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► **To cite this version:**

Sophie Thiebaud-Roux, Romain Richard, Brigitte Dubreuil, Laurent Prat. Development of continuous processes for vegetable oil alcoholysis in microfluidic devices. Journée Chevreul 2012 : Chimie du Végétal et Lipochimie, Société Française pour l'Etude des Lipides (SFEL). FRA., Jun 2012, Maisons-Alfort, France. pp.24 slides. hal-02746651

HAL Id: hal-02746651

<https://hal.inrae.fr/hal-02746651>

Submitted on 3 Jun 2020

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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

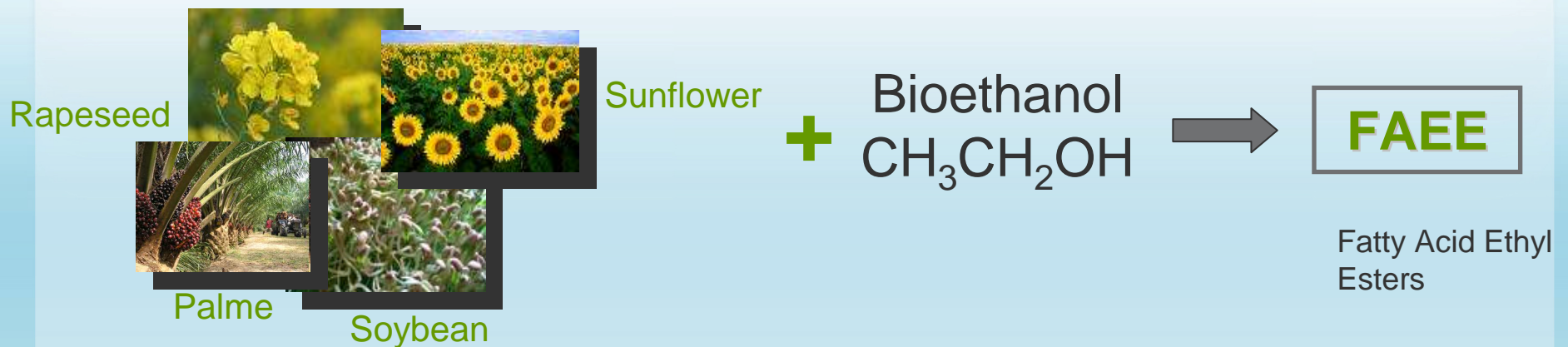
3. Reaction modelisation and simulation

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

5. Conclusion & Perspectives

Context and objectives

Vegetable oils



- **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**

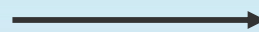
Limits of FAEE production processes

- 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

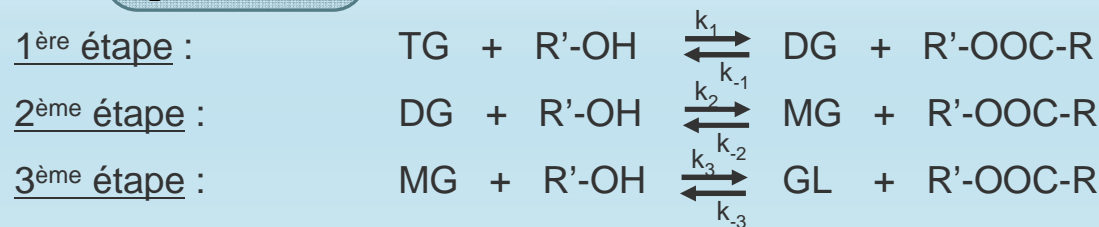
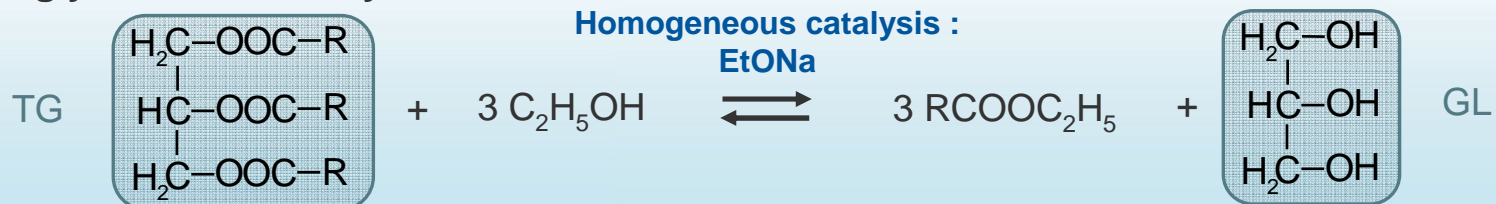


Continuous process

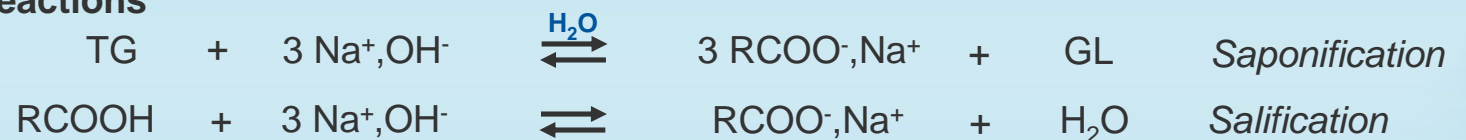
Transesterification : a complex system

Reactions

Triglycerides ethanolysis *



Secondary reactions **



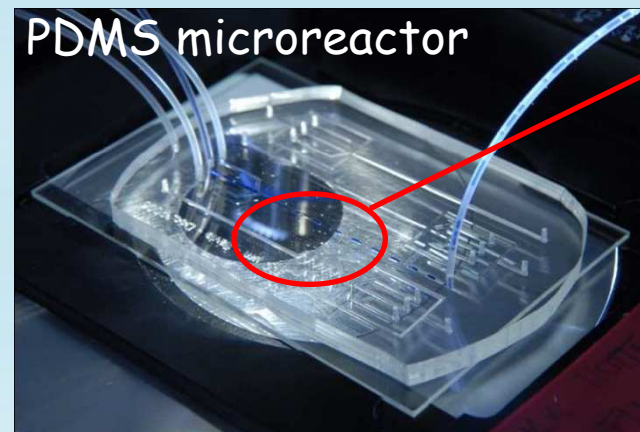
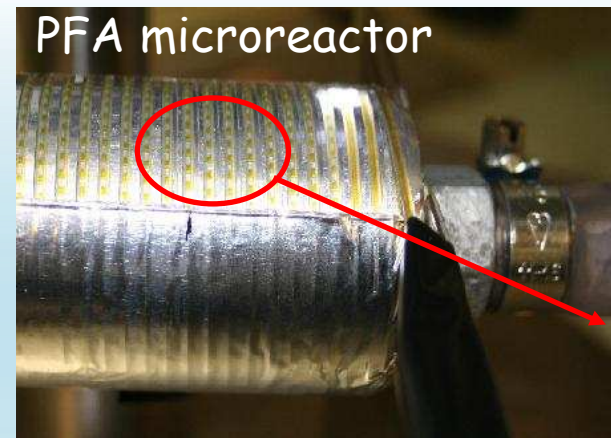
Phase equilibrium changes

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

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 $\mu\text{L/h}$ 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



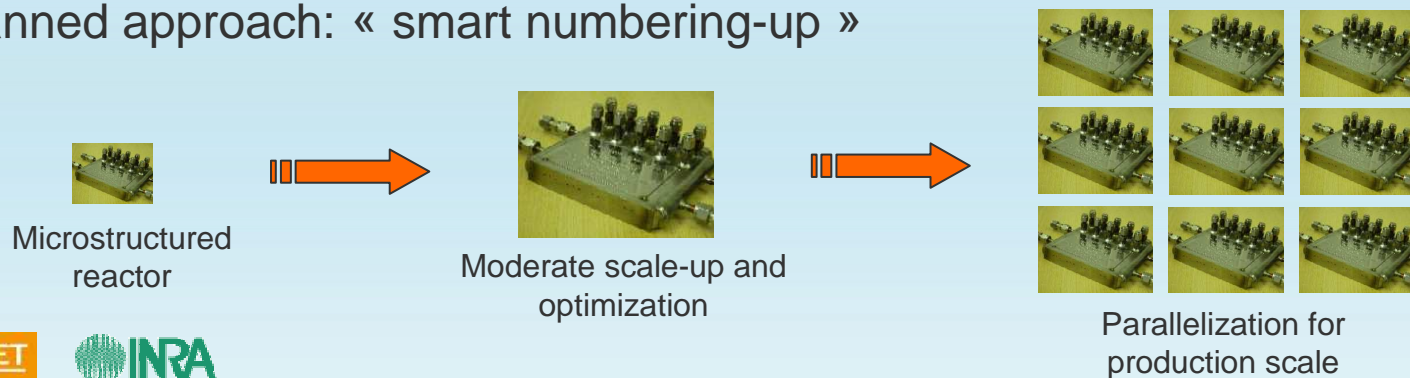
Reaction
generating
droplets

Transposition to a continuous process in microreactors

- Parallelize the microreactors to produce (“numbering-up” vs scaling-up) : a faster extrapolation
 - current approach: « scale-up »

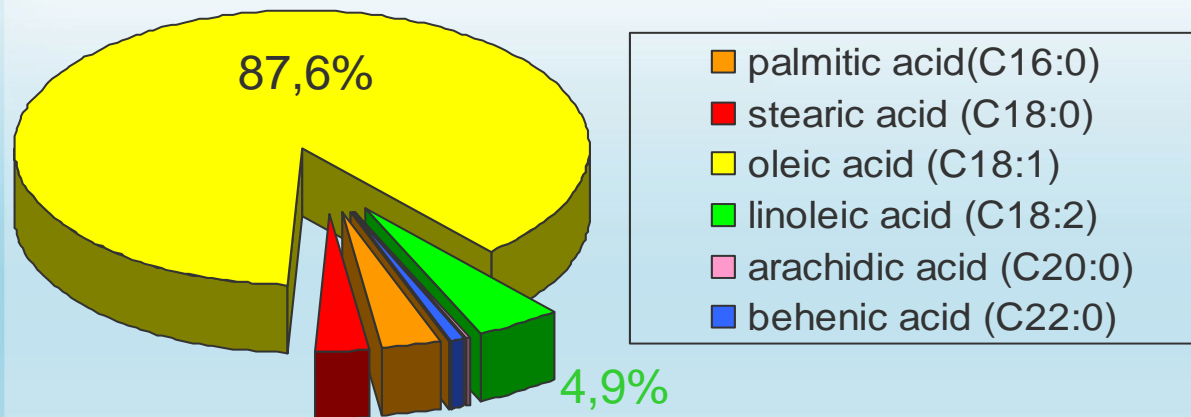


- planned approach: « smart numbering-up »



Materials and methods

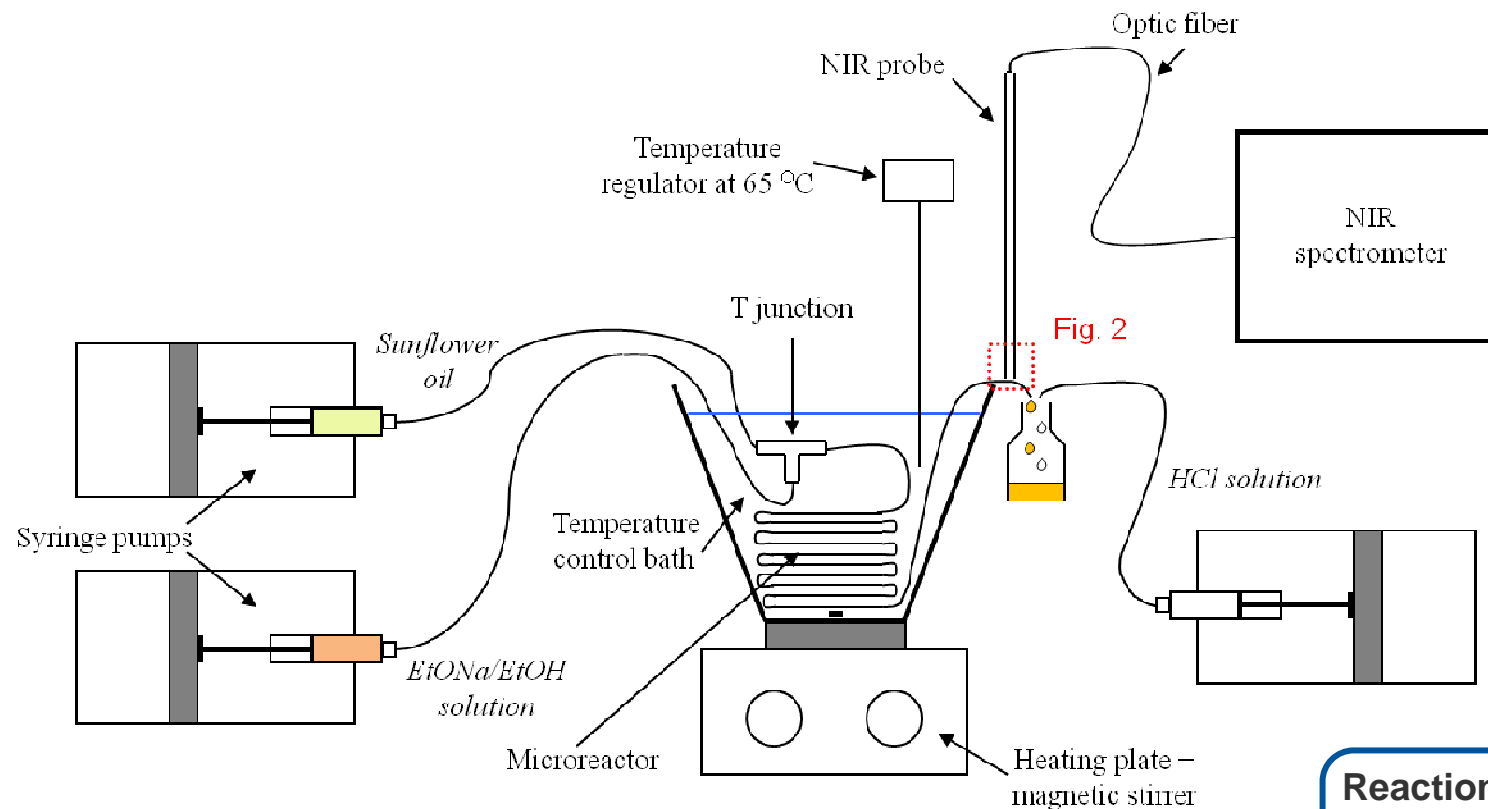
- High oleic sunflower oil (TG)



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)

Experimental device



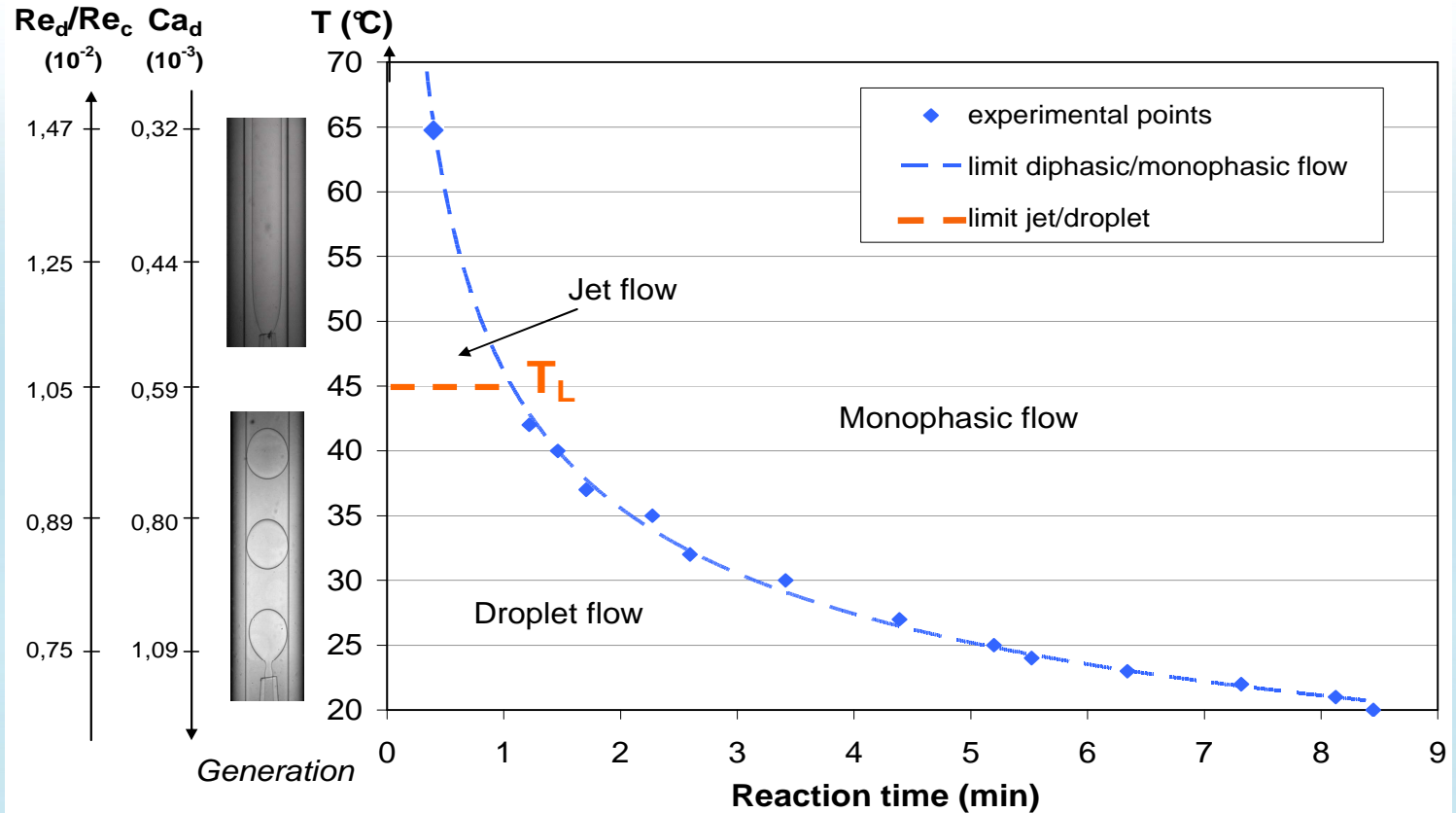
- Each tube length corresponds to a reaction time : the tube was cut to obtain lower reaction times

Reaction is quenched by adding HCl to neutralize the basic catalyst

Effect of temperature on the flow

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

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

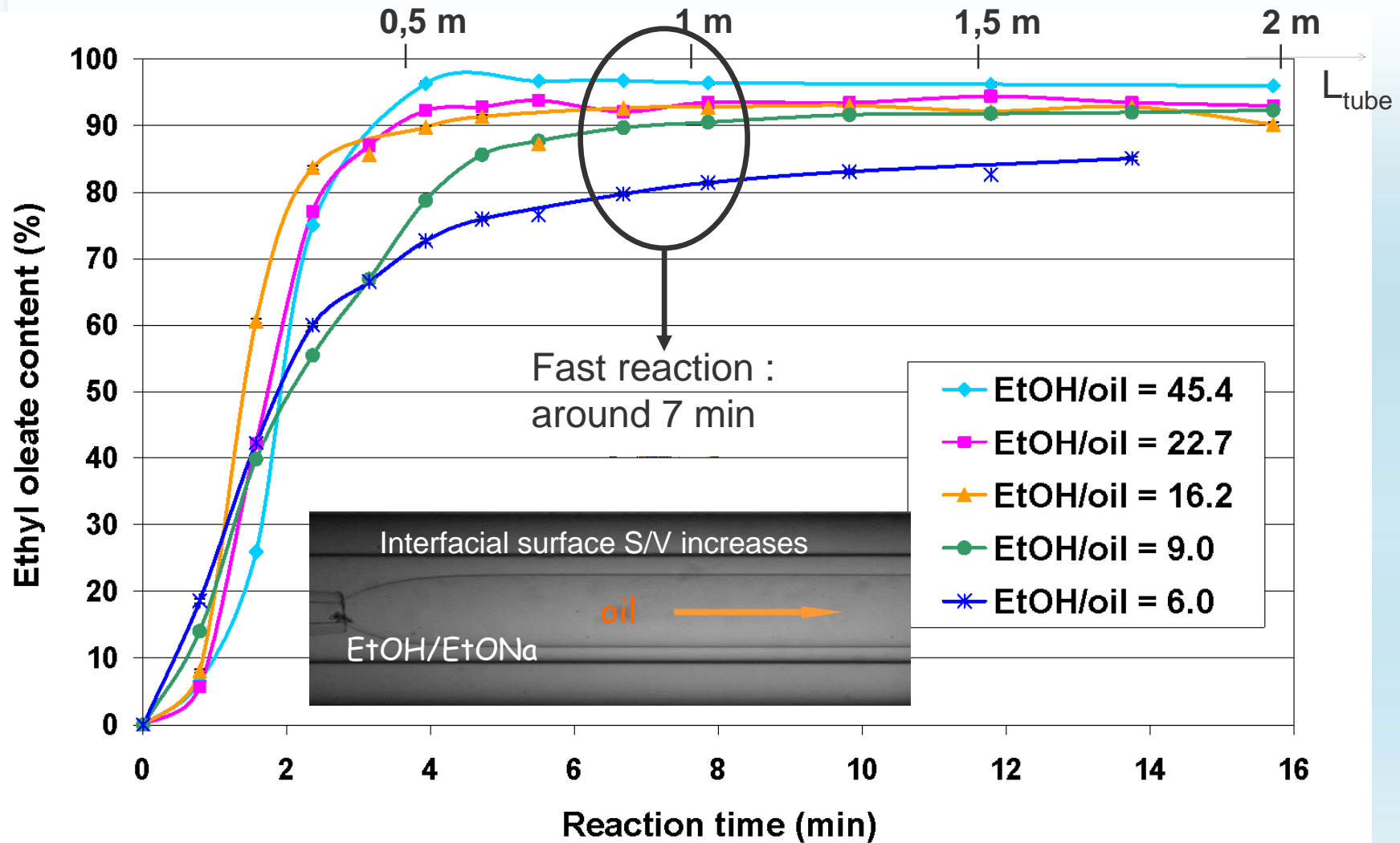


$Q_{tot} = 1,5 \text{ mL.h}^{-1}$
 Molar ratio EtOH/huile = 45,4
 Catalyst EtONa = 1%
 Water content = 0,08%



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**



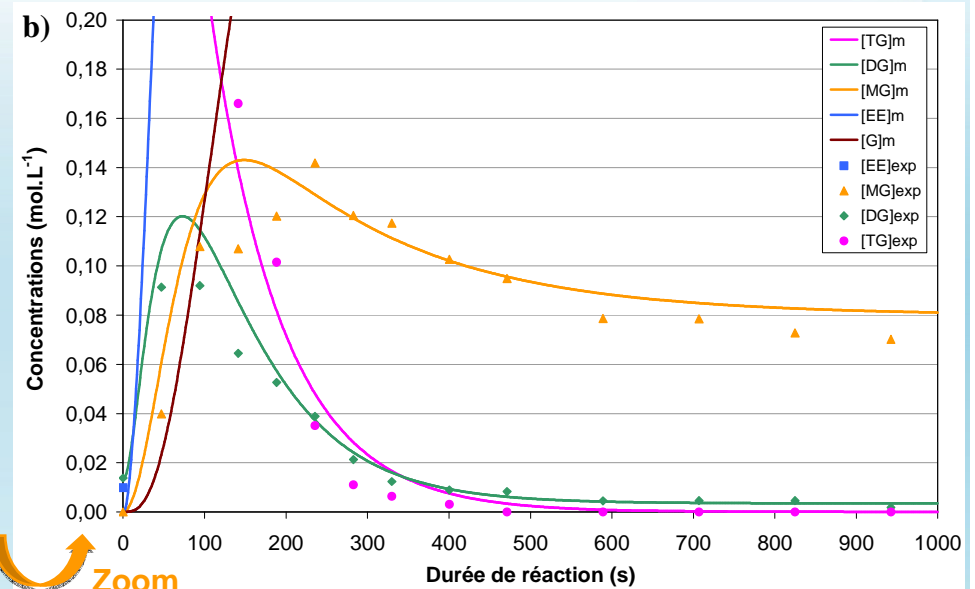
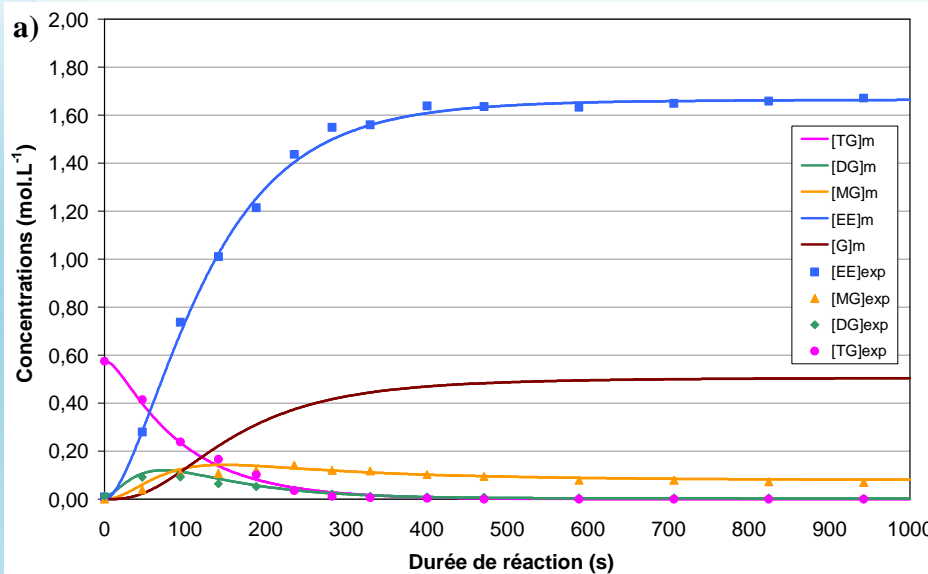
Modelling the kinetics



**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



k_1	$1,0 \cdot 10^{-1}$
k_{-1}	$8,7 \cdot 10^{-11}$
k_2	$1,1 \cdot 10^{-1}$
k_{-2}	$1,2 \cdot 10^{-2}$
k_3	$4,5 \cdot 10^{-2}$
k_{-3}	$9,2 \cdot 10^{-3}$

$k_{L(TG)}$	$1,8 \cdot 10^{-6}$
$k_{L(DG)}$	$1,9 \cdot 10^{-5}$
$k_{L(MG)}$	$6,3 \cdot 10^{-7}$

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

...



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'' ($d_i = 508 \mu\text{m}$)

➡ Reactions limited by chemical kinetics

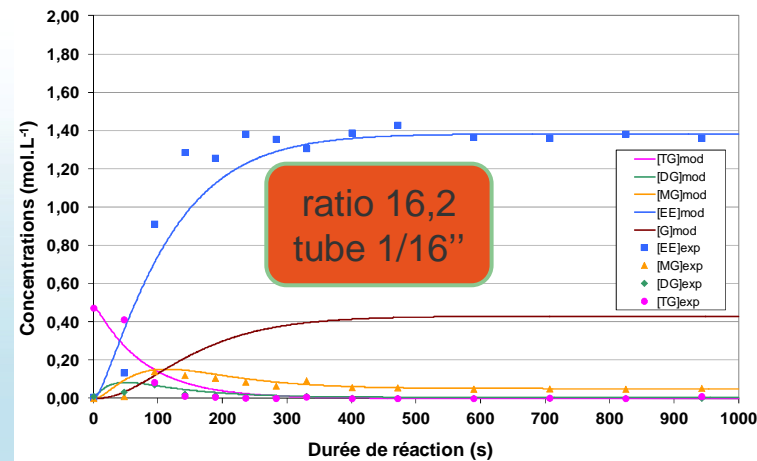
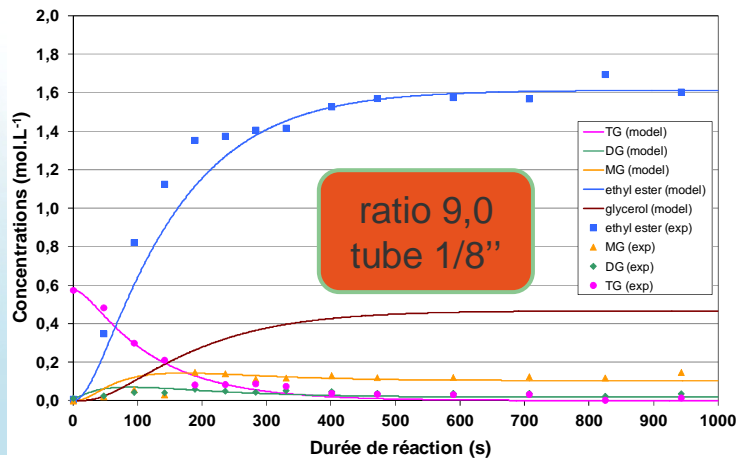


Scale change

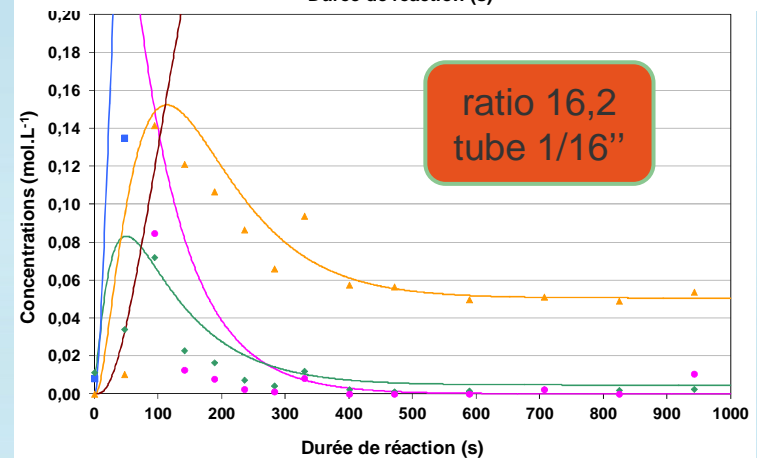
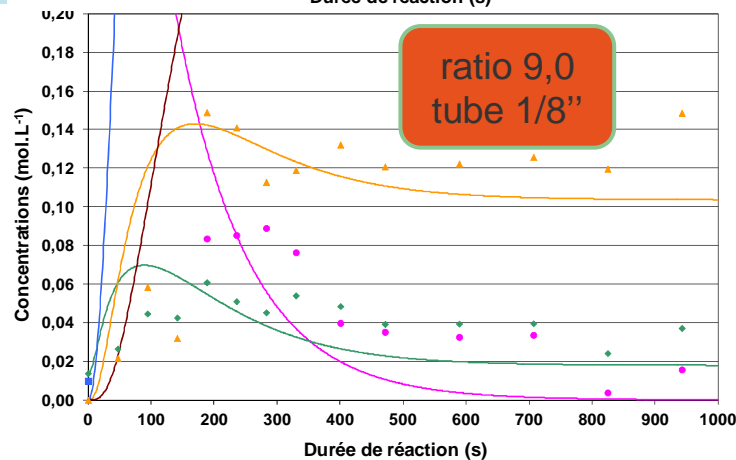
Reaction where mass transfer is more limiting in order to determine a set of parameters satisfactory whatever the molar ratio used and the size of the tubular reactor

➡ Reaction in millireactor : tube 1/8'' ($d_i = 2,362 \text{ mm}$)

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

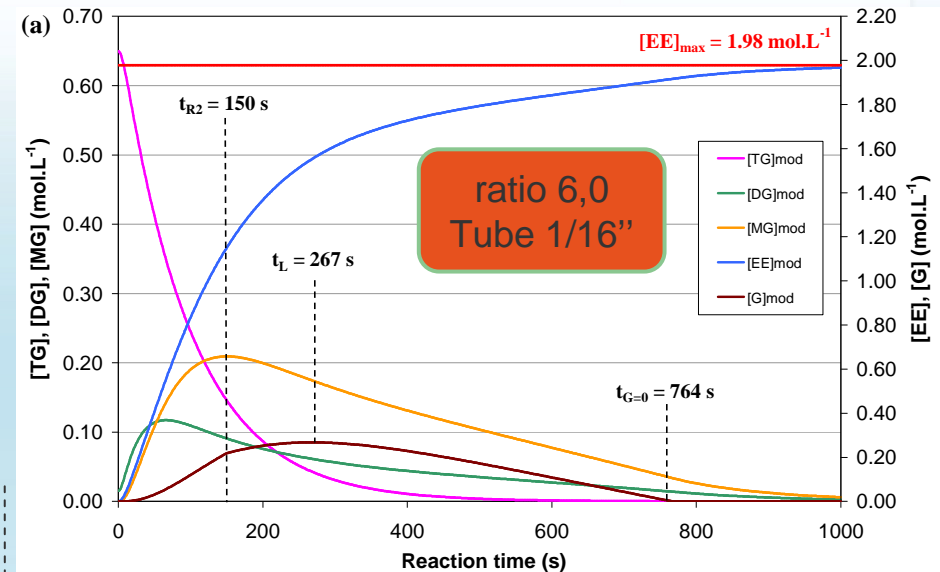
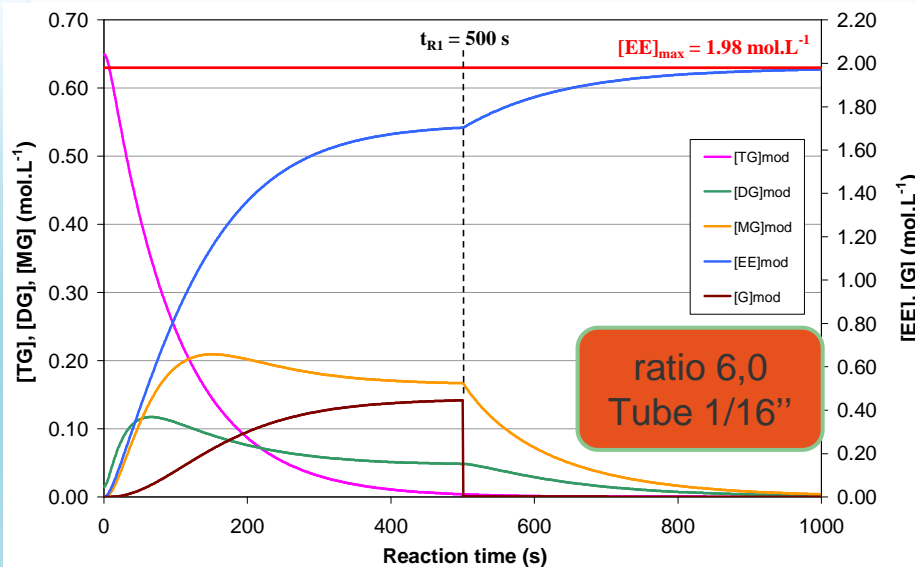
Simulations by using the model

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)



Total glycerol removal :

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

Constant continuous removal ($0,001 \text{ mol.s}^{-1}$):

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

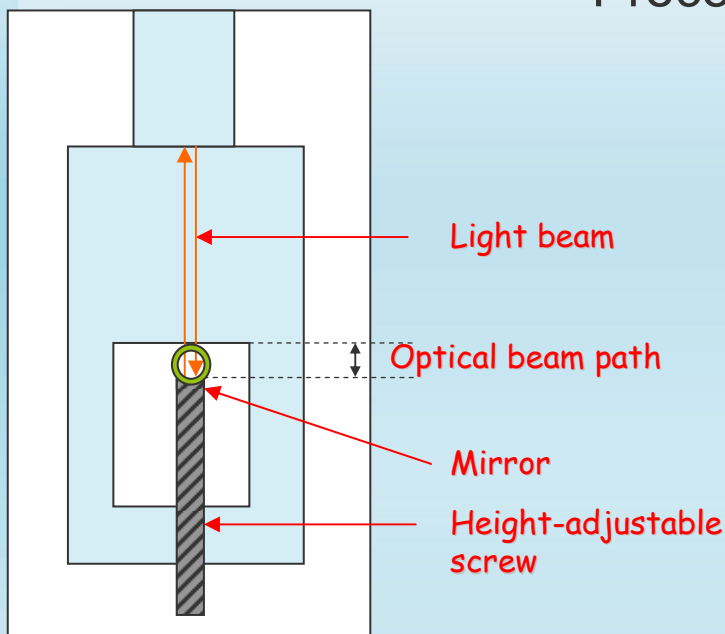
$[\text{GL}] \nearrow$ until $t = t_L = 267 \text{ s}$,
then for $t > t_L$, $[\text{GL}] \searrow$ until 0

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**

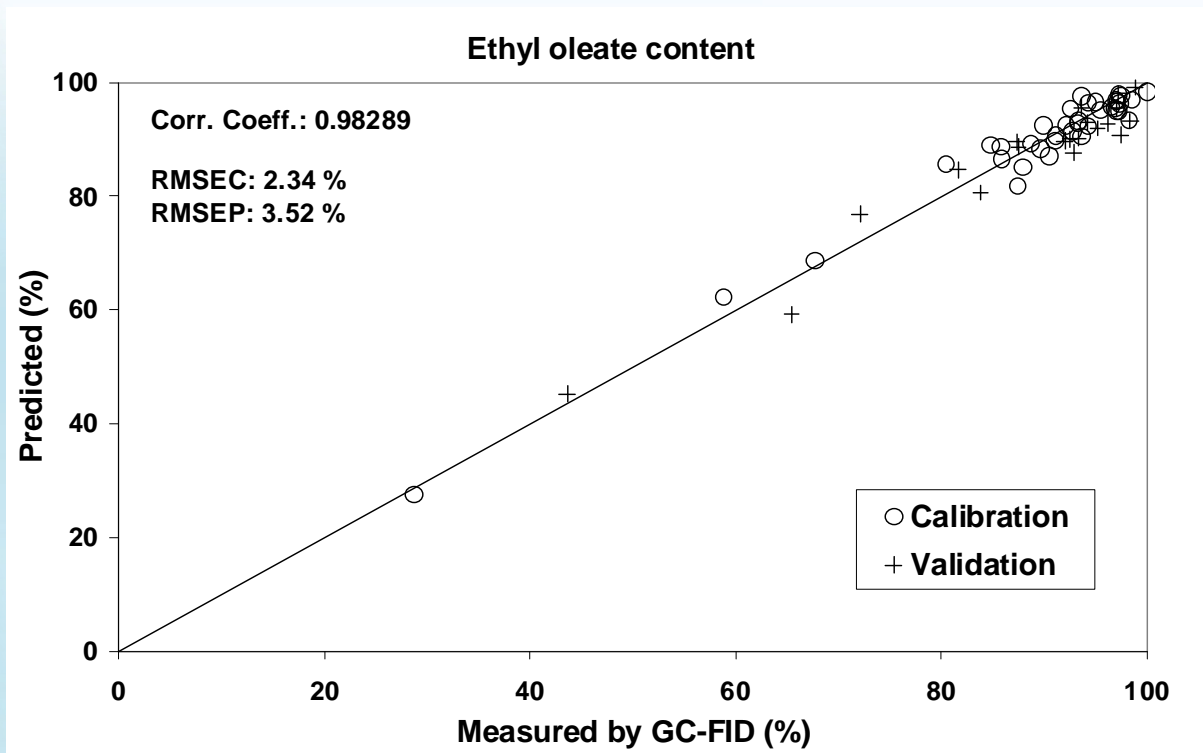
NIR Spectroscopy Analysis

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



- **Fiber-optic probe working by transreflectance**
- **Analysis parameters:**
 - Wavenumber range: 10000 – 4000 cm^{-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

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°C < T°C < 70°C	1L-batch reactor ^[4] Repetability 70°C
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)**



Thank you for your attention

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Acknowledgements for
co-financial support :

