

Biodiesel: Improvement on Standards, Co-ordination of Producers & Ethanol Studies

VEROLLET J., ALFOS C., POUILLOUX Y., MARTY A.

Introduction

The objective is to work on the process of production of ethyl esters (FAEE) in order to identify technical barriers that still have to be overcome and to improve the process so that actual industrial fatty acid methyl esters (FAME) based equipment could be used to produce them. Three different processes must be compared at laboratory scale using different catalysts (homogeneous, heterogeneous and enzymatic). These works must be done at :

- ITERG (homogeneous catalyse)
- LACCO (heterogeneous catalyse)
- INSA (enzymatic catalyse)

Partners

**Homogeneous catalyse****Heterogeneous catalyse****Enzymatic catalyse**

Materials and Methods

Several parameters were tested for the production of FAEE. It includes:

- temperature
- type of catalyst
- reaction time
- quality of EtOH
- addition of a co-solvent
- ratio EtOH/oil

- temperature
- reaction time
- addition of a co-solvent
- ratio EtOH/oil

- 3 commercial immobilised lipases
- 2 quality of ethanol (absolute / 95%)
- 2 temperatures 40°C & 60°C
- 3 ratio EtOH / oil = 3, 4 & 3+1 (3 at the beginning + 1 during reaction)

Results

The best results obtained for each catalyse were reported in a summary table.



Parameters	ITERG	LACCO	INSA	FAME specifications (EN 14103)
Temperature	80°C	230°C	40°C	
Catalyst	MeONa (1% w/w oil)	new catalyst (confidential)	lipase (20 g/L)	
Quality of ethanol	absolute	absolute	absolute	
Ratio EtOH/oil	4,5	18	3+1	
Time reaction	2h	7h	6h	
Yield	97,5%	100%	95,1%	96,5%



Table 1: Optimum conditions for the synthesis of FAEE at lab scale



Temperature had no detectable effect on the ultimate conversion to ester. However, higher temperatures decrease the time required to reach maximum conversion.

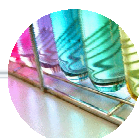


The highest ester content (100%) was obtained with a new catalyst after 7h of reaction. This new catalyst is presently in development at LACCO and is part of the know-how of LACCO (confidential). It enables to use a temperature of 230°C and a ratio alcohol/oil of 18.

NB : pressure was near 32 bars for all trials.



It was shown that ethanol must not contain water. The best temperature was determined (40°C). The best results were obtained with a ratio of ethanol/oil of 3 plus 1 added during the reaction.



Discussion

Concerning **homogeneous catalyse**, ester content is superior to 97% after washings. Partial glyceride contents of the ester phase are low and respect the specifications (according to EN 14 214) for FAME. The disadvantages of homogeneous catalyse is the fact that :

- catalyst can not be reused,
- soaps are created and must be remove thanks to several water washings,
- glycerol phase is brown and contains soaps and partial glycerides.

FAEE can be produced in FAME reactors according to the results obtained in this study.

The advantages of **heterogeneous catalyse** is the fact that glycerol phase is purer (no soaps). High yields (around 97%) were obtained after optimisation of the temperature, the ratio alcohol/oil and the reaction time. It must be kept in mind that heterogeneous catalysts are expensive and therefore it is essential to reuse them and avoid losses (by lixivation for example). FAME equipment can be used to produce FAEE because ratio alcohol/oil can be reduced to 18 (instead of 26 classically used for FAME). The process must be evaluated from an economical point of view to validate the cost of FAEE.

Enzymatic catalyse implies lower ester content (94%). Glycerol phase is very pure (no partial glyceride in it) but its obtaining requires 3 centrifugations (lab scale process) and some additional ethanol to recycle enzymes. An other drawback is the cost of enzymes.

Conclusion

To sum up, if the three processes had to be compared, the homogeneous catalyse would be the easiest process to develop at the moment. From a technical point of view, heterogeneous catalyse is a very promising process because it produces less by-products than homogeneous catalyse. New catalysts developed by Lacco indicate that it is possible to obtain very pure products with high yields. So heterogeneous catalyse might be the future process for FAEE production. Enzymatic catalyse still needs some development to obtain purer esters, higher yields and economically viable process.