Development of continuous processes for vegetable oil ethanolysis in microfluidic devices

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Outline

1. Context and objectives
Why transesterification reaction in microreactors ?

2. Materials and methods
Transesterification of high oleic sunflower oil with ethanol

3. Reaction modelisation and simulation

4. On-line monitoring of the transesterification using Near Infrared spectroscopy

5. Conclusion & Perspectives

Context and objectives

Vegetable oils

+ Bioethanol CH_3CH_2OH → **FAEE**

Fatty Acid Ethyl Esters

- **FAEE : considered as 100% biosourced**
- **FAEE used for applications principally in food and cosmetic industry**
- **To open the application field to biofuels or biosolvents (as Methyl Esters), the process efficiency has to be developed to be economically profitable**
- **Transfer of the batch or semi-batch transesterification into a continuous device**

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Limits of FAEE production processes

- **Constant amount of monoglycerides at the end of the reaction (not negligible contrary to DG and TG) : stable equilibria**

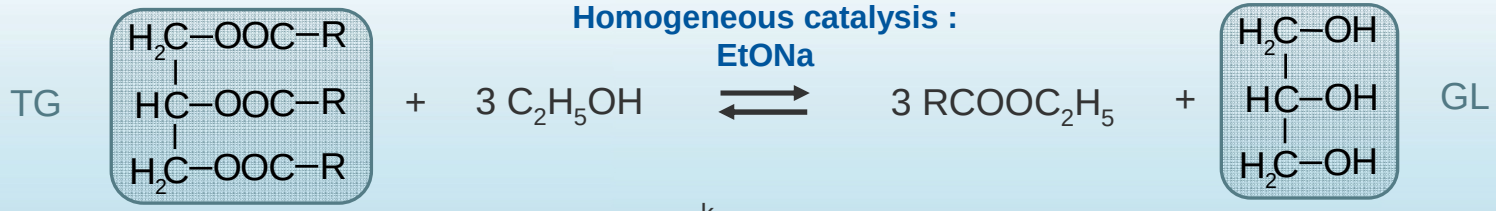
- **Numerous steps in the ethanolysis process in order to shift the reaction equilibria (in comparison to methanolysis processes) :**
  - **Transesterification reaction**
  - **Separation of ethyl esters from glycerol, by-product of the reaction : quite difficult**
  - **Refill with ethanol and catalyst**
  - **2nd reaction…**

Expensive process

Batch process → Continuous process

Transesterification : a complex system

- **Reactions**
  - **Triglycerides ethanolysis ***



1ère étape : TG + R'-OH $\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ DG + R'-OOC-R

2ème étape : DG + R'-OH $\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}$ MG + R'-OOC-R

3ème étape : MG + R'-OH $\underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}}$ GL + R'-OOC-R

  - **Secondary reactions ****

TG + 3 Na^+,OH^- $\overset{H_2O}{\rightleftharpoons}$ 3 $RCOO^-,Na^+$ + GL *Saponification*

RCOOH + 3 Na^+,OH^- $\rightleftharpoons$ $RCOO^-,Na^+$ + H_2O *Salification*

- **Phase equilibrium changes**
- **Two immiscible phases are present at the beginning of the reaction (oil and ethanol phases) and at the end of the reaction (ester and glycerol phases with ethanol in excess in both phases)**
- **Simultaneous presence of various phenomena : mixing, heat and mass transfers, principal and competitive reactions**

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Transposition to a continuous process in microreactors

- Implementation of small volumes (widths between 1 µm and 1000 µm)

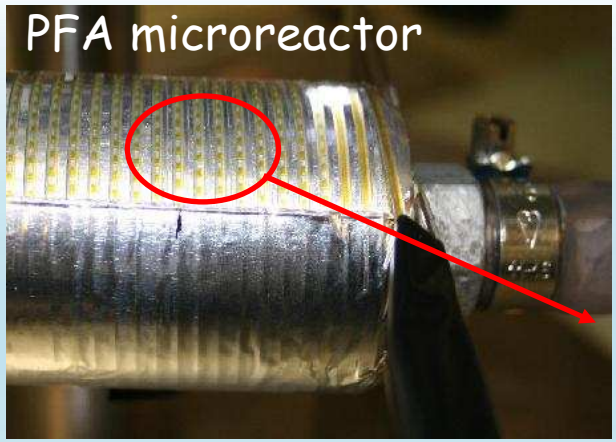
  ➡ safety is increased

- Perfect control of the flows (between 1 µL/h and several L/h)

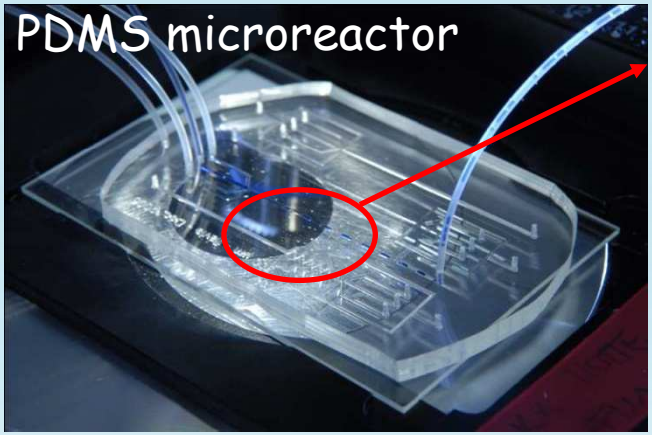
- Very high surface/volume (S/V) ratio which increases heat and mass transfer

- Control of the initial mixing time which does not depend on the feeding procedure

- Access to low characteristic times



Reaction generating droplets



Transposition to a continuous process in microreactors

- Parallelize the microreactors to produce (“numbering-up” vs scaling-up) : a faster extrapolation

  - current approach: « scale-up »

laboratory

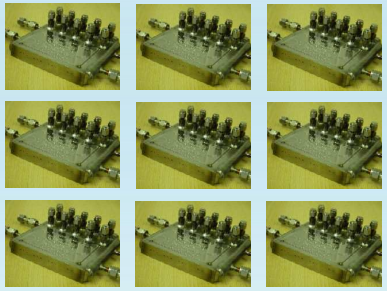
pilot

Industrial scale

  - planned approach: « smart numbering-up »

Microstructured reactor

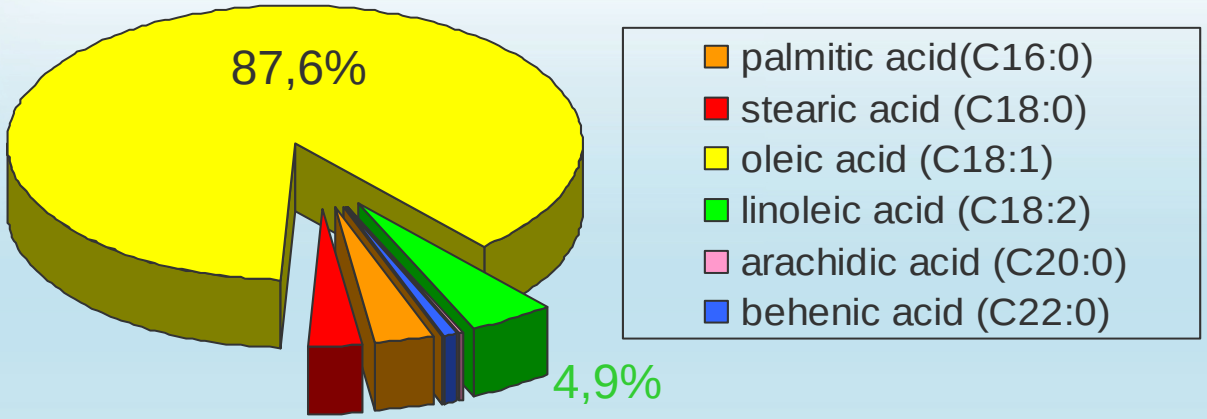
Moderate scale-up and optimization



Parallelization for production scale

Materials and methods

- High oleic sunflower oil (TG)



Fatty acids composition obtained by gas chromatography analysis (CPG)

- Ethanol (99,9%)
- Catalyst : Sodium ethanolate EtO^-,Na^+
  (commercial solution at 21wt% in EtOH)
- Hydrochloric acid HCl
  (for the catalyst neutralization at the end of the reaction)

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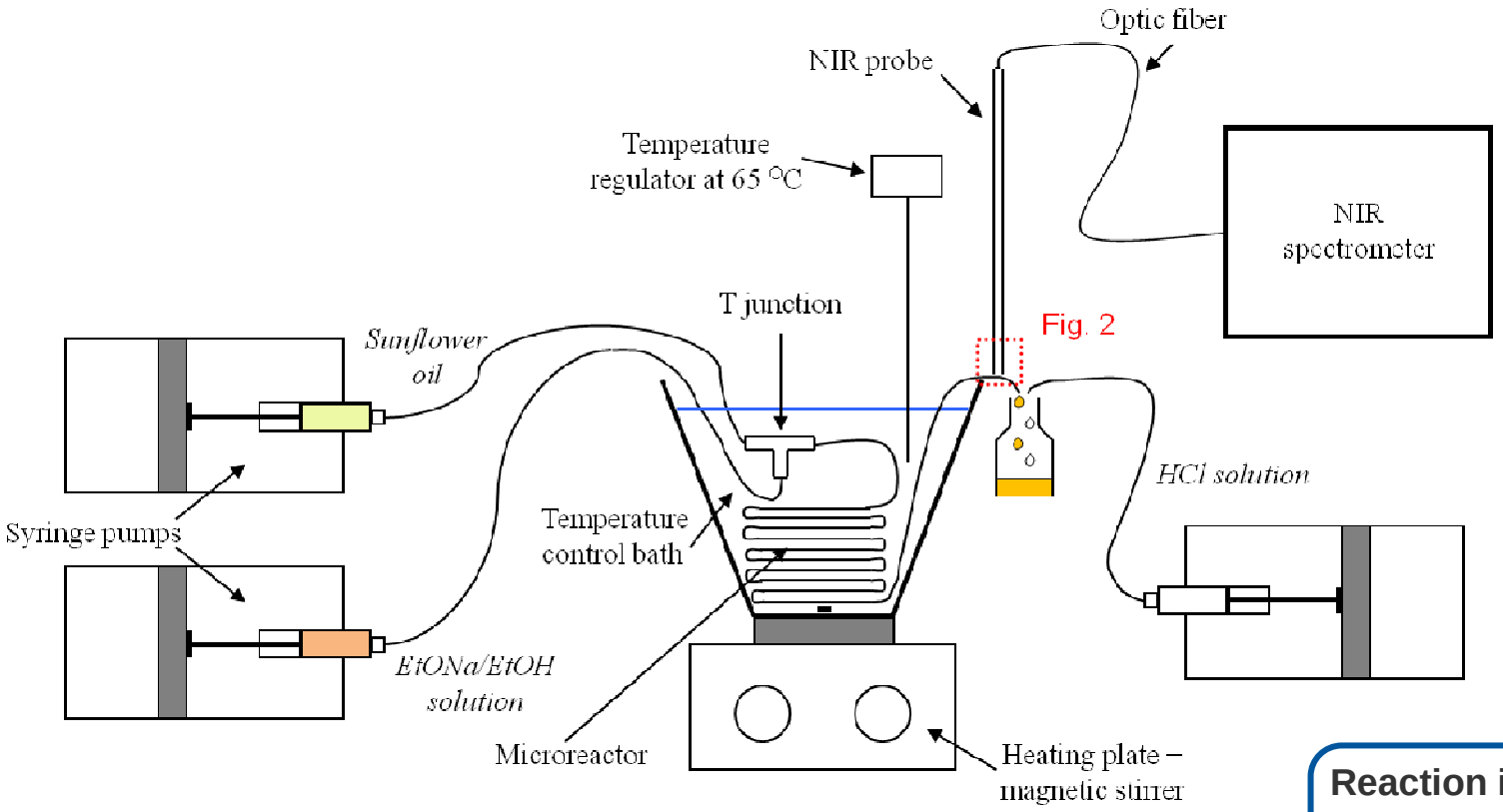
Experimental device



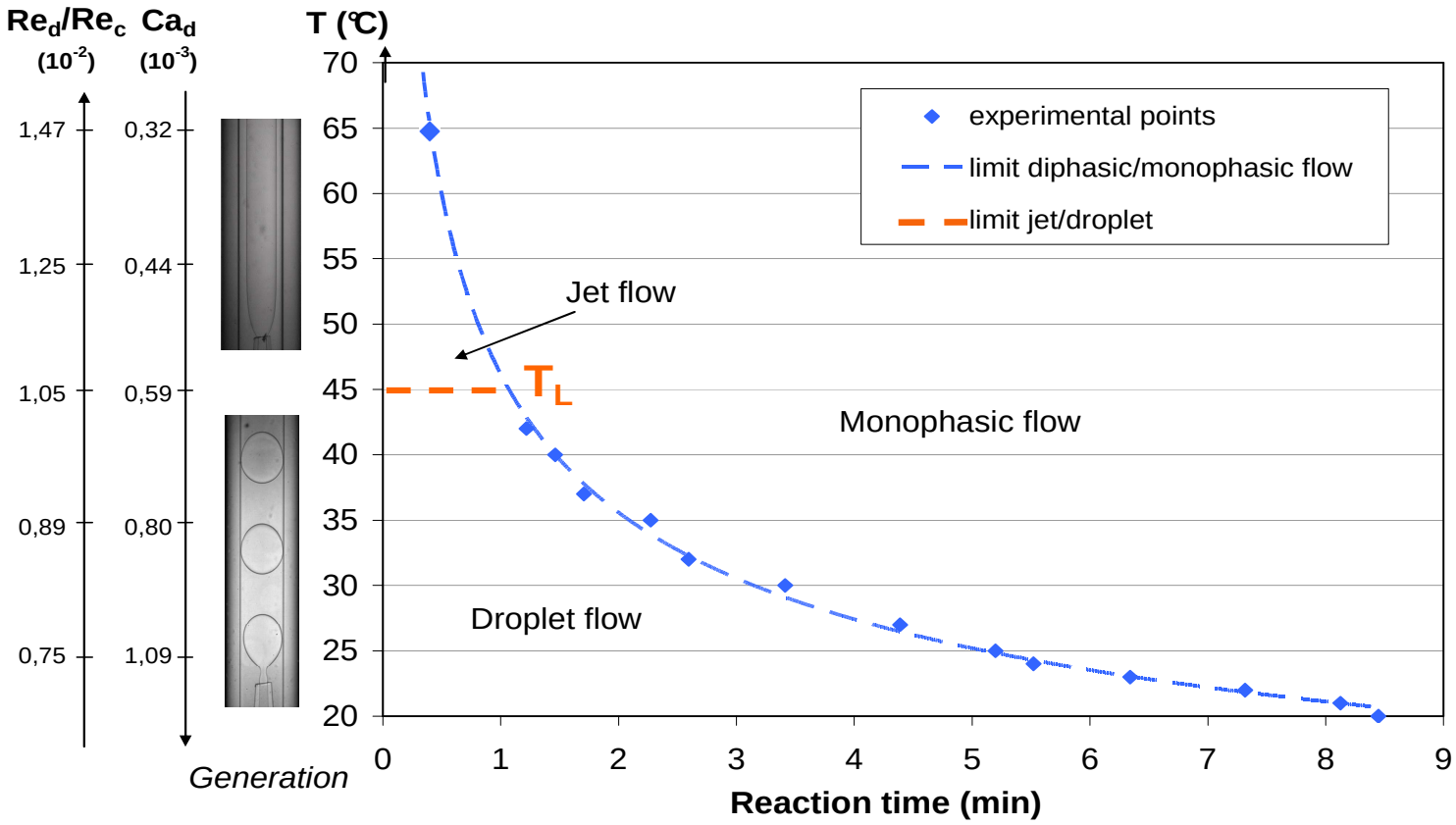
- Each tube length corresponds to a reaction time : the tube was cut to obtain lower reaction times

Reaction is quenched by adding HCl to neutralize the basic catalyst

Effect of temperature on the flow

$$Re_c = \frac{\rho_c U_c d}{\eta_c}$$

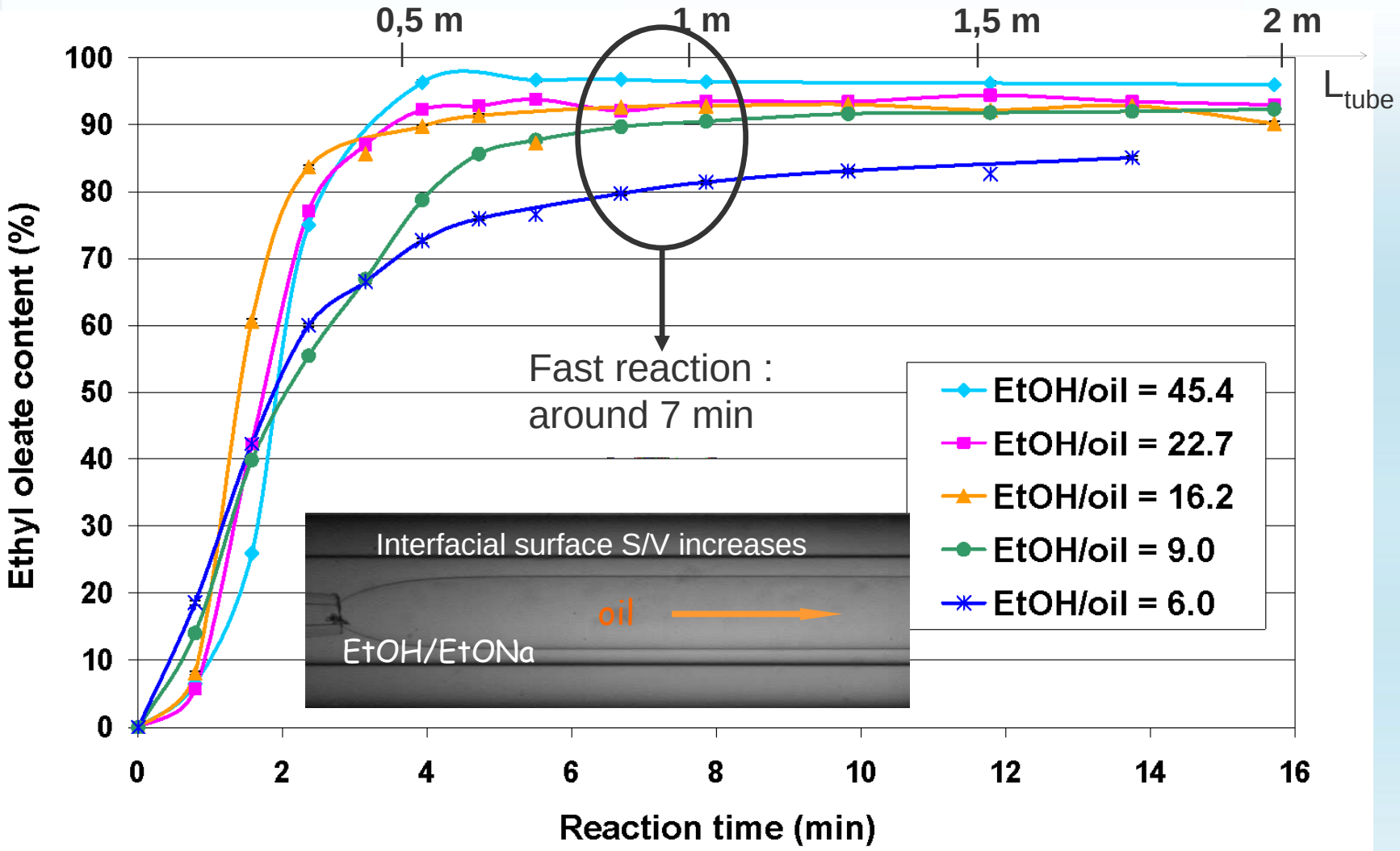
$$Ca_d = \frac{\eta_d U_d}{\sigma_d}$$



Q_{tot} = 1,5 mL.h^{-1}
Molar ratio EtOH/huile = 45,4
Catalyst EtONa = 1%
Water content = 0,08%

From T = T_L, no drops are observed : coflowing jet

FAEE contents for different EtOH:oil molar ratios



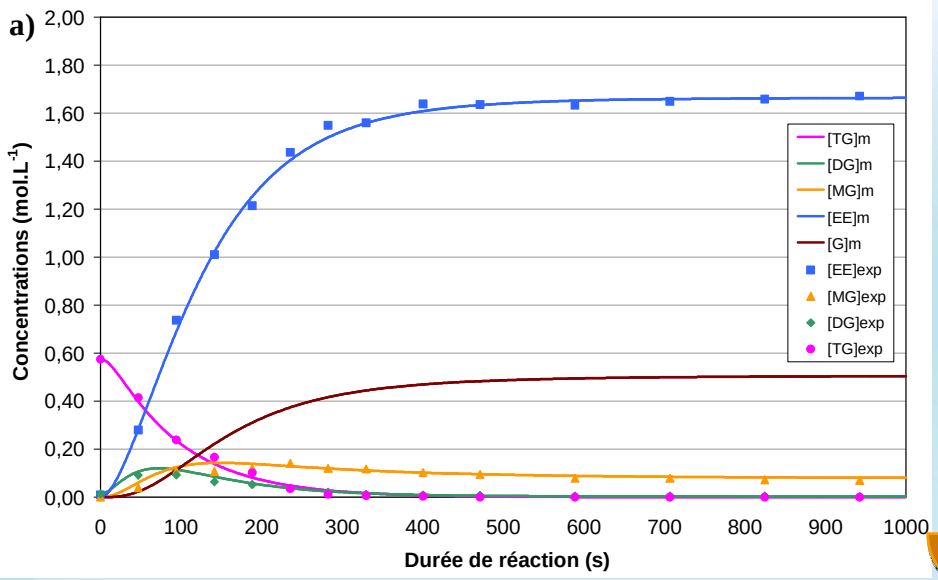
Acquisition of experimental data at very weak characteristic times

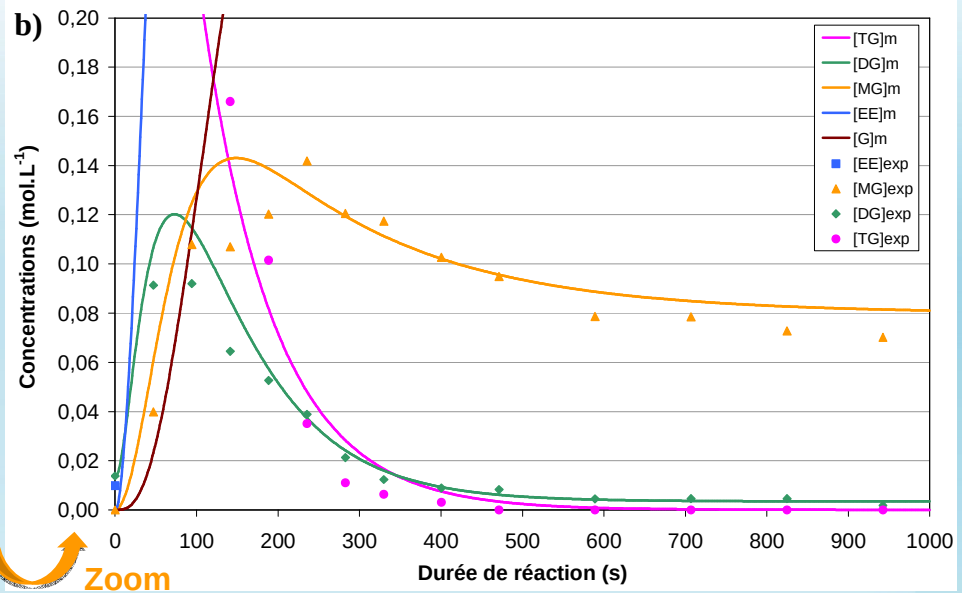
Modelling the kinetics

Building of a mathematical model able to represent the behavior of the reaction medium for various ethanol to oil molar ratios

Parameters identification for each molar ratio

Example of model and experimental data for molar ratio EtOH/oil = 9,0





Zoom

k_1	$1{,}0.10^{-1}$
k_{-1}	$8{,}7.10^{-11}$
k_2	$1{,}1.10^{-1}$
k_{-2}	$1{,}2.10^{-2}$
k_3	$4{,}5.10^{-2}$
k_{-3}	$9{,}2.10^{-3}$

$(mol^{-2}.L^2.s^{-1})$

$k_{L(TG)}$	$1{,}8.10^{-6}$
$k_{L(DG)}$	$1{,}9.10^{-5}$
$k_{L(MG)}$	$6{,}3.10^{-7}$

$(m.s^{-1})$

$$\frac{d[TG]_E}{dt} = -k_1[TG]_E[EtOH][Cata] + k_{-1}[DG]_E[EE][Cata] + k_L a_{(TG)}([TG]_O - [TG]_E)$$

…

The model enables the representation of the evolution of the reaction medium composition as a function of reaction time

Global parameters identification

Determination of the kinetics constants and mass transfer coefficients for each ethanol to oil molar ratio

Different reactions were conducted in a tube 1/16'' (d_i = 508 µm)

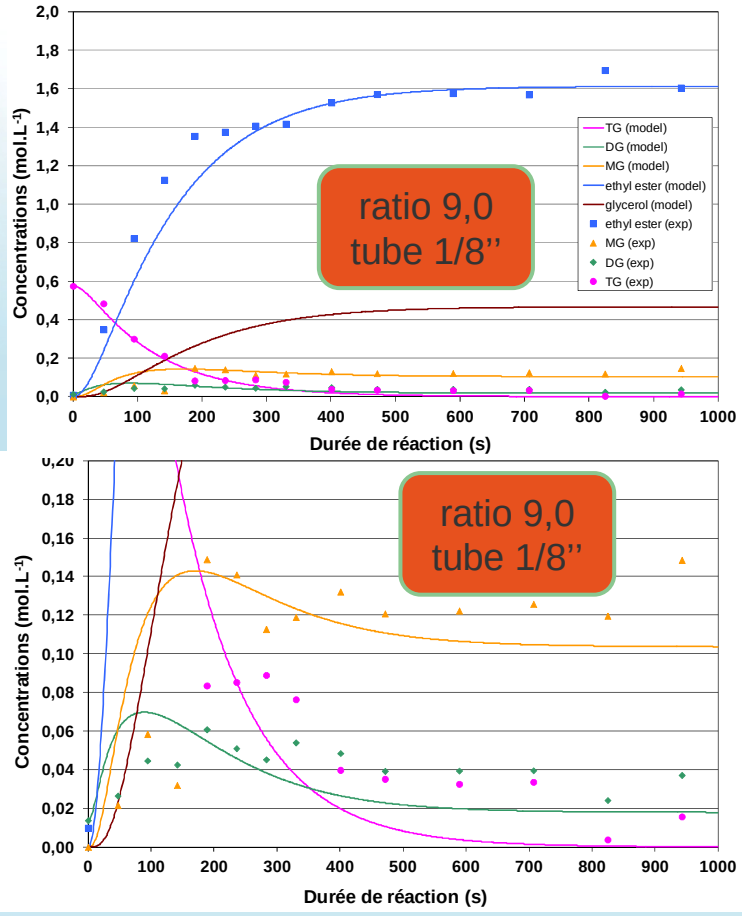
➡ Reactions limited by chemical kinetics

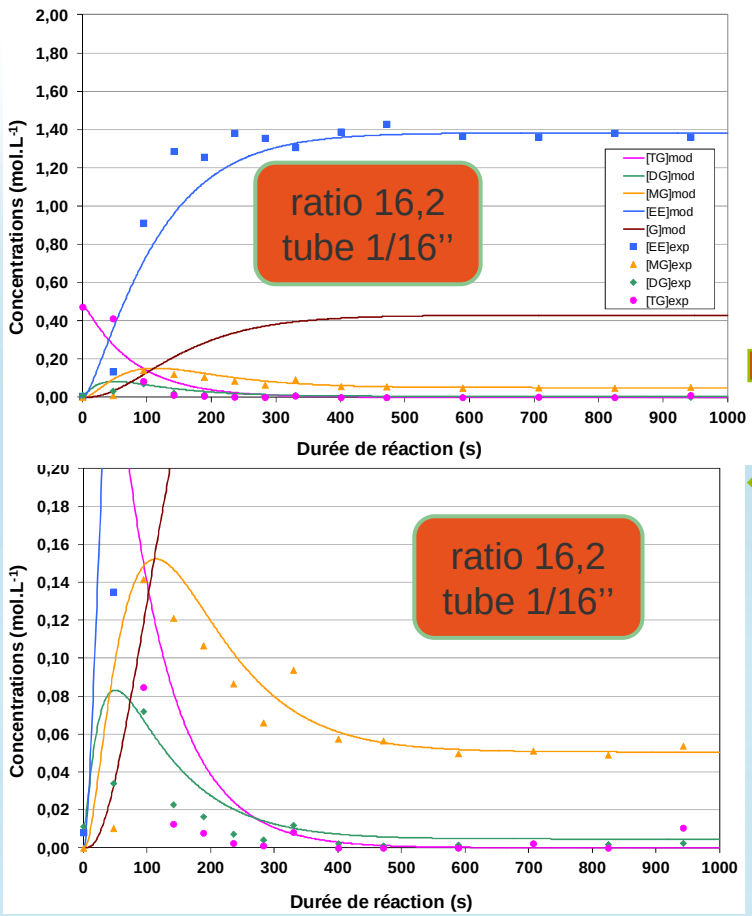
⬇ Scale change

Reaction where mass transfer is more limiting in order to determine a set of parameters satisfactory whatever the molar ratio used and the size of the tubular reactor

➡ Reaction in millireactor : tube 1/8'' (d_i = 2,362 mm)

Global parameters identification





Zoom

Determination of a **global** set of parameters able to represent **the concentration evolutions for all components** whatever the molar ratio used for **all** experiments limited by chemical kinetics or mass transfer

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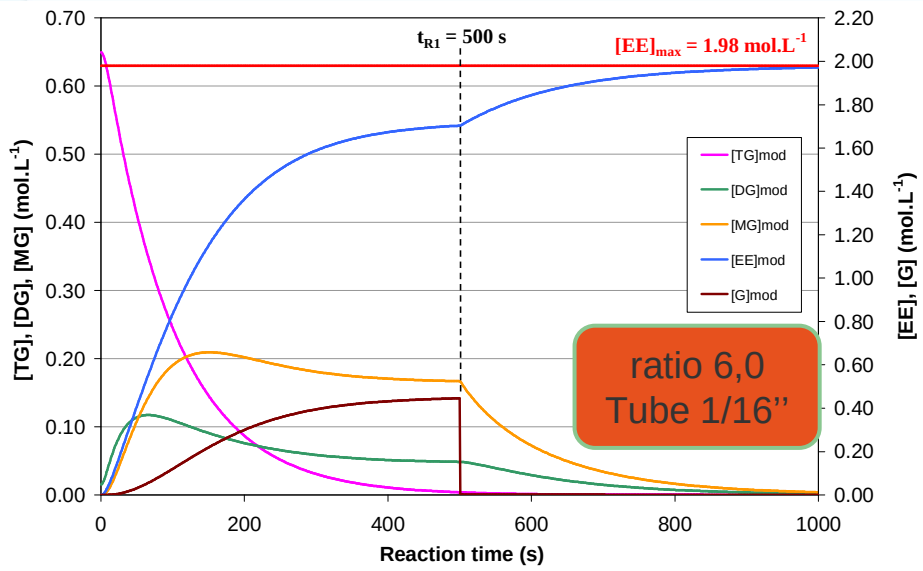
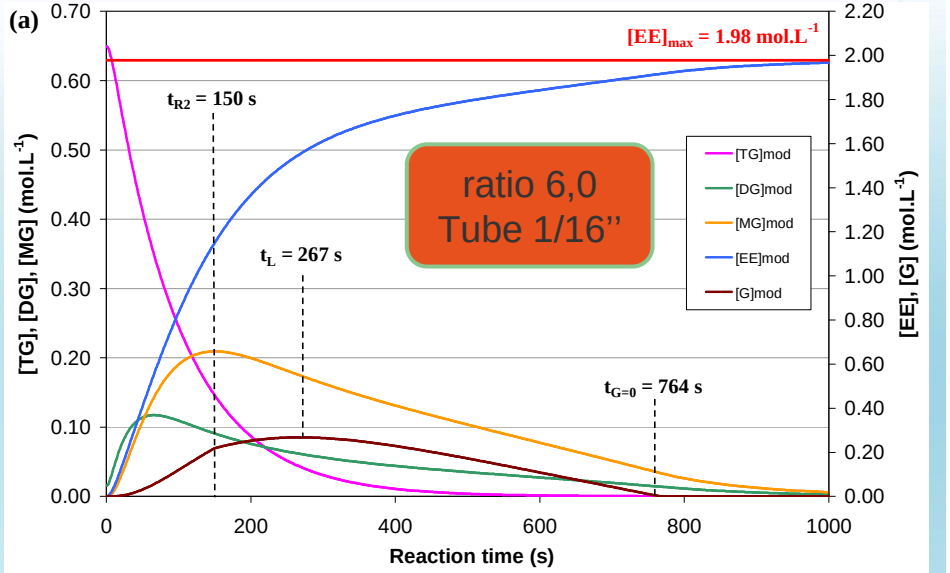
Simulations by using the model

It is possible to simulate different conditions of reaction and separation

- Ethanolysis using other molar ratios
- Transesterification in other tubes with higher or lower sizes
- Glycerol separation during the reaction in order to shift the equilibrium towards FAEE formation

Total or continuous removal of glycerol (simulation)





<u>Total glycerol removal</u> :

For $t > t_R$, GL removal flux (0.5 mol.s^{-1}), higher than the GL amount in the reaction medium

Shifting of the reaction equilibrium towards FAEE formation

<u>Constant continuous removal</u> (0,001 mol.s^{-1}):

At $t = t_R$ = 150 s: $F_{GLremoval} < F_{GLformation}$

[GL] ↗ until $t = t_L$ = 267 s,

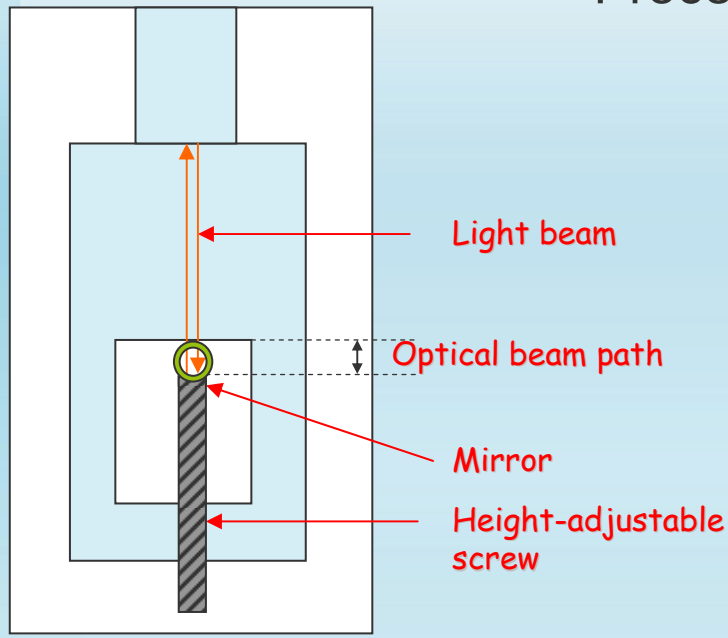
then for $t > t_L$, [GL] ↘ until 0

A new on-line method based on Near Infrared spectroscopy and a multivariate approach

- **Advantages:**
  - **Fast**
  - **Reliable**
  - **Inexpensive**
  - **Non-destructive**
  - **No quench needed**
  - **No sample preparation needed**

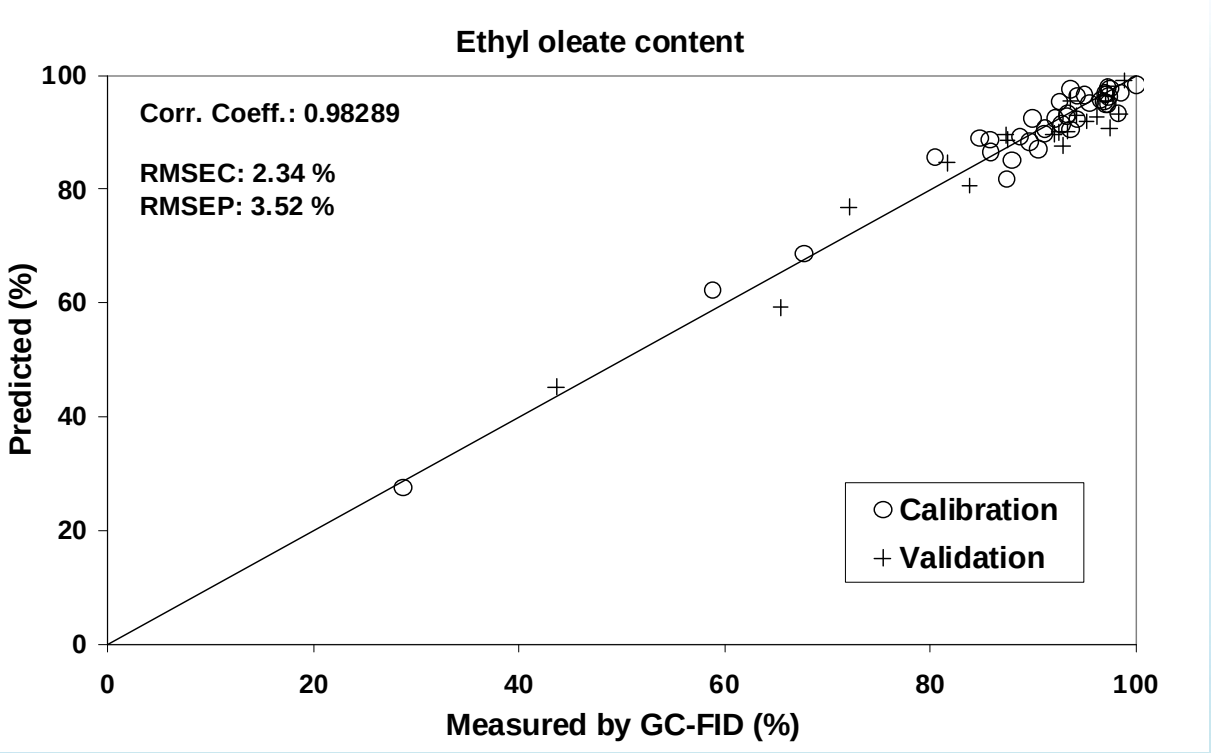
NIR Spectroscopy Analysis

- **Material :** NIR Spectrometer Antarix MX FT-NIR Process Analyzer from Thermo Fisher Scientific, USA



- **Fiber-optic probe working by transflectance**
- **Analysis parameters:**
  - Wavenumber range: 10000 – 4000cm^{-1} (800 - 2500 nm)
  - Optical beam path: 3 mm
  - 32 scans
  - Spectral resolution: 2 cm^{-1}
- **Monitoring of the reaction** through sequential scans and with GC reference method

Correlation between NIR spectral data and GC-FID analysis



61 samples:
40 for calibration 21 for validation

Pre-processing methods:
Baseline correction,
Savitzky-Golay smoothing
First derivative
Mean-centering + variance scaling

PLS regression : model capable to predict ethyl ester content of the reaction mixtures obtained with same ethanol to oil molar ratio (45.4) at 65°C

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Correlation between NIR spectral data and GC-FID analysis

PLS Model	Microreactor 6 < EtOH/oil < 45,4	Microreactor Repetability 45,4	1L-batch reactor[4] 30℃ < T℃ < 70℃	1L-batch reactor[4] Repetability 70℃
Probe	reflection	transflectance	transflectance	transflectance
R^2	0.98471	0.98289	0.99361	0.98244
RMSEC*	4.08%	2.34%	1.26%	0.378%
RMSEP**	4.10%	3.52%	1.74%	0.433%

- For the 2 models in microreactors, errors are lower in the case of samples used with the same EtOH/oil molar ratio (45.4) because the range of composition is more restricted.

- Errors are lower in batch reactor because the probe is directly dipped in the reactor whereas the optical beam is altered when passing through the PFA tube due to dispersion

Conclusion

- Transesterification reaction was successfully transposed into continuous microreactors
- Access to very low characteristic times : it allows to build kinetics models and NIR calibration and prediction models
- The kinetics model of the ethanolysis was validated for all tested molar ratios : kinetics constants and mass transfer coefficients were precisely determined.
- This model can be used to simulate other operating conditions such as glycerol removal
- On-line monitoring of the transesterification reaction was developed : errors on calibration and prediction are lower than 5%, which is acceptable

Future prospects

- **The NIR method elaborated at laboratory-scale: could be used at industrial scale, either in batch systems or continuous systems**
- **Works on separation of products at the end of the reaction: Ethyl esters, Glycerol and EtOH excess** by using an appropriate membrane separation technology
- **Use of heterogeneous catalysts (grafted on the tube wall)**

LABORATOIRE DE CHIMIE AGRO-INDUSTRIELLE

Thank you for your attention

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