BIOCARMAT

Alternative method for the preparation of vegetable oil ester through an enzymatic process





The project team is constituted of researchers from three laboratories of the molecular physic and chemistry Institute "Jean Barriol" of the Lorraine University and one researcher from "I'Institut Français du Pétrole (IFP)



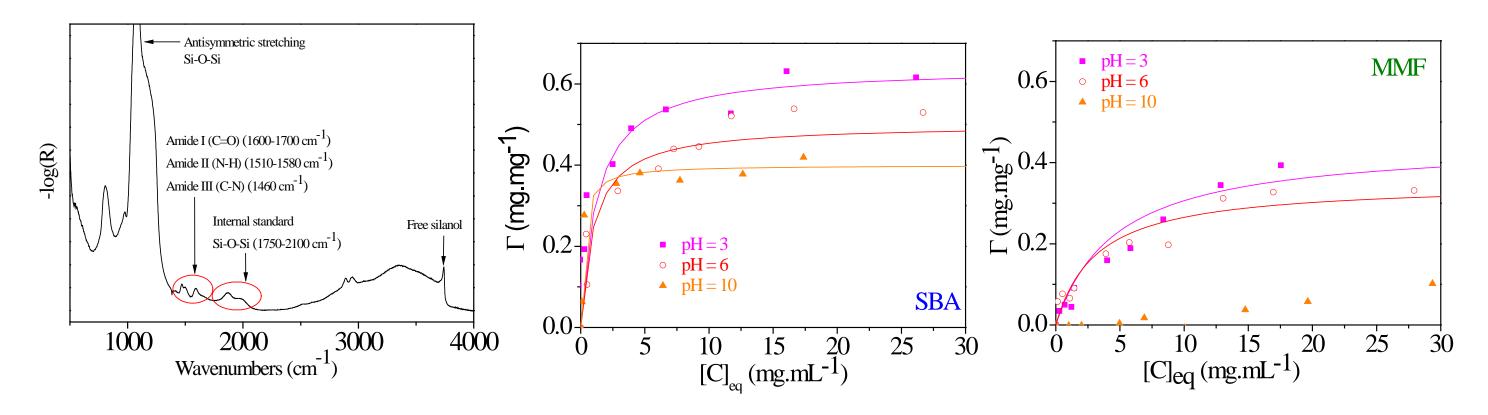
Introduction

From the past decade, biodiesel has attracted considerable attention as a renewable, biodegradable and non-toxic fuel. Moreover, one interesting way to prepare biodiesel is to use waste oil. In our work, biodiesel is obtained by immobilizing an enzyme (lipase Mucor Miehei) in a mesoporous material which plays the role of catalyst. This group form a bioreactor which is the seat of the reaction of transesterification. Two materials were prepared from micellar solutions based block copolymer (material SBA-15) and fluorinated surfactants (material MMF).

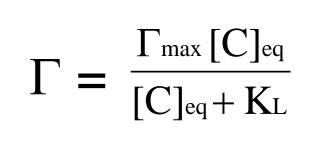


Adsorption of lipase on the material

- o dissolution of the enzyme in a buffer solution
- o variation of the lipase concentration (from 2 to 30mg/mL)
- o addition of silicate support (0.025g)
- o after filtration of support, washing with buffer solution
- o air drying in room temperature



Langmuir model used to fit the experimental curve:



where Γ is the amount of lipase adsorbed Γ_{max} the maximum amount of adsorbed lipase, K_L the equilibrium constant and $[C]_{eq}$ the concentration of lipase

Materials		pH = 3	pH = 6	pH = 10
SBA-15	$K_L (mg.mL^{-1})$	1.27	1.02	0.23
	Γ max (mg.mg ⁻¹)	0.64	0.5	0.40
MMF	K _L (mg.mL ⁻¹)	4.7	3.2	_
	Γ max (mg.mg ⁻¹)	0.45	0.5	_

- → pH → quantity adsorbed adsorption
 →
- Adsorption on SBA-15 > adsorption on MMF

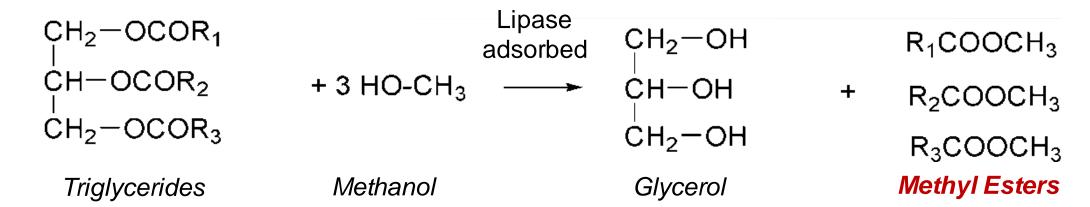
Weaker affinity between the supports and the lipase when pH > 6

| Maximal adsorption | Enzyme | Zero point charge of silica: pH = 3
| Isoelectric point of Mucor Miehei = 4.5

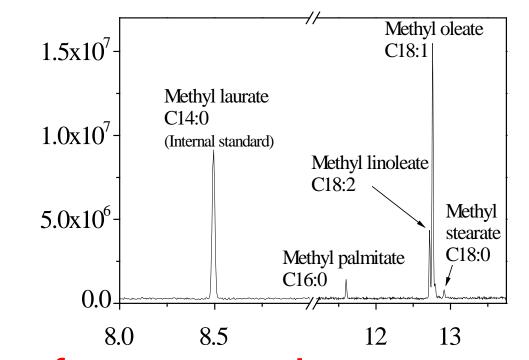
Between the isoelectric points of silica and lipase ⇒ existence of pH range where adsorption is maximal

Production of methyl esters

Transesterification of triglycerides (colza oil) with methanol:



 Analysis of Methyl Esters by Gas Chromatography coupled to mass spectrometry (GC-MS)



24 | Methanol/oil molar ratio = 1 | Reaction time : 24 hours |

8 | 16 | | 8 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 | | 4 |

Water added (%)

No water

• 5 wt.% of water

- Addition of water ⇒ increase of the transesterification yield
- Transesterification yield ≈ 22% reached after 15 hours of reaction
- Lipases also catalyze hydrolysis in aqueous media
- Excess water stimulates the competing hydrolysis reaction ⇒ transesterification yield



0 10 20 30 40 50 60 70

Reaction time (hours)

Ordered mesoporous silica materials can be used as matrix for the immobilization of lipase to form a bioreactor. The bioreactor can effectively be used for transesterification of colza oil with methanol.

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Yield (%)



