

BODIESEL PRODUCTION FROM VEGETABLE FRYING OIL AND ETHANOL USING ENZYMATIC CATALYSIS

Ferreira, P.J.¹, Sousa, H.S.², Caetano, N.S.³

¹ Chemical Engineering Dpt., School of Engineering (ISEP), Polytechnic Institute of Porto, Portugal
1000501@isep.ipp.pt

² Chemical Engineering Dpt., School of Engineering (ISEP), Polytechnic Institute of Porto, Portugal
1000982@isep.ipp.pt

³ LEPAE –Chemical Engineering Dpt., School of Engineering (ISEP), Polytechnic Institute of Porto, Portugal
nsc@isep.ipp.pt

ABSTRACT

The aim of this work was the evaluation and optimization of conditions for Fatty Acid Ethyl Ester (FAEE) production. The influence of variables such as catalyst (NaOH, Lipozyme RM IM, Lipozyme TL IM, Novozym 435), alcohol (methanol, ethanol 96% v/v, ethanol 70% v/v), reaction temperature (35 – 38°C), oil: alcohol molar ratio (1:3; 1:9; 1:18) and reaction time (8 and 24h) was studied.

Comparing alkaline homogeneous with enzymatic catalysis, we could observe that the former one produced a higher yield and lower selectivity, in addition to minor problems related to corrosion of the equipment used in the process.

Enzymatic catalysis also presents another benefit, which is the fact that it allows no side reactions producing byproducts, therefore reducing the costs on subsequent purification. In this context, enzymatic catalysts have been studied as an alternative to FAEE production, so that separation processes can be simplified and associated costs reduced. Experimental runs when Lipozyme TL IM was used lead to the best results. Yields ranging from 21 to 60% were achieved in 8 hours reaction time. However, the highest yield (90%) was obtained using 96% v/v ethanol, an alcohol : oil ratio of 1:3, 24 hours reaction time and temperature range of 35-38°C.

Keywords: Biodiesel, FAEE, Lipase, Enzymatic Catalysis

INTRODUCTION

In a global context, biofuels will supply an important part of the world demand in the near future, driven primarily by environmental considerations, the increase in oil prices in the international market and the uncertainty in the fossil fuels supply in a medium and long term.

Biofuels are products derived from agricultural crops (sugar cane, cereals and organic material), which can be used as fuel alone or be mixed with conventional fuels. The most common examples in this category are biodiesel, bioethanol and biomethanol.

Biodiesel is a biodegradable alternative fuel for diesel oil, produced from renewable sources of energy (mainly alcohol and vegetable oil or animal fat), free of sulphur in its composition. It can be used in diesel engines without the need of any kind of adjustment, without significant loss of performance and contributes to improving the life of the engine (because its lubricant capacity is better than the one from diesel oil). Biodiesel has clean burning (pollutants production from biodiesel is lower than the one from diesel oil combustion). There are dozens of plant species from which oil can be extracted to produce biodiesel, such as sunflower, soybean, palm, corn and all oils and animal fats.

Besides environmental benefits, where reducing greenhouse gas emissions can be highlighted as its most expressive capacity, biodiesel has a low risk of explosion, since it needs a heat source of above 150°C to explode, which facilitates transport and storage.

As a fuel, biodiesel is already a reality in expansion. It benefits the farmers and contributes to the economic growth of deserted land, therefore reduces fuel dependency from imports, preserving the national interest and promoting the exploitation of energy resources.

However, if world consumption of biodiesel raw materials is for a larger scale it will require plantations in large agricultural areas. Countries that do not adequately monitor their forest resources will have a high degree of deforestation to make room for plantations. With cereals use for biodiesel production, prices of this raw material will inevitably increase in the near future.

Transesterification Reaction

Transesterification process is the most currently used for biodiesel production. It consists in a chemical reaction of vegetable oils or animal fats with a short chain alcohol (ethanol or methanol) encouraged by a catalyst, which also draws glycerin, a product with different applications in chemical industry. To obtain biodiesel, transesterification reaction of vegetable oils with primary alcohols can be processed both in acidic or in basic environment:

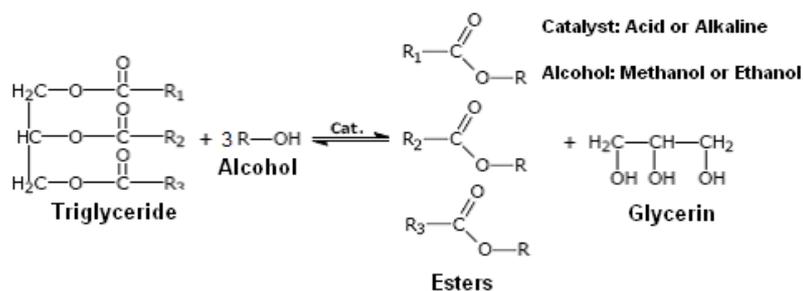


Figure 1 – Transesterification Reaction

Despite biodiesel can be produced with different alcohols, the most commonly used is methanol. In spite of its higher toxicity, it is the most reactive and affordable. Ethanol can be used, but is less reactive, which requires greater reaction times and energy consumption [1].

Alcoholise with methanol is technically more feasible than with ethanol, particularly if it corresponds to the hydrated ethanol, in which water content (4-6%) slows the reaction. Use of anhydrous ethanol in this reaction will minimize this inconvenient, although not implicating a solution for the inherent problem of glycerin separation in the reaction, which in the case of methyl esters can be easily obtained by means of a simple decantation.

In addition to this, while a fuel, biodiesel requires some technical characteristics that can be considered essential: the transesterification reaction must be complete, causing total absence of fatty acids and the biofuel must be highly purified, not containing traces of glycerine, residual catalyst or surplus alcohol from the reaction.

Catalysis

Biodiesel can be produced through homogeneous or heterogeneous catalysis. Homogeneous catalysis is divided into acidic or basic catalysis, but in industrial terms the last one stands out, because it allows for faster reaction rate and milder operating conditions. In heterogeneous catalysis, glycerin is produced with higher purity, but this process has some disadvantages, such as higher initial investment costs, due to the catalysts usage. The main heterogeneous catalysts used for biodiesel production are enzymes, titanium silicate, alkaline-earth metals compounds and resins.

The priority choice to biodiesel production has been the alkaline homogeneous catalysis, where the most used catalysts are sodium hydroxide (NaOH) and potassium hydroxide (KOH). Its widespread usage is primarily due to its good performance in alkaline transesterification and its low cost. Moreover, homogeneous catalysis presents a problem of the difficult catalyst separation at the reaction end. In this context, heterogeneous catalysts, which can be kept in fixed bed or when mixed to reactants can be separated from the final products by simple procedures such as filtration, have been studied as an alternative to reduce costs, simplify and reduce impacts on separation processes.

Heterogeneous catalysts utilization is a more economically viable option because in addition to avoiding the saponification problem, it also produces a fraction of glycerin less contaminated, which does not require large capital investments to achieve a high standard on the market. Another advantage comes from the fact that heterogeneous catalysts do not produce corrosion or emulsion,

thus facilitating products separation. Among various heterogeneous catalysts studied, resins and enzymes can be highlighted.

Enzymatic catalysis synthesizes specifically alkyl esters, which allows for the simple recovery of glycerol, transesterification of glycerides with high fatty acids content, total transesterification of free fatty acids, and the use of milder conditions in the process, with yields of at least 90%, therefore becoming a more commercially profitable alternative [2].

The advantages of this process are: the absence of alkali aqueous rejects, lower production of other contaminants, greater selectivity and good yields, which motivates research, aiming at a decrease of the main disadvantage of the methodology: relatively high cost of the pure enzymes. The high cost of the purification and extraction procedures of macromolecules in solution and its instability represent an obstacle to biocatalyst recovery after use.

Actually, biodiesel commercial production process is mainly chemical, but enzymes have aroused the interest of the scientific community. The common aspect of these studies consists in the optimization of reaction conditions, to establish characteristics that will make them available for industrial applications.

Process for biodiesel production

The procedures relating to the preparation of the raw material for its conversion into biodiesel aims to create the best conditions for the implementation of transesterification reaction, with the maximum conversion rate. First, it is necessary for the raw material to have a minimum moisture and acidity level. This is possible by treating acid oils or fats to a neutralization process, with an alkaline solution of sodium or potassium hydroxide, followed by an operation of drying or dehumidification. The specific procedures of this treatment will depend on the nature and conditions of fat used as raw material. The transesterification reaction is the conversion stage, itself, of oil or fat, on ethyl or methyl esters of fatty acids, which is the biodiesel.

After the transesterification reaction that converts the fat into esters (biodiesel), the final reaction mass consists of two phases, separable by decantation or by centrifugation. The heavier stage is composed of crude glycerin, imbued with the excesses of alcohol, water and impurities inherent to the raw material. The less dense phase consists of a mixture of ethyl or methyl esters (depending on the nature of the alcohol originally adopted) impregnated with excess alcohol and impurities.

The heavy phase containing water and alcohol is subjected to a process of evaporation, eliminating from the crude glycerin phase these volatile constituents, whose vapours are liquefied in an appropriate condenser. Similarly, but separately, residual alcohol is recovered from the upper phase, releasing for the following steps the ethyl or methyl esters. The residual alcohol excess, after the recovery process, contains significant amounts of water, requiring a separation. The dehydration of alcohol is normally made by distillation.

Esters can be washed or separated by centrifugation and dehumidified later, resulting finally in biodiesel, which should have its characteristics defined in the specifications of the technical standards established for biodiesel as fuel for use in diesel engines.

Crude glycerin emerging in the biodiesel production process, even with some impurities, is a saleable subproduct. However, the market is much more profitable for purified glycerin, when its value is enhanced. The purification of the crude glycerin is made by the vacuum distillation, resulting in a clear and transparent product, known commercially as distilled glycerin.

EXPERIMENTAL PROCEDURES

Materials and methods

Oil used in this study was vegetable, with no soybean oil added, by Alvolino. Ethanol used in this study had two different grades: 96% (V/V, by AGA) and 70% (V/V) by AGA. Three different supported enzymes, kindly offered by Novozymes Spain, S.A., were used in the study: Lipozyme TL IM; Lipozyme RM IM and Novozym 435 (Figure 2).

Biodiesel produced in the study was tested for several parameters according to the methods suggested in EN 14214:2003 E: density, kinematic viscosity, water (Coulometric Karl Fisher titration method), acid value and iodine value.

Procedure

300g of oil are weighted into a screw cap flask and heated on a hotplate with magnetic stirring to

the desired temperature. A certain amount of ethanol was added to the flask, mixed thoroughly and the enzyme was added to the mixture. The closed reaction flask was left in the stirring heater for the reaction time (8 or 24 h). After this time, mixture was poured into a separating funnel in order to provide a separation between phases.

When the separation of phases was not clearly visible, a centrifugation was conducted, followed by a vacuum filtration (to remove some supported enzyme that could be in the mixture). At the end of the work the enzyme recovery was carried out. All the biodiesel samples were characterized with no further purification, washing or drying.



Figure 2 – Different enzymes test in this work: Novozyme 435, Lipozyme RM IM and Lipozyme TL IM

Table 1 summarizes the experiments that were conducted to screen for the influence of several parameters (oil: ethanol ratio; oil: enzyme ratio, type of enzyme, temperature, reaction time, ethanol grade).

Table 1 – Lipase catalyzed experiments conducted for biodiesel production from vegetable oil and ethanol.

Test n°.	Ethanol [% v/v]	Oil : Ethanol Ratio	Enzyme	Enzyme [g]	Temperature [°C]	Reaction Time [h]
1	70%	1:3	Lipozyme RM IM	≈ 7	45°C	8
2	70%	1:3	Lipozyme TL IM	≈ 7	45°C	8
3	70%	1:3	Novozym 435	≈ 7	45°C	8
4	70%	1:3	Lipozyme RM IM	≈ 7	35°C – 38°C	8
5	70%	1:3	Lipozyme TL IM	≈ 7	35°C – 38°C	24
6	96%	1:3	Lipozyme RM IM	≈ 7	35°C – 38°C	24
7	96%	1:3	Lipozyme TL IM	≈ 7	35°C – 38°C	24
8	96%	1:3	Novozym 435	≈ 7	35°C – 38°C	24
9	96%	1:9	Lipozyme TL IM	≈ 7	35°C – 38°C	24
10	96%	1:9	Lipozyme TL IM	≈ 10	35°C – 38°C	24
11	96%	1:18	Lipozyme TL IM	≈ 7	35°C – 38°C	24
12	96%	1:9	Lipozyme TL IM	≈ 7	35°C – 38°C	8
13	96%	1:9	Lipozyme TL IM used in test n°. 9	≈ 7	35°C – 38°C	24

In tests 1 to 3, the flasks were heated using a thermostatic bath with continuous stirring at 70 rpm, while the remaining experiments were conducted on a heating plate under magnetic stirring (Fig 3).

In tests n°.1 to 4, n°.6 and n°.8 it was not possible to achieve enough biodiesel production to perform its full characterization, suggesting that 8h reaction time was not enough for biodiesel production in significant amounts. Also it seems that the best lipase to be used is Lipozyme TL IM. Thus the results only express the characterization of the remaining trials.



Figure 3 – Experiments run under different stirring conditions.

EXPERIMENTAL RESULTS

The effect of ethanol purity (water content) on the reaction could be tested for Lipozyme TL IM, by comparing the reaction product from experiments n^o.5 vs n^o.7 (biodiesel characterization in table 2). Analyzing the experimental results, we could conclude that the best experimental conditions corresponded to the one chosen for run n^o.7, when ethanol 96% and Lipozyme TL IM were used at 35-38°C for 24h reaction time. The oil: alcohol molar ratio used was 1:3, corresponding to a yield of 90.31%. This is a very good yield and means that there was a good reaction between oil and ethanol, clearly forming two phases, biodiesel and glycerin.

Table 2 – Effect of ethanol purity (70% vs 96% V/V) and of the oil: alcohol molar ratio on production and characteristics of biodiesel.

Parameter	Ethanol 70% n ^o .5	Ethanol 96% n ^o .7	Ethanol 96% n ^o . 9	Ethanol 96% n ^o .11
Density at 20° C [kg/m ³]	889	891	883	867
Water Content [mg/kg]	800	4,506	24,127	40,502
Kinematic viscosity at 20° C [mm ² /s]	5,76	5,28	4,79	3,46
Acid value [mg KOH / g]	-----	6,88	6,45	5,57
Iodine value [g iodine/100g]	121	112	106	71
Yield [%]	68,5	90,3	41,2	21,7

Regarding the iodine number, both tests are within the limits allowed in the European Standards, as well as density and viscosity. It should be noticed that, despite biodiesel obtained from 70% ethanol corresponded to a relatively good yield, the phase separation was not so clearly visualized as for the biodiesel produced with 96% ethanol.

The effect of the oil: alcohol molar ratio on biodiesel production could be studied in experiments n^o.7, 9 and 11, and results are presented in Table 2.

These tests are within the limits allowed by the European Standard, regarding to iodine value, as well as to density and viscosity. Regarding yield, it is clear that rising the oil: alcohol ratio leads to worst results (1:3 corresponds to the stoichiometric ratio need for the reaction) and the best results were obtained exactly at the stoichiometric conditions. This also suggests that by rising the reaction time, it could probably be possible to reach higher yields.

The effect of the amount of lipase used in the reaction could be tested in experiments n^o.9 and 10. Corresponding results are presented in Table 3. The results show that there is no significant difference in any of the evaluated parameters so, 7g of lipase should be enough for the amount of oil used in the experiments.

Table 3 - Results obtained for lipase catalyzed transesterification of vegetable oil with 96% ethanol using different amounts of Lipozyme TL IM (24h reaction time and 1:9 oil: alcohol ratio), different reaction times and fresh versus used catalyst

Parameter	Ethanol 96% nº. 9	Ethanol 96% nº. 10	Ethanol 96% nº.12	Ethanol 96% nº.13
Density at 20° C [kg/m ³]	883	880	894	820
Water Content [mg/kg]	24,127	24,845	-----	-----
Kinematic viscosity at 20° C [mm ² /s]	4,79	4,08	4,52	2,57
Acid value [mg KOH / g]	6,45	6,41	8,21	1,06
Iodine value [g iodine/100g]	106	96	101	123
Yield [%]	41,2	41,6	36,6	-----

The effects of reaction time and of catalyst usage were tested in experiments nº.9 vs nº.12 and nº.9 vs. nº.13. Results are presented in Table 3.

Experiment nº. 13 was conducted with the same catalyst used in experiment nº.9 with no kind of treatment prior to usage. After a 24h reaction time, it could not be observed any significant formation of biodiesel. We recommend therefore that for a new laboratory work where the objective is the reutilization of the enzyme, we should first of all make a pre-treatment for the enzyme recovery.

Regarding the biodiesel obtained with a reaction time of 8h, it appears again that the studied parameters are within the limiting values. However, Comparing the yields between biodiesel produced with 1:9 oil: ethanol ratio and 7g of enzyme, using different reaction times (8 and 24h), we can see that longer reaction time leads to higher yield, allowing to conclude that the reaction time can influence oil to biodiesel conversion.

CONCLUSIONS

Through the analysis of this study we concluded that water presence in the alcohol could decrease the reaction yield.

Also an oil: ethanol (96% v/v) molar ratio of 1: 3 combined with 42,8:1 oil to lipase mass ratio gave the best yield, corresponding to about 90% conversion, under mild reaction conditions (35-38 °C), with 24 h reaction time. However the use of low oil: alcohol molar ratio also makes glycerin separation more difficult.

This work presents encouraging results since biodiesel production from ethanol by homogeneous catalysis presents some difficulties and the high yields obtained are very promising, suggesting the need to continue this study.

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