Università degli Studi di Milano

Doctorate School in Chemical Sciences and Technologies
Doctorate in Industrial Chemistry – XXVIII Cycle

Reduction of the carbon footprint of fuels and petrochemicals starting from vegetable oils

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Doctorate Thesis – A.Y. 2015-2016

dedicated to

my Advisor: a wise guide and a sincere friend.

Carlo

"Considerate la vostra semenza:

fatti non foste a viver come bruti,

ma per seguir virtute e canoscenza"

Dante Alighieri, 1472

"La Divina Commedia", Inferno, Canto XXVI.

Summary

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Publication list

Scientific publications belonging to the major of the thesis

1. C Pirola, **F Galli**, M Corbetta, F Manenti, "Robust kinetic modeling of heterogeneously catalyzed free fatty acids esterification in monophasic liquid/solid packed bed reactor: rival model discrimination", Clean Technologies and Environmental Policy, 17 (2015) 1139-1147, DOI: 10.1007/s10098-015-0925-x.
2. C. Pirola, **F. Galli**, A. Comazzi, F. Manenti, C.L. Bianchi, "Preservation of carotenes in the deacidification of crude palm oil", RCS Advances, 4 (2014) 46922-96925, DOI: 10.1039/c4ra09575h.
3. **Galli F**, Corbetta M, Pirola C, Manenti F, "Robust Kinetic Modeling of Heterogeneously Catalyzed Free Fatty Acids Esterification in (Monophasic Liquid)/Solid Packed-bed Reactor: Rival Model Discrimination, Chemical Engineering Transactions, 39, (2014), 979-984, DOI:10.3303/CET1439164
4. D.C. Boffito, C Pirola, **F Galli**, A. Di Michele, CL Bianchi, "Free fatty acids esterification of waste cooking oil and its mixtures with rapeseed oil and diesel", Fuel 108 (2013) 612–619; DOI: 10.1016/j.fuel.2012.10.069.
5. **Galli F**, Nucci S, Pirola C, Bianchi C L, "Epoxy Methyl Soyate as Bio-Plasticizer: Two Different Preparation Strategies", Chemical Engineering Transaction, 37 (2013) 601-606; DOI: 10.3303/CET1437101.
6. Pirola C, Manenti F, **Galli F**, Bianchi C L, D.C. Boffito, Corbetta M, "Heterogeneously catalyzed Free Fatty Acids esterification in (monophasic liquid)/solid Packed Bed Reactors (PBR)", Chemical Engineering Transaction, 37 (2013) 553-558; DOI: 10.3303/CET1437093.
7. D.C. Boffito, **F. Galli**, C. Pirola, C.L. Bianchi, G.S. Patience, "Ultrasonic free fatty acids esterification in tobacco and canola oil", Ultrasonic Sonochemistry, 21 (2014) 1969-1975; DOI: 10.1016/j.ultsonch.2014.01.026
8. C. Pirola, F. Galli, C.L. Bianchi, D.C. Boffito, A. Comazzi, F. Manenti, "Vegetable Oil Deacidification by Methanol Heterogeneously Catalyzed Esterification in (Monophasic Liquid)/Solid Batch and Continuous Reactors", Energy and Fuels, 28 (2014) 5236-5240; DOI: 10.1021/ef501397h

Other scientific publications

1. C.L. Bianchi, C Pirola, **F Galli**, M. Stucchi, Morandi S, Cerrato G, Capucci V, “Nano or micro-TiO2 for the photodegradation of ethanol: experimental data and kinetic modelling”, RCS Adv, 2015, 5, 53419-53425; DOI: 10.1039/C5RA05385D
2. C Pirola, **F Galli**, F Manenti, M Corbetta, C.L. Bianchi, “Simulation and Related Experimental Validation of Acetic Acid/Water Distillation Using p-Xylene as Entrainer”, Ind. Eng. Chem. Res., 2014, 53 (46), pp 18063–18070, DOI: 10.1021/ie502758v
3. A. Di Fronzo, C Pirola, A Comazzi, **F Galli**, C L Bianchi, A Di Michele, R Vivani, M Nocchetti, M Bastianini, DC Boffito, “Co-based hydrotalcites as new catalysts for the Fischer–Tropsch synthesis process”, Fuel 119 (2014) 62–69; DOI: 10.1016/j.fuel.2013.11.014.
4. Pirola C, **Galli F**, Bianchi C L, Carvoli G, “Heterogeneous Distillation of the System Water-Acetic Acid p- Xylene: Study of its Fluid Phase Equilibria, Micro-Pilot Column Experimental Results and Computer Simulation”, Chemical Engineering Transaction 32 (2012) 1897-1902; DOI: 10.3303/CET1332317.
5. C L Bianchi, Pirola C, **Galli F**, Cerrato G, Morandi S, Capucci V, “Pigmentary TiO2: A challenge for its use as photocatalyst in NOx air purification”, Chemical Engineering Journal, (2014), DOI: 10.1016/j.cej.2014.03.078.
6. Pirola C, Scavini M., **Galli F**, Vitali S., Comazzi A, Manenti F, Ghigna P, “Fischer-Tropsch synthesis: EXAFS study of Ru and Pt bimetallic Co based catalysts”, Fuel, 132 (2014) 62-70; DOI: 10.1016/j.fuel.2014.04.063.

Contributions to national and international Congresses

1. Di Michele A, Pirola C, Di Fronzo A, Comazzi A, Galli F, Bianchi C.L. “Co based bimetallic catalysts for Fischer-Tropsch synthesis prepared by high-power ultrasound”. “XIth European Congress on Catalysis” Lion, France 1-6 September 2013, Poster presentation.

2. Di Michele A, Pirola C, Di Fronzo A, Comazzi A, Galli F, Bianchi C.L. “Sonochemical synthesis of Co based bimetallic catalyst for Ficher-Tropsch synthesis”. “XVII Congresso Nazionale di Catalisi e XI Congresso Nazionale di Scienza e Tecnologia delle Zeoliti” Riccione, Italia 15-18 September 2013, Poster presentation

3. C. Pirola, A. Di Fronzo, F. Galli, D. C. Boffito, G. Carvoli, “Separation of water and acetic acid by distillation using p-xylene as entrainer: experimental data and computer simulation”, XVIII congresso Nazionale della Divisione di Chimica Industriale, 11-14 June 2012, Firenze. Poster presentation

4. C. Pirola, G. Carvoli, F. Galli, “Distillazione estrattiva eterogenea della miscela acqua-acido acetico con p-xilene come solvente estrattore: risultati sperimentali e di simulazione”, convegno GRICU, Montesilvano, 16-19 settembre 2012. Poster presentation

5. C. Pirola, F. Galli, C. L. Bianchi, G. Carvoli, “Heterogeneous distillation of the system water-acetic acid- p-xylene: study of its phase equilibria, micro-pilot column experimental results and computer simulation”, ICheaP-11 Congress, 2-5 June 2013 – Milano. Oral presentation

6. F. Galli, C. Pirola, C. L. Bianchi, G. Carvoli, “Heterogeneous catalyzed FFA esterification of soybean oil in a pressurized PFR reactor”, XVII National Congress on Catalysis GIC 2013 and XI National Congress of Zeolites Science and Technology, Riccione, 2013. Poster presentation

7. F. Galli, C. Pirola, G. Carvoli, C.L. Bianchi, “Heterogeneous catalyzed free fatty acids esterification in crude palm oil, a study of the catalyst stability”, 11. Europacat (European Congress on Catalysis), Lyon (France), 2013. Poster presentation

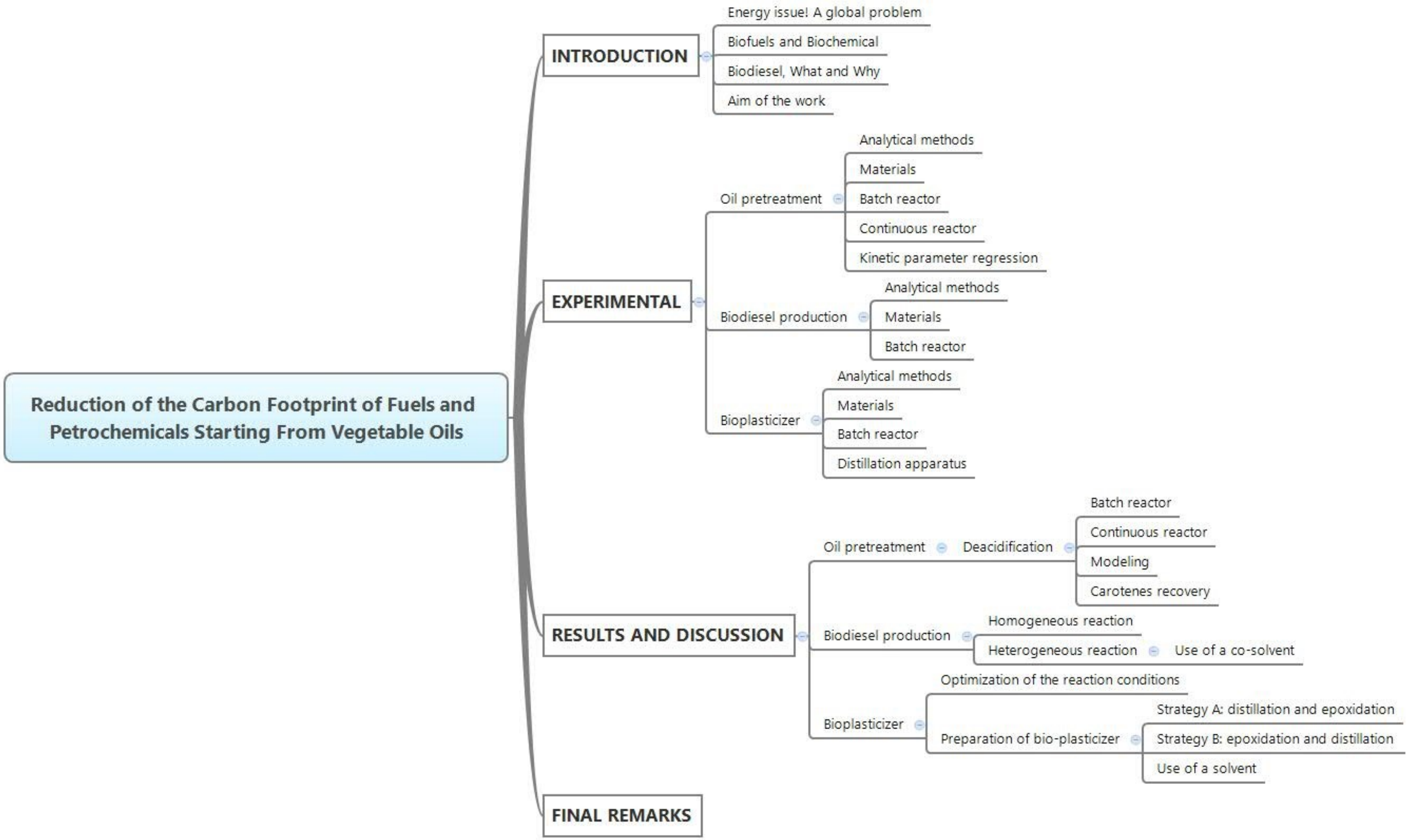
8. C. Pirola, A. Di Fronzo, A. Comazzi, F. Galli, A. Di Michele, C. L. Bianchi, “Co based bimetallic catalysts for Fischer-Tropsch synthesis prepared by high power ultrasound”, 11 Europacat European Congress on Catalysis, Lyon (France), 2013. Poster presentation

9. C. Pirola, F. Manenti, F. Galli, C. L. Bianchi, D. C. Boffito, M. Corbetta “Heterogeneously catalyzed free fatty acid esterification in (monophasic liquid)/solid Packed Bed Reactors (PBR), International Congress on Biomass, 4-7 may 2014, Florence, Italy. Oral presentation

10. C. Pirola, A. Di Fronzo, F. Galli, C. L. Bianchi, A. Comazzi, F. Manenti “Biogas conversion by Fischer-Tropsch synthesis: experimental results and multi-scale simulation of a PBR with high Fe loaded supported catalysis”. International Congress on Biomass, 4-7 may 2014, Florence, Italy. Poster presentation

11. F. Galli, S. Nucci, C. Pirola, C.L. Bianchi “Epoxy methyl soyate as bio-plasticizer: two different preparation strategies” International Congress on Biomass, 4-7 may 2014, Florence, Italy. Poster presentation

Conceptual map



THESIS ABSTRACT

1. INTRODUCTION

Biodiesel, i.e. fatty acid methyl esters (FAME) derived from vegetable oil or from animal fat, has been produced as alternative fuel since 1991 (Pahl, 2008). However, its production is still noncompetitive compared to fossil fuels for different reasons. In this work I focused on different aspects of the biodiesel production, trying to understand the critical points of the processes and proposing improvements to the existing technology.

The first one belongs to the oil pretreatment technologies. Since one of the main drawback in using edible oils for producing fuels relies in their costs and the agricultural land usage, vegetable oils obtained from non-edible seeds or wastes were used. However, this feedstock is characterized by a great amount of free fatty acids (FFA), which should be eliminated because represent a problem in the transesterification step. One of the more advantageous solution proposed relies in the FFA esterification (Pirola, et al., 2015). It consists in eliminating FFA by making them react with alcohol (methanol) to give ester and water. However, the reaction conditions used are not yet standardized and optimized (Son, et al., 2011), (Kouzu, et al., 2011). In my work both batch and continuous experiments were performed using ion exchange resin as catalyst, i.e. Amberlyst 46 resin, changing different key parameters, i.e. temperature, methanol amount and reaction time in order to optimize the operative variable and developing a comprehensive kinetic model able to describe the reaction kinetics and the non-ideality of the mixture exanimated.

In a second step, the work focused on the core process of the biodiesel production, i.e. the transesterification reaction. In this step usually a homogeneous basic catalyst is used, generally NaOH or KOH (Jain, et al., 2011). Together with the great advantage of the very low reaction time needed for achieving complete oil conversion, the typical disadvantage of the homogeneous catalysis are non-negligible, i.e. their separation from the reacting mixture and their disposal. In detail, I studied the heterogeneous transesterification of second generation oils using CaO as heterogeneous catalyst. Instead of developing costly and complicated catalysts, whose cost affects the operative expenses of the process, I focused on enhancing the biodiesel yield trying to use a cosolvent (among acetone, tethrahydrofuran, chloroform, ethyl acetate, dichloromethane and heptane) for oil and methanol (that shows a very low solubility in triglycerides), in order to eliminate the external mass transfer limitation. This, as far as I know, is an innovative solution for the biodiesel synthesis technology. I tested the transesterification in seven different solvents, performing the reactions at 60°C in a batch reactor. Among the solvents tested, THF showed the best results.

Finally, since in the end the main limitation to the biodiesel usage are the economic limitations, I tried to develop methods for the recovery of high added value molecules, for instance beta carotenes from palm oil and used biodiesel as a reactant for the production of plasticizers using hydrogen peroxide generated in situ, following different strategies for the epoxidation reaction yield maximization in order to improve the economic balance of the whole production. In particular crude palm oil was treated with heterogeneous catalyst at low temperature and pressure in order to preserve the carotenes content while for what concern the epoxidation of biodiesel I optimized the reaction conditions and tried different strategies form increasing the plasticizer power of the final product, achieving results comparable to the available commercial bio plasticizers.

2. RESULTS AND DISCUSSION

2.1 Oil pretreatment, deacidification

I chose Amberlyst 46 catalyst because of its peculiar properties for the esterification reaction between FFA and methanol to give FAME and water. In fact, it is a sulphonic acid resin characterized by the presence of the active acid sites only at the catalyst surface, property that reduce the internal diffusional limitations. In a previous work this catalyst was found to be the best among a series of heterogeneous catalyst.

All the results obtained in the FFA deacidification of oil gave the indication that a monophasic reacting mixture is the best choice for undergoing deacidification reaction, since the double phase formation limits the biodiesel yield and the catalyst performance in a packed bed reactor. The methanol:oil molar ratio equal to 5 was found to be the best for obtaining high FFA conversions.

In Figure 1 the main results concerning the batch deacidification experiments are reported (Galli et al., 2014).

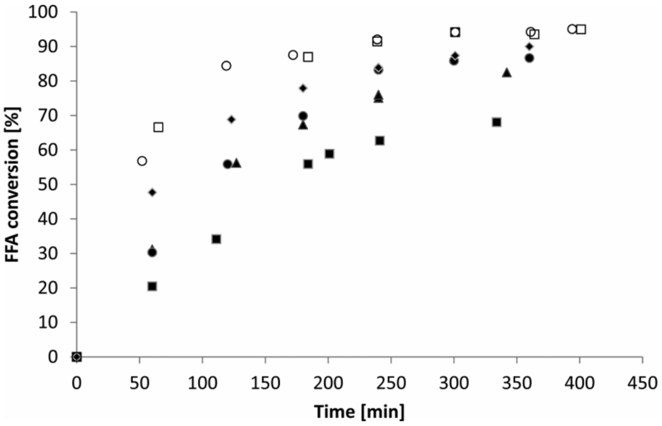


Figure 1: Experimental FFA conversion at different methanol/FFA molar ratios: (+) 1.96, (■) 2.99, (▲) 5.00, (●) 10.06, (◆) 13.38, (○) 94.32), and (□) 149.35. Full symbols indicate the present of only one liquid phase, and empty symbols indicate the presence of two liquid phases.

In Figure 2 the main results obtained concerning the continuous oil deacidification varying the reaction temperature are summarized, together with the kinetic regression (Galli et al., 2015).

Two different models, pseudo-homogeneous and adsorption-based, were proposed and the corresponding kinetic parameters were regressed. In particular two different thermodynamic approaches were considered, i.e. considering the liquid mixture ideal and non-ideal, calculating the activity coefficients using the UNIQUAC model (Abrams & Prausnitz, 1975). The equations of these two models are reported hereinafter:

$$r_{PSEUDO} = \frac{d\xi}{dt} * C_{FFA}^{0} = k_{1}^{0} * a_{FFA} * a_{MeOH} - k_{-1}^{0} * a_{FAME} * a_{H2O} \qquad \text{Equation 1}$$

in which ξ represents the conversion of FFA, C_{FFA}^{0} the initial FFA concentration, k_{i}^{0} the kinetic constant of either the direct or inverse reaction and a_i the activity of the component i. The expression of the reaction rate considering the adsorption based model is reported in Equation 2

$$r_{ADS} = \frac{d\xi}{dt} * C_{FFA}^{0} = \frac{k_{1}^{0} * a'_{FFA} * a'_{MeOH} - k_{-1}^{0} * a'_{FAME} * a'_{H2O}}{\left(a'_{FFA} + a'_{MeOH} + a'_{FAME} + a'_{H2O}\right)^{2}} \qquad \text{Equation 2}$$

in which a'_i are the activities considering the adsorption affinity constant between the component I and the resin, reported in (Popken, et al., 2000) and (Rehfinger & Hoffmann, 1990). For both the models the temperature dependence of the kinetic constants was considered adopting the Arrhenius model.

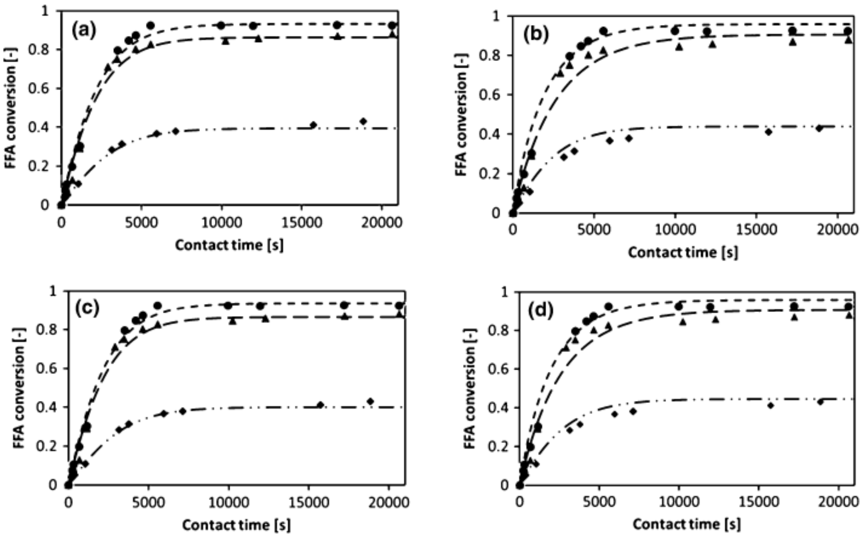


*Figure 2: Experimental FFA esterification, experimental data (points) at 95°C (circles), 85°C (triangles), and 54°C (diamonds) and simulated curves using **(a)** the adsorption-based model with UNIQUAC, **(b)** the pseudo-homogeneous model with UNIQUAC, **(c)** the adsorption-based model with IDEAL (activity coefficients = 1), **(d)** the pseudo-homogeneous model with IDEAL (activity coefficients = 1), taken from (Galli et al., 2015)*

The best fitting was obtained using the adsorption based model taking into account the calculation of the liquid activities. The calculation of the activities considering the UNIQUAC model does not have a great influence on the fitting probably because the experimental amount of methanol used was chosen in order to have only a monophasic liquid mixture and then corresponding to mixture compositions only lightly non-ideal. Nevertheless, being the system oil/FFA/FAME/methanol/water highly non-ideal for others several compositions, a possible formation of two liquid phases can be calculated only using this more realistic thermodynamic approach, and thus its use is preferable. The use of UNIQUAC model in order to take into account the non-ideality of the liquid medium is consequently advantageous when using starting vegetable oils characterized by higher FFA content. In this case, with the UNIQUAC adsorption-based model, it is possible to predict the behavior of the system, and it is possible to design a series of packed bed reactor (PBRs) each of which dimensioned in order to avoid the liquid demixing. Proper water separation procedures will be necessary between two consecutive reactors.

In addition, since the stability of a catalyst is a crucial and important point for an industrial process, the catalyst was used for more than 600 hours without discharging it. It and showed no chemical and mechanical degradation because the result obtained in the first run was reproduced twice at the end of all the experiments proving once again that Amberlyst 46 is a suitable industrial catalyst for the oil pretreatment.

2.2 The biodiesel production, transesterification

The results of transesterification reaction between triglycerides and methanol to give FAME and glycerol obtained with CaO working without using a cosolvent are reported in Table 1. The tests were performed in a batch reactor using sunflower oil as feedstock at a temperature of 60°C varying the amount of methanol in the reactor.

Table 1: summary of the results obtained in the heterogeneous catalyzed transesterification reaction

		FAME YIELD [%]			
	Time [min]	**60**	**120**	**180**	**240**
MeOH/Oil	**3**	22	45	58	74
	6	23	50	65	82
	10	25	58	70	85
	12	42	66	77	90
	22	49	63	75	91

The first consideration to be made is that the time needed to achieve a high oil conversion is higher than 4 hours. This observation confirms and highlight the main restriction of the heterogeneous catalysis for the transesterification reaction, i.e the diffusional limitation. Another important aspect of the results obtained is that the experiment performed with a MeOH/oil of 12 gave almost the same results of the one performed at a ratio of 22. This means that a too high excess of methanol does not affect the oil conversion and this is due for the same reason exposed previously, the formation of a two liquid phase system.

In Figure 3 are reported the best results obtained for the reaction in the presence of different co-solvents. The reaction was performed in a batch reactor and using a fixed amount of catalyst (10% by weight based on the oil phase). The amount of co-solvent, instead, was varied in order to find the optimized value for obtaining the highest biodiesel yield.

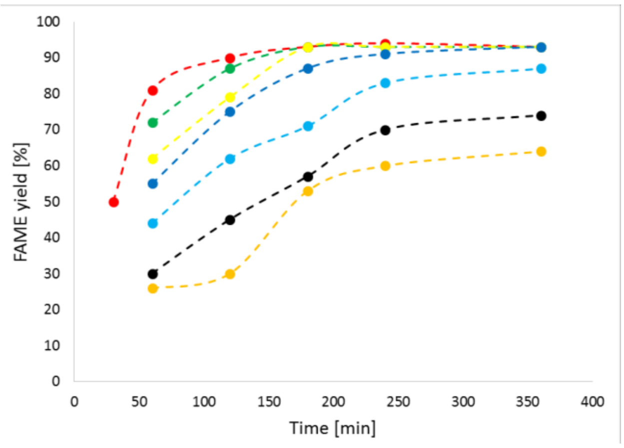


Figure 3: Reaction rate of the best results obtained with each cosolvent: acetone (orange, 10%w), heptane (black, 20%w), no solvent (light blue), chloroform (blue, 30%w), ethyl acetate (yellow, 20%w), dichloromethane (green, 30%w), THF (red, 30%w).

The reaction rates with acetone and heptane are lower than without a co-solvent. FAME yields are higher with THF, ethyl acetate and the chlorinated ones showed higher FAME yield, and the rate of reaction are faster compared to the two-phase system (no solvent). The yield and reaction rates were lowest for acetone; ketones self-condense when in contact with basic catalysts (noted also from the GC analysis). Thus less methanol was consumed and the FAME yield was slightly better. THF and the catalyst was recycled for three consecutive batch reactions. The equilibrium conversion was identical for each batch, which demonstrates that the catalyst performance is stable. Summarizing, THF is the most promising co-solvent for heterogeneous catalysis. The performances of this new process are comparable to the one of the homogeneous catalyzed process, giving good prospective for the application of the heterogeneous catalysis for the biodiesel synthesis (Galli, et al., 2015).

2.3 Biodiesel economic enhancement, carotenes recovery and bioplasticizer synthesis

The final part of the work was dedicated to the economical enhancement of the whole biodiesel process. Two different approaches were studied, the first one concerning the carotenes recovery from crude oils. Carotenoids are important commercial products and, being accepted as a food-grade additive, are exempt from certification. Another important use of carotenes is in cosmetic preparations.

The methanol to FFA molar ratio equal to 5 resulted to be good for preserving the carotenes content in crude palm oil. A series of bacth deacidification reactions of crude pam oil using an esterification reaction with methanol catalyzed by an acid ion exchange resin (Amberlyst 46) was performed. Temperature, initial FFA content and methanol amount was varied without discharging the heterogeneous catalyst.

The adsorption of carotenes on the resin surface was observed and satisfactory free fatty acid conversion was always obtained, as shown in Figure 4. Moreover, carotenes resulted more stable towards air oxidation when adsorbed on the catalyst.

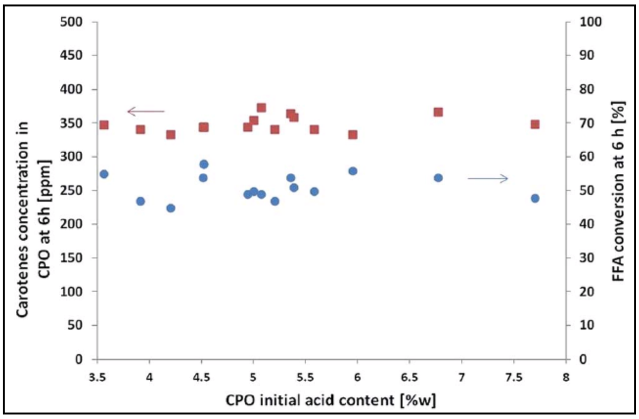


Figure 4: Experimental FFA conversion (blue points) and final carotenes content (red squares) versus initial FFA content in crude palm oil

Again, the catalyst resulted stable after 200 hours of work and satisfactory FFA conversions were always obtained (Galli et al., 2014).

A second research I performed was aimed to use biodiesel as reagent to produce bioplasticizers. Among two different strategies proposed, concerning the concentration of double bond in the feedstock by distillation of the satured esters contained in biodiesel (strategy A) or the concentration of epoxide in the final product by distillation of the unreacted molecules (strategy B), I found in the biodiesel distillation, followed by the epoxidation reaction the best condition for maximizing the plasticizer yield, considered the reaction used for the epoxidation of biodiesel and the separation technique adopted, i.e. batch distillation. In particular the performances in terms of oxirane oxygen (OO) content of two commercial bioplasticizers and the ones prepared with the two strategies are reported in Table 2:

Table 2: experimental oxirane oxygen content of two commercial plasticizer and the ones prepared starting from biodiesel

Sample	OO [gO/100g]
NPPX®	4.96
REFLEX-100	6.38
Strategy A (using hexane)	4.78
Strategy B	3.14

The best commercial product is the one of Arkema, which is a leader company in chemicals. However, the bio-plasticizer prepared with Strategy A possesses an amount of epoxides similar to the one of NPPX and thus it is already a good product. Moreover the reduced number of satured compounds compared to NPPX makes it a higher grade plasticizer because phenomena like the diffusion of these latter compounds through the polymer matrix.

Considered the reaction used for the epoxidation of biodiesel and the separation technique adopted, i.e. batch distillation, the Strategy A resulted the best for obtaining the highest OO bio plasticizer. Further improvements in the epoxidation reaction are necessary to reach a product comparable to the best bioplasticizer commercially available (REFLEX 100), but the results are very promising (Galli, et al., 2014).

3. CONCLUSIONS

Even if the biodiesel production process has been known for years, some innovations and contribution to the state of the art could be found from this work.

The operative conditions used for both the deacidification and the transesterification are not yet standardized and optimized. In particular it was demonstrated that some works were operated in disadvantageous operative conditions, i.e. using a too high excess of methanol. Working in a monophasic system for both the deacidification (limiting the amount of methanol to a molar methanol:free fatty acid ratio of 5) and the transesterification (using a cosolvent) lead to very satisfactory results, obtaining an oil suitable to be transesterified and an heterogeneous transesterification process that gave yields comparable to the homogeneous catalyzed process. At the same time, it was demonstrated that at mild operative conditions, the high added value products contained in crude oils could be separated making the whole process economically sustainable.

Finally, a possible improvement of biodiesel to valuable chemical was studied. In particular the synthesis of epoxidized biodiesel was firstly optimized and then performed on biodiesel and distilled biodiesel, obtaining with this latter substrate a product with an epoxide content comparable to a commercial product, giving positive suggestion for its application as bioplasticizer.

Introduction

The Energy Issue, a Global Problem

Every natural and artificial process, either spontaneous or not, requires energy.

Humans, due to their nature, changed the world using the most powerful tool at their disposal: their intelligence.

Since AD 1800, the era of the industry has begun. With the efficient production of every kind of good, the life quality of the population (at least the Europeans at the beginnings) increased. However, the need for energy has continuously increased and the high consumption of fossil fuels (carbon, oil and natural gas) led to geo-economic and environmental changes. In the modern era, fossil oil is the principal source of energy together with natural gas. Their consumption is continuously increasing because of the increasing energy demand of both developed Countries and “Emerging Countries”, i.e. Brazil, China, India, Colombia and the South Arabian Countries. In Figure 1 and Figure 2 it is reported the World production of fossil fuel.

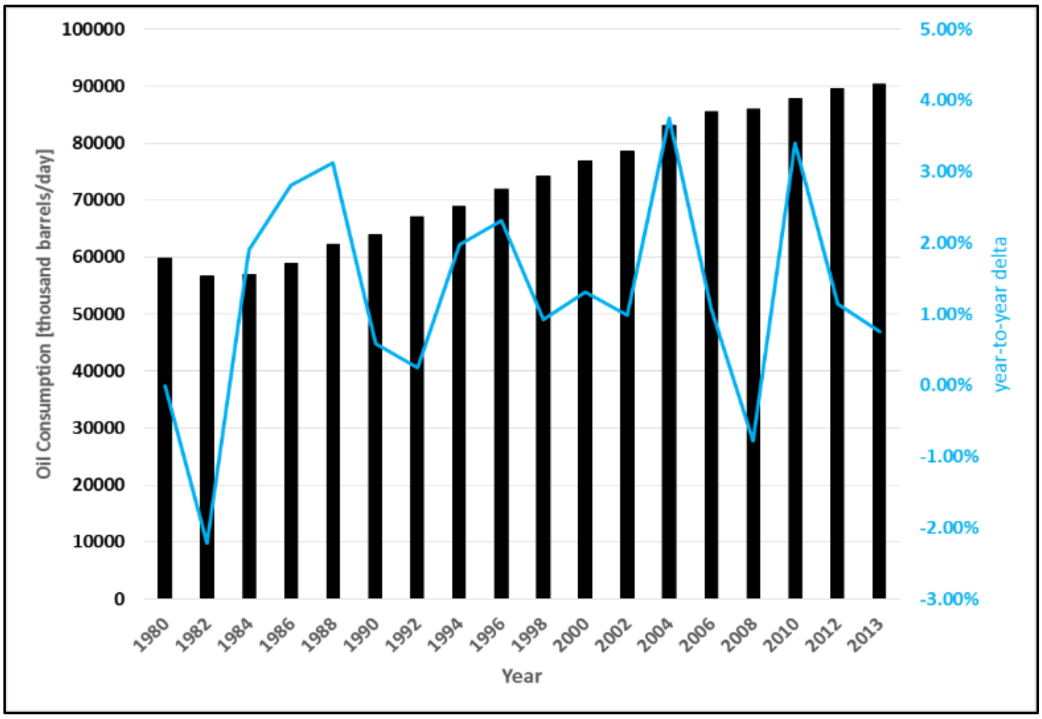


Figure 4: World oil consumption

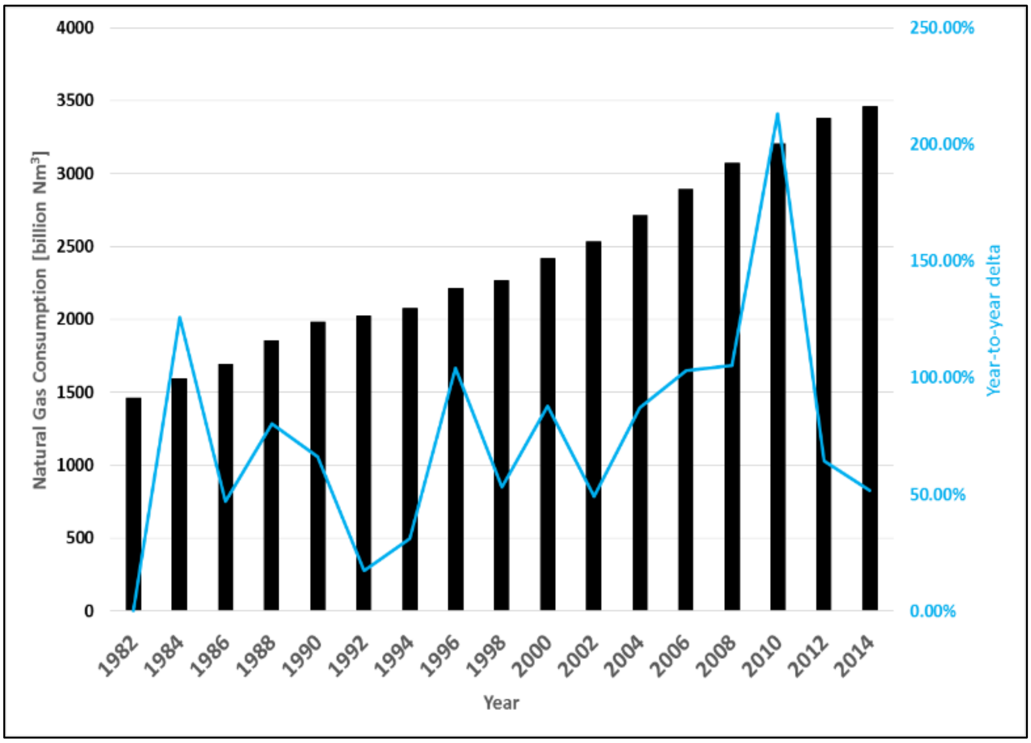


Figure 5: World natural gas consumption

It is possible to observe that the global trend of consumption for both the energy sources is increasing. Focusing on the environmental problems, burning such high quantities of oil and natural gas leads to huge CO_2 emissions. These have a great and catastrophic impact on vegetation (Krupa & Kickert, 1989), ocean (Haruko, et al., 2004) and agriculture (Alvaro, et al., 2013) because carbon dioxide influences the global temperature and the pH of both soil and water. For this reason different policies were adopted trying to reduce the CO_2 emission and preserve di environment, from the Kyoto protocol, signed in 2005 to more recent oriented grants like the LIFE+ program, part of the European HORIZON 2020 strategic plan, aimed to develop action for the CO_2 reduction to improve the quality of the environment.

Among the strategies to reach this objective there are:

- Optimization of the engines/processes: the process optimization and intensification is an important tool for saving energy and thus for reducing the CO_2 emissions (Reay, 2008).
- CO_2 sequestration from either the atmosphere or a process stream: carbon dioxide could be captured and stored, avoiding its emission into the atmosphere (Abu-Khadera, 2006).

- The development of technologies able to fixate carbon dioxide, by transforming it into chemicals, avoiding the use of “fresh” petroleum compounds (Aaron, et al., 2013).
- The reduction of carbon dioxide emission using biofuels (Demirbas, 2009).

This latter strategy is one of the most explored and cited. Using natural products, i.e. oils, lignin, sugars etc. it is possible to create fuels and chemicals whose emission are already compensated by the nature of the substrate they were made from. Several examples of biofuels and biochemical exist, and technologies are already applied. In the next section, a focus on the state of the art of the biofuels and the biochemical is presented.

Biofuels and Biochemicals

According to the Oxford Dictionary, a biofuel is “a fuel derived immediately from living matter”. This living matter is of course a vegetable, which is able to fix carbon dioxide into sugars, i.e. energy carriers, through the photosynthesis process. All over the World, industries and academy are giving more and more attention to biofuels, this is simply demonstrated by searching the keyword “biofuel” into the database SciFinder Scholar®, filtering the results year per year. The results of this research are reported in Figure 6:

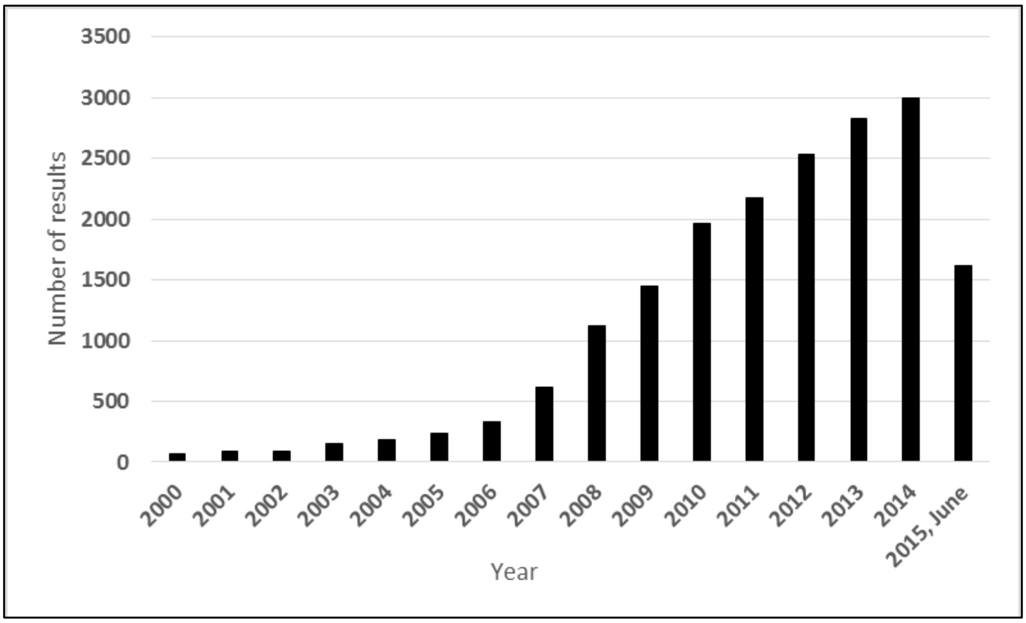


Figure 6: Number of scientific articles containing the keyword “biofuel” published per year

From 2006 researchers have been focusing on biofuels and their impact on the environment. This statement does not mean that this field is already understood and the technology is established because different biomasses are considered as feedstock and the biofuels changed as described hereinafter.

Some of the most popular types of biofuels are (Demirbas, 2008):

- Vegetable oil: these kinds of oil can be used either for cooking purpose or even as feedstock for fuel synthesis. The main fact that determines the usage of this oil is the quality. In most of the countries, vegetable oil is mainly used for the production of biodiesel.
- Biogas: Biogas is produced by the anaerobic digestion of the organic materials, such as crop. In Lombardy (region in the northern part of Italy), for example, 216 biogas plants were operating in 2012 and the number was expected to increase by the 200% in 5 years (Adani, 2012). The residue or the by product of the digestion can be easily used as manure or fertilizers for agricultural use. The biogas produced is very rich in methane (from 60 to 80% by volume), which can be easily recovered through the use of separation techniques like the water absorption of CO_2 (Pirola, et al., 2015). A less clean form of biogas is the one obtained in the fermentation of landfill waste.
- Bio-alcohols: These are alcohols produced by the use if enzymes and micro organisms through the process of fermentation of starches and sugar. Ethanol is the most common type of bio-alcohol. Biobutanol is sometimes also referred to as a direct replacement of gasoline because it can be directly used in the various gasoline engines.
- Syngas: it is a mixture of hydrogen and carbon oxide. By pyrolysis process biomass is converted to syngas and then into diesel through the Fischer Tropsch process.

According to the sources of these biomasses, biofuels can be divided into different “generation”. In particular, first generation biofuels feedstock are the most developed. They are obtained from cultures that directly compete with the human alimentation. This kind of biomass, either edible or not, is cultivated and grown instead of cultivation dedicated to agriculture. This creates a competition between the need for energy and the need for food, leading to land consumption and social impacts, which can be related to an increase in the food prices (Rathmann, et al., 2011).

The second generation biomasses are considered not in conflict with the agriculture since the feedstock used for their production is made of wastes, which have not any influence on the food market. Some examples of second generation feedstock are lignin, i.e. the residue of the paper industry, waste cooking oil, i.e. oil already used for alimentation purposes and ready to be disposed, agricultural wastes, that can be gasified to produce green diesel and non edible plants that grow at a high rate, in water-poor environments and whose seeds like Jatropha.

Even if this kind of feedstock solve the problem of the land consumption, they production rates are slow and most of all the processes used are the same of the first generation fuels, i.e. energy demanding and less sustainable compared to the ones that are now developing for the next generation biofuels.

The third generation of biofuel in fact is characterized by the use of microorganism like bacteria (Akhtar & Jones, 2015), microalgae (Singh, et al., 2011) or enzymes (Klein-Marcuschamer, et al., 2012), in order to have, in a bioreactor, the rapid synthesis of biofuel from wastes avoiding the use of high amount of energy. However, since this generation has been developed only in recent year, several LCA studies concluded that the energy conversion efficiency ratio obtained for microalgae is relatively lower than the one of first and second generation (terrestrial feedstock), which means that at the moment their production is less sustainable (Lam & Lee, 2012).

The lack of technologies makes the third generation biomasses not appealing for industries, but second generation feedstock rapidly substituted first generation biomasses in the existing plants.

Depending on their physical state, biofuels are divided into three main categories: solid, liquid and gas. Solid biofuels are simply waste that are burned to generate energy. Lignin is one of the examples. Currently, lignin is burned only in small part for heat integration because it is generally preferred to generate biochemical that possess high added value instead of simply produce heat. Liquid biofuels are biodiesel, green diesel and bio-alcohols. Biodiesel will be discussed throughout this thesis. For this reason, the Reader can see the next paragraph, *Biodiesel, What and Why*, in which a description of the state of the art of this biofuel is presented. Finally, gaseous biofuels are biogas and biosyngas. The first one is burned, while the second is either treated to obtain fuel (green diesel) or used to synthetize bio-methanol.

Fossil oil is a valuable resource not only because it has been the only source of fuel for years, but also because from its fractions a huge number of chemicals can be obtained, from the building blocks for polymer synthesis, to the aromatic compounds, that are the molecules at the basis of the fine chemicals. The same trend, i.e. the migration to the fossil-based chemicals to the bio based one, has been observed in recent years, for the same reason: the production of environmentally sustainable chemicals, in order to reduce the carbon dioxide emission and preserve the environment. There is a plenty of examples regarding the preparation of biochemical (Xu, et al., 2015) and it is out of the scope of this thesis a full description of every example. Here I report just two examples: the preparation of phenols from lignin (Pandey & Kim, 2011) and the preparation of plasticizer from vegetable oil (Goud, et al., 2006).

For what concern lignin, instead of burning it, it is transformed into phenolic compounds by thermochemical methods, to give very important building blocks for polymers, or substrates for the synthesis of high added value molecules. The same concept is applied to oil, that are epoxidized to obtain secondary plasticizer for PVC. These molecules confer impressive properties to the polymer and have the great advantages that are non-toxic, differently from phthalates.

The point is that there is a new trend both for the research and for industries: the shift from a fossil-oil oriented chemistry to a green oriented chemistry.

Together with this very promising prospective, however, some criticism arose. Some researchers believe that biofuel and in general biochemistry is more harmful to the social and agricultural background (Giampietro & Mayumi, 2009). Less dramatic but enough strong is the consideration about the volume of fuel and commodity chemicals needed to the global market. Figure 1 reports the global annual oil consumption. In 2013 it was about 90,000 barrels per day, i.e. about 88 metric ton per day (considering an average density of the crude oil of 0.82 kgL^{-1}). Now, considering that about 40% of the crude oil is simply burned as a fuel, about 35.2 metric tons of fuel (gasoline, diesel, naphtha and jet fuel) are needed per day. How much biomass should be necessary to satisfy completely the world need for fuel? The same question could be asked for what concern biochemical.

My personal opinion to this issue is that biomasses difficulty will substitute crude oil, but in the near future the percentage of crude oil usage must decrease because of the environmental issue discussed more than the fossil-oil depleting. In any case a middle-long term research campaign is surely ongoing to go beyond the biofuels, but since that time, it is imperative to make a lot of effort in the biofuel study, optimizing the technologies and the yields to improve the quality, even if a little, of the world environment. Since a direct and immediate impact on the carbon dioxide emission is needed, the research should focus not only on the new generation biomasses, but also on the existing technologies, trying to improve them for making them competitive. The next paragraph will give all the details about one of the most used biofuel, biodiesel, the object of this thesis.

Biodiesel, What and Why

Biodiesel is defined as "mono-alkyl esters of long chain fatty acids derived from vegetable oils or animals fats". The root of the word *Biodiesel* comes from the inventor of the homonymous engine, Rudolf Diesel (Songstad, et al., 2009). In 1937, G. Chavanne published one of the first patent on the use of vegetable oil as fuels. This describes the transesterification of palm oils using ethanol (Chavanne, 1937). During World War II (1939 to 1945), when petroleum fuel supplies were interrupted, vegetable oil was used as fuel by several countries, including Brazil, Argentina, China, India, and Japan. However, when the war ended and petroleum supplies were again cheap and plentiful, vegetable oil fuel use dropped to zero until 1970s, when the petroleum oil embargo caused many countries to look to vegetable oil as a possible fuel.

The first biodiesel manufacturing plant opened in 1985 at an agricultural college in Austria. Since 1992, biodiesel has been manufactured across Europe, with Germany being the largest producer while in the United States biodiesel was first manufactured commercially in 1991 in Kansas City, Missouri (Pahl, 2008). In Figure 7 the production of biodiesel is reported for different countries.

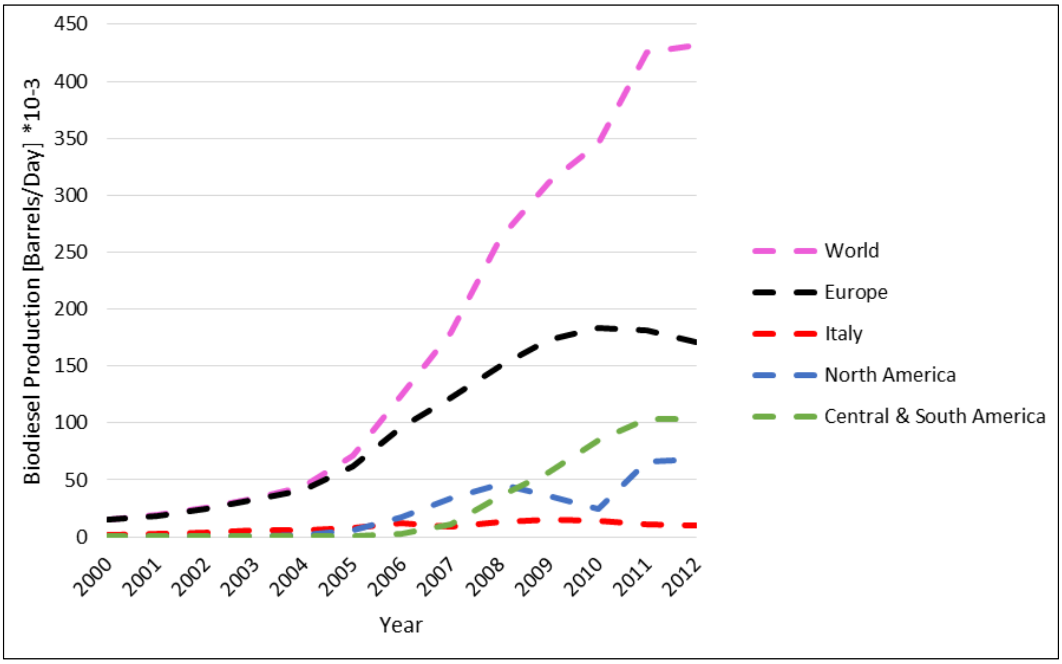


Figure 7: Biodiesel production rates for different Countries

Europe, since 2005, has been the main (almost the only) biodiesel producer, whereas from 2006 the production if methyl esters increased in South and North America, especially in Brazil and USA and Canada respectively. The decrease in North American biodiesel production

(Figure 7, blue line) is likely due to changes in the Federal subsidies. Similarly, in Europe the production dropped from 183,142 to 170,923 barrels per day for the same reason. However, as stated before, biodiesel production is going to increase, hopefully favored by incentives.

There are two main ways for producing biodiesel from either refined or waste oils:

- Thermochemical conversion
- Chemical conversion

Among these two, the transesterification of oil (chemical conversion of triglycerides into methyl fatty esters) is the most commonly used and applied (Okoronkwo, et al., 2012), and it is the method that was studied during this thesis. In the following part of the paragraph, I will discuss the methodologies used for biodiesel production by transesterification.

Generally, transesterification is a reaction in which an ester and an alcohol react to give the respective ester and alcohol with the alcoxy group switched. It is an equilibrium reaction. This is the reason why the reaction is typically performed in two steps: the first one to reach about 90-93% of fatty ester yields, the latter to complete the reaction (Çaylı & Küsefoğlu, 2008).

This reaction could be catalyzed by either strong acid or strong base. In this case, we talk about catalytic transesterification. Depending on the catalyst, the reaction mechanism changes, from the protonation of the ester, the nucleophilic attack of the alcohol and the alcohol (glycerol in this case) elimination in the first case, to the formation of al alcoxide, its nucleophilic attack to the ester and the elimination of the alcohol with the regeneration of the catalyst in the second case.

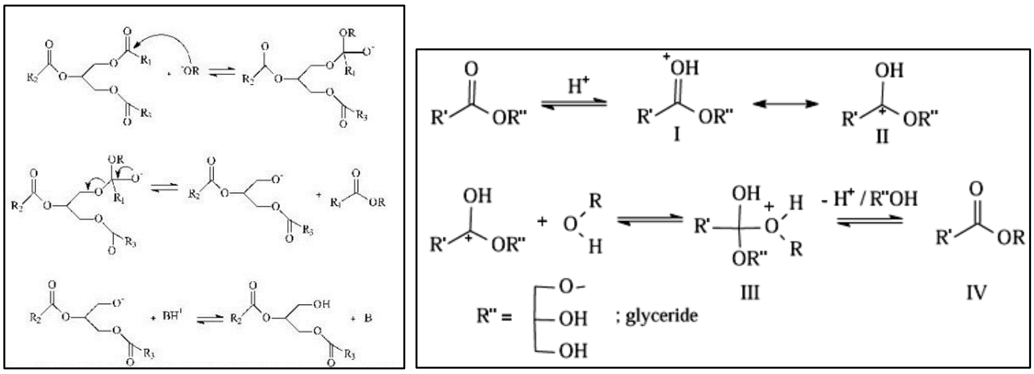


Figure 8: Base (left) and acid (right) catalyzed transesterification mechanism

Catalytic transesterification may be performed using homogeneous, heterogeneous or enzymatic catalysis. The first one is the most common because it is the most economical.

Typically, basic catalysts are used because show higher reaction rates compared to the acid ones (Jain, et al., 2011). Moreover, they pose fewer corrosion problems. The most used catalysts are sodium methoxide or potassium hydroxide.

This process shows few drawback, the main one is that the free fatty acid contained in the oils, especially in waste cooking oils, could lead to the formation of soaps when put in contact with a homogeneous base. These soaps make difficult the separation between biodiesel and glycerol, usually generating emulsions. In order to overcome this aspect, a pre step based on the elimination of these free fatty acids is carried out. This pre step could be an elimination by washing with either water or a basic solution, a molecular distillation (Martins, et al., 2006), or a pre esterification of these free fatty acid to obtain biodiesel already at this preliminary step (Pirola, et al., 2014), as shown in Figure 9

$$R_1COOH + CH_3OH \xrightleftharpoons{\text{Catalyst}} R_1COOCH_3 + H_2O$$

Figure 9: Reaction scheme of the free fatty acid esterification

Homogeneous acid catalyzed transesterification obviously does not show this problem. Usually, sulphuric acid or hydrochloric acid are used to catalyze this reaction. However, as already written, this process is unfavorable since high amount of alcohol is needed, the catalyst must be used at high concentration and great corrosion problem are to be accounted. The main advantage of this process is that acid oils (free fatty acid content higher than 5% by weight) could be treated directly (Zheng, et al., 2006).

Recently also the heterogeneous transesterification process has been studied and developed. Heterogeneous catalysts offer some advantages (Ertl, et al., 2008), they are noncorrosive, environmentally benign, recyclable, show fewer disposal problems (Tanabe & Holderich, 1999), are easily separated, show higher selectivity and longer catalyst lifetimes. The main catalyst used are supported alkali metal (Benjapornkulaphong, et al., 2009), zeolites (Suppes, et al., 2004), and hydrotalcites (Silva, et al., 2012) but calcium oxide (Kouzu, et al., 2008) is the most common because it has both good physical properties and strong basic OH– Bröensted sites (Boey, et al., 2011). Even if compared with traditional homogeneous catalyst the heterogeneous process is unfavorable, all the advantages previously explained are of a great interest. Part of this thesis work is aimed to find the best operative condition at which good biodiesel yield (comparable or better than homogeneous process) could be obtained.

Literature reports also the use of biological catalyst, i.e. enzymes, for the synthesis of biodiesel. Lipase-catalyzed transesterification is a green reaction and produce high purity grade glycerol even if high acid content oils are used (Fjerbaek, et al., 2008) but shows low reaction rate (Zhang, et al., 2003) and their cost is order of magnitude higher compared to the typical catalysts (Jaeger & Eggert, 2002). These are the two main limits to the use of enzymes in the industrial processes.

Together with the catalyzed transesterification some non-catalytic processes exists. The most important one is the supercritical transesterification. More in detail, operating at temperatures ranging from 200 to 400°C with pressures higher than 200 bar the alcohol (methanol or ethanol) reaches the supercritical conditions, giving some advantages like the higher miscibility and high reaction rates (Bunyakiat, et al., 2006). The presence of moisture generally is non-relevant to the reaction. However, the high-energy cost makes difficult the diffusion of this technology (Ganesan, et al., 2009).

The main advantages of this fuel are, among others, its biodegradability (Schleicher, et al., 2009), the net reduction in CO_2 concentration in the atmosphere, due to the fact that the plant fixes carbon dioxide for growing (Yee, et al., 2009), low particulate emission, due to presence of oxygen atoms in the molecular structure (Szybist, et al., 2007) and a low Sulphur content (Knothe, et al., 2006), that results in a very low emission of SO_x, a class of dangerous chemical for the atmosphere.

Biodiesel has never been used for the production of chemicals except rare cases because it was simply burned. However, since it derives from oil, a fraction that is dependent from the oil that originated it, is constituted by unsatured molecules, that can be functionalized to give high added value chemicals.

In any case, the high research, industrial and Governments interests towards biodiesel is still high and more developments are needed in the field.

Aim of the Work

This thesis is inserted in the context above described.

Studies on the entire biodiesel chain, from the pretreatment and valorization of the raw materials to the biodiesel production and its use as feedstock for the preparation of bio plasticizer were made. The objectives can be summarized as follows:

1. Test and optimize the deacidification of oils in different reactors, studying the catalyst stability and developing a comprehensive kinetic model able to predict in the reaction performances in a wide range of conditions. In this part, attention was also devoted to the analysis of the stability of carotenes in crude palm oil.
2. Develop and optimize the heterogeneous transesterification of oil in order to make more competitive the process compared the homogeneous one. In particular, we tried the use of co-solvents in order to make the system monophasic and thus increasing the concentration of methanol in contact with the oil. In this part, I also evaluated the possibility to produce biodiesel in fluidized gas phase reactor.
3. Study the epoxidation of biodiesel to obtain bioplasticizer developing different strategies in order to enhance the epoxide yield and minimize the amount of satured esters to improve the product final performances. Together with the optimization of the synthesis, I studied the distillation of epoxy biodiesel to improve its characteristics.

Experimental

Oil Pretreatment, deacidification of vegetable oils

This part of the thesis is dedicated to the study of the deacidification pretreatment. This, as already explained in the Introduction section, is a reaction catalyzed by acids, either homogeneous or heterogeneous, aimed to convert the free fatty acids (FFAs) contained in the oil into biodiesel. This process is important because in the transesterification step, if the oil contains a too high amount of FFA, problems due to the soap generation could be generated. I studied both in batch and continuous reactor the deacidification of first and second generation oils, using a solid acid resin, Amberlyst 46$^{®}$. This reaction is well known in literature, the first report comprising a strong acid ion-exchange resin SPC 108 for the esterification of 13% FFA in crude palm kernel oil dates back to the year 1985 (Marchal, et al.).

However, the reaction conditions used are not yet standardized and optimized. This statement is confirmed by a brief search in the literature. For example, in the work of Son (2011) the esterification of oil was carried out using methanol between the 25-50 % based on volume, vaporizing the alcohol and feeding it into a tubular reactor. Kouzu (2011), used a volumetric methanol:oil ratio of 1:3, leaving the catalyst in contact with the alcohol for two hours before the reaction. These differences are found in a lot of papers.

Considering that the methanol solubility into the oil is about the 7-9% by weigh depending on the temperature and the kind of oil, in all this experiments the researchers dealt with a two liquid phase system. This feature gives some problems: first of all, the second alcoholic phase extracts part of the FFA dissolved in the oil, this is a great drawback because the biodiesel yield is decreased and the rest of the alcohol needs to be purified. Secondly, great diffusional problems result when a heterogeneous catalyst is used. For all of these reasons I performed the deacidification of vegetable oils working in a monophasic liquid mixture, showing that a quantity of methanol of five times the moles of FFA is enough to reach satisfactory oil acidity.

The operating parameters (temperature and methanol amount) were varied in order to develop a kinetic model able to fit the experimental data obtained. This part of the work was made collaborating with the Politecnico di Milano, in particular with Prof. Flavio Manenti and Dott. Michele Corbetta. We modeled the deacidification using two rival models: the pseudo homogeneous model, which considers the catalyst in the same phase of the reactant and an adsorption-based model, which accounts the reactants and products adsorption on the resin by means of an equilibrium constant. Moreover we considered either the liquid phase ideal, i.e. used the molar fraction of the components in the differential equation, or the liquid non-ideality, using the UNIQUAC (Abrams & Prausnitz, 1975) model to calculate the activity coefficients of the components.

Considering also the deacidification of second generation oils, I experimented the crude palm oil deacidification. This oil contains minor components, about the 1% by weight, including carotenoids, tocopherols, sterols, triterpene alcohols, phospholipids, glycolipids and terpenic and paraffinic hydrocarbons (Goh, et al., 1985) that are of great interest because of their commercial prize. It is important indeed to try not to destroy or decompose these molecules in the deacidification step. Two main strategies for their recovery (with particular attention to carotenes) are available: the molecular distillation of crude palm oil, made after the transesterification (Ooi, et al., 1994) or their supercritical extraction (Davarnejad, et al., 2008). Both these techniques show the drawback of the intense energy required, the first for the heating and the vacuum, the second for the compressor. I found preliminary but encouraging results about the carotene adsorption on the Amberlyst 46 surface, which could lead to a selective extraction of these molecules in the same reactor in which deacidification takes place.

Hereinafter I will describe all the analytical methods, the materials used and the protocols followed.

Materials

In this section all the materials (reagents and catalyst used for the deacidification studies) will be described.

I studied the preparation of fatty acid methyl esters, thus the alcohol used both for the deacidification and transesterification step was methanol. It was purchased from Sigma Aldrich (>99.8%, anhydrous) and the water content of this reagent was constantly checked. When the water contained exceeded 600 ppm we used molecular sieves to reduce it.

As already said, different vegetable oils were used to study the deacidification to study a possible influence of the acidic composition of the oil on the catalyst and reaction performance. In particular four kind of oils were used: soybean oil, available in the lab because of a previous collaboration with Agri 2000 srl, sunflower oil, purchased in a local market and crude palm oil, that was available in the lab due a previous collaboration and waste cooking oil, supplied by a local restaurant. These feedstock belong either to first or second generation biomasses and are characterized by different FFA amount.

To study the deacidification of oil of very high FFA content, palmitic acid (>99%, Sigma Aldrich product) and oleic acid (>93%, Sigma Aldrich product) was used to modify and increase the initial acidity. I used a mixture of these acid trying to maintain the average FFA molecular weight similar to the one of the oil as it is.

The catalyst used for the heterogeneous deacidification of the oils is a Dow® product, Amberlyst 46. It is a macro porous ion exchange resin functionalized with strong acid groups. The matrix is a copolymer of styrene-divinylbenzene with a high degree of cross linking, and it is characterized by the presence of active sites only at the surface. This particular feature of the catalyst permits to avoid the side reaction inside the catalyst pores. Moreover, since the oil molecule are particularly sterically hindered, having the active sites on the surface is advantageous. The catalyst main feature (manufacturer data) are reported in Table 3 (The Dow Chemical Company):

Table 3: Amberlyst 46 main features, manufacturer data

Polymer Matrix		Macroporous cross-linked polystyrene
Physical Form	-	Opaque, spherical beads
Ionic form (as shipped)	-	H^+
Shipping weight	(gL^{-1})	600
Acid Sites	($meqg^{-1}$)	0.8 – 1.3
Water content	(%)	26 - 36
Fines Content (<0.425 mm)	(%)	< 1
Surface Area	(m^2g^{-1})	> 75
Average Pore Size	(Å)	235

Analytical Methods

FFAs content determination, colorimetric titration

To determine the percentage of FFA either referred to volume or to the weight contended in the oils colorimetric titrations were used. If not specified directly in the text, all the titrations were carried out using potassium hydroxide in ethanol solution 0.1 N (Fluka product, solution denatured with toluene). A weighted amount of oil (usually about 2 g) was diluted with about 5 mL of isopropanol (99.5%, Sigma Aldrich product, anhydrous) to make it act as cosolvent between oil and methanol and facilitate the titration. Phenolphthalein (2% solution in ethanol, Fluka product) was used as indicator. The weight percentage of FFA was calculated using Equation 1:

$$\%_{w,FFA} = \frac{V * N * \overline{MW}}{W} * 100 \qquad \textit{Equation 1}$$

In which V is the volume of KOH solution used, N the normality of the titrating solution (0.1, equimolar reaction), $\overline{\mathrm{MW}}$ the average molecular weight of the acids in the oil, calculated from a weighted average of the fatty acid ester composition of the oil, obtained by gas-chromatographic analysis (see Analytical Methods of the second part of the Experimental section) of the oil after the homogeneous transesterification with methanol performed for 24 hours. Finally, W is the weight of the sample in mg.

Moreover, the amount of FFA was used to calculate the reaction conversion, simply comparing the amount of FFA at time t (or at a certain reactor length in the case of the continuous reactor) to the one of time zero, following Equation2:

$$\%conversion_{FFA} = \frac{FFA_{t=0} - FFA_{t=t}}{FFA_{t=0}} * 100 \qquad \textit{Equation 2}$$

Also the acidity of the heterogeneous catalyst (whose properties are described in the next section of this part of the Experimental) was determined by titration. In this case, since the resin is a polymeric material which shows at its surface SO3H acid groups the procedure of the total ion exchange: in particular a weighted amount of resin (about 10 g) was put in 50 mL of a satured NaCl solution overnight under agitation, in order to let the sodium cation fully exchange with the acid protons of the resins. After this procedure, a precise volume of solution is titrated using KOH and phenolphthalein as indicator and the results are expressed ad meq of H+ per gram of resin. In all cases, the acidity value obtained from the analysis of the resin, either in its dry or wet form, confirmed the declared value of the supplier.

Water amount determination, Karl Fischer analysis

Karl Fischer analysis permits to detect the amount of water (to the ppm level) in an organic solution. The amount of water is essential since the esterification reaction is an equilibrium (see Figure 6) and even traces of water can shift towards FFA the reaction. Moreover, as explained in the next part of the thesis, Amberlyst 46 resin activity, like all the sulphonic type rensins, is very influenced by the presence of water, that strongly adsorb on its surface. This is why the measurement of the water concentration is important.

To perform this analysis we used an Amel titrator (model 231, dead stop titrator) and HYDRANAL solvent. The automatic titration was simply activated by pressing the “start” button after the calibration of the instrument, made titrating a solution of known concentration of sodium tartrate dihydrate.

Carotenes analysis

I determined the carotenes content during the deacidification of crude palm oil, see *Crude Palm Oil Esterification: Preservation of the Carotenes Content* section at the end of this paragraph, using an T60 (PG LTD) UV-vis spectrophotometer. Carotenes absorbs with a high extinction molar coefficient in the visible light (maximum absorption at 443 nm) of about 130000 (Biheler, et al., 2010). In order to have a value of absorbance below 2 and greater than 0.2 in all the samples (range in between the instrument response is linear) a dilution of 1:70 v/v with n-hexane was necessary.

In order to evaluate the amount of carotenes adsorbed onto the catalyst surface, a solid-liquid extraction was performed using a Soxhlet extractor and n-hexane as solvent. All the extractions lasted overnight to ensure the total yield.

Batch Reactor

With the generic name "*Batch Reactor*", it is intended a tank in which reactants are charged, let react for a certain time and then discharged after a certain time. This procedure is intrinsically time dependent and is the conceptual difference between the continuous reactors, which at the stationary conditions temperature, concentrations and pressure are stable. The reactions in batch reactor were carried out in a three way flask equipped with a reflux condenser and a thermometer. A mechanical stirrer was used to ensure a good mixing. The reactor was heated by a thermostatic bath. Generally the protocol followed for each experiment was:

Oil charge and thermostat bath turned on at the desired temperature

Initial FFA content measurement and eventually acidity correction by the addiction of either oleic acid or palmitic acid

1. Addiction of methanol
2. Stirrer turned on and after 5 min addiction of the catalyst, which corresponded to time zero.
3. The procedure to withdrawn a sample was simple:
4. stop the agitation
5. wait for 30 seconds

withdrawn an amount of about 1-2 mL of reactant mixture. When there was the presence of two phases, the oil phase was sampled.

A picture of the batch reactor is reported in Figure 10:

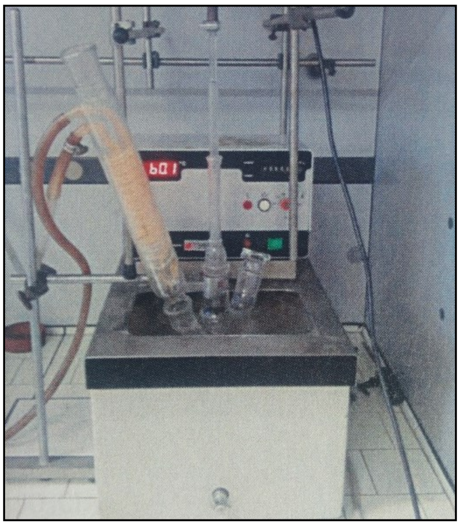


Figure 10: Picture of the batch reactor used

The operative temperature was varied between 35 and 60°C, in order to not reach the limit imposed by the boiling temperature of methanol, i.e. 64°C. This because the reactor is open (pressure of 1 bar) and thus working at higher temperature is useless. Moreover studies on the influence of the second phase formation were carried out, changing the molar ratio methanol: FAA from 2 to 135.

Continuous Reactor

In this kind of reactor, reactants are continuously fed in the system and products continuously withdrawn. The reactants mixture flows through the catalyst bed, which is fixed. In this way, of the catalyst is saved from the mechanical stress of the stirrer and its life is prolonged. In Figure 11 is reported the scheme and the picture of the Packed Bed Reactor:

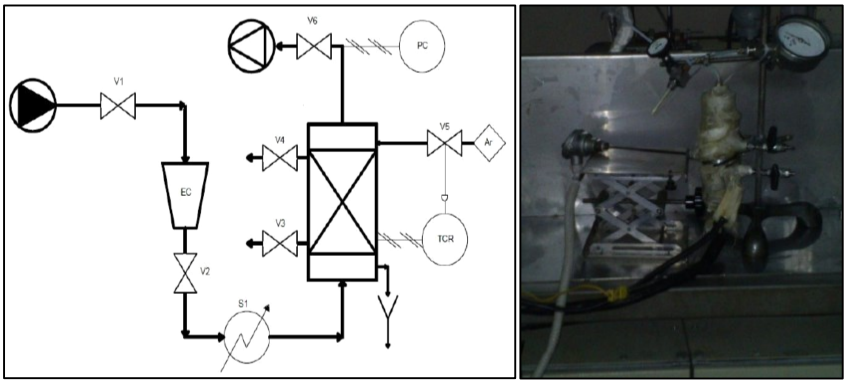


Figure 11: Scheme (left) and picture (right) of the continuous packed bed reactor

The reactor is a cylinder 203 mm long with a diameter of 43 mm. it is made of stainless steel. The catalyst in its wet form is placed 40 mm from the bottom for a volume of 60 cc, and it is packed using glass sphere and glass wool. In this way the catalytic bed results placed 20 mm from the bottom of the reactor. The reactants are charged into a feeding chamber (steel, volume of 1.8 L) and via pressurized air they are fluxed through the reactor (from the bottom to the top to be sure that the catalyst bed is in contact in all the parts with the reagents). In this way the pressure inside the reactor was controlled and kept at a value of 5 bar. The reagents are pre-heated and then enter the reactor, which is heated by an external jacket controlled by a thermocouple placed in the middle of the catalytic bed. From the two valves (50 mm from the bottom and 90 mm from the bottom) and the top of the reactor samples of oil were withdrawn to be analyzed. Different deacidification runs were performed, varying the temperature between 54 and 105 °C using different kind of oils. I decided to work with a fixed amount of methanol (5 times the FFA on molar basis) to have a monophasic liquid system, avoiding the problem to have part of the catalytic bed surrounded by the methanol-rich phase.

Kinetic Parameter Regression

The kinetic modeling is an essential part of the experimental work. It is the description of an event by equations, whose parameters are regressed by experimental data. The main advantage of the model based simulation is that a great number of experiments can be saved, thus saving costs and energies. This is true if the parameters that describe the reaction studied are well determined.

For the esterification reaction of FFA I collaborated with the group of Prof. Manenti, from the Chemical Engineering Department of Politecnico di Milano. The kinetic parameters regression on experimental data was performed by means of the set of very robust optimizers belonging to the BzzMath Library. This software works in object-oriented programming with Turbo C++, allowing a significant improvement of numerical methods and easiness of implementation. (Buzzi-Ferraris & Manenti, 2012).

The FFA esterification kinetic modeling has already been performed by some authors, for example Tesser et al. (2005). The main issue in this work is that the parameters were obtained considering experimental data gathered with the catalyst swelled in methanol, which is not representative of a typical esterification run because, as shown in the *Results and Discussion* section, the performances of the resin decrease in the first 3-4 runs and then become stable, due to the water adsorption on its surface. This means that using methanol to increase the reaction rate leads to wrong kinetic parameters that overestimate the reaction rates. For this reason, we used data obtained only with equilibrated resin, i.e. after a reaction time of the catalyst of about 24 h.

For what concern the models, two different kinetic models were considered and compared, a pseudo-homogeneous and an adsorption based one, following a research paper by Popken et al. (2000). The first model, the pseudo-homogeneous one, is simpler because its assumption is that the heterogeneous reaction is assimilated to be a homogeneous one, i.e. considering the catalyst homogeneous. In this model, the reaction rate is proportional to the bulk concentration of the components. In Equation 3 the expression of the reaction rate for the FFA esterification is reported:

$$r_{PSEUDO} = \frac{d\xi}{dt} * C_{FFA}^{0} = k_{1}^{0} * a_{FFA} * a_{MeOH} - k_{-1}^{0} * a_{FAME} * a_{H2O} \qquad \textit{Equation 3}$$

in which ξ represents the conversion of FFA, C_{FFA}^{0} the initial FFA concentration, k_{i}^{0} the kinetic constant of either the direct or inverse reaction and a_{i} the activity of the component i.

The second model, the adsorption based one, considers the actual concentration of the reactants on the resin surface by means of an equilibrium constant. In Equation 4 the expression of the reaction rate according to the adsorption model is reported:

$$r_{ADS} = \frac{d\xi}{dt} * C^{0}_{FFA} = \frac{k^{0}_{1} * a'_{FFA} * a'_{MeOH} - k^{0}_{-1} * a'_{FAME} * a'_{H2O}}{\left(a'_{FFA} + a'_{MeOH} + a'_{FAME} + a'_{H2O}\right)^{2}}$$ *Equation 4*

in which a'_i are the activities of the components calculated as reported in Equation 5:

$$a'_i = \frac{K_i * a_i}{MW_i}$$ *Equation 5*

in which MW_i is the molecular weight of the component i and K_i the adsorption affinity constant od the component i, reported in Table 4:

Table 4: binary adsorption affinities Ki

Component (i)	Binary Adsorption Affinity (Ki)
Water	5.24
Methanol	5.64
FFA	1.61
FAME	1.61

This equation is derived (Song, et al., 1998) from the Langmuir–Hinshelwood–Hougen–Watson (LHHW) model by considering instead of a constant number of moles adsorbed onto the resin a constant mass. Popken (2000) studied the adsorption on Amberlyst 15 of water, methanol, ethyl acetate, and acetic acid. Considering that the polymeric substrate of Amberlyst 46 is the same of Amberlyst 15, the constant of water and ethanol can be used. As suggested in a work by Rehfinger and Hoffmann (1990), the adsorption constant of methyl oleate (FAME) and oleic acid (FFA) could be calculated from the one of methanol divided by a factor of 3.5.

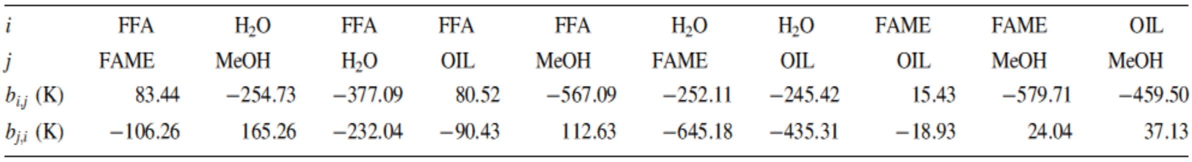
For both the models the temperature dependence of the kinetic constants was considered adopting the Arrhenius model.

Another important feature of this kinetic model approach is the thermodynamic model chosen. We compared the IDEAL model, in which the activity coefficients are equal to 1 and the UNIQUAC (Abrams & Prausnitz, 1975) model in order to account for the non-ideality of the mixture. The system studied is in fact highly non ideal indeed it forms two liquid phases. UNIQUAC binary interaction parameters τ_{ij} were calculated following Equation 6:

$$\tau_{ij} = exp\left(\frac{b_{ij}}{T}\right)$$ *Equation 6*

where the binary b ij parameters were taken from the AspenPlus^{TM} database and reported in Table 5:

Table 5: UNIQUAC binary interaction parameters from the AspenPlus database[a]



i	FFA	H_2O	FFA	FFA	FFA	H_2O	H_2O	FAME	FAME	OIL
j	FAME	MeOH	H_2O	OIL	MeOH	FAME	OIL	OIL	MeOH	MeOH
$b_{i,j}$ (K)	83.44	−254.73	−377.09	80.52	−567.09	−252.11	−245.42	15.43	−579.71	−459.50
$b_{j,i}$ (K)	−106.26	165.26	−232.04	−90.43	112.63	−645.18	−435.31	−18.93	24.04	37.13

a: taken from (Pirola, et al., 2014)

The regression of the kinetic parameters were made by minimizing the sum of the squared errors (SSE) using the robust method of the BzzMath Library, able to detect outliers (Buzzi-Ferraris & Manenti, 2010).

Crude Palm Oil Esterification: Preservation of the Carotenes Content

As previously written in the *Introduction* section, oils can contain, together with triglycerides, molecules of high added value that, if properly extracted, can be sold and sustain economically the whole production process. In detail, I used crude palm oil during my research. The adjective crude stand for not refined. It is an high viscous oil, with a characteristic red color. This is due to the carotenes and tocopherols conteined in the oil. In particular they are present in crude palm oil ranging from 500-1000 ppm and 500-2000 respectively (Gibon, et al., 2007). About the 90% of the carotenes are constituted by α- and β-Carotene.

β-Carotene is the precursor of Vitamin A in humans and studies demonstrated its efficacy against some types of cancer, promoting the immune system (Verwaal, et al., 2007). For this reason this molecule is a food additive, and more than the 85% of the available β-carotene is synthetized chemically. A process able to maintain the carotenes content and eventually separate them from the crude palm oil while it is processed for the biodiesel production is essential. The current methods used for the carotenes extraction are based either on the supercritical solvent-extraction, but are time consuming and need a large use of solvent and expensive (Davarnejad, et al., 2008). Another possibility is represented by molecular distillation, but this unit operation is characterized by high implant costs (Ooi, et al., 1994).

In my research, I conducted some tests to assess the carotenes stability at the operative condition used for the esterification. Moreover, I noted that Amberlyst 46 were able to adsorb preferentially carotenes on their surface.

The deacidification reaction were run in the batch reactor, charging about 200 g of crude palm oil per experiment. Thirty-one experiments were run changing the FFA content of the palm oil, adding palmitic acid before the start of the reaction to understand if the acid contained in the oil could degrade carotenes. The carotenes content was measured every two hours by monitoring the value of absorbance at 443 nm diluting each sample 1:70 v/v in n-hexane (99%, Sigma Aldrich product). The catalyst used the first run was never discharged and reused every successive experiment. At the end it was characterized using an optic microscope. Each experiment duration was 6 h.

Biodiesel Production, heterogeneous transesterification of vegetable oils

This second part of the thesis is dedicated to the study of the heterogeneous transesterification of oils. This is the core of the biodiesel synthesis process. As explained in the *Introduction* section, the oil with a reduced amount of FFA undergoes the transesterification reaction typically catalyzed y a homogeneous base, in particular either sodium hydroxide or potassium hydroxide. The advantages of using such catalysts are well known and evident: first of all and most important of all their cost. These catalyst are cheap compared to any other, especially compared with enzymes. Another important aspects is that these two are both very strong basis and are able to speed up the transesterification reaction more than other catalysts.

However, these homogeneous catalysts possess some disadvantages. Firstly, they are not reusable: in a typical biodiesel production plant a specific and dedicated unit operation should be designed and operated only for the final product neutralization, made usually by water washing. This generates costs that in a heterogeneous process wouldn’t exist. Secondly the homogeneous catalyst are more aggressive towards the plant, generating corrosion problems.

The use of heterogeneous catalysis is the answer. They offer high basicity and surface areas and are easily separated being solids. However, these are not applied because even if they offer great advantages (see *Introduction* section), the reaction rates obtained are in every case slower compared to homogeneous catalysts.

This is reasonable, since a catalyst in the same phase of the reagents do not give problems like the diffusion of products and reactants. In any case the efforts are still strong. In my thesis I studied the transesterification of oil using CaO, which is a well-known heterogeneous catalyst for the transesterification reaction and, instead of trying to develop a modified catalyst able to increase the biodiesel yield of few percentage, I tried to reduce the causes that makes the heterogeneous reaction slower, in particular the double phase between oil and methanol. Similarly to the FFA esterification, the presence of two liquid phases hinders, due to diffusional problems, the reaction. With a three phase system (solid-liquid-liquid) the problem is one order of magnitude higher.

After a brief survey on the heterogeneous catalysts that could be used, I dedicated my time to search a solvent able with which the heterogeneous reaction is faster like the homogenous one, with great results. In the following part of this section I described the materials and the reactor used for the study of the transesterification reaction.

Analytical Methods

Biodiesel acidic composition, Gas-chromatographic analysis

To determine the amount of each methyl ester produced a gas-chromatographic analysis was used, following the EN 14103 (2011). We used a Hawlett-Packard HP 5890 GC-FID, equipped with a capillary column Supelco Omegawax 320 (length 30 m, internal diameter 0.32 mm, film thickness 0.25 μm). Helium was used as carrier, while the other operative condition are reported in Table 6:

Table 6: Setting parameters for the GC analysis

Carrier Pressure	25 psi
Split ratio	1:100
Oven temperature	200°C, isotherm
Injector temperature	280°C
Detector temperature	280°C
Injection volume	1 μL
Internal standard	Iso-octane (>99%, Sigma Aldrich product)
Internal standard concentration	1.67 % w/w

The BD yield, expressed as a mass fraction of FAME, was calculated according to Equation 7:

$$C_{BD} = \frac{\sum A - A_{C19}}{A_{C19}} \frac{C_{C19} V_{C19}}{m}$$ *Equation 7*

where A is the total peak area of the FAME, A_{C19} is the peak area corresponding to methyl nonadecanoate; C_{C19} is the concentration (mg mL^{-1}), of the methyl nonadecanoate solution used as as standard; V_{C19} is the volume (mL) of the methyl nonadecanoate solution; m is the mass, in mg, of the sample.

Catalysts preparation and characterizations

As previously briefly described, a study on the performances of a set of catalyst was conducted. In particular, together with the homogeneous catalysts sodium hydroxide and potassium hydroxide, calcium oxide (bulk and supported over Al_2O_3) and catalyst on which both calcium oxide and strontium oxide were supported with different percentage on Al_2O_3.

Hereinafter I describe briefly the preparation of each catalyst:

- Calcium oxide bulk (CaO): CaO is widely available in nature in the form of limestone and it is a low cost catalyst. According to Iizuka et al. (1971), who studied the basicity of CaO by IR spectroscopy, the strength of the oxide anion species on CaO is strong, following this order MgO < CaO < SrO < BaO, while the number of sites per weight follows this order: BaO < SrO < MgO < CaO. We purchased CaO from Fluka (99%) and kept it in oven at 120°C to avoid contamination of water.
- Calcium oxide supported on alumina (CaO/Al_2O_3): a catalyst with low surface area, like CaO, is typically supported on a high surface inert oxide, in order to have a final catalyst with a great specific surface area. This is the reason why I prepared CaO/Al_2O_3, using the wet impregnation method reported by Zabeti et al. (2009), and using calcium acetate (>99%, Sigma Aldrich product) as precursor for CaO. 10 g of γ-Alumina, previously left overnight at 600°C in an oven and 10 g of calcium carbonate were put in 50 mL of distilled water for 4 hours at room temperature. After, the powder was filtrated and dried at 120°C overnight. Finally the catalyst was calcined at 718 °C for 5 h.
- Mixed supported calcium oxide and strontium oxide over alumina ($CaO+SrO/Al_2O_3$): the synthesis of this catalyst is similar to the one previously described, i.e. the method of the wet impregnation was used. As precursor of SrO strontium carbonate was used. Three different catalyst were prepared using different mass ratio between the two precursors. The amount used are summarized in Table 7:

Table 7: Quantities of precursors used for the mixed CaO SrO supported catalysts synthesis

	$CaO_{75}SrO_{25}$	$CaO_{50}SrO_{50}$	$CaO_{25}SrO_{75}$
$(CH_3COO)_2Ca$ [g]	3.0167	4.021	3.0161
$SrCO_3$ [g]	1.0084	4.0215	1.0052

The catalysts prepared were characterized using different techniques.

The specific surface area was obtained by adsorption of nitrogen at the temperature of liquid nitrogen, using a typical BET apparatus, while the analysis of the surface atomic composition was performed using a XPS, analysis that is able to give the atomic percentage in the first atomic layers. The spot size of investigation for survey analyses is 200x750 μm, and pass energy of 1 eV/pt, while high resolution analyses were performed on a spot size of 200500 µm and pass energy 0.03 eV/pt. The internal reference used for the peak shift correction was the 1s energy level of contaminant carbon, at 284.6 eV. The curve fittings were performed by using Gaussian's peaks and Shirley's baseline. The output of this analysis was essential to understand if the synthesis of the mixed oxide was properly made, or if on the supported catalyst the active species (CaO) was actually exposed at the surface.

Batch Reactor

All the experiments were performed in a 250 mL flask, equipped with a mechanical stirrer. The reactions were performed if not specified at 60°C. Samplings were made by turning off the agitation and, after waiting for 30 seconds, the oil phase was withdrawn. Before the gas chromatographic analysis the sample was subjected to waster washing if homogeneous catalyst was used or to a centrifugation if heterogeneous catalyst was used. After, it was put under vacuum to eliminate the excess of methanol.

Bioplasticizer, green chemicals of high added value

A plasticizer improves the plasticity of plastics, paints and adhesives (Wypych, 2004). It is added to the polymeric matrix in different quantities and take the general name external additives. The external plasticizer can be divided into two main categories: 1) Primary, which are added up to the 30 %vol and 2) Secondary, which reduce the polymer rigidity but have got poorer performances. These are used in smaller quantities.

With particular reference to polyvinylchloride (PVC), which is one of the most produced and used polymer, the phthalate family is the most important class of primary plasticizer. These are esters of phthalic acid and a primary alcohol, for example octil alcohol. Unfortunately, due to recent research, UE forbade their use because phthalates have effect on human health, in particular they can induce prostate cancer (Lee, et al., 2014). Due to this, alternatives to phthalates were developed, some of them synthetized from biomasses. Among these the most economically and sustainable chemical products are epoxidized vegetable oils (EVO), (Park, et al., 2004). These are easily biodegraded and possess good plastic properties. Moreover they possess low diffusion coefficient in the polymer, low volatility and a good lubricant power. The main drawback of these materials is their low solubility in the polymeric matrix, hence they are used mainly as secondary plasticizers (Goud, et al., 2006).

To improve the product disadvantages, new bio-plasticizer should be developed. An alternative that seems valid is represented by epoxidized biodiesel. Due to the lower molecular weight, epoxidized biodiesel is more soluble in PVC and it also could be used as precursor for bio-lubricants. The epoxide group (an oxygen bridge between two consecutive carbons) is of course obtained only from unsatured molecules. Dealing with biodiesel, only methyl oleate, linoleate and linolate can react to give epoxide.

This creates an issue.

The satured methyl esters have less affinity towards the polymeric matrix and thus tend to migrate at the PVC surface giving transudation problems. For this reason in my thesis work I studied the in situ epoxidation reaction with hydrogen peroxide catalyzed by sulphuric acid and, after a brief investigation on the optimization of the reaction conditions, two different strategies for preparing low satured molecules content epoxybiodiesel.

The first one (Strategy A) consisted in the satured methyl esters distillation and then in the epoxidation of the residue, rich in unsaturation. The second strategy (B) consisted in the epoxidation of biodiesel as it is and then in the complete distillation od the unreacted compounds. The product obtained using both the strategies were compared in order to choose the best way to produce an epoxidized biodiesel with the highest oxyrane content possible.

Materials

All the reagents for the synthesis and the analytical part were purchased from Sigma Aldrich and were used without further purifications. The epoxidation reaction was studied using soybean biodiesel as substrate, supplied by Oil.B srl.

For the epoxidation reaction the following reagents were used: glacial acetic acid, hydrogen peroxide (30% v/v), sulphuric acid (96-98%), sodium bicarbonate and n-hexane.

For the analysis it was used crystal violet (1% solution in acetic acid) as the indicator for the oxirane oxygen content, HBr solution (33%w solution in acetic acid) and methyl octanoate (>99%), used as internal standard for the GC analysis alredy reported in the *Biodiesel Production, heterogeneous transesterification of vegetable oils-Analystical methods* section.

Analytical Methods

Determination of the unsaturation contend, iodine number

In order to have a measure of the insaturation content and be able to calculate th double bond conversion the iodine number was measured. The method consists in the retro titration of the iodine that is left after the complete reaction with all the double bond present with tiosulphate. Practically a weighted amount of biodiesel, about 0.2 g, is put in a flask with 10 mL of cyclohexane, 10 mL of acetic acid and exactly 25 mL of Wijs reagent. The solution is left in dark condition for 2 hours. Than 20 mL of a KI solution (100 gL^{-1}) is added, together with 150 mL of distilled water. The titrant is a solution of sodium tiosulphate 1 M. the iodine number is then expressed as grams of iodine per 100 grams of substrate and it calculated using the formula reported in Equation 8:

$$IN = \frac{25.48 * M * (V_1 - V_b)}{m} * 100 \qquad \textit{Equation 8}$$

In which 25.48 is the molecular weight of iodine already corrected by a factor that consider the change in the unit of measure, M the title of the tiosulphate solution, V_1 the volume of titrant used, V_b the volume of titrant used in the blank titration and m the mass of sample. As previously stated, the iodine number measurements were used to calculate the double bond conversion, simply subtracting the initial IN value to the one obtained at a certain time and dividing the results for the IN value at time zero.

Determination of the epoxide contend, oxirane oxygen number

The quantity of epoxide in a certain amount of substrate is given by the oxirane oxygen content (OO). Its value is expressed as grams of oxygen (oxiranic) per 100 g of sample. The most used method for the OO calculation for epoxides of fatty acids is the addiction of an alyde HX to the epoxide ring, i.e. an hydroalogenation. Dubertaky (1956) reported a direct method for the OO determination. The titrant is a solution of bromidic acid in acetic acid while the indictaor is a solution of crystal violet in acetic acid. This method is reported in a large number of publications as AOCS Method Cd 9-57.The sample is dissolved in a non acqueous, water-free solvent, i.e. toluene or glacial acetic acid. One drop of indicator is added and the titration should be made under vigorous stirring. The experimental OO obtained (OO_{exp}) is than used together with the theoretical one (OO_{the}) calculated considering the IN to have the reaction selectivity. More in detail, Equation 9 shows the formula used for the calculation of OO_{the}:

$$OO_{the} = \left\{\frac{[(IN_0 - IN_t)/PM_{I2}]}{100 + [(IN_0 - IN_t)/PM_{I2}] * PA_0}\right\} * PA_0 * 100 \qquad \textit{Equation 9}$$

In which IN_0 is the initial iodine number, IN_t is the iodine number at time t and $PM_{I2}$and $PM_O$the molecular weight of iodine and oxygen respectively. The reaction selectivity is then calculated as shown in Equation 10:

$$Selectivity = \frac{OO_{exp}}{OO_{the}} * 100 \qquad \text{Equation 10}$$

Batch Reactor

The epoxidation reaction, either on biodiesel or on distilled biodiesel, was carried out in a 1 L flask, thermostaded and agitated by a mechanical stirrer. The scheme of the reactor is reported in Figure 12:

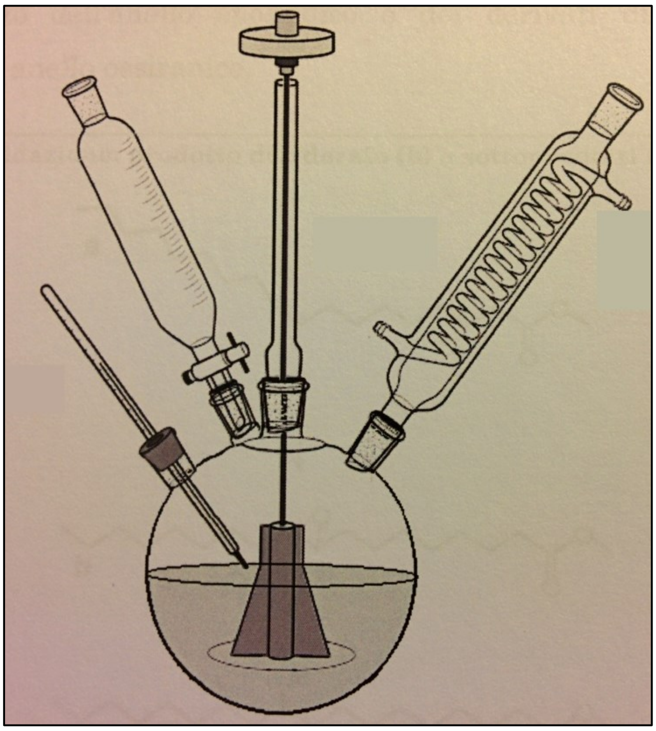


Figure 12: Epoxidation batch reactor scheme

In the reactor the substrate to be epoxidized is charged together with acetic acid in different proportions, depending on the reaction conditions. In a funnel the hydrogen peroxide and the sulphuric acid and the mixture was added dropwise at 40°C in 15-20 minutes to the flask under strong agitation. The temperature was controlled and kept at 40°C because the generation of acetic peroxide evolves heat. At the end of the addition (time zero), the temperature is raised to the desired value.

The molecule that effectively epoxidases the double bonds is peracetic acids, which forms after the reaction between acetic acid and hydrogen peroxide catalyzed by sulphuric acid. This is the rate determining step since the epoxide formation is a very fast reaction. The epoxides are very reactive and thus in the presence of acids or esters can condensate and generate by-product, decreasing the reaction selectivity.

At the end of the reaction (typically 6 hours of reaction) the acid is neutralized together with the hydrogen peroxide abated using sodium bicarbonate solution. The two liquid phases are separated and the organic phase is washed several times with 10 mL of deionized water, until neutral pH is reached. The product is then dehydrated using sodium sulphate, filtrate and finally put under vacuum.

Samples were withdrawn every hour. The work-up is the same above described.

Distillation apparatus

The distillation of soybean biodiesel was made with the aim to concentrate the unsatured molecules. It consisted of a vacuum batch distillation, using a Claisen apparatus equipped with a vigreaux column (25 cm height). In order to minimize heat dispersions, both reboiler (a 250 mL flask) and vigreaux column were thermally insulated with glass wool, aluminum sheets and high temperature resistant Teflon. The scheme of the distillation apparatus is reported in Figure 13:

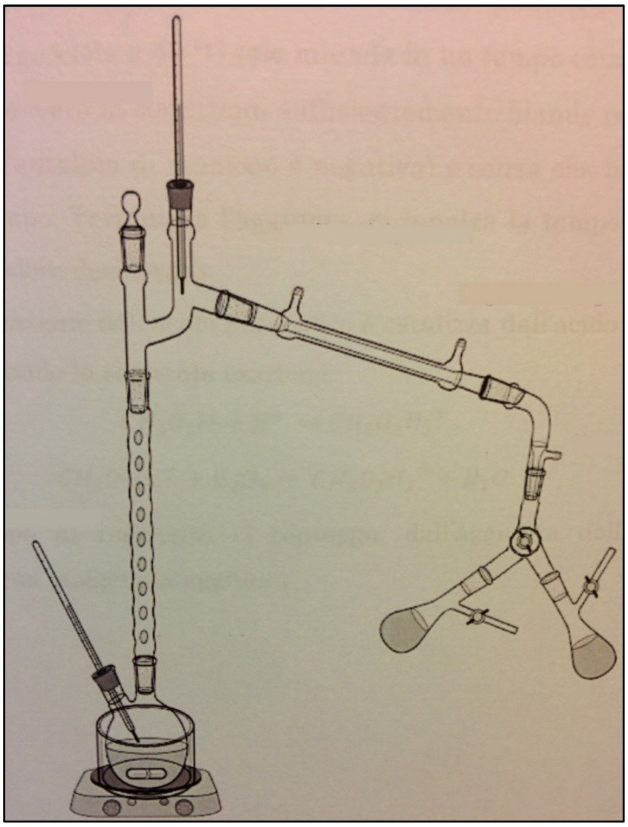


Figure 13: Scheme of the distillation apparatus for the unsatured methyl esters concentration

To collect different fraction of distillate, a system based on two alternate collective flasks was studied, which made possible the withdrawn of samples without pressurizing the system. In general the typical distillation protocol is described hereinafter:

1. Charge of biodiesel (about 200g);
2. Addiction of the magnetic stirrer and agitation turned on;
3. Set up of the distillation equipment;
4. Set the reboiler temperature, using an oil bath, at 200°C while turning on the vacuum pump

Once the distillation of the satured esters is finished, the content of the reboiler is further purified by simple distillation (without vigreaux), in order to remove the traces of biodiesel degraded, i.e. the by-products formed after the high temperature oligomerization of biodiesel.

Results and Discussion

Oil Pretreatment, deacidification of vegetable oils

In this part of the thesis all the results obtained regarding the deacidification of vegetable oils are reported. Firstly, the study of the monophasic deacidification of FFA is reported, investigating the disadvantages that result when a double liquid system due to the excess of methanol forms. Moreover, it was noted that the catalyst performances are not stable, but in the first experiments (about the first 30 h of work) tend to decrease. This is associated with the water adsorption on the resin. This aspect was considered together with the deacidification performed in a packed bed reactor for developing a robust kinetic model, which considers the high non ideality of the system and the adsorption of both reactant and products on the resin.

Batch Reactor, study on the monophasic FFA esterification

As previously reported in the *Introduction* section, the FFA esterification is an equilibrium reaction, in which one mole of acid reacts with one mole of alcohol (methanol) to give one mole of ester and one of water. However, usually, an excess of methanol is used to shift the equilibrium towards the product (FAME). Object of this part of the work was the optimization of the methanol quantity, trying to understand if the formation of a double phase system was beneficial or not to the FFA conversion.

In the test performed sunflower oil was used. It was purchased from a local market. From a GC analysis the acidic composition of the oil was determined, and it is reported in Table 8:

Table 8: Sunflower oil acidic composition

Component	Retention time [min]	Concentration [%w]
STD	1.93	-
Methyl myristate	3.27	0.00
Methyl palmitate	4.72	6.41
Methyl stearate	7.43	4.28
Methyl oleate	7.93	19.04
Methyl linolate	8.91	70.57
Methyl linolenate	10.54	0.00
Average FFA molecular weight $\overline{MW}$ [g mol-1]	279.40	

The value of average molecular weight was used for the calculation of the FFA conversion, according to Equation 1.

A total of eleven experiments were performed with the following aims:

- One test without catalyst, in the presence of two phases, in order to evaluate the equilibrium repartition of FFA in the phases (whether it exists). In the operative condition chosen the autocatalytic reaction is very slow, and the system could be considered non reacting, governed only by a physical equilibrium.
- Three tests performed with catalyst changing the agitation rate, in order to study the influence of the external diffusion and operating the next tests avoiding this problem.
- Seven tests changing the methanol:FFA molar ratio (MeOH/FFA), to study the influence of the methanol amount on the FFA conversion, either in the presence of one or two liquid phases. These tests were useful also for determinating a rough range of methanol concentration at which, at the operative conditions chosen, the second liquid phase starts to form.

It is important to say that for each test fresh catalyst was used, to maintain the same condition, even if the catalyst at the first reaction converts more than the one at the equilibrium.

Test 1

The operative conditions are summarized in Table 7:

Table 9: Test 1, operative parameters

Oil mass [g]	202.5
Methanol mass [g]	74.0026
Catalyst mass [g]	-
T [°C]	59
Agitation [rpm]	100

The experimental results are reported in Figure 14 and **Errore. L'origine riferimento non è stata trovata.**:

Table 10: Test 1, experimental results

Time [min]	Sample mass [g]	V KOH [mL]	FFA [%w]	Extraction [%]
0	1.7355	2.22	3.33	0
11	2.149	2.13	2.58	22.5
38	2.224	2.13	2.49	25.1
63	2.357	2.23	2.46	26

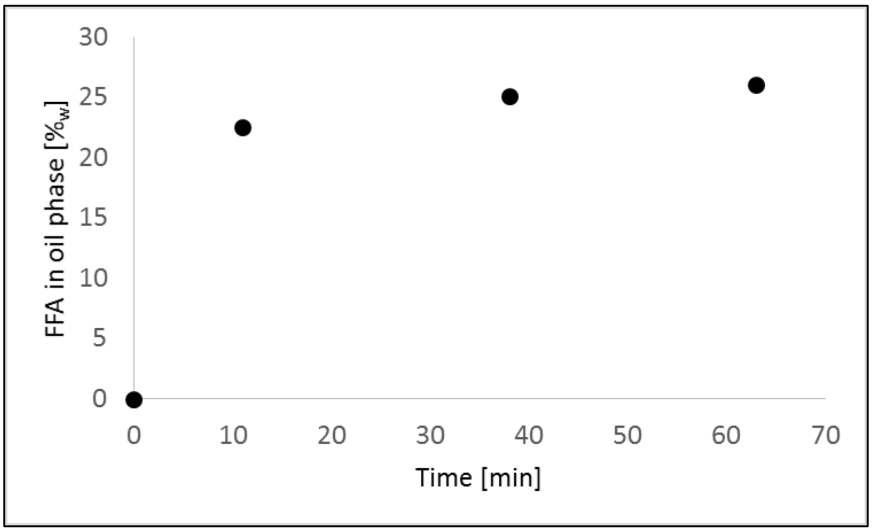


Figure 14: Test 1, experimental results

The equilibrium distribution of FFA is reached about in one hour at the operative condition chosen. The result indicates that about the 26 % of the FFA are dissolved in methanol. This considerable part thus in the presence of a double phase system, is not converted into FAME but remains dissolved in methanol. Therefore, when two liquid phases are present, a not negligible quantity of FFA cannot be converted into FAME, as it is not in contact with the catalyst.

Test 2

This test is the first of a set of three in which the agitation rate was varied. The operative conditions are reported in Table 11:

Table 11: Test 2, operative conditions

Oil mass [g]	204.48
Methanol mass [g]	11.496
Catalyst mass [g]	20.275
T [°C]	59
Agitation [rpm]	100

The results obtained are reported in Table 12 and in Figure 15:

Table 12: Test 2, experimental results

Time [min]	Sample mass [g]	V KOH [mL]	FFA [%w]	Conversion [%]
0	1.7766	2.35	3.45	0
60	1.965	1.36	1.8	47.7
123	2.328	0.96	1.07	68.8
180	2.0883	0.61	0.76	77.9
240	1.734	0.37	0.56	83.9
301	1.675	0.28	0.44	87.4
360	1.888	0.25	0.34	90

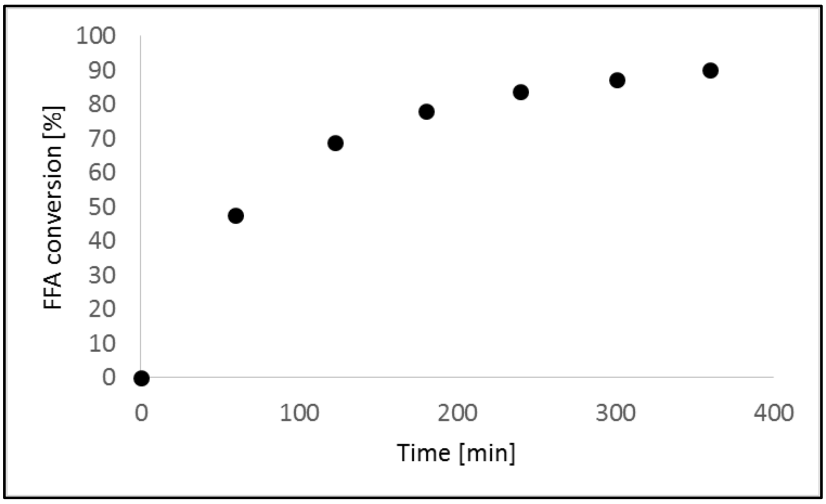


Figure 15: Test 2, experimental results

Test 3

The operative parameters are reported in Table 13:

Table 13: Test 3, operative parameters

Oil mass [g]	204.17
Methanol mass [g]	10.3470
Catalyst mass [g]	20.4245
T [°C]	59
Agitation [rpm]	200

The results obtained are reported in Table 12 and Figure 16:

Table 14: Test 3, experimental results

Time [min]	Sample mass [g]	V KOH [mL]	FFA [%w]	Conversion [%]
0	1.8047	2.22	3.20	0.0
107	2.0261	0.88	1.13	64.7
153	2.2990	0.74	0.84	73.8
245	1.7425	0.34	0.51	84.1
311	2.0190	0.29	0.37	88.3
379	2.1405	0.27	0.33	89.7

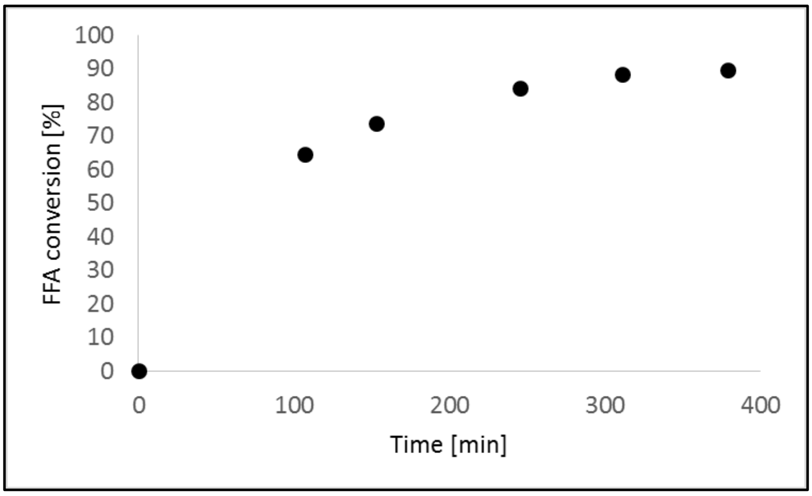


Figure 16: Test 3, experimental results

Test 4

The operative parameters of Test 4 are reported in Table 15:

Table 15: Test 4, operative parameters

Oil mass [g]	204.01
Methanol mass [g]	10.3500
Catalyst mass [g]	20.4028
T [°C]	59
Agitation [rpm]	300

The results are reported in Table 16 and Figure 17:

Table 16: Test 4, experimental results

Time [min]	Sample mass [g]	V KOH [mL]	FFA [%w]	Conversion [%]
0	1.9585	2.46	3.27	0.0
60	1.9994	1.31	1.71	47.8
120	2.0760	0.81	1.02	68.9
180	1.8405	0.48	0.68	79.2
240	2.0810	0.38	0.48	85.5
300	2.0160	0.31	0.40	87.8
360	2.1080	0.27	0.33	89.8

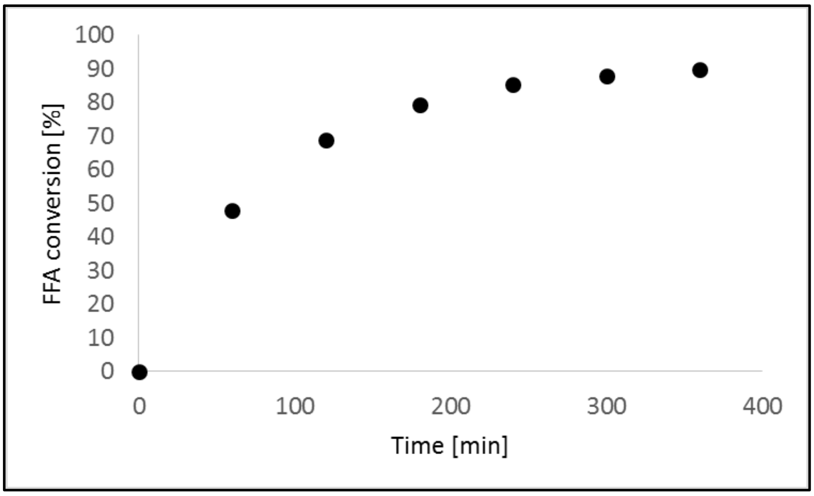


Figure 17: Test 4, experimental results

In Figure 16 the results of Test 2-4 are reported together.

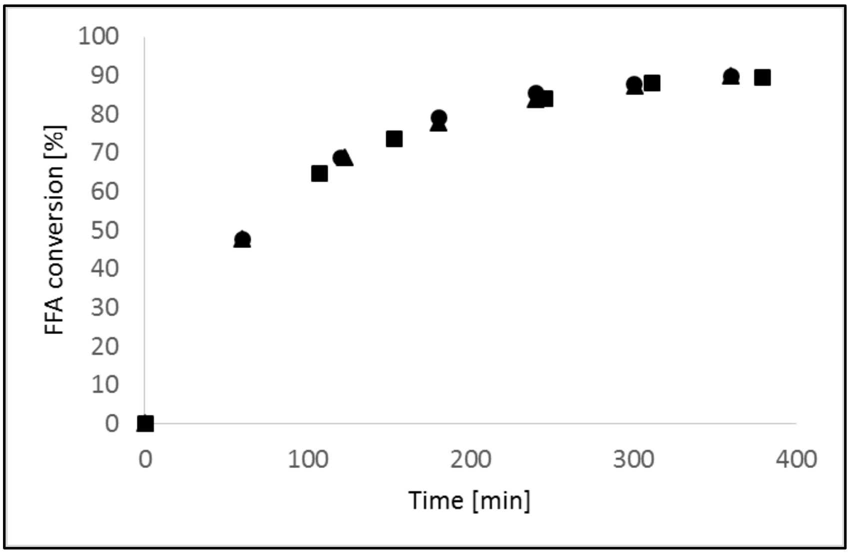


Figure 18: Comparison between the results of Test 2 (circles), Test 3 (triangles) and Test 4 (squares)

The perfect overlap between the experimental data permit to exclude the presence of external diffusion.

For this reason, all the remaining tests were performed at an agitation rate of 200 rpm.

Test 5

In this set of experiments, the amount of methanol was varied to change the MeOH/FFA ratio. In this Test, it was set to 2, and only one liquid phase was present. The operative parameters are reported in Table 17:

Table 17: Test 5, operative parameters

Oil mass [g]	201.57
Methanol mass [g]	1.5458
Catalyst mass [g]	20.3080
T [°C]	59
Agitation [rpm]	200
MeOH/FFA	2

Table 18 and Figure 19 report the experimental data obtained:

Table 18: Test 5, experimental results

Time [min]	Sample mass [g]	V KOH [mL]	FFA [%w]	Conversion [%]
0	1.4742	1.80	3.18	0.0
60	1.8776	1.76	2.44	23.2
118	2.0449	1.52	1.94	39.1
179	1.9911	1.28	1.67	47.3
253	2.1150	1.20	1.48	53.5
299	2.3207	1.28	1.44	54.8
355	2.3309	1.28	1.43	55.0

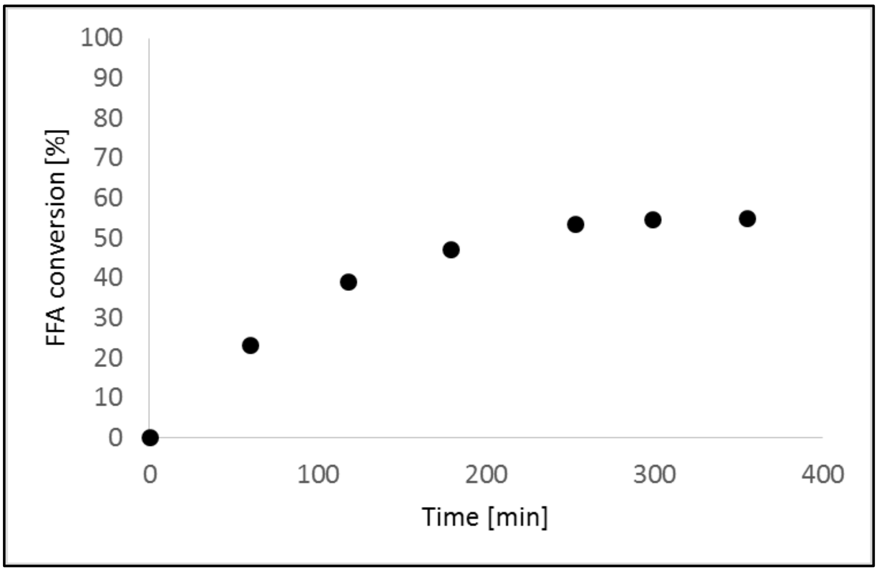


Figure 19: Test 5, experimental results MeOH/FFA=2

Test 6

In Test 6 the MeOH/FFA was fixed to 3, only one liquid phase was observed. The operative parameters are reported in Table 19:

Table 19: Test 6, operative parameters

Oil mass [g]	202.33
Methanol mass [g]	2.2618
Catalyst mass [g]	20.4113
T [°C]	59
Agitation [rpm]	200
MeOH/FFA	3

The experimental results are reported in Table 20 and Figure 20:

Table 20: Test 6, experimental results

Time [min]	Sample mass [g]	V KOH [mL]	FFA [%w]	Conversion [%]
0	1.7985	2.10	3.04	0.0
60	2.0890	1.94	2.42	20.5
111	2.1063	1.62	2.00	34.1
184	2.2535	1.16	1.34	55.9
201	1.6453	0.79	1.25	58.9
241	1.9048	0.83	1.14	62.7
303	1.9970	0.79	1.10	64.0
334	2.2516	0.84	0.97	68.0

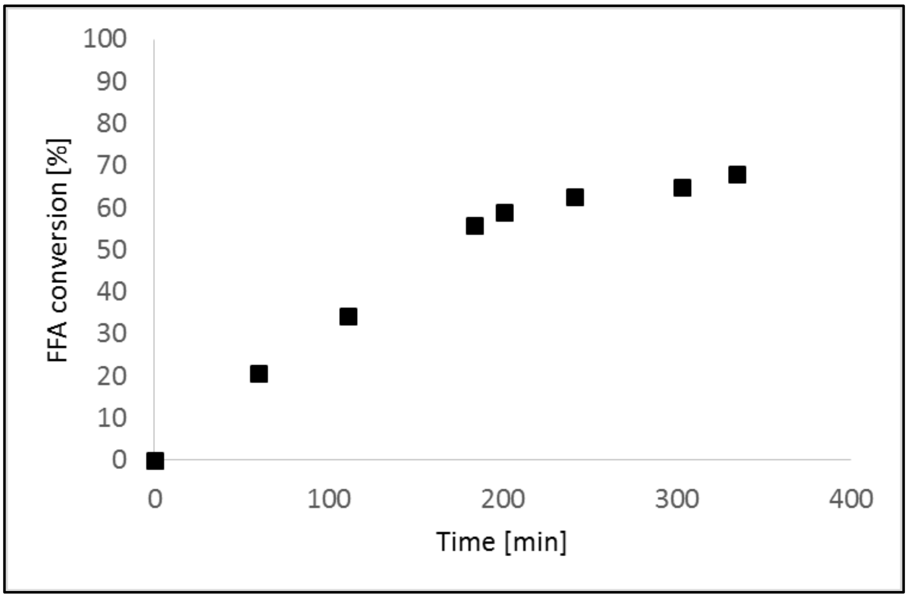


Figure 20: Test 6, experimental results MeOH/FFA=3

Test 7

The operative conditions of Test 7 are reported in Table 21. The MeOH/FFA molar ratio was fixed to 5.

Table 21: Test 7, operative parameters

Oil mass [g]	203.66
Methanol mass [g]	3.8471
Catalyst mass [g]	20.4362
T [°C]	59
Agitation [rpm]	200
MeOH/FFA	5

The results obtained are reported in Table 22 and Figure 21:

Table 22: Test 7, experimental results

Time [min]	Sample mass [g]	V KOH [mL]	FFA [%w]	Conversion [%]
0	0.6454	0.76	3.07	0.0
60	2.1228	1.72	2.11	31.2
127	2.5240	1.30	1.34	56.3
180	1.9235	0.74	1.00	67.3
240	2.5827	0.73	0.74	76.0
342	3.2928	0.68	0.54	82.5

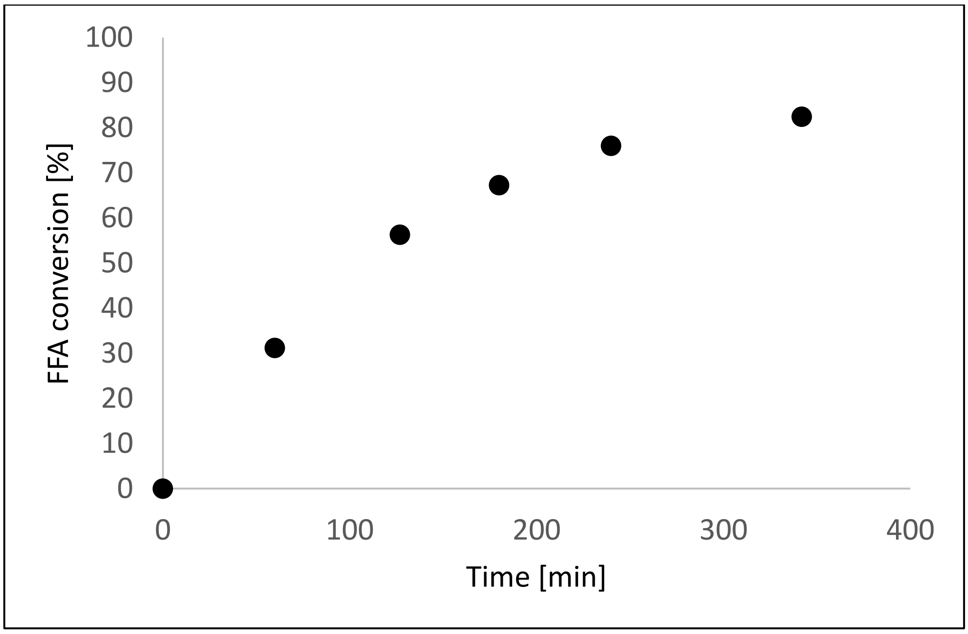


Figure 21: Test 7, experimental results MeOH/FFA=5

Test 8

In this Test the MeOH/FFA was fixed to 10. Also in this case only one liquid phase was observed.

The operative parameters are reported in Table 23:

Table 23: Test 8, operative parameters

Oil mass [g]	203.16
Methanol mass [g]	7.5852
Catalyst mass [g]	20.3274
T [°C]	59
Agitation [rpm]	200
MeOH/FFA	10

The results are reported in Table 24 and Figure 22:

Table 24: Test 8, experimental results

Time [min]	Sample mass [g]	V KOH [mL]	FFA [%w]	Conversion [%]
0	0.8633	1.00	3.02	0.0
60	2.1309	1.72	2.10	30.3
120	1.9174	0.98	1.33	55.9
180	2.0609	0.72	0.91	69.8
240	2.0609	0.40	0.51	83.2
300	2.0126	0.33	0.43	85.8
360	2.1990	0.34	0.40	86.7

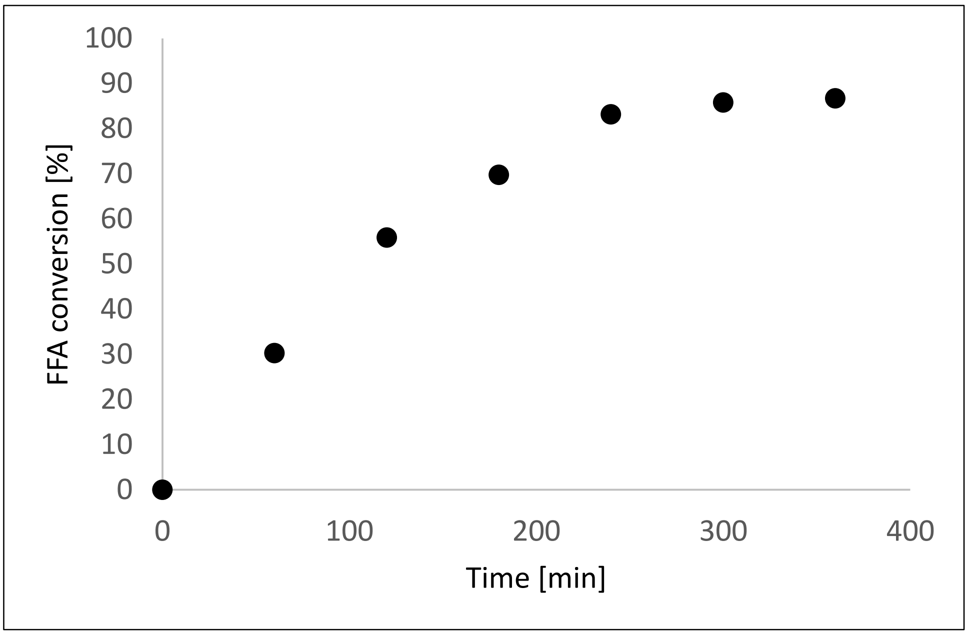


Figure 22: Test 8, experimental results MeOH/FFA=10

Test 9

Test 9 is actually Test 3, since the MeOH/FFA was set to 13 in the first 3 Tests. For this reason the results obtained (reported

Table 14 in and Figure 16) were useful also in this set of experiments.

Test 10

MeOH/FFA molar ratio for Test 1o was fixed to 95. In these conditions two liquid phases were observed. The operative parameters are reported in Table 25:

Table 25: Test 10, operative parameters

Oil mass [g]	203.32
Methanol mass [g]	70.3201
Catalyst mass [g]	20.4188
T [°C]	59
Agitation [rpm]	200
MeOH/FFA	95

The results obtained are reported in Table 26 and Figure 23:

Table 26: Test 10, experimental results

Time [min]	Sample mass [g]	V KOH [mL]	FFA [%w]	Conversion [%]
0	0.8913	1.02	2.98	0.0
52	2.1037	1.04	1.29	56.8
119	2.2405	0.40	0.47	84.4
172	2.6652	0.38	0.37	87.5
239	2.3082	0.21	0.24	92.0
301	2.0897	0.14	0.17	94.1
361	2.1116	0.14	0.17	94.2
394	2.4744	0.14	0.15	95.1

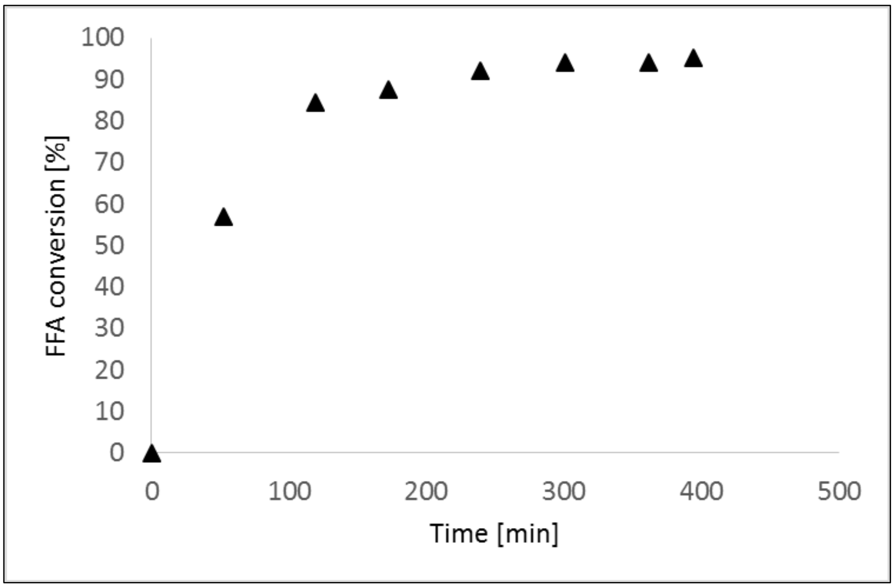


Figure 23: Test 10, experimental results MeOH/FFA=95

Test 11

In this last Test the MeOH/FFA molar ratio was fixed to 150. Again, the liquid system was biphasic. The operative parameters are reported in Table 27:

Table 27: Test 11, operative parameters

Oil mass [g]	201.86
Methanol mass [g]	107.4204
Catalyst mass [g]	20.4188
T [°C]	59
Agitation [rpm]	200
MeOH/FFA	150

The results obtained are reported in Table 28 and Figure 21:

Table 28: Test 11, experimental results

Time [min]	Sample mass [g]	V KOH [mL]	FFA [%w]	Conversion [%]
0	2.2481	2.50	2.90	0.0
65	2.9340	1.09	0.97	66.6
120	1.9085	0.50	0.68	76.4
184	1.9990	0.29	0.38	87.0
239	2.3208	0.22	0.25	91.5
301	2.3043	0.15	0.17	94.1
364	2.0841	0.15	0.19	93.5
401	2.3233	0.13	0.15	95.0

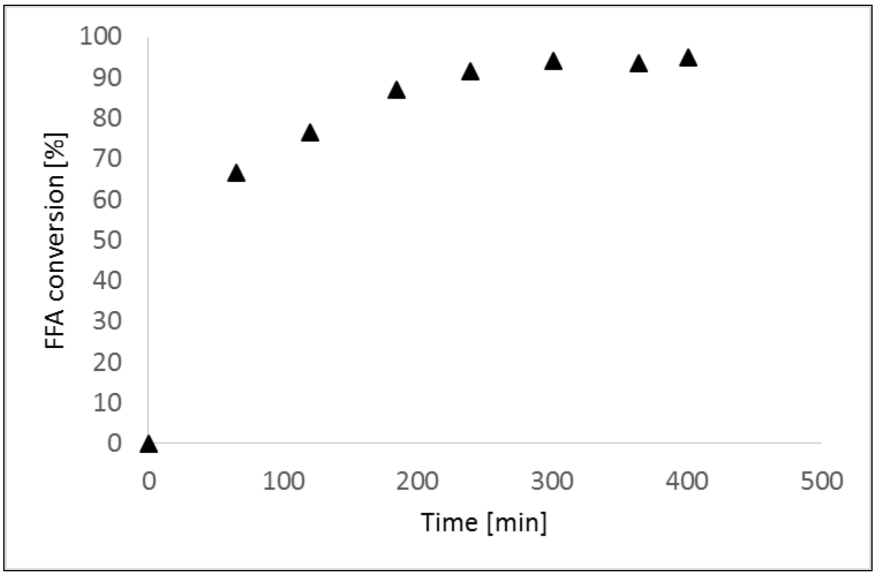


Figure 24: Test 11, experimental results MeOH/FFA=105

A comparison between the results obtained in Tests 5-11 is reported in Figure 25.

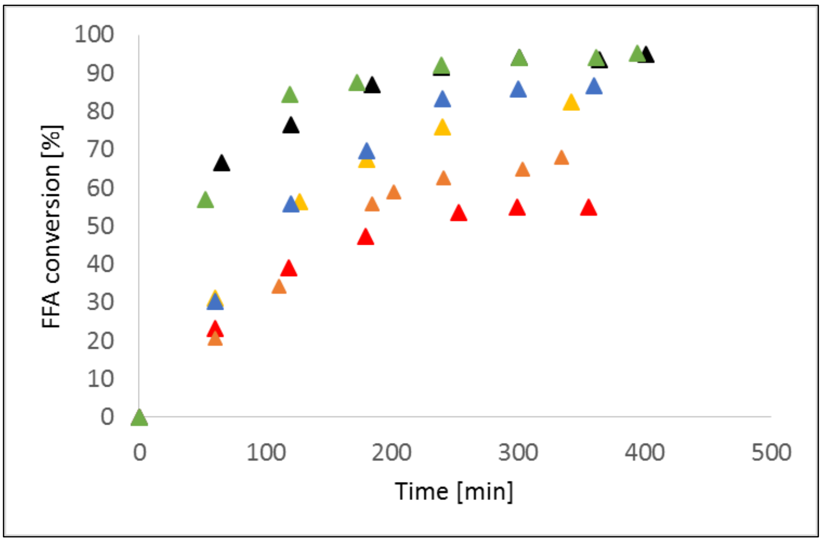


Figure 25: Comparison between the experimental results of Test 5 (red), Test 6 (orange), Test 7 (yellow), Test 8 (blue), Test 10 (green) and Test 11 (black)

The experimental conversions are coherently ordered respect the MeOH/FFA ratios, in other word, the higher the amount of methanol, the higher the conversion. Differently, when a double phase system forms, the amount of methanol in the oil phase remains constant at a fixed temperature. As a consequence, the reaction rate maximizes and remains constant at any methanol/FFA molar ratio.

In Figure 26 it is shown a comparison with the experimental data of Test 10 (MeOH/FFA=95) without considering the FFA dissolution in the methanol phase and considering it by calculating the real FFA amount, i.e. considering by the extraction percentage observed in Test 1.

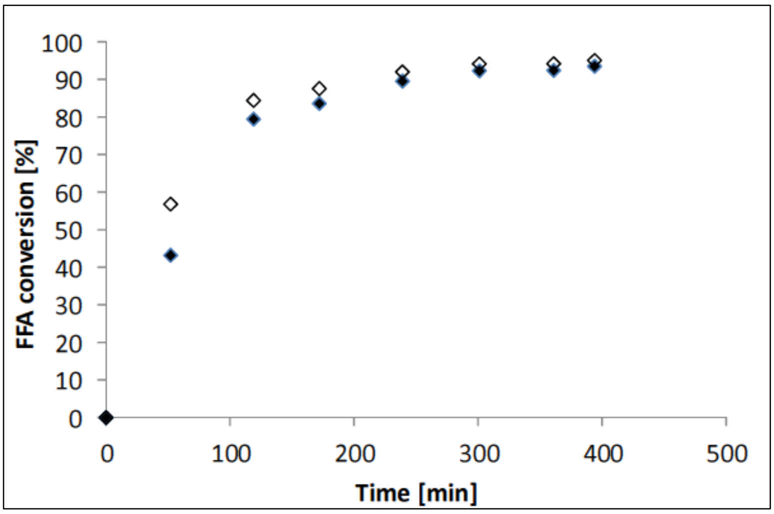


Figure 26: Comparison between experimental data of Test 10 taking (full symbols) or not (empty symbols) into account the extraction phenomenon

A conversion after 60 min of 43.15% is calculated, which is consistent with the data of Test 9, where the MeOH/FFA ration was set to 13, meaning that the excess of methanol used was in the end wasted and only extracted FFA from the oil phase.

All these data collected in a batch reactor demonstrate the efficacy to perform the esterification reaction using limited amount of methanol, i.e. operating in a (monophasic liquid)/solid system. From a kinetic point of view, being the temperature always kept constant, the conversion at a certain time is only proportional to the amount of methanol.

In Figure 27 the experimental FFA conversion at 240 min is reported versus the MeOH/FFA molar ratio.

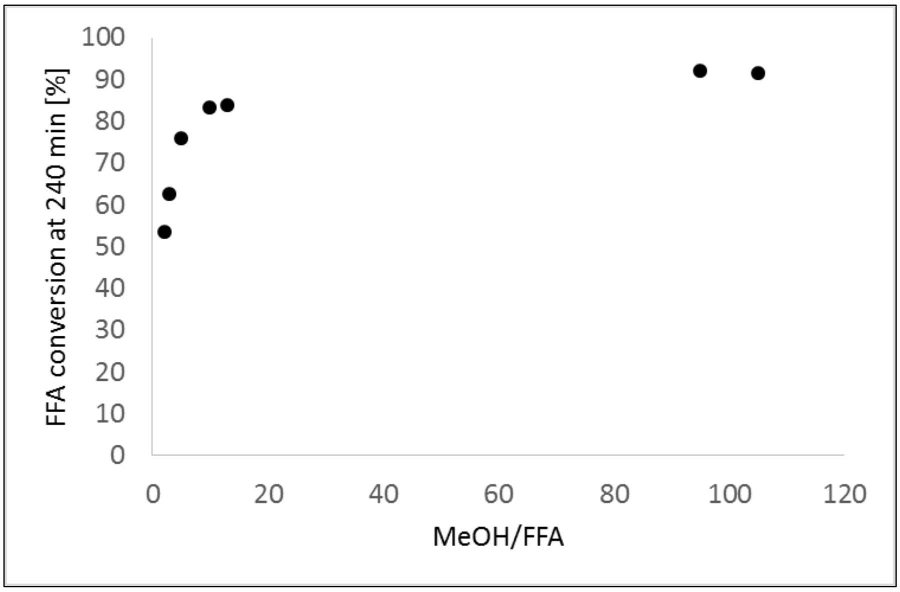


Figure 27: FFA conversion at 240 min vs MeOH/FFA molar ratio

When the system is monophasic, the methanol concentration in the oil phase (the phase in which the catalyst is present) increases if the MeOH/FFA increases, but when the critical concentration is reached, the excess of methanol forms the second phase, while its concentration in the oil remains constant. This concept are well represented in Figure 22.

The data were fitted using a function represented generically in Equation 11:

$$f(x) = \frac{A*x}{B*x+1} \qquad \textit{Equation 11}$$

Which is a simple equation that reaches a plateau value. The best A and B value were found to be 67.8105 and 0.7247 respectively, giving a satisfactory fitting.

From this analysis it can be concluded that the second phase forms at the transition between the linear behavior (low MeOH/FFA ratio) and the plateau, i.e. between a MeOH/FFA of 20 or 30. Converting these values in percentage by weight of methanol it results a range of 6.8%-10.2%$_{w.}$ Of course the exact value can only be found with dedicated experiments but it is out of the scope of this work.

These simple tests showed that it is not convenient, due to the disadvantages already described, working with an excess of methanol which leads to the formation of a double phase system, but it is more effective to work in a monophasic liquid, considered also that high FFA conversions could be obtained, differently from a lot of works found in literature (Russbueldt & Hoeldrich, 2009), (Son, et al., 2011), (Ding, et al., 2012).

Batch Reactor, study on the catalyst stability

Another important study performed concerned the stability of the Amberlyst 46 catalyst at the operative condition. For this test rapeseed oil was used and a MeOH/FFA ratio of 5, in order to maintain the system monophasic. A total of 9 deacidification reactions were performed changing the temperature and using always the same resins, without discharging them from the reactor. Before running these 9 Tests three reactions were performed at 60°C in order to make the equilibrium of reactants and product be established on the resin surface.

This is not a negligible aspect to be considered. In Figure 28 the comparison between the first and the third equilibrium reactions are reported.

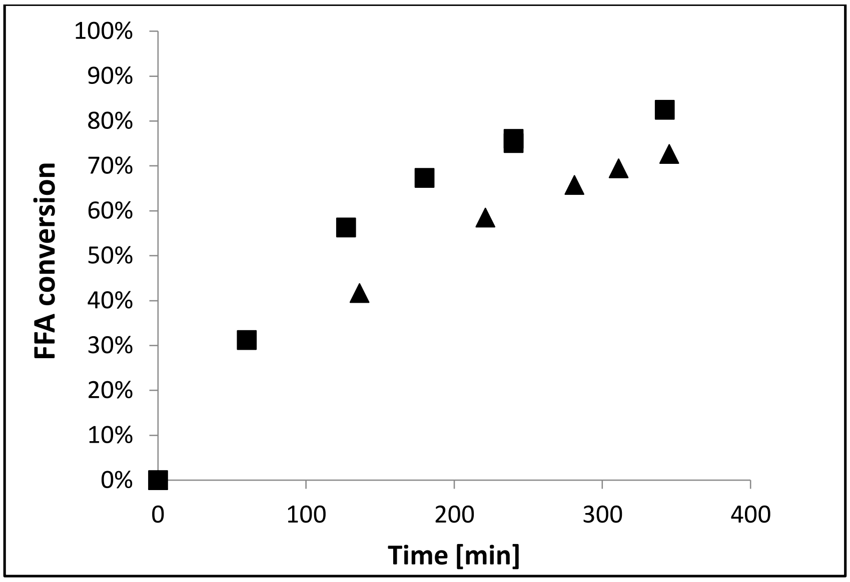


Figure 28: Comparison between FFA conversion obtained with fresh resins (squares) and equilibrated resins (triangles)

This phenomenon was always observed every time fresh catalyst was used. The explanation is simple, water formed as by-product of the esterification remains adsorbed on the resin and thus the reaction rate results enhanced because water is subtracted from the mixture.

All the results of the nine experiments are reported hereinafter.

Tests 1-5

Tests1-5 were performed at 60 °C. in the following Tables all the experimental results are reported, while in Table 29 the masses of oil and methanol used are shown:

Table 29: Tests 1-5 amount of oil and methanol used

Operative conditions of	Reagent	Mass [g]
Test 1	Oil	205.26
	Methanol	2.8534
Test 2	Oil	203.52
	Methanol	2.6106
Test 3	Oil	203.69
	Methanol	2.7018
Test 4	Oil	209.10
	Methanol	2.7059
Test 5	Oil	204.53
	Methanol	2.6911

Table 30: Test 1, experimental results

Time [min]	Sample mass [g]	V KOH [mL]	FFA [%w]	Conversion [%]
0	2.1706	1.88	2.45	0.0
136	2.4536	1.24	1.43	42.1
221	2.4747	0.89	1.02	59.2
281	2.3621	0.70	0.84	66.6
311	2.6072	0.69	0.75	70.5
345	2.6590	0.63	0.67	73.3

Table 31: Test 2, experimental results

Time [min]	Sample mass [g]	V KOH [mL]	FFA [%w]	Conversion [%]
0	4.3007	3.4	2.23	0.0
60	2.7734	1.82	1.85	17.7
120	2.7112	1.36	1.41	37.0
180	2.8508	1.12	1.11	50.9
240	2.9250	0.96	0.93	58.4
300	2.6148	0.76	0.82	63.3
336	2.4872	0.64	0.73	67.4

Table 32: Test 3, experimental results

Time [min]	Sample mass [g]	V KOH [mL]	FFA [%w]	Conversion [%]
0	2.3233	1.92	2.33	0.0
30	2.2314	1.54	1.95	17.4
65	2.4038	1.46	1.72	27.6
125	2.1368	1.20	1.59	32.0
138	2.1464	0.98	1.29	45.5
205	2.3560	0.82	0.98	58.5
263	2.3670	0.70	0.84	64.1
330	2.2776	0.58	0.72	69.2

Table 33: Test 4, experimentla results

Time [min]	Sample mass [g]	V KOH [mL]	FFA [%w]	Conversion [%]
0	2.3787	1.90	2.26	0.0
15	2.5896	1.92	2.09	7.1
30	2.6547	1.86	1.98	12.0
60	2.3520	1.48	1.78	21.8
120	2.3908	1.18	1.39	38.8
195	2.2151	0.84	1.07	53.4
270	2.2608	0.68	0.85	62.7
330	2.3731	0.62	0.74	67.5
390	2.1158	0.50	0.67	70.4

Table 34: Test 5, experimental results

Time [min]	Sample mass [g]	V KOH [mL]	FFA [%w]	Conversion [%]
0	2.1878	1.70	2.20	0.0
13	2.2525	1.70	2.13	3.0
30	2.3862	1.70	2.01	8.2
58	2.1967	1.40	1.80	18.7
119	1.9782	1.00	1.43	35.4
215	1.9625	0.70	1.01	54.0
255	2.0413	0.64	0.89	60.8
338	2.2957	0.56	0.69	69.3
403	2.5990	0.56	0.61	72.3

All the results of Tests 1-5 are plotted together in Figure 29:

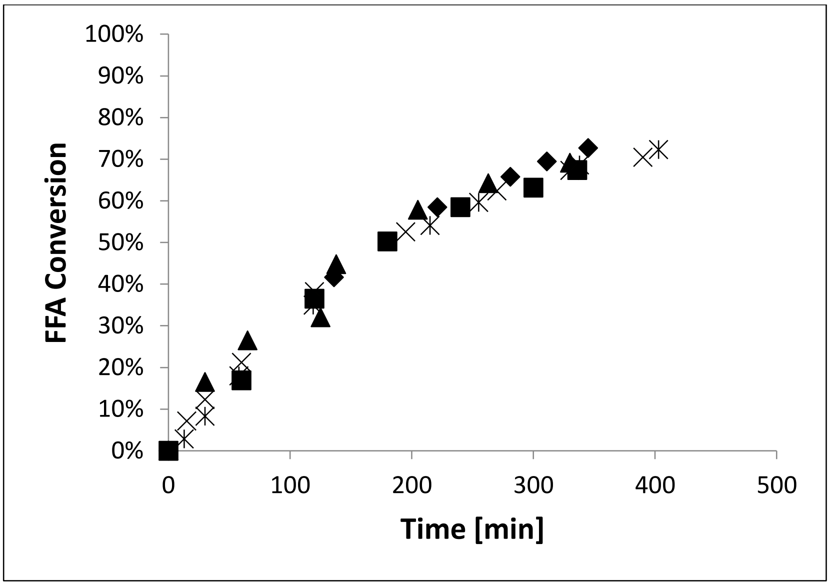


Figure 29: Experimental FFA conversion at 60°C, diamonds: Test 1, squares: Test 2, triangles: Test 3, X: Test 4, stars: Test 5

After the resin equilibration is reached, the catalyst performance resulted stable for 300 hours of work. After this first set of experiments, three tests were performed at 50°C and one last experiment at 40°C, which resulted very useful for the regression of the kinetic parameters (see *Kinetic Modelling* paragraph).

Tests 6-8

As previously introduced, these three tests were performed at lower temperature, i.e. 50°C. Since the catalyst was not discharged, Table 35 reports only the amount of methanol and rapeseed oil used for each Test.

Table 35: Tests 6-8 amount of methanol and oil used

Operative conditions of	Reagent	Mass [g]
Test 6	Oil	203.24
	Methanol	2.8191
Test 7	Oil	204.24
	Methanol	2.7920
Test 8	Oil	205.36
	Methanol	2.7251

In the following three Tables the experimental results are reported:

Table 36: Test 6, experimental results

Time [min]	Sample mass [g]	V KOH [mL]	FFA [%w]	Conversion [%]
0	2.5526	2.24	2.48	0.0
20	2.2901	1.96	2.42	3.5
34	2.3900	1.96	2.32	7.7
95	2.4213	1.84	2.15	13.8
190	2.8200	1.87	1.87	24.1
240	2.0338	1.28	1.74	30.8
280	2.4531	1.37	1.58	36.3
340	2.3404	1.17	1.41	43.7
1253	2.2238	0.34	0.43	83.4
1440	2.1098	0.30	0.40	84.9
1632	2.2365	0.28	0.35	85.7

Table 37: Test 7, experimental results

Time [min]	Sample mass [g]	V KOH [mL]	FFA [%w]	Conversion [%]
0	2.5526	2.24	2.48	0.0
15	2.2901	1.96	2.42	3.1
30	2.3900	1.96	2.32	7.4
60	2.2907	1.84	2.27	9.5
120	2.6224	1.87	2.01	19.9
214	2.0738	1.28	1.74	30.6
270	2.4531	1.37	1.58	36.6
331	2.3404	1.17	1.41	43.3
1460	2.1203	0.26	0.35	86.2
1682	2.1602	0.26	0.34	86.3

Table 38: Test 8, experimental results

Time [min]	Sample mass [g]	V KOH [mL]	FFA [%w]	Conversion [%]
0	2.1193	1.58	2.11	0.0
30	2.4553	1.72	1.98	6.4
60	2.4787	1.67	1.90	10.8
123	2.3455	1.43	1.72	18.3
180	2.5282	1.41	1.58	25.2
240	2.1476	1.08	1.42	33.3
300	2.1150	0.96	1.28	39.4
350	2.1810	0.93	1.20	43.9
1330	2.8941	0.35	0.34	86.0
1464	2.4019	0.26	0.31	87.2
1671	3.1538	0.30	0.27	87.2

In Figure 30 the comparison between the results obtained is shown:

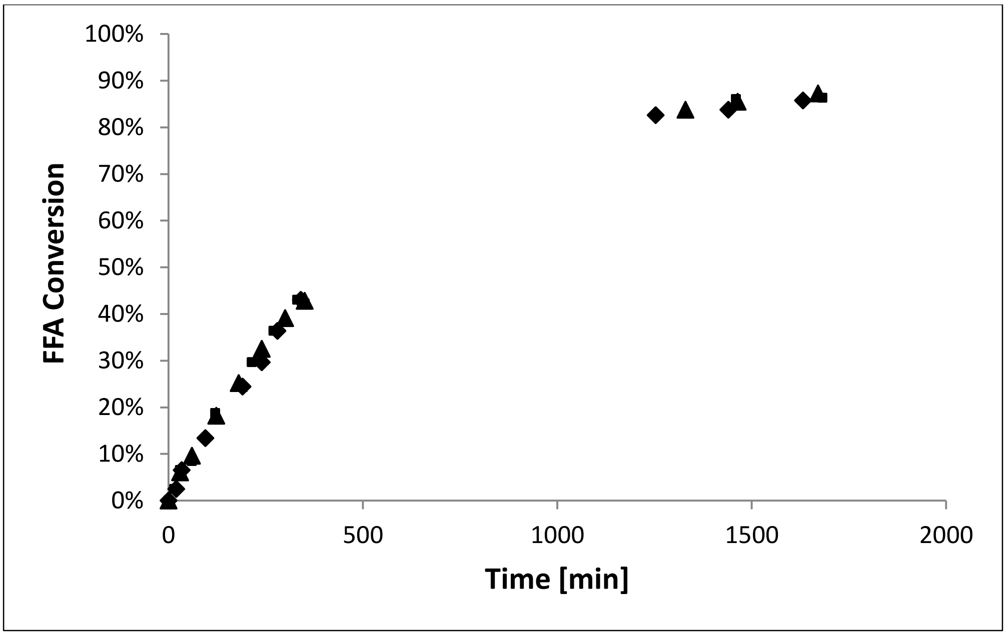


Figure 30: FFA experimental conversion for Test 6 (diamonds), Test 7 (squares) and Test 8 (triangles)

Again, the results are perfectly reproducible. Naturally, the Tests were carried out for longer time since the rate of reaction is slowed due to the low temperature (50°C).

Tests 9

This last Test was performed at 40°C. even if the temperature is too low, since the reaction made at 50°C needed more than 24 hours to reach the equilibrium, this experiment is still useful because increases the range of operative conditions at which the kinetic model is valid.

In Table 39 the amount of oil and methanol used are reported:

Table 39: Amount of methanol and oil used in Test 9

Operative conditions of	Reagent	Mass [g]
Test 9	Oil	205.15
	Methanol	2.6853

In Table 40 the experimental results are reported:

Table 40: Test 9, experimental results

Time [min]	Sample mass [g]	V KOH [mL]	FFA [%w]	Conversion [%]
0	2.4069	1.92	2.65	0.0
60	2.1894	2.02	2.61	2.1
150	2.0170	1.74	2.44	8.8
270	2.3404	1.80	2.18	18.5
479	2.9906	1.40	1.99	25.2
4260	1.8696	0.24	0.36	86.9
4380	2.1135	0.24	0.32	88.0
4530	2.6747	0.32	0.34	87.3

In Figure 31 a comparison between Test 1, Test 6 and Test 9 results is reported:

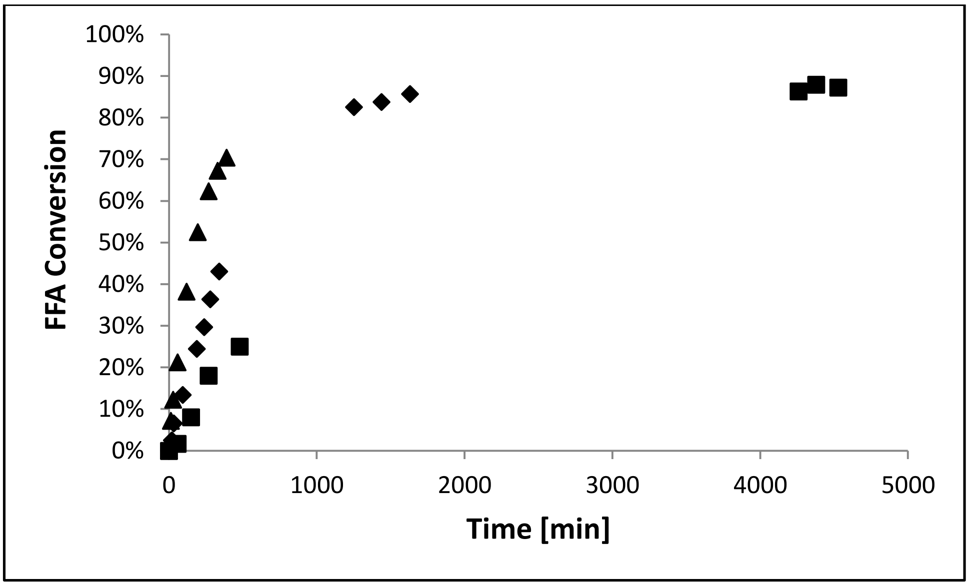


Figure 31: Comparison between FFA conversion at different temperatures, 40°C (squares), 50°C (diamonds) and 60°C (triangles)

The trend of all the experiments results seems reasonable and coherent. Moreover, from the observation seems that the equilibrium conversion is not strongly dependent from temperature in the range 40-60°C.

After about 200 hours of work the catalyst performance remained stable, meaning that at the operative condition used no degradation of the polymeric matrix and no loss (leaching) of active sites was observed. The catalyst life time is a crucial and underestimated factor that is very important for an eventual large scale application of every catalytic process. In this case Amberlyst 46 demonstrated to be both very active and stable for the deacidification reaction in a system that was voluntary kept monophasic in order to have all the disadvantages of the double phase system.

Continuous Reactor

In this section the results of the continuous reactor are shown. As reported in the *Experimental* section the reactor is a packed bed reactor that works at 5 bar. It was chosen to work in a pressurized system in order to make reactions at a temperature higher than the one of the normal boiling point of methanol. Of course, higher temperature allows a higher reaction rate and a more rapid equilibrium. Similarly to the tests performed in batch reactor concerning the catalyst life time, the Amberlyst 46 charged in the reactor was never changed or treated with pure methanol in order to study its mechanical and chemical stability.

Also in these tests a molar MeOH/FFA ratio of 5 was used and the reactant volumetric flux was varied in order to have residence times between few minutes and six hours. The temperature range studied was 54-105°C, and the deacidification reactions were performed on sunflower and soybean oils.

In order to make easy the reading of the following Tables and Figures, all the data obtained with the packed bed reactor will be shown as FFA conversion versus reactant residence time, calculated dividing the volume of the catalytic bed (at the sampling point height) by the volumetric flow of the reagents.

In the reactor the catalyst Amberlyst 46 was charged in its wet form. The very first data obtained were performed at 55°C using sunflower oil are reported in Figure 32, plotted as FFA content (weight perchentage) sampled at the reactor outlet versus time. In this peculiar run, the time axis represents the working time, i.e. the time the reactor was continuously working:

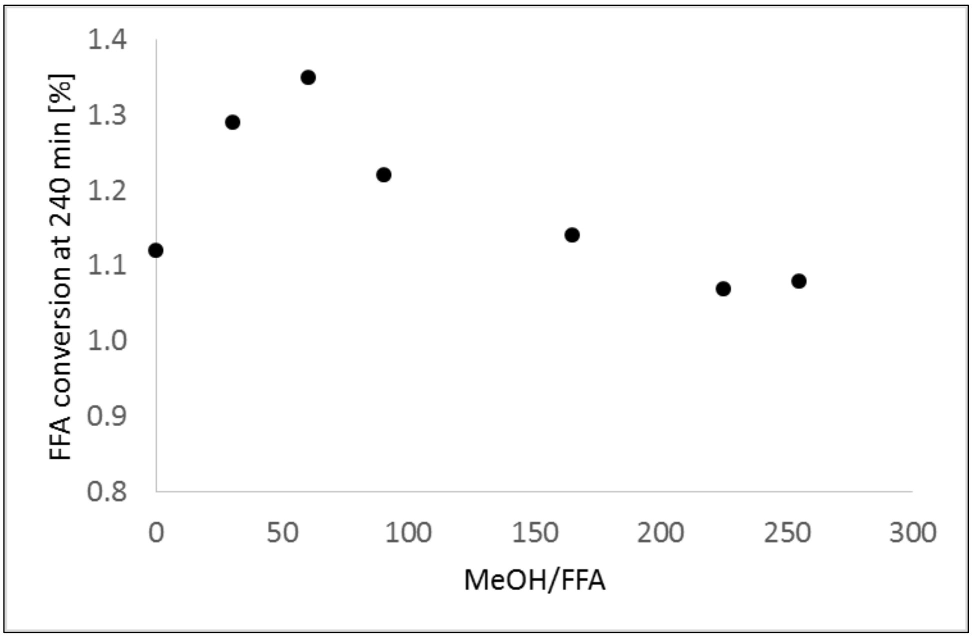


Figure 32: FFA content of the outlet flow of the reactor

The phenomenon of the resin equilibration was observed again in this test, only with opposite effects. FFA content instead of decreasing, in the first hours tend to increase. This because the water adsorbed on the resin exceeded the equilibrium quantity and thus was released by the catalyst acting on the chemical equilibrium. When the real equilibrium between all the four species involved in the deacidification reaction was reached, the FFA content starts to decrease and reach the real equilibrium value, with a positive conversion.

After this first observation, two tests were performed trying to measuring the water content of the oil. This was possible using the Karl Fischer analysis.

After the instrument calibration, we noticed that on oil samples the water content analysis was not reproducible. This because of the too high viscosity of the oil, which was difficulty dissolved by the Karl-Fisher solvent. For this reason the protocol analysis was modified using as solvent for the titration a mixture of toluene (about 20 mL for each titration) and the dedicated Hydranal® solvent (about 10 mL for each titration).

Both the tests were performed at 65°C, changing the volumetric flowrate and thus the results are reported altogether in Table 41:

Table 41: Determination of the water concentration at different residence time

Residence time [min]	Water concentration [ppm]
0	695
2.5	692
5	784
7.5	690
10	623
30	977
60	991
90	996
120	961
180	1019
210	1005
270	1173

The water content varies with a certain error, but its trend is clear. Water formed from the deacidification reaction tends to reach a stable value of about 1000 ppm, that could be approximated to the solubility of water in the oil at 65°C.

In order to investigate this aspect two batch reactions were performed following both the FFA conversion and the water content in the samples. It was chisen to work in a batch reactor because the sampling procedure was easier. The first experiment was carried out at 50°C, the results obtained are reported in Table 42, in which, together with the conversion calculated on FFA ($\text{Conversion}_{\text{FFA}}$), also the conversion calculated on the water formed is reported ($\text{Conversion}_{\text{W}}$):

Table 42: FFA deacidification test with the determination of water content, 50°C

Time [min]	FFA [%w]	$\text{Conversion}_{\text{FFA}}$ [%]	Water [ppm]	$\text{Conversion}_{\text{W}}$ [%]
0	4.17	0.0	779	0.0
20	3.57	14.2	-	-
40	3.34	20.8	-	-
60	3.20	23.7	1038	25.1
120	2.80	33.5	994	22.6
180	1.30	42.5	-	-
300	1.68	60.3	1021	24.9
1560	0.32	92.0	995	22.6

Unfortunately the initial water content in the oil was near to the critical 1000 ppm value. Due to this, only the first point gives a reasonable water based conversion compared to the FFA conversion.

Table 43 reports the results obtained in the second batch experiment, performed at 60°C and using soybean oil. In this experiment the oil was first put under stron agitation in vacuum condition, in order to evaporate the maximum quantity of water avoiding reaching the plateau water concentration in the first minutes of reaction:

Table 43: FFA deacidification test with the determination of water content, 60°C

Time [min]	FFA [%w]	Conversion$_{FFA}$ [%]	Water [ppm]	Conversion$_{W}$ [%]
0	2.98	0.0	426	0.0
60	2.92	2.9	453	6.0
120	2.43	19.5	679	37.4
180	1.85	38.8	650	34.5
240	1.37	54.1	751	43.3
300	1.19	60.7	740	42.8

Except the second experimental point, the first three determinations seem coherent. However, the too high error in the water analysis, that is common when dealing with highly viscous and hydrophobic substances (the demonstration could be found in literature, or better could not be found since no one reported experimental data on water content in this kind of reaction) could only lead to gross error.

In order to evaluate whether the viscosity influences the water content analysis, three last deacidification tests were performed on acidified sunflower oil (using oleic acid, see *Experimental* section) blended with toluene (1:1 and 1:0.2 by weight) and diesel (1:1 by weight). Also in these three tests, the oil was subjected to a vacuum treatment overnight in order to remove the highest quantity of water possible.

In Table 44 the results concerning the experiment using toluene 1:1 by weight are reported, the test was carried out at 50°C:

Table 44: FFA deacidification of sunflower blended with toluene 1:1 by weight

Time [min]	FFA [%w]	Conversion [%]	Water [ppm]
0	4.40	0.0	449
60	4.09	7.2	668
120	3.75	15.3	1147
180	3.57	19.6	1501
240	3.40	23.4	1317
300	3.20	27.7	1322
495	2.85	35.8	1218
1380	1.79	59.1	1220
1740	1.11	75.1	1241

In Table 45 the results of the test performed with an oil:toluene blend of 1:0.2 by weight are reported. The test was carried out at 60°C

Table 45: FFA deacidification of sunflower blended with toluene 1:0.2 by weight

Time [min]	FFA [%w]	Conversion [%]	Water [ppm]
0	4.40	0.0	450
60	3.62	18.0	858
120	2.86	35.4	1574
180	2.34	47.4	1854
240	1.71	61.3	1635
300	1.58	64.9	1719
490	1.05	76.7	1705

Comparing the results obtained in these two experiments, the FFA conversion reaches the same equilibrium value and the final water content is coherent with the temperature used in the tests, i.e. it is higher at higher temperature. The value of equilibrium water concentration is slightly higher compared the test with only pure oil (about 1000 ppm). This could be due to the effect of toluene, which increases the water solubility in the oil mixture because is more polar. In any case, when the equilibrium value is reached, a great fluctuation of the results is always experimented.

The last test was performed at 60°C, Table 46 reports the results obtained:

Table 46: FFA deacidification of sunflower blended with diesel 1:1 by weight

Time [min]	FFA [%w]	Conversion [%]	Water [ppm]
0	4.40	0.0	450
60	3.63	18.4	1218
120	287	35.8	1007
180	2.28	48.0	989
240	1.98	55.5	965
300	1.54	65.1	1015
360	1.24	72.2	996

In this case the equilibrium water content reached is very similar to the one obtained with pure oil, this because diesel is a mixture of hydrocarbon and thus is completely apolar.

These tests demonstrated that the water measurement is a very critical point, and that the maximum solubility of water is dependent on the temperature and not strongly dependent by the kind of oil and in any case affected by a high error.

For this reason the water content was not measured in the following tests and when it is present, it should be used only as an indication.

The results obtained with the packed bed reactor are reported in the following. A total of 7 different reaction temperatures were experimented, in particular in the range 54-105°C, the pressure for all these tests was set to 5 bar.

Test 1

Test 1 was performed at 54°C, the results are reported in Table 47:

Table 47: Test 1, results of the FFA deacidification in packed bed reactor at 54°C

Residence time [min]	FFA [%w]	Conversion [%]
0.0	4.41	0.0
3.5	4.26	3.5
6.5	4.18	5.2
17.4	3.93	10.9
52.5	3.16	28.3
62.9	3.02	31.5
99.2	2.79	36.7
119.0	2.73	38.1
262.4	2.60	41.1
314.2	2.51	43.1

Test 2

Test 2 was operated at 65°C. The results obtained are reported in Table 48:

Table 48: Test 2, results of the FFA deacidification in packed bed reactor at 65°C

Residence time [min]	FFA [%w]	Conversion [%]
0.0	4.70	0.0
3.5	4.47	5.0
9.7	4.25	9.6
18.2	3.86	17.9
51.1	3.16	32.8
62.9	2.90	38.3
102.0	2.25	52.2
119.0	2.07	56.0
262.4	1.95	58.5
314.2	1.83	61.0

Test 3

Test 5 was operated at 75°C. This test is performed at a temperature higher than the normal boiling point of methanol but, being in a pressurized system, no problems due to evaporation of methanol were detected. In Table 49 are shown the experimental results:

Table 49: Test 3, results of the FFA deacidification in packed bed reactor at 75°C

Residence time [min]	FFA [%w]	Conversion [%]
0.0	4.70	0.0
3.5	4.56	3.0
6.5	4.34	7.65
18.2	4.07	13.5
49.5	3.30	29.8
59.9	2.96	37.0
99.2	2.45	47.8
119.0	2.24	52.3
262.4	1.54	67.3
314.2	1.42	69.8

Test 4

In this Test the temperature was set to 85°C. The experimental results collected are reported in Table 50:

Table 50: Test 4, results of the FFA deacidification in packed bed reactor at 85°C

Residence time [min]	FFA [%w]	Conversion [%]
0.0	4.34	0.0
3.2	4.09	5.8
5.3	3.96	8.8
11.9	3.54	18.4
21.0	3.08	29.1
48.2	1.26	71.0
57.6	1.05	75.8
80.0	0.84	80.7
95.9	0.75	82.8
179.8	0.66	84.7
215.6	0.61	86.0
315.0	0.56	87.1
377.5	0.49	88.7

Test 5

In this test a temperature of 95°C was set. The results obtained are reported in Table 51:

Table 51: Test 5, results of the FFA deacidification in packed bed reactor at 95°C

Residence time [min]	FFA [%w]	Conversion [%]
0.0	4.34	0.0
3.8	4.01	7.6
5.1	3.88	10.6
11.2	3.48	19.8
19.0	3.02	30.5
58.2	0.89	79.6
69.8	0.66	84.8
77.3	0.54	87.5
92.6	0.33	92.5
166.0	0.33	92.5
199.0	0.33	92.3
286.7	0.32	92.6
343.6	0.32	92.6

Test 6

Test 6 was performed at 105 °C. This is the highest temperature tested during the experiments. The results collected are reported in Table 52:

Table 52: Test 6, results of the FFA deacidification in packed bed reactor at 105°C

Residence time [min]	FFA [%w]	Conversion [%]
0.0	4.34	0.0
4.2	3.89	10.4
5.1	3.67	15.5
10.6	3.25	25.2
17.2	2.58	40.5
63.8	0.65	85.0
76.5	0.41	90.6
77.1	0.42	90.4
92.4	0.36	91.6
159.9	0.37	91.4
191.7	0.37	91.5
259.1	0.37	91.5
310.6	0.37	91.5

Compared to Test 5, the equilibrium conversion at 105°C resulted, even if only by one unity, less than the one obtained at 95°C. This result could be ascribed to the higher water solubility in the oil.

Test 7

In Test 7 the operative conditions of Test 4, i.e. temperature of 85°C, was repeated, changing the oil type, from soybean oil to acidified sunflower oil. Oleic acid was added to maintain a similar FFA content. The results obtained are reported in Table 53:

Table 53: Test 7, results of the FFA deacidification in packed bed reactor at 85°C, sunflower oil

Residence time [min]	FFA [%w]	Conversion [%]
0.0	4.41	0.0
3.2	4.15	5.8
5.1	4.04	8.4
11.3	3.85	12.8
19.0	3.12	29.2
48.5	1.28	71.0
58.1	1.10	75.1
77.3	0.87	80.3
92.8	0.76	82.8
170.8	0.68	84.5
204.8	0.63	85.8
287.1	0.58	86.9
344.3	0.53	88.0

In Figure 33 is reported a comparison between the two homologue Tests.

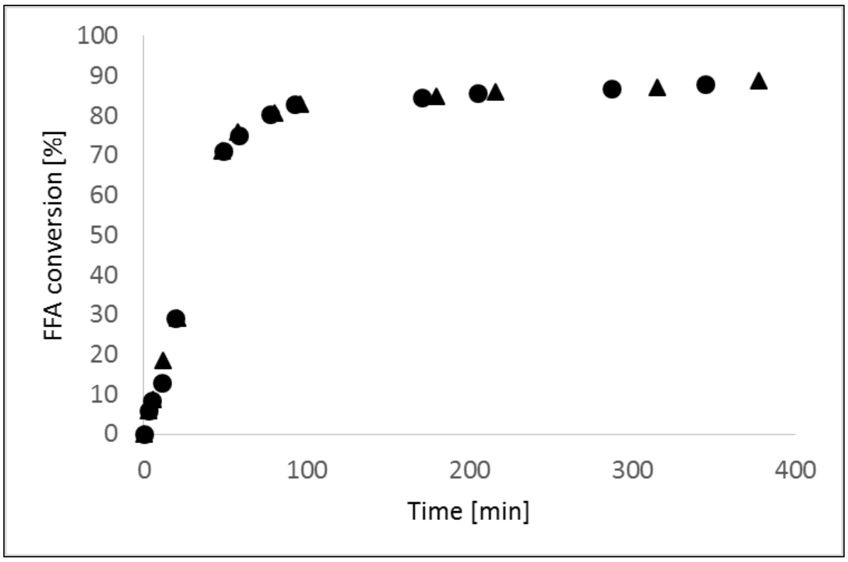


Figure 33: Comparison between the experimental results of Test 7 (circles) and Test 4 (triangles)

A very good overlap between these two experiments meaning that the acidic composition of the oil, i.e. the different FFA species possess the same behavior towards the resin and the reaction, which is logic since they are all long chain fatty acid, belonging to an homologues series.

Test 8

Test 8 is a repetition of Test 2 (deacidification at 65°C) that was performed to establish if the catalyst had lost its activity towards the deacidification reaction. In Table 54 the results of this final test are reported:

Table 54: Test 8, results of the FFA deacidification in packed bed reactor at 65°C

Residence time [min]	FFA [%w]	Conversion [%]
0.0	4.41	0.0
3.9	4.17	5.4
8.67	3.98	9.8
21.6	3.62	17.9
59.0	2.77	37.3
70.8	2.57	41.7
130.6	2.04	53.8
156.7	1.91	56.6
324.5	1.65	62.6
389.1	1.57	64.4

In Figure 34 a comparison between the results of Test 2 and Test 8 is reported:

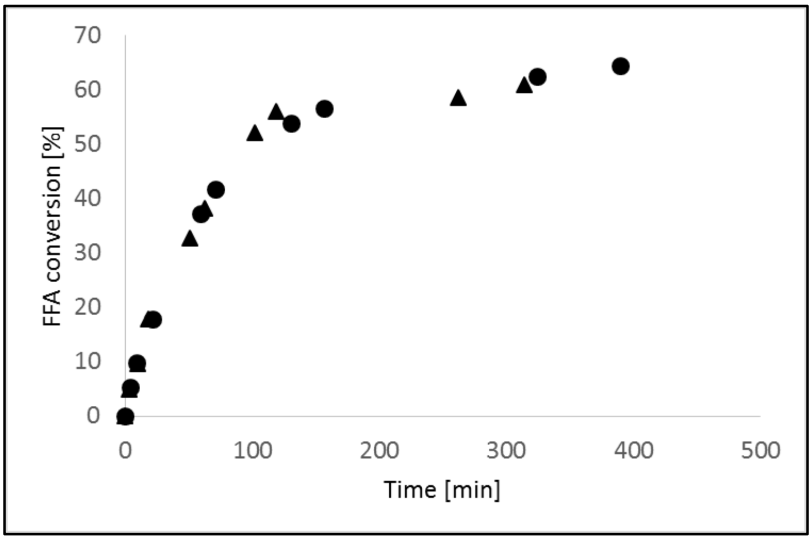


Figure 34: Comparison between the experimental results of Test 2 (triangles) and Test 8 (circles)

After about 600 hours of work, considered not only the cumulated time of reaction but also the time needed for reaching the temperature, the equilibration of the resin and the set of the reactant volumetric flowrate, the performance of the catalyst remained comparable and stable, demonstrating once again the good choice of the catalyst and its potentiality to be used in a real process.

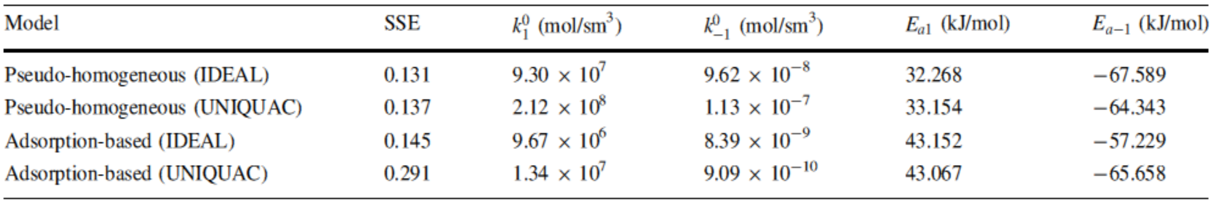
Kinetic Modelling

As previously introduced, in this part of the work two different kinetic models were considered, a pseudo-homogeneous and an adsorption based one which accounts for the different affinities toward the polymeric matrix of all the species involved in the reaction and the solvent (triglycerides) following the same approach proposed by Popken et al. (2000).

For both the models, the ideal and non ideal behaviors of the mixture were considered, and the results were compared. A good kinetic interpretation is essential for the optimization of the process, because the simulation of the reactor behavior in a vast range of operative configurations is possible (Myint & El-Halwagi, 2009).

On the basis of the experimental results obtained in the previous section, two different models, pseudo-homogeneous and adsorption-based, were proposed and the corresponding kinetic parameters were regressed. The optimized parameters for both models are reported in Table 55 in with the residual errors (SSE):

Table 55: Optimized kinetic parameters for the FFA esterification using pseudo-homogeneous and adsorption-based models, taken from (Pirola, et al., 2015)



Model	SSE	k_1^0 (mol/sm^3)	k_{-1}^0 (mol/sm^3)	E_{a1} (kJ/mol)	E_{a-1} (kJ/mol)
Pseudo-homogeneous (IDEAL)	0.131	9.30×10^7	9.62×10^{-8}	32.268	−67.589
Pseudo-homogeneous (UNIQUAC)	0.137	2.12×10^8	1.13×10^{-7}	33.154	−64.343
Adsorption-based (IDEAL)	0.145	9.67×10^6	8.39×10^{-9}	43.152	−57.229
Adsorption-based (UNIQUAC)	0.291	1.34×10^7	9.09×10^{-10}	43.067	−65.658

It is important to highlight that all the activation energies for the heterogeneously catalyzed reaction calculated in this work are apparent activation energies, not the true values for the chemical reaction. In fact, these energies correspond to the sum of all the micro-steps involved in the heterogeneous catalytic process. For this reason, the negative value of the activation energies obtained for the inverse reaction should be considered not astonishing.

Even if the pseudo-homogeneous model does not consider the adsorption of both reactants and products, its use permits to better calculate the experimental trends, especially for the runs performed at high temperatures, respect to the more sophisticated adsorption-based model. This is probably due to the not-correct values of the adsorption constants, which were measured for the binary non-reactive mixtures at a fixed temperature (25 °C), far from the experimental operative conditions. Moreover, these numerical values were obtained for a similar, but different, catalyst, i.e., Amberlyst 15. For these reasons, a regression of the adsorption-based model kinetic parameters together with the binary adsorption constants of water and methanol was performed, assuming valid that $K_{OIL} = 0$ and $K_{FAME} = K_{FFA} = \frac{K_{MeOH}}{3.5}$

The final optimized parameters are reported in Table 55:

Table 56: Adsorption-based model kinetic parameter, regressed together with the water and methanol adsorption equilibrium constants, taken from (Pirola, et al., 2015)

Adsorption-based model	SSE	k_1^0 (mol/sm^3)	k_{-1}^0 (mol/sm^3)	E_{a1} (kJ/mol)	E_{a-1} (kJ/mol)	K_{H_2O}	K_{MeOH}
IDEAL	0.09	3.22×10^6	6.96×10^{-1}	40.467	−55.796	1.74×10^{-2}	8.04×10^5
UNIQUAC	0.09	5.52×10^5	1.20×10^2	35.398	−58.339	5.16×10^{-7}	4.03×10^5

A comparison between some experimental data and the calculated behavior is shown in Figure 35.

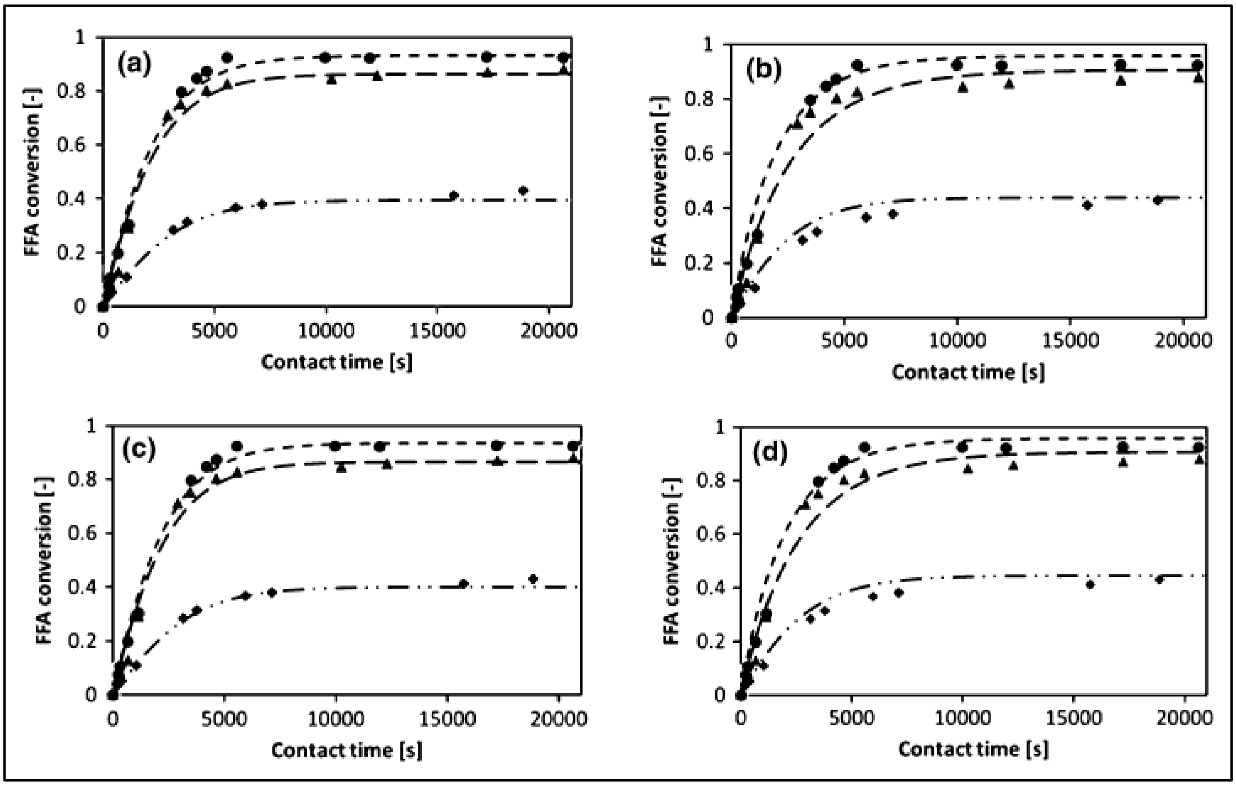


*Figure 35: Experimental FFA esterification, experimental data (points) at 95°C (circles), 85°C (triangles), and 54°C (diamonds) and simulated curves using **a** the adsorption-based model with UNIQUAC, **b** the pseudo-homogeneous model with UNIQUAC, **c** the adsorption-based model with IDEAL (activity coefficients = 1), **d** the pseudo-homogeneous model with IDEAL (activity coefficients = 1), taken from (Pirola, et al., 2015)*

From this Figure, it is clear how an adsorption-based model better fits the experimental data reported, that is particularly true near the equilibrium condition. The calculation of the activities considering the UNIQUAC model does not influence the overall SSE probably because the experimental amount of methanol used was chosen in order to have only a monophasic liquid mixture and then corresponding to mixture compositions only lightly non-ideal. Nevertheless, being the system oil/FFA/FAME/methanol/water highly non-ideal for others several compositions, a possible formation of two liquid phases can be calculated only using this more realistic thermodynamic approach, and thus its use is preferable.

The use of UNIQUAC model in order to take into account the non-ideality of the liquid medium is consequently advantageous when using starting vegetable oils characterized by higher FFA content. In this case, with the UNIQUAC adsorption-based model, it is possible to predict the behavior of the system, and it is possible to design a series of PBRs each of which dimensioned in order to avoid the liquid demixing. Proper water separation procedures will be necessary between two consecutive reactors. A detailed optimization of this kind of process will be considered in future works

Carotenes recovery from Crude Palm Oil

As previously introduced, the aim of this part of the work was to investigate the possibility to perform the deacidification reaction of crude palm oil preserving the stability of carotenes. Deacidification tests were conducted by monitoring both the FFA and carotenes content.

The oil was characterized by a FFA content of 3.50$\%_w$ and a concentration of carotenes of 350 ±5 ppm.

A first set of 15 experiments were carried out at 60 °C and at an agitation of 250 rpm. A second set of 16 batch experiments was performed increasing the initial FFA content by the addiction of palmitic acid with the aim to study the stability of carotenes at different FFA concentrations (from 3.50 $\%_w$ up to 7.70 $\%_w$).

The catalyst used in the first experimental run was always reused for all the 31 runs to study the stability of the resin during the esterification reaction.

In Figure 36 the results of some runs belonging to the first set are reported. It was avoided a full detailed report of the data because these observation are the same reported in the first part of the "*Batch Reactor, study on the catalyst stability*" section.

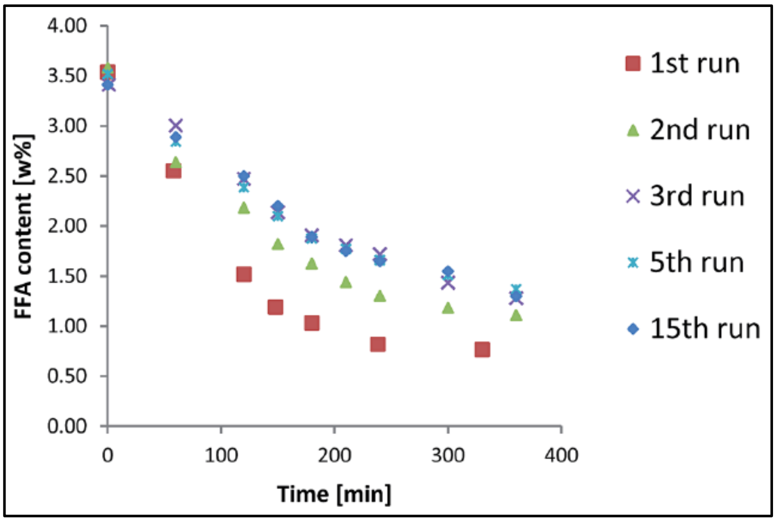


Figure 36: CPO deacidification results, FFA weight percentage versus time, taken from (Pirola, et al., 2014)

The FFA content in oil decreases faster in the first and in the second experimental run due to the adsorption of water onto the resins. In fact, the catalyst was charged in its dry form the first time and the water produced by the reaction equilibrated onto the catalyst surface.

In Figure 37 the final concentration of carotenes is reported at the end of the reactions (each experiment lasted 6 h) versus the number of the first set of experimental runs.

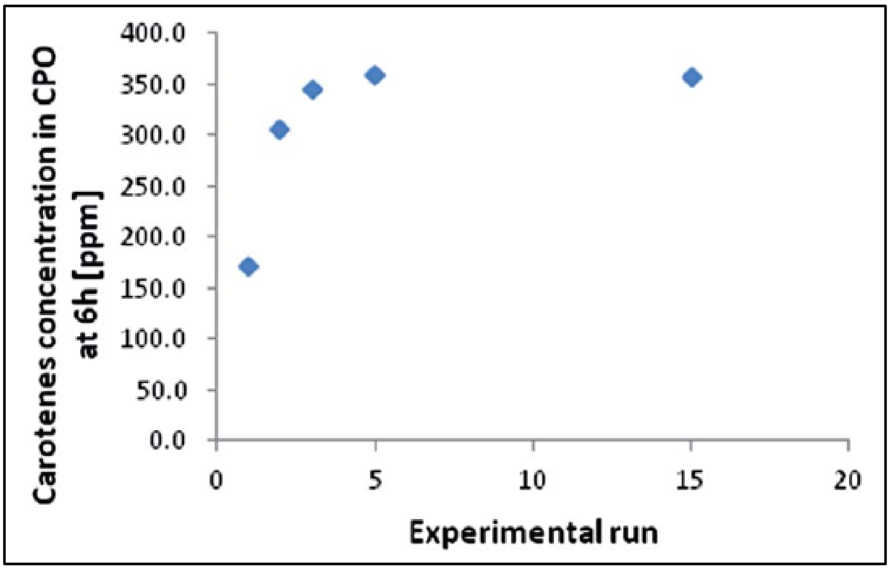


Figure 37: Carotenes concentration at the end of the first set of experimental runs, taken from (Pirola, et al., 2014)

In the first 5 runs, i.e. in the first 300 hours of work, the final concentration of carotene resulted lower compared the average one of crude palm oil, while for the others it reaches a plateau. This observed decrease in carotenes concentration could be ascribed to their adsorption on the catalyst particles.

Fig. 5 shows both the final FFA conversion and the carotenes content in CPO versus the initial acidity of CPO.

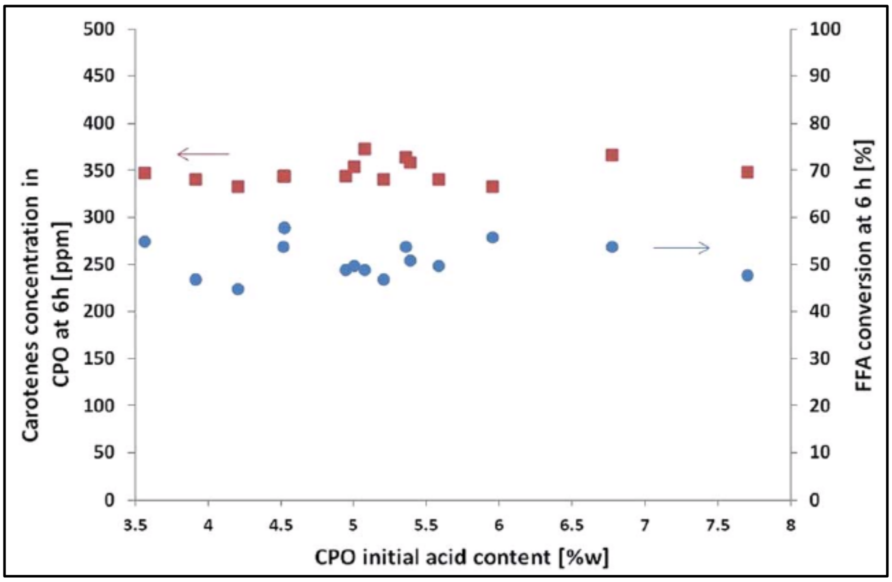


Figure 38: Experimental FFA conversion (blue points) and final carotenes content (red squares) versus initial FFA content in CPO, taken from (Pirola, et al., 2014)

The concentration of carotenes remained stable and thus the presence of FFA does not influence the carotenes degradation. This result is very important because the FFA content in crude palm oil is not constant, but varies depending on the type of oil, the harvesting period and the manufacturing process (O'Brien, 2008). On the other hand, the final conversion of FFA tends to remain stable, showing that the performances of the catalyst are not affected by the carotenes adsorption.

In order to investigate the adsorption of carotenes on the catalyst surface, a sample of fresh resin and one of the same after all the experimental determination were observed using an optic microscope. Figure 39 reports the images:

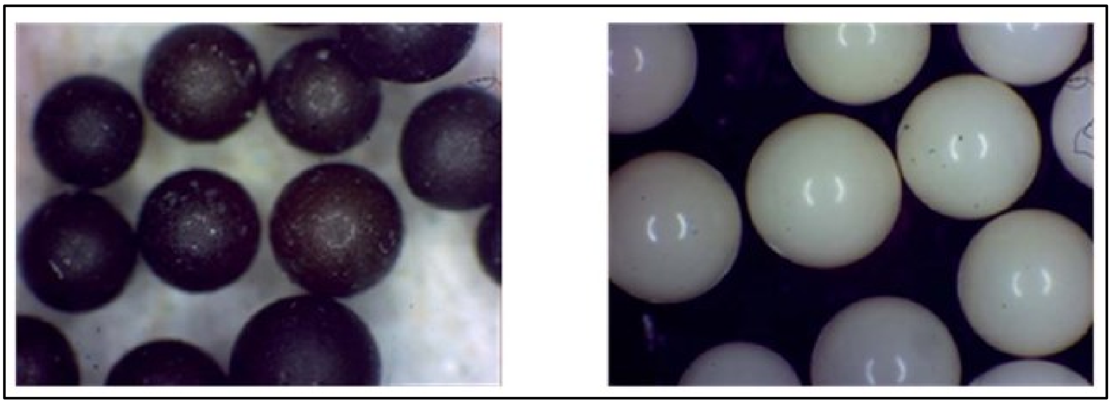


Figure 39: Amberlyst 46 images (x15) after (left) and before (right) all the experimental CPO deacidification tests. Taken from (Pirola, et al., 2014)

The magnifications show clearly that onto the resin surface there are species adsorbed. In a Soxhlet apparatus the total extraction of these products was carried out using n-hexane as solvent and then measuring the UV-vis spectra we noticed the presence of the typical carotenes absorption band. This result confirms that the carotenes are adsorbed on the resin, probably because of the chemical affinity between carotenes and the polymeric matrix of the catalyst.

Finally, the stability of the carotene adsorbed on the resin was evaluated by putting two samples of 2 g each of used catalyst in inert (N_2) and oxidizing (O_2) static atmosphere respectively. After 6 days an extraction using 15 mL of n-hexane was made and the absorbance for both the samples was registered. The results are shown in Figure 40:

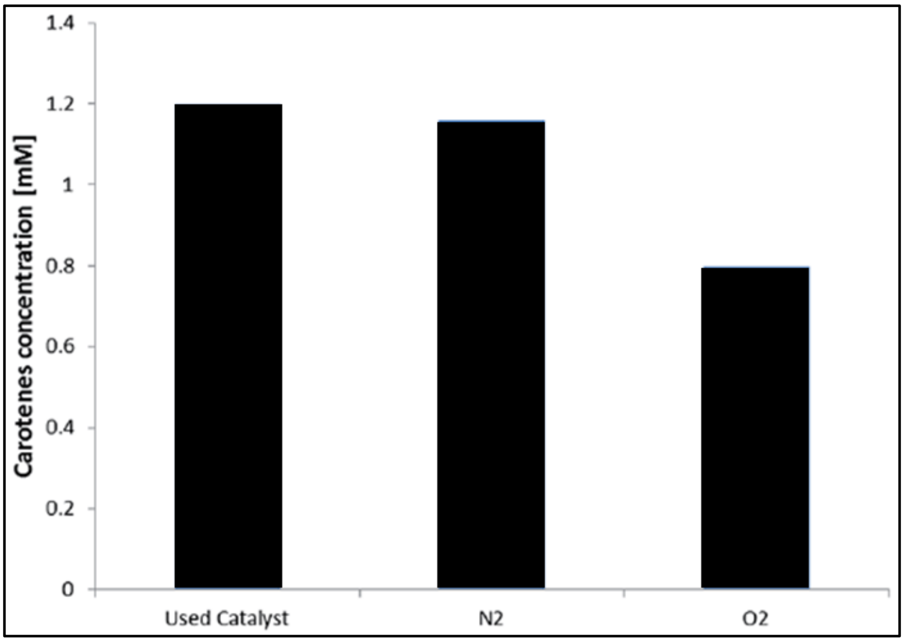


Figure 40: Carotenes concentration in 15 mL n-hexane extracts for 2 g of: (i) used catalyst after all the experimental runs; (ii) used catalyst in inert atmosphere (N2); and (iii) in oxidizing atmosphere (O2). Taken from (Pirola, et al., 2014)

The amount of carotenes remained stable after 6 days on the resin, meaning that the acid sites of the catalyst do not act on the degradation of carotenes. Differently, under oxygen atmosphere, the degradation of carotenes occurred and about the 40% of carotenes molecules were oxidized.

Considering a work by Henry et al. (1998) the time necessary to achieve this degradation value is about 9.4 days, however, considering that our experimental determination was made under an oxygen partial pressure of 1 atm, instead of about 0.2 atm, it can supposed that the adsorption on the resin surface limits the carotenes degradation.

Moreover, considering Figure 37 and using the molecular weight of beta-carotene as representative for all the carotenes group, a total of 71 mg of carotenes were adsorbed onto the resin surface. This estimation was made calculating an amount of 200 g of crude palm oil were used each experiment. From the first column of Figure 40 it is possible to calculate the amount of carotenes captured by the catalyst, which is 68 mg of carotenes, confirming the mass balance of the collected experimental data.

In conclusion, carotenes content was preserved in the deacidification of crude palm oil using an esterification reaction with methanol catalyzed by an acid ion exchange resin (Amberlyst A46). Moreover the adsorption of carotenes on the resin surface was observed satisfactory free fatty acid conversion was obtained and the catalyst performance was proved to be stable even after 186 hours of work.

Biodiesel Production, heterogeneous transesterification of vegetable oils

Homogeneous vs Heterogeneous catalyzed reaction

Homogeneous transesterification of oil is well known (Abbaszaadeh, et al., 2012) technique for obtaining biodiesel. For this reason only few reaction with different substrate conditions were performed using sunflower oil as feedstock, in order to be able to compare these results to the one obtained with heterogeneous catalysis.

In particular two Tests were performed on sunflower oil as it is, i.e. containing FFA and deacidified oil.

Test 1

In this Test the transesterification of sunflower oil using sodium hydroxide was performed. In Table 57 the operative conditions are reported:

Table 57: Test 1, operative conditions of the transesterification of sunflower oil

Oil mass [g]	100.04
Catalyst mass [g]	1.0056
FFA content [%w]	4.3
T [°C]	60
Agitation [rpm]	350

The results are reported in Table 58 and Figure 41:

Table 58: Test 1, experimental results

Time [min]	Oil conversion [%]
5	2.82
10	1.78
30	2.67
45	2.76
60	3.34
90	5.20

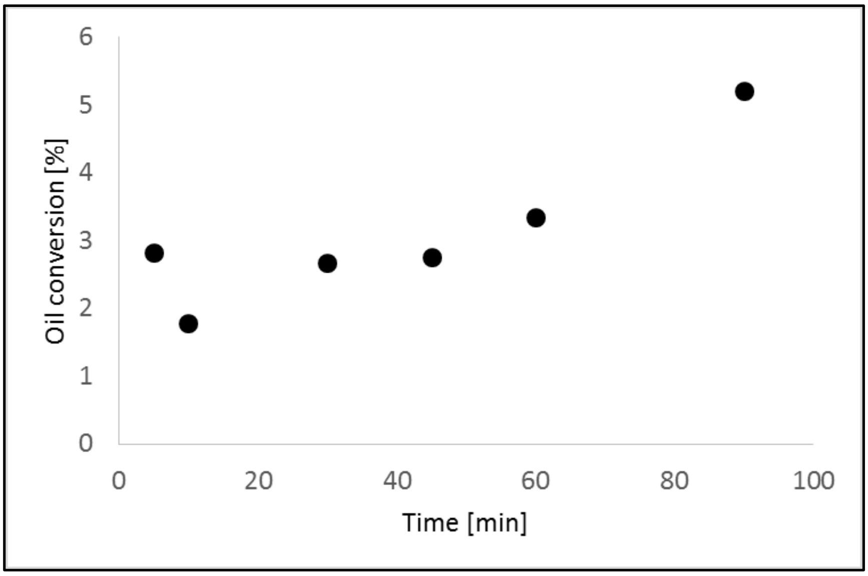


Figure 41: Test 1, experimental results

Very likely, the result obtained at 5 minutes is affected by an error. From it is evident how the FFA influences the conversion, since they neutralize the catalyst, and the oil conversion resulted very low.

Test 2

In the second Test deacidified oil was used. In Table 59 the operative conditions are shown:

Table 59: Test 2, operative conditions of the transesterification of decidified sunflower oil

Oil mass [g]	100.13
Catalyst mass [g]	1.0012
FFA content [%w]	0.3
T [°C]	60
Agitation [rpm]	350

In Table 60 and in Figure 42 the results obtained are reported:

Table 60: Test 2, experimental results

Time [min]	Oil conversion [%]
15	89.90
20	96.44
25	97.09
30	97.57
60	97.28

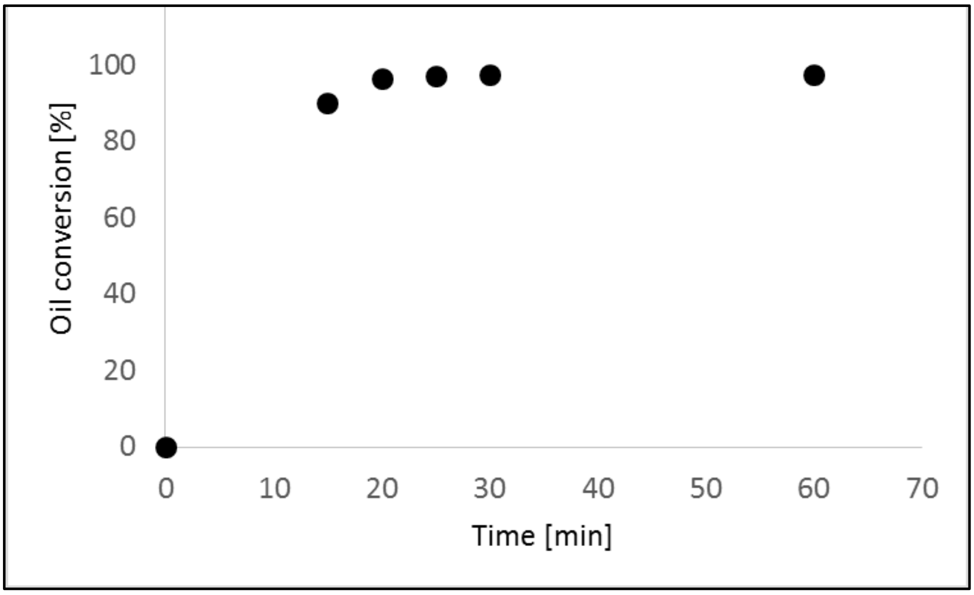


Figure 42: Test 2, experimental results

The results shown that the amount of FFA highly impacts on the oil conversion and that the deacidification process is essential.

After the heterogeneous transesterification was tested. The first catalyst used was the CaO. In particular it was conducted a study changing the molar ratio MeOH/oil, similarly to the experiments described in the "*Batch Reactor, study on the monophasic FFA esterification*" section.

In Table 61 the experimental conditions are reported for all the tests. The agitation was set to 600 rpm avoiding the influence of the external diffusion and the temperature was fixed to 60°C:

Table 61: Operative conditions of the transesterification reaction performed with CaO as catalyst

Oil mass [g]	Methanol mass [g]	MeOH/Oil
50.35	5.81	3
49.33	11.17	6
49.39	18.34	10
50.12	22.96	12
50.65	41.03	22

All the results obtained are reported in Table 62 and in Figure 43:

Table 62: Experimental results obtained in the heterogeneous transesterification of oil using CaO as catalyst

		Oil Conversion [%]			
	Time [min]	60	120	180	240
MeOH/Oil	3	22.56	45,33	58,77	74,36
	6	23,69	50,36	65,77	82,87
	10	25,68	58,30	70,98	85,25
	12	42,80	66,34	77,25	90,72
	22	49,90	63,24	75,64	91,82

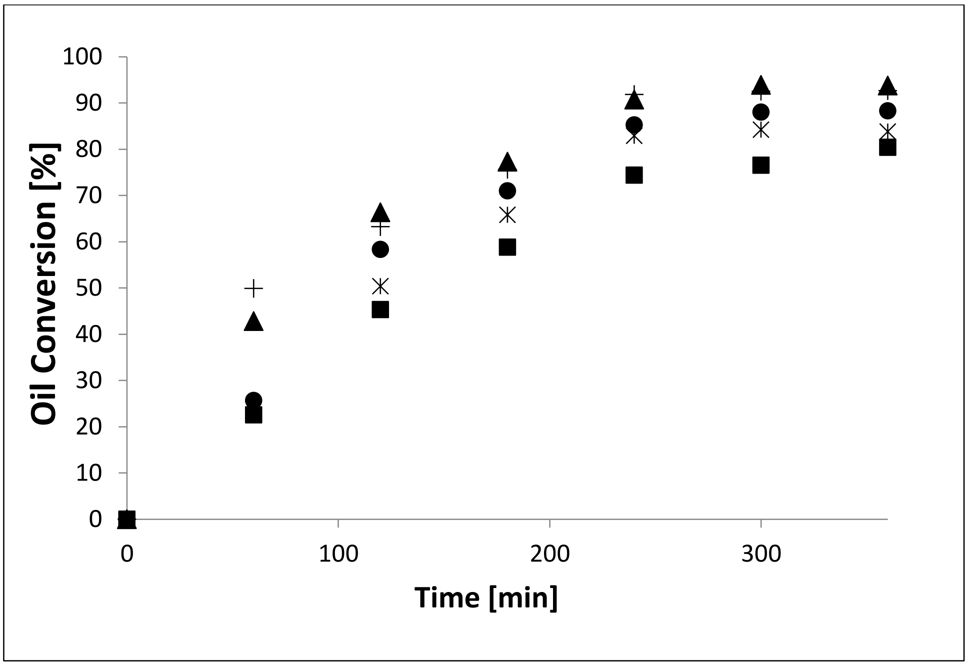


Figure 43: Experimental results of the heterogeneous transesterification of oil using CaO at different MeOH/oil ratios: 3 (squares), 6 (*), 10 (circles), 12 (triangles) and 22 (+)

The first consideration to be made observing Figure 43 is that a larger time is needed to achieve a high oil conversion, that is in any case not sufficient after 4 hours of reaction. This observation confirms and highlight the main restriction of the heterogeneous catalysis for the transesterification reaction. Another important aspect of the results is that the experiment performs with a MeOH/oil of 12 gave almost the same results of the one performed at a ratio of 22. This means that a too high excess of methanol does not affect the oil conversion and this is due for the same reason exposed previously, the formation of a two liquid phases system.

The CaO/Al_2O_3 catalyst gave very poor performances. In particular in a test performed at a MeOH/oil of 12 a conversion of 88% was obtained after 15 hours of reaction (at 60°C). This observation led to the conclusion to avoid using this catalyst.

For what concern the mixed oxides catalyst the reactions conditions used for the three tests performed are summarized in Table 63:

Table 63: Operative conditions of the tests performed using the mixed phase SrO and CaO catalyst

	Catalyst		
	25% SrCO3	50% SrCO3	75% SrCO3
Oil mass [g]	42,08	42,1	42,14
Methanol mass [g]	58,22	57,94	58,00
Catalyst mass [g]	1,4709	1,4741	1,4712

In Figure 44 the results in terms of oil conversion after 15 h of reaction are reported for these catalysts:

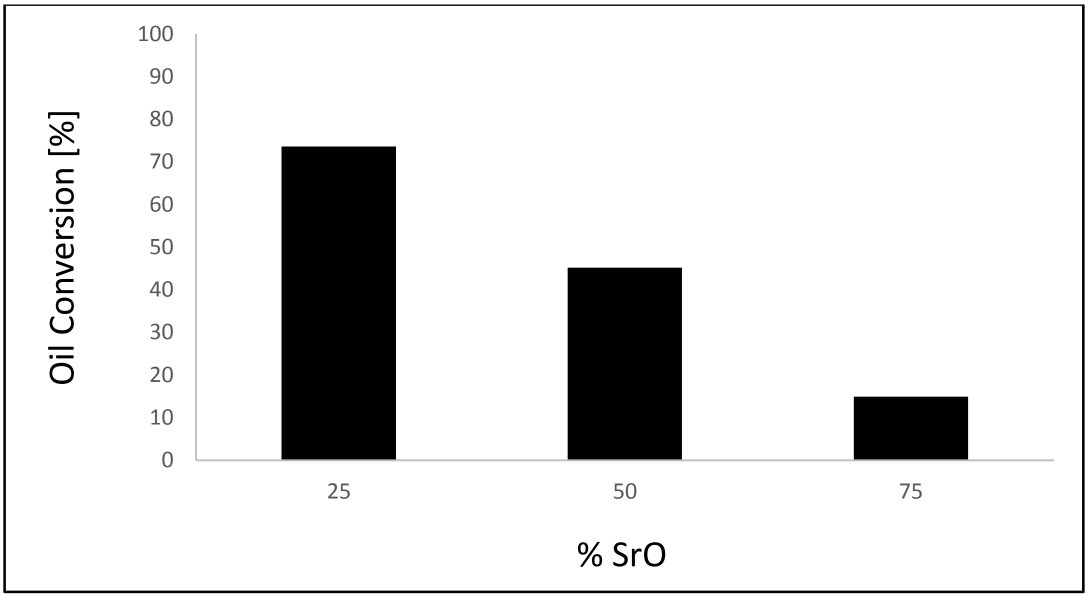


Figure 44: Experimental results of the heterogeneous transesterification of oil using mixed phase oxides

The oil conversion decreases when the amount of strontium oxides increases in the mixed oxide. Even if both CaO and SrO are strong bases, SrO does not contributes to catalyze the transesterification reaction.

The hypothesis that the SrO was not exposed at the catalyst surface was discarded by interpreting the XPS results. Figure 45 shows the XPS analysis of the sample $_{75\%}SrO_{25\%}CaO$, that evidences the presence of both the oxides at the catalyst surface. This result was the same for all the three samples.

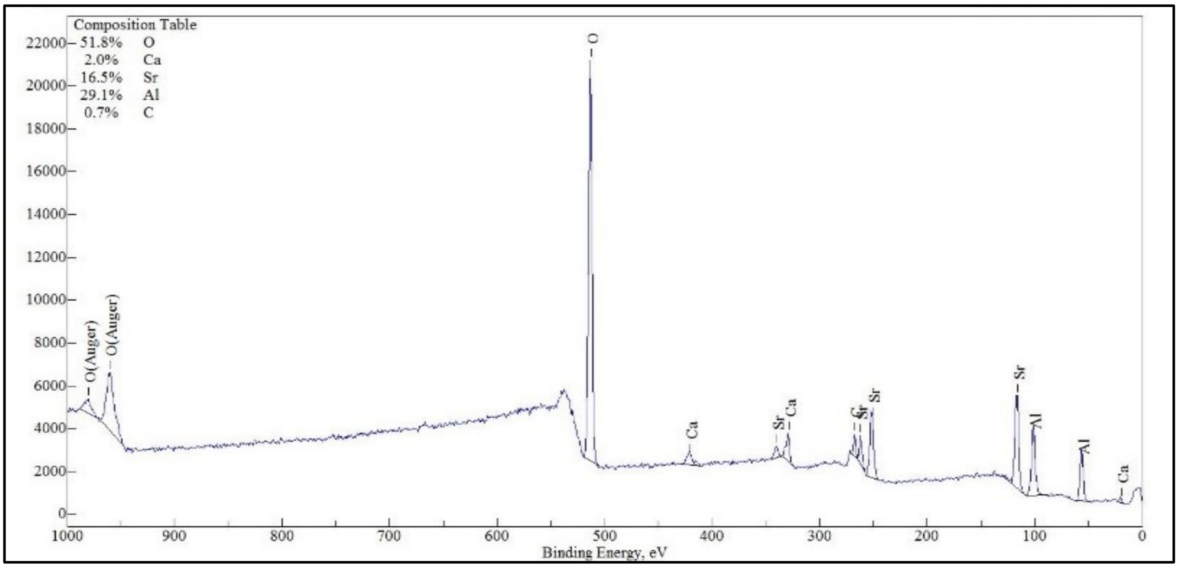


Figure 45: XPS spectrum of the sample $_{75\%}SrO_{25\%}CaO$

All the experiments performed with the heterogeneous catalysts highlighted their disadvantages compared to the homogeneous ones. Among the one tested, bulk CaO demonstrated to be the best alternative because it converts oil into FAME in half the time required by the other catalysts. Suitable strategies should be developed to make more competitive the use of heterogeneous catalysts since the too long time needed to reach an high oil conversion inhibits their use. In my thesis work a solution was proposed: the use of a co-solvent able to make the reactant system homogeneous permitting to increase the MeOH/oil ratio effectively, and thus increasing the reaction rate.

Co-solvent for the heterogeneous catalyzed transesterification

As previously introduced, under typical reaction conditions, i.e. methanol:oil molar ratio between 6:1 and 12:1 (Ma & Hanna, 1999), a biphasic liquid system forms. Together with the poor immiscibility, the catalyst must straddle both phases to react and if improperly agitated much of it might remain at the bottom of the vessel (Maeda, et al., 2010). The incentive for heterogeneous catalysts is clear but a step change in reaction rate is required for this process to compete with homogeneous catalysis.

Introducing a co-solvent to form a single phase solution could possibly increase the reaction rates to be competitive with a homogeneous catalyst.

A total of six different solvents were tested, i.e. acetone, tetrahydrofuran, chloroform, ethyl acetate, dichloromethane and heptane. In Table 64 the solubility of the two transesterification products (FAME and glycerol) are reported for all the solvents

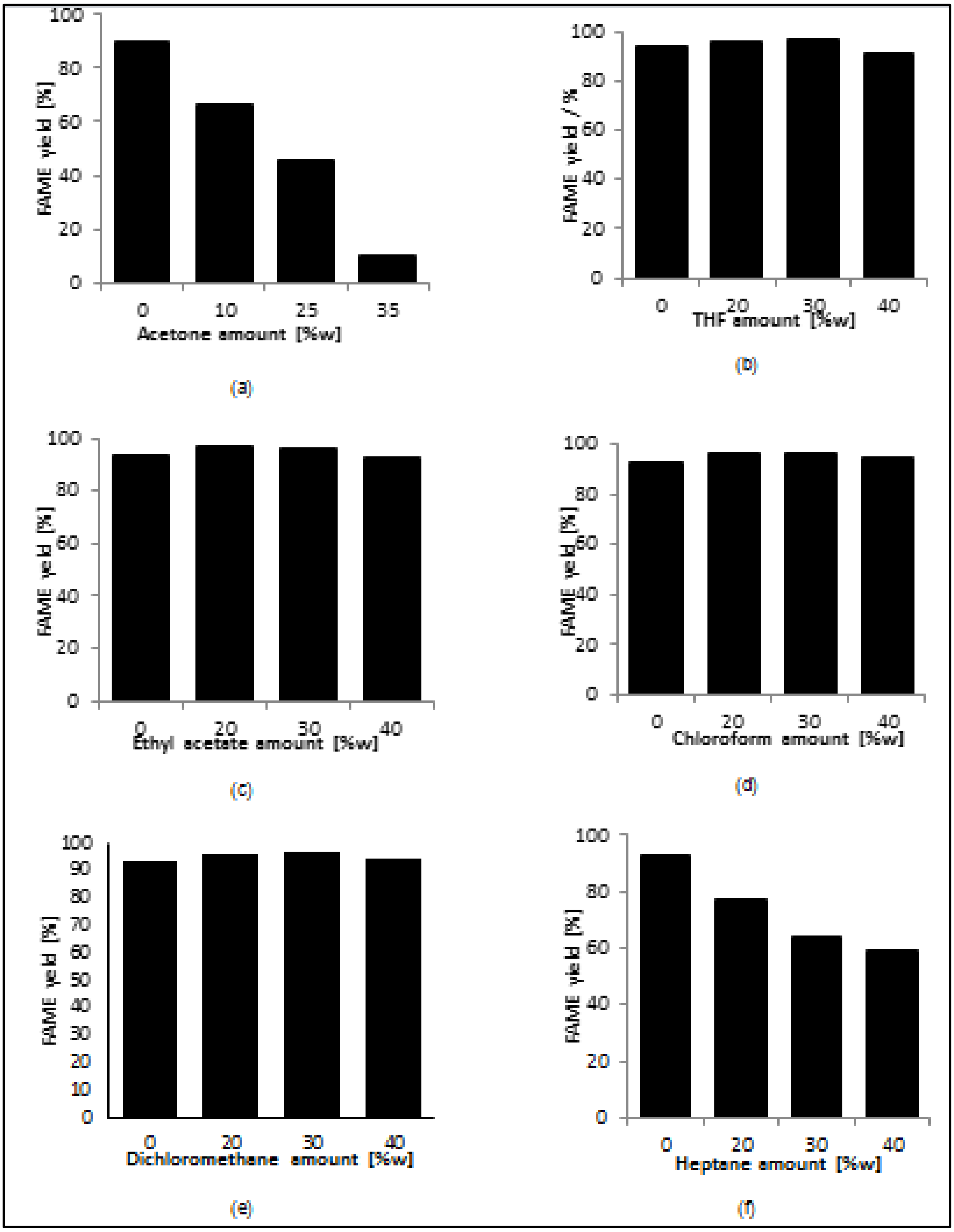
Table 64: Solubility at 60°C of FAME and glycerol in the six solvents tested: (S) soluble, (NS) non soluble.

	Solvents		
	Acetone	Chloroform	Tetrahydrofuran
FAME	S	S	S
Glycerol	NS	S	NS
	Heptane	Ethyl acetate	Dichloromethane
FAME	S	S	S
Glycerol	S	NS	NS

Tetrahydrofuran (THF) is one of the most promising co-solvents because it completely dissolves methanol and triglycerides but not glycerol (Boocock, et al., 1998), which simplifies the recovery of this co-product.

Previous studies considered THF as a co-solvent with a homogeneous catalyst, for which separation issues remain (Kim, et al., 2004). In another work, Sawangkeaw et al. (2007) used THF and supercritical methanol to transesterify palm oil.

A first study on the amount of solvent on the biodiesel yield after 6 hours of reaction (60°C, 600 rpm) was made. The results are reported in Figure 46:



(a) (b) (c) (d) (e) (f)

Figure 46: FAME yield Vs cosolvent amount after a reaction time of 6 h , (a):Acetone, (b) THF, (c):Ethyl acetate, (d): Chloroform, (e) Dichloromethane, (f): Heptane

The FAME yield is relatively insensitive for THF, ethyl acetate, chloroform dichloromethane above 90 %. It drops significantly with increasing mass fraction of acetone and heptane.

In particular, in Table 65 the results of the test performed with the 10% by weight are reported and in Figure 47 it is shown a comparison between the results of this test and the one performed without acetone, i.e. using only CaO and thus working in a biphasic system:

Table 65: Experimental results of the test performed with 10% by weight of acetone

Time [min]	Conversion [%]
0	0.0
60	27.0
140	33.8
190	57.6
262	64.3
360	66.9

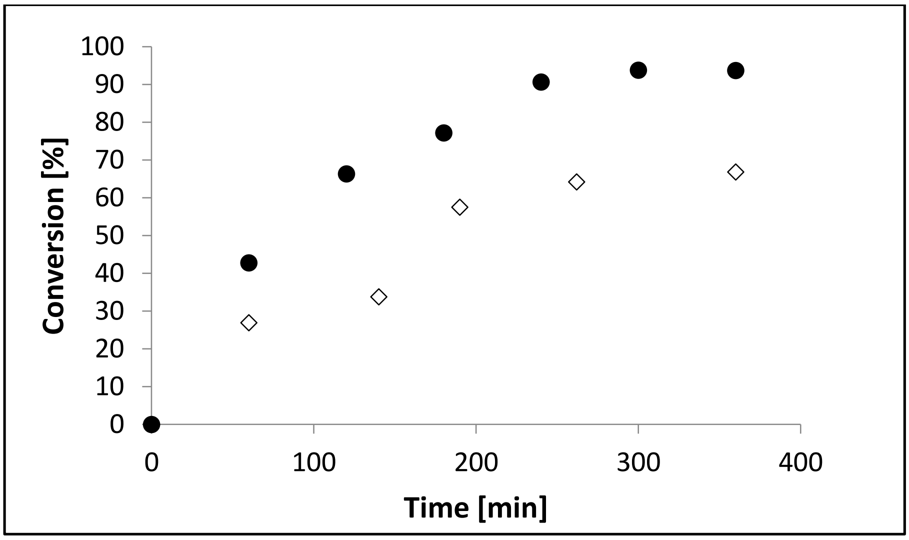


Figure 47: Comparison between the results performed with 10% by weight of acetone (empty points) and the ones performed with the typical heterogeneous catalytic process

The lower conversion obtained with acetone could be ascribed to the reaction between acetone and methanol to give a hemiacetal, shown in Figure 48:

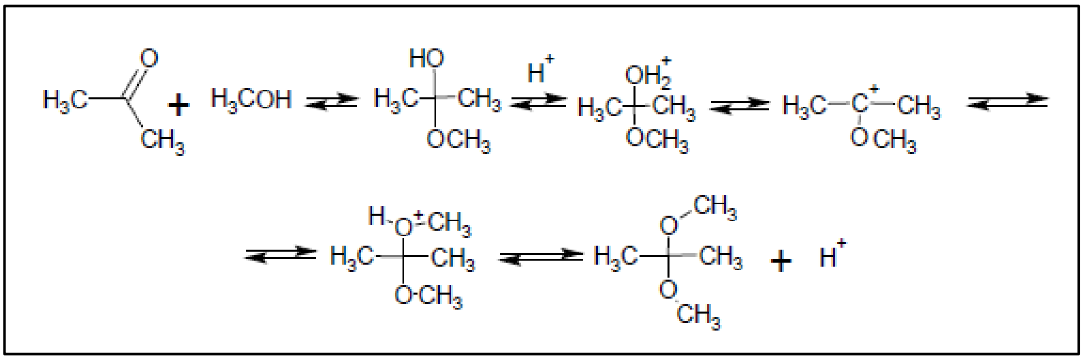


Figure 48: Hemiacetal formation reaction scheme

This hypothesis was considered the most probable since a GC analysis after 6 hours of a mixture of methanol and acetone in the presence of catalyst gave as results, together with the peaks of the substances, two other peaks belonging to the hemiacetal and the acetal. The Chromatogram is reported in Figure 46:

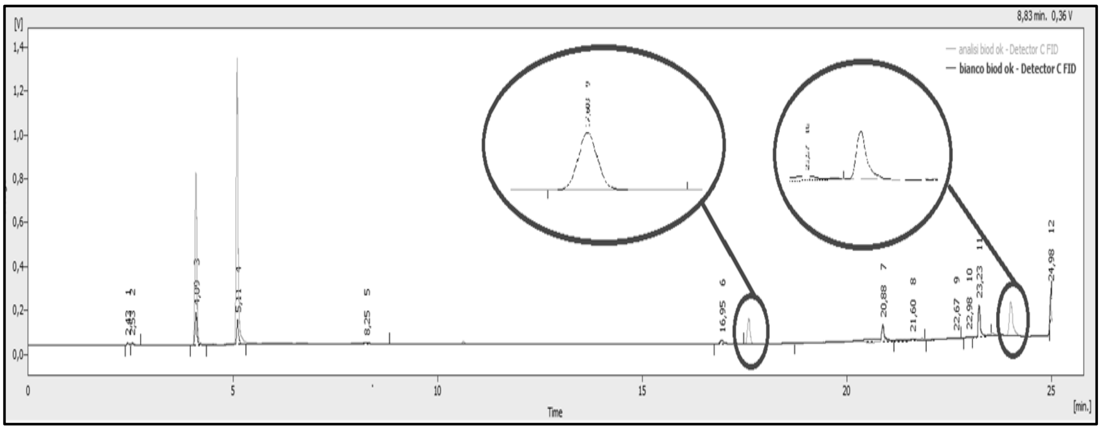


Figure 49: Chromatogram of the mixture methanol acetone in the presence of CaO after 6 hours

Figure 50 compares the FAME yield after 6 h for each co-solvent for which the yield was at the maximum.

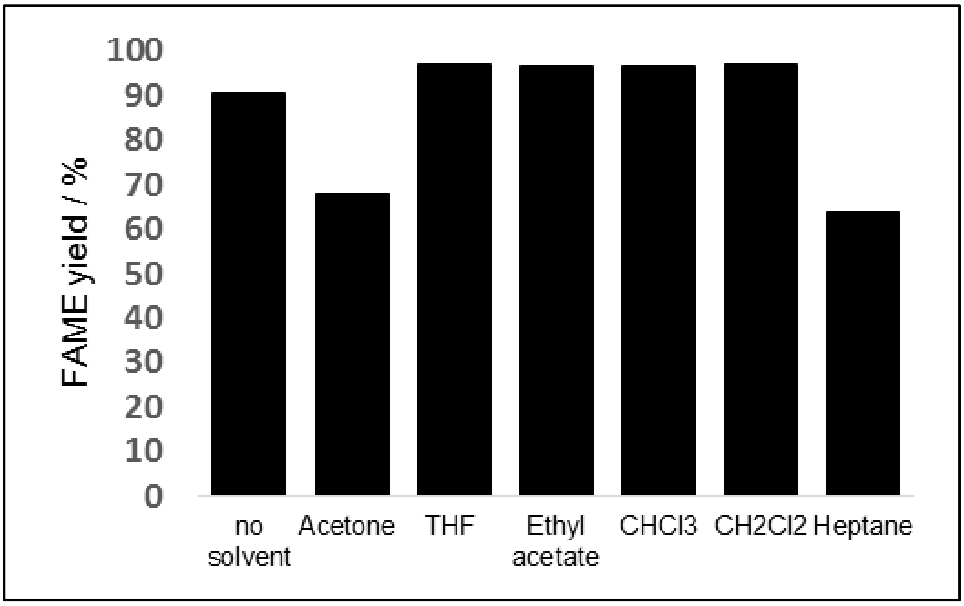


Figure 50: FAME yield obtained using different co-solvents after 6h of reaction time.

Figure 51 compares the reaction rates with each co-solvent, for which the yield was at the maximum.

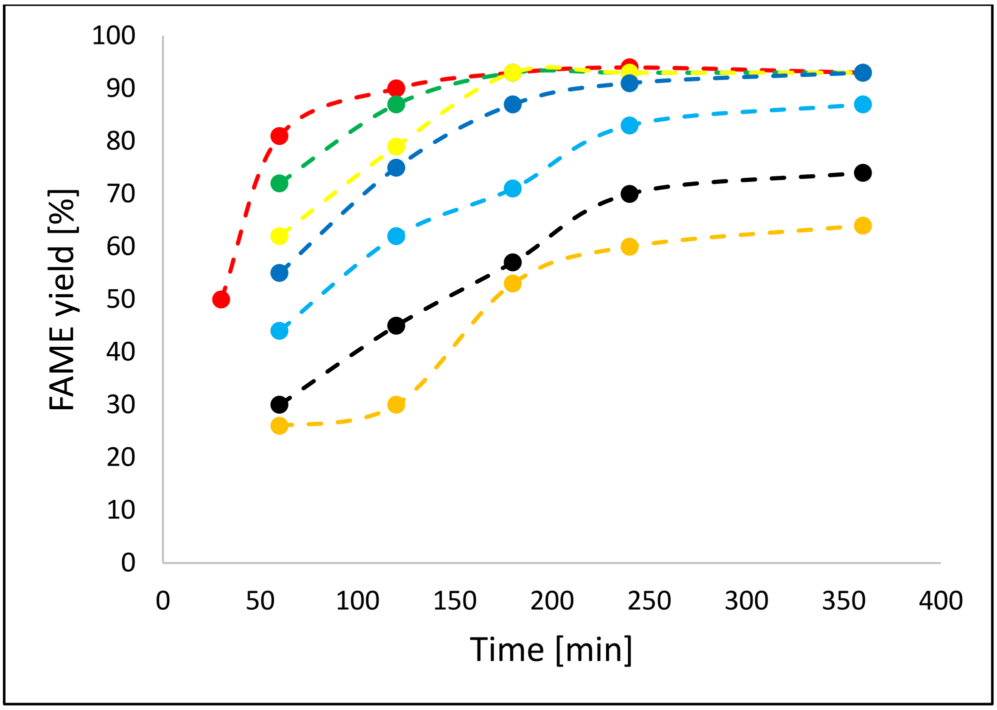


Figure 51: Reaction rate of the best results obtained with each cosolvent: acetone (orange, 10%w), heptane (black, 20%w), no solvent (light blue), chloroform (blue, 30%w), ethyl acetate (yellow, 20%w), dichloromethane (green, 30%w), THF (red, 30%w).

The reaction rates with acetone and heptane are lower than without a co-solvent. FAME yields are higher with THF, ethyl acetate and the chlorinated ones showed higher FAME yield, and the rate of reaction are faster compared to the two-phase system (no solvent).

n-Heptane is most likely a poorer co-solvent such that the oil and methanol essentially remains as a two-phase system. Higher concentrations of n-heptane exacerbate the system and may further dilute interfacial concentration between the MeOH in the oil, which reduces the reaction rate. Chlorinated solvents, even with high molecular weights, are known to be effective solvents and indeed increase FAME yield but are unlikely candidates for this application due to their toxicity.

The yield and reaction rates were lowest for acetone; ketones self-condense when in contact with basic catalysts (noted also from the GC analysis, see ESI). Moreover, methoxide ions generated by the catalyst, can attack the carbonylic part of acetone since they are nucleophilic, which removes methanol from the transesterification reaction. We confirmed that ketones were poor co-solvents in a test with cylclohexanone; after 6 h, the yield of FAME was only 41%. Since the molecular weight of cyclohexanone is greater than that of acetone, we added less moles and maintained the same mass. Thus less methanol was consumed compared and the FAME yield was slightly better.

Another important feature that makes THF a promising solvent relates to its physic-chemical properties. Its normal boiling point is similar to that of methanol (66°C and 64.2 °C, respectively) and they form an azeotrope (Russbueldt & Hoeldrich, 2009) that facilitates their separation from oil/BD at low temperature (57 °C), resulting in energy savings. Furthermore, both THF and methanol are recycled so there is no need to separate them. Recycling THF reduces any toxicity issues related to purifying it after each batch. We recycled catalyst and THF for three consecutive batch reactions. The equilibrium conversion was identical for each batch, which demonstrates that the catalyst performance is stable.

In conclusion to this thesis part, heterogeneous catalysts is advantageous versus homogeneous catalysts. However, both yield and reaction rates are lower. Adding co-solvents improve the immiscibility between the methanol and oil phase thereby reducing the mass transfer resistance. Not only is the reaction rate comparable to the homogeneous catalyst system the yield of FAME is slightly higher. THF is the most promising co-solvent for heterogeneous catalysis. Moreover, glycerol is insoluble in THF which makes it easier to separate and recover unreacted methanol and THF. Yields and reaction rates were lowest with ketones and hydrocarbons.

Bioplasticizer, green chemicals of high added value

As previously written in the *Experimental* section, firstly a brief study on the optimization of the operative conditions of the epoxidation reaction was performed, and the best operative parameters were chosen to prepare the bioplasticizer and evaluate which synthetic strategy is the best for obtaining a product with the highest OO possible. Firstly, the biodiesel was characterized by GC-FID analysis in order to obtain the acidic composition, its iodine number and the moles of double bonds (DL) per 100 g of substrate. The results are reported in Table 66:

Table 66: GC-FID analysis of soybean biodiesel

Component	Retention time [min]	Area [-]	Concentration [%w]
STD	1.93	106920.7	-
Methyl myristate	3.27	3330.2	0.44
Methyl palmitate	4.72	144658.5	19.50
Methyl stearate	7.43	30378.7	4.12
Methyl oleate	7.93	278909.1	37.07
Methyl linolate	8.91	241452.8	34.65
Methyl linolenate	10.54	26945.0	4.22
Equivalent IN		102.44 gI2/100g	
Moles DL/100g		0.25 mol/100g	

Soybean biodiesel main satured compound is represented by palmitic acid. Only a small fraction is constituted by methyl stearate that, having the same number of carbon of methyl oleate, is for sure very difficult to be distilled. The great part of the unsatured compounds is constituted by methyl oleate (one double bond per mole) and methyl linolate (two double bonds per mole).

Epoxidation Reaction Condition Optimization

In this paragraph the results on the optimization of the epoxidation reaction conditions are presented.

In detail, the main parameters optimized were the amount of acetic acid, the amount of hydrogen peroxide, both expressed as molar ratio considering the moles of double bonds and the quantity of sulphuric acid (expressed as weight percentage on the aqueous phase). A total of ten experiments were performed and the results are reported in the following.

Test 1

The first test was performed in the absence of catalyst, i.e. sulphuric acid. The operative conditions are summarized in Table 65:

Table 67: Test 1, operative conditions

MolesDB/100g	0.25
Moles AA/ moles DL	1
Moles HP/ moles DL	1
Weight H2S04/weight AP	0 %
T [°C]	60
Agitation [rpm]	250

The results obtained are reported in Table 68 and Figure 52:

Table 68: Test 1, experimental results

Time [h]	IN [gI2/100g]	OOthe [gO/100g]	OOexp [gO/100g]	Conversion [%]	Selectivity [%]
0	67.63	0.00	0.00	0.00	0.00
2	65.98	0.10	0.10	2.58	98.58
4	62.60	0.30	0.27	7.58	89.48
6	58.75	0.52	0.35	13.26	67.34
18	47.27	1.20	0.80	30.21	66.51
27	31.40	2.15	1.03	53.64	47.79

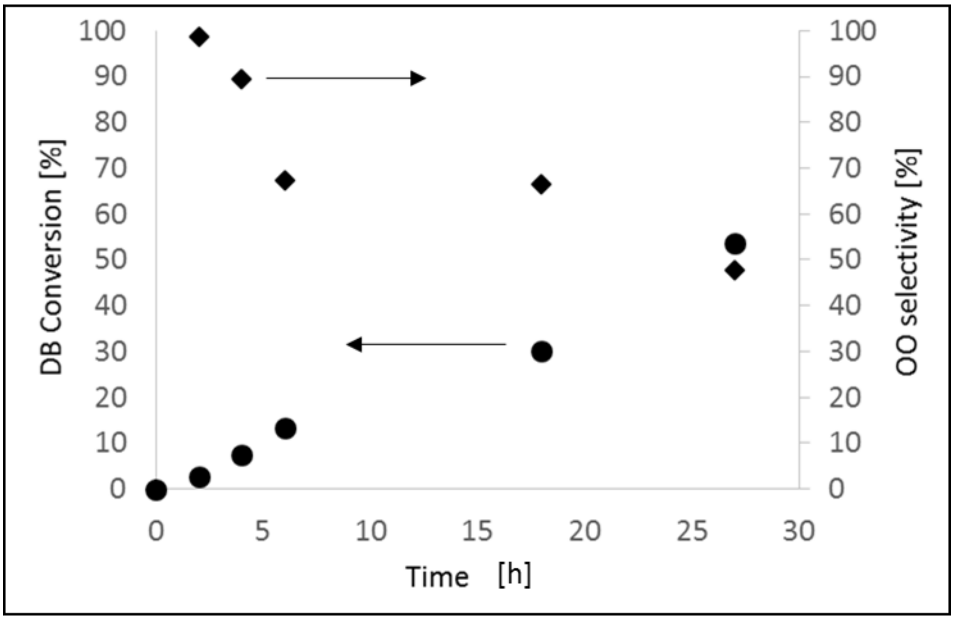


Figure 52: Test 1 experimental results, DB conversion (circles) and OO selectivity (diamonds)

As it can be observed, the absence of a catalyst slows the reaction, in fact a double bond conversion of 53% was obtained after 27 hours of reaction, while the selectivity drops since the epoxides formed further react to give by-products.

Test 2

The second test was performed adopting the same operative condition but using sulphuric acid as catalyst. The operative conditions are reported in Table 69:

Table 69: Test 2, operative conditions

MolesDB/100g	0.25
Moles AA/ moles DL	1
Moles HP/ moles DL	1
Weight H2S04/weight AP	1 %
T [°C]	60
Agitation [rpm]	250

Table 70 and Figure 53 summarize the experimental results.

Table 70: Test 2, experimental results

Time [h]	IN [gI2/100g]	OOthe [gO/100g]	OOexp [gO/100g]	Conversion [%]	Selectivity [%]
0	67.73	0.00	0.00	0.00	0.00
1	56.10	0.68	0.46	17.16	67.06
2	48.29	1.14	0.88	28.71	76.99
3	43.42	1.43	1.14	35.90	79.75
4	38.70	1.71	1.44	42.85	83.28
5	36.67	1.84	1.53	45.85	83.28
6	33.74	2.01	1.71	50.19	85.19

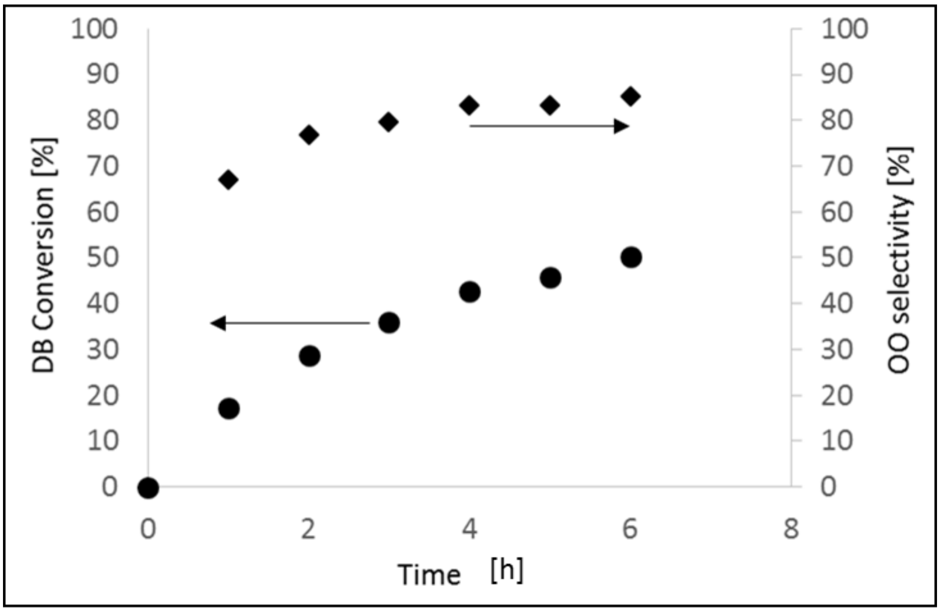


Figure 53: Test 2 experimental results, DB conversion (circles) and OO selectivity (diamonds)

From the comparison between the results obtained in Test 1 and Test 2 results necessary to operate with a catalyst, in order to maintain the selectivity of the process high. This results was also confirmed from literature in a study on the epoxidation of vegetable oils (Abdullah & Salimon, 2010).

Test 3

The operative parameters are reported in Table 71:

Table 71: Test 3, operative conditions

MolesDB/100g	0.25
Moles AA/ moles DL	0.5
Moles HP/ moles DL	1.5
Weight H2S04/weight AP	1 %
T [°C]	60
Agitation [rpm]	250

The experimental results are reported in Table 72 and Figure 54:

Table 72. Test 3, experimental results

Time [h]	IN [gI2/100g]	OOthe [gO/100g]	OOexp [gO/100g]	Conversion [%]	Selectivity [%]
0	64.07	0.00	0.00	0.00	0.00
1	57.22	0.40	0.39	10.68	96.32
2	50.67	0.79	0.83	20.91	105.17a
3	44.40	1.16	1.11	30.69	96.02
4	37.08	1.60	1.49	42.12	93.07
5	34.67	1.74	1.66	45.89	94.98
6	30.62	1.99	1.86	52.21	93.29

a: this value is for sure overestimated due to an experimental error

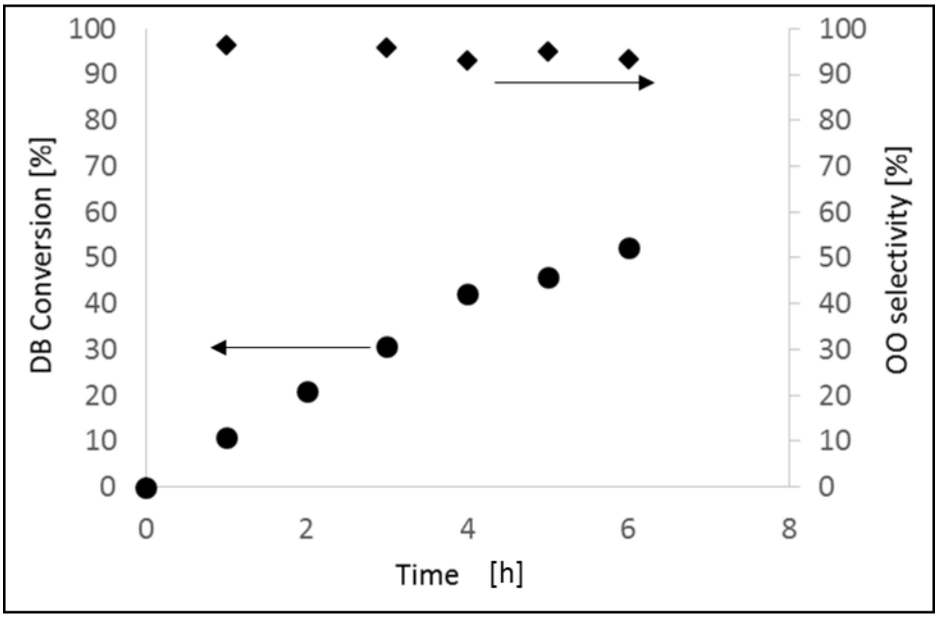


Figure 54. Test 3 experimental results, DB conversion (circles) and OO selectivity (diamonds)

Test 4

In Test 4 the amount of hydrogen peroxide was increased. In Table 73 the operative parameters are reported:

Table 73: Test 4, operative conditions

MolesDB/100g	0.25
Moles AA/ moles DL	0.5
Moles HP/ moles DL	2.5
Weight H2S04/weight AP	1 %
T [°C]	60
Agitation [rpm]	250

The results obtained are reported in Table 74 and Figure 55:

Table 74: Test 4, experimental results

Time [h]	IN [gI2/100g]	OOthe [gO/100g]	OOexp [gO/100g]	Conversion [%]	Selectivity [%]
0	67.73	0.00	0.00	0.00	0.00
1	57.97	0.57	0.46	14.41	81.29
2	44.73	1.35	1.14	33.96	84.49
3	37.18	1.80	1.65	45.10	91.54
4	29.23	2.29	2.06	56.85	90.21
5	23.52	2.63	2.39	65.28	90.70
6	17.18	3.02	2.61	74.63	86.37

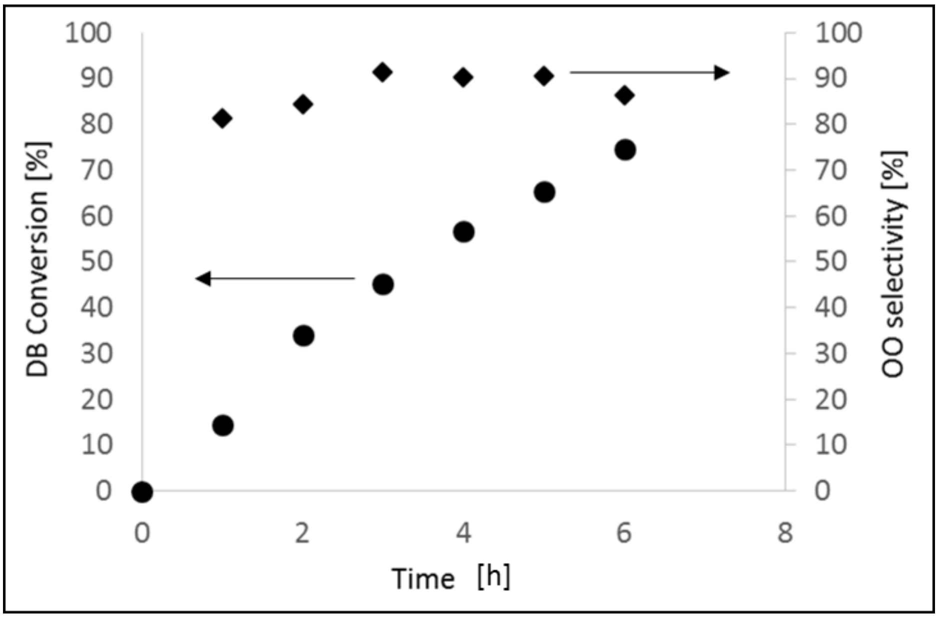


Figure 55: Test 4 experimental results, DB conversion (circles) and OO selectivity (diamonds)

Comparing the results between Test 3 and Test 4 is useful to understand that the formation of peracetic acid is the rate determining step: in fact, increasing the amount of hydrogen peroxide results in higher double bonds conversion, while the selectivity remains high (93% and 86% respectively at 6 hours).

Test 5

In this experiment the amount of acetic acid was decreased compared to the one of Test 4. The operative conditions are summarized in Table 75:

Table 75: Test 5, operative conditions

MolesDB/100g	0.25
Moles AA/ moles DL	0.25
Moles HP/ moles DL	2.5
Weight H2S04/weight AP	1 %
T [°C]	60
Agitation [rpm]	250

The experimental results are reported in Table 76 and Figure 56:

Table 76: Test 5, experimental results

Time [h]	IN [gI2/100g]	OOthe [gO/100g]	OOexp [gO/100g]	Conversion [%]	Selectivity [%]
0	67.73	0.00	0.00	0.00	0.00
1	59.83	0.25	0.27	11.66	107.19a
2	54.25	0.58	0.51	19.90	89.50
3	50.36	0.81	0.77	25.65	96.10
4.25	44.21	1.17	1.10	34.72	94.03
5.25	40.94	1.37	1.33	39.55	97.06
6	38.24	1.53	1.50	43.54	97.85

a: this value is for sure overestimated due to an experimental error

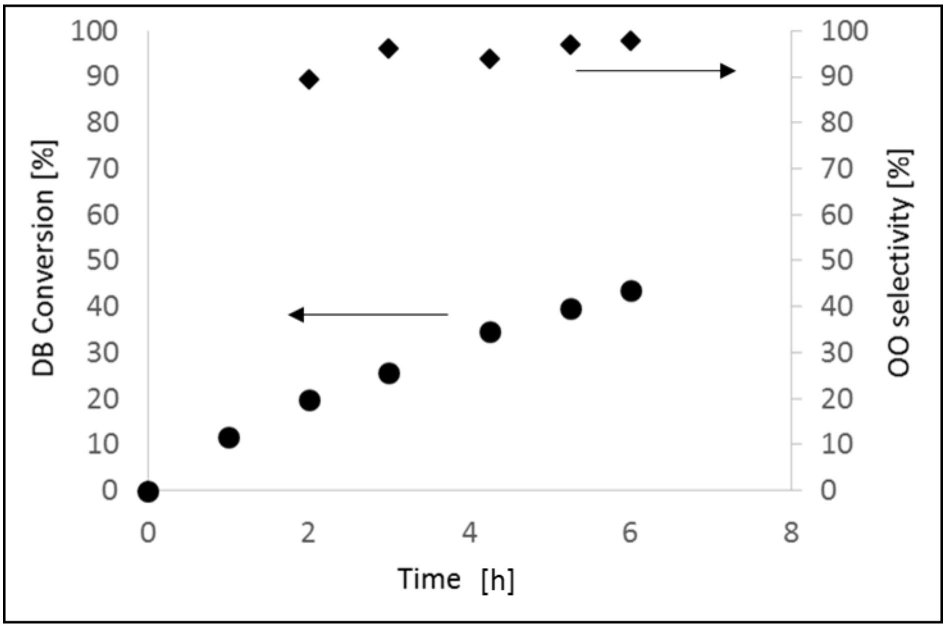


Figure 56. Test 5 experimental results, DB conversion (circles) and OO selectivity (diamonds)

<u>Test 6</u>

In this experiment the amount of acetic acid was increased, according to the operative parameters reported in Table 77:

Table 77: Test 6, operative parameters

MolesDB/100g	0.25
Moles AA/ moles DL	1
Moles HP/ moles DL	2.5
Weight H2S04/weight AP	1 %
T [°C]	60
Agitation [rpm]	250

The results are reported in Table 78 and Figure 57:

Table 78: Test 6, experimental results

Time [h]	IN [gI2/100g]	OOthe [gO/100g]	OOexp [gO/100g]	Conversion [%]	Selectivity [%]
0	67.73	0.00	0.00	0.00	0.00
1	52.87	0.66	0.54	21.93	82.87
2	46.02	1.06	1.27	32.06	119.23a
3.5	21.69	2.53	2.07	67.97	81.75
4	20.21	2.62	2.25	70.16	85.78
5	15.52	2.91	2.51	77.08	86.20
6	11.16	3.18	2.67	83.53	83.53

a: this value is for sure overestimated due to an experimental error

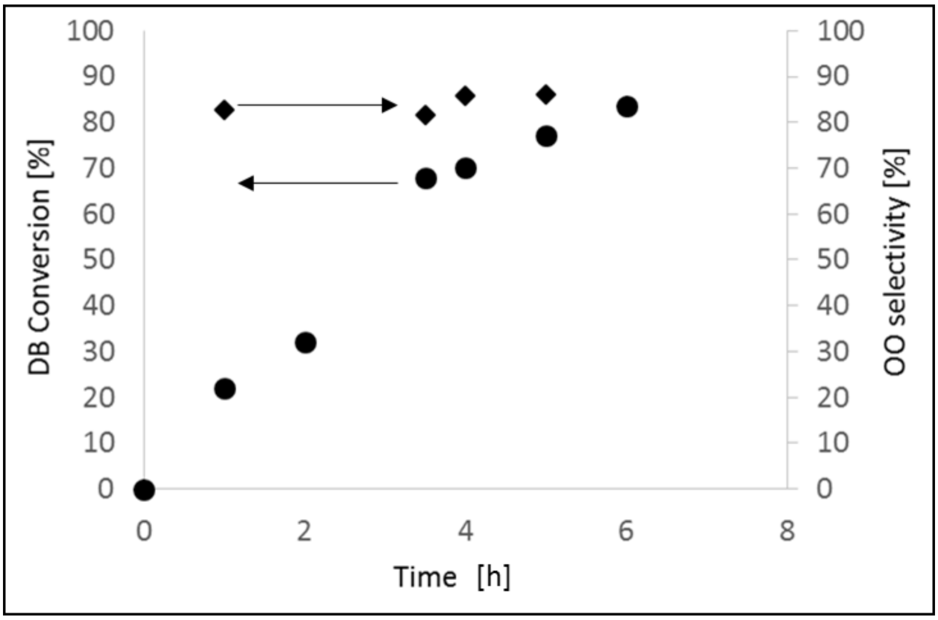


Figure 57: Test 6 experimental results, DB conversion (circles) and OO selectivity (diamonds)

Tests 4-6 differ for acetic acid per double bond amount, from 0.25 to 1.

Acetic acid takes part to every reaction involved in the system: from the synthesis of the epoxidizing agent, i.e. the peracetic acid, to the reactions that generate by-products, i.e. oxirane ring opening. In fact, double bond conversion and epoxide selectivity show invers trends.

Test 7

In this experiment the effect of temperature on the reaction was investigated. Milchert et al. (2009) for the epoxidation of rapeseed oil, identifying the optimal range between 50-60°C. The Authors found that increasing the temperature over 60°C the degradation of the epoxide ring occurred. For this reason I performed Test 7 at 50°C. In Table 79 the operative parameters are summarized:

Table 79: Test 7, operative parameters

MolesDB/100g	0.25
Moles AA/ moles DL	0.25
Moles HP/ moles DL	2.5
Weight H2S04/weight AP	1 %
T [°C]	50
Agitation [rpm]	250

The results obtained are reported in Table 80 and Figure 55:

Table 80: Test 7, experimental results

Time [h]	IN [gI2/100g]	OOthe [gO/100g]	OOexp [gO/100g]	Conversion [%]	Selectivity [%]
0	67.73	0.00	0.00	0.00	0.00
1	63.62	0.24	0.13	6.06	52.52
2	58.75	0.52	0.28	13.26	53.72
3	54.00	0.80	0.47	20.28	58.54
4	52.71	0.88	0.57	22.17	65.14
5	49.75	1.05	0.73	26.54	68.93
6	47.89	1.16	0.84	29.29	72.09

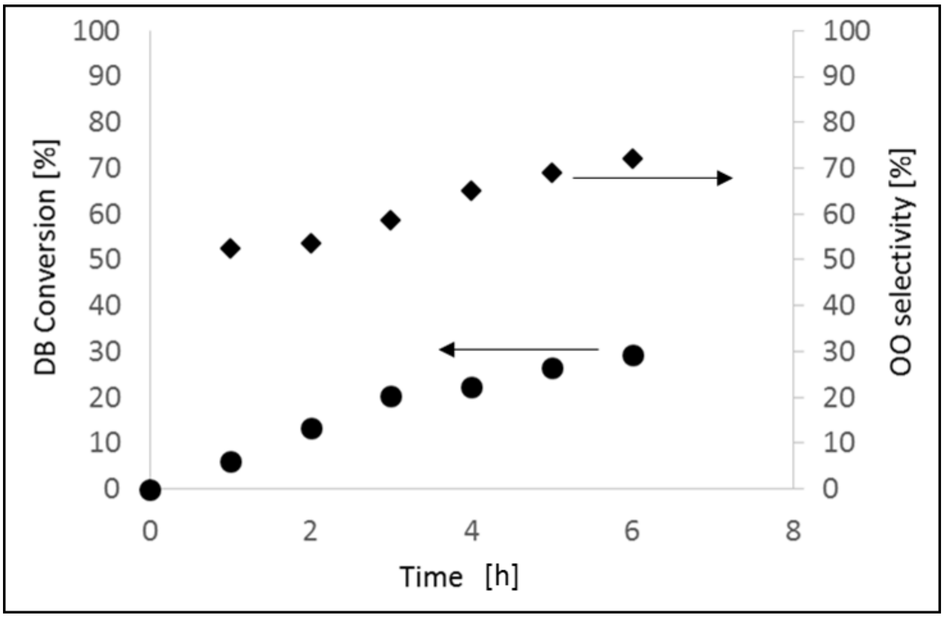


Figure 58: Test 7 experimental results, DB conversion (circles) and OO selectivity (diamonds)

Comparing Test 6 and Test 7, of course increasing the temperature a higher conversion is obtained since the reaction rates are enhanced. While at 60°C the selectivity remains constant, at 50°C the selectivity increases from time 0 to 6 hours. This could be explained considering a kinetic reason, either, because the formation of the epoxide is slowed down too or a physical reason, because of the lower solubility of peracetic acid in the biodiesel phase.

Test 8

In Tests 8-10 the epoxidation reactions were repeated with an higher amount of catalyst. The operative conditions of this test are reported in Table 81:

Table 81: Test 8, operative conditions

MolesDB/100g	0.25
Moles AA/ moles DL	0.25
Moles HP/ moles DL	2.5
Weight H2S04/weight AP	2 %
T [°C]	60
Agitation [rpm]	250

The results are reported in Table 82 and Figure 56:

Table 82: Test 8, experimental results

Time [h]	IN [gI2/100g]	OOthe [gO/100g]	OOexp [gO/100g]	Conversion [%]	Selectivity [%]
0	67.73	0.00	0.00	0.00	0.00
2	54.61	0.48	0.28	13.04	58.35
3.5	41.23	1.28	0.95	34.35	74.23
4	31.75	1.85	1.32	49.44	71.73
5	23.53	2.35	1.59	62.53	67.78
6	17.92	2.69	1.70	71.46	63.18

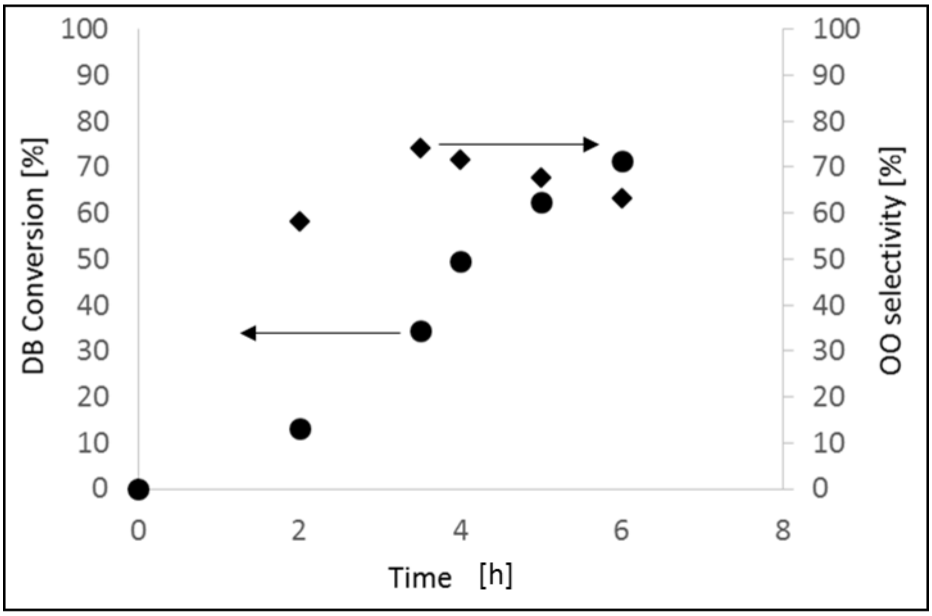


Figure 59: Test 8 experimental results, DB conversion (circles) and OO selectivity (diamonds)

Test 9

The operative conditions are summarized in Table 83:

Table 83: Test 9, operative parameters

MolesDB/100g	0.25
Moles AA/ moles DL	0.5
Moles HP/ moles DL	2.5
Weight H2S04/weight AP	2 %
T [°C]	60
Agitation [rpm]	250

The experimental results are reported in Table 84 and Figure 60:

Table 84: Test 9, experimental results

Time [h]	IN [gI2/100g]	OOthe [gO/100g]	OOexp [gO/100g]	Conversion [%]	Selectivity [%]
0	67.73	0.00	0.00	0.00	0.00
2	49.41	0.79	0.67	21.33	85.24
3	24.67	2.28	1.75	60.72	76.77
4	11.67	3.08	1.95	89.57	54.96
5	6.55	3.40	1.87	89.57	54.96
6	2.31	3.66	1.98	96.31	54.15

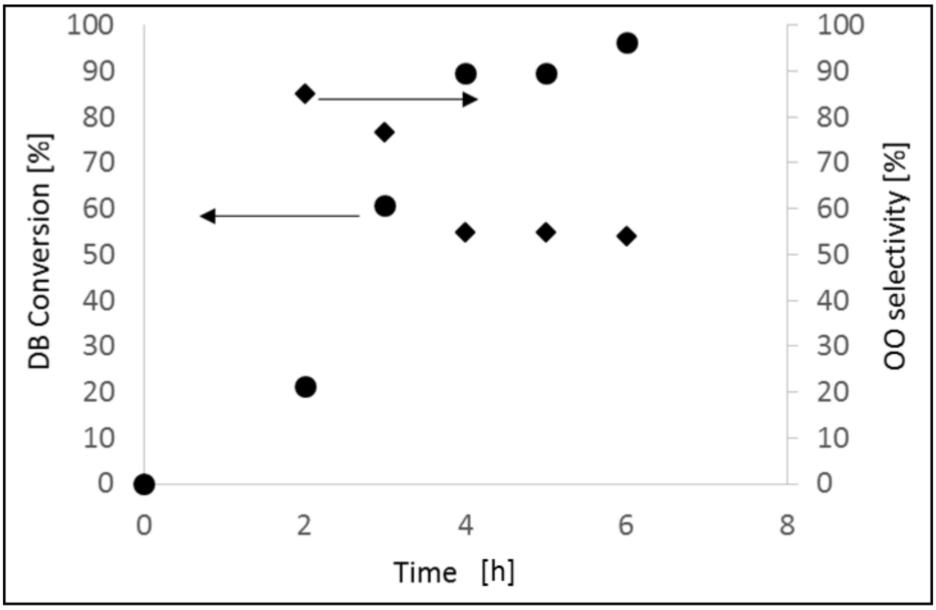


Figure 60: Test 9 experimental results, DB conversion (circles) and OO selectivity (diamonds)

Test 10

The operative conditions are reported in Table 85:

Table 85: Test 10, operative conditions

MolesDB/100g	0.25
Moles AA/ moles DL	1
Moles HP/ moles DL	2.5
Weight H2S04/weight AP	2 %
T [°C]	60
Agitation [rpm]	250

The experimental results are reported in Table 86 and Figure 61:

Table 86: Test 10, experimental results

Time [h]	IN [gI2/100g]	OOthe [gO/100g]	OOexp [gO/100g]	Conversion [%]	Selectivity [%]
0	67.73	0.00	0.00	0.00	0.00
1	34.29	1.77	1.12	45.40	63.21
2	9.44	3.25	2.46	84.96	75.58
3	2.98	3.63	2.36	95.26	65.06
4	0.49	3.78	1.65	99.22	43.63
6	0	3.81	1.12	100	29.34

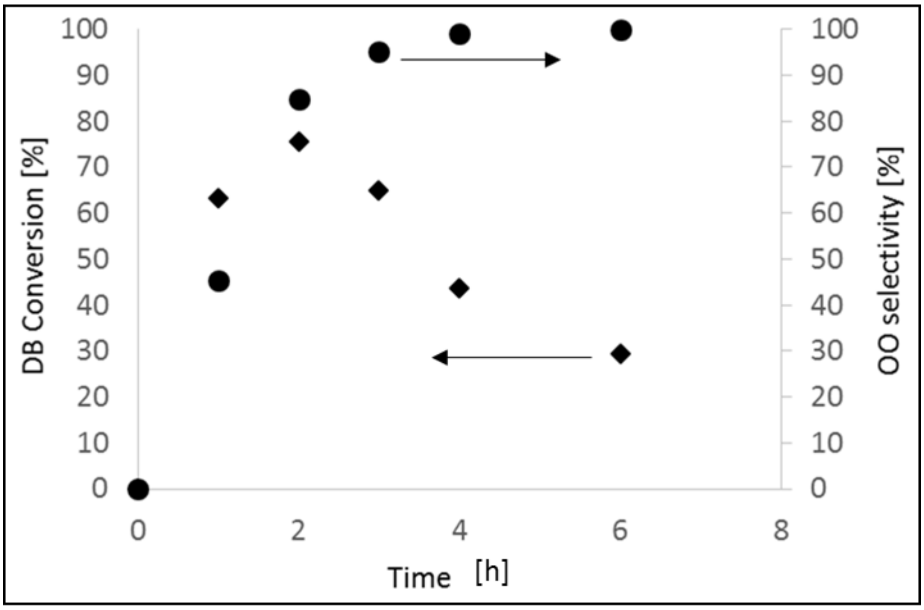


Figure 61: Test 10 experimental results, DB conversion (circles) and OO selectivity (diamonds)

In Table 87 is reported a comparison between the conversions and selectivity obtained in Tests 4-6 and Tests 8-10:

Table 87: Double bond conversion and oxirane selectivity comparison

	Test 4	Test 5	Test 6	Test 8	Test 9	Test 10
DB Conversion [%]	43.54	71.46	74.63	96.31	83.53	100
OO Selectivity [%]	97.85	63.18	86.37	54.15	83.83	29.40

The higher the catalyst concentration, the higher the double bond conversion. The peracetic acid formation is of the first order towards acetic acid, hydrogen peroxide and H^+ concentration (Zhao, et al., 2007). On the other hand, the presence of a high acid ambient promotes the formation of by-product. For this reason, the selectivity decreases when the concentration of sulphuric acid is raised.

All the experimental results, together with the reaction yields are summarized in Table 88:

Table 88: Summary of the experiments performed for the epoxidation reaction optimization

Test	Molar ratios			Results at time= 6 h			
	AA	HP	Catalyst	OO [gO/100g]	Conversion [%]	Selectivity [%]	Yield [%]
1	1	1	-	1.03	53.64	47.79	25.63
2	1	1	1	1.71	50.19	85.19	42.75
3	0.5	1.5	1	1.86	52.21	93.29	48.71
4	**0.5**	**2.5**	**1**	**2.61**	**74.63**	**86.37**	**64.46**
5	0.25	2.5	1	1.50	43.54	97.85	42.60
6	1	2.5	1	2.67	83.53	83.83	70.02
7	0.25	2.5	1	0.84	29.29	72.09	21.11
8	0.25	2.5	2	1.70	71.46	63.18	45.15
9	0.5	2.5	2	1.98	96.31	54.15	52.16
10	1	2.5	2	1.12	100	29.34	29.34

The best operative conditions chosen are the one of Test 4, because both the conversion and the selectivity resulted high (higher than 80 %), obtaining a final epoxidation yield of 64%. In addition, Test 6 results was very good, but the lower (even if of a little) selectivity towards OO pushed me to choose the conditions of Test 4.

Strategy A: Distillation and Epoxidation

After the experimental conditions for achieving the highest epoxide yield possible, the next part of the work was aimed to the study of the best strategy in order to obtain a final product with a high OO. The first strategy considered consisted in the biodiesel distillation, in order to remove the satured methyl esters and epoxidize a substrate rich in double bonds.

The distillation is a promising separation since great part of the satured esters is constituted by the more volatile molecules, i.e. methyl myristate and methyl palmitate. Methyl stearate shows unfortunately a volatility very similar to the one of methyl oleate and thus is more difficult to be separated. Another technique that could be very useful for separating methyl stearate and methyl palmitate is the crystallization (Duane, 2012).

A first distillation was performed evaporating all the biodiesel except the products impossible to be distilled (that resulted the 5% by weight), i.e. polar lipids, phytosterols, tocopherol, high molecular weight hydrocarbons, pigments and minerals (Yu, et al., 1998). This was due to study the influence of these products on the epoxidation reaction.

In Table 89 the results of the total distillation of biodiesel is reported:

Table 89: Results of the total distillation of biodiesel

Component	Concentration in Biodiesel [%w]	Concentration in Totally Distilled Biodiesel [%w]
Methyl myristate	2.09	1.79
Methyl palmitate	24.87	24.61
Methyl stearate	17.18	16.81
Methyl oleate	39.94	40.38
Methyl linolate	14.58	14.99
Methyl linolenate	1.33	1.42

This substrate, that hereinafter will be called total distilled biodiesel, was epoxidized at different conditions, in order to study at different conditions the double bond conversions and epoxide selectivity. The results are reported in the following.

Test 11

In Test 11 I used the same operative conditions of Test 4, reported in Table 73. The experimental results are reported in Table 90 and Figure 62:

Table 90: Test 11, experimental results

Time [h]	IN [gI2/100g]	OOthe [gO/100g]	OOexp [gO/100g]	Conversion [%]	Selectivity [%]
0	56.27	0.00	0.00	0.00	0.00
1	47.24	0.53	0.58	16.06	109.32a
2	40.42	0.94	1.05	28.18	111.12a
3.25	31.70	1.47	1.47	43.67	100
4.25	26.78	1.77	1.81	52.40	102.80a
5	21.97	2.06	1.98	60.96	95.97
6	17.72	2.32	2.21	68.52	95.08

a: this value is for sure overestimated due to an experimental error

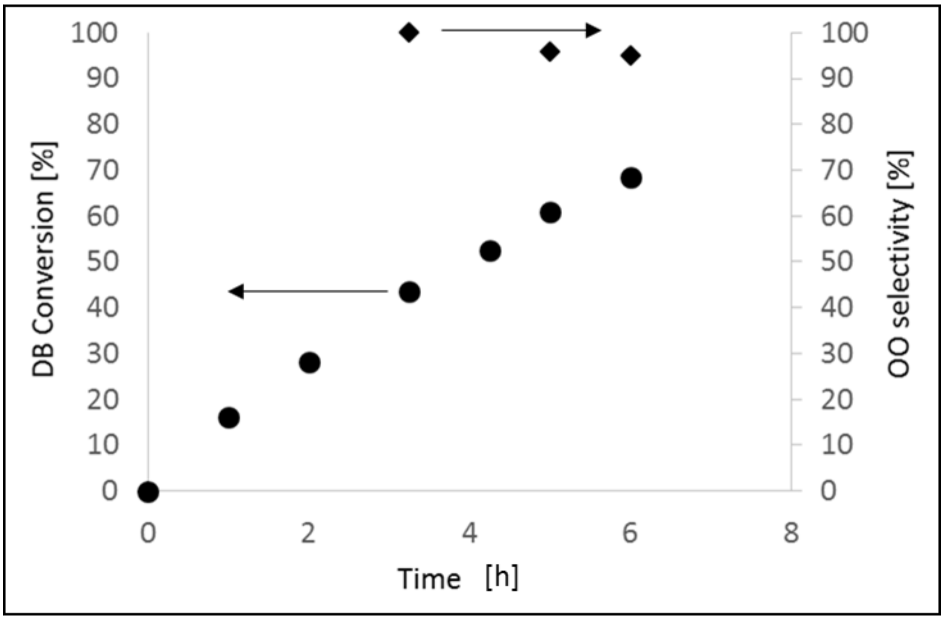


Figure 62: Test 11 experimental results, DB conversion (circles) and OO selectivity (diamonds)

Test 12

In Test 12 the same operative conditions of Test 5 were used, reported in Table 75.

The experimental results are shown in Table 91 and Figure 63:

Table 91: Test 12, experimental results

Time [h]	IN [gI2/100g]	OOthe [gO/100g]	OOexp [gO/100g]	Conversion [%]	Selectivity [%]
0	64.07	0.00	0.00	0.00	0.00
2	54.25	0.58	0.51	15.32	89.50
3	50.36	0.81	0.77	21.40	96.10
4	44.21	1.17	1.10	30.99	94.03
5	40.94	1.37	1.33	36.09	97.06
6	38.24	1.53	1.50	40.31	97.85

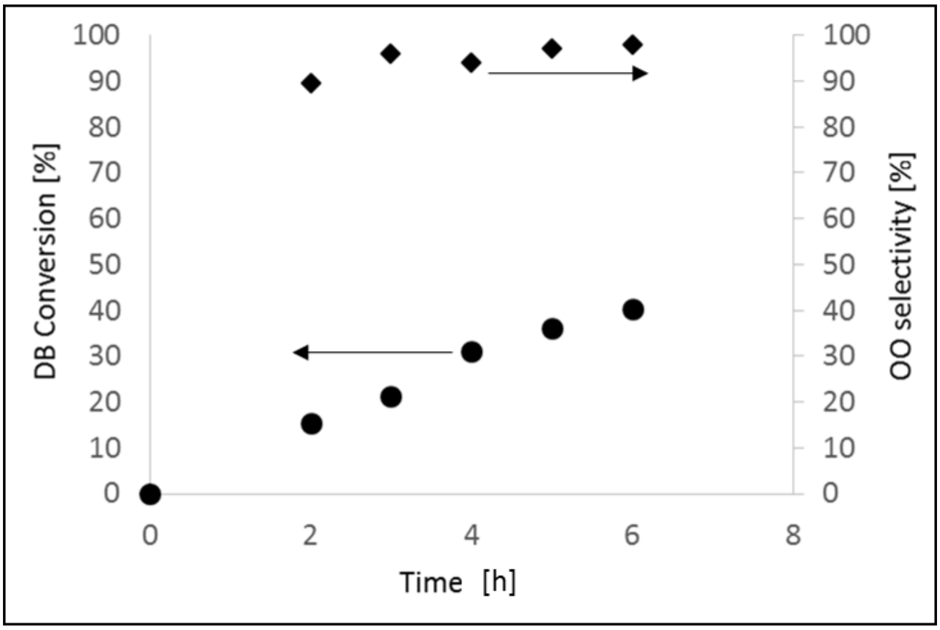


Figure 63. Test 12 experimental results, DB conversion (circles) and OO selectivity (diamonds)

Test 13

In Test 13 the operative conditions of Test 3 were repeated on total distilled biodiesel, following the operative conditions reported in Table 71. The experimental results obtained are reported in Table 92 and Figure 64:

Table 92: Test 13, experimental resuts

Time [h]	IN [gI2/100g]	OOthe [gO/100g]	OOexp [gO/100g]	Conversion [%]	Selectivity [%]
0	62.31	0.00	0.00	0.00	0.00
1	53.41	0.52	0.60	14.26	115.33a
2	45.90	0.97	1.05	26.34	108.91a
3.3	36.30	1.54	1.62	41.75	104.91a
3.9	33.97	1.68	1.77	45.48	105.30a
5.5	26.27	2.15	2.20	57.84	102.10a

a: all the values are for sure overestimated due to an experimental error, the selectivity can be supposed equal to 100%

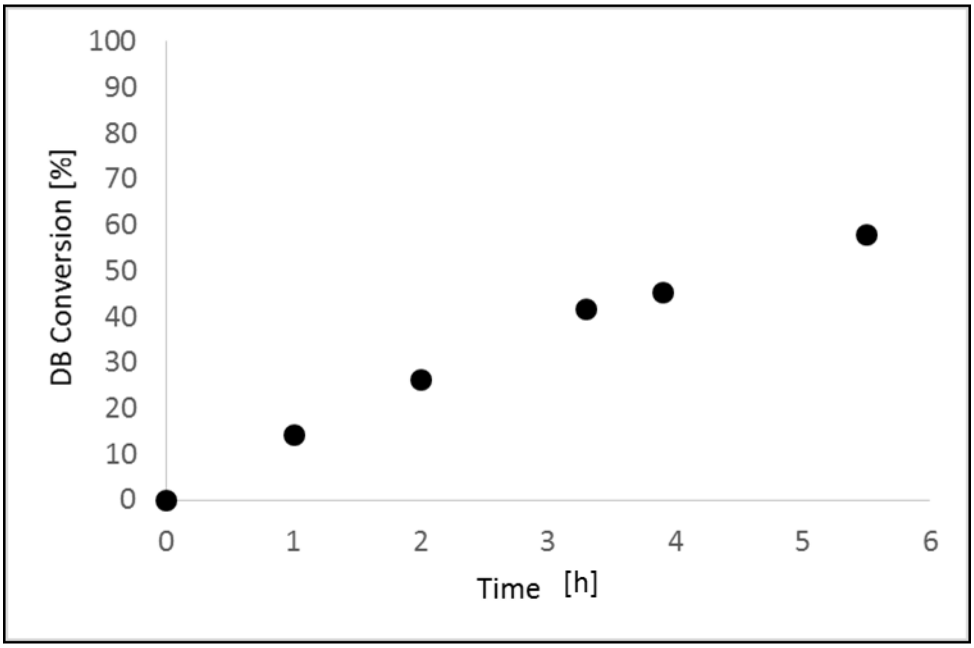


Figure 64. Test 13 experimental results

Test 14

This last Test was performed using the same conditions of Test 6, reported in Table 77.

The experimental results are reported in Table 93 and Figure 65:

Table 93: Test 14, experimental results

Time [h]	IN [gI2/100g]	OOthe [gO/100g]	OOexp [gO/100g]	Conversion [%]	Selectivity [%]
0	62.19	0.00	0.00	0.00	0.00
1	52.38	0.58	0.62	15.77	108.12
2	37.36	1.47	1.55	39.92	105.46
3.75	22.06	2.40	2.40	64.53	99.94
4.25	17.00	2.71	2.50	72.66	92.15
5	12.44	2.99	2.68	80.00	89.55
6	8.06	3.27	2.86	87.05	87.56

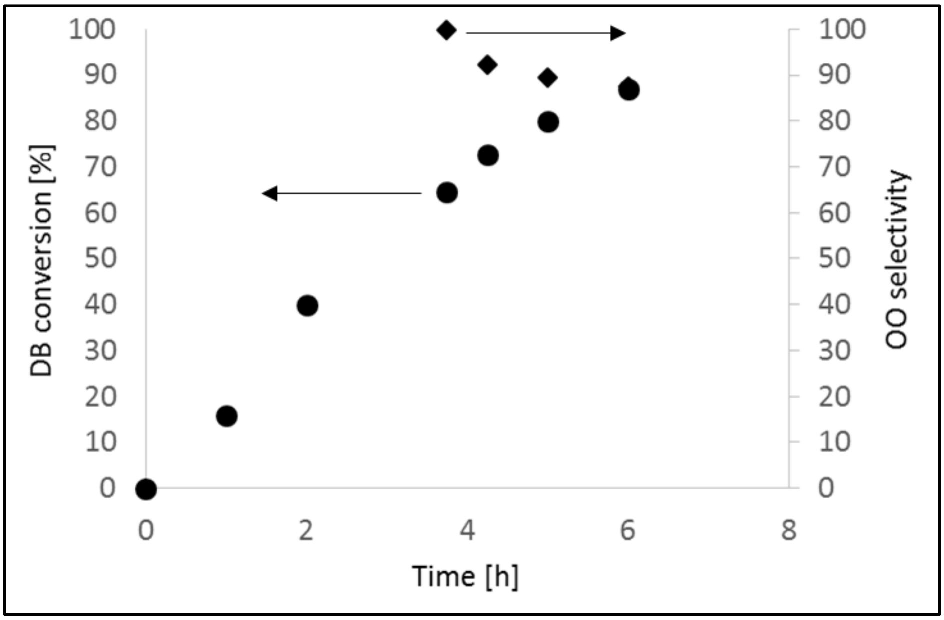


Figure 65. Test 14 experimental results, DB conversion (circles) and OO selectivity (diamonds)

The epoxidation reaction results are reported for both biodiesel and total distilled biodiesel in Table 94:

Table 94: Comparison between the epoxidation of biodiesel and total distilled biodiesel

Operative conditions of	Substrate	OO at 6 h [gO/100g]	Conversion at 6 h [%]	Selectivity at 6 h [%]	Yield [%]
Test 4	Biodiesel	2.61	74.63	86.37	64.46
	Total distilled biodiesel	2.21	68.52	95.08	65.14
Test 5	Biodiesel	1.50	43.54	97.85	42.60
	Total distilled biodiesel	1.50	40.31	97.85	39.44
Test 3	Biodiesel	1.86	52.21	93.29	48.70
	Total distilled biodiesel	2.20	57.84	>99	57.84
Test 6	Biodiesel	2.67	83.53	83.83	70.02
	Total distilled biodiesel	3.27	87.05	87.56	76.22

The results showed that a possible influence of this traces compound exists. In particular for the optimized reaction conditions (last raw of Table 94) the selectivity of the reaction is significantly higher which means that one of more of these components (probably the polar lipids since that they are present in the biodiesel phase and possess a charge that can open the epoxide ring) act on the epoxide ring formed decreasing the selectivity of the reaction. This information is in any case very interesting for understanding the epoxidation reaction.

Another important aspect is that, since also pigments were separated from the mixture, a pale yellow product was obtained, where the non distilled biodiesel is orange. The color of the substrate seem a meaningless thing, but it is a very important aspect of the final product.

After this experiment, a brief investigation on the distillation of biodiesel was carried out. In particular a distillation curve was obtained, to understand at which temperature operate the fractionation of biodiesel. More in detail, the pressure of the apparatus was kept at a constant value of 450 mtorr and the reboiler temperature fixed to a certain value and raised only when the mixture in the reboiler was not boiling. This because, since the more volatile components distillate, the mixture in the reboiler changes its composition during the distillation and, since the concentration of heavier components increase, a higher temperature is needed to make the mixture boil again. Every fraction was collected and analyzed.

The experimental results of this first distillation curve are reported in Table 95 and Figure 66:

Table 95: Distillation curve of soybean biodiesel

Fraction		0 (initial biodiesel)	1	2	3	4	5	6
Mass [g]		180.56	6.80	7.03	10.28	7.41	133.11	15.93
Temperature [°C]		25	176.8	182	184.2	185.3	193	200
Molar Fraction	C14*	0.44	6.27	1.34	0.15	0.35	0.00	0.00
	C16	19.50	70.19	68.75	67.97	63.89	11.53	0.00
	C18	4.12	0.73	14.33	15.31	17.17	4.06	10.98
	C18:1	37.07	10.71	14.06	14.96	16.77	41.37	52.08
	C18:2	34.65	10.88	1.52	1.61	1.82	38.78	33.26
	C18:3	4.22	1.22	0.00	0.00	0.00	4.26	3.68

*: the acronyms reported in this column represents the same component of Table 89. in particular the first number is the number of carbon of the FFA while the second number, after :, is the number of insaturations present in the molecule.

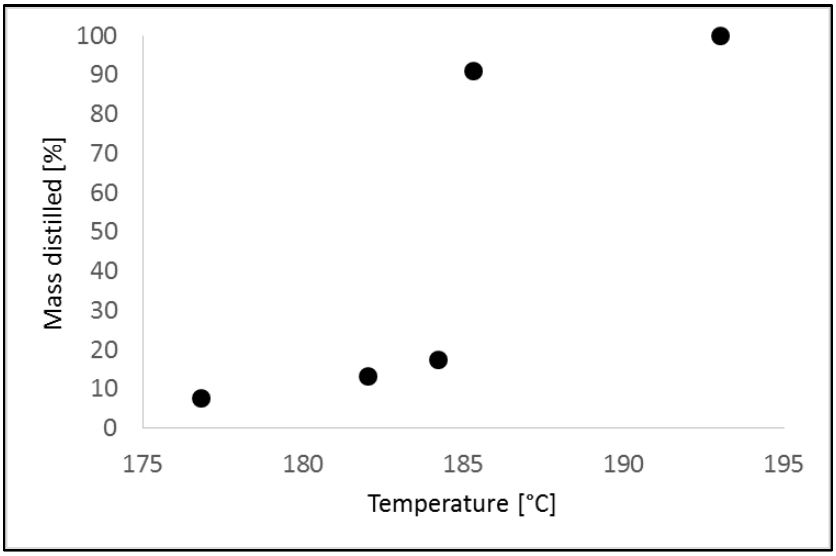


Figure 66: Biodiesel distillation curve, experimental results

A reboiler temperature of 188 °C was chosen to make all the distillations.

A comparison between the biodiesel as it is and a sample of distilled biodiesel with the operative condition described (P= 450 mtorr and T= °C) is reported in Table 94:

Table 96: Distillation of biodiesel, experimental results and comparison between non distilled biodiesel

Component	Concentration in Biodiesel [%w]	Concentration in Distilled Biodiesel [%w]
Methyl myristate	2.09	0.00
Methyl palmitate	24.87	0.85
Methyl stearate	17.18	3.43
Methyl oleate	39.94	58.84
Methyl linolate	14.58	29.33
Methyl linolenate	1.33	7.56

From the comparison of the results in Table 96, it could be concluded that the conditions used permitted to obtain a substrate with a high IN, i.e. highly concentrated in double bonds, that is very promising for obtaining a high value bio-plasticizer.

The epoxidation reaction with the operative condition of Test 4 (see Table 73) gave the results reported in Table 97 and Figure 64:

Table 97: Epoxidation of distilled biodiesel, experimental results

Time [h]	IN [gI2/100g]	OOthe [gO/100g]	OOexp [gO/100g]	Conversion [%]	Selectivity [%]
0	120.60	0.00	0.00	0.00	0.00
1	93.80	1.66	1.19	22.23	71.69
2	63.44	3.48	2.19	47.39	63.05
3	43.77	4.62	3.01	63.71	65.26
4	25.98	5.63	3.61	78.46	64.16
5	17.18	6.12	3.92	85.75	64.10
6	9.55	6.54	4.25	92.08	64.97

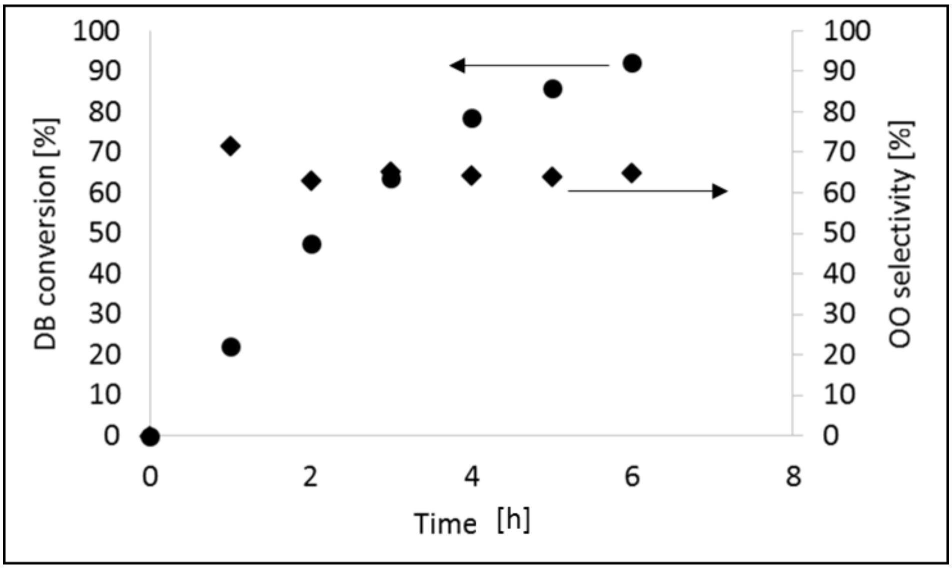


Figure 67. Experimental results of the distilled biodiesel epoxidation, DB conversion (circles) and OO selectivity (diamonds)

Compared to Test 4, the epoxidation of distilled biodiesel gave a higher conversion of double bonds but a lower selectivity (even if the value is stable during the time compared to the one of Test 4 that decreases). A possible explanation could be the double bounds concentration, that in distilled biodiesel is doubled, and this can lead to a higher conversion and thus also to an increased number of by-products.

Another hypothesis is that the satured part, that was almost completely removed from the substrate, could not play a "solvent effect" role.in other words the satured methyl esters might act such in a way to decrease the oxirane ring opening, probably decreasing the solubility of polar molecules like water in the biodiesel phase.

To deeply investigate this aspect, some experiments were performed for understanding the effect of the satured components performing the epoxidation reaction on distilled biodiesel in the presence of a solvent.

Effect of satured fatty acid esters

In order to choose the most convenient solvent a simulation on the solubility of acetic acid in biodiesel in presence of some solvents was carried out using PRO/II, setting as thermodynamic system the model UNIFAC (Fredenslund, et al., 1975).

In particular in the simulation the same amount of reagents of Test 4 was set and 4 different kind of solvents were tested, i.e. hexane, cyclohexane, toluene and methyl dodecanoate, this latter was considered a substitute of the satured methyl esters.

The results in terms of solubility of acetic acid in the organic (biodiesel) phase was:

Hexane<Cyclohexane<Toluene<Methyl dodecanoate

In other words the higher the polarity of the molecule, the higher the solubility of acetic acid in the mixture is. Since the satured esters were eliminated by distillation, the acetic acid solubility was enhanced by the presence of unsatured compounds, that are slightly more polar.

It was then decided to operate an epoxidation using hexane as solvent, using it in the same quantity of the methyl esters distilled. The same operative conditions of Test 4 were used. In this case, before the analysis of every sample, the solvent was evaporated al low temperature under vacuum. The experimental results are reported in Table 98 and Figure 68:

Table 98: Epoxidation of distilled biodiesel using hexane as solvent. Experimental results

Time [h]	IN [gI2/100g]	OOthe [gO/100g]	OOexp [gO/100g]	Conversion [%]	Selectivity [%]
0	120.60	0.00	0.00	0.00	0.00
1	95.23	1.57	1.05	21.03	66.59
2	60.23	3.67	2.29	50.06	62.50
3	43.64	4.63	3.03	63.81	65.78
4	29.70	5.42	3.63	75.37	67.01
5	19.76	5.98	4.09	83.62	68.39
6	10.93	6.47	4.78	90.93	73.99

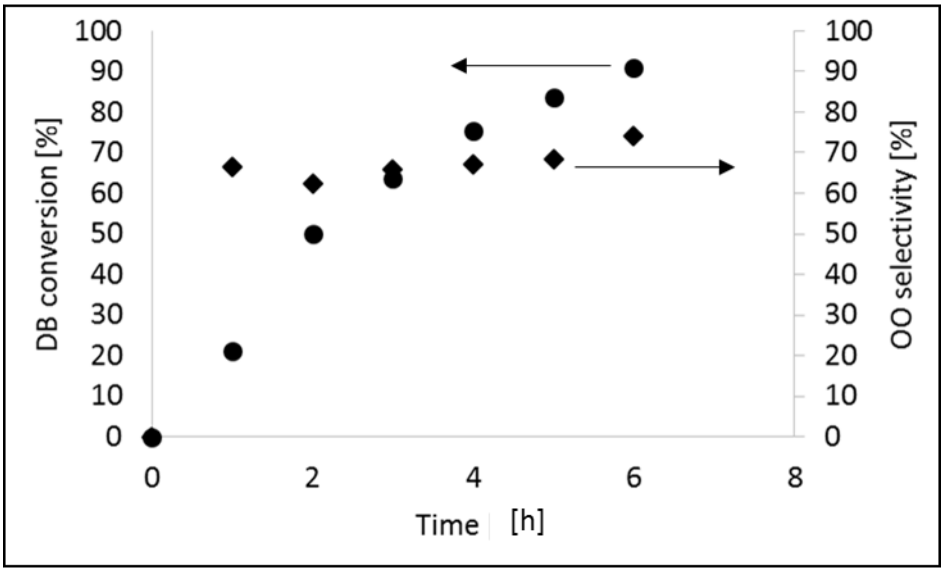


Figure 68: Epoxidation of distilled biodiesel using hexane as solvent. Experimental results. DB conversion (circles) and OO selectivity (diamonds)

While the double bonds conversion does not change dramatically, the selectivity towards the epoxide is increased, showing that the presence of a solvent is positive for obtaining a bioplasticizer with a high OO. Moreover, the great advantage of a solvent like hexane is that it can be very easily separated from the mixture and reused.

Strategy B: Epoxidation and distillation

Another strategy for increasing the OO value of epoxidized biodiesel, that is not comparable to the one of commercial bio plasticizer as reported in the following, is the separation of the unreacted molecules after the epoxidation reaction.

The epoxidized molecules, due to the presence of the oxygen, result far less volatile than the methyl esters and for this reason remain concentrated in the reboiler. Epoxidized biodiesel obtained from Test 4 was distilled using the batch apparatus described in the *Experimental Section*. In order to avoid high residence time in the reboiler of the bio plasticizer the reboiler temperature was set to 190 °C. Considering the conversion obtained, about the 30% of the mixture should be distilled. No samples were withdrawn. The experimental results are reported in Table 99:

Table 99: Distillation of bio plasticizer, experimental results

Sample	OO [gO/100g]
Sample Test 4	2.21
Reboiler	3.14
Distillate	1.07

The results showed that the efficiency of the distillation equipement was insufficient to avoid the epoxidized compound to evaporate. However, using the vigreaux, the time needed for the distillation was too high and all the epoxide degraded.

Some improvements that could help the process are:

- The optimization of the distillation, increasing the stages number using a structured packing instead of a vigreaux column.
- The reduction of the time needed for completing the distillation, further decreasing the pressure of the system, which reduces the tboiling temperature of the mixture and increase the volatility between non reacted components and epoxides.
- The use of alternative separation techniques, i.e. crystallization or the thin layer evaporation.

Another important aspect that should be highlighted, is that the color of the bio plasticizer in the reboiler change from a pale yellow to brown, depending on the time needed for the distillation.

Comparison between commercial samples

Finally, a comparison between the two bio plasticizer prepared with the two strategies were compared with two commercial bioplasticizer.

The first one considered is NPPX, a product that is commercialazied in India and China. It is characterized by a high viscosity and a pale yellow color. The second one is an Arkema® product, named REFLEX-100, which is colorless and with a medium viscosity. The oxirane oxygen number of these two plasticizer is compared to the ones of the two bio-plasticizer prepared with the two strategies in Table 100:

Table 100. Comparison between the OO content of commercial bioplasticizer and the ones prepared with the two strategies

Sample	OO [gO/100g]
NPPX®	4.96
REFLEX-100	6.38
Strategy A (using hexane)	4.78
Strategy B	3.14

The best commercial product is the one of Arkema, which is a leader company in chemicals. However, the bio-plasticizer prepared with Strategy A possesses an amount of epoxides similar to the one of NPPX and thus it is already a good product. Moreover the reduced number of satured compounds compared to NPPX makes it a higher grade plasticizer because phenomena like the diffusion of these latter compounds through the polymer matrix.

Considered the reaction used for the epoxidation of biodiesel and the separation technique adopted, i.e. batch distillation, the Strategy A resulted the best for obtaining the highest OO bio plasticizer.

Further improvements in the epoxidation reaction are necessary to reach a product comparable to REFLEX-100, but the results are very promising.

Conclusions

In conclusion, to this thesis it is possible to say that, even if the biodiesel production process has been known for years, some innovations and contribution to the state of the art could be found from this work.

The operative condition used for both the deacidification and the transesterification are not standardized and optimized from literature. In particular it was demonstrated that some works were operated in disadvantageous operative conditions, i.e. using a too high excess of methanol. Working in a monophasic system for both the deacidification (limiting the amount of methanol to a molar methanol:free fatty acid ratio of 5) and the transesterification (using a cosolvent) lead to very satisfactory results, obtaining an oil suitable to be transesterified and an heterogeneous transesterification process that gave yields comparable to the homogeneous catalyzed process.

At the same time, it was demonstrated that at mild operative conditions, the high added value products contained in crude oils could be separated making the whole process economically sustainable.

Finally, a possible improvement of biodiesel to valuable chemical was studied. In particular the synthesis of epoxidized biodiesel was firstly optimized and then performed on biodiesel and distilled biodiesel, obtaining with this latter substrate a product with an epoxide content comparable to a commercial product, giving positive suggestion for its application as bioplasticizer.

Generally, since the society and the scientific committee are giving more and more attention towards biofuels and biochemical, and this work hopefully contributes to the advances of our society to a new and more sustainable World.

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