Economic impact of CalB immobilization method to be used in continuous oil transesterification.

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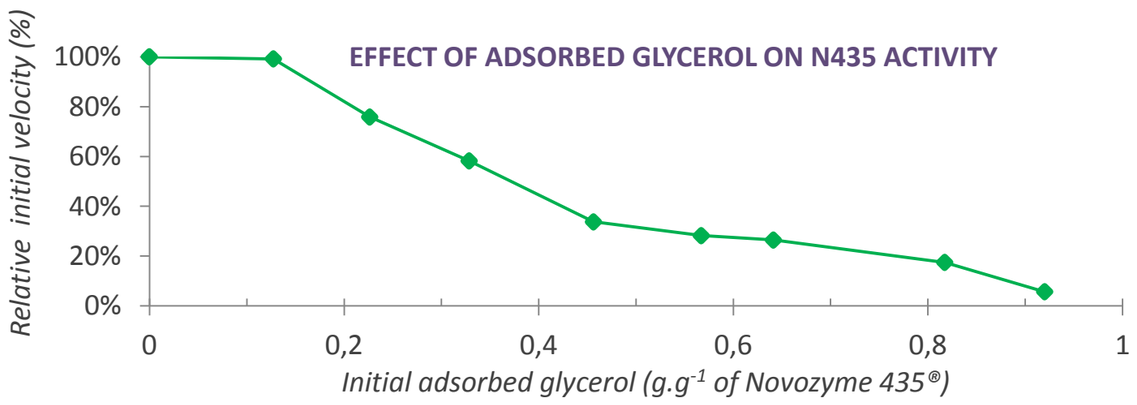
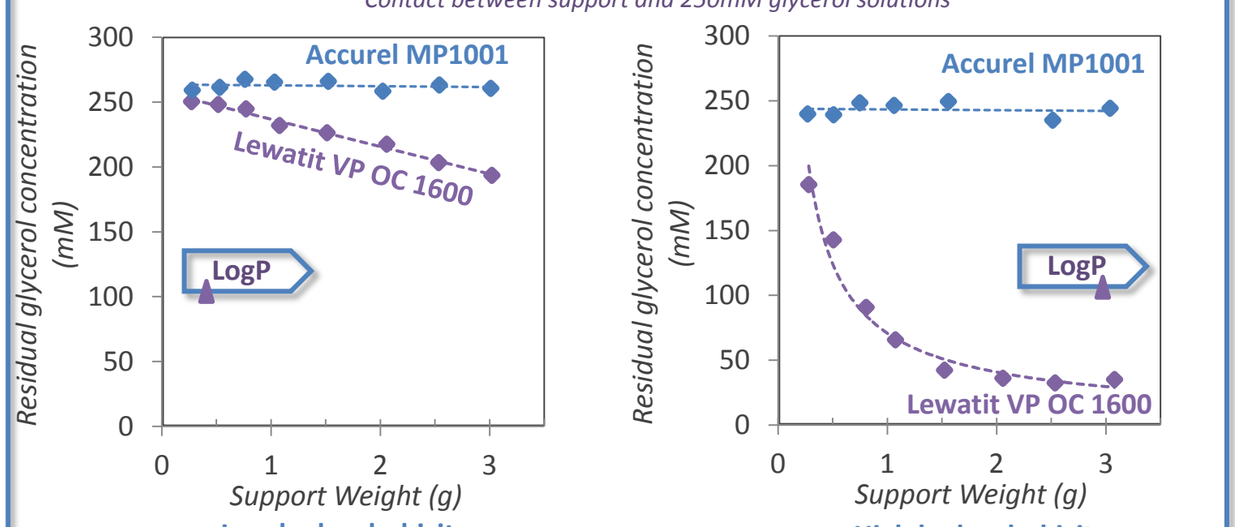
Context of the study

Fatty Acid Alkyl Esters (FAAE) may be obtained by transesterification reaction between triacylglycerols and alcohols resulting in glycerol release as by-product. Lipase the most commonly used is Novozyme 435 (N435), the lipase B from *Candida antarctica* (CalB) adsorbed on Lewatit VP OC 1600. Its price and the medium hydrophobic nature of its supports may be limiting for continuous process development : glycerol is able to form a hydrophilic layer around the enzyme resulting in low enzyme stability [1]. Then, we developed an immobilization strategy of CalB (Lipozyme CalB-L) using Accurel MP, a very hydrophobic macroporous propylene, that avoids glycerol adsorption. An economical approach was expanded in order to explore and rationalize the impact of immobilization on the development of an industrial packed bed reactor (PBR).

Glycerol Adsorption *vs* Enzymatic Transesterification





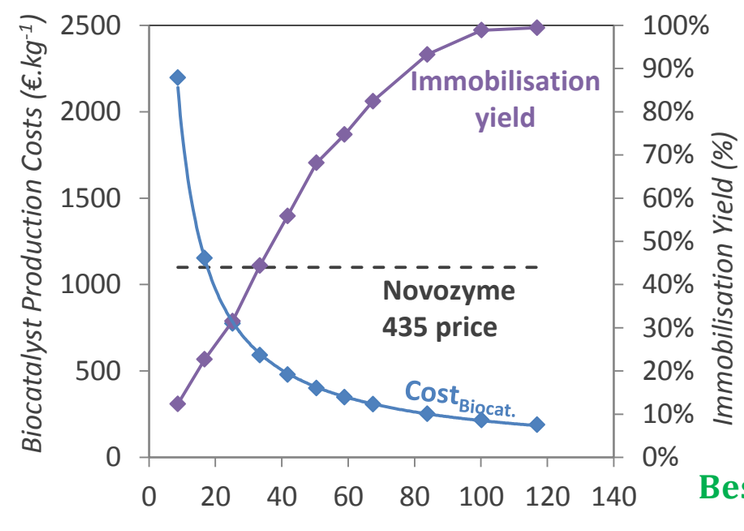
Immobilization procedure with variation of support/enzyme

20 min contact with Acetone → Direct Addition of Lipozyme CalB-L → 48h of gentle stirring at room temperature → Filtration and washing (x3)

Volumes of lipase (Lipozyme CalB-L) and additives were kept constant
The ratio between Support and Enzyme quantities varied from 0 $g.L^{-1}$ to 120 $g.L^{-1}$

Immobilization Yield vs Biocatalyst Production Costs

$$Cost_{biocat.} = \frac{m_{MP1001} \times cost_{MP1001} + m_{CalB} \times cost_{CalB} + cost_{additives} + cost_{operation}}{m_{biocat.}}$$



Support/Enzyme ↑
Immobilisation yield ↑
Enzyme loss ↓
Production Costs ↓

$Best\ Price_{Biocat.} \approx Price_{Novozyme\ 435}/6$

PBR design & capital cost estimate

The biocatalyst weight W_{ENZ} (Kg) needed in PBR is estimated according the activity measured in batch reactions [2].

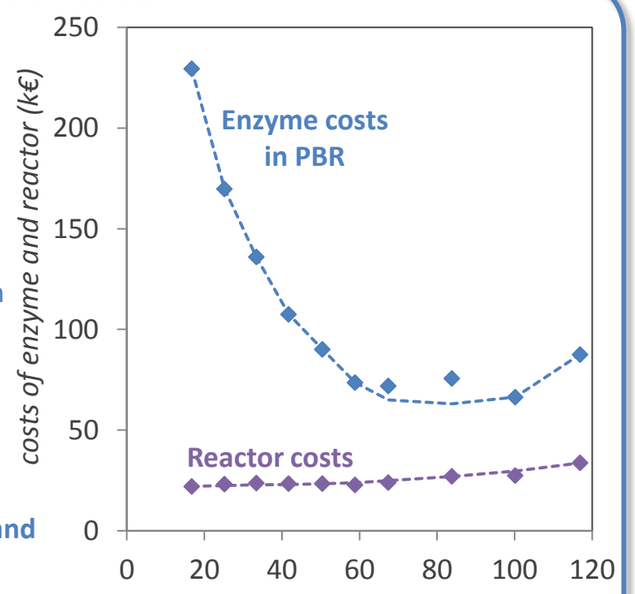
$$W_{ENZ} = q.\frac{W_{batch}.t_{batch}}{V_{batch}}$$

- q : flow rate in PBR ($L.min^{-1}$)
- W_{batch} : enzyme weight used in batch reaction (kg)
- t_{batch} : time necessary for conversion in batch reaction (min)
- V_{batch} : volume of batch reaction (L)

PBR volume was deducted from W_{ENZ} and Accurel MP1001 density.

The average investment costs for the PBR were computed by using three different methods (accuracy of these methods around 25%):

- **Chauvel *et al.* method [3],**
- **Peters *et al.* method [4]**
- **Turton *et al.* method [5]**



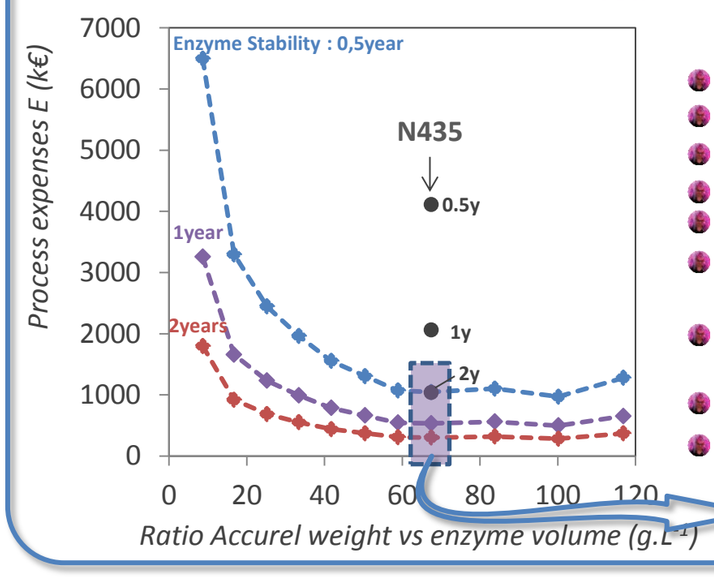
Enzyme costs >> Reactor Costs
(Factor 2 to 10)

Maximization of the Net Present Value (NPV)

$$NPV = -I_{process} + \sum_{p=1}^{t_d} \frac{(R_{process} - E_{process} - D_{process})(1-a) + D_{process}}{(1+i)^p} - \sum_{p=0}^{E(t_d/t_{enz})} \frac{nC_{enz}}{(1+i)^{pt_{enz}}}$$

Considering a constant production rate, the NPV is maximized if the total expenses E_{tot} are minimized. E_{tot} can be simplified to the only investments made for PBR design and costs of catalyst spent over the reactor lifetime.

$$E = I_{PBR} + \sum_{p=0}^{E(t_d/t_{ENZ})} \frac{nC_{ENZ}}{(1+i)^{pt_{ENZ}}} + \sum_{p=1}^{t_d} \frac{-aD_{PBR}}{(1+i)^p}$$



- t_D : depreciation time (commonly 10 years)
- t_{ENZ} : enzyme lifetime
- a : tax rate (33% for France)
- i : price deflator (10% over 10 years)
- I_x : Investments (€)
- $R_{Process}$: global incomes associated with the process operating
- E_x : Expenses ($E_{process}$ are operating costs (raw materials, utilities, labour, etc.)
- D_x : Depreciation charges
- C_{ENZ} : costs due to the catalyst.

Best compromise between activity, volume and process economy

Conclusion

We have developed an immobilization system on a very hydrophobic polymer, Accurel MP1001. An economic evaluation enables the optimization of the ratio between the quantity of support and the quantity of enzyme used for immobilization. From an economic point of view, the protein adsorption yield has to be maximized, even if the catalyst is less active and the reactor volume higher. The new immobilized enzyme allowed to avoid glycerol (and other polar compounds) adsorption, and would permit long-lasting continuous transesterification reactions.

REFERENCES

[1] Dossat, *et al.* Journal of Biotechnology (2002);97:117–24..
[2] Séverac, *et al.* Enzyme and microbial technology 48.1 (2011): 61-70.
[2] Chauvel, *et al.* Publications de l'Institut Français du Pétrole (2001)
[4] Peters, *et al.* Prentice Hall, Old Tappan (2003)
[5] Turton *et al,* McGraw-Hill Science/Engineering/Math, New York (1991)