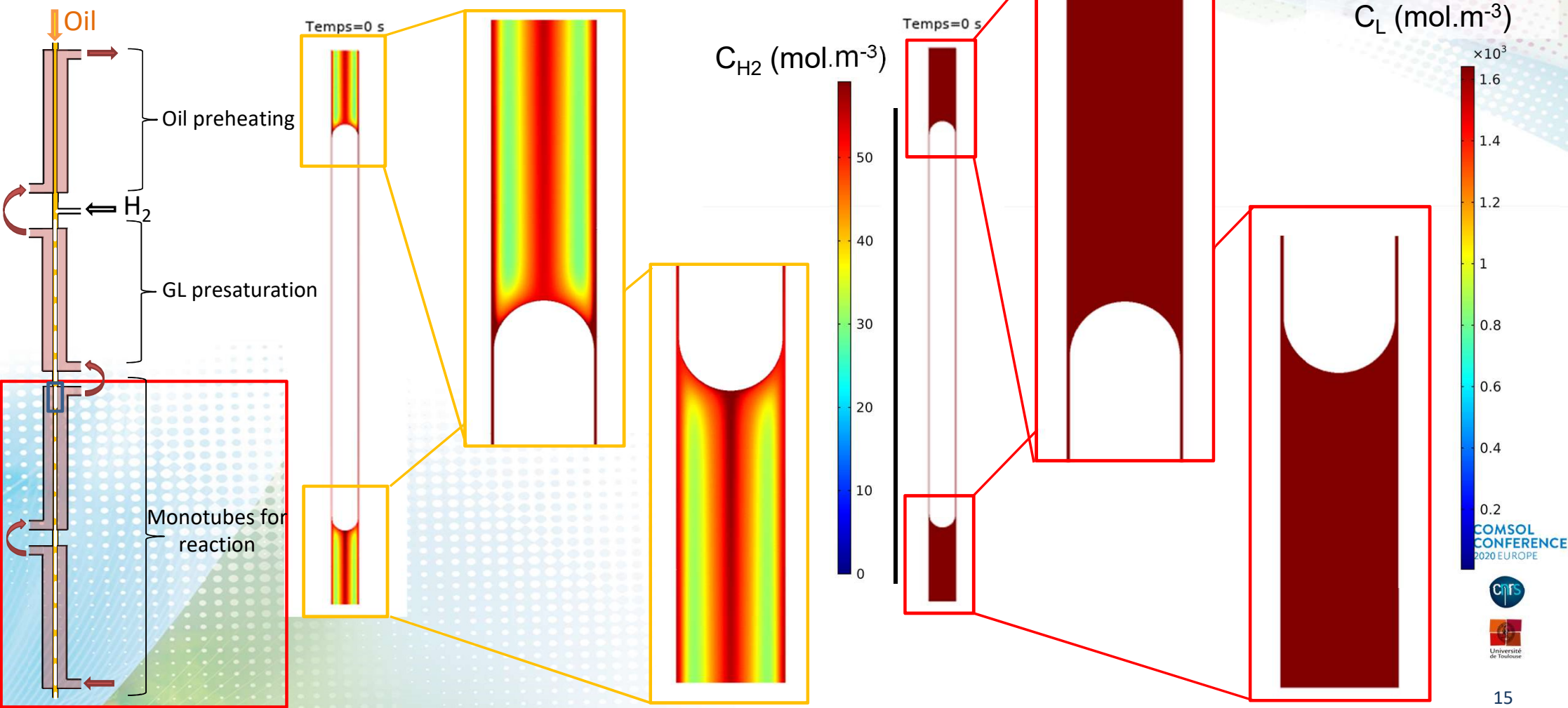
Concentration fields in the reactive section

160°C – 21 bar – $\alpha = 1$



Concentration fields in the reactive section

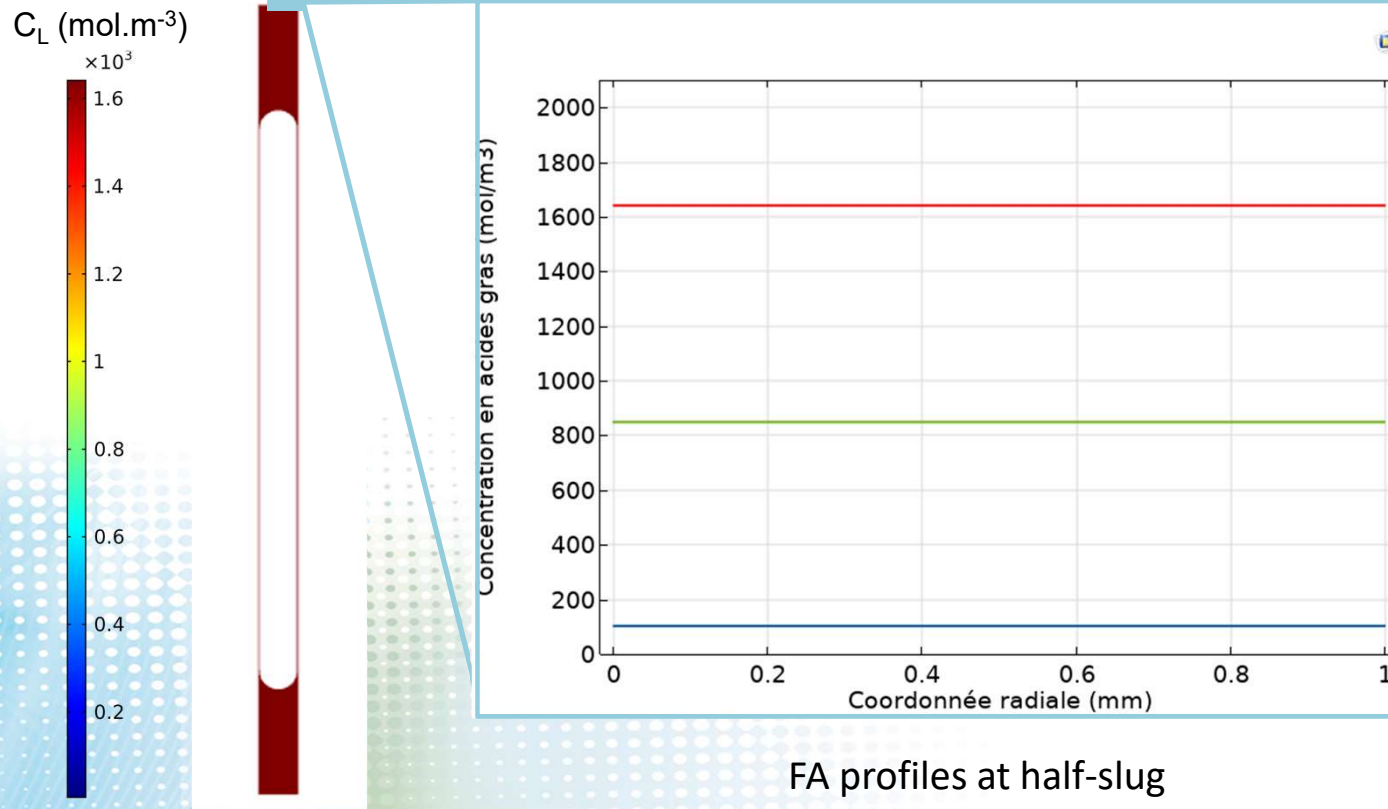
160°C – 21 bar – $\alpha = 1$



Radial concentration profiles

160°C – 21 bar – $\alpha = 1$

Temps=0 s



FA profiles at half-slug

Analysis:

- TAG radial transfer to/from the wall is driven by diffusion
- But, TAG diffusivity is very low:
→ Strong mass TAG mass transfer resistance
→ Intermediate (C18:1) is consumed at the wall

Species:

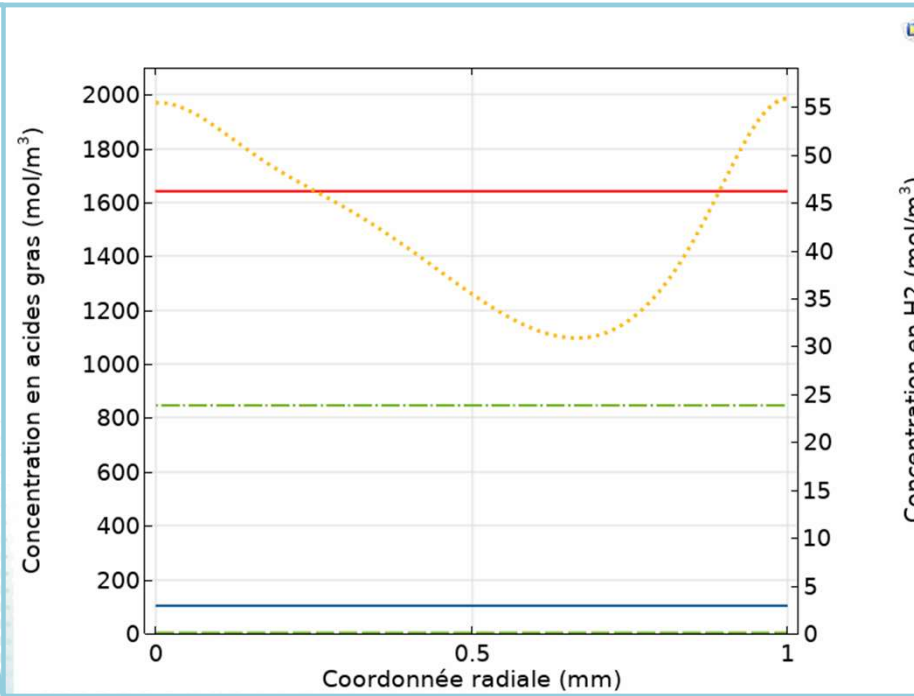
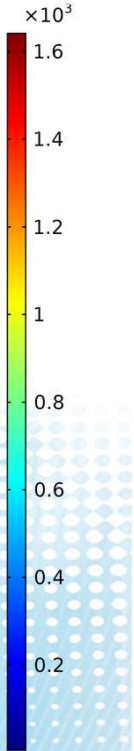
- C18:2 (L)
- C18:1 (M)
- C18:0 (S)

Radial concentration profiles

160°C – 21 bar – $\alpha = 1$

Temps=0 s

C_L (mol.m⁻³)



FA and H₂ profiles at half-slug

Analysis:

- Here, H₂ transfer is limiting as well!
→ Isomerisation of C18:1 *cis* to C18:1 *trans*

Species:

C18:2 (L)

C18:1 *cis* (C,- · -) and *trans* (T,- - -)

C18:0 (S)

H₂ (second axe)

Conclusions

Results :

- CFD highlighted transport phenomena limitations in monolith type reactor:
 - Mass transport limitation for TAG from liquid to wall
 - Production of saturated FA 😞
 - ... but also for H₂ at low pressure and high catalysis activity
 - Production of *trans* FA 😞
- **Monolith type reactor are not suitable for edible hydrogenation**

Thanks for your attention

