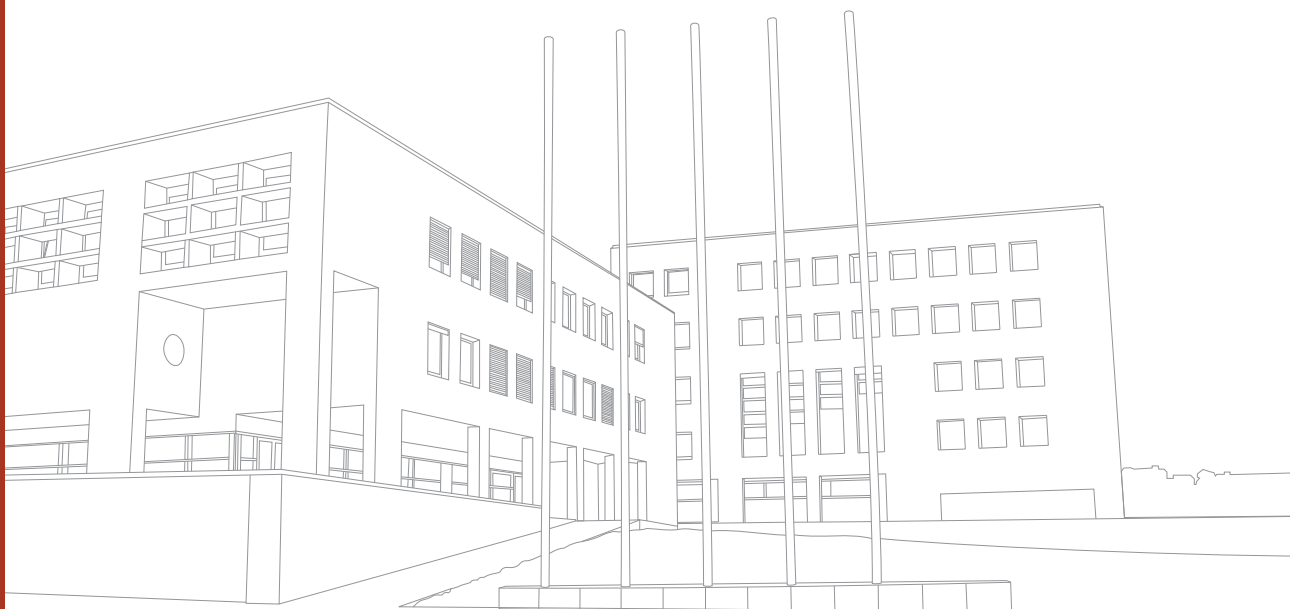




Biodiesel Production from Wastes: Process Development and Quality Control

Joana Maia Moreira Dias
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BIODIESEL PRODUCTION FROM WASTES:
PROCESS DEVELOPMENT AND QUALITY CONTROL

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BIODIESEL PRODUCTION FROM WASTES: PROCESS DEVELOPMENT AND QUALITY CONTROL

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FCT Fundação para a Ciência e a Tecnologia

MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E ENSINO SUPERIOR



To my family and friends,
for always believing in me

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ABSTRACT

The present work aimed to provide increased knowledge regarding biodiesel production by transesterification, focusing on diversifying raw materials and improving production process, in order to take advantage of current investments made in biodiesel production plants.

Using sunflower oil, soybean oil and waste frying oil as raw materials and NaOH, CH₃ONa and KOH as catalysts, the results showed that: i) biodiesel production using virgin oils results in higher yields (reaching 97 wt.%) compared to the production using waste frying oils (reaching 92 wt.%); ii) biodiesel kinematic viscosity and purity were important quality properties to select catalytic conditions to be used; using KOH as catalyst, minimum purity was not obtained; and iii) depending of the raw material and the sodium based catalysts used, to ensure a product with quality, 0.6 or 0.8 wt.% of catalyst should be used.

Using mixtures of pork lard and soybean oil as raw materials for biodiesel production: i) using raw material mixtures the product yield varied from 81.7 to 88.8 (wt.%) and enough purity was not obtained, being however close to the limit; ii) a linear model could be used to estimate the composition and some biodiesel quality properties, based on the weighted average of those properties for each component of the mixture.

Biodiesel production from acid waste lard (14.57 mg KOH g⁻¹) was enabled by studying a two-step process, including acid esterification followed by basic transesterification. In the two step synthesis, the best reaction conditions led to a purity of 99.6 wt.%; however, low yield was obtained (65 wt.%). Basic transesterification of a raw material mixture resulted in a yield of 77.8 wt.%, showing that blending might be an interesting alternative to enable homogeneous transesterification of acid raw-materials.

Several heterogeneous catalysts were studied for biodiesel production and results showed that: i) the basicity and catalyst calcination play a very important role in its performance; ii) CaO and the mixed oxide of calcium and manganese (Ca_{0.9}Mn_{0.1}O) presented the best results; iii) using CaO, higher reaction rates were observed compared to when using Ca_{0.9}Mn_{0.1}O; however, the mixed oxide catalyst needed lower activation temperature; iv) carbonation was probably responsible for the deactivation of CaO catalyst whereas hydration was responsible for the deactivation of the mixed oxide of calcium and manganese; v) temperature and interaction between temperature and catalyst concentration mostly influenced product purity obtained from pork lard using calcium manganese oxide as catalyst; vi) calcium manganese oxide was reused without loss of activity but there were evidences of residual catalyst leaching to biodiesel; however, catalytic behaviour could be classified as essentially heterogeneous.

Using different raw materials, after 8 h of reaction, heterogeneous catalysis (calcium manganese oxide) led to better product quality compared to homogeneous catalysis (NaOH); the higher reaction times might be compensated by reduced purification steps.

The developed work can be used to improve biodiesel production using homogeneous catalysis and presents relevant results to support research regarding heterogeneous catalysis.

KEYWORDS: Vegetable oils, animal fats, wastes, mixtures, transesterification, heterogeneous catalysts.

RESUMO

O presente trabalho pretendeu acrescentar conhecimento ao processo de produção de biodiesel através de transesterificação, focando-se na diversificação de matérias-primas e na melhoria do processo e traduzindo-se em possíveis adaptações às actuais fábricas, contribuindo para uma melhoria da sua viabilidade económica.

Utilizando óleo de girassol, óleo de soja e óleo de fritura usado como matérias-primas e NaOH, CH₃ONa, e KOH como catalisadores, os resultados mostraram que: i) utilizando óleos virgens conseguem-se maiores rendimentos na produção de biodiesel (atingindo 97 % (m/m)), do que utilizando óleos de fritura usados (atingindo 92 % (m/m)); ii) a viscosidade cinemática e a pureza são parâmetros de elevada importância para a selecção das condições catalíticas; utilizando KOH como catalisador, a pureza mínima não foi obtida; iii) uma concentração de 0.6 ou 0.8 % (m/m) de catalisador à base de sódio foi necessária, dependendo da matéria-prima e do catalisador utilizado, de forma a assegurar um produto com qualidade.

Utilizando misturas de banha de porco e óleo de soja como matérias-primas para a produção de biodiesel: i) o rendimento do produto variou entre 81.7 e 88.8 % (m/m) e a pureza mínima não foi obtida, estando no entanto próxima do limite mínimo; ii) um modelo linear pôde ser utilizado para estimar a composição e propriedades do biodiesel tendo em conta a média pesada dessas propriedades nos componentes da mistura.

A produção de biodiesel utilizando banha ácida, com uma acidez de 14.57 mg KOH g⁻¹, foi possível através de um processo em dois estágios: esterificação ácida seguida de transesterificação básica. As melhores condições reaccionais permitiram a obtenção de um produto com 99.6 % (m/m) de pureza, no entanto, com um baixo rendimento (65 % (m/m)). A transesterificação básica de uma mistura de matérias-primas resultou num produto com um rendimento de 77.8 % (m/m), mostrando que a mistura pode ser uma alternativa atractiva para permitir a transesterificação homogénea de matérias-primas ácidas.

Vários catalisadores heterogéneos foram estudados para a produção de biodiesel. Os resultados mostraram que: i) a basicidade do catalisador e a calcinação prévia apresentam um papel decisivo no seu desempenho; ii) o óxido de cálcio (CaO) e o óxido de cálcio e manganês (Ca_{0.9}Mn_{0.1}O) apresentaram os melhores resultados; iii) utilizando CaO, a reacção progride mais rapidamente do que utilizando Ca_{0.9}Mn_{0.1}O; contudo, o óxido misto necessitou de uma menor temperatura de activação do que o óxido de cálcio; iv) a carbonatação foi provavelmente responsável pela inactivação do CaO enquanto que a hidratação foi responsável pela inactivação do óxido misto; v) utilizando óxido de cálcio e manganês como catalisador na reacção de transesterificação de banha de porco, a temperatura e a interacção entre a temperatura e a quantidade de catalisador influenciaram maioritariamente a pureza do produto obtido; vi) o óxido misto foi utilizado sem perda de actividade no entanto verificaram-se evidências de lixiviação de cálcio para o biodiesel; apesar disso, o comportamento catalítico pôde ser classificado como essencialmente heterogéneo.

Em ensaios de transesterificação de 8h, utilizando diferentes matérias-primas, verificou-se uma melhor qualidade do produto utilizando a catálise heterogénea (óxido misto) do que a catálise homogénea (NaOH); os elevados tempos de reacção poderão ser compensados pela minimização dos estágios de purificação.

O trabalho realizado pode ser utilizado para melhorar a produção de biodiesel através de catálise homogénea e apresenta resultados relevantes para suportar investigação futura em catálise heterogénea.

PALAVRAS-CHAVE: Óleos vegetais, gorduras animais, resíduos, misturas, transesterificação, catálise heterogénea.

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LIST OF ACRONYMS

AC	Activated carbon
ASS	Anhydrous sodium sulphate
AWL	Acid waste lard
BaFeOx	Barium and iron oxide
BaMnOx	Barium and manganese oxide
Bio-ETBE	ethyl-tertio-butyl-ether
Bio-MTBE	methyl-tertio-butyl-ether
CaCeOx	Calcium and cerium oxide
CaFeOx	Calcium and iron oxide
CaMnOx	Calcium and manganese oxide
CaZrOx	Calcium and zirconium oxide
CCD	Central composite design
CFPP	Cold filter plugging point
CI	Cetane index
CN	Cetane number
CO ₂ e	CO ₂ equivalents
EEA	European Environment Agency
FAME	Fatty acid methyl ester / fatty acid methyl esters
FID	Flame ionization detector
GC	Gas chromatography
GHG	Greenhouse gas / greenhouse gases
HC	Unburned hydrocarbons
ME	Methyl ester / methyl esters
pH _{PZC}	pH of the point of zero charge
PL	Pork lard

PM – Particulate matter

r^2 – determination coefficient

RSM – Response surface methodology

SBO – Soybean oil

SFO – Sunflower oil

TG – Thermogravimetric

toe – Tonnes of oil equivalents

VOF – Volatile organic fraction

WFO – Waste frying oil / waste frying oils

CHAPTER 1 INTRODUCTION

1.1 FRAMEWORK

1.1.1 RELEVANCE OF THE STUDY

The society depends on energy to be able to function and the amount of spent energy is closely related with each country activities and the life quality of its inhabitants (Tester, 2005). Accordingly, the need for development and the continuous increase in world population causes even higher needs for energy resources.

Throughout the world, around 85% of the commercial energy is obtained from fossil fuels, non renewable fuels such as petroleum, coal and natural gas (Tester, 2005). Because several countries are deficient in fossil fuel reserves, they are dependent upon imports. The costs associated with the imports significantly increased not only due to increasing consumption but also due to external factors such as variation in price (caused by reduction of fossil fuel reserves), and in exchange rates (McGowan et al., 2009).

There is no doubt that the most important fossil fuel worldwide is petroleum, extracted in some countries and mostly consumed in the industrialised ones. Between 1991 and 1999 crude Brent petroleum prices were fairly constant being in the range of 10-20 €/barrel (Figure 1.1); however, after 1999, they have started to rise in a very significant way reaching in 2008 a peak price of around 85 €/barrel. Between 2008 and 2009 the prices started to decrease but a rapid rise was again observed in the following year; petroleum price in May 2010 was around 62 €/barrel.

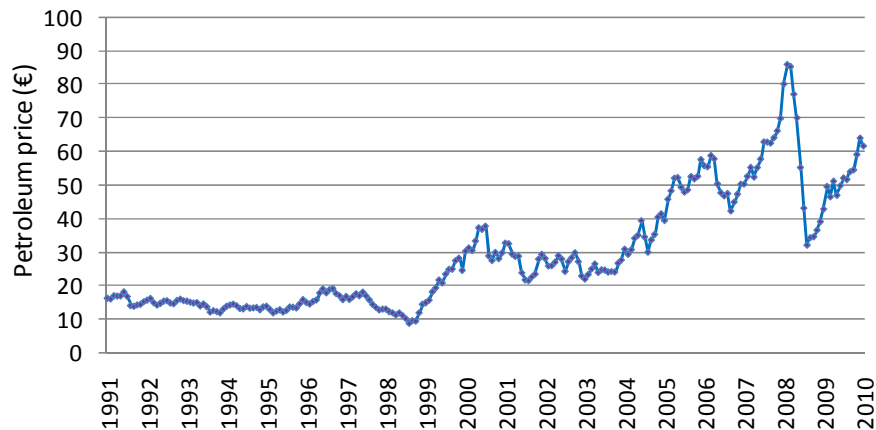


Figure 1.1. Evolution of petroleum prices (€/barrel) throughout the years (ECB, 2010).

The transport sector has been the great final consumer of petroleum throughout the world, showing higher expression over the years (Figure 1.2); also, the activity of this sector has increased significantly due to transport demand (for freight and passengers) and preference for road rather than other less polluting transport options (EEA, 2009).

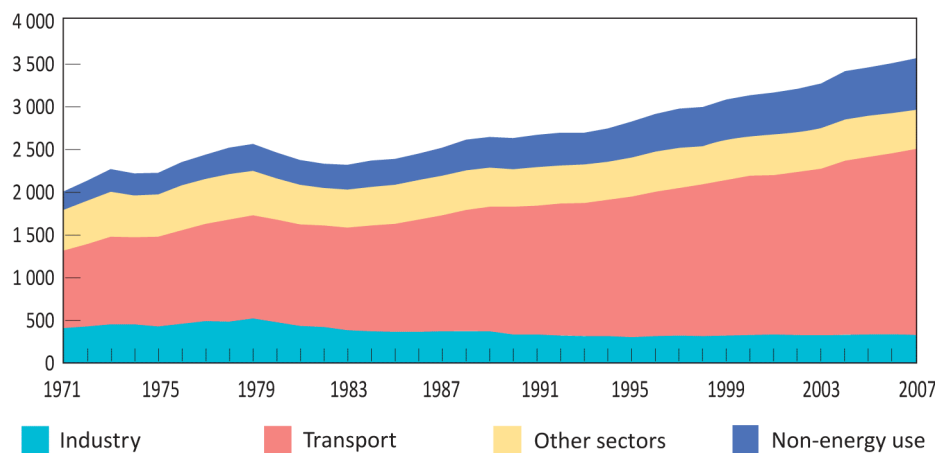


Figure 1.2. World evolution (1971-2007) of petroleum consumption, in millions of tonnes of oil equivalents (Mtoe), by activity sector; adapted from IEA (2009).

The high consumption of petroleum and intense activity of the transport sector are responsible for significant environmental impacts, reflected by high emissions of greenhouse gases (GHG), which trap heat in the atmosphere. In Europe, the transport sector is certainly the most problematic emission sector with upward emission trends, being 26% higher in 2001 compared to 1990 (EEA, 2009). The production of public electricity and heat from fossil fuel combustion by the energy industry and the road transportation have the most responsibility on the emission of GHG in Europe; in 2007, the road transportation emitted 17% of the total emissions (Figure 1.3).

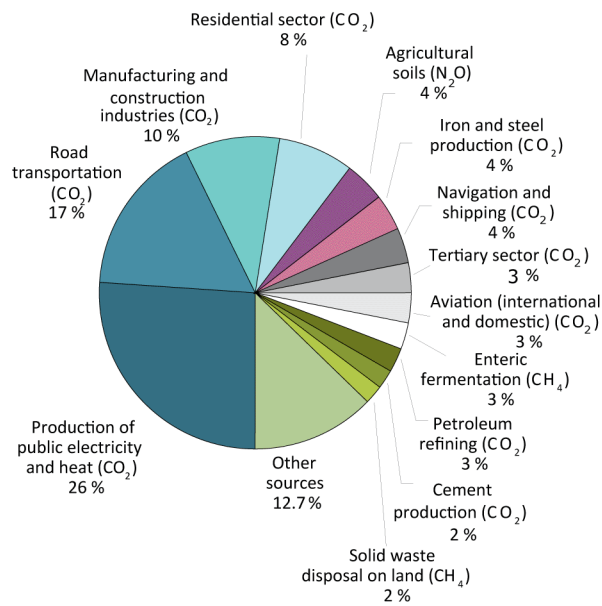


Figure 1.3. Greenhouse gas emissions in the EU-27 by main source activity in 2007;
adapted from EEA (2009).

In order to reduce the fossil fuel dependency and the high associated environmental impacts (namely regarding GHG emissions), it is of extreme importance to rationalise the consumption and diversify the energy sources. Additionally, the development of renewable energy for the transport sector should be one of the main priorities.

Biofuels, renewable fuels derived from biomass, are certainly key contributors for the diversification of energy sources in the transport sector. Therefore, the present work studied biodiesel production, a biofuel which might be used as an alternative to fossil diesel in the transport sector, focusing on improving production process by considering both, raw material diversification and process development.

1.1.2 OBJECTIVES

The present work aimed to provide increased knowledge regarding biodiesel production. The main objectives were to understand biodiesel processing constraints, to enable the diversification of currently used raw materials, as well as, to improve production diagram aiming the substitution of the currently used processes.

Studies considering the application of alternative raw materials included the use of edible and non-edible vegetable oils, animal fats (with low and high acidity) as well as their mixtures. Process improvement was studied focusing on the chemical reaction (selection of best conditions and development of alternative catalysts) as well as on the product quality.

1.1.3 OUTLINE

The outline of the work, including the description of main subjects approached in each chapter, is presented in Table 1.1.

Table 1.1: Outline of the work

CHAPTERS	DESCRIPTION
CHAPTER 1 Introduction	Presents subject relevance, objectives and outline of the work; Provides an overall view of energy in Portugal and the importance of biofuels production; Details biodiesel fundamentals regarding production, advantages and disadvantages, raw materials as well as process improvement.
CHAPTER 2 Edible and Non-edible Vegetable Oils for Biodiesel Production	Studies biodiesel production from edible and non-edible vegetable oils using different homogeneous alkali catalyst; Evaluates the influence of reaction conditions on biodiesel quality.
CHAPTER 3 Biodiesel Production from Vegetable oil/Animal fat Mixtures	Evaluates biodiesel production using vegetable oils mixed with animal fat; Analyses variations in composition and quality aiming its prediction when different mixtures are used as raw materials.
CHAPTER 4 Biodiesel Production from Acid Waste Lard	Studies biodiesel production from acid waste lard evaluating esterification as pre-treatment to reduce raw material acidity; Evaluates product quality and the use of raw material mixtures for biodiesel production with and without pre-treatment.
CHAPTER 5 Biodiesel Production from Animal fat Through Heterogeneous Catalysis	Studies different heterogeneous catalysts for pork lard transesterification; Evaluates the influence of the reaction conditions on biodiesel purity, namely using response surface methodology ; Analyses the re-use and the leachability of the catalyst.
CHAPTER 6 Calcium manganese oxide for Biodiesel Production using Different Raw materials	Compares biodiesel production using calcium manganese oxide and other catalysts; Analyses biodiesel heterogeneous synthesis using calcium manganese oxide and different raw materials, such as animal fat, waste frying oil and their mixture; Evaluates product quality according to EN 14214.
CHAPTER 7 Conclusions and Future Work	Presents the main conclusions and suggests future studies to complement the work and continue its development.

1.2 ENERGY IN PORTUGAL

1.2.1 ENERGY DEPENDENCY AND POLLUTANT EMISSIONS

Portugal is a country with scarce energetic resources; therefore, the economy is significantly dependent on the import of fossil fuels. The economic growth and population increase intensified this state of dependency; accordingly, the domestic production represented in 2006 only about 16% of the one consumed (Figure 1.4). The major contribution clearly corresponds to petroleum, which in 2007 represented around 80% of the Portuguese energetic imports, followed by natural gas with 10% (Figure 1.5).

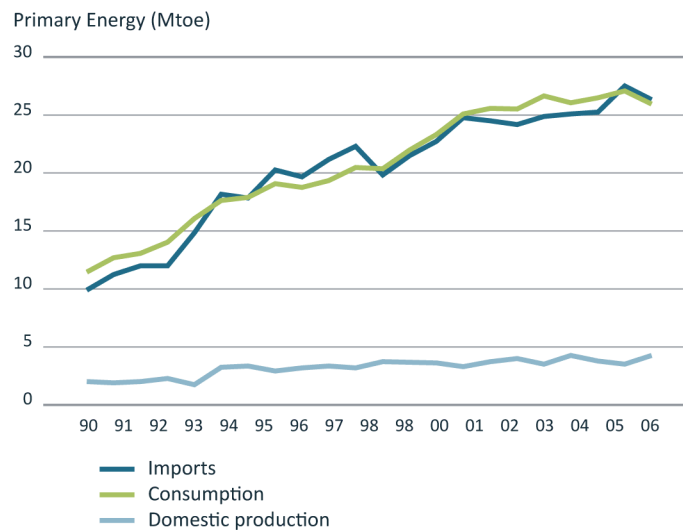


Figure 1.4. Domestic production, imports and consumption of primary energy in Portugal in 2006; adapted from APA (2008).

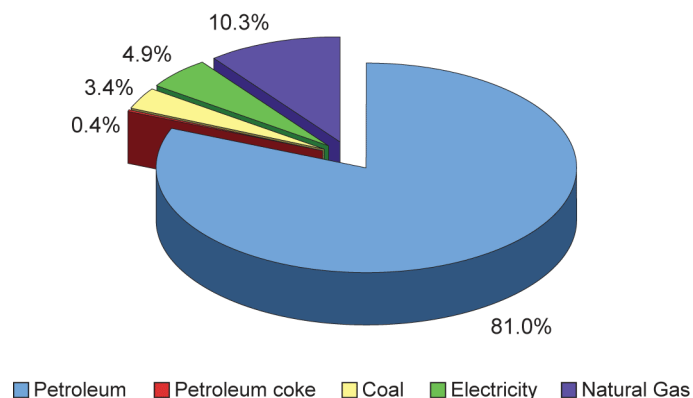


Figure 1.5. Energy imports structure in 2007; adapted from DGEG (2008a).

In Portugal, the transport sector was responsible for the consumption of 42% of the imported petroleum in 2007 (MEI, 2007). In agreement with the world and European trends, this sector has been growing very significantly; the number of vehicles in circulation increased 86% from 1990 till 2007 (APA, 2009).

In terms of the transport sector contribution for pollutant emissions, Figure 1.6 clearly shows the Portuguese negative situation, since in 2006 higher GHG emissions were emitted by Portugal in comparison with the European Union-27 (EU-27).

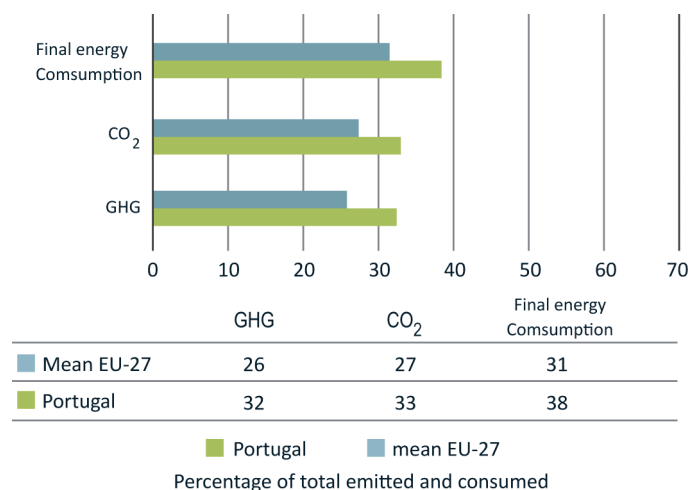


Figure 1.6. Relative contribution of the transport sector for the emissions of the main pollutants (GHG and CO₂) and final energy consumption adapted from APA (2008).

GHG include CO₂, CH₄, N₂O and fluorinated gases (hydrofluorocarbons, perfluorocarbons and sulphur hexafluoride); CO₂ is certainly the main GHG, presenting the higher emissions amongst all. According to the European Environment Agency (EEA, 2009), the predominant role of CO₂ in GHG emissions is directly related with the combustion of fossil fuels and their derived fuels; CH₄ and N₂O mainly result from agricultural and waste management activities and the fluorinated gases from industrial processes. The Portuguese GHG emissions in 2006 were about 39% higher than the ones of 1990 (considering CO₂, CH₄ e N₂O and excluding emission and capture by forest and changes in land use). According to the Kyoto Protocol, an international agreement aiming GHG emission reduction, Portugal should limit to 27% the increase of GHG emissions relatively to 1990 within the period of 2008-2012. GHG emissions, in terms of CO₂ equivalents (CO₂e), where in 2006 12% higher than the Kyoto Protocol goal (Figure 1.7). The most recent information on Portugal GHG emissions shows a 2% reduction in 2007 compared to 2006 (APA, 2009); however, emissions are still 10% above the imposed limit for that year, meaning that the target regarding GHG emission reduction is far from being reached.

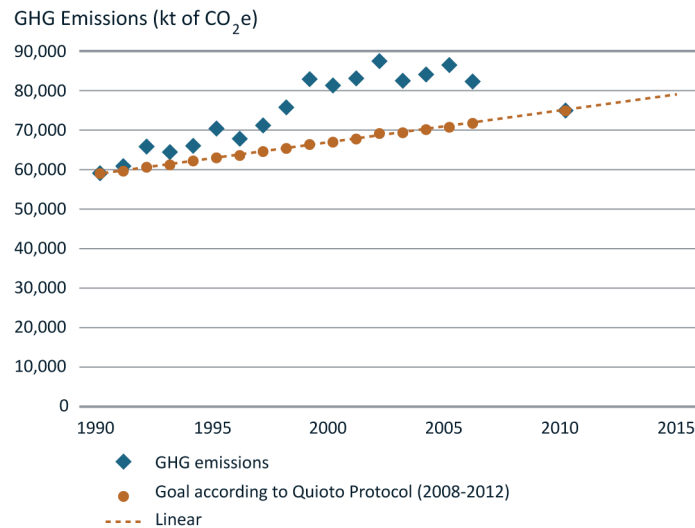


Figure 1.7. Portugal greenhouse gases emissions, considering CO₂, CH₄ and N₂O, until 2006 and commitment for the 2008-2012 period; adapted from APA (2008).

1.2.2 ENERGY FROM RENEWABLE SOURCES

The Portuguese energy production from renewable sources increased 25.9% between 2002 and 2006, and, currently, domestic production of primary energy is mostly ensured by renewable energy sources, as demonstrated in Figure 1.8.

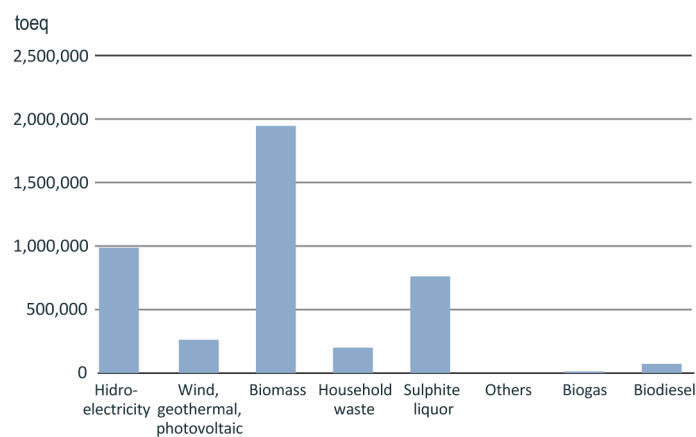


Figure 1.8. Domestic production of primary energy by source ; adapted from APA (2008).

The main sources are biomass and hydroelectricity. Biomass (wood and forest wastes) accounts for electricity production; however, is mostly used for heat generation in cogeneration plants of the forestry sector industries (which require large amounts of thermal power to function). Hydroelectricity, wind, geothermal and solar photovoltaic energy are mostly used for electricity production as demonstrated in Figure 1.9.

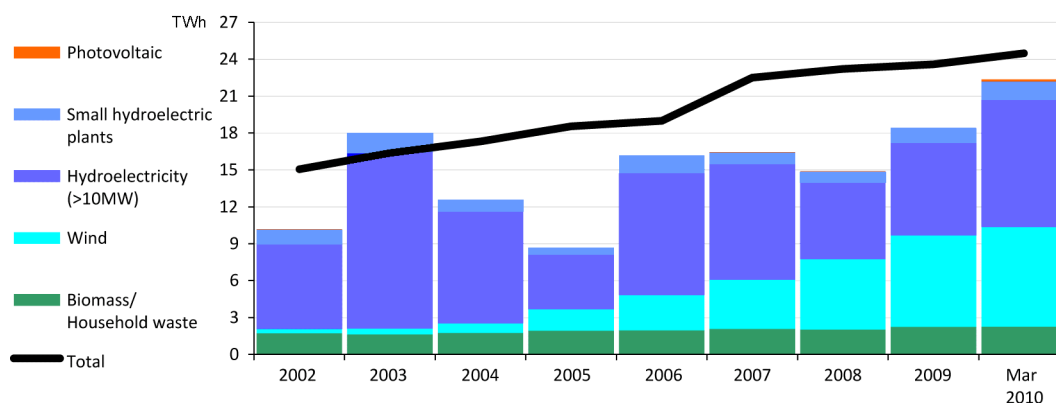


Figure 1.9. Evolution of renewable energy sources in electricity production, total corrected takes into account the productivity index of hydroelectricity; adapted from DGEG (2010b).

Other sources, with smaller representation, include household waste, sulphite liquor (a fluid resulting from wood processing), biogas and biodiesel. Household waste and sulphite liquor are also used for heat and/or electricity generation. Biogas and biodiesel can be used as alternative fuels, namely for transport purposes.

Portugal expects to increase significantly the production of renewable energy; the perspectives regarding renewable energy production, mostly for the present year (2010), are presented in Table 1.2.

In order to increase Portuguese endogenous production and achieve the expectations for the present year (Table 1.2) renewable energy production increased.

Table 1.3 shows the present situation regarding renewable energy production and a comparison with the previous perspectives will be made from now on.

In March 2010, the renewable energy installed capacity in Continental Portugal was 9 229 MW (DGEG, 2010b); however, the present capacity is below the perspectives for 2010.

In addition to the Continental Portugal renewable energy production, it should be emphasised the geothermal production in the archipelago of Azores (island of São Miguel); there are two geothermal electric power stations operating with an installed capacity of 23 MW, divided by *Ribeira Grande* (13 MW) and *Pico Vermelho* (10 MW) which account for 44% of the total power generation in São Miguel.

The wind energy installed capacity increased but additional efforts are essential to fulfil the 2012 target; also, the hydroelectricity production target was not fulfilled.

Table 1.2: Perspectives regarding renewable energy production capacities in Portugal for 2010/2012

	
RENEWABLE ENERGY	PERSPECTIVES
	<i>INFORMATION AND FIGURES IN MEI (2007)</i>
Wind energy	To reach 5 100 MW of installed capacity by 2012 (a 1950 MW increase).
Hydroelectric energy	To reinforce infrastructures to reach 5 575 MW of installed capacity in 2010.
Biomass	To attribute further 100 MW capacity, increasing electricity target capacity to 250 MW by 2010.
Solar photovoltaic	To construct the biggest worldwide photovoltaic power station (<i>Moura</i> photovoltaic plant); To connect with microgeneration and solar hot water policies and objectives.
Micro-generation	To promote the installation of 50 000 systems by 2010, namely encouraging the installation of solar hot water in buildings.
Wave power	To create a pilot area with an operating capacity of 250 MW for the development of new prototypes and their commercialisation.
Biofuels	To achieve a target of 10 vol.% of biofuels in road fuels by 2010; To reach 100 MW of installed capacity for anaerobic digestion of wastes.

New biomass thermoelectric plants significantly increased installed capacity (103 MW actual versus 24 MW in 2008 according to DGEG (DGEG, 2010b)) and several other plants are expected to be functioning in the future in order to reach 250 MW of installed capacity. However, the 2010 target is still far from being reached.

Solar photovoltaic energy and microproduction increased significantly and a very large plant (the largest of the world when constructed) is currently operating in Portugal, presenting a capacity of 46 MWp.

The Council of Ministries communicated recently (17 June 2010) the approval of a Resolution regarding the exploitation of a pilot area for the production of electric energy from waves; the project is therefore in its starting stage, as expected. Biogas installed capacity is still much smaller than the target capacity (21 MW compared to 100 MW).

Table 1.3: Present situation regarding renewable energy production capacities in Continental Portugal, March 2010 (DGEG, 2010b)

	
RENEWABLE ENERGY	PRESENT SITUATION <i>FIGURES IN MEI (2007)</i>
Wind energy	Installed capacity of 3 725 MW (204 wind parks, 1 956 aerogenerators, 39% share attributed to parks with capacity ≤ 25 MW).
Hydroelectric energy	Installed capacity of 4 821 MW by March 2010.
Biomass	Installed capacity of 103 MW from thermoelectric plants: Operating plants: <i>EDP Bio Constância</i> (13 MW) and <i>Bio Figueira da Foz</i> (30 MW); <i>Rodão Power</i> (14 MW); <i>ENERPULP Setúbal</i> (12,5 MW) and <i>Cacia</i> (12,5 MW); <i>Terras Santa Maria</i> (10 MW); <i>Mortágua</i> (9 MW) and <i>Centroliva</i> (5 MW) (APREN, 2010). Note: In 2009 the Portuguese government launched a public competition for the construction of 15 thermoelectric plants using biomass to create a network of plants presenting 250 MW of capacity. Installed capacity of 88 MW from household waste incinerators.
Solar photovoltaic and Microgeneration	Installed capacity of 108.7 MW (DGEG, 2010b); Main operating photovoltaic plants: <i>Moura</i> (46 MWp (megawatt peak)) and <i>Serpa</i> (11MWp).
Wave power	Installed capacity of 4.2 MW.
Biofuels	Biogas: Installed capacity of 21 MW; Biodiesel: Installed production capacity of around 600 000 t/year Main operating plants: <i>Biovegetal</i> (120 000 t/year); <i>Iberol</i> (120 000 t/year); <i>Prio</i> (100 000 t/year); <i>Sovena</i> (100 000 t/year) and <i>Torrejana</i> (100 000 t/year). Small dedicated producers (<3000 t/year): around 20 The following are the current small dedicated producers operating in Portugal: <i>Dieselbase</i>, <i>Bio valouro</i>, <i>Space</i>, <i>Norgen</i>, <i>Multirecolha</i>, <i>Avibom</i>, <i>Hardlevel</i>, <i>Socipole</i>, <i>Supermatéria</i>, <i>T.P.G</i>, <i>Ares Lusitani</i>, <i>Ecocomb</i>, <i>USV</i>, <i>Enercalis</i>, <i>Paisagem a Óleo</i> and <i>Biosarg</i> and more recently, <i>Leveforma</i>, <i>Bioprincipio</i>, <i>EGL</i>, <i>Biocanter</i>, and <i>Biomove</i> (DGEG, 2010a).

Despite the efforts made so far, the Portuguese endogenous production is far from responding to the energetic demands (APA, 2008) and most efforts performed so far focus on the diversification of renewable energy sources for electricity production.

The last formal information regarding the incorporation of biofuels is presented in the "Fifth national report on promoting the use of biofuels or other renewable fuels in transport in Portugal – Directive 2003/30/EC" (DGEG, 2008b), which relates to biofuels production and incorporation in 2007.

The report shows that biodiesel was the only biofuel incorporated in road transport; accordingly, in 2007 an amount of 195 884 t was produced from which 189 836 t was incorporated. In the same year, 1 589 306 t of gasoline and 4 864 016 t of road diesel were sold, which correspond to around 5 842 662 m³ of diesel and 7 968 823.7 m³ of fossil road fuels^{*}.

The amount incorporated in 2007 corresponds to approximately 3.7 vol.%[†] (3.37% on a energy basis[‡]) incorporation in diesel and 2.7 vol.% (2.54% on a energy basis) incorporation in total road fuels.

More recent information is provided by the European Biodiesel Board (EBB, 2010). According to this, the Portuguese biodiesel production from 2007 and 2008 was 175 000 t and 268 000 t, respectively[§]. Such information shows a clear increase in biodiesel production from 2007 to 2008 (53.1%).

Considering the same amount of road diesel sold in 2007, if all the biodiesel produced in 2008 (according to the European Biodiesel Board) was incorporated in diesel, it would correspond to around 5.2 vol.% (4.8% on a energy basis) incorporation in diesel and 3.8 vol.% (3.6% on a energy basis) in total road fuels. This means that a growth is being observed; however, Portugal was still in 2008 very far from reaching the 10 vol.% target incorporation in total road fuels for 2010.

Currently, Portuguese biodiesel production capacity allows a much higher incorporation; in fact, considering the same amounts of fossil fuels sold in 2007, the use of the total production capacity (considering 600 000 t) would allow an incorporation of approximately 8.6 vol. % (8% on a energy basis) in total road fuels.

The reason why most Portuguese plants are working significantly below their capacity relates with the scarce endogenous production of the vegetable oils (raw material currently used for biodiesel production) and also the need for those materials to respond to the food market. Currently, used oils include soybean oil, sunflower and rapeseed oil which are mostly imported; therefore, raw materials costs sometimes do not compensate biodiesel production (1 litre of oil is sometimes more expensive than 1 litre of biodiesel).

Additionally, even when vegetable oil prices allow production, companies are extremely dependent upon tax incentives (exemption of tax over petroleum products) to be able to sell their fuel at a competitive price; Portuguese legislation defines exempted amounts.

^{*} Considering a mean density of 747.5 kg m⁻³ for gasoline and 832.5 kg m⁻³ for diesel, according to *Decreto-Lei 89/2008*.

[†] Considering a mean density of 880 kg m⁻³ for biodiesel according to EN 14214 (2003).

[‡] Considering 6 986 883 GJ of biodiesel (36.8 GJ/t) and 275 348 958 GJ of diesel (42.6 GJ/t) and gasoline provided by DGEG (2008b).

[§] The information for 2007 corresponds to a production 11% less than the one published by DGEG (2008b) (195 884 t); therefore, it should not be considered very rigorous.

Regarding biofuels production, namely for incorporation in the transport sector (replacement of diesel and gasoline), only biodiesel is being produced mainly due to the deficit in diesel production compared to the surplus in gasoline production. Accordingly, tax incentives for bioethanol production (for incorporation in gasoline) do not exist. The installed biodiesel production capacity allows higher incorporations but production is extremely dependent upon variation of raw material prices and tax incentives. This means that if biodiesel economic efficiency is not ensured, it is necessary to stop production.

In the near future, through legislation and national incentives, a greater impact in the development of alternative fuels for the transport sector is expected. Along with the regulations, research should be performed aiming the reduction of biodiesel production costs to make it more economically competitive, namely the development/application of alternative raw materials as well as the improvement of production processes efficiency.

1.2.3 LEGISLATION AND NATIONAL INCENTIVES

According to the Directive 2001/77/EC, relative to the production of electricity from renewable sources, Portugal should ensure a 39% share of all the consumed electricity in 2010. Because it was considered to be of strategic importance, the Portuguese government in its last national allocation plan for emissions allowances, approved by legislation (*Resolução do Conselho de Ministros n.º 1/2008*), changed this target to 45%. In 2009, the incorporation of renewable energy in the Portuguese electric energy consumption was 45%, being already in agreement with the 2010 target (DGEG, 2010b).

In fact, as previously mentioned, Portugal presents a good performance regarding the electric energy production from renewable sources; however, in what regards biofuels production, it has still a medium behaviour and a very unstable legal framework.

The reference documents for current legislation regarding biofuels production are the “Biomass action Plan” (COM (2005) 628) adopted in 2005 and the document “An EU Strategy for Biofuels” (COM (2006) 34) released in 2006 which emphasise the need to promote biofuels use in Europe and developing countries.

Currently, the Directive 2009/28/EC, the ultimate European legislation on the promotion of the use of energy from renewable sources, sets new mandatory national targets for the overall share of energy from renewable sources in the final energy consumption; the main definitions regarding renewable energy sources according to this directive are presented in Table 1.4.

Table 1.4: Definitions according to Directive 2009/28/EC

TERM	DEFINITION
Energy from renewable sources	Energy from renewable non-fossil sources, namely wind, solar, aerothermal, geothermal, hydrothermal and ocean energy, hydropower, biomass, landfill gas, sewage treatment plant gas and biogases.
Aerothermal energy	Energy stored in the form of heat in the ambient air.
Geothermal energy	Energy stored in the form of heat beneath the surface of solid earth.
Hydrothermal energy	Energy stored in the form of heat in surface water.
Biomass	Biodegradable fraction of products, waste and residues (biological origin) from agriculture (vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and household waste.
Biofuels	Liquid or gaseous fuel for transport produced from biomass.
Bioliquids	Liquid fuel for energy purposes other than for transport, including electricity, heating and cooling, produced from biomass.

According to this, biofuels are liquid and gaseous products used for transport, produced from biomass. Liquid fuels that are not used for transport purposes and that are produced from biomass are defined as bioliquids. This Directive also sets targets for the energy obtained from renewable sources specifically in the transport sector; therefore, for the first time, the biofuels are included in European evaluation of the share of renewable energy for transports in final energy consumption, which indicates that greater evolutions are to be expected in the future regarding biofuels production.

The national global objectives are in agreement with the introduction of at least 20% of energy from renewable sources in the final energy consumption of the European community until 2020. In the case of Portugal, by 2020 a 31% share of renewable energy in the final energy consumption should be ensured. Additionally, each member state must guarantee that the share of renewable energy consumed by all transportation means represents, in 2020, at least 10% of the final energy consumption. Each member state should soon present an action plan to support measures and allow the fulfilment of such targets (30th June 2010). As previously mentioned, the development of alternative fuels for the transport sector in Portugal is currently based on biodiesel production.

A resume of main Portuguese legislation regarding biofuels production is presented in Table 1.5.

Table 1.5: Portuguese Legislation concerning biofuels production

NO.	LEGISLATION	DESCRIPTION	CONNECTIONS
1	<i>Decreto-Lei n.º 62/2006</i>	Creates mechanisms for biofuels promotion; Regulates biofuels production and creates conditions for small dedicated producers, namely the ones recycling waste frying oils.	Transposes Directive 2003/30/EC
2	<i>Decreto-Lei n.º 66/2006</i>	Establishes the creation of a tax incentive (reduction/ exemption) for biofuels.	
3	<i>Portaria n.º 3-A/2007</i>	Establishes the amount of tax exemption for biofuels until 31 December 2007 (small scale production until 31 December 2010).	
4	<i>Portaria n.º 1554-A/2007</i>	Regulates the process of tax exemption attribution to the economic operators that introduce biofuels in Portuguese consumption (period 2008-2010).	Revokes No. 3
5	<i>Resolução do Conselho de Ministros n.º 21/2008</i>	Approves the strategy for fulfilling national objectives regarding biofuels incorporation in fossil derived fuels.	
6	<i>Decreto-Lei n.º 89/2008</i>	Establishes technical specifications and quality control regulations for road fuels and conditions for commercialisation of fuels with incorporated biofuels (> 5 vol.%).	Changes No. 1
7	<i>Despacho n.º 22061/2008</i>	Defines a model for the obligatory inscription to be placed in equipments at the service stations that supply fuels with incorporated biofuels (> 5% vol.).	
8	<i>Decreto-Lei n.º 206/2008</i>	Inclusion of public entities in the category of small dedicated producers.	Changes No. 1
9	<i>Portaria n.º 13/2009</i>	Establishes (for a 1 year period) the tax exemption for biofuel as diesel substitute (with effects from 1 Jan 2008).	Follows No. 4 and 6
10	<i>Portaria n.º 134/2009</i>	Establishes the tax exemption for biofuel as diesel substitute (with effects from 1 Jan 2009).	
11	<i>Decreto-Lei n.º 49/2009</i>	Establishes a minimum share of biofuels for incorporation in road diesel and the procedures for monitoring and control: Targets: 6 vol% in 2009; 10 vol.% in 2010.	
12	<i>Portaria n.º 353-E/2009</i>	Establishes maximum prices and volumes of biofuels from which the entities responsible for introducing road diesel for consumption are exempted from obligatory incorporation and selling.	
13	<i>Portaria n.º 69/2010</i>	Same as No. 12	Updates No. 12

The legal framework was established since the Directive 2003/30/EC on the promotion of the use of biofuels or other renewable fuels for transport was implemented, being after transposed to the Portuguese law (Decreto-Lei n.º 62/2006). According to this directive, Member States should ensure a minimum proportion of biofuels and other renewable fuels in their market.

The following national indicative targets, regarding the incorporation (calculated on the basis of energy content) of biofuels in all gasoline and diesel used for transport purposes, were set: i) 2 % by 31 December 2005; and ii) 5.75 % by 31 December 2010. As mentioned in sub-section 1.2.2, in 2007 the incorporation was 2.54%; the values reported for 2008 indicate an incorporation of 3.6%; being significantly below the target for 2010 but higher than the target for 2005.

Portugal was very ambitious regarding biodiesel production and established through legislation (*Decreto-Lei n.º 49/2009*) that, by the end of 2010, fossil diesel should have at least 10 vol.% of biodiesel. However, up until recently, quality specifications for diesel (EN 590 (2009)) only allowed the incorporation of 5 vol.% of biodiesel. To help the fulfilment of the targets regarding biodiesel incorporation in Europe, the latest EN 590 specification standard set a maximum allowed incorporation percentage of 7 vol.%.

Therefore, the “at least 10 vol.%” target for Portugal is presently adjusted to “up to 7 vol.%”. In 2010, the national legislation fixed the biodiesel amounts that can be sold free of tax (Table 1.6), aiming the exemption of approximately that incorporation percentage in diesel (7 vol.%).

It should be however emphasised that it is possible to sell diesel with higher biodiesel incorporation percentages, namely up to 10, 15 and 20% if the service stations present the obligatory inscription according to specific legislation (*Despacho 22061/2008*). The consumer is then responsible for the use of that fuel and should confirm vehicle compatibility. At present, several light vehicles and most heavy ones can in fact use higher percentages of biodiesel, up to 30%.

The biofuel produced and imported destined to be integrated in petroleum derivative products (gasoline and diesel) in Portugal has to be exclusively delivered by petroleum and energy bonded terminal holders, to be later introduced into the marketplace.

Table 1.6: Maximum amounts (m³), by producer, of biofuels that can be sold free of tax according to Portuguese legislation (*Portaria n.º 69/2010*)

PRODUCER	2009	2010
<i>Iberol</i>	76 159	82 426
<i>Torrejana</i>	66 691	77 654
<i>Biovegetal</i>	54 700	68 993
<i>Prio</i>	52 498	67 111
<i>Sovena</i>	37 024	62 981
Total	287 072	359 165

Exceptions include the small dedicated producers (recognised by the responsible entities). A small dedicated producer is the one that presents a maximum annual production of 3 000 t and which production is made using waste raw materials or projects presenting technological advances aiming the production of less pollutant products; all the production must however be delivered to regular consumers which have a contract with the producer (*Decreto-Lei n.º 62/2006*). Therefore, small dedicated producers are not dependent upon biodiesel delivery by petroleum and energy bonded terminal holders, but are however obliged to communicate to the responsible entities the amount of biofuels produced in the previous trimester, as well as, the identification of the consumers and the respective delivered amounts.

1.3 BIOFUELS

1.3.1 DEFINITIONS

From the perspective of several authors, biofuels are obtained from biomass, being applicable to all kinds of final energy transformation, which includes electricity, heat generation and use as fuel in the transport sector. Examples of fuels that might be used are wood, straw, forest wastes, animal wastes, household wastes, synthetic gas derived from plant and animal matter, black liquor (sulphite liquor), biogas, biodiesel and bioethanol (Tabak, 2009). On the other hand, specific legislation regarding biofuels separates these from others not specifically used for transport purposes (Table 1.4). In the present work, when referring to biofuels, the biofuels legislation definition applies. Table 1.7 presents the definitions of the different types of biofuels according to the Directive 2003/30/EC, on the promotion of biofuels for transport. Table 1.8 presents a resume of the biofuels production methods and the respective applications.

Table 1.7: Definitions of biofuels according to the Directive 2003/30/EC

BIOFUEL	DEFINITION
Biodiesel	Methyl-ester produced from vegetable or animal oil, of diesel quality, to be used as biofuel.
Bioethanol	Ethanol produced from biomass and/or the biodegradable fraction of waste, to be used as biofuel.
Biomethanol	Methanol produced from biomass, to be used as biofuel.
Biodimethylether	Dimethylether produced from biomass, to be used as biofuel.
Bio-ETBE (ethyl-tertio-butyl-ether)	ETBE produced on the basis of bioethanol. The percentage by volume of bio-ETBE calculated as biofuel is 47 %.
Bio-MTBE (methyl-tertio-butyl-ether)	Fuel produced on the basis of biomethanol. The percentage by volume of bio-MTBE calculated as biofuel is 36 %.
Biogas	Fuel gas produced from biomass and/or from the biodegradable fraction of waste, that can be purified to natural gas quality, to be used as biofuel, or woodgas.
Synthetic biofuels	Synthetic hydrocarbons or mixtures of synthetic hydrocarbons, which have been produced from biomass.
Biohydrogen	Hydrogen produced from biomass, and/or from the biodegradable fraction of waste, to be used as biofuel.
Pure Vegetable oil	Oil produced from plants through pressing, extraction or comparable procedures, crude or refined but chemically unmodified, when compatible with the type of engines involved and the corresponding emission requirements.

Table 1.8: Biofuels production methods and applications in the transport sector

BIOFUEL	PRODUCTION METHOD	APPLICATIONS FOR TRANSPORT
Biodiesel	Transesterification of vegetable oils and animal fats ^{a)} .	Compression ignition engines (diesel substitute)
Bioethanol/ Biomethanol	Fermentation of sugar crops ^{b)} .	Spark ignition engines (gasoline substitute)
Bio-ETBE Bio-MTBE	Chemical reaction between alcohols and isobutylene.	Spark ignition engines (gasoline substitute)
Biodimethylether	Methanol dehydration and CO/CO ₂ hydrogenation.	Adapted vehicles (Liquefied petroleum gas substitute)
Biogas	Anaerobic digestion of organic material.	Adapted vehicles
Synthetic biofuels	Gasification and synthesis using lignocellulosic material.	Compression ignition engines (diesel substitute)
Biohydrogen	Gasification of biologic processing of lignocellulosic material.	Adapted vehicles
Pure vegetable oil	Physical/Chemical extraction from plants.	Compatible vehicles

^{a)} Raw materials: soybean, rapeseed, sunflower, pork lard, beef tallow, poultry fat; ^{b)} Sugarcane, corn, cassava, sweet sorghum, sweet sugar beet.

At present, the biofuels mostly used at a commercial scale are biodiesel, produced from rapeseed oil and soybean oil and bioethanol, produced from sugarcane, corn or sugar beet. Bioethanol or methanol can be further chemically converted in Bio-ETBE or Bio-MTBE biofuels.

Biodimethylether production can be made from methanol or derived methanol from synthesis gas (produced by biomass gasification) through catalytic methanol dehydration (Hassanpour et al., In press) or CO/CO₂ hydrogenation (Zhang et al., 2010).

Biogas (CH₄) production from the anaerobic digestion of wastes is an established technology; however, a very small contribute is observed in its use as transportation fuel in Portugal, most being produced at the waste management units and used for electricity and heat production (fulfilling the energetic/heat demands and selling the excess) rather than for transportation purposes.

The production of synthetic biofuels via biomass pyrolysis and hydrogenation of carbohydrates, lignin or triglycerides is also being studied for future applications (Vertés et al., 2010).

Biohydrogen combustion is extremely attractive because it yields zero CO₂ emissions (Vertés et al., 2010). Common processes of producing biohydrogen include biomass thermal gasification and biological production, namely by anaerobic fermentative bacteria which decompose carbohydrates, generating hydrogen and small organic acids (Gressel, 2008). Hydrogen has a very high energetic value by mass; however, in normal conditions of temperature and pressure, it remains in the gaseous state and the very low density of the gas makes its energetic content by volume very low in comparison with other fuels; accordingly, there is a need to store high volumes of hydrogen to ensure the energetic requirements (SPF, 2006). To allow the storage of high volumes, compression and liquefaction can be used but they consume high amounts of energy. Additional constraints relate with the logistics of transportation (due to high amounts) and safety issues (very high flammability) (SPF, 2006). Through electrochemical processes, the hydrogen can be converted to electricity in fuel cells with very high efficiencies; fuel cells can further be used in the transport sector and currently several car manufacturers are developing prototype vehicles for its application (Oliveira, 2009). The development of more efficient routes to produce, store and transport hydrogen along with the reduction of the technology costs might enable a larger application of fuel cells in the transport sector in the future.

The use of vegetable oils as direct fuel is not new; over 100 years ago, Rudolf Diesel (1858-1913) developed an engine working on vegetable oils. In fact, in 1900 he showed in an exhibition in Paris a engine working using peanut oil (Demirbas, 2003).

However, the direct use of vegetable oils presents a series of inconvenient namely increase of carbon deposits, injector coking, thickening and gelling of the engine lubricating oil amongst others (Rakopoulos et al., 2006).

The application of some of the existing biofuels in the transport sector is dependent upon vehicle adaptation. As previously referred, most commonly used biofuels are bioethanol and biodiesel, which can be used in conventional vehicles, usually incorporated with fossil derived fuels without need of vehicle adjustments. Bioethanol is usually used incorporated with gasoline, with incorporation percentages around 5-10 vol.%; however, Flexi-fuel vehicles can use up to 85 vol%. Biodiesel can be used pure but usually, incorporation percentages up to 30% in diesel are used.

North and South America are the main producers of bioethanol, with Brazil and the United States producing more than 80%; almost all the ethanol produced is consumed domestically, although trade is beginning to grow (Vertés et al., 2010). Regarding biodiesel production in Europe during 2005, a 20-fold higher production than the United States was observed; however, the production of the United States showed a dramatic increase and in 2007 it was the second-largest biodiesel producer of the world, after Germany. The European Union and the United States account for more than 95% of the global biodiesel demand (Vertés et al., 2010). Because bioethanol and biodiesel are at present the most important biofuels, the next sections will essentially focus on both.

1.3.2 PROPERTIES

Engine manufacturers develop their products taking into account the properties of the used fuel; therefore, the introduction of bioethanol and biodiesel in the fuel market led to very strict quality control and the need for full characterisation of these fuels. The characterisation enables vehicle adaptation, namely to guarantee the same atomisation and combustion as when conventional fuels are used; this fact naturally led to a high resistance by several vehicle producers to implement biofuels (Vertés et al., 2010).

The main reason why biofuels can replace fossil derived fuels relates with their relatively similar properties; however, some important differences exist. The fundamental properties of biofuels and petroleum-derived fuels are presented in Table 1.9, being highlighted the properties of gasoline and diesel fuel.

Table 1.9: Biofuels properties compared to petroleum-based fuels, adapted from Vertés et. al. (2010)

FUEL	LOWER HEATING VALUE (MJ kg ⁻¹)	STOICHIOMETRIC AIR/FUEL RATIO	OXYGEN CONTENT (Wt.%)	LATENT HEAT OF VAPORISATION (kJ kg ⁻¹)	REID VAPOR PRESSURE (kPa)	CETANE RATING	OCTANE RATING	
							RON ^{a)}	MON ^{b)}
Gasoline	42.7-44.0	14.6	0	350-356	48-103	-	91-99	82-90
Methane	49.9	17.2	0	507	-	-	130	130
Natural gas	44.8	16.2	0	-	-	-	>120	120- 127
Liquefied petro- leum gas	46.0	15.8	0	428	-	-	104	89
Methanol	19.9	6.5	50.0	1103-1186	32	3	106- 112	91-92
Ethanol	26.9	9.0	34.8	842	22	8	107- 111	89-92
Hydrogen	119.4	34.3	0	-	-	-	-	-
Diesel	43.2	14.5	0	207-286	-	40-65	-	-
Soybean Biodiesel	37-39.8	12.5	10.8	320	-	46.2-51	-	-
Rapeseed Biodiesel	37.3	12.7	9.9	320	-	52.9	-	-
Sunflower Bio- diesel	38.1-38.6	12.2	11.4	320	-	49	-	-
Tallow biodiesel	39.9	12.5	11.3	313	-	58	-	-

^{a)} RON –Research octane test; ^{b)} MON - Motor octane test.

The physical properties are determinant to guarantee an efficient combustion as they influence the mixture of the air with the fuel; the mixture depends on the atomisation and consequent dispersion of the fuel at the intake of the engine or at the combustion chamber. The most relevant properties regarding bioethanol use in spark ignition engines and biodiesel use in internal combustion engines will be described in the following subsections.

SPARK IGNITION ENGINES

Spark ignition engines mostly work by injection of the fuel into the inlet port immediately before the inlet valve; the mixture then occurs when the fuel and the air enter the cylinder. For an efficient mixing, it is important that the fuel is sufficiently volatile.

The energy content of the fuels is usually represented by the lower heating value ^{**}; ethanol has much lower heating value than gasoline which means that for a certain amount of fuel, a lower distance can be travelled using ethanol compared with diesel.

The Reid vapour pressure is a test that works as an indicator of the fuel volatility. Ethanol presents much lower Reid vapour pressure than gasoline; however, it is well known that the addition of ethanol to gasoline increases the volatility, essentially due to splash blending of ethanol in gasoline; however, high incorporations are avoided because volatility also influences evaporative emissions (Vertés et al., 2010).

The latent heat of vaporisation determines how much heat is required for the fuel to vaporise and this property is much higher in bioethanol than in gasoline, which means that a higher amount of heat is required in order to volatilise bioethanol. This is indicated as one of the major reasons why the maximum incorporation percentage is fixed in around 85%, in order to ensure a sufficient amount of fuel efficiently volatile, which is very important at cold start (Vertés et al., 2010).

Adapted engines might use only gasoline for cold start and after mixing the alcohol, therefore allowing higher incorporation percentages (100%). One very important advantage of using 100% bioethanol is that up to 5% of water is tolerated in the fuel, therefore the bioethanol production costs are reduced (no need of additional purification steps to reduce water content). When mixed with gasoline, ethanol needs to have a very low water content, or else, mixture is not complete and phases (alcohol and gasoline) tend to separate (Vertés et al., 2010).

^{**} Relates with the determination method used: when combustion takes place, water is formed and appears in the form of vapour; as the gases expand and cool, the water condensates releasing a certain amount of heat; this heat is discounted from total heat measured leading to the lower heating value, which is in fact the useful heat.

COMPRESSION IGNITION ENGINES

Because the time for fuel injection in the combustion chamber is very short using these engines (few time for mixing with air and atomisation); the atomisation of the fuel is critical.

Amongst the physical properties that influence atomisation are the viscosity and the density of the fuel, which essentially relate to the fuel composition. Usually, biodiesel presents higher viscosity and density than diesel; in fact, density of biodiesel is usually around 7% higher than that of diesel (Vertés et al., 2010).

The differences in viscosity of biodiesel to diesel also influence the fuel atomisation. Because viscosity significantly varies with temperature, one way to overcome this issue might be the adjustment of the temperatures to ensure that at the time of injection the fuel has similar viscosity than the diesel fuel. At low incorporation percentages (up to 5 vol%) this differences are, however, negligible (Vertés et al., 2010).

The cetane number indicates the ignition quality and it is relatively similar between diesel and biodiesel; however, depending on the raw material used for biodiesel production, different values can be obtained. Because the cetane number is inversely related with the number of double bonds, biodiesel from fats presents usually higher cetane number (Mittelbach et al., 2004). The lower heating value of biodiesel is around 9% lower than the one of diesel, the difference being much smaller than the bioethanol/gasoline differences. However, we should consider that we are comparing heating values on a weight basis and the densities of the fuels, as previously mentioned, are significantly different. The energy content by weight and by volume of several biofuels is presented in Table 1.10.

Table 1.10: Energy content of transport fuels (Directive 2009/28/EC)

FUEL	LOWER HEATING VALUE (MJ/kg)	LOWER HEATING VALUE (MJ/l)
Bioethanol	27	21
Biomethanol	20	16
Bio-ETBE	36	27
Bio-MTBE	35	26
Biodiesel	37	33
Biogas	50	-
Gasoline	43	32
Diesel	43	36

Because biodiesel density is higher than the one of diesel, the energy content by weight is smaller; however if we compare it on a volumetric basis the differences are much smaller. The measure by mass has a high meaning from a scientific point of view; however, in the case of bio-fuels, the measure by volume is more relevant because the space in the transport to be used is limited and also logistics for transport purpose are crucial (one of the main problems with hydrogen). However, a difference around 8% still exists and according to that, the use of 100% biodiesel should influence the fuel consumption.

1.3.3 QUALITY STANDARDS

It is essential to evaluate the quality of biofuels to ensure engine-fuel compatibility and reliability; therefore, quality standards were developed. The fulfilment of the standard specifications is essential because vehicle engines are optimised considering those properties. Some considered most important quality parameters of bioethanol and biodiesel will be described from now on.

BIOETHANOL

Amongst the most important bioethanol quality parameters are the denaturant, ethanol and water contents and the acidity.

In the United States of America, bioethanol needs to be denatured to make it undrinkable before being possible to blend it with gasoline. The denaturing usually involves adding a bitter chemical called Bitrex® and methanol. The denaturant content needs to be such that effectively denaturises the alcohol but not too much that can affect engine performance.

The ethanol content is also an important quality as it indicates the purity of bioethanol; higher purities are desirable but the increase of the purity has great reflection on bioethanol production costs (ASTM D4806 (2009) sets a minimum of 92.1 vol.%).

The water content is also a very important parameter and due to the possibility of phase separation at certain water content, it must be limited.

The acidity indicates the presence of low-weight organic acids, measured in term of the acetic acid content, that might lead to corrosion problems by use (Vertés et al., 2010).

Table 1.11 presents main quality standards currently in place regarding bioethanol quality as well as their description.

Table 1.11: Main quality standards regarding bioethanol quality

APPLICATION	STANDARD	DESCRIPTION
United States of America	ASTM D4806 (2009)	Anhydrous denaturated fuel to be blended with leaded and unleaded gasoline at 1-10 vol.% ^{a)} .
United States of America	ASTM D5798 (2010)	Quality specification for E85 - 85% denaturated bioethanol (finalised in 2001).
Europe	EN 15376 (2007+A1:2009)	For undenaturated ethanol to be used as a blending component with gasoline up to 5 vol.% (finalised in 2008).
Brazil	<i>Resolução ANP n.º 36</i> (2005)	For undenaturated ethanol to be blended up to 25 vol%.

^{a)} This standard has been in place since 1999 and it has been used as reference standard for many countries such as Canada, Australia and China.

BIODIESEL

Amongst the most important biodiesel quality parameters are the methyl ester content, the flash point, the viscosity, the water content and the cold filter plugging point.

The purity of biodiesel samples is measured in terms of their methyl ester content, being a very important parameter to ensure biodiesel quality, namely it controls the effectiveness of the production process and the illegal mixture of other substances (Mittelbach et al., 2004).

Flash point is the temperature at which the fuel ignites when exposed to a flame. The flash point of biodiesel (>120 °C according to EN14214 (2003)) is higher than the conventional fuel (flash point > 50 °C according to Decreto-Lei 89/2008) which makes it safer (Meher et al., 2006). Low flash points will also indicate the presence of methanol which shows the effectiveness of the biodiesel purification steps; it is therefore a very important parameter to be determined considering handling, storage and safety of the fuel (Encinar et al., 2005; Srivastava et al., 2000).

As previously mentioned, viscosity is very important for fuel atomisation and efficient combustion; also, it is well correlated with the methyl ester content (Allen et al., 1999; De Filippis et al., 1995), therefore, also indicating effective production process and conversion of the oil into the ester.

The water content is a very important parameter. Excess water affects biodiesel oxidation stability (Leung et al., 2006), being therefore relevant to determine the storage life of the fuel.

The cold filter plugging point measures the ability of the fuel to flow through the injection system and it is a very important parameter for cold countries.

This parameter is extremely related with the raw materials, namely, biodiesel produced from animal fat presents higher cold filter plugging point (the temperature at which filtration is difficult is higher) as compared to biodiesel from vegetable oils; therefore, it might not be adequate to use it 100% pure in vehicles during cold weather (Lebedevas et al., 2006).

The most important standards regarding biodiesel quality are the ones from the United States of America and Europe, being presented in Table 1.12. Most countries tended to develop their standards according to these two.

Table 1.12: Main quality standards regarding biodiesel quality

APPLICATION	STANDARD	DESCRIPTION
United States of America	ASTM D6751 (2003)	Specifies requirements and test methods of 100% biodiesel to be used as blend component with diesel fuel oils (first publication in 2002)
Europe	EN 14214 (2003)	Specifies requirements and test methods for fatty acid methyl esters to be used as automotive fuel for diesel engines at 100% concentration or as an extender in accordance with the requirements of EN 590 (approved in 2003)

1.4 BIODIESEL

The main reasons that led to the production of biodiesel were the previously reported problems associated with the direct application of the vegetable oils in diesel engines.

Viscosity is a key physical property of the fuel to ensure good atomisation and further complete combustion. The viscosity of the vegetable oils is around 10 to 20 times higher than the viscosity of diesel (Mittelbach et al., 2004). The viscosity of the vegetable oil or animal fat can vary significantly depending of their composition.

1.4.1 COMPOSITION OF VEGETABLE OILS

Triglycerides are the main components of vegetable oils and animal fats (90-98%); additionally, a small amount of mono- and diglycerides might also exist (Srivastava et al., 2000). Chemically, triglyceride molecules consist of three long chain fatty acids radicals that are ester bonded to a single glycerol molecule (Figure 1.10).

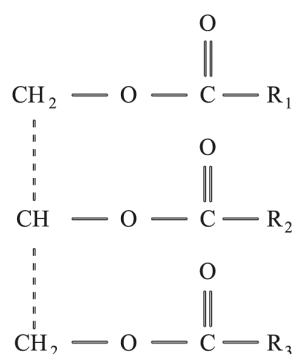


Figure 1.10. Triglyceride molecule (R_1 , R_2 and R_3 are the radicals which vary according to the fatty acid composition of the oil).

Different fatty acids exist, varying in the carbon chain and in the number, orientation and position of double bonds, depending on the raw materials. The fatty acid composition of some vegetable oils and animal fats is presented in Table 1.13.

Table 1.13: Examples of fatty acid composition (wt.%) of some vegetable oils and animal fats^{a)} (Mittelbach et al., 2004)

RAW MATERIAL	C12:0	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	Others
Rapeseed Oil ^{b)}	-	-	3-5	-	1-2	55-65	20-26	8-10	1.5-2.5
Soybean Oil	-	-	11-12	-	3-5	23-25	52-56	6-8	-
Sunflower Oil	-	-	6	-	3-5	17-22	67-74	-	0.6
Lard	-	1-2	23-30	3	12-18	43-50	7-13	1	2.6
Beef tallow	0.5	2-8	25-38	4-5	15-28	40-50	1-5	0.5	2.3
Poultry fat	-	0.5	23	8.4	5.4	42	17	1	1-2

^{a)} Cx:y means x carbons and y double bonds; ^{b)} Low erucic acid (C22:1).

The unsaturated content of the fats is much lower than the vegetable oils; reason why fats are usually solid at room temperature contrary to vegetable oils, which are in the liquid state. This property is also related with the viscosity; and, in fact, fats present much higher viscosities than vegetable oils.

1.4.2 PRODUCTION OF RENEWABLE DIESEL SUBSTITUTES

In order to change the vegetable oil physical properties, mainly the viscosity, production processes were developed to approximate the properties of the obtained fuel from those of diesel.

CONVENTIONAL TECHNOLOGIES

The most widely used conventional technologies aiming viscosity reduction of vegetable oils/fats for the production of renewable diesel substitutes are pyrolysis, microemulsification and transesterification (Mittelbach et al., 2004).

Pyrolysis

Pyrolysis is a thermal technology used to decompose materials in the absence of oxygen. In fact, the pyrolysis of different triglycerides was used for fuel supply in different countries during the First and Second World Wars (Lima et al., 2004).

Pyrolysis is usually conducted at temperatures around 400 °C, in the presence of a solid catalyst and yields a mixture of products, namely alkanes, alkadienes, aromatics and carboxylic acids, similar to hydrocarbon-based diesel (Mittelbach et al., 2004).

This thermal reaction increases the cetane index of the obtained fuel compared with vegetable oil; however, several physical parameters of the fuel are still not adequate for use as diesel substitute. Namely, the viscosity is high, the cold flow properties are poor, and it presents higher values of ash and carbon residue than fossil diesel (Mittelbach et al., 2004).

Microemulsification

While some vegetable oils are soluble in alcohol others are completely insoluble (Trevithick et al., 1929); additionally, solubility will depend upon alcohol concentration and temperature (Kaparathi et al., 1959).

The microemulsification consists in the formation of a stable dispersion of two not usually miscible liquids (Mittelbach et al., 2004). A microemulsion can be made using vegetable oils, an ester and a co-solvent, or vegetable oils, an alcohol and a surfactant. Additionally, diesel fuel can be added to the emulsion (Srivastava et al., 2000).

Microemulsification can lead to an increase in the cetane index of the microemulsion relatively to the oil (Srivastava et al., 2000).

The use of microemulsions of oils and alcohols have however proven to lead to incomplete combustion and also the formation of carbon deposits around the orifices of the injector nozzles (Mittelbach et al., 2004).

Transesterification

Chemically, biodiesel might be produced by transesterification, also called alcoholysis, which is a three-step reversible reaction that converts the initial triglyceride into a mixture of esters (biodiesel) and glycerol, in the presence of a catalyst, usually a homogeneous base such as NaOH or KOH (Vicente et al., 2007). During reaction, the triglyceride is converted step by step into a diglyceride, monoglyceride and glycerol; at each step, one mol of ester is produced. The overall reaction is presented in Figure 1.11.

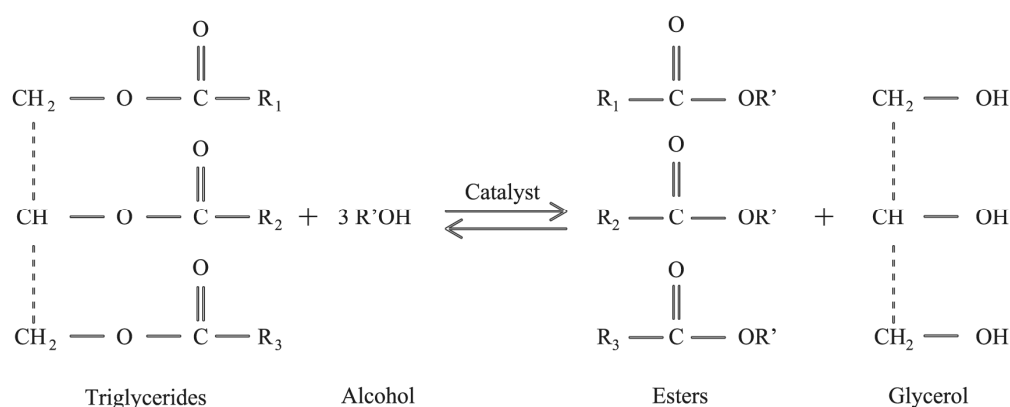


Figure 1.11. Transesterification reaction of triglycerides (overall reaction).

The reaction between low molecular weight alcohols (usually used) and triglycerides to produce free glycerol and fatty acid esters of the respective alcohol was first described in 1852 (Duffy, 1852). The first patents related to biodiesel production were by Hartman (1980) and Tanaka (1980).

The most widely used alcohol is methanol, reason why sometimes this reaction is called methanolysis. Besides being cheaper, one of the major advantages of using methanol is that the products, fatty acid methyl esters (FAME) and glycerol, can be very easily separated. Biodiesel produced by methanolysis shows very similar properties to fossil diesel.

Ethanolysis is often mentioned as a more environmentally friendly process because bioethanol can be used presenting very low toxicity as opposed to methanol.

The problems relate with high difficulties in phase separation as ethyl esters are much more soluble than the corresponding methyl esters in glycerol; also, residual amounts of water significantly affect product yield making this process very expensive relatively to methanolysis (Mittelbach et al., 2004).

ADVANCED TECHNOLOGIES

Amongst the most promising advanced technologies for the production of renewable diesel substitutes are non-catalytic transesterification of vegetable oils or fats, Fischer-Tropsch synthesis of lignocellulosic biomass and hydrotreatment, namely of vegetable oils and or fats.

Non-catalytic Transesterification

An alternative technology for biodiesel production is non-catalytic transesterification with methanol under supercritical conditions. The reaction is fast, presenting high conversions in short time (50–95% after 10 min reaction) but high temperatures (250–400 °C) and pressures (up to 82.7 bar) difficult its commercialisation due to high production costs and energy consumption (Helwani et al., 2009).

Fischer-Tropsch Synthesis

The Fischer-Tropsch synthesis is used to produce chemicals, gasoline and diesel fuel by converting a syngas (a mixture of hydrogen and carbon monoxide which can be produced from biomass gasification) into a range of hydrocarbons, being therefore an alternative process for the production of liquid fuels (Dry, 2004; Fernandes et al., 2007).

According to Lapuerta (In Press), for its application, this technology needs to be integrated in the overall biomass-to-fuel production system (biomass gasification, gas cleaning, water–gas-shift reaction for an optimal H_2/CO adjustment, amongst others); therefore, high investments are expected before the cost of the final products is reduced to competitive levels.

Hydrotreatment

Vegetable oils can be hydrotreated to produce liquid alkanes with high cetane numbers (80–100) and improved fuel properties. Hydrotreatment occurs by hydrogenation of the C=C bonds of the vegetable oils. The resulting free fatty acids, diglycerides, monoglycerides and waxes can go further different pathways to produce the alkanes. Namely, through decarbonylation, normal liquid alkanes, CO/CO₂ and propane are produced (the least amount of hydrogen is required); dehydration/hydrogenation produces a liquid alkane and propane (Huber et al., 2007).

The alkanes can further undergo isomerisation and cracking to produce lighter isomerised alkanes with improved fuel qualities.

Hydrotreatment is an expensive process because it requires H_2 . Currently, the objective of hydrotreating in a petroleum refinery is to remove sulphur, nitrogen, metals and oxygen from pol-
yaromatics from the heavy gas oil feedstock. This reaction is performed using catalysts, typically sulphided Co-Mo and Ni-Mo, and reaction conditions are usually 300-450 °C and pressures of 35-170 bar H_2 (Huber et al., 2007). Because petroleum refineries already perform hydrotreatment, this technology can be more easily implemented for renewable fuel production in such units.

The application of advanced technologies might be a solution in a long term; however, so far the costs and complexity difficult their application to the production of alternative diesel fuel.

From all the technologies applied, the transesterification has been demonstrated to be the best aiming to reduce the triglyceride viscosity and obtain a product presenting properties similar to those of diesel fuel (Mittelbach et al., 2004); accordingly, most plants throughout the world use this process for the production of biodiesel. In fact, biodiesel is referred as the FAME, a diesel substitute product resulting from the methanolysis of triglycerides.

The following sections will focus on describing the current FAME production in Europe and the advantages and disadvantages of its application.

1.4.3 BIODIESEL PRODUCTION IN EUROPE

According to EBB (2010), biodiesel production in Europe was 5 713 kt in 2007 and 7 755 kt in 2008. The evolution of the production from 2002 to 2008 is presented in Figure 1.12.

From 2002 to 2008, biodiesel production increased more than 6 times; whereas from 2007 to 2008 it increased around 36%.

Throughout the years, it is clear the introduction of several countries in the biodiesel market. While in 2002 only six countries were producers (Germany, France, Italy, Denmark, Austria and United Kingdom), in 2008, 24 countries were producing biodiesel.

The major European biodiesel producer is Germany, followed by France and Italy. The increase of capacity of several operating countries is reducing the expression of Germany in the biodiesel market; accordingly, while the production accounted for 50.6% of the European production in 2007, in 2008 accounted for 36.4%. Despite that reduction, Germany is clearly the main European biodiesel producer.

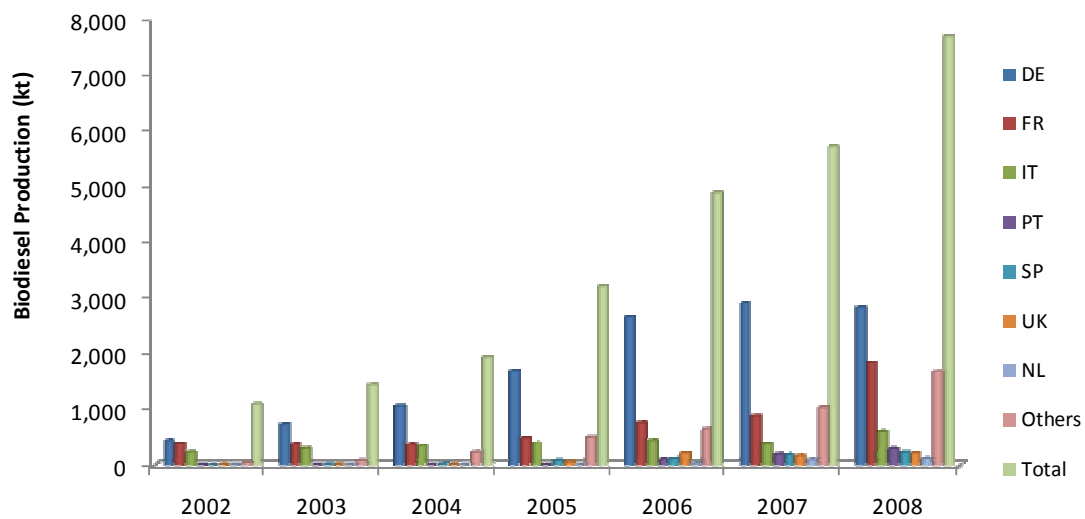


Figure 1.12. Biodiesel production in Europe from 2002-2008 (EBB, 2010).

In 2007, the France and Italy production represented 15.3% and 6.35% of the total production, respectively. In 2008, France share increased to 23.4% of the total production, whereas Italy production increased to 7.7%.

According to the same source (EBB, 2010), Portuguese production was 175 kt in 2007 and 268 kt in 2008, representing around 3.1% in 2007 and 3.5% in 2008 of the total biodiesel production in Europe.

1.4.4 ADVANTAGES AND DISADVANTAGES OF BIODIESEL

Biodiesel is an efficient alternative to fossil diesel. Amongst the diverse advantages of its application, the following remain of major importance (Chand, 2002): i) safe use in any diesel engine; ii) engine performance similar to the one obtained using fossil diesel; iii) higher lubrication; iv) absence of toxicity and reduced inflammability; and v) reduction of pollutants emissions, namely CO₂, unburned hydrocarbons, carbon monoxide and particles.

Biodiesel blends with fossil diesel are usually denoted by BXX, where XX represents the percentage (usually by volume) of biodiesel incorporated.

Table 1.14 shows the exhaust emissions regarding the use of B20 and B100.

Table 1.14: Exhaust emissions for B20 and B100 (Vertés et al., 2010)

TEST ENGINE	TEST ENGINE	HC ^{a)}	CO	NOx	PARTICULATE EMISSIONS		
					Total PM ^{b)}	VOF ^{c)}	Soot
Cummins N-14	B100	-95.6	-45.3	+13.1	-28.3	+42.8	-60.9
Cummins N-14	B20	-17.4	-14.7	+4.2	-3.80	+31.4	-20.3
Detroit diesel Series 50	B100	-83.3	-38.3	+11.3	-49.0	+10.3	-71.4
Detroit diesel Series 50	B20	0	-7.4	+3.60	-13.7	+13.8	-23.8
Cummins B5.9	B100	-74.2	-38.0	+4.30	-36.7	+14.6	-62.9
Cummins B5.9	B20	-32.3	-21.5	+1.90	-14.8	-8.30	-20.0

^{a)} HC – unburned hydrocarbons; ^{b)} PM – particulate matter; ^{c)} VOF – volatile organic fraction

Biodiesel use presents zero sulphur emissions due to the absence of sulphur compounds in its composition.

Also, biodiesel use provides benefits regarding decreased net CO₂ emissions because the plants that provide the oil can reuse CO₂ for growth. To determine overall reductions it is however determinant to consider the emissions resulting from crop production, harvesting, transporting and manufacturing the biofuel. According to the Directive 2009/28/EC, the use of soybean oil, rapeseed, sunflower and residual oil sources for biodiesel production results in a net typical GHG reduction of 40%, 45%, 58% and 88%, respectively.

The use of biodiesel in replacement of diesel provides very significant reductions in unburned hydrocarbons, CO and particulate emissions; these advantages have been in fact great contributors for the promotion of biodiesel use.

Most studies show, however, an increase in NOx emissions by using biodiesel. There are still several doubts regarding the reason for NOx increase; while most authors attribute this fact to the higher oxygen content of biodiesel and the increase in the availability of well-mixed oxygen during combustion; others relate this fact to the higher reached temperatures or to certain physical properties of the fuel (Mittelbach et al., 2004).

Due to stringent limitations regarding NOx emissions, there are currently processes that can be used to reduce the emissions namely by using DeNOx catalysts, precious metal-coated or zeolite-coated devices aiming the reaction of NOx with unburned hydrocarbons to produce N₂ and H₂O; NOx-adsorber catalysts, which oxidise NO to NO₂, storing it in the form of nitrates in the storage unit and selective catalytic reduction, which reduce NOx to N₂ using ammonia, usually from urea (Mittelbach et al., 2004).

Because the exhaust after-treatment devices will certainly reduce emissions to low levels, regardless of the biodiesel incorporation percentage used, this should not be a significant problem (Vertés et al., 2010).

Regarding particle emissions, they are significantly reduced but when disaggregating emissions in the volatile organic fraction (VOF) and the soot the increase of VOF is clear when biodiesel is used. According to Vertés (2010), the large decrease in soot, even considering the increase in VOF, should be an important advantage because soot is much more toxic.

Biodiesel presents a high net energy balance; for instances, considering soybean-oil biodiesel, it produces a 93% energy gain, compared with 25% obtained from corn ethanol (Vertés et al., 2010).

The main disadvantages of biodiesel use are the following (Wardle, 2003): i) NO_x emission increase; ii) frozen in cold weather; iii) degradation of the fuel when stored for long periods; iv) poor materials compatibility; and v) obstruction of filters during initial use (related with the solvent capacity of the FAME that cleans some residual sediments, remaining by previous fuel use).

The operability temperature of biodiesel can be adjusted by blending it with fossil diesel and also by the use of additives such as malan-styrene esters and polymethacrylate (Vertés et al., 2010); additionally, the control by heating fuel tanks, fuel lines and filters (Mittelbach et al., 2004) can be performed.

The material compatibility might be solved by replacement of materials prone to degradation by the solvent (namely natural or nitrile rubber compounds, polypropylene, polyvinyl and Tygon materials) by compatible ones such as Teflon, Viton, and Nylon which have very little reaction to biodiesel (NBB, 2010).

Filter obstruction can be easily controlled by frequent replacement during beginning of biodiesel use in the vehicle (Wardle, 2003).

The transesterification has in fact demonstrated to be the best aiming to attain a product presenting similar properties as the diesel fuel; therefore, the next section will focus on the improvement of the transesterification process.

1.4.5 IMPROVEMENT OF THE TRANSESTERIFICATION PROCESS

The most important steps in a transesterification process are the transesterification reaction and the purification steps of the resulting products. An example of a methanolysis process is presented in Figure 1.13.

Usually, the methoxide solution, resulting from mixing methanol with the catalyst, is added to the reactor; the transesterification reaction occurs under selected conditions, and after reaction, the ester is separated from the glycerol by decantation.

Both phases still present contaminants and a purification process needs to be further performed. Usually, an acidulation of the glycerol is performed to break the soaps formed, releasing the free fatty acids and the salt resulting from the acid-base reaction (Mittelbach et al., 2004).

Because methanol is added in excess to promote the formation of FAME, there is a need to recover the methanol from both phases; which is usually made by heating/distillation.

For the removal of residual catalyst from the ester phase, a liquid-liquid extraction, conventionally called “washing step” is performed. Residual water is then separated from the partially hydrated FAME which is finally dried leading to the purified product.

Regarding the amount of the obtained products; stoichiometric methanolysis of 1 kg of triglycerides leads roughly to 1 kg of FAME and 100 g of glycerol. Regarding the produced glycerol, it might have good value in the pharmaceutical industry as well as in the cosmetic industry if purified; this is a great advantage because it brings higher value to the production process. The increased activity of the biodiesel market led to high amounts of glycerol produced across the world; accordingly, the destination of glycerol can sometimes be a huge problem.

The glycerol has been used in industrial boilers for heating and also as supplement in animal feed. The use of crude glycerol for heating is interesting but it becomes not economically effective due to the low heating value; the use as animal feed supplement is also being restricted as the high purification needed makes it ineffective from an economic point of view.

Several alternative processes for the use of glycerol are being studied, namely chemical and biological transformations. Amongst the resulting products with added value are: 1,2-propanediol (propilenoglycol), propionic acid, acrylic acid, propanol, isopropanol, allylic alcohol and acrolein (Watanabe et al., 2007). The 1,2- propanediol is one of the more studied products which can be directly used as additive in food products, cosmetic products, solvents for dyeing and flavouring, as well as for dehydration, lubrication and antifreeze.

In order to take advantage of the large investments made on the currently existing plants and avoid high costs of implementing new advanced technologies, the most attractive alternative solutions in the short term are the ones that can easily substitute and improve conventional processes in place.

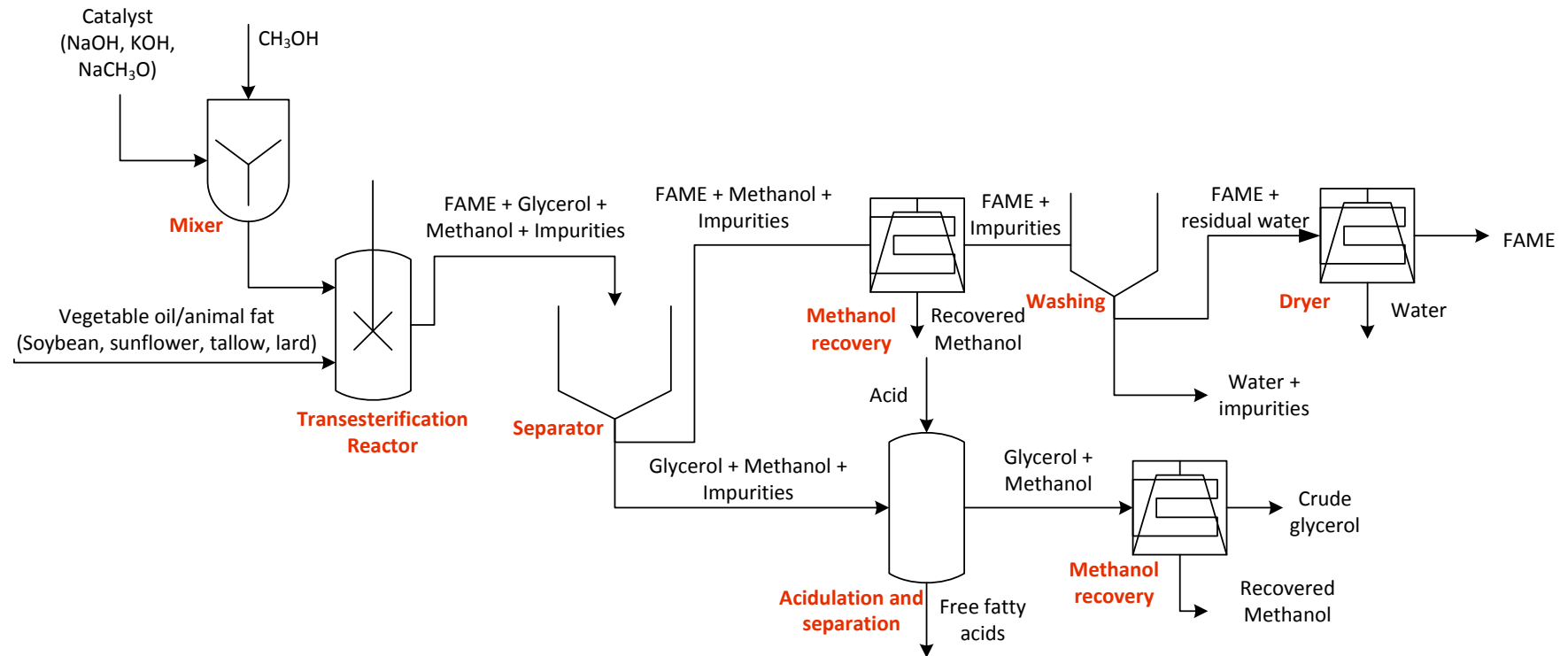


Figure 1.13. General diagram of biodiesel production process through basic transesterification.

Considering the improvement of the overall transesterification process; aiming to diversify the raw material sources, which is of extreme importance, the impact of using different raw materials should be assessed. Process improvement needs to consider the reaction conditions and the purification steps used. Therefore, the following subsections will focus on raw materials and process improvement (mostly studied from the perspective of reaction improvement).

RAW MATERIALS

As previously reported, biodiesel is a biofuel that might be produced from the transesterification of vegetable oils (edible or non-edible) and animal fats, being possible to use it in diesel engines (compression ignition engines) in mixture with fossil diesel.

Usually, virgin vegetable oils are used as raw materials (Antolin et al., 2002; Dias et al., 2008a). Most common plants used for oil extraction are soybean, rapeseed, palm, corn, sunflower, peanut, cotton, castor and *Jatropha curcas*; the extraction can be made by mechanical press or using solvents, depending upon the installed capacity of the production units (Ma et al., 1999; Van Gerpen, 2005).

Approximately 80% of biodiesel production costs relate with the costs of the feedstock oil used (Vertés et al., 2010); currently, food oils such as soybean oil account for the majority of the production. There is a great discussion regarding the use of food oils for the production of biodiesel and accordingly, studies are being conducted with the objective of using non-edible oils as well as by-products from the refining of the vegetable oils (Veljkovic et al., 2006), shifting the research interests towards production of so called second and third generation biodiesel.

There are several different approaches regarding the definition of such generations. From the author perspective, second generation biodiesel results from the application of alternative feedstock such as non-edible oils and wastes as well as advanced technologies such as oil hydrotreatment and gasification/Fischer-Tropsch synthesis of lignocellulosic biomass. Third generation biodiesel results from the application of advanced raw materials, with much greater productivities, such as microalgae and cyanobacteria.

In order to improve transesterification process, most promising raw materials are alternative triglyceride sources, which can be processed similarly, such as algae and cyanobacteria, as well as non-edible vegetable oils and waste raw materials.

The productivities that might be achieved using third generation raw materials might in the future enable a greater impact on overall biodiesel production amounts; however, their application in a short term is limited due to high associated costs, namely during harvesting.

Cost reduction might be possible in the future by using a biorefinery approach, genetic engineering and advances in photobioreactors engineering (Chisti, 2007). Also, the fulfillment of quality standards currently in place, namely the oxidation stability, is generally not possible using such raw materials due to high content in polyunsaturated fatty acids (Knothe, 2006).

Regarding second generation raw materials, non-edible oils are dependent upon land availability and some to specific climacteric conditions, similarly to what happens with the first generation ones (Gui et al., 2008); additionally, the fulfillment of biodiesel quality standards might be difficult due to the differences in the composition of some oils, namely castor and rubber seed oil, in comparison with edible vegetable oils (Gui et al., 2008).

Biodiesel can also be produced from waste frying oils (Felizardo et al., 2006; Tomasevic et al., 2003; Zheng et al., 2006) and other greasy wastes, such as pork lard, beef tallow and poultry fat which do not compete with the food market; the use of waste materials has a very important role both in the reduction of biodiesel production costs and environmental impacts caused by incorrect management of such wastes. The use of such wastes as raw materials adds value to the wastes, which otherwise present no value and need to be further eliminated. Also, the research performed so far enables their immediate application in currently existing plants leading to a product in agreement with biodiesel quality standards. The use of waste raw material mixtures is also important as they allow raw material management according to availability, being even possible to create benefits regarding product quality specifications.

According to recent legislation considering the management of waste frying oils (Decreto-Lei n.º 267/2009), between 43 000-65 000 t of these oils are produced in Portugal.

Contact with the oil production industries indicates, however, that these values are quite over estimated (around 100 000 t of liquid oil are sold in Portugal and a large part of the oil remains with the food and it cannot be recovered). Regarding the waste animal fats, greater amounts should be produced at several slaughterhouses and other meat processing units. In fact, considering the amount of animals slaughtered and approved for consumption in the country, around 90 000 t of waste fat (based on data from 2007 and 2008) can be obtained (Projecto QREN 3491, 2009).

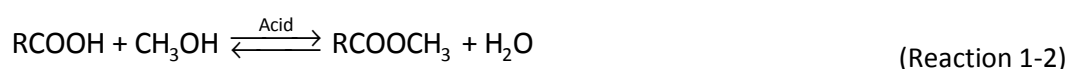
Animal fats had a common application as animal feeds but this practice strongly decreased due to the possibility of severe animal disease and the consequent obligation to effectively discard or recycle them (Ngo et al., 2008). Such fats can alternatively be used for biodiesel production, which constitutes no harm or danger to human and animal health.

One of the operational problems related with the use of wastes is their frequently high acidity resulting from hydrolysis and degradation processes. When raw materials present high acid values, the basic catalyst reacts with the free fatty acids and this is a limiting factor, because it leads to the formation of soaps that reduce biodiesel yield. Sodium soap formation by reaction of NaOH (one of the most common catalyst used) with free fatty acid is described by Reaction 1-1.



Accordingly, when considering the use of a basic transesterification, a pre-treatment is needed to reduce acidity to acceptable values. For that, a saponification reaction might be induced by reacting a basic hydroxide with the free fatty acids to form soaps which are further removed; however, this procedure only makes sense for low free fatty acid contents because it causes a decrease in biodiesel yield, due to the fact that the fatty acids discarded might be used as raw material for biodiesel production.

A more interesting option is the pre-esterification of the free fatty acids through reaction with methanol in the presence of an acid catalyst, more commonly H_2SO_4 , to form FAME and water (Reaction 1-2), therefore taking advantage of all the raw material for biodiesel production.



Alternatively, an acid transesterification can be used to avoid soap formation and the need of pre-processing. Bhatti et al. (2008) showed that biodiesel production from waste tallow by acid catalysis might have higher yields than basic catalysis.

However, greater amounts of sulphuric acid (25 or 50% of fat weight), higher molar ratio of methanol to fat (30:1) and much longer reaction time (24 h) were used as compared with basic transesterification.

It is also necessary to consider that even when using the same vegetable oil, different behaviour might be found regarding production processes due to different refinement processes adopted in its production, reason why it is essential to know and understand feedstock composition (Freedman et al., 1984).

The use of different raw materials, such as waste oils or fats will have also an impact in product quality essentially by changing the physical properties of the obtained biodiesel. Biodiesel European Standard EN 14214 clearly specifies the quality parameters for FAME. Table 1.15 presents the specifications according to EN 14214 and Table 1.16 shows the main properties of oils, fats, and their derived methyl esters.

Table 1.16 clearly shows the great differences between the densities and viscosities of the oils and the respective methyl esters (ME) regardless the raw material used; in fact, viscosity can be higher in the oil more than ten times.

Some oils, namely those from rapeseed and palm, present high acidity; accordingly, as explained previously, there is a need for raw material pre-treatment to perform alkali transesterification.

It is clear the difference between the engine performance, translated by the higher cetane index/number in the ME compared with the oils and fats. Compared with biodiesel from vegetable origin, biodiesel from animal fats has the advantage of a higher cetane number (Lebedevas et al., 2006).

Generally, animal fats have a significant content of saturated fatty acids and therefore the fuel produced has high cold filter plugging point; therefore, it might not be adequate to use it 100% in vehicles during cold weather. The obtained fuel might however be used 100% pure in boilers for heat generation. Alternatively, fats might be mixed with other raw materials to get a biodiesel obeying such quality specifications, being even possible to improve some biodiesel properties, such as the iodine value and the combustion emissions, by incorporation of fats in other raw material (Canoira et al., 2008; Dias et al., 2008b).

PROCESS IMPROVEMENT

There are many parameters affecting the transesterification reaction. The ones known to greatly influence the reaction are: temperature, methanol/oil molar ratio, mixing rate, catalyst type and amount and reaction time (Ma et al., 1999; Meher et al., 2006).

The homogeneous alkaline process is the established technology throughout the world. Usually, the following reaction conditions are used:

- Temperature: optimum tends to be the one which is the closest to the boiling point of the alcohol used (usually between 60 °C and 65 °C when using methanol);
- Methanol/oil molar ratio: excess alcohol is necessary to promote a good conversion (6:1 is considered as the best methanol/oil molar ratio by many authors);
- Mixing rate: should be as high as possible to promote the mixture of the reactants, which is particularly important due to the fact that the system behaves as a two phase system (oil, and alcohol with dissolved catalyst);
- Catalysts: usually sodium and potassium hydroxides (NaOH, KOH), sodium and potassium methoxides (CH_3ONa , CH_3OK) as well as sodium and potassium carbonates (NaCO_3 , KCO_3) are normally used; metal alkoxides generally show better performances;

Table 1.15: Quality specifications for biodiesel according to EN 14214

PROPERTY	LIMITS	TEST METHOD
Ester content (wt.%)	> 96.5	EN 14103
Density @ 15 °C (kg m ⁻³)	860-900	EN ISO 3675 EN ISO 12185
Viscosity @ 40 °C (mm ² s ⁻¹)	3.50-5.00	EN ISO 3104
Flash point (°C)	>120	prEN ISO 3679
Sulphur content (mg kg ⁻¹)	<10.0	prEN ISO 20846 prEN ISO 20884
Carbon residue (on 10% distillation residue) (wt.%)	<0.30	EN ISO 10370
Cetane number	>51.0	EN ISO 5165
Sulphated ash content (wt.%)	<0.02	ISO 3987
Water Content (mg kg ⁻¹)	<500	EN ISO 12937
Total contamination (mg kg ⁻¹)	<24	EN 12662
Copper strip corrosion (3h @ 50 °C)	Classe 1	EN ISO 2160
Oxidation stability, 110°C (h)	>6.0	EN 14112
Acid value (mg KOH g ⁻¹)	<0.50	EN 14104
Iodine value (g I ₂ 100g ⁻¹)	<120	EN 14111
Linolenic acid methyl ester (wt.%)	<12.0	EN 14103
Polyunsaturated (>= 4 double bonds) methyl esters (wt.%)	<1	-
Methanol content (wt.%)	<0.20	EN 14110
Monoglyceride content (wt.%)	<0.80	EN 14105
Diglyceride content (wt.%)	<0.20	EN 14105
Triglyceride content (wt.%)	<0.20	EN 14105
Free glycerol (wt.%)	<0.02	EN 14105 EN 14106
Total glycerol (wt.%)	<0.25	EN 14105
Alkaline metals (Na+K) (mg kg ⁻¹)	<5.0	EN 14108 EN 14109
Group II metals (Ca,Mg) (mg kg ⁻¹)	<5.0	prEN 14538
Phosphorus content (mg kg ⁻¹)	<10.0	EN 14107

Table 1.16: Properties of oils, fats, and methyl esters (ME) obtained (Mittelbach et al., 2004)

	DENSITY (T°C) (kg m ⁻³)	VISCOSITY (T°C) (mm ² s ⁻¹)	FLASH POINT (°C)	CFPP ^{a)} (°C)	CETANE NUMBER (CN)/ CETANE INDEX (CI)	ACID VALUE (mg KOH g ⁻¹)	MEAN MOLECULAR WEIGHT (g mol ⁻¹)
Rapeseed oil	910 (20)	37.7 (38)	300-324	-5-(-14)	CN: 39-44	< 8	883
Rapeseed oil ME	875-900 (15)	3.50-5.00 (40)	153-179	-19-(-8)	CN: 49-62 CI: 52	-	296
Soybean oil	916-922 (25)	32.6 (38)	254-282	-	CN: 38	0.3-3	-
Soybean oil ME	884 (25)	3.05-4.08 (40)	141-171	-2	CN: 45.0-54.8 CI: 47	-	293
Sunflower oil	914 (25)	37.1 (38)	274	-	CN: 37.1	0.6	883
Sunflower oil ME	885 (15)	4.20-4.40 (40)	164-183	-3	CN: 45-61 CI: 47-51	0.3	294
Palm oil	920-927 (20)	26.8-39.6 (38)	267	9	CN: 42-62 CI: 38-40	6.9	847
Palm oil ME	859-875 (15)	4.3-6.3 (40)	155-174	9-11	CN: 50-70 CI: 55	0.3	283
Olive oil	914-919 (15)	46.5 (40)	225	-	-	< 2	868.53
Olive oil ME	880 (15)	4.7 (40)	> 110	-6	CN: 61	-	-
Tallow	919.8 (15)	51.15 mPa/s (40)	201	-12	CI: 40.1	-	-
Tallow ME	877.2 (15)	7.3 (40)	167	9-14	CN: 58 CI: 50.2-57.8	-	-
Lard ME	876 (25)	-	-	-	CN: 63.6	-	-
Castor oil	958-969 (15)	297 (38)	260	-	CN: 42.3	< 2	921.2
Castor oil ME	908 (20)	15.2-17.1 (40)	180	-3	-	0.25	-

^{a)} CFPP – Cold filter plugging point.

- Catalyst amount: might vary from 0.2-2 wt.%, the typical value is 1 wt.%;
- Reaction time: depending on other reaction conditions and raw materials used, reaction can be completed after 15 min; however, common reaction time is 1 h.

The catalyst is needed to increase reaction rate mainly because the triglyceride and the alcohol are not miscible. As previously mentioned, basic catalysts are usually preferred because the acid homogeneous catalysts such as HCl, H₂SO₄ do not efficiently influence the velocity of the reaction.

Because there is a necessity to remove this catalyst after biodiesel production (great corrosivity of such materials), the washing of the product is currently performed (Figure 1.13), leading to product loss and the production of great amounts of wastewater, significantly increasing both production costs and environmental impacts (namely if wastewater is incorrectly managed) (Wei et al., 2009).

The use of homogeneous basic catalysts brings other operational problems: i) the reaction of the hydroxide with the alcohol which originates the formation of water (Equation 1-3); (ii) the presence of water that causes the hydrolysis of the esters and the consequent formation of fatty acids (Equation 1-4) which react with the hydroxide to form soaps according to Equation 1-1.



This fact opens an important field of study, the process improving by using a different catalyst that enables less separation costs and environmental impacts.

A lot of interest was initially devoted to the development of enzymatic catalysts, namely the use of lipases due to great advantages in the elimination of the purification steps required which leads to FAME and glycerol presenting high purity. However, the cost of the enzymes and their instability that frequently leads to inactivation are great barriers to their application at an industrial scale (Mittelbach et al., 2004).

Among research works considering the improvement of the currently used production processes, heterogeneous catalysis appears as a very important contribute aiming to simplify the process as well as to reduce the purification costs associated with the dissolution of the homogeneous catalysts in the final product.

The use of heterogeneous catalysts might bring easier production process (separation by simple filtration), improved product quality (homogenous catalysts react with free fatty acids to form soaps), and also lack of corrosion and toxicity problems (caused by residual homogenous catalyst in the fuel) (Wei et al., 2009). Additionally, acid raw materials might be more easily applied (Kawashima et al., 2009).

The preparation of a highly effective heterogeneous catalyst seems to be complex and difficult to achieve, also requiring experienced people to operate it (Wei et al., 2009).

The costs of fabricating the heterogeneous catalyst should be evaluated and might be of critical importance to make its application economically effective.

In most experiments using heterogeneous catalysts, the reaction is slow as compared to the one using basic homogeneous catalysts. This fact is mainly due to diffusion problems, because this heterogeneous media behaves as a three-phase system (oil/alcohol/catalyst).

As previously mentioned common basic transesterification reaction conditions are: 60-65 °C; 1 wt.% catalyst concentration, methanol to oil/fat molar ratios of 6:1 and reaction time of 1h.

As compared with the homogeneous catalysis, heterogeneous catalytic reactions are performed using:

- Temperatures similar and lower (Kawashima et al., 2009; Liu et al., 2008a; Liu et al., 2008c) but in some cases much higher (120 °C, 200 °C) (López et al., 2007; Sunita et al., 2008);
- Much higher catalyst concentrations, ranging from 2 (Umdur et al., 2009) to 20 wt% (Liu et al., 2007);
- Methanol to oil/fat molar ratios of 6:1 (Huaping et al., 2006; Martyanov et al., 2008) being commonly higher, such as 12:1 (Gao et al., 2008) and 30:1 (Liu et al., 2007);
- Much higher reaction times, from 3 h (Liu et al., 2008a; Liu et al., 2008b; Liu et al., 2008c) to 24 h (Arzamendi et al., 2007; Arzamendi et al., 2008).

The most currently studied heterogeneous catalysts are:

- Calcium oxide, both pure or supported in different materials (silica and alumina, amongst others) (Albuquerque et al., 2008; Granados et al., 2007; Huaping et al., 2006; Kawashima et al., 2009; Kouzu et al., 2008; Liu et al., 2008a; Liu et al., 2008b; Liu et al., 2008c; Martyanov et al., 2008; Umdur et al., 2009; Wei et al., 2009);
- Supported sodium, potassium, and their hydroxides (Noiroj et al., 2009; Suppes et al., 2004; Vyas et al., 2009; Xie et al., 2007; Xie et al., 2006);

- Zirconia (ZrO) based catalysts (Garcia et al., 2008; López et al., 2008; López et al., 2007; Sree et al., 2009; Sunita et al., 2008);
- Hydrotalcite ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$) (Barakos et al., 2008; Gao et al., 2008; Liu et al., 2007);
- Dolomite ($\text{CaMg}(\text{CO}_3)_2$) based catalysts (Ngamcharussrivichai et al., 2007; Wilson et al., 2008);
- Oxides such as the ones of zinc, aluminium, iron and titanium (Bournay et al., 2005; Kawashima et al., 2008; Vyas et al., 2009; Yang et al., 2007).

Due to the wide range of reaction conditions and materials used for the heterogeneous transesterification of tryglicerides it remains important to perform research aiming to find/select the best reaction conditions and catalysts for a more efficient biodiesel production process.

The objective of the present work was, therefore, to study the transesterification process aiming the substitution/improvement of the currently used process, considering the application of alternative raw materials and improvement of the chemical reaction by selection of best conditions and development of alternative heterogeneous catalysts.

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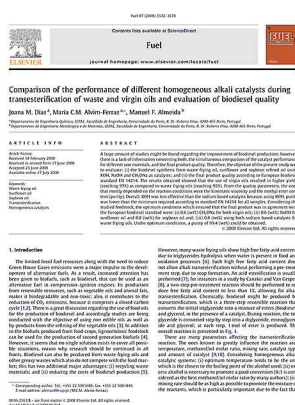
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CHAPTER 2 EDIBLE AND NON-EDIBLE VEGETABLE OILS FOR BIODIESEL PRODUCTION



This chapter was based on:

Dias, J. M., Alvim-Ferraz, M. C. M. and Almeida, M. F. (2008). *Comparison of the performance of different homogeneous alkali catalysts during transesterification of waste and virgin oils and evaluation of biodiesel quality. Fuel* **87**: 3572-3578.

ABSTRACT

A large amount of studies might be found regarding the improvement of biodiesel production; however, there is a lack of information concerning both, the simultaneous comparison of the catalyst performance for different raw materials, and the final product quality. The present study evaluated: i) biodiesel synthesis from waste frying oil, sunflower and soybean refined oil using KOH, NaOH and CH_3ONa as catalysts; and ii) final product quality according to European biodiesel standard EN 14214. The results obtained showed that the use of virgin oils resulted in higher yields (reaching 97 wt.%) as compared to waste frying oils (reaching 92 wt.%). From the quality parameters, the ones that mostly depended on the reaction conditions were the kinematic viscosity and the methyl ester content (purity). Overall, KOH was less effective than the sodium based catalysts; using KOH, purity was lower than the minimum required according to standard EN 14214 for all samples. Considering the studied feedstock, the optimum conditions which ensured that the final product was in agreement with the European biodiesel standard were: i) 0.6 wt.% CH_3ONa for both virgin oils; ii) 0.6 wt.% NaOH for sunflower oil and 0.8 wt.% for soybean oil and; iii) 0.8 wt.% using both sodium based catalysts for waste frying oils. Under best conditions, a purity of 99.4 wt.% could be obtained.

2.1 SCIENTIFIC RELEVANCE

Currently, biodiesel production is performed using virgin vegetable oils also used as food resource; accordingly, research is making efforts to find alternative raw materials that do not compete with the food market.

Raw materials currently used account for 80% of biodiesel production costs (Van Gerpen, 2005); amongst the alternative raw materials, waste oil sources are the cheapest ones and despite in less amounts, their use for biodiesel production is fundamental as it simultaneously reduces waste management costs and environmental impacts.

Studies should therefore focus on the application of non-edible oil sources such as waste oils and compare them with the virgin vegetable oils to support its use as total or partial substitute of currently used vegetable oils.

Transesterification reaction is currently applied for biodiesel production from triglycerides; the most relevant reaction conditions, which need control, are: temperature, methanol/oil molar ratio, mixing rate, catalyst type and amount of catalyst (Ma et al., 1999; Meher et al., 2006). The most widely employed catalytic systems consist on the application of homogeneous basic catalysts such as NaOH and KOH, due to their high efficiency. There are many studies focused on the optimization of biodiesel production by studying the influence of the reaction conditions (Antolin et al., 2002; Tomasevic et al., 2003; Felizardo et al., 2006; Zheng et al., 2006; Vicente et al., 2007). Additionally, a large amount of studies are being made on the application of different catalytic systems and different raw materials. Due to the fact that studies tend to focus either on the use of different raw materials using a specific catalyst (Çetinkaya et al., 2004; Encinar et al., 2005; Veljkovic et al., 2006), or different catalytic systems for a specific raw material (Yang et al., 2007; Kawashima et al., 2008), there is a lack of supporting information regarding the simultaneous comparison of the performance of different raw materials and different catalysts.

Product quality is a key issue regarding biodiesel production and its evaluation is critical in the related studies. In the few studies which considered raw material and catalyst performance (Leung et al., 2006), the evaluation of the final product quality was limited.

The present study aims to evaluate biodiesel synthesis using different raw materials and catalysts as well as the final product quality. Waste frying oil, sunflower and soybean virgin oils were used as raw materials; the virgin oils were selected because they are the ones mostly produced and consumed in the country, and would therefore serve as comparison to the waste frying oil used.

2.2 SPECIFIC OBJECTIVES

- To evaluate biodiesel synthesis by comparing simultaneously the performance of three raw materials (waste frying oil, sunflower oil and soybean oil) and three types of homogeneous basic catalysts (KOH, NaOH and CH_3ONa);
- To evaluate the final product quality according to the European biodiesel standard EN 14214.

2.3 MATERIALS

Refined oils used were donated by Sovena, SA, Portugal. The sunflower oil (SFO) was from the brand “3Ás equilíbrio”, whereas the soybean oil (SBO) was from the brand “olisoja”. These oils were in agreement with the Portuguese specifications for food oil.

The waste frying oil (WFO)^{††} was obtained from a voluntary collection system implemented at *Faculdade de Engenharia da Universidade do Porto* and consisted of WFO from different domestic sources. WFO was filtered under vacuum, after dehydrated using anhydrous sodium sulphate (left over night) and finally again filtered under vacuum, prior to use (Figure 2.1).



Figure 2.1. Pre-treated waste frying oil.

The reagents used during synthesis and purification procedures were: methanol 99.5% (analytical grade, Fischer Scientific), sodium hydroxide powder 97% (reagent grade, Aldrich), sodium methoxide solution 30% in methanol (synthesis grade, Panreac), potassium hydroxide 85% powder (purum grade, Fluka), hydrochloric acid 37% (ACS reagent, Aldrich) and anhydrous sodium sulphate 99% (analytical grade, Panreac).

^{††} Waste frying oil used was always from the same prepared mixture.

2.4 METHODS

2.4.1 BIODIESEL PRODUCTION

Biodiesel production was performed according to the diagram presented in Figure 2.2. Production presented two major steps: synthesis and purification.

SYNTHESIS

Synthesis of biodiesel was carried out by transesterification.

A defined amount of methanol (6:1 molar ratio to oil) was pre-mixed with the different catalysts (KOH, NaOH and CH_3ONa). The amounts of catalyst varied from 0.2 to 1% of the oil mass for virgin oils and 0.4 to 1.2% of the oil mass for the WFO.

It should be noted that higher catalyst concentrations were tested during synthesis of WFO. This option was related with assumed less conversion of the used oils under the same catalyst concentrations when compared with virgin oils. In fact, preliminary experiments showed that when using WFO: i) at 0.2 wt.% catalyst concentrations the washing of the product was very difficult to perform (appearance of emulsions very difficult to break) which might indicate the presence of impurities which have higher water solubility and; ii) using the same amount of catalyst as for the virgin oils, viscosities tended to be higher which is known to be related with smaller conversion.

The mixture of methanol and catalyst was then added to the reactor, which already had 200 g of the oil (SFO 227.4 mmol, SBO 228.8 mmol and WFO 227.9 mmol) preheated at the reaction temperature (60 °C). At this point, the reaction started.

To perform the reaction, an acrylic bath was designed to allow controlled heating and magnetic stirring as well as observation of reaction progression; a reactor, consisting of a 1 L flat-bottom flask equipped with a water-cooled condenser was immersed in the bath as shown in Figure 2.3.

Reaction occurred for 60 min under vigorous stirring; at the end of the reaction, products were left to settle for 2 hours to ensure the separation of the two phases: biodiesel and glycerol.

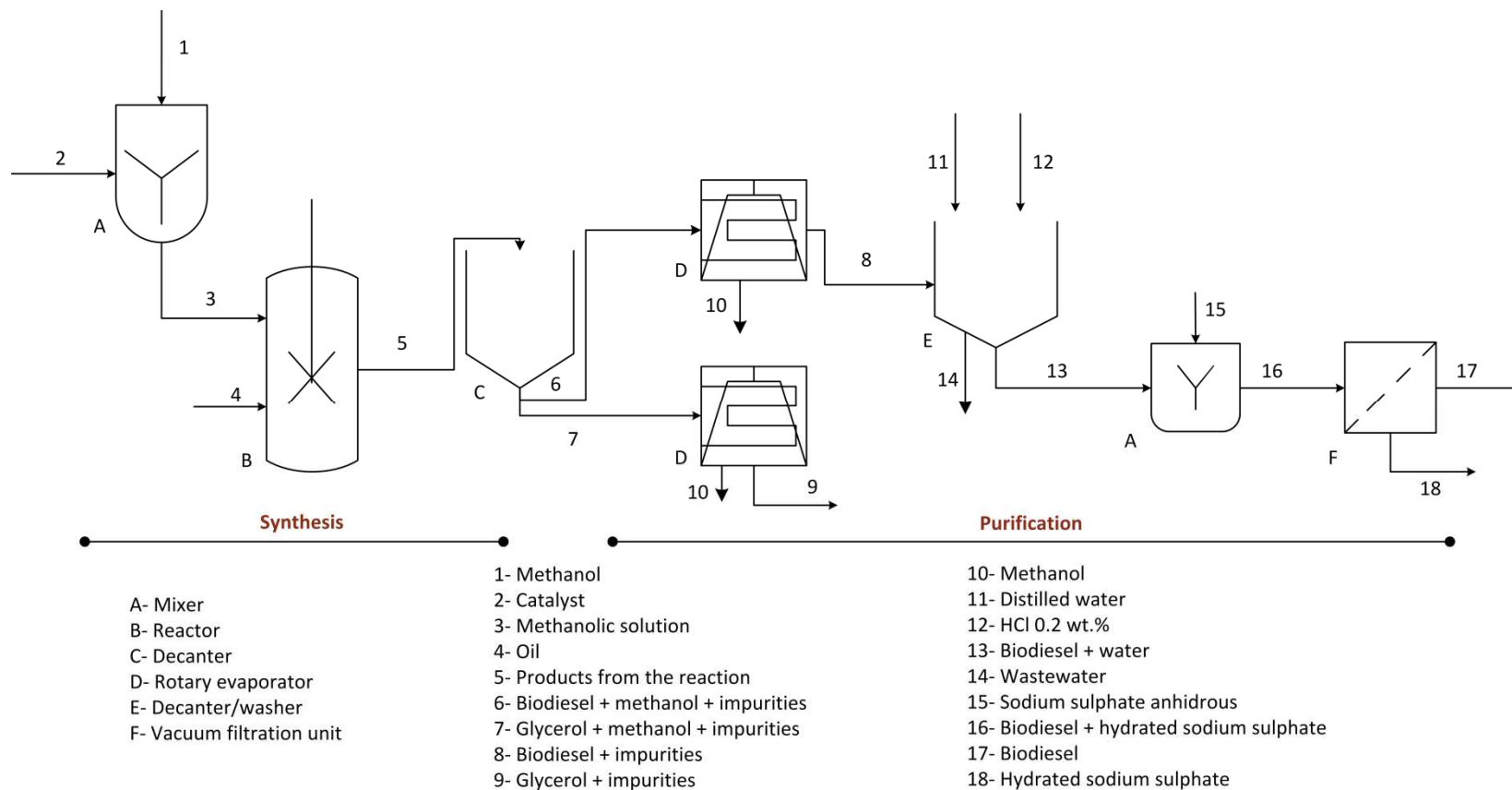


Figure 2.2. Diagram adopted for biodiesel production using edible and non edible oils.



Figure 2.3. Reactor used for homogeneous synthesis and designed acrylic bath.

PURIFICATION

The separation and purification steps are illustrated in Figure 2.4. After settlement, both phases were separated and excess methanol was recovered from each phase separately, using a rotary evaporator under reduced pressure (Figure 2.4B).

The biodiesel phase was then washed, first with 50 vol.% of an acid solution (HCl 0.2 wt.%) and after repeatedly with 50 vol.% of distilled water until the pH of the washing water was the same as the distilled water (Figure 2.4C).

To remove residual water, biodiesel was after dried over anhydrous sodium sulphate (30 wt% relatively to biodiesel weight), left over night, and finally filtered under reduced pressure to obtain the final product Figure 2.4D.



Figure 2.4. Separation and purification of biodiesel: A. phase separation; B. methanol recovery; C. washing; and D. drying.

2.4.2 ANALYTICAL METHODS

Raw material properties as well as biodiesel quality parameters were determined.

RAW MATERIALS

The following raw material properties (considered the most relevant) were determined:

- Composition: using gas chromatography (GC) according to EN 14103 (2003) and NP EN ISO 5508 (1996);
- Acid value: by volumetric titration according to the standard NP EN ISO 660 (2002);
- Iodine value: by volumetric titration using Wijs reagent, according to the standard ISO 3961 (1996);
- Water content: using coulometric Karl Fischer titration according to ISO 8534 (1996).

BIODIESEL

Biodiesel quality was evaluated according to the European biodiesel standard EN 14214 (2003).

The following properties ^{**} were determined:

- Acid value: by volumetric titration according to the standard EN 14104 (2003);
- Kinematic viscosity: determined at 40 °C using glass capillary viscometers according to the standard ISO 3104 (1994);
- Density: determined using a hydrometer method according to the standard ISO 3675 (1998);
- Flash point: using a rapid equilibrium closed cup method, according to the standard ISO 3679 (2004);
- Copper corrosion: using a copper strip test according to the standard ISO 2160 (1998);
- Water content: by Karl Fischer coulometric titration according to the standard NP EN ISO 12937 (2003);
- Ester and linolenic acid methyl ester content: by gas chromatography (GC) according to the standard EN 14103 (2003);
- Iodine value: determined from the ester content according to annex B of EN 14214 (2003).

Regarding chromatographic analysis, a Dani GC 1000 DPC gas chromatograph (DANI Instruments S.p.A.) with an AT-WAX (Heliflex capillary, Alltech) column was used. The injector temperature was set at 250 °C, while the flame ionization detector (FID) temperature was set at 255 °C. The following temperature program was used: 120 °C, heating at a rate of 4 °C min⁻¹ until 220 °C and holding at that temperature for 10 min.

The equipments used for the analytical methods are presented in Appendix A.

2.5 RESULTS AND DISCUSSION

2.5.1 RAW MATERIAL CHARACTERISATION

The composition and the mean molecular weight (calculated from the composition) of the oil samples are presented in Table 2.1. An example of the mean molecular weight calculation is presented in Appendix B. With the objective of increasing the accuracy of the results, the use of correction factors in gas chromatography analysis was evaluated and being presented in Appendix C.

^{**} The properties were selected considering major relevance and budget for equipment acquisition.

Table 2.1: Methyl ester composition (wt.%) and mean molecular weight of the waste frying oil, sunflower oil and soybean oil

<i>Methyl ester composition, wt.%^{a)}</i>	WFO	SFO	SBO
Palmitate (C16:0)	8.4	5.7	11
Stearate (C18:0)	3.7	4.0	3.3
Oleate (C18:1)	34.6	35.2	25.4
Linoleate (C18:2)	50.5	53.5	53.6
Linolenate (C18:3)	0.6	0.1	5.3
Behenate (C22:0)	0.8	0.7	0.4
Docosadienoate (C22:2)	-	0.1	0.2
Others	1.3	0.9	1.0
<i>Mean molecular weight (g mol⁻¹)</i>	877.5	879.5	874.0

^{a)} Totals might not equal 100% due to rounding.

Considering the typical composition of vegetable oils as determined using GC (Rossel, 1986), namely considering the content in methyl oleate and linoleate, the waste frying oil composition indicates that both soybean and sunflower oil might be present; the low methyl linolenate content and the higher content in methyl oleate might indicate that sunflower is present in a higher amount (see also Table 1.13 for fatty acid composition of vegetable oils and animal fats).

In WFO composition, smaller content of C18:1 and C18:2 would be expected due to oxidation reactions with temperature; however, this was not the case and similar results have also been found in related studies. Çetinkaya and Karaosmanoğlu (2004) attributed this fact to SFO exposed to high temperature for a short period of time. Because the WFO used in this study was from a domestic source, this might justify these findings.

SFO had an acid value of 0.08 mg KOH/g and an iodine value of 123 g I₂/100 g; SBO had an acid value of 0.21 mg KOH/g and an iodine value of 127 g I₂/100 g; and WFO had an acid value of 0.82 mg KOH/g and an iodine value of 117 g I₂/100 g.

The acid value of the virgin oils was lower than the WFO; however, much higher acid values have been reported in WFO; the previously discussed low variation in composition, which indicates smaller degree of oxidation reactions, should be related with such small difference found.

The water content was 0.05 wt.% for the waste frying oil and 0.04 wt.% for both virgin oils. In the case of the virgin oils low water contents were expected, the low content also found on the WFO was due to the pre-treatment procedure.

2.5.2 YIELD

SODIUM BASED CATALYSTS

Biodiesel Yields $\left(\frac{\text{weight of product}}{\text{weight of raw material}} \times 100 \right)$ varied between 76.0 and 97.1 wt.%. As it can be seen

from Figure 2.5, the lowest yields were generally obtained at the lowest (0.2 wt.%) and highest (1.0 wt.%) catalyst concentration using both refined oils and both sodium based catalysts. In what relates the waste frying oils, the lowest yield was obtained using a 1.2 wt.% catalyst concentration; for 0.2 wt.% catalyst concentration a small yield would also be expected.

The lower yields obtained at the higher catalyst concentrations might be associated with the formation of soaps (Reaction 1-1) which are known to frequently occur under homogeneous alkali catalysis (Vicente et al., 2007). For all raw-materials tested, higher yields were generally obtained using 0.4 wt.% catalyst concentration; when that did not occur, differences between the highest yield and the one at 0.4 wt.% were less than 2%. Generally, for the same catalyst concentrations, yields were lower when using waste frying oil as compared with virgin oils.

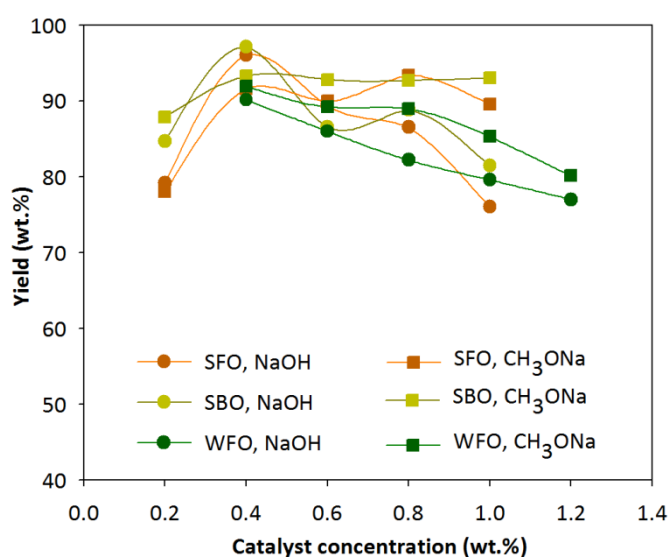


Figure 2.5. Biodiesel yield (wt.%) using waste frying oil, sunflower oil and soybean oil and different sodium based catalysts.

KOH

When using KOH as catalyst, yields varied from 78.6 to 94.1 (wt.%). Therefore, differences between yield using the two different sets of catalysts were not relevant.

The lowest yield was obtained when using 1.2 wt.% catalyst concentrations and waste frying oil as raw material (Figure 2.6). As for the sodium catalysts, lower yields were obtained when using waste frying oils as compared to virgin oils (for the same catalyst concentration) and the highest yields were generally observed at 0.4 wt.% catalyst concentration.

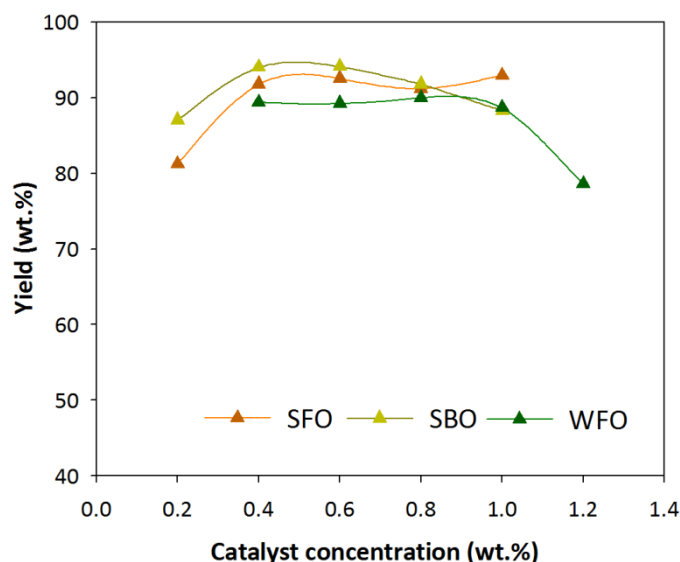


Figure 2.6. Biodiesel yield (wt.%) using waste frying oil, sunflower and soybean oil and KOH as catalyst.

Same behaviour as for sodium catalyst was also observed for the lowest yields when using soybean oil; however, the highest yield occurred for the highest catalyst concentration when using sunflower oil (difference between this and the one at 0.4 (wt.%) was less than 1%).

The obtained results showed that 0.4 (wt.%) could be chosen as the best concentration, under the conditions studied, to obtain the highest product yield using all catalysts and raw materials studied.

2.5.3 BIODIESEL CHARACTERISATION

ACID VALUE

The acid value is defined as the mass (mg) of potassium hydroxide required to neutralise the free fatty acids present in 1 g of sample. High levels of free fatty acids will affect biodiesel stability.

The established limit for biodiesel samples according to EN 14214 is 0.5 mg KOH/g.

The biodiesel produced using soybean oil and 0.8 wt.% of NaOH showed an acid value similar to the limit (0.51 mg KOH/g); nevertheless, all the other samples showed an acid value lower than the limit, with values ranging from 0.04 to 0.36 mg KOH/g. Therefore, the selected production process was effective to obtain a product having an acid value in agreement with European biodiesel standard, for all conditions tested (i.e., varying catalyst type and concentration as well as feedstock).

KINEMATIC VISCOSITY AT 40 °C

Methyl ester content has been correlated with viscosity (De Filippis et al., 1995; Allen et al., 1999), which allows using it as indicator of the conversion of oils to esters.

The viscosity of the fuel controls the performance of the injectors. High viscosities lead to negative impacts on fuel injector performance (Meher et al., 2006), leading to carbon deposition on the injectors (Encinar et al., 2005). Viscosity is also important for transport purposes, namely to guarantee good conditions for oil flow into pipelines (Srivastava et al., 2000), as well as to predict cold weather behaviour (Bozbas, 2008). The acceptable range for biodiesel samples according to the European biodiesel standard is 3.5-5.0 mm² s⁻¹.

Viscosity is very related to the chemical structure of the fuel; therefore, viscosity of biodiesel from fats is higher than from vegetable oils due to their saturation levels (Canakci et al., 2008). Accordingly, it is generally expected that the waste frying oils show higher viscosity due to oxidation reactions that alter their composition.

SODIUM BASED CATALYSTS

The kinematic viscosity decreased with increasing catalyst concentration, values ranged from 4.42 to 5.48 mm² s⁻¹.

Decrease was more evident when changing from 0.2 to 0.4 (wt.%) catalyst concentration for virgin oils and 0.4 to 0.6 (wt.%) for waste frying oils (Figure 2.7).

The limit was fulfilled for catalyst concentrations of at least 0.4 (wt.%) for virgin oils and 0.6 (wt.%) for waste frying oil. For the same catalyst concentrations, viscosities were always higher when using waste frying oil as raw material.

KOH

As expected, the kinematic viscosity also decreased with increasing catalyst concentration (Figure 2.8). Viscosity ranged from 4.40 to 6.03 $\text{mm}^2 \text{s}^{-1}$.

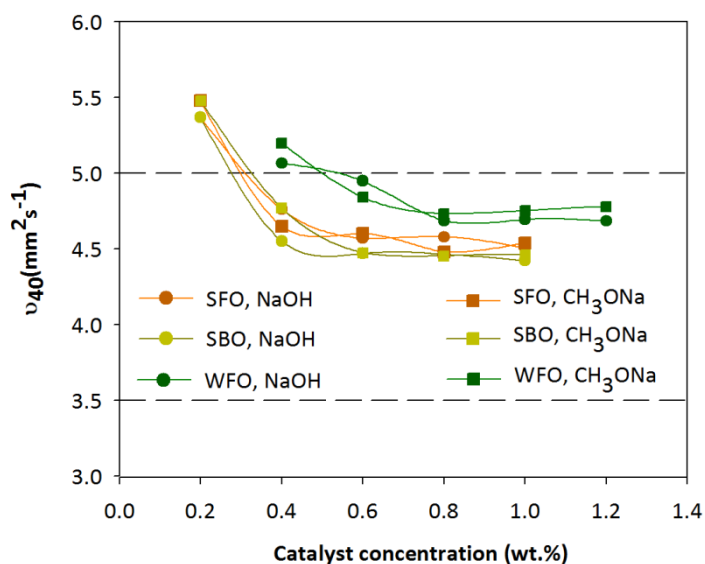


Figure 2.7. Biodiesel kinematic viscosity (v , $\text{mm}^2 \text{s}^{-1}$) using waste frying oil, sunflower oil and soybean oil and different sodium based catalysts; dashed lines indicate maximum and minimum limits according to European standard EN 14214.

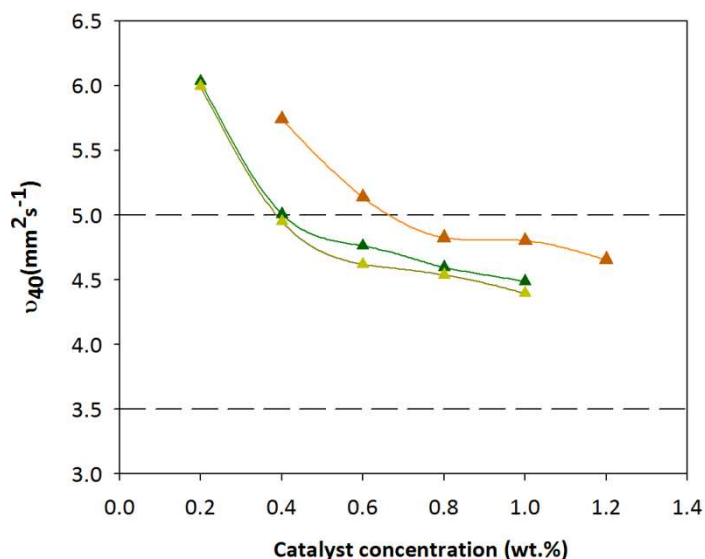


Figure 2.8. Biodiesel kinematic viscosity (v , $\text{mm}^2 \text{s}^{-1}$) using waste frying oil, sunflower oil and soybean oil and KOH as catalyst; dashed lines indicate maximum and minimum limits according to European standard EN 14214.

As for the sodium based catalysts, decrease was more evident when changing from 0.2 to 0.4 wt.% catalyst concentration for virgin oils and 0.4 to 0.6 wt.% for WFO.

However, viscosity at 0.4 wt.% for the virgin oils was almost equal than the European standard upper limit which indicates that higher concentration should be used to ensure minimum quality.

According to the results, it is recommended that concentrations equal or higher than 0.6 wt.% are used for the conversion of the studied virgin oils and equal or higher than 0.8 wt.% for the conversion of the studied WFO.

Viscosities were also always higher when using waste frying oil as raw material. Differences between the viscosity of biodiesel resulting from waste and virgin oils were more evident when using this catalyst.

The differences found in viscosity comparing waste frying oils and vegetable oils could be explained by the differences in their compositions; however, it was already discussed previously that such differences were not relevant and for this raw material the contribution to the higher viscosity appears to be irrelevant. Therefore, higher viscosities seemed to indicate smaller conversions, later emphasized by lower purity of samples produced using the waste frying oil.

For the same concentrations of catalyst, under the conditions studied, KOH was shown to be less effective than the sodium based catalysts for obtaining a product with a proper viscosity. When using virgin oils, a catalyst concentration of either 0.4 wt.% of NaOH or CH_3ONa or 0.6 wt.% of KOH could be used. For the WFO, a catalyst concentration of either 0.6 wt.% of NaOH or CH_3ONa or 0.8 wt.% of KOH could be adopted.

DENSITY AT 15 °C

The density might also serve as an indicator of the completeness of the transesterification reaction (Al-Widyan et al., 2002) and additionally influences the injection performance of the fuel.

For all analysed samples, density was within the established standard limits, which are set between 860 and 900 kg m^{-3} . Values ranged from 878.7 to 889.3 kg m^{-3} . Considering the results, under the conditions studied, this was not a limiting parameter.

FLASH POINT

Flash point is the temperature at which the fuel ignites when exposed to a flame. The flash point of biodiesel is higher than the conventional fuel which makes it safer (Meher et al., 2006).

For all analysed samples, flash point was much higher than the minimum limit according to EN 14214 (120 °C); values ranged from 174 to 182 °C.

Such high values indicate that excess methanol was successfully recovered, because otherwise methanol would significantly decrease the flash point.

COPPER CORROSION

It is a measure to assess corrosivity of biodiesel, generally indicating the presence of sulphur compounds in the fuel (Srivastava et al., 2000). For all analysed samples, no copper corrosion was verified and therefore all samples were according to the specifications: classification 1A, ISO 2160 (1998). According to the results, this was also a non limiting parameter under the conditions studied.

WATER CONTENT

High water contents will improve biodiesel degradation due to hydrolysis (Leung et al., 2006), therefore affecting the storage life of the fuel.

The maximum water content according to the European biodiesel quality standard is 500 mg/kg (0.05 wt.%). The adopted diagram production included a step that intended to reduce the water content of biodiesel samples resulting from the washing stage.

This step consisted on using a dehydrated salt (anhydrous sodium sulphate). However, the use of this salt was shown to be very ineffective. Water content of biodiesel samples varied from 0.09 to 0.19 (wt.%) and, therefore, none of the samples fulfilled the established limit.

It is however curious to observe that the water content generally decreased with increasing catalyst concentration (Figure 2.9), mostly at the lowest catalyst concentrations, probably related with the fact that poor conversion of the oils leads to the existence of impurities which have higher water solubility and difficult biodiesel dehydration.

To reduce water content to acceptable values, a different procedure was adopted. Two samples of biodiesel obtained from SFO (water content of 0.10 wt.%) and SBO (water content of 0.12 wt.%) were subjected to evaporation under reduced pressure, using a rotary evaporator.

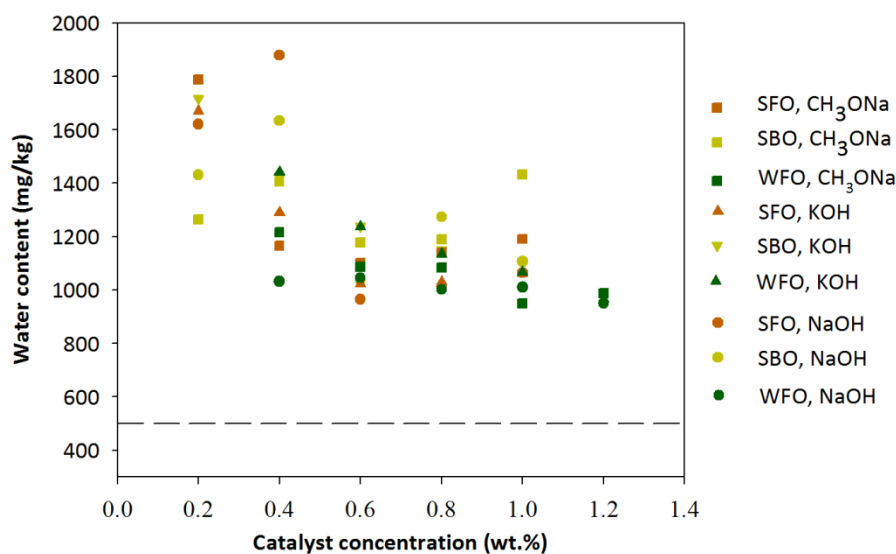


Figure 2.9. Water content (mg/kg) using waste frying oil, sunflower oil and soybean oil and all studied catalysts; dashed line indicates maximum limit according to European standard EN 14214.

Two temperatures were tested, 40 and 60 °C, at the same pressure (163 mbar) during 45 min. The water content of the biodiesel obtained from SFO was reduced to 0.04 (wt.%) at 40 °C and to 0.02 (wt.%) at 60 °C, whereas the water content of the biodiesel from SBO was reduced to 0.04 (wt.%) at 40 °C and 0.03 (wt.%) at 60 °C. Therefore, evaporation under reduced pressure at 40 °C allowed the fulfilment of the required standard limit for water content.

LINOLENIC ACID METHYL ESTER CONTENT

In what relates the linolenic acid methyl ester content, as it depends on the raw material, it was practically constant for all samples produced using the same starting material.

Values were always below the maximum limit of 12.0 wt.%, set by the European biodiesel standard, being 0.1 wt.%, 5.4 wt.% and 0.6 wt.% for the SFO, SBO and WFO, respectively.

METHYL ESTER CONTENT

The purity of biodiesel samples is measured in terms of their methyl ester content (wt.%), being a very important parameter to ensure biodiesel quality. The European biodiesel standard EN 14214 establishes a minimum purity of 96.5 wt.%.

The results obtained for this parameter will be discussed in detail from now on.

Sodium Based Catalysts

Methyl ester content of biodiesel samples increased with increasing catalyst concentration and tended to stabilize in most cases at the highest catalyst concentrations studied. Values ranged from 85.5 to 99.4 wt.% (Figure 2.10).

Using virgin oils, for catalyst concentrations higher than 0.6 wt.%, samples showed purity equal or higher than the established limit.

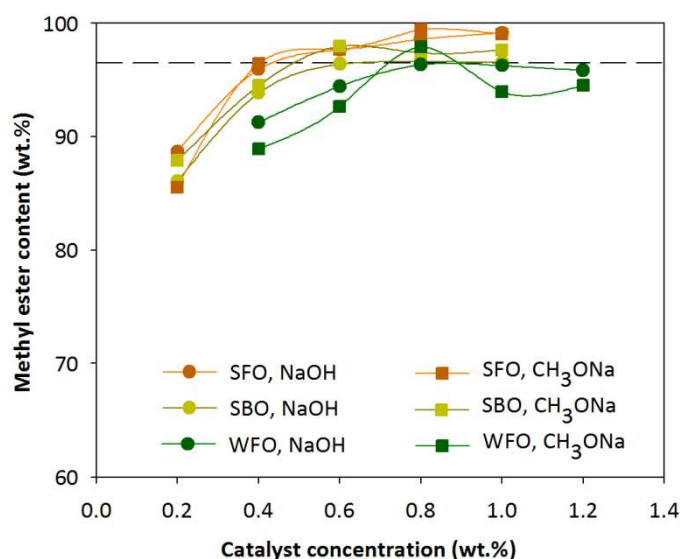


Figure 2.10. Methyl ester content (wt.%) using waste frying oil, sunflower oil and soybean oil and different sodium based catalysts; dashed line indicates minimum limit according to European standard EN 14214.

It is relevant to notice that, when using virgin oils, the samples produced using CH₃ONa generally showed the best results and the maximum purity of 99.4 wt.% was obtained using 0.8 wt.% of this catalyst. Samples produced using waste frying oil showed lower purity than those produced using virgin oils. For those samples, minimum purity was obtained using 0.8 wt.% CH₃ONa and it was close to the limit for 0.8 and 1 wt.% NaOH.

KOH

As for the sodium based catalysts, biodiesel purity increased with increasing catalyst concentration; however none of the samples fulfilled the standard limit for this parameter. Purity varied from 81.8 to 95.9 wt.% (Figure 2.11).

Samples showed values close to the limit when using 1 wt.% catalyst concentration and sunflower oil and 1.2 wt.% catalyst concentration and waste frying oil. Values were 95.9 and 95.8 wt.%, respectively.

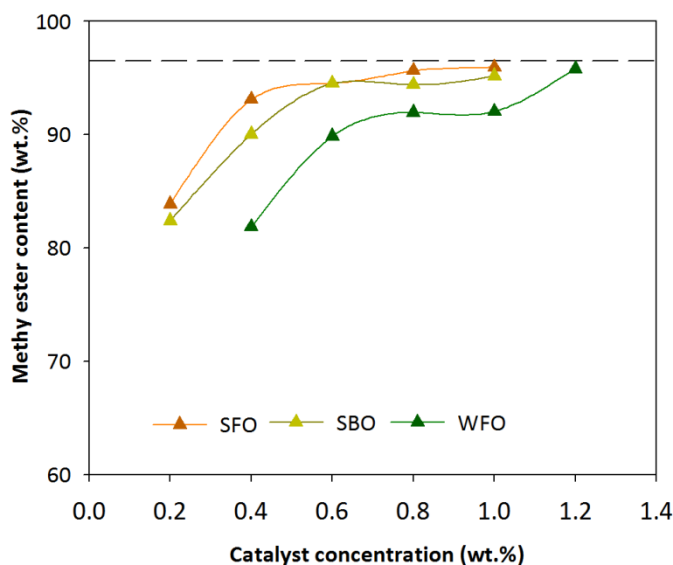


Figure 2.11. Methyl ester content (wt.%) using waste frying oil, sunflower oil and soybean oil and KOH as catalyst; dashed line indicates minimum limit according to European standard EN 14214.

Considering the obtained results, it was clear that the studied homogeneous sodium based alkali catalysts were more effective than the KOH to obtain a pure biodiesel according to the European biodiesel standard EN 14214. Because purity at the highest concentrations was close to the limit, best results would be expected by increasing catalyst concentration (≥ 1.2 wt.%).

Regarding the sodium based catalysts, optimum conditions were: i) 0.6 wt.% CH_3ONa for both virgin oils; ii) 0.6 wt.% NaOH for sunflower oil and 0.8 wt.% for soybean oil; and iii) 0.8 wt.% using both catalysts for waste frying oils.

IODINE VALUE

The iodine value gives a measure of the degree of unsaturation of the biodiesel samples. The existence of double bonds might lead to polymerization of glycerides by heating, which could lead to gum formation (Encinar et al., 2005), possibly creating deposits on injector nozzles. The increase in double bonds will worsen this problem. Highly unsaturated compounds also tend to have lower oxidation stability, leading to the formation of degradation products which can affect engine performance (Mittelbach et al., 2004). A maximum limit of 120 g $\text{I}_2/100$ g was imposed by European biodiesel standard EN 14214 to ensure biodiesel quality. As this parameter depends only on the raw material used, samples obtained using the same vegetable oil should present similar iodine value.

The results obtained were in agreement with the characterization made for the raw materials. Taking into account the results, soybean oil is not an attractive raw material concerning iodine value (127 g I₂/100 g). Sunflower oil showed an iodine value of 124 g I₂/100 g, which is close to the maximum limit.

The waste frying oil was, among the used raw materials, the most adequate to be used, presenting an iodine value of 117 g I₂/100 g, because it probably resulted from the mixture of oils with less unsaturated fatty acid content.

One way to reduce the iodine value of the virgin oils could be, therefore, to mix them with other oils which composition has less unsaturated fatty acids. For instances, rapeseed oil which presents an iodine value between 94 and 120 g I₂/100 g (Lapuerta et al., 2009) or fats, such as lard, with an iodine value around 70 g I₂/100 g (Dias et al., 2008; Dias et al., 2009).

2.6 CONCLUSIONS

The results of this study can be used for improving biodiesel production processes using the same raw materials (sunflower oil, soybean oil and waste frying oil) and catalysts (NaOH, CH₃ONa, KOH).

Results revealed that biodiesel production using virgin oils results in higher yields as compared to waste frying oils (97 wt.% compared with 92 wt.%).

In terms of iodine value, the most attractive raw material was the waste frying oil (117 g I₂/100 g). Iodine value of soybean oil was above the established limited and sunflower oil showed an iodine value close to limit.

The production diagram adopted ensured that most biodiesel samples fulfil the required standard limits in terms of acid value, density, flash point, copper corrosion and linolenic acid methyl ester content. High flash points (from 174 to 182 °C) were obtained for all produced samples and indicate efficient excess methanol recovery and high safety.

Anhydrous sodium sulphate was not effective to ensure that biodiesel water content was according to the standard limit; however, evaporation at reduced pressure (40 °C, 150 mbar, 45 min) was effective.

Amongst the studied biodiesel properties, the kinematic viscosity and the methyl ester content were the most important for the selection of the best catalyst type and concentration.

Using sodium based catalysts, namely CH_3ONa and NaOH , the optimum conditions which ensured that studied parameters fulfilled the required limits according to the European biodiesel standard EN 14214, were: i) 0.6 wt.% CH_3ONa for both virgin oils; ii) 0.6 wt.% NaOH for sunflower oil and 0.8 wt.% for soybean oil; and iii) 0.8 wt.% using both catalysts for waste frying oils.

KOH catalyst was less effective than the sodium based catalysts. A catalyst concentration of 0.6 wt.% for virgin oils and 0.8 wt.% for waste frying oils ensured that viscosity was within the limits, but purity was lower than the minimum required according to the European biodiesel standard EN 14214. Because at the highest catalyst concentrations purity was generally very close to the limit, best results would be expected by increasing the catalyst concentration.

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CHAPTER 3 BIODIESEL PRODUCTION FROM VEGETABLE OIL/ANIMAL FAT MIXTURES

ENERGY & FUELS

Article
Mixtures of Vegetable Oils and Animal Fat for Biodiesel Production: Influence on Product Composition and Quality
Joana M. Dias, Maria C. M. Alvim-Ferraz, and Manoel F. Almeida
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ABSTRACT

The use of raw material mixtures, by incorporating wastes, is an environmental friendly alternative to reduce biodiesel production costs and improve product quality. The present work studied: i) biodiesel production using vegetable oils mixed with animal fat; ii) variations in biodiesel composition aiming its prediction when mixtures are used as raw materials; and iii) the influence of mixture composition in biodiesel quality. Product yields varied from 81.7 to 88.8 (wt.%). Biodiesel fulfilled most of the determined quality specifications according to EN 14214; however, methyl ester content (purity) and iodine value were not fulfilled in some cases. Minimum purity was only achieved when using waste frying oil or soybean oil alone as raw material; however, it ranged from 93.9 to 96.6 (wt.%), being always close to the limit (96.5 wt.%). A model was developed to be used for predicting composition and some quality parameters of biodiesel resulting from mixtures; accordingly, the use of at least 12 wt.% lard in a soybean oil/lard mixture would be expected to reduce biodiesel iodine value to an acceptable value. The waste frying oil used has proven to be good raw material to reduce biodiesel production costs and obtain a product with quality.

3.1 SCIENTIFIC RELEVANCE

There are many studies reporting the transesterification of different types of vegetable oils for biodiesel production; but fewer studies can be found regarding the conversion of animal fat. This is probably due to the fact that animal fat use at a larger scale is limited; also, high degree of free fatty acids tends to difficult production processes (Ngo et al., 2008).

The use of mixtures as raw material might be very relevant for biodiesel production because it allows management according to availability and can even improve product quality. In a study by Meneghetti (2007) the use of castor oil, which had a viscosity of $225.8 \text{ mm}^2 \text{ s}^{-1}$ at 40°C was enabled for biodiesel production by mixing it with either soybean oil or cottonseed oil. In a study by Lebevedas (2006) the use of three component mixtures also allowed the reduction of emission and harmful components of the fuel.

The great amounts of waste animal fat, produced at several slaughter houses and other meat processing units, might be an attractive and cheap raw material additive. Besides the acidity, one of the great concerns regarding the use of animal fat as raw material for biodiesel production is its cold weather properties and oxidation stability; however, it is known that the obtained fuel might be used in 100% in boilers for heat generation. Additionally, its use in mixture dilutes the effect of such properties in the final product.

Soybean oil has a high iodine value; therefore, the product obtained using this raw material most of the times does not fulfil the European biodiesel standard EN 14214. Because animal fat has a low iodine value, its use in mixture with soybean oil will probably result in a fuel with improved iodine value (lower than the maximum limit).

Other waste materials that can be used for biodiesel production are the waste frying oils (Al-Widyan et al., 2002; Felizardo et al., 2006; Wang et al., 2006; Zheng et al., 2006). Due to the scarce availability of these low cost materials, their use at an industrial scale is limited; however, their mixture with other raw materials might be an attractive alternative.

As far as it is known, the current knowledge regarding the use of mixtures of raw materials including wastes is very scarce; aiming to improve this knowledge, the present work studied biodiesel production using mixtures of vegetable oils (virgin and waste) and animal fats.

3.2 SPECIFIC OBJECTIVES

- To study biodiesel production using vegetable oils (virgin and waste) mixed with animal fat;
- To analyze the variations in biodiesel composition aiming its prediction when mixtures with different fat contents are used as raw materials;
- To understand how mixture composition influences biodiesel quality.

3.3 MATERIALS

The SBO and the WFO used were the same presented in Chapter 2. The pork lard (PL) was from the brand “*Dilop Carnes*”, and it was purchased at the food market (Figure 3.1).



Figure 3.1. Commercial pork lard used.

The reagents used during synthesis and purification procedures were the same presented in Chapter 2.

3.4 METHODS

3.4.1 BIODIESEL PRODUCTION

Biodiesel production was made by adjusting previously reported diagram (Figure 2.2); in this case, production presented three steps: pre-treatment, synthesis and purification (Figure 3.2).

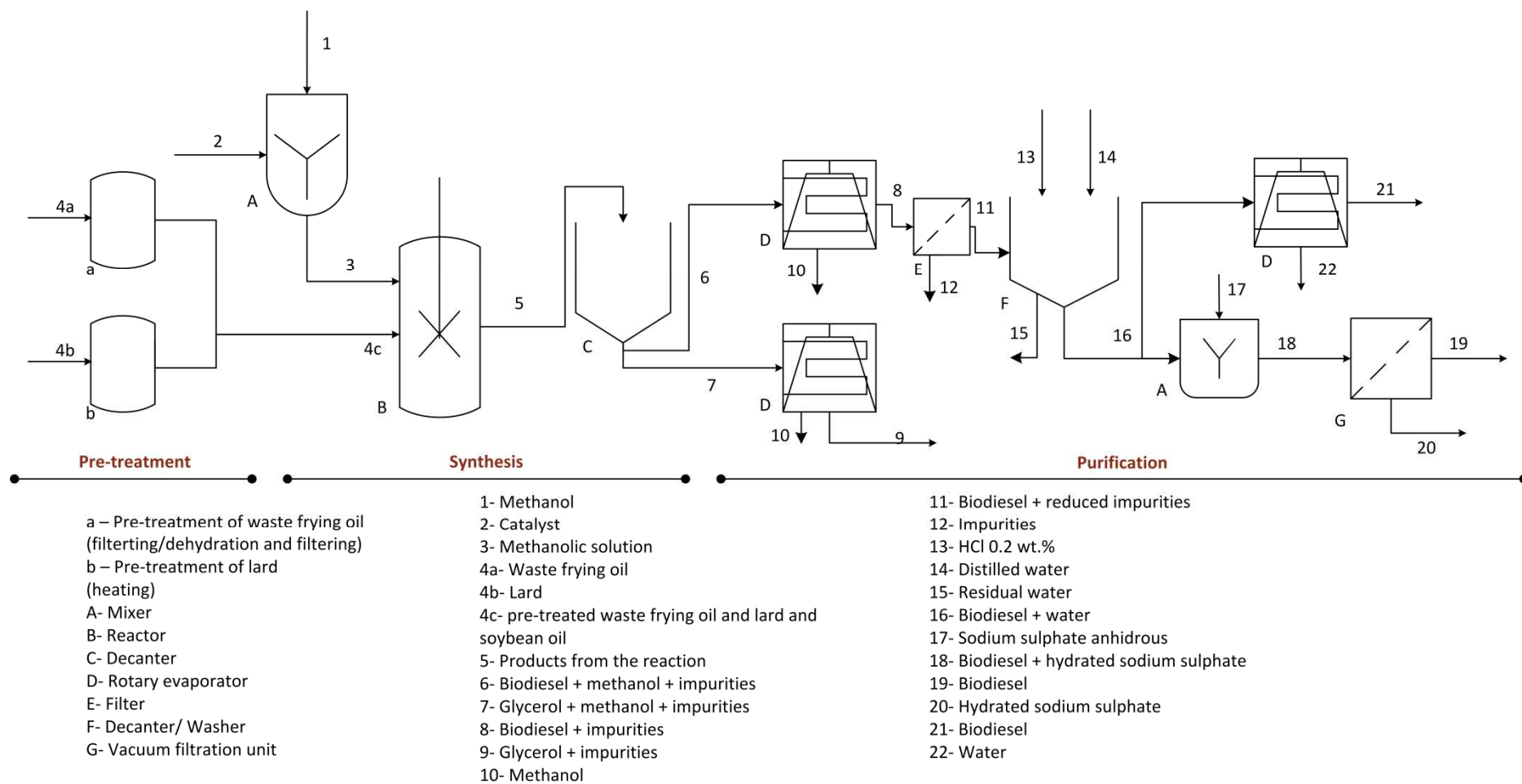


Figure 3.2. Diagram adopted for biodiesel production using vegetable oil/animal fat mixtures.

PRE-TREATMENT

Pre-treatment was performed to vaporize residual water and reduce sample heterogeneity. WFO was filtered under vacuum, after dehydrated using anhydrous sodium sulphate (left over night) and finally again filtered under vacuum. The PL was first heated at 100 °C to eliminate residual water and after cooled to near the reaction temperature (60 °C).

SYNTHESIS

Synthesis of biodiesel was carried out by transesterification.

The mixtures of vegetable oil and fat were prepared considering the increase in the fat fraction of the mixture, varying from 0-1(w/w), in 0.2 intervals.

The reaction conditions were chosen according to a previous study by Dias et al. (2008). A defined amount of methanol (6:1 molar ratio to oil) pre-mixed with NaOH (0.8 wt.% of the starting mixture weight) was added to the reactor, which already had 100 g of the raw material mixture, pre-heated at the reaction temperature (60 °C); the reaction occurred for 1 hour at vigorous mixing.

The reactor and acrylic bath was the same used in experimental work described in Chapter 2 (Figure 2.3).

PURIFICATION

Methanol recovery and washing was conducted in the same way as presented in Chapter 2 (Figure 2.4); however, between methanol recovery and washing, biodiesel was this time filtered (S&S, grade 589/1). The filtering stage was adopted due to the fact that it significantly improved the washing stage, reducing emulsion formation.

Regarding biodiesel dehydration, and according to the results presented in Chapter 2, different procedures were adopted to evaluate which would be the best one. Such procedures were based on the use of an anhydrous salt and evaporation at reduced pressure under different conditions.

3.4.2 ANALYTICAL METHODS

Raw material properties as well as biodiesel quality parameters were determined.

The following raw material properties were determined: composition, acid value, iodine value and water content. Specific methods and related standards were presented in section 2.4.2.

Biodiesel quality was evaluated according to the European biodiesel standard EN 14214 (2003); the parameters evaluated were: acid value, kinematic viscosity, density, flash point, copper corrosion, water content, ester and linolenic methyl ester content and iodine value. Specific methods and related standards were presented in section 2.4.2.

3.5 RESULTS AND DISCUSSION

3.5.1 RAW MATERIAL CHARACTERISATION

Raw material composition and other measure properties are presented in Table 3.1.

The properties of the WFO and the SBO were previously discussed in Chapter 2.5.1.

Regarding the PL, it presented low acid value, probably resulting from pre-treatment processes; however, commonly referred value for commercial lard according to the *Codex Alimentarius Commission* is slightly higher, being 1.3 mg KOH/g fat (CAC, 2001).

The high saturation levels found on biodiesel from PL (38.1 wt.%) were reflected, as expected, in lower iodine values compared with SBO and WFO.

The water content of the PL was very low due to the pre-treatment procedure.

3.5.2 YIELD

Biodiesel production yields are presented in Table 3.2. Yields varied from 81.7 to 88.8 (wt.%).

The lower yields were obtained when using waste frying oil or lard alone as raw materials for biodiesel production.

Considering all oil/lard mixtures, the differences between yields were less than 3.4% (varying from 85.2 to 88.6 wt.%).

Table 3.1: Starting raw materials properties including acid value, iodine value, water content, methyl ester composition (wt.%) and mean molecular weight

RAW MATERIAL PROPERTIES	SBO	PL	WFO
<i>Acid value (mg KOH/g)</i>	0.21	0.71	0.82
<i>Iodine value (g I₂/100 g)</i>	127	67	117
<i>Water content (wt.%)</i>	0.04	0.03	0.05
<i>Methyl ester composition (wt.%)^{a)}</i>			
Miristate (C14:0)	n.d	1.3	n.d
Palmitate (C16:0)	11.0	23.7	8.4
Palmitoleate (C16:1)	n.d	2.2	0.2
Stearate (C18:0)	3.3	12.9	3.7
Oleate (C18:1)	25.4	41.4	34.6
Linoleate (C18:2)	53.6	15.0	50.5
Linolenate (C18:3)	5.3	1.0	0.6
Eicosenoate (C20:1)	0.3	0.9	0.4
Others	1.1	1.5	1.5
<i>Mean molecular weight (g/mol)</i>	874.0	861.6	877.5

^{a)} Totals might not equal 100% due to rounding; n.d. not detected.

Table 3.2: Biodiesel production yields (wt.%) using different vegetable oil/lard mixtures as raw materials

LARD FRACTION (w/w)	SBO/PL	WFO/PL
0	88.8	82.2
0.2	87.4	87.1
0.4	85.2	87.6
0.6	87.6	85.2
0.8	88.6	88.0
1	81.7	81.7

In the present study, each sample produced was subjected to a different dehydration treatment aiming to select an appropriate dehydration method.

The following treatments were performed:

- Addition of 30 wt.% of anhydrous sodium sulphate (ASS);
- Evaporation (163 mbar) including heating at 40 °C during 45 min (Ev_{40/45});
- Evaporation (163 mbar) including heating at 45, 65 and 80 °C during 90 min (Ev_{45/90}, Ev_{65/90}, Ev_{80/90});

- Evaporation (163 mbar) including heating at 90 °C during 120 min (Ev_{90/120}) and during 210 min (Ev_{90/210}).

Table 3.3 shows which samples were used in each treatment as well as the final water contents.

Table 3.3: Dehydration methods used and final water contents of the biodiesel samples

LARD FRACTION (w/w)	SBO/PL			WFO/PL		
	SAMPLE NUMBER	DEHYDRATION METHOD	WATER CONTENT (wt.%)	SAMPLE NUMBER	DEHYDRATION METHOD	WATER CONTENT (wt.%)
0	1	ASS	0.127	7	ASS	0.100
0.2	2	Ev _{40/45}	0.154	8	Ev _{90/210}	0.040
0.4	3	Ev _{65/90}	0.095	9	Ev _{80/90}	0.100
0.6	4	Ev _{45/90}	0.153	10	Ev _{90/120}	0.045
0.8	5	Ev _{40/45}	0.155	11	Ev _{90/120}	0.056
1	6	Ev _{40/45}	0.114		-	

The same dehydration treatment led to different final water contents (samples 2, 5 and 6 by evaporation treatment; samples 1 and 7 by anhydrous salt treatment) probably due different water contents after the washing stage. Nevertheless, a qualitative analysis was performed in order to select a dehydration method which leads to a product compatible with the European biodiesel standard EN 14214.

When evaporating during 90 min, the effect of increasing the temperature seems to be mainly noted when temperature increases from 45 to 65 °C (samples 4 and 3), than from 65 °C to 80 °C (sample 9). The increase in evaporation time from 45 to 90 min was not reflected in lower water contents at temperatures of 40 and 45 °C (samples 2, 5 and 6 compared to sample 4).

When using 80 °C during 90 min (sample 9), water content obtained was 0.1 wt.%; however, when temperature increased to 90 °C and time to 120 min (sample 10 and 11), a significant decrease in the water content was observed, being 0.045 and 0.056. Using higher evaporation times at 90 °C, the difference was not very high (sample 8), but under such conditions the lowest water content was achieved (0.04 wt.%).

Considering the obtained results, evaporation at 90 °C using a holding time of 210 min (163 mbar) was selected as the safest of the studied methods to obtain a biodiesel according to EN 14214.

3.5.3 BIODIESEL COMPOSITION

Biodiesel composition resulting from the transesterification of SBO and WFO mixed with PL was evaluated aiming its prediction when mixtures with different lard contents are used as raw materials.

It was postulated that the methyl ester composition of biodiesel corresponded to the weighted average of the composition of each component of the mixture, therefore:

$$C_{\text{mix}} = C_{\text{oil}} X_{\text{oil}} + C_{\text{lard}} X_{\text{lard}} \Leftrightarrow C_{\text{mix}} = (C_{\text{lard}} - C_{\text{oil}}) X_{\text{lard}} + C_{\text{oil}} \quad (\text{Equation 3-1})$$

where:

C_{mix} – methyl ester composition (wt.%) of the mixture;

C_{oil} – methyl ester composition (wt.%) of the oil;

C_{lard} – methyl ester composition (wt.%) of the lard;

X_{oil} – weight fraction of the oil;

X_{lard} – weight fraction of the lard.

In fact, it was found that the methyl ester composition was linearly correlated with the mass fraction of lard incorporated in the raw material with determination coefficient $r^2 > 0.88$ and p -value < 0.05 (using an F-test) for the main methyl esters, which corresponded to more than 96% of the methyl ester composition.

Figure 3.3 and Figure 3.4 show the variation in methyl ester composition (main methyl esters) with incorporation fraction of lard in SBO and WFO, respectively. In these figures it is evident the variation of the wt.% of each methyl ester; in fact, such variation appears to be linear and an example of a linear correlation plot presented in the Figures confirms that fact.

Table 3.4 shows the linear regression parameters. From those, it was possible to verify that the slope (a) was similar to the difference between the methyl ester content in fat and oil ($C_{\text{lard}} - C_{\text{oil}}$); also, the intercept (b) was similar to the methyl ester content in the oil (C_{oil}) and differences were lower than 5%. Such results show that Equation 3-1 might be used to predict the methyl ester content of biodiesel resulting from mixtures of soybean oil/lard and waste frying oil/lard when different lard contents are used.

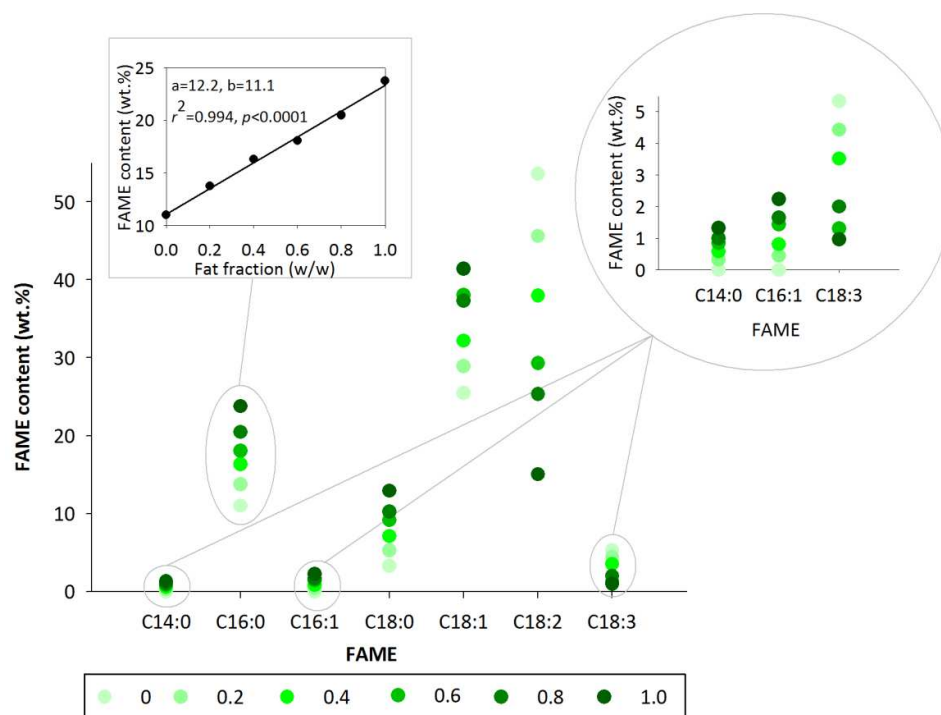


Figure 3.3. Methyl ester content variation with incorporation of lard 0-1.0 (w/w) in soybean oil including example of linear correlation regarding methyl palmitate (C16:0) content.

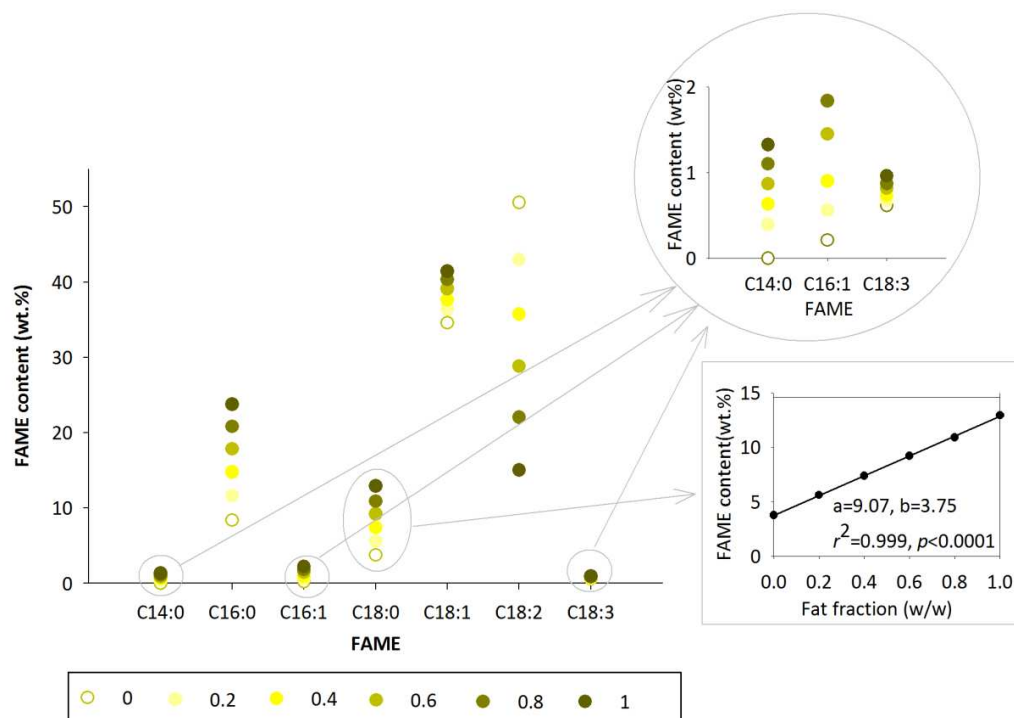


Figure 3.4. Methyl ester content variation with incorporation of lard 0-1.0 (w/w) in waste frying oil; including example of correlation regarding methyl oleate (C18:0) content.

Table 3.4: Fitting of methyl ester composition (wt.%) of biodiesel versus lard mass fraction incorporated in the oil - linear regression parameters

METHYL ESTER	MIXTURE	a	b	r^2	p-value	C _{oil}	C _{lard}	C _{lard} -C _{oil}
C14:0	SBO/PL	1.3	0.0	0.991	<0.0001	n.d	1.3	1.3
	WFO/PL	1.3	0.1	0.989	<0.0001	n.d	1.3	1.3
C16:0	SBO/PL	12.2	11.1	0.994	<0.0001	11.0	23.7	12.7
	WFO/PL	15.3	8.5	1.000	<0.0001	8.4	23.7	15.4
C18:0	SBO/PL	9.3	3.3	0.993	<0.0001	3.3	12.9	9.6
	WFO/PL	9.1	3.8	1.000	<0.0001	3.7	12.9	9.2
C18:1	SBO/PL	15.8	26.0	0.952	<0.001	25.4	41.4	16.0
	WFO/PL	6.8	34.8	0.994	<0.0001	34.6	41.4	6.9
C18:2	SBO/PL	-37.5	53.2	0.993	<0.0001	53.6	15.0	-38.6
	WFO/PL	-35.3	50.2	1.000	<0.0001	50.5	15.0	-35.5
C18:3	SBO/PL	-4.5	5.2	0.892	<0.05	5.3	1.0	-4.4
	WFO/PL	0.3	0.6	0.995	<0.0001	0.6	1.0	0.3
C20:0	SBO/PL	-0.1	0.4	0.987	<0.0001	0.4	0.2	-0.1
	WFO/PL	-0.2	0.4	0.997	<0.0001	0.4	0.2	-0.2
C20:1	SBO/PL	0.6	0.3	0.985	<0.0001	0.3	0.9	0.6
	WFO/PL	0.5	0.4	0.996	<0.0001	0.4	0.9	0.5
C22:0	SBO/PL	-0.5	0.5	0.878	<0.01	0.5	n.d	-0.5
	WFO/PL	-0.9	0.9	1.000	<0.0001	0.8	n.d	-0.8

C_{oil} – methyl ester content of oil; C_{lard} – methyl ester content of lard; a – slope; b – intercept; r^2 – determination coefficient; p – probability value (using an F-test); SBO – soybean oil; WFO – waste frying oil; PL – pork lard; n.d – not detected.

3.5.4 BIODIESEL QUALITY

As it can be observed in Table 3.5, all produced samples fulfilled the European standard limit in terms of acid value, kinematic viscosity, density, flash point, copper corrosion and linolenic methyl ester content.

High flash points indicate effective methanol recovery, which should be reflected in low methanol contents of biodiesel.

Table 3.5: Quality parameters of biodiesel from oil/lard mixtures and the respective standard limits according to EN 14214

PROPERTY	RESULTS	EN 14214
Acid value (mg KOH/g)	0.02-0.10	<0.5
Kinematic viscosity at 40 °C (mm ² s ⁻¹)		
Lard/Soybean oil mixture	4.46-4.71	3.50-5.00
Lard/Waste frying oil mixture	4.67-4.77	
Density at 15 °C (kg m ⁻³)	875.7-883.6	860-900
Flash point (°C)	174-179	>120
Copper corrosion (3 h/50 °C)	All samples- Class 1a	Class 1
Methyl ester content (wt.%)	93.9-96.6	>96.5
Linolenic methyl ester content (wt.%)		
Lard/Soybean oil mixture	1.0-5.3	<12.0
Lard/Waste frying oil mixture	0.6-1.0	
Iodine value (g I ₂ /100 g) ^{a)}		
Lard/Soybean oil mixture	67-127	<120
Lard/Waste frying oil mixture	67-117	

^{a)} Calculated from the methyl ester composition.

Kinematic viscosity was slightly higher for mixtures using waste frying oil; however, it was always within the standard limits according to EN 14214.

Among the measured parameters, methyl ester content (purity) and iodine value were the ones that were not fulfilled by all samples.

It was verified that the minimum purity of biodiesel (96.5 wt.%) was only achieved when using waste frying oil or soybean oil alone as raw material (Figure 3.5); when using 100% of lard, lowest purity was obtained (94.4%).

The lowest purity obtained using lard alone led to a decrease in biodiesel purity with increased incorporation of lard, despite the high yields obtained.

However, it should be referred that purity might be improved, namely by increasing either catalyst concentration, for instance 1 wt.%, or temperature, for instance 65 °C (Leung et al., 2006; Dias et al., 2008).

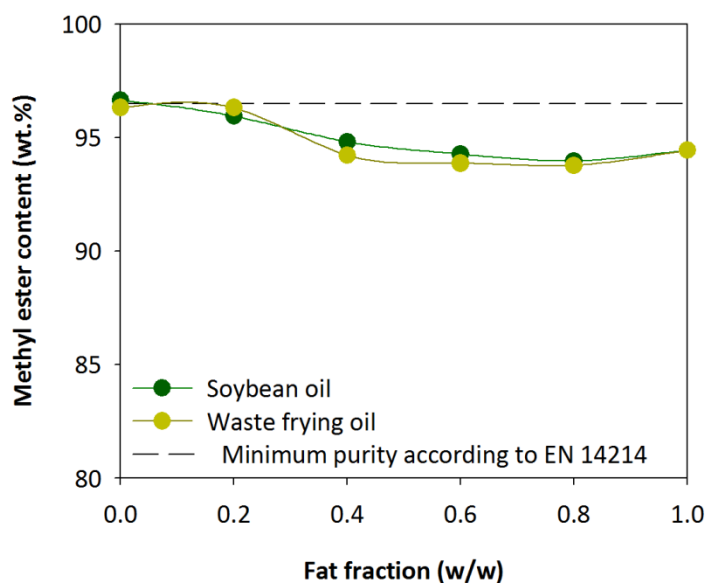


Figure 3.5. Methyl ester content (wt.%) of biodiesel samples obtained using different mixtures of vegetable oil and pork lard.

As for the composition, it was postulated that the quality parameter of the biodiesel obtained from the mixture corresponded to the weighted average of the quality parameter of biodiesel resulting from each component; therefore:

$$P_{\text{mix}} = P_{\text{oil}} X_{\text{oil}} + P_{\text{lard}} X_{\text{lard}} \Leftrightarrow P_{\text{mix}} = (P_{\text{lard}} - P_{\text{oil}}) X_{\text{lard}} + P_{\text{oil}} \quad (\text{Equation 3-2})$$

where:

P_{mix} – quality parameter of biodiesel from the mixture;

P_{lard} – quality parameter of biodiesel from the lard;

P_{oil} – quality parameter of biodiesel from the vegetable oil;

X_{oil} – weight fraction of the vegetable oil;

X_{lard} – weight fraction of the lard.

In fact, a linear correlation was also found between some of the quality parameters and the lard fraction incorporated in the oil; those parameters were: iodine value, density, viscosity, methyl ester content and linolenic methyl ester content.

Such correlations had $r^2 > 0.79$ ($p < 0.05$) except in the case of viscosity and methyl ester content of biodiesel resulting from the mixture of waste frying oil and lard.

Table 3.6 shows the linear regression parameters of the fitting.

Table 3.6: Fitting of some quality parameters of biodiesel from oil/lard mixtures versus incorporated lard fraction - linear regression parameters

PROPERTY	MIXTURE	a	b	r^2	p-value	P _{oil}	P _{lard}	P _{lard} -P _{oil}
Iodine value (g I ₂ /100 g)	SBO/PL	-59	127	0.991	<0.0001	127	67	-60
	WFO/PL	-50	118	1.000	<0.0001	117	67	-50
Density (kg m ⁻³)	SBO/PL	-7.9	883.4	0.993	<0.0001	883.6	875.7	-7.8
	WFO/PL	-7.4	883.4	0.989	<0.0001	883.4	875.7	-7.6
Viscosity (mm ² s ⁻¹)	SBO/PL	0.25	4.46	0.815	<0.05	4.46	4.71	0.25
	WFO/PL	0.02	4.70	0.040	0.705	4.69	4.71	0.02
Methyl ester content (wt%)	SBO/PL	-2.5	96.3	0.788	<0.05	96.6	94.4	-2.2
	WFO/PL	-2.5	96.1	0.615	0.0647	96.3	94.4	-1.9
Linolenic methyl ester content (wt%)	SBO/PL	-4.5	5.2	0.892	<0.05	5.3	1.0	-4.4
	WFO/PL	0.3	0.6	0.995	<0.05	0.6	1.0	0.3

P_{oil} – property of oil, P_{lard} – property of lard, a – slope, b – intercept, r^2 – determination coefficient, p – probability value (using an F-test), SBO – soybean, WFO – waste frying oil.

It was possible to verify that, considering the fittings with determination coefficients > 0.8, the slope (a) was similar to the difference between the property in fat and oil (P_{lard}-P_{oil}); also, the intercept (b) was similar to the property of the oil (P_{oil}) (differences were less than 3.5 %). The very low determination coefficient found regarding biodiesel viscosity resulting from waste frying oil/lard mixtures might be explained by the fact that biodiesel samples obtained from these two raw materials had very similar viscosities and experimental errors were much more reflected.

The results showed that Equation 3-2 might be used to predict the following properties of biodiesel resulting from mixtures of soybean oil/lard and waste frying oil/lard when mixtures with different lard contents are used: iodine value, density, viscosity (considering soybean/lard mixtures only), methyl ester content (considering soybean/lard mixtures only) and linolenic methyl ester content.

As expected, the increase in the lard fraction led to a decrease in the iodine value. In the case of mixture with soybean oil, this had a positive effect because biodiesel obtained from soybean oil alone does not meet the standard specification according to EN 14214. From the linear model, it was possible to estimate that the use of 12 wt.% of lard in the soybean/lard mixture would decrease biodiesel iodine value to the maximum limit according to EN 14214.

Therefore, the incorporation of lard in the soybean oil was found to be effective in reducing the iodine value of biodiesel to acceptable values, as predicted.

Overall, in terms of using virgin or waste oil, the mixture behaviour was not very different which can indicate that incorporating waste frying oil might be a good alternative to obtain a biodiesel fulfilling European standard at a lower cost.

3.6 CONCLUSIONS

Synthesis of biodiesel by transesterification of several raw material mixtures of pork lard with virgin and waste frying oil resulted in yields varying from 81.7 to 88.8 (wt.%).

Evaporation at 90 °C, 163 mbar and during 3 h 30 min was established as an efficient dehydration method for biodiesel production using such raw material mixtures.

Biodiesel met the European biodiesel quality standard EN 14214 in terms of acid value, viscosity, density, flash point, copper corrosion and linolenic acid methyl ester content using different lard incorporation fractions in soybean oil and waste frying oil.

Methyl ester content (purity) and iodine value were the ones that were not fulfilled in some cases. Minimum purity was achieved when using waste frying oil or soybean oil alone as raw material; however, it was always close to the limit (93.9-96.6 wt.%).

It was postulated and confirmed by a linear model that: (i) the methyl ester composition of biodiesel corresponds to the weighted average of the composition of each component of the mixture, and (ii) the quality parameter of biodiesel obtained from the mixture corresponded to the weighted average of the parameter of biodiesel resulting from each component. For the first, it could be applied for the main methyl esters, which corresponded to more than 96% of the methyl ester composition (linear fittings with determination coefficient $r^2 > 0.88$, $p\text{-value} < 0.05$). For the second, it could be applied for iodine value, density, viscosity (considering soybean/lard mixtures), methyl ester content (considering soybean/lard mixtures) and linolenic methyl ester content (linear fittings with determination coefficient $r^2 > 0.79$, $p\text{-value} < 0.05$).

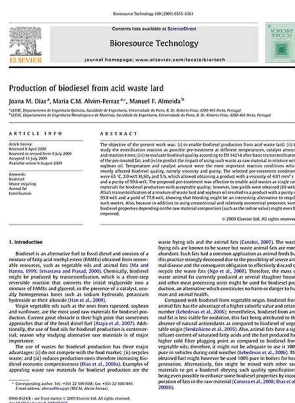
It was predicted that the use of at least 12 wt.% of lard in a soybean oil/lard mixture would be effective in reducing the iodine value of biodiesel to the maximum limit according to EN 14214.

There was not much difference regarding the use of refined or waste vegetable oil, which can indicate that the use of waste frying oil might be a good alternative to obtain a biodiesel fulfilling European standard EN 14214 at a lower cost.

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CHAPTER 4 BIODIESEL PRODUCTION FROM ACID WASTE LARD



This chapter was based on:

Dias, J. M., Alvim-Ferraz, M. C. M. and Almeida, M. F. (2009). *Production of biodiesel from acid waste lard*. *Bioresource Technology* 100: 6355-6361.

ABSTRACT

The use of fat wastes as raw material for biodiesel production through transesterification is appealing, namely due to their low cost, but high acidity is usually a very limiting factor. The present work studied: (i) biodiesel production from acid waste lard; (ii) esterification reaction as possible pre-treatment to reduce the raw material acid value, using different temperatures, catalyst concentrations and reaction times; (iii) biodiesel quality according to EN 14214 after basic transesterification of the pre-treated fat; and (iv) the impact of using such waste as raw material in mixture with soybean oil. Temperature and catalyst amount were the most important reaction conditions affecting biodiesel quality, namely viscosity and purity. The selected pre-treatment conditions were 65 °C, 2.0 wt.% H₂SO₄ and 5 h, which allowed obtaining a product with a viscosity of 4.81 mm² s⁻¹ and a purity of 99.6 wt.%. The proposed pre-treatment was effective to enable acid wastes as single raw materials for biodiesel production with acceptable quality; however, low yields were obtained (65 wt.%). Alkali transesterification of a mixture of acid waste lard and soybean oil resulted in a product with a purity of 99.8 wt.% and a yield of 77.8 wt.%, showing that blending might be an interesting alternative to recycle such wastes.

4.1 SCIENTIFIC RELEVANCE

Virgin vegetable oils such as the ones from rapeseed, soybean and sunflower, are the most used raw materials for biodiesel production. Current great obstacle is their high price that sometimes approaches that of the fossil diesel fuel (Ataya et al., 2007). Additionally, the use of food oils for biodiesel production is controversial, reason why studying alternative raw materials is of major importance.

The use of wastes has great advantages namely by reduction of biodiesel production costs and environmental impacts. Examples of appealing waste raw materials for biodiesel production are the waste frying oils and the animal fats (Canakci et al., 2008). The waste frying oils are known to be scarce but waste animal fats are more abundant which make them more attractive.

Up to date, few studies relate to biodiesel production from animal fats and some of the existing focus on the use of edible grade fat presenting low acid value (Sendzikiene et al., 2005; Lebedevas et al., 2006) which is more expensive and scarce. Unless the fat is almost immediately extracted from fresh generated fatty wastes, the acid value of the fat will be high as a result of hydrolysis, due to presence of water and degradation processes.

Aiming the biodiesel production from waste animal fat at a larger scale, the high content of free fatty acids of the raw material should be considered as a limiting factor, because they react with the catalyst during basic transesterification, causing the formation of soaps (Ngo et al., 2008).

One of the most interesting options is the pre-esterification of the free fatty acids through reaction with methanol in the presence of an acid catalyst, more commonly H_2SO_4 , to form ester and water, therefore taking advantage of all the raw material for biodiesel production.

As for the transesterification, amongst the parameters which mostly influence the esterification reaction are catalyst amount, reaction temperature, reaction time and molar ratio of methanol to oil. To enable biodiesel production from acid raw materials in a more cost-effective way, the study of such reaction is necessary. As far as it is known, few studies were developed regarding the evaluation of the pre-treatment acid esterification reaction.

Lin et al. (2009) evaluated the influence of the molar ratio of methanol to oil and the reaction time in the acid value of the esterified product, when crude rice bran oil was used as raw material. A two-step pre-treatment with 1 wt.% of H_2SO_4 at 50 °C was used. A 6:1 and 7:1 molar ratio of methanol to oil and 60 min and 30 min reaction time were selected as optimum for the first and second pre-treatment, respectively.

The acid value was reduced from 40 mg KOH g⁻¹ to less than 1 mg KOH g⁻¹ oil and the alkali transesterification led to a product complying with biodiesel quality specifications.

Issariyakul et al. (2007) studied biodiesel production from waste fryer grease with 5-6 wt.% free fatty acids through an esterification pre-treatment monitored by acid value decrease using 50 and 60 °C, 2 wt.% H₂SO₄ and 5 h; an ester content of 96 wt.% could be obtained after basic transesterification using KOH.

Canoira et al. (2008) studied biodiesel production from soybean oil mixed with low grade animal fat (50 vol.%). The mixture reduced the raw material acidity from 13.6 mg KOH g⁻¹ to 7.2 mg KOH g⁻¹ and the pre-treatment using a strong organic acid under fixed reaction conditions (60 °C, 0.5 wt.% catalyst, 4 h and 6:1 molar ratio of methanol to fat) was used to reduce the acid value to 0.6 mg KOH g⁻¹; according to the authors, the biodiesel produced by further transesterification using sodium methoxide had a low cost and acceptable quality.

Ngo et al. (2008) studied a series of diarylammonium catalysts for the acid esterification of greases containing 12 - 40 wt.% of free fatty acids, reducing that content to less than 1 wt.%; the reaction temperature and time were fixed (90 °C, 2 h) and the amount of methanol and catalyst were evaluated; best conditions were selected for 2-3 mol% of catalyst and 5-20 equiv of methanol.

The existing studies reviewed which considered the use of waste animal fats for biodiesel production evaluated the pre-esterification reaction conditions by considering mostly the acid value decrease; the influence of the process parameters on final biodiesel quality was rarely analysed. Therefore, the present work studied both pre-esterification reaction conditions and product quality obtained by acid esterification followed by basic transesterification of acid waste lard.

4.2 SPECIFIC OBJECTIVES

- To enable biodiesel production from acid waste lard;
- To study the esterification reaction as possible pre-treatment using different temperatures, catalyst concentrations and reaction times;
- To evaluate biodiesel quality according to the European Biodiesel Standard EN 14214 after basic transesterification of the pre-treated fat;
- To predict the impact of using such wastes as raw materials in mixture with soybean oil also considering the elimination of the pre-treatment step.

4.3 MATERIALS

Pork wastes (mainly consisting of fat and residual skin and meat) were collected at a local butchery and the fat extraction was made by heating until the fat was melted and separating it from the solid remaining residue; this product was finally filtered at reduced pressure.

Due to the known heterogeneity of the raw material, a calculated amount of fat wastes, enough for the execution of all experiments, was treated and homogenised to ensure reproducibility of the results.

The fat yield was calculated relatively to the mass of pork wastes $\left(\frac{\text{weight of fat}}{\text{weight pork wastes}} \times 100 \right)$. The extracted fat was kept in the freezer at 4 °C during the experimental period (Figure 4.1).



Figure 4.1. Extracted acid waste pork lard.

The SBO used was the same presented in Chapter 2 (section 2.3).

The reagents used during biodiesel synthesis and purification were: methanol 99.5% (analytical grade, Fischer Scientific), sulphuric acid 95 – 98% (ACS reagent, Aldrich), sodium hydroxide powder 97% (reagent grade, Aldrich), and hydrochloric acid 37% (ACS reagent, Aldrich).

4.4 METHODS

4.4.1 BIODIESEL PRODUCTION

Synthesis was made by acid esterification followed by basic transesterification. The production process included the following steps: pre-treatment, acid esterification, purification of intermediate products, basic transesterification and purification of final products according to Figure 3.2.

PRE-TREATMENT

Before the synthesis, the waste lard was heated at 100 °C to vaporize residual water and after cooled to near the reaction temperature (45 - 65 °C).

ACID ESTERIFICATION

Esterification conditions varied among experiments; the following reference conditions were selected according to literature (Ma et al., 1999; Tashtoush et al., 2004; Issariyakul et al., 2007): 55 °C, 2.0 wt.% catalyst, 5 h and 6:1 molar ratio of methanol to lard. The variables studied were the catalyst amount, the temperature and the reaction time. When one parameter was studied, all the others were fixed as in the reference conditions.

For the esterification, 120.0 g of the dehydrated lard were weighted and added to the reactor which was set at the reaction temperature (45, 55 or 65 °C). After reaching the reaction temperature, a defined amount of methanol (6:1 molar ratio to lard) pre-mixed with H₂SO₄ (1.0, 2.0, 3.0 or 4.0% of lard weight) was added to the reactor; at this point the reaction started.

The reactor and acrylic bath was the same used in experimental work described in Chapter 2 (Figure 2.3). As soon as the reaction started, samples of 3 mL were taken periodically and the acid value was measured to evaluate the reaction progress, 6 samples were taken during each experiment (excluding the sampling at the end of the reaction time).

Reaction occurred during 3, 5 or 6 h under vigorous stirring. At the end of the reaction, products were decanted for 0.5 h and two phases could be identified; the upper phase consisted of methanol, H₂SO₄ and impurities and the lower phase mainly consisted of lard and the esterified fatty acids, containing also H₂SO₄, residual methanol and impurities (Canoira et al., 2008).

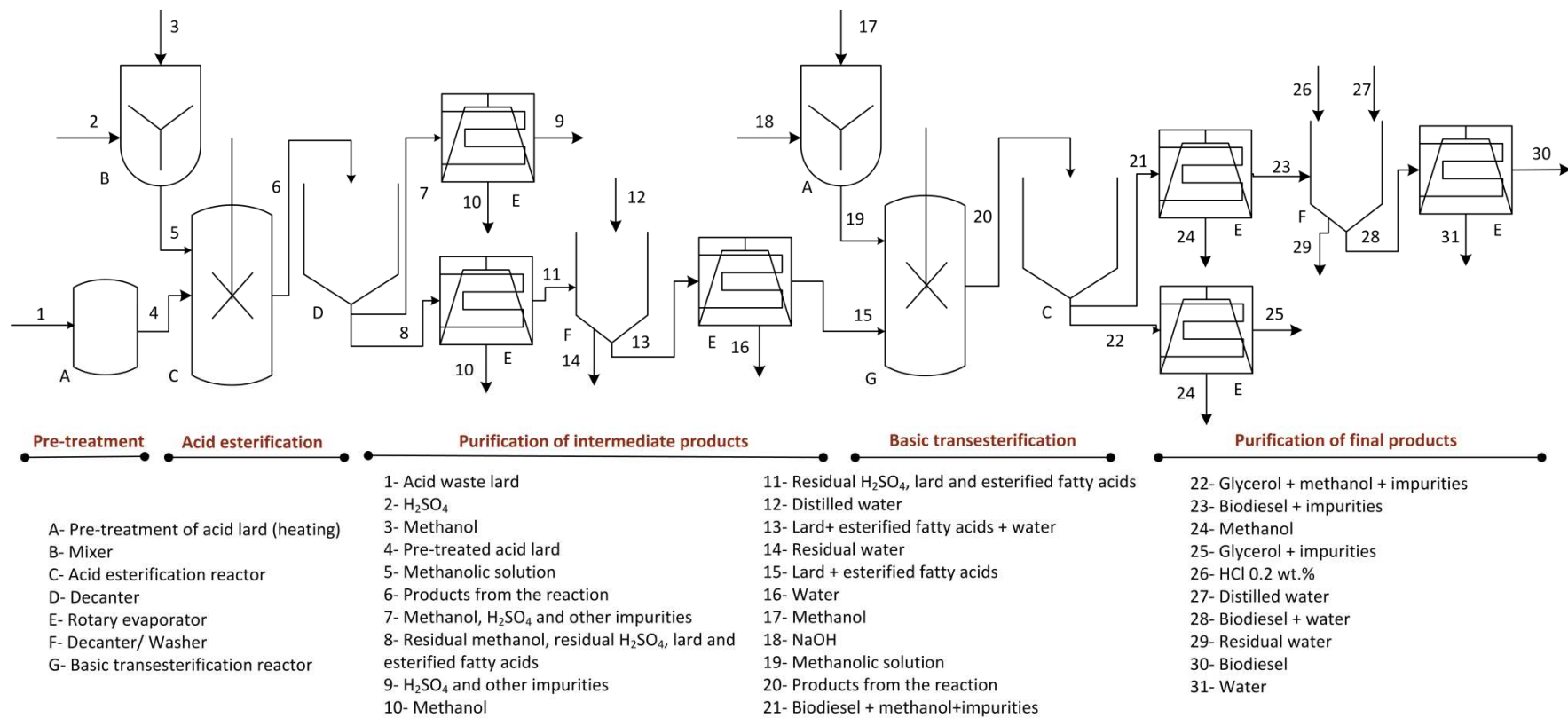


Figure 4.2. Diagram adopted for biodiesel production from acid waste lard.

PURIFICATION OF INTERMEDIATE PRODUCTS

The phases were separated and excess methanol was recovered from each one using a rotary evaporator under reduced pressure. To avoid washing and drying to remove the residual acid, the use of silica gel for dehydration and excess of basic catalyst to neutralise the acid was evaluated (Issariyakul et al., 2007), but soap production after the addition of the basic catalyst impaired the transesterification reaction. Alternative dehydration at 90 °C under reduced pressure and addition of excess basic catalyst was also evaluated, but results were similar.

Therefore, the esterified product needed to be washed with distilled water to remove residual H_2SO_4 and after dried at 90 °C during 1 h in a rotary evaporator at reduced pressure to enable further basic transesterification.

BASIC TRANSESTERIFICATION

The washed and dried product was then submitted to basic transesterification at 65 °C, 1 wt.% NaOH and a 6:1 molar ratio of methanol to lard during 1 h, according to previously published procedure (Dias et al., 2008), and the products from the reaction were decanted overnight.

PURIFICATION OF FINAL PRODUCTS

Biodiesel and glycerol purification was performed according to Dias et. al. (2008); regarding biodiesel dehydration, the procedure was the evaporation at reduced pressure at 90 °C during 2 h.

ADDITIONAL EXPERIMENTS

Determination of the Acid value of the Esterified Product

After selecting the best acid esterification conditions, the reaction was repeated under those conditions for determination of the acid value of the esterified product.

Use of Raw Material Mixtures

A mixture of the acid waste lard with soybean oil was also studied as possible raw material for biodiesel production.

Aiming to obtain a biodiesel with an iodine value according to EN 14214 ($<120 \text{ g I}_2/100 \text{ g}$), the percentage of lard to be incorporated was calculated using a model previously developed (Dias et al., 2008); accordingly, to obtain a biodiesel iodine value of $115 \text{ g I}_2/100 \text{ g}$, 25 wt.% of waste lard was used.

With the raw material mixture two experiments were performed:

- Two-step process (pre-esterification and transesterification) under the esterification reaction conditions previously selected;
- One-step process^{§§} (basic transesterification) under the same synthesis and purification procedures applied in the two-step treatment (regarding the transesterification process).

4.4.2 ANALYTICAL METHODS

Raw material properties as well as biodiesel quality parameters were determined.

The following raw material properties were determined: composition, acid value and iodine value. Specific methods and related standards were presented in section 2.4.2.

Biodiesel quality was evaluated according to the European biodiesel standard EN 14214 (2003); the parameters evaluated were: acid value, kinematic viscosity, water content, ester and linolenic methyl ester content and iodine value. Specific methods and related standards were presented in section 2.4.2.

4.5 RESULTS AND DISCUSSION

4.5.1 RAW MATERIAL CHARACTERISATION

The yield of fat extraction was 70 wt.%. The acid waste lard (AWL) had an acid value of $14.57 \text{ mg KOH g}^{-1}$ and one-step basic transesterification of this raw material alone at 65°C , 1 wt.% NaOH and 6:1 molar ratio of methanol to lard resulted in immediate soap production. The acid value of the AWL was, as expected, much higher than that of SBO ($0.21 \text{ mg KOH g}^{-1}$).

^{§§} Raw material mixture was dehydrated (heating at 100°C and cooling to near the reaction temperature) prior to the basic transesterification reaction.

The iodine value of AWL (79 g I₂/100 g) was significantly lower than that of SBO (127 g I₂/100 g), in agreement with the higher saturation levels found on biodiesel from waste lard (33.7 wt.%) as compared with the one from soybean oil (15 wt.%). The composition and other chemical properties of the soybean oil were previously reported in Chapter 2 (section 2.5.1).

Table 4.1 shows the composition of biodiesel obtained from both the AWL and the raw materials mixture (25 wt% of waste lard and 75 wt% soybean oil). As expected, the methyl ester composition of the mixture showed higher content of linoleate and lower contents of oleate and palmitate, compared with the AWL, due to the increased content of soybean oil.

Table 4.1: Methyl ester composition obtained using acid waste lard and a 75 wt.% soybean oil and 25 wt.% waste lard raw materials mixture

METHYL ESTER COMPOSITION, wt%	AWL	75SBO/25AWL
Myristate (C14:0)	1.1	0.3
Palmitate (C16:0)	21.6	14.1
Palmitoleate (C16:1)	1.5	0.4
Stearate (C18:0)	11.0	5.2
Oleate (C18:1)	40.6	29.5
Linoleate(C18:2)	21.2	45.1
Linolenate (C18:3)	1.4	4.0
Others	2.3	1.3

In fact, regarding the main methyl esters, their content in the mixture corresponded to the weighted average of its content in each component of the mixture (differences were less than 5%), as confirmed with other mixtures studied in previous developed work (Dias et al., 2008).

4.5.2 ESTERIFICATION OF ACID WASTE LARD

MONITORING THE ACID ESTERIFICATION REACTION

Figure 4.3 shows the acid value decrease with time using different reaction temperatures.

The acid values are high due to the presence of H₂SO₄ in the reaction media. The initial acid value varied between 21 and 26 mg KOH g⁻¹ due to experimental difficulties on the sampling for time zero, indicating that the reaction progresses fast immediately after addition of the alcohol/acid mixture.

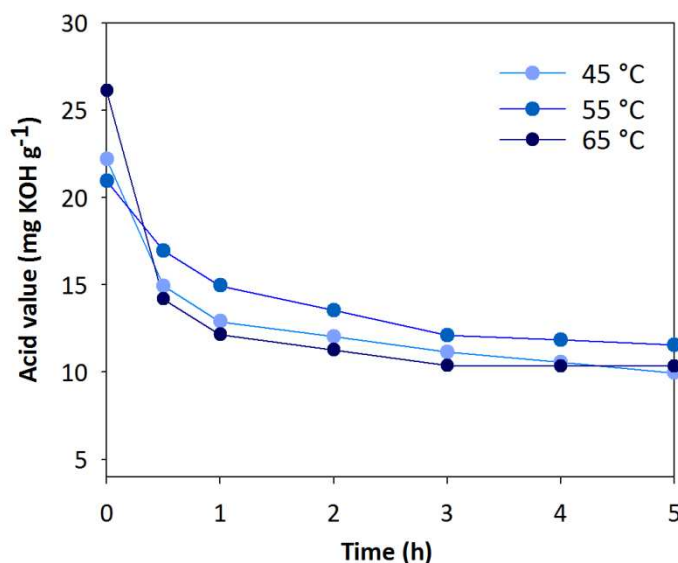


Figure 4.3. Evolution of waste lard acid value during the esterification reaction at different temperatures (2.0 wt.% H_2SO_4 , 6:1 molar ratio of methanol to lard).

The decrease of the acid value was high in the first hour and then tended to stabilise, indicating that the esterification of the free fatty acids was almost complete during the first hour of reaction.

After 3 hours at 55 °C, the acid value was about 11 mg KOH g⁻¹. The lowest acid value achieved using the esterification pre-treatment was obtained at both 45 °C and 65 °C for a reaction time of 5 h, being 10.3 mg KOH g⁻¹. The acid value was also determined for a longer acid esterification reaction time (6 h at 55 °C) and it was found to be similar to the one obtained for 5 h at both 45 °C and 65 °C (10.0 mg KOH g⁻¹). Such result might indicate that no significant esterification of free fatty acids was occurring after 5 hours.

INFLUENCE OF ESTERIFICATION REACTION CONDITIONS IN BIODIESEL QUALITY

The range of results regarding the quality parameters of biodiesel obtained using different acid esterification conditions followed by transesterification are presented in Table 4.2.

Regarding the water content determination, it was found to be essential ensuring that all the material used was prevented from any contamination (careful manipulation and oven dried glass material always used) that might lead to incorrect results.

Among the measured parameters, the acid value, the kinematic viscosity and the methyl ester content were the ones that did not agreed with EN 14214 for all conditions studied.

Table 4.2: Quality parameters of biodiesel from acid waste lard and the respective requirements according to EN 14214

PARAMETER	RESULTS	EN 14214
Water content (wt %)	0.034 - 0.047	<0.05
Acid value (mg KOH g ⁻¹)		
1 wt % H ₂ SO ₄	1.13	<0.50
Other esterification conditions	0.03 - 0.25	
Kinematic viscosity at 40 °C (mm ² s ⁻¹)	4.64 - 7.73	3.50 - 5.00
Methyl ester content (wt %)	69.6 - 99.6	>96.5
Linolenic methyl ester content (wt %)	1.4	<12.0
Iodine value ^a (g I ₂ /100 g)	77	<120

^a Calculated from the methyl ester composition.

The acid value varied between 0.03 and 1.13 mg KOH g⁻¹, the highest value found was obtained for 1.0 wt.% H₂SO₄, being always below 0.25 mg KOH g⁻¹ for all the other conditions, therefore in agreement with EN 14214. This fact indicates that when 1.0 wt.% H₂SO₄ was used, the decrease of the raw material acid value during the pre-treatment step was not enough, since after alkali transesterification of the resulting product, biodiesel had an acid value higher than the maximum, according to EN 14214.

The iodine value and the linolenic methyl ester content were constant in all samples, as expected, because such parameters relate with the composition of the raw material used. Both parameters were within the requirements set by EN 14214. The iodine value obtained from the methyl ester composition agreed with the one determined using the Wijs method.

Biodiesel viscosity and methyl ester content (purity) were found to be the quality parameters that mostly depended on the esterification conditions used.

INFLUENCE OF ACID ESTERIFICATION CONDITIONS ON BIODIESEL VISCOSITY

For the same raw material, differences in viscosity indicate insufficient methyl ester conversion due to the fact that FAME have much lower viscosity than triglycerides. The range of biodiesel viscosity was 4.64 - 7.73 mm²s⁻². Figure 4.4 shows the influence of catalyst amount, time and temperature on biodiesel viscosity after transesterification of the pre-esterified AWL.

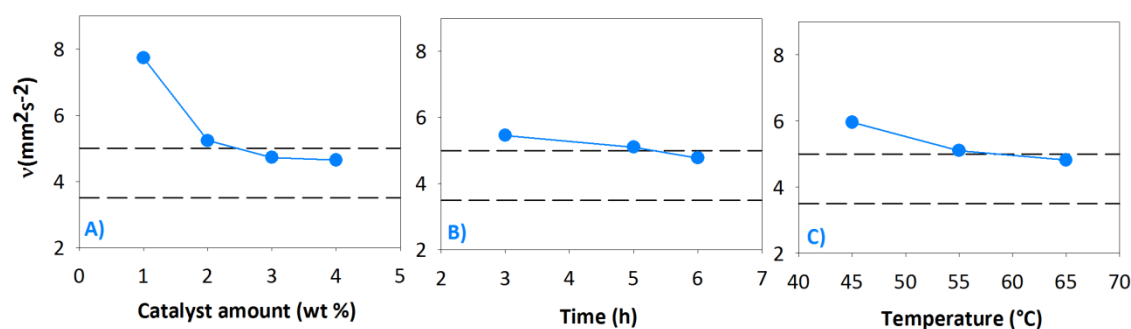


Figure 4.4. Viscosity of biodiesel from waste lard using different pre-esterification conditions at 6:1 molar ratio of methanol to lard: A) 55 $^{\circ}\text{C}$, 5 h; B) 55 $^{\circ}\text{C}$, 2.0 wt.% H_2SO_4 ; C) 2.0 wt.% H_2SO_4 , 5 h (dashed lines indicate minimum and maximum requirements according to EN 14214).

It can be seen that the parameter which mostly influenced biodiesel viscosity was the catalyst amount (Figure 4.4A), needing to be higher than 3 wt.% (at 50 $^{\circ}\text{C}$ and during 5 h) to obtain a biodiesel viscosity in agreement with EN 14214.

However, when temperature and time varied, differences were not so relevant except at 45 $^{\circ}\text{C}$ (biodiesel viscosity was higher: 6.0 mm^2s^{-2}).

An increase in both temperature and time showed a decrease of biodiesel viscosity; for 2.0 wt.% catalyst, the biodiesel viscosity was according to EN 14214 only at a temperature of 65 $^{\circ}\text{C}$ or for a reaction time of 6 h.

Lower biodiesel viscosities reflect better conversions; therefore, the results indicated that more efficient esterification of the raw material occurred when higher catalyst amount, temperature and reaction time were used; consequently, lower biodiesel viscosities were obtained after further transesterification of the pre-treated raw material.

BIODIESEL PURITY DETERMINATION

The range of purity values determined according to European Standard EN 14103 (2003), defined by EN 14214, was 67.6-97.6 wt.%. This analytical method uses methyl heptadecanoate as internal standard.

Due to the existence of methyl heptadecanoate in some animal fats, a correction might be needed when using the method proposed by EN 14214 for biodiesel purity determination. In fact, even if existing in small amounts, methyl heptadecanoate content might affect the results leading to lower purities (Canoira et al., 2008).

Using commercial lard (Chapter 3), the methyl heptadecanoate content was very low (area smaller than the minimum); however, biodiesel obtained from the waste lard showed the presence of this methyl ester (Figure 4.5).

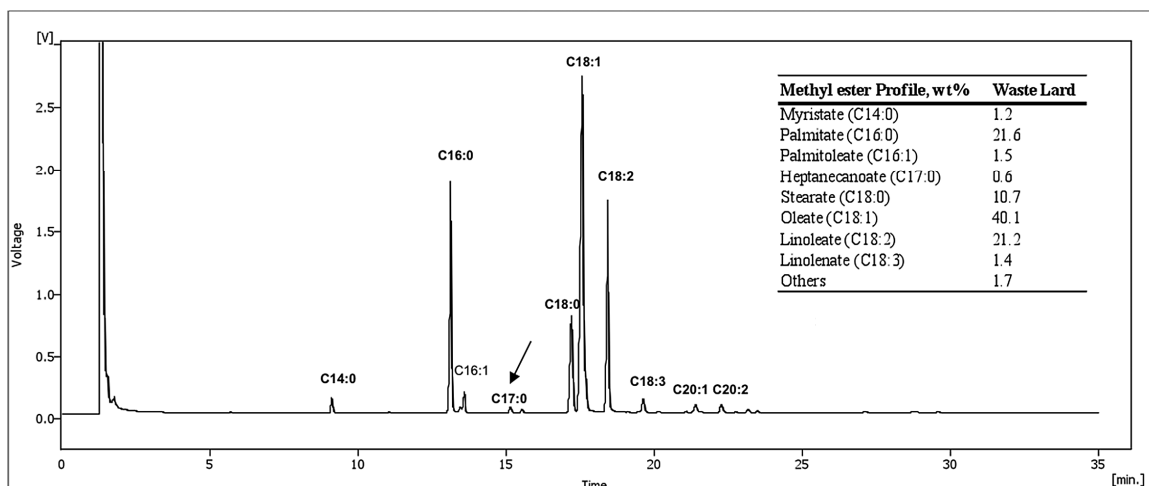


Figure 4.5. GC chromatogram of waste lard FAME.

The GC analysis showed that the methyl ester composition included 0.6 wt.% of heptadecanoate. By applying a simple correction proposed by Schober et al. (2006), taking into account the peak area of the heptadecanoate present in the sample, a 2% increase of biodiesel purity was obtained (from 93.7 to 95.8 wt%). The results therefore confirmed that the method proposed by EN 14214 is not very rigorous for purity determination when some fats are used as raw materials and that a correction should be performed.

INFLUENCE OF CATALYST CONCENTRATION IN BIODIESEL PURITY

Figure 4.6 shows the influence of catalyst amount, temperature and time on biodiesel purity after transesterification of the pre-esterified AWL.

The stronger influence of catalyst amount on biodiesel purity was confirmed and a purity above the minimum of 96.5 wt.% according to EN 14214 was only achieved at 65 °C (99.6 wt.%) using 2.0 wt.% catalyst and was almost achieved at 55 °C (95.0 wt.%) using 3 wt.% catalyst. Those results confirm what was verified for the viscosity, that in fact lower viscosities were indicating more effective conversions.

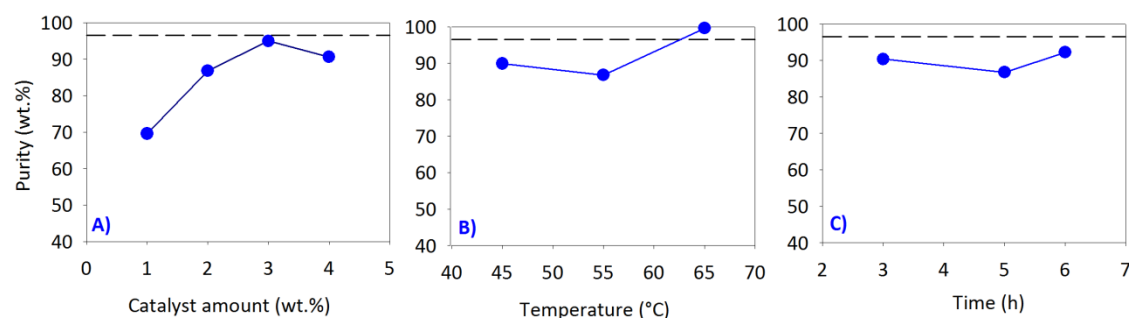


Figure 4.6. Purity of biodiesel from acid waste lard using different reaction conditions at 6:1 molar ratio of methanol to lard: A) 55 °C, 5 h; B) 55 °C, 2.0 wt.% H_2SO_4 ; C) 2.0 wt.% H_2SO_4 , 5 h (dashed line indicates minimum purity according to EN 14214).

Despite the higher viscosity found at 45 °C as compared to the one at 55 °C, purity of biodiesel was slightly higher at 45 °C (89.9 wt.% compared to 86.8 wt.%). Figure 4.3 showed that a lower acid value was achieved after 5 h reaction at 45 °C as compared to 55 °C; this fact might justify the higher purity of biodiesel obtained at 45 °C. However, in both cases (using 2.0 wt.% catalyst), purity was far from the minimum according to EN 14214.

PRODUCTION OF BIODIESEL USING SELECTED ACID ESTERIFICATION CONDITIONS

According to the results above stated, the best conditions for biodiesel production were 65 °C, 5 h and 2.0 wt.% H_2SO_4 , considering the use of a 6:1 molar ratio of methanol to lard.

The esterification reaction was repeated under the selected conditions to determine the acid value of the esterified product. The acid value was 3 mg KOH g^{-1} . Therefore, under the selected conditions, the acid value of the raw material was reduced to around 20% of the initial value (14.57 mg KOH g^{-1}) using the esterification pre-treatment.

Due to the fact that catalyst amount seemed to have the greatest influence in the product quality, it was further postulated that good results could be obtained considering the use of 65 °C, 6:1 molar ratio of methanol to lard, lower reaction time (3 h) and higher catalyst amount (3.0 wt.% H_2SO_4). To confirm this hypothesis, one experiment was performed to evaluate the yield and biodiesel quality using such reaction conditions. Results are presented in Table 4.3.

Biodiesel viscosity was according to EN 14214, however, purity was lower than the minimum of 96.5 wt.% required; therefore, a further experiment was conducted during 5 h, and results, also presented in, show that under these conditions purity was closer to EN 14214 requirements and biodiesel yield was 19.0 wt.% higher.

Table 4.3: Product yield, viscosity and purity of biodiesel from acid waste lard using a two step treatment considering the use of the following esterification conditions: 65 °C, 3 wt.% H₂SO₄, 6:1 molar ratio of methanol to lard and 3/5 hours

REACTION TIME	YIELD (wt.%)	$\nu_{40\text{ °C}}$ (mm ² s ⁻¹)	PURITY (wt.%)
3 h	47.2	4.72	92.0
5 h	66.2	4.50	95.7

Because results using 65 °C at higher catalyst concentrations were not so advantageous (using 5 h, purity was smaller than the one obtained using 2.0 wt.% catalyst), it was concluded that a lower catalyst concentration could be used if temperature was set at 65 °C.

Therefore, according to the obtained results the best conditions were 65 °C, 2.0 wt.% H₂SO₄, 5 h and 6:1 molar ratio of methanol to lard.

STATISTICAL ANALYSIS

To better evaluate the obtained results, a statistical analysis using the JMP5 software was further performed to find the best model describing the influence of the three parameters, individually or combined, in the viscosity and purity of biodiesel.

Two predictive models were obtained and the corresponding coefficients were calculated from the experimental responses through least squares regression.

Regarding the viscosity, the model which better described the data was a linear model which presented a determination coefficient (r^2) of 0.89. All obtained coefficients were statistically significant ($p < 0.05$) and negative, the values being -0.28, -0.18, -0.052 and 9.5 for the catalyst concentration, time, temperature and intercept, respectively.

Such results indicate that the increase of each parameter led to a decrease in the viscosity; which is in agreement with what was expected. Also, considering the range of values for each parameter, the predictive model showed that, within the experimental range, the temperature and the catalyst concentration were the parameters that mostly influenced the viscosity of the obtained biodiesel.

Regarding the purity, the model which better described the data was a second-degree polynomial (relatively to catalyst concentration) with $r^2 = 0.83$. The coefficients obtained were: -6.7, 39, 0.20, 1.6 and 20 for the catalyst concentration (second and first order), temperature, time and intercept, respectively.

However, in this model, only the coefficients related with the catalyst concentration and the intercept were statistically significant ($p < 0.05$), meaning that the data did not allow taking significant conclusions regarding the relevance of the time and temperature variables. However, the predictive model showed that, for the experimental data obtained, the catalyst concentration was the parameter that mostly influenced purity which increased with increasing catalyst concentration until a maximum was reached.

For both responses, viscosity and purity, the models which considered the combined effects of the studied variables led to coefficients that were not statistically significant ($p > 0.05$), showing that, when considering the data from the present study, the individual effects of the variables had the greatest impact on the response.

PRODUCTION OF BIODIESEL FROM A SOYBEAN OIL/ACID WASTE LARD MIXTURE

In order to assess the impact of recycling AWL wastes by mixing them with virgin vegetable oils commonly used to produce biodiesel, a mixture of AWL with SBO was used as raw material to produce biodiesel.

As biodiesel iodine value is usually high when SBO is used alone as raw material, it was also intended to reduce iodine value to a value according to EN 14214 ($< 120 \text{ g I}_2/100 \text{ g}$) by using such mixture.

The percentage of AWL that can be incorporated aiming to achieve a product with an iodine value according to EN 14214, was calculated using a model previously developed by the authors (Dias et al., 2008); according to that model, it was previewed that a mixture containing 25 wt% of waste lard would allow to obtain a biodiesel iodine value of $115 \text{ g I}_2/100 \text{ g}$.

For this raw material mixture, the final selected acid esterification conditions were used to produce biodiesel using two-step synthesis; because the acid value of the SBO was very low, transesterification alone in a one-step process, was also evaluated.

Results of biodiesel viscosity, purity, iodine value and product yield using a one step and two-step synthesis are presented in Table 4.4.

Regarding the two-step process, the yield was not very high (64.4 wt.%) and agreed with the one obtained using the previously studied conditions and waste lard alone as raw material (Table 4.3). On the other hand, the alkali transesterification of the soybean oil/waste lard mixture showed a yield of 77.8 wt.%.

Table 4.4: Product yield, iodine value, viscosity and purity of biodiesel obtained by pre-esterification followed by transesterification (E + T) and transesterification alone (T) of a mixture of waste lard (25 wt.%) and soybean oil

REACTION	YIELD (wt.%)	IODINE VALUE ^a (g I ₂ /100 g)	$\nu_{40^\circ\text{C}}$ (mm ² s ⁻¹)	PURITY (wt.%)
E + T	64.4	115	4.44	95.3
T	77.8	115	4.30	99.8

^a Calculated from the methyl ester composition.

The lower yield of the two step synthesis might be justified by the greater number of reaction steps and namely the inclusion of an additional washing stage that led to yield losses.

It was confirmed that the mixture composition previewed by the model allowed obtaining the aimed biodiesel iodine value of 115 g I₂/100 g, therefore in agreement with EN 14214.

It was observed that when the two step reaction was performed, biodiesel purity was very close to the minimum required of 96.5 wt.% whereas a purity of 99.8 wt.% was obtained using the one-step process.

When the two-step process was applied, an overnight decantation time was used after transesterification, whereas for the one-step process, only a 1 h of decantation was used. In fact, if residual water existed in the reaction media (namely by reaction of sodium hydroxide with methanol), hydrolysis of FAMES might have occurred during longer decantation time, leading to lower conversion and consequently lower purity.

In both processes, viscosities were in agreement with EN 14214, being smaller than the ones obtained using waste lard alone, which was expected due to the less saturated content of the soybean oil.

The production of biodiesel from AWL could only be enabled using a two-step synthesis; however, the obtained results showed that the methodology of blending AWL with vegetable oils reduces the acidity of the raw material, enabling the use of a one-step process. Therefore, blending might be an interesting alternative to recycle wastes, namely because conventional and relatively economical processes might be used. Additionally, some properties which relate with the raw material composition (such as the iodine value) can be improved, selecting adequately the wastes to be recycled.

4.6 CONCLUSIONS

Biodiesel production from acid lard was effectively enabled by a two-step synthesis.

The influence of the pre-esterification conditions in biodiesel quality was studied and two predictive models were further obtained.

Catalyst amount and temperature mostly affected biodiesel quality. The selected conditions, which led to a product viscosity of $4.81 \text{ mm}^2 \text{ s}^{-1}$ and a purity of 99.6 wt.%, were: 65 °C, 2.0 wt.% H_2SO_4 and 5 h.

A mixture of waste lard and soybean oil was used to produce biodiesel using a one step synthesis and the good results obtained indicated that blending might be an interesting alternative to recycle wastes and even improve some product properties.

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CHAPTER 5 BIODIESEL PRODUCTION FROM ANIMAL FAT THROUGH HETEROGENEOUS CATALYSIS



This chapter was based on:

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ABSTRACT

In order to contribute for a more sustainable biodiesel production, its synthesis from animal fat through heterogeneous catalysis was studied, by focusing on: i) selecting an heterogeneous catalyst for pork lard transesterification; ii) studying the influence of the reaction conditions on biodiesel purity, namely by using Response Surface Methodology (RSM); and, iii) evaluating the re-use of the catalyst. Calcium manganese oxide was the selected heterogeneous catalyst for the transesterification of lard obtained from a meat processing industry. RSM studies allowed the development of a second-order model representing the influence of the reaction conditions on biodiesel purity; temperature and the interaction between temperature and catalyst concentration were the conditions which mostly influenced product purity. The maximum predicted methyl ester content was 99.6 wt.% using 60 °C, 1 wt.% catalyst and 21:1 methanol to fat molar ratio. Catalyst was reused without loss of activity indicating that catalytic behaviour was heterogeneous.

5.1 SCIENTIFIC RELEVANCE

The use of waste raw materials for biodiesel production, namely animal fats, might be of great value due to the fact that their use combines the substitution of edible food sources by cheap available waste sources with improved biodiesel production costs and reduced environmental impacts (concerning the management of such wastes). Additionally, it adds value to a material which otherwise needs to be further eliminated.

As previously mentioned, transesterification is the most common process for biodiesel production and it occurs by chemical reaction between an alcohol and a triglyceride. Because the reagents are not miscible, a catalyst is needed to perform the reaction faster. Basic catalysts are usually preferred as they present higher catalytic activities than the acid ones; usually, homogeneous strong bases such as sodium hydroxide, potassium hydroxide or their alkoxides are applied (section 1.4.2 and 1.4.5 present additional information).

The use of homogeneous basic catalysts has great disadvantages because there is a necessity to remove it after the reaction, usually using water as extraction media, which leads to the production of great amounts of wastewater, significantly increasing both production costs and environmental impacts (if not properly managed) (Wei et al., 2009).

Amongst other alternatives (enzymatic catalysis and catalyst free reaction), the use of heterogeneous basic catalysts has been studied as a promising alternative to solve this problem; however, the preparation of highly effective materials seems to be complex and difficult to achieve, also requiring experienced people to operate it (Wei et al., 2009). A detailed review of literature regarding heterogeneous catalysis in biodiesel production is presented in Appendix D.

Amongst the most currently studied heterogeneous catalysts, calcium oxide and supported calcium oxide catalysts, seem to be the most promising, presenting high basicity, low solubility, acceptable reaction conditions and also low price (Huaping et al., 2006; Kawashima et al., 2009).

Huapping et al. (2006) achieved vegetable oil conversions up to 93 wt.% using thermally treated calcium oxide at 70 °C, 2.5 h, 1.5 wt.% catalyst and 9:1 methanol to oil molar ratio. Kousu et al. (2008) achieved similar vegetable oil conversions using calcium oxide at 65 °C, 1 h, using 8 wt.% catalyst and a 12:1 methanol to oil molar ratio and no conversion using calcium carbonate or magnesium oxide. Liu et al. (2008) showed high conversions (98 wt.% yield) using calcium methoxide; reaction conditions were 65 °C, 2 h, 4 wt.% catalyst and 1:1 (v/v) of methanol to oil.

Usually, there is a need to activate the catalysts through thermal treatment prior to use. Albuquerque et al. (2008) supported calcium oxide in different materials and concluded that without activation (800 °C) all catalysts were inactive.

Kawashima et al. (2008) studied the application of a great variety of mixed metal oxide catalysts for rapeseed oil transesterification clearly showing that the ones containing calcium had the best performance, namely CaO-CeO_2 , CaZrO_3 , $\text{Ca}_2\text{Fe}_2\text{O}_5$, CaMnO_3 and CaTiO_3 with product methyl ester contents from 79 to 92 wt.% at 60 °C after 10 h of reaction and using around 6:1 molar ratio of methanol to oil.

While a great amount of studies were already performed regarding homogeneous catalytic synthesis of WFO and some performed regarding their heterogeneous catalytic transesterification (Kouzu et al., 2007; Chung et al., 2008; Guan et al., 2009), biodiesel production using animal fats is still understudied (Dias et al., 2009) regarding homogeneous but even more considering heterogeneous synthesis.

In a study by Liu et al. (2007), the use of heterogeneous basic catalysts derived from an Mg–Al hydrotalcite was evaluated for the transesterification of poultry fat with methanol. Conversions were higher than 90 wt.%, but reaction conditions were relatively extreme; reaction occurred at 120 °C, during 8 hours, using 10 wt.% of catalyst and a 30:1 methanol to fat molar ratio. Also, Venkat Reddy et al. (2006) showed a 100% conversion using nanocrystalline calcium oxide for the conversion of poultry fat to biodiesel. In that study, reaction temperature was close to ambient (25 °C), and reaction occurred for 7 h, using 1 mmol of catalyst to 3 g of fat (around 1 wt.% catalyst) at high molar ratios of methanol to fat (around 70:1). The different conditions used in these studies might be due to both catalyst performance and the raw material used, reason why optimization should be performed for each raw material and catalyst applied.

Response surface methodology (RSM) is a widely used statistical tool which has great advantages, namely for the optimization of reaction conditions and the study of interactions among experimental variables; which allows a better understanding of the process while reducing the experimental time (Hameed et al., 2009). Jeong et al. (2009) studied the use of RSM for the optimization of animal fat transesterification through homogeneous catalysis showing an optimum conversion of 98.6 wt.% using 65 °C, 1.26 wt.% catalyst (KOH), and a methanol to fat molar ratio of 7.5:1 within 20 min reaction time.

Aiming to achieve increased knowledge among the previously described issues and specifically in the behaviour of animal fats in biodiesel production using heterogeneous catalysts, the present work focused on animal fat transesterification by heterogeneous catalysis and on the understanding of the influence of reaction conditions using RSM.

5.2 SPECIFIC OBJECTIVES

- To select an heterogeneous catalyst for pork lard transesterification;
- To evaluate the influence of the reaction conditions (temperature (40-60 °C), catalyst concentration (1-5 wt.% of fat), and methanol/fat molar ratio (9:1-27:1)) on biodiesel purity, namely using response surface methodology;
- To evaluate the re-use of the catalyst.

5.3 MATERIALS

Pork lard was supplied by *Irmãos Monteiro S.A*, a Portuguese meat processing industry, being kept in the freezer at 4 °C during the experimental period (Figure 5.1).



Figure 5.1. Pork lard supplied by *Irmãos Monteiro, S.A.*

The SBO used was the same presented in Chapter 2 (section 2.3).

Methanol 99.5% (analytical grade, Fischer Scientific) was used for biodiesel synthesis and n-Heptane (analytical grade, Merck) was used for catalyst cleaning and chromatographic analysis.

The oxides used to prepare the mixed oxide catalysts, namely CaO, BaO, ZrO₂ and CeO₂ were supplied by Sigma-Aldrich and Fe₂O₃ and MnO₂, were supplied by Riedel-de-Haën. Syringe filters used (polypropylene, 25 mm diameter and 0.2 µm pore size) were supplied by VWR.

5.4 METHODS

5.4.1 CATALYST PREPARATION

PRELIMINARY STUDIES

As a preliminary study, the activity of several materials, prepared by supporting metals commonly used in heterogeneous catalysis (such as Zn, Ni, Ag, Na amongst others) on different materials (activated carbon, aerogel and zeolite), was evaluated for the transesterification reaction of SBO; however, the reaction did not occurred. Figure 5.2 shows several of the studied catalysts.



Figure 5.2. Heterogeneous catalysts studied.

Table 5.1 presents a brief description of the catalyst preparation and reaction conditions used as well as some observations.

The experiments were initially performed with the perspective of implementing basic homogeneous conditions previously studied in Chapter 2 (e.g. catalyst 1); however, because no reaction occurred, additional experiments were performed using more “extreme” conditions by increasing methanol/oil molar ratio (e.g. 5 and 10), catalyst concentration (e.g. catalyst 4 and 6), reaction temperature (e.g. catalyst 6-9) and time (catalyst 11), mostly simultaneously.

Table 5.1: List of preliminary studied catalysts with no results in biodiesel conversion; all catalysts were oven dried at 100 °C prior to use.

	N.º	CATALYST	ASPECT	PREPARATION	REACTION CONDITIONS STUDIED <i>Molar ratio ^{a)}, catalyst concentration (wt%) ^{b)}, reaction time (h), temperature (°C)</i>	OBSERVATIONS
BASED IN AC ^{c)}	1	AC/Zn	Black granules	10 g of AC mixed with 0.5 L of the cation solution (0.5 g/L) during 48 h	▪ 6:1, 0.6, 1, 60 ▪ 6:1, 0.6, 3, 60 (100 g vegetable oil)	-
	2	AC/Ce	White granules	= catalyst 1 Further calcination under nitrogen atmosphere at 400 °C during 2 h	▪ 20:1, 2, 6, 65 (80 g vegetable oil)	-
	3	AC/La	Black granules	= catalyst 2	= catalyst 2	Difficult to separate catalyst afterwards
BASED IN AEROGEL	4	Aerogel/Na	Black pellets	Water (8.75 mL) + resorcinol (6.5 g) + formaldehyde (8.75 mL) + metal nitrate	▪ 12:1, 0.6, 3, 60 ▪ 24:1, 3, 6, 60 (100 g vegetable oil)	-
	5	Aerogel/Zn	Orange pellets	= catalyst 4	▪ 24:1, 0.6, 4.4, 60 (100 g vegetable oil)	-
	6	Aerogel/La	Black pellets	= catalyst 4 Further calcination under nitrogen atmosphere at 400 °C during 2 h	▪ 15:1, 2, 6.3, 70 (50 g vegetable oil) ▪ 15:1, 4, 6.3, 70 (80 g vegetable oil)	Catalyst disaggregation occurred
	7	Aerogel/Ag	Black pellets	= catalyst 6	▪ 13:1, 1.6, 6.3, 70 (80 g vegetable oil)	-
	8	Aerogel/Ce	Black pellets	= catalyst 6	▪ 13:1, 2, 6.3, 70 ▪ Suspended catalyst support (250 g vegetable oil)	Some catalyst disaggregation
	9	Aerogel/Ni	Black pellets	= catalyst 6	▪ 13:1, 2, 6, 70 ▪ Suspended catalyst support (250 g vegetable oil)	Catalyst well preserved after reaction

Table 5.1: List of preliminary studied catalysts with no results in biodiesel conversion; all catalysts were oven dried at 100 °C, prior to use (*Continued*).

BASED IN ZEOLITE ^{d)}	N.º	CATALYST	ASPECT	PREPARATION	REACTION CONDITIONS STUDIED <i>Molar ratio ^{a)}, catalyst concentration (wt%) ^{b)}, reaction time (h), temperature (°C)</i>	OBSERVATIONS
	10	Zeolite/Zn	White powder	10 g of commercial zeolite mixed with 0.5 L of the cation solution (0.5 g/L) during 48 h	▪ 24:1, 0.6, 4.5, 60 (100 g vegetable oil) ▪ 20:1, 2, 4, 65 (80 g vegetable oil)	-
	11	Zeolite/La	White granules	= catalyst 10 Further calcination under nitrogen atmosphere at 400 °C during 2 h	▪ 20:1, 2, 6, 65 ▪ 20:1, 2, 24, 65 (80 g vegetable oil)	Difficult to separate catalyst afterwards
	12	Zeolite/Ni	White granules	= catalyst 11	▪ 20:1, 2, 6, 65	Difficult to separate catalyst afterwards
	13	Zeolite/Ce	White granules	= catalyst 11	= catalyst 12	Difficult to separate catalyst afterwards
	14	Al ₂ O ₃ /Zn	White powder	10 g of Al ₂ O ₃ mixed with 0.5 L of the cation solution (0.5 g/L) during 48 h	▪ 24:1, 0.6, 3, 60 (100 g vegetable oil)	-

^a Molar ratio of methanol to oil; ^b Percentage relative to oil weight; ^c Commercial activated carbon (SORBO-Norit); ^d High silica zeolite ZSM-5 (Ratio SiO₂/Al₂O₃ 1000, CAS 308081-08-5), supplied by Acros Organics.

To understand the absence of success during first experiments, the basicity of some of the materials was evaluated through the measurement of the pH of the point of zero charge (pH_{PZC}) (Ferro-García et al., 1998). The ones supported in AC (activated carbon) had a pH_{PZC} around 8, zeolite catalysts all presented acidic nature ($4.7 < \text{pH}_{\text{PZC}} < 6.6$); the aerogel catalyst of lanthanum presented acidic nature ($\text{pH}_{\text{PZC}} = 3.8$) whereas the one of Na presented a pH_{PZC} around 8.

It was therefore hypothesised that the materials need to have a greater basicity in order to present catalytic activity; therefore, Ag and Ni as well as La and Ce were supported in the same materials and further calcined (around 1000 °C during 4 h) to be present as oxides with higher basicity; after, pH_{PZC} was maximum around 8 and the progression of the reaction was still not observed (catalysts 2, 3, 6-9, 11-13).

Because it was considered to be difficult obtaining enough basicity using the metal supported catalysts and also due to difficulties in separation and also disaggregation of the materials, non-supported metal oxides were further studied.

PREPARATION OF METAL OXIDES

The following mixed oxide catalysts were studied: calcium iron oxide (CaFeOx), barium iron oxide (BaFeOx), calcium manganese oxide (CaMnOx), barium manganese oxide (BaMnOx), calcium zirconium oxide (CaZrOx) and calcium cerium oxide (CaCeOx). The oxides were prepared conducting a solid-state reaction by mixing in an agate mortar each oxide in an equimolar proportion followed by calcinations at 900 °C during 4 h under N_2 atmosphere in a tubular furnace (Figure 5.3).



Figure 5.3. Tubular furnace used for catalyst calcination.

When catalyst was not immediately used, calcination procedure was repeated to avoid its deactivation by carbonation and/or hydration. When CaO was used as catalyst alone, it was prepared from CaCO_3 which was calcined according to previously described procedure. After, catalyst was kept for few minutes in a desiccator under vacuum before use.

The thermogravimetric (TG) analysis were performed in a equipment Setaram, model 92-16.18.

5.4.2 BIODIESEL PRODUCTION

Synthesis was made by heterogeneous basic transesterification. The production process included pre-treatment, basic transesterification and purification of final products according to Figure 5.4.

PRE-TREATMENT

Similarly to what was reported in previous chapters (3 and 4), in this study the PL was pre-treated by heating at 100 °C and after cooled to near the reaction temperature, which in the present case varied from 40 to 60 °C.

BASIC TRANSESTERIFICATION

Biodiesel synthesis was performed in a glass reactor consisting of a 250 mL round-bottom flask with three necks immersed in a temperature controlling bath previously presented (section 2.4.1); the reactor was equipped with a water-cooled condenser, a magnetic stirrer, a septum for syringe sample collection, an entrance for nitrogen and a dropping funnel (Figure 5.5).

For transesterification, 70 g of PL were kept at the reaction temperature (40, 50 or 60 °C); catalyst (1, 3 or 5 wt.% relative to fat weight) was placed into the reactor which was under controlled nitrogen atmosphere; the necessary amount of methanol (methanol to fat molar ratio of 9:1, 18:1 or 27:1) was added to the catalyst using the dropping funnel and kept under mixing until reaching the reaction temperature; finally, the lard was slowly added also using the dropping funnel. The starting of the reaction was considered to be after the addition of all the lard into the reactor; at that time, mixing of the reactants was changed from medium to vigorous.

The experimental planning was made by JMP software, using a central composite design (CCD) and two central points. The central values (zero level) chosen for experimental design were: temperature 50 °C, catalyst concentration 3 wt.% and methanol to fat molar ratio of 18:1.

Sampling for Evaluation of Reaction Progression

Samples were taken at 0.25, 0.5, 1, 2, 4 and 8 h. The sampling was made through the septum using a syringe. Each time, around 1 mL was taken and filtered through a syringe filter to remove residual catalyst and immediately inserted in a ice bath to ensure the reaction end. After, the reaction mixture was distilled under vacuum, in a rotary evaporator.

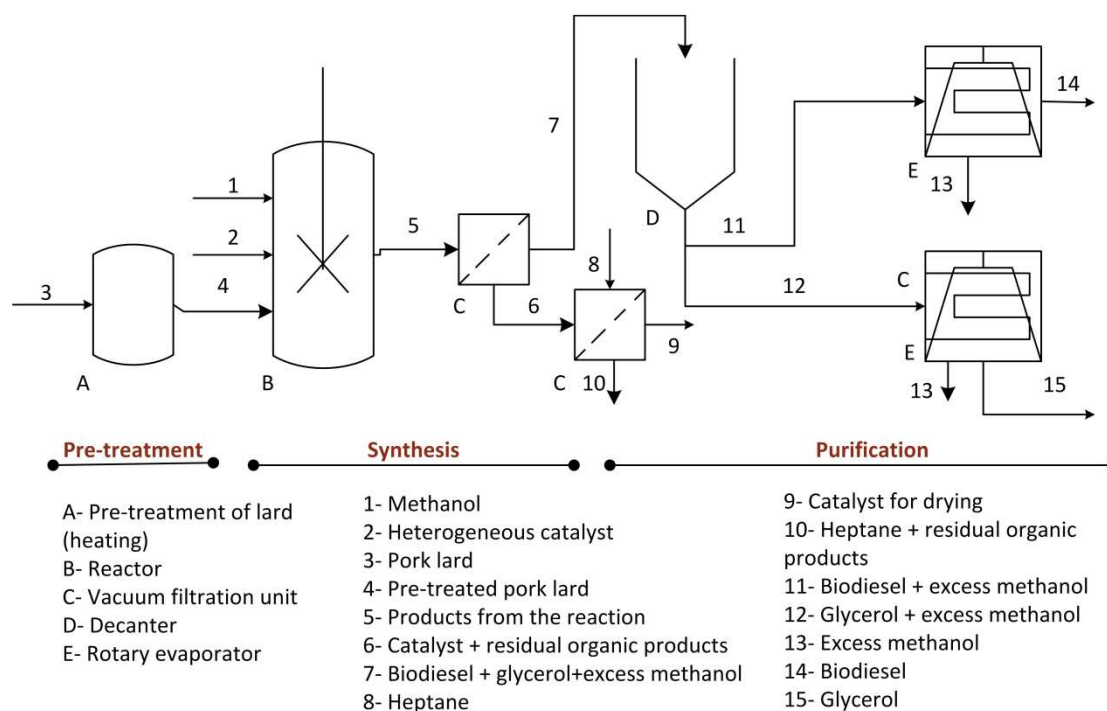


Figure 5.4. Diagram adopted for heterogeneous biodiesel production from pork lard.

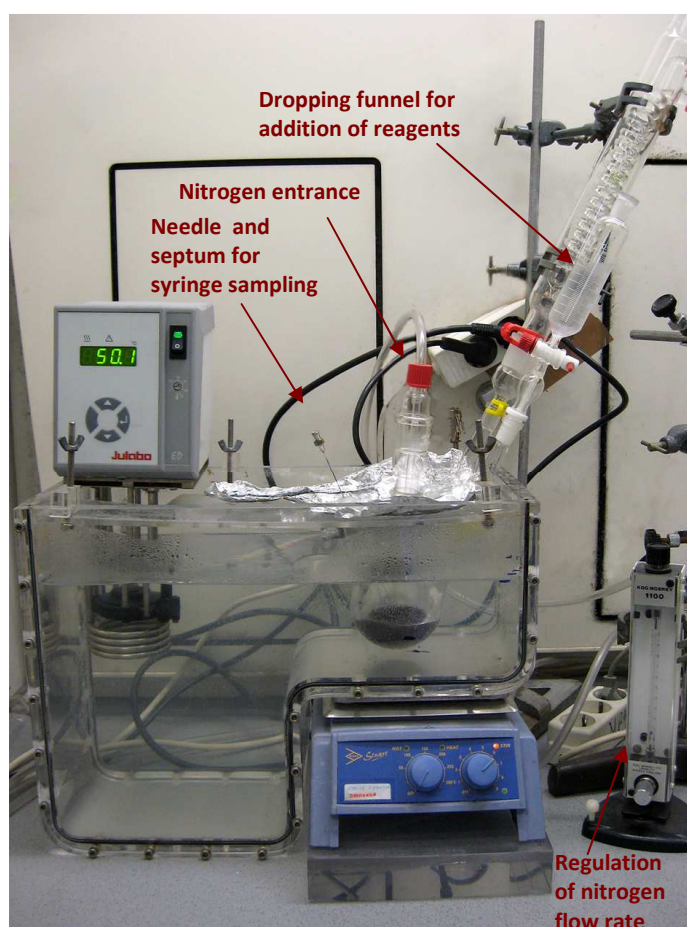


Figure 5.5. Reactor used for heterogeneous synthesis and designed acrylic bath.

A sample was taken from the lighter phase and further treated according to EN 14103 (2003) for determination of methyl ester content by chromatographic analysis.

PURIFICATION

After the 8 h sampling, the reaction mixture was filtered under vacuum and left to complete phase separation overnight. The catalyst was washed with 40 mL of heptane using vacuum filtration and left to dry in the oven at 100 °C.

Phases were finally separated and excess methanol was recovered from each separately.

Biodiesel yield $\left(\frac{\text{weight of product}}{\text{weight of fat}} \times 100 \right)$ was determined afterwards. Note that biodiesel yield is valid for comparison among experiments due to the fact that sampling was performed leading to product loss.

5.4.3 ANALYTICAL METHODS

Raw material properties, biodiesel conversion and biodiesel calcium content were determined.

The following raw material properties were determined: composition, acid value and iodine value. Specific methods and related standards were presented in section 2.4.2.

The evaluation of biodiesel conversion was performed by measuring product methyl ester content according to the method and related standard presented in section 2.4.2.

5.5 RESULTS AND DISCUSSION

5.5.1 CATALYST SELECTION

Due to both raw material availability and simplicity of the process, the selection of the catalyst and reaction conditions range was performed using soybean oil as raw material.

Table 5.2 presents the obtained results; the experiments showed that only some of the materials containing calcium presented catalytic activity.

Table 5.2: Results regarding the catalytic activity of calcium oxide and mixed oxides in the transesterification of soybean oil and respective pH_{PZC} .

CATALYST	REACTION CONDITIONS	pH_{PZC}	PRODUCT METHYL ESTER CONTENT (wt.%)
	<i>Molar ratio ^{a)}, catalyst concentration (wt.%) ^{b)}, reaction time (h), temperature (°C)</i>		
CaMnOx	20:1, 4, 6.5, 50 / 20:1, 5, 9, 60	12.7	89.5 / 98.0
BaMnOx	20:1, 5, 7, 50	11.0	0.0
CaFeOx	20:1, 5, 9, 50	12.7	4.5
BaFeOx	20:1, 5, 7, 50	12.3	0.0
CaZrOx	20:1, 5, 7, 50	12.7	0.0
CaCeOx	20:1, 5, 7, 50	12.7	0.0
CaO	20:1, 3, 9, 50 / 20:1, 5, 9, 60	12.8	51.0 / 94.6

^{a)} Molar ratio of methanol to oil, ^{b)} Percentage relative to oil weight.

All the catalysts showed much greater basicity than the ones previously developed, the pH_{PZC} was similar to the pH resulting from contacting NaOH (most commonly used homogeneous catalyst) with decarbonated ultrapure water ($\text{pH}=12.8$). The best results were obtained using CaO and CaMnOx.

Due to the fact that there are very few studies regarding the use of calcium manganese oxide for biodiesel production, especially if compared with the ones using CaO (Appendix D), the CaMnOx catalyst was selected for the following studies. Additionally, results were quite promising for the selected catalyst if we compare with the 92 wt.% methyl ester content in a study by Kawashima et al. (2008), using CaMnO_3 for rapeseed oil transesterification with less alcohol (around 7:1 molar ratio), but using 60 °C, a reaction time of 10 h and 10 wt.% catalyst. However, under the conditions studied, results concerning BaFeOx and CaCeOx differed completely from the ones obtained with BaFeO₃ and CaCeO₃ in the mentioned study (around 90 wt.% methyl ester yields). This fact highlights the great sensibility of the heterogeneous catalytic process.

In order to define the best suited catalyst calcination temperature, a TG analysis of the selected catalyst was also performed. According to the results, the selected calcination temperature was 750 °C (heating rate of 20 °C min⁻¹) using a holding time of 45 min.

5.5.2 RAW MATERIAL PROPERTIES

The pork lard (mean molecular weight of 860.5 g/mol), presented an acid value of 0.71 mg KOH/g fat and an iodine value of 68 g I₂/100 g fat, values similar to the ones of commercial lard, showing very low degree of oxidation (Dias et al., 2008).

The mean composition of the raw material might be evaluated considering the methyl ester composition presented in Table 5.3 which was also very close to the one obtained when using commercial pork lard as raw material for biodiesel production (Table 3.1).

Table 5.3: Methyl ester composition obtained using pork lard as raw material

METHYL ESTER COMPOSITION	wt.%
Myristate (C14:0)	1.5
Palmitate (C16:0)	23.9
Palmitoleate (C16:1)	2.1
Stearate (C18:0)	12.2
Oleate (C18:1)	42.5
Linoleate (C18:2)	15.1
Linolenate (C18:3)	0.9
Others	1.8

5.5.3 INFLUENCE OF INERT CONDITIONS IN BIODIESEL PRODUCTION

As described in the experimental section, biodiesel production was performed under inert atmosphere.

Figure 5.6 shows that this was in fact a critical factor, because when such conditions were not present, a great difference was found regarding the progression of the reaction. This is most probably related with carbonation and hydration of the catalyst due to the contact with air leading to the reduction of catalytic activity (Granados et al., 2007).

5.5.4 EXPERIMENTAL PLANNING USING RSM

In order to evaluate the influence of the studied variables (temperature, catalyst concentration and methanol to fat molar ratio), experimental planning was conducted by JMP software, using CCD as previously described.

The response variables evaluated were the product methyl ester content

$$\left(\frac{\text{weight of methyl esters}}{\text{weight of product}} \times 100 \right) \text{ at 4 h } (Y_1) \text{ and 8 h } (Y_2) \text{ as well as the product yield } (Y_3)$$

$$\left(\frac{\text{weight of product}}{\text{weight of fat}} \times 100 \right).$$

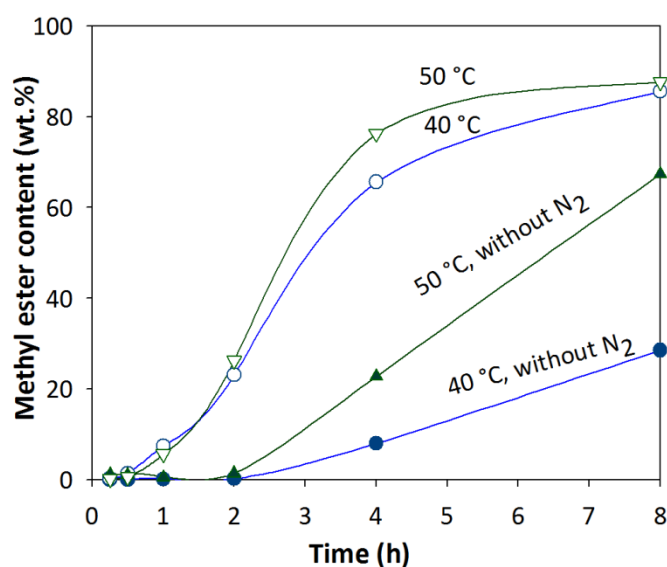


Figure 5.6. Influence of inert atmosphere in methyl ester conversion: product methyl ester yield as function of time at 40 °C (5 wt.% catalyst, 9:1 methanol to fat molar ratio); and 50 °C (3 wt.% catalyst, 18:1 methanol to fat molar ratio) with and without inert atmosphere.

A design of the three factors at three levels (variables coded by (-1), 0 and 1) was conducted. The dimensionless variables were designated by x_1 , x_2 and x_3 . The results and experimental planning used are presented in Table 5.4.

5.5.5 INFLUENCE OF REACTION CONDITIONS ON CONVERSION

Apart from the interaction between variables, the effect of some of the variables isolated in biodiesel conversion was analysed for more clear understanding, being presented in the following sub-sections.

INFLUENCE OF REACTION TEMPERATURE

Temperature greatly influences the heterogeneous transesterification reaction progression and kinetics (Figure 5.7A). Under similar operational conditions, reaction progressed much faster at 60 °C than at 50 and 40 °C; at 60 °C, after 4 h, maximum methyl ester yield was almost reached (92.4 wt.% compared to 95.8 wt.% at 8 h reaction). A great difference was observed at 4 h of reaction using different temperatures. At 40 °C, the maximum methyl ester yield was obtained at 8 h, being 80.5 wt.%.

Table 5.4: Results for experimental planning using central composite design (T – temperature (°C), C – catalyst concentration (wt.% of fat) and M – methanol to fat molar ratio; Y – responses: Y_1 – product methyl ester yield after 4 h reaction (wt.%); Y_2 – product methyl ester yield after 8 h reaction (wt.%); Y_3 – product yield (wt.%)).

RUN	T	C	M	x_1	x_2	x_3	Y_1	Y_2	Y_3
1	50	3	18	0	0	0	76.3	87.6	81.9
2	40	1	9	-1	-1	-1	6.1	59.2	82.2
3	60	5	27	1	1	1	90.6	89.3	74.2
4	50	1	18	0	-1	0	37.9	87.3	79.1
5	60	5	9	1	1	-1	73.2	74.9	57.1
6	60	3	18	1	0	0	92.4	95.8	73.4
7	40	5	27	-1	1	1	43.1	81.1	77.6
8	60	1	9	1	-1	-1	84.6	87.0	74.6
9	50	3	18	0	0	0	81.9	92.5	82.0
10	60	1	27	1	-1	1	92.0	92.3	75.2
11	40	1	27	-1	-1	1	2.8	43.7	61.7
12	40	3	18	-1	0	0	35.7	80.5	78.5
13	50	3	27	0	0	1	79.5	88.4	74.3
14	50	5	18	0	1	0	89.2	89.9	63.7
15	50	3	9	0	0	-1	56.8	84.5	76.2
16	40	5	9	-1	1	-1	65.6	85.5	73.6

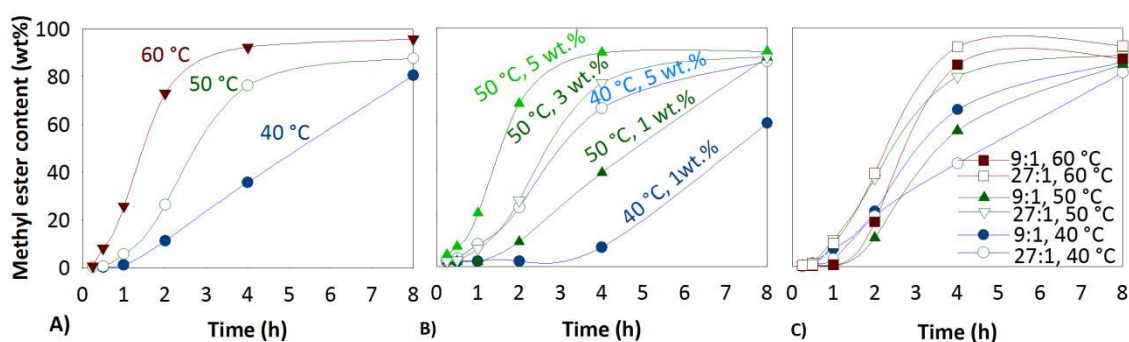


Figure 5.7. Influence of the reaction conditions in product methyl ester yield. A) temperature, using 3 wt.% catalyst and 18:1 methanol to fat molar ratio; B) catalyst amount using 40 °C (9:1 methanol to fat molar ratio) and 50 °C (18:1 methanol to fat molar ratio); C) methanol to fat molar ratio, using 40 °C (5 wt.% catalyst), 50 °C (3 wt.% catalyst) and 60 °C (1 wt.% catalyst).

INFLUENCE OF CATALYST CONCENTRATION

Figure 5.7B shows the influence of catalyst concentration for 40 and 50 °C, the influence at 60 °C will be further addressed. The influence of catalyst concentration at 40 and 50 °C was evident; in fact, using different temperatures, the higher the catalyst concentration, the faster the reaction and the higher the conversion achieved.

INFLUENCE OF METHANOL TO FAT MOLAR RATIO

Figure 5.7C shows the influence of the methanol to fat molar ratio in biodiesel conversion at different temperatures. Results seem to indicate that, at the lower temperature studied (40 °), when a higher catalyst amount was used (5 wt.%), an increase in methanol to fat molar ratio had no effect in biodiesel conversion, with even smaller conversion observed at 4 h of reaction. As temperature increases and catalyst amount decreases, the effect becomes positive being the best at the central point conditions (T=50 °C and catalyst amount of 3 wt.%), where an increase in methanol to fat molar ratio significantly increased biodiesel conversion.

5.5.6 MODEL FITTING

After performing the experiments, each response variable was fitted to a second-order model in order to correlate it with the independent variables. The model presented in the following equation, which considered the linear, quadratic and the interaction effects of the variables, was used for the preliminary regression fits.

$$Y = \beta_0 + \sum_{i=1}^3 \beta_i x_i + \sum_{i=1}^3 \beta_{ii} x_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 \beta_{ij} x_i x_j \quad (\text{Equation 5-1})$$

Preliminary fits for the methyl ester content at 4 h and the product yield resulted in predictive models with determination coefficients (r^2) of 0.94 and 0.85, respectively, suggesting relatively good adjustments. However, for both responses, the model parameter estimates were mostly not significant (p value > 0.05, using an F test), reason why the models were considered to be statistically invalid.

Regarding the methyl ester content at 8 h, the preliminary fit showed that the linear effect of the methanol to fat molar ratio (x_3) was not significant.

The interaction term of methanol to fat molar ratio and catalyst concentration (x_3x_2) and the quadratic term of catalyst concentration (x_2^2) showed low significance (p value < 0.10). Therefore, a reduced model was used to fit experimental data.

Despite being non significant, the linear effect of the methanol to fat molar ratio need to be included in the model, to support hierarchy, due to the significance of the quadratic term; all the other parameters were statistically valid with 95% confidence, except the quadratic term regarding methanol to fat molar ratio which was statistically valid, however, at slightly lower level of confidence (p value = 0.0581). The regression model showed a r^2 of 0.94 and the final equation, in terms of coded factors, is given by Equation 5-2.

$$Y_2 = 90.9 + 8.93x_1 + 5.12x_2 + 0.370x_3 - 5.89x_1^2 - 7.59x_3^2 - 9.85x_1x_2 + 4.95x_1x_3 \quad (\text{Equation 5-2})$$

Figure 5.8 shows the experimental results versus the results obtained by the model. A line of unit slope, corresponding to zero error between experimental and predicted values is also presented. This figure shows that the model represents a relatively good description of the experimental data regarding methyl ester content at 8 h reaction time.

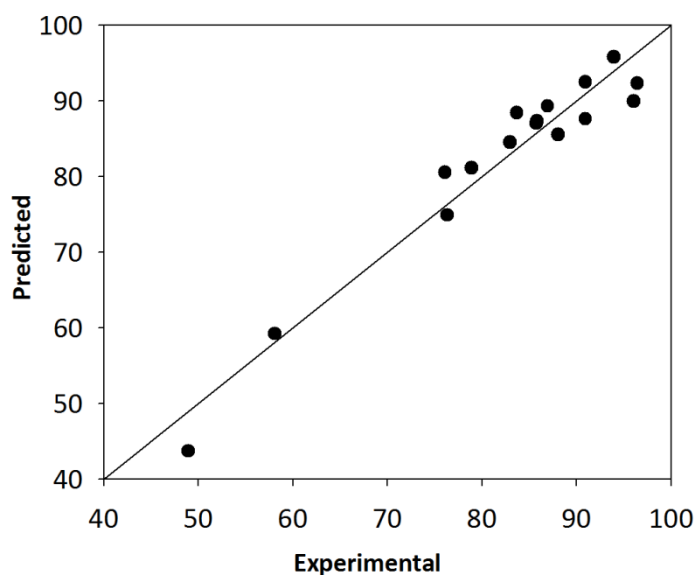


Figure 5.8. Predicted versus experimental product methyl ester content (wt.%) after 8 h of reaction (line corresponds to zero error between experimental and predicted).

The modelling results showed that the most significant effect was the linear effect of temperature and the interaction between temperature and catalyst concentration. The other effects showed similar but smaller significance.

In fact, when studied in isolation, an increase in catalyst concentration and temperature is known to have a positive effect in methyl ester content; however, the model indicates that when both increase (for values higher than the central point conditions: 50 °C, 3 wt.% catalyst), a decrease in product methyl ester content occurs. This fact suggested an interaction between the temperature and the catalyst active site under such conditions. Kansedo et al. (2009) attributed similar effect in acid heterogeneous catalysis to the fact that the equilibrium is more rapidly established at higher concentrations and that after a certain time, transesterification reactions may become stagnant or start to reverse.

Figure 5.9 shows the progression of the reaction at 60 °C for the highest and lowest catalyst concentration showing that in fact for the highest catalyst concentration reaction progresses much faster but after 2 hours it starts to stabilize and even decrease showing at 8 h (values predicted by the model) lower methyl ester content than with smaller catalyst concentrations.

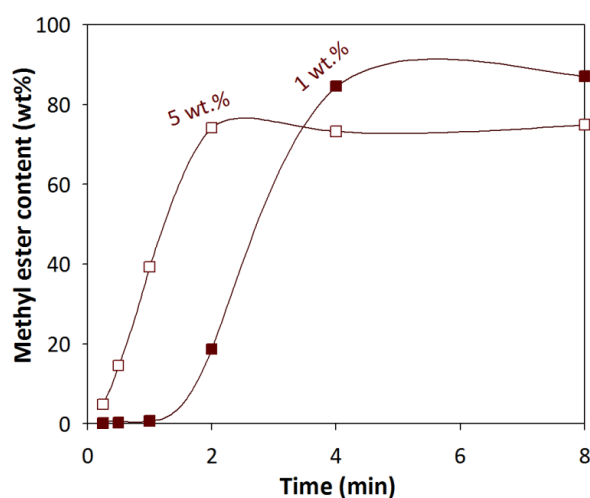


Figure 5.9. Product methyl ester content (wt.%) over time at 60 °C using 9:1 methanol to fat molar ratio and different catalyst concentrations.

Other explanation for this finding might be that the fast conversion leads to a high concentration of products, namely glycerol, which might interfere by blocking the catalyst, which is more available and less dispersed due to high concentration (at low methanol to fat molar ratio), reducing its activity and therefore the methyl ester content after 8 h of reaction.

The determination of the critical points was accessed using JMP; a saddle point was found ($x_1 = 0.52$ (55 °C); $x_2 = 0.38$ (3.8 wt.%) and $x_3 = 0.19$ (20:1)), which corresponds to product methyl ester content of 94.2 wt.%; therefore, due to the nature of this point, it could not be assumed as the optimum value. In order to find the maximum value of the function, a different approach was performed using iterative methods (Microsoft Excel Solver), according to defined constraints (maximum and minimum values for the variables). The maximum was found to be at $x_1 = 1$ (60 °C); $x_2 = -1$ (1 wt.%) and $x_3 = 0.32$ (21:1), predicting a maximum product methyl ester content of 99.6 wt.%. Figure 5.10 represents the conditions leading to the maximum methyl ester content; which are obtained at the limit of two of the studied variables (x_1 and x_2).

It is also interesting to observe Figure 5.11, which represents the model behaviour for the lowest studied temperature (40 °C). As previously reported, when such temperature is used, an increase in catalyst concentration leads to higher conversion, reason why a higher catalyst amount should be used.

However, under such conditions, the maximum methyl ester content was lower than the one obtained at higher temperature, reason why the linear effect of temperature was one of the most significant factors affecting methyl ester content after 8 h, according to the predictive model.

5.5.7 EFFECT OF REUSING THE CATALYST

In order to determine possible loss of catalyst activity by reuse, further experiments were conducted to evaluate catalyst behaviour after reuse under similar conditions.

Prior to reuse, the catalyst was heated at 550 °C in the presence of O₂ to ensure complete organic removal and further activated by calcination at 750 °C under N₂ atmosphere as described in section 5.4.1.

Two experiments were performed, one in the conditions of the central point of the experimental design (run 1, Table 5.4) and another at 60 °C (run 6, Table 5.4), to evaluate possible differences considering variation of experimental conditions. Figure 5.12 shows the evolution of methyl ester content with time in both cases before and after catalyst reuse. Results showed that, in fact, it is possible to reuse the catalyst without significant loss of its activity independently of the experimental conditions used, which indicates that catalytic behaviour was essentially heterogeneous (this subject will be further evaluated).

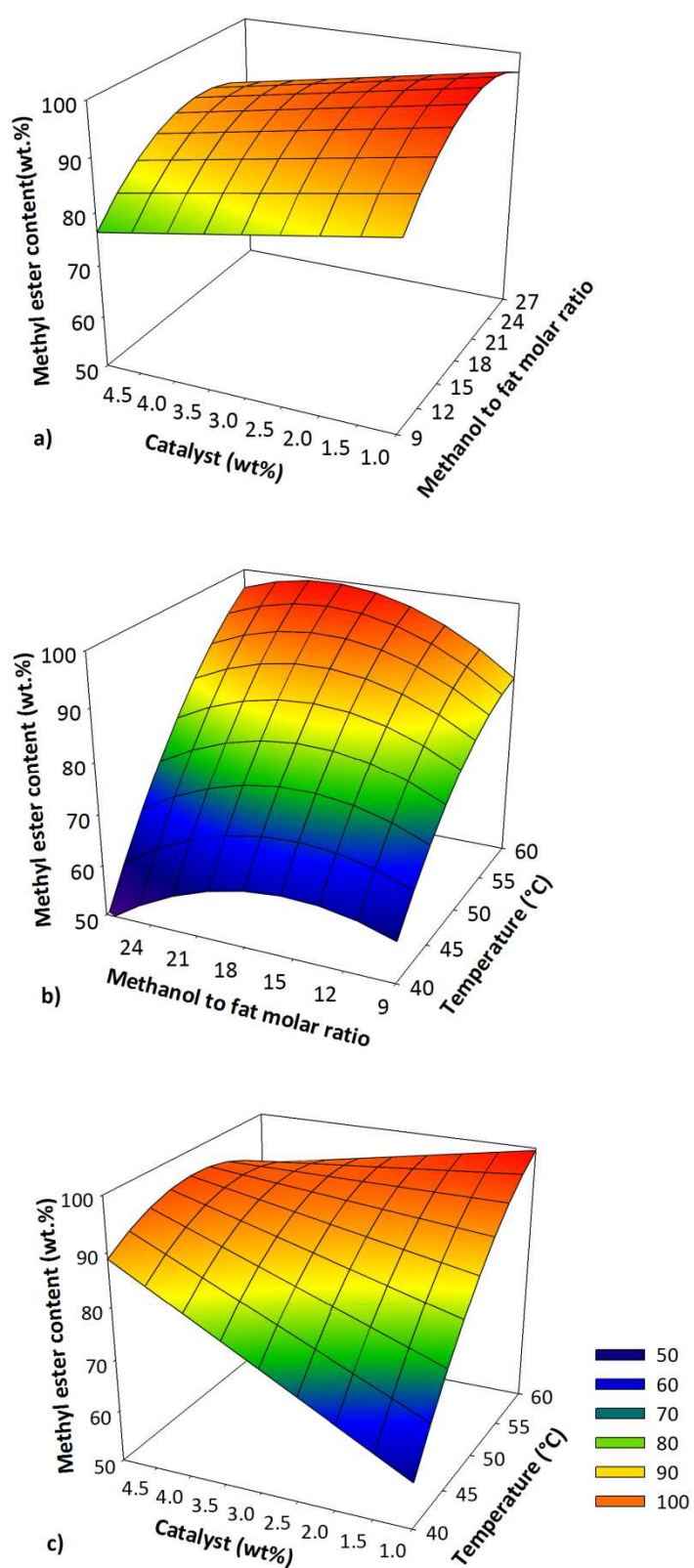


Figure 5.10. Response surface for product methyl ester content (8 h): (a) temperature of 60 °C; (b) catalyst concentration of 1 wt.%; and (c) 21:1 methanol to fat molar ratio.

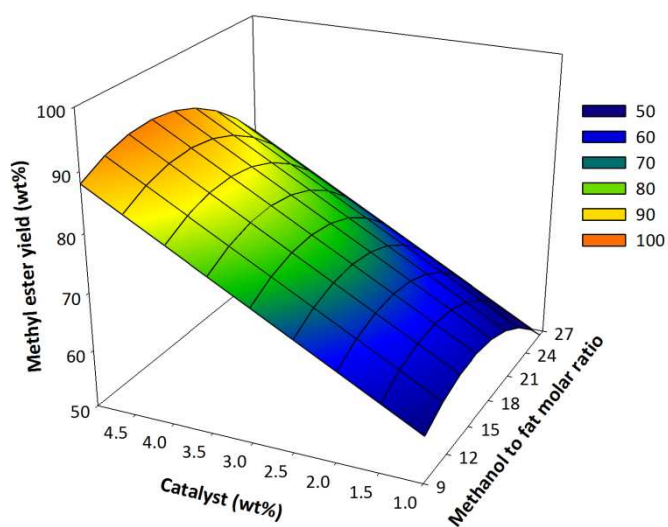


Figure 5.11. Response surface for product methyl ester content (8 h) at 40 °C.

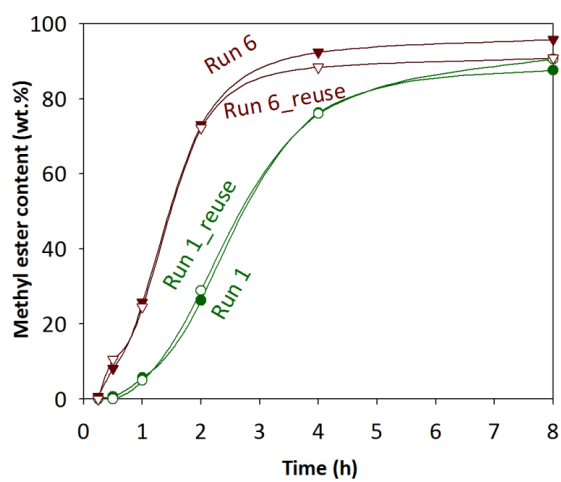


Figure 5.12. Product methyl ester content (wt.%) over time at run 1 (50 °C, 3 wt.%, 18:1 methanol to fat molar ratio) and run 6 (60 °C, 3 wt.%, 18:1 methanol to fat molar ratio) and after catalyst reuse in each experiment.

5.6 CONCLUSIONS

Several materials were prepared with the objective of applying them as catalysts for the transesterification of triglycerides; however, most revealed inactive on the reaction.

The mixed oxide catalysts were the ones presenting the highest basicities ($\text{pH}_{\text{pzc}} > 11$) and catalytic activity was only observed in some of those materials, namely calcium oxide, calcium manganese oxide and calcium barium oxide.

Among the studied potential heterogeneous catalysts, CaO and calcium manganese oxide showed the best results, the last being selected for detailed studies using response surface methodology.

A second-order model, describing the influence of reaction conditions in methyl ester content (purity), was obtained; temperature and the interaction between temperature and catalyst concentration were the parameters which mostly influenced product purity.

As it was possible to reuse the catalyst without loss of its activity, results indicated that catalytic behaviour was essentially heterogeneous.

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CHAPTER 6 CALCIUM MANGANESE OXIDE FOR BIODIESEL PRODUCTION USING DIFFERENT RAW MATERIALS



This chapter was based on:

Dias, J. M., Alvim-Ferraz, M. C. M., Almeida, M. F., Díaz, J. D. M., Sánchez-pólo, M. and Rivera-Utrilla, J. Submitted for publication. *Calcium manganese oxide for Biodiesel Production using Different Raw materials: Impacts on Product Quality*.

ABSTRACT

Calcium manganese oxide was previously studied as heterogeneous catalyst for biodiesel production from animal fat; however, some key aspects remained unclear, namely the differences between this and other catalysts, its behaviour in the synthesis using different raw materials as well as the impacts of its use on product quality; therefore, the present study: i) compared biodiesel production using calcium manganese oxide and other catalysts also considering heterogeneous catalyst leachability; ii) analysed biodiesel heterogeneous synthesis using calcium manganese oxide and different raw materials; and iii) evaluated raw material and catalyst impact on product quality according to EN 14214. After 8 h of reaction, product purity was similar using different catalysts, being 92.5 wt.% using both NaOH and calcium manganese oxide and 93.8 wt.% using CaO. The leaching results showed that catalytic behaviour could be classified as essentially heterogeneous. The reaction was slower when lard was used for biodiesel synthesis using calcium manganese oxide. Heterogeneous synthesis using calcium manganese oxide led to similar results regarding reaction progression and better results regarding product quality compared to the homogeneous one (NaOH); however, much higher reaction time was needed. A global evaluation of production time will determine the impacts of increased reaction time.

6.1 SCIENTIFIC RELEVANCE

As previously mentioned, biodiesel production relies on the use of first generation plants whereby vegetable oils, generally used as food resources, are converted chemically into a diesel substitute, by a simple transesterification reaction using a basic homogeneous catalyst.

In order to reduce economical and social constraints and to sustain future biodiesel production, most important developments regarding the adaptation of currently existing plants (to take advantage of the large investments already made) relate with the substitution of food resources used as raw materials and improvement of the production process by using more environmentally friendly and less costly solutions.

The use of waste materials, more specifically animal fat wastes (alone or as additives), has been seen as a very important contribute aiming to reduce the dependency upon food resources, the costs of production and the environmental impacts caused by incorrect management of such wastes (Dias et al., 2008b; Dias et al., 2009; Dias et al., Submitted for publication).

Amongst research works considering the adaptation of currently used production processes, heterogeneous catalysis appears as a very important contribute aiming to simplify the process as well as to reduce the purification costs associated with the dissolution of the homogeneous catalyst in the final product.

In order to substitute raw materials and improve conventional processes currently used for biodiesel production, calcium manganese oxide was studied as heterogeneous catalyst for biodiesel production through transesterification of lard (Dias et al., Submitted for publication); however, some key aspects remained unclear, namely the differences between this and other catalysts, its behaviour in the synthesis using different raw materials as well as the impacts of its use on product quality. The present work was performed aiming to respond to such questions.

6.2 SPECIFIC OBJECTIVES

- To compare biodiesel production using calcium manganese oxide and other catalysts;
- To evaluate the leachability of the heterogeneous catalysts;
- To analyse biodiesel heterogeneous synthesis using calcium manganese oxide and different raw materials, including animal fat, waste frying oil and their mixture;
- To evaluate raw material and catalyst impact on product quality according to EN 14214.

6.3 MATERIALS

The raw materials used were: PL, WFO and a mixture of WFO (78 wt.%) and PL (78WFO/22PL). The raw material mixture was prepared aiming to reduce the WFO iodine value considering that the iodine value obtained from the mixture corresponds to the weighted average of the iodine value of each component used (Dias et al., 2008b).

PL was the same presented in section 5.3. The WFO was a different lot than the one presented in section 2.3, was obtained in the same manner and after filtered under vacuum prior to pre-treatment.

Methanol for biodiesel synthesis and n-Heptane for catalyst cleaning and chromatographic analysis were the same presented in section 5.3.

Heterogeneous catalysts were prepared using CaCO_3 , CaO (both supplied by Sigma-Aldrich) and MnO_2 (supplied by Riedel-de-Haën); Ca(OH)_2 used was supplied by Sigma-Aldrich.

6.4 METHODS

6.4.1 CATALYST PREPARATION

CaO was prepared calcinating CaCO_3 at the selected temperature, using a heating rate of $20\text{ }^\circ\text{C min}^{-1}$ and a holding time of 45 min in a tubular furnace (Figure 5.3) under N_2 atmosphere.

Calcium manganese oxide was prepared conducting a solid-state reaction by mixing in an agate mortar both oxides (CaO and MnO_2) in an equimolar proportion followed by calcination at $900\text{ }^\circ\text{C}$ under N_2 atmosphere in a tubular furnace during 4 h.

Both catalysts were activated by calcination prior to use; calcination temperatures differed, being selected after TG analysis of the materials in a Setaram (model 92-16.18) thermobalance using a heating rate of $20\text{ }^\circ\text{C min}^{-1}$.

When catalyst was not immediately used, calcination procedure was repeated to avoid catalyst deactivation. After calcination, catalyst was kept for a few minutes in a desiccator under vacuum before use.

6.4.2 BIODIESEL PRODUCTION

HETEROGENEOUS PROCESS

Heterogeneous synthesis was made by basic transesterification and the production process was the same as presented in section 5.4.2 but this time both the waste frying oil, the pork lard and the mixtures were pre-treated (Figure 6.1).

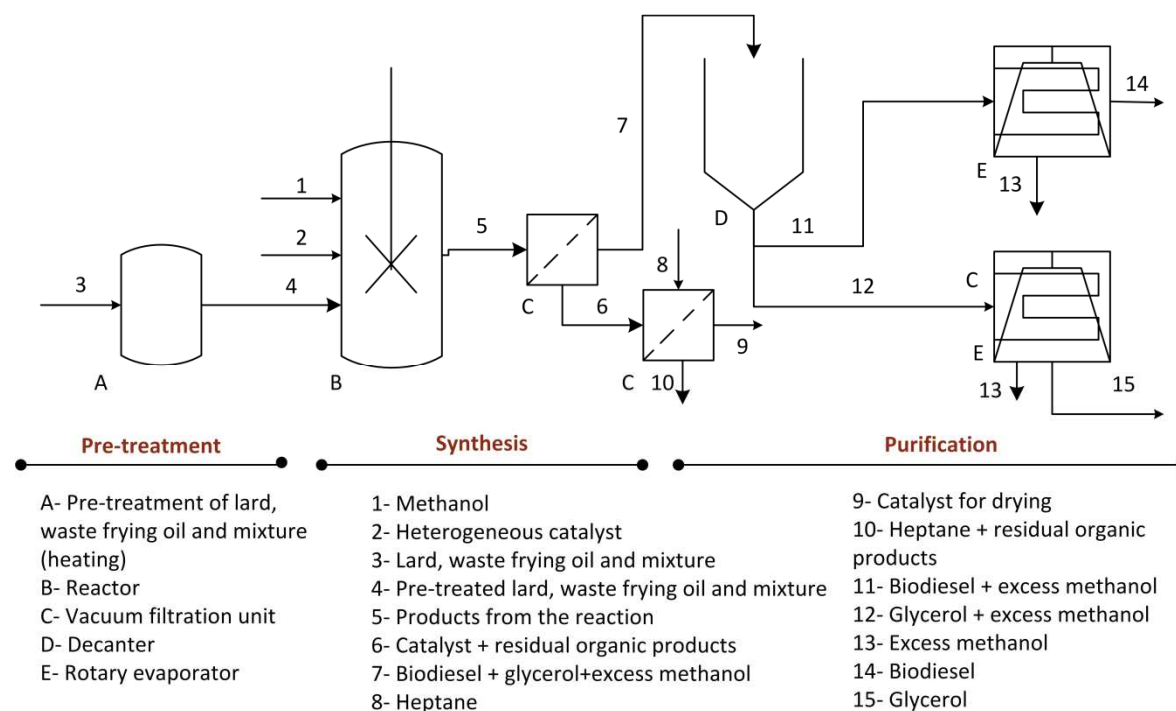


Figure 6.1. Diagram adopted for heterogeneous biodiesel production from lard, waste frying oil and their mixture.

Pre-treatment

The raw materials were pre-treated by heating at 100 °C and after cooled to near the reaction temperature (50 °C).

Basic Heterogeneous Transesterification

Biodiesel synthesis was performed using the reactor and setup presented in section 5.4.2. The same amount of raw material was used (70 g) and in this case the reaction conditions were fixed at the central values chosen for experimental design in the previous chapter: temperature 50 °C, catalyst concentration 3 wt.% and methanol to fat molar ratio 18:1.

When the progression of the reaction was evaluated, the method used was the same presented in section 5.4.2.

Purification

The same method presented in section 5.4.2.

HOMOGENEOUS PROCESS

Biodiesel homogeneous synthesis from lard was performed for comparison in the same reactor without using nitrogen atmosphere.

The same amount of dehydrated lard used in the homogeneous process was used (70 g) in the homogeneous reaction.

The production process was performed according to Figure 3.2.

The reaction conditions were the same as presented in section 3.4.1 (0.8 wt.% of NaOH, relative to fat weight, 6:1 methanol to fat molar ratio and a temperature of 60 °C).

In order to evaluate the progress of the homogeneous reaction, samples were taken at 0.25, 0.5, 1, 2 and 4 h. After each period, 1 g of the reaction mixture was added to 1 mL of HCl solution (prepared considering a calculated amount of HCl needed to stop the reaction). The organic phase was extracted, washed with 2 mL of distilled water and dried in a rotary evaporator at 90 °C being finally treated according to EN 14103 (2003) for determination of methyl ester content by GC.

6.4.3 ANALYTICAL METHODS

Raw material properties, biodiesel conversion and catalyst analysis were performed.

The raw material properties and biodiesel conversion was performed according to the methods and related standards presented in section 5.4.3.

Catalyst was analysed by X-ray diffraction analysis (BRUKER D8 Advance) in order to identify the compounds in the catalysts structure.

The calcium content of biodiesel was determined through atomic absorption spectrophotometry at an external laboratory; the sample used for analysis was obtained using a biodiesel sample subjected to evaporation, calcination at 550 °C and nitric acid attack.

6.5 RESULTS AND DISCUSSION

6.5.1 RAW MATERIAL PROPERTIES

The WFO presented an acid value of 0.91 mg KOH/g WFO and an iodine value of 129 g I₂/100 g WFO. The acid value of the WFO might be explained by humidity during storage of this raw material which might lead to triglycerides hydrolysis and acid value increase.

The iodine value of the WFO was higher than the maximum according to biodiesel quality standard (120 g I₂/100 g); therefore, a raw material mixture was prepared aiming to reduce such iodine value (Dias et al., 2008b). The determined iodine value of the mixture was 117 g I₂/100 g, close to the estimated one, which was 115 g I₂/100 g.

The properties of the PL were presented in section 5.5.2.

The composition of the WFO and 78WFO/22PL might be analysed from the methyl ester composition presented in Table 6.1.

Table 6.1: Methyl ester composition obtained using waste frying oil and a mixture of waste frying oil and lard as raw materials and respective mean molecular weight of raw materials

RAW MATERIAL COMPOSITION	WFO	78WFO/22PL
<i>Methyl ester composition, wt. %</i>		
Myristate (C14:0)	0.1	0.4
Palmitate (C16:0)	7.3	10.7
Palmitoleate (C16:1)	0.1	0.6
Stearate (C18:0)	4.0	5.4
Oleate (C18:1)	26.9	31.5
Linoleate (C18:2)	60.0	50.2
Linolenate (C18:3)	0.5	0.7
Others	1.1	0.5
<i>Mean molecular weight (g mol⁻¹)</i>	877.7	873.6

The WFO showed a composition relatively different from other previously studied (Table 2.1) because it results from a voluntary collection system, being heterogeneous and varying according to the frying oil sources. The composition of the mixture was, as expected (Dias et al., 2008b), a reflection of the composition of each component alone.

6.5.2 CATALYSTS CHARACTERISATION

In order to identify the active species, X-ray diffraction analysis was performed in the materials prior to calcination. Calcium carbonate material was mainly constituted by CaCO_3 and a small amount of Ca(OH)_2 (Figure 6.2).

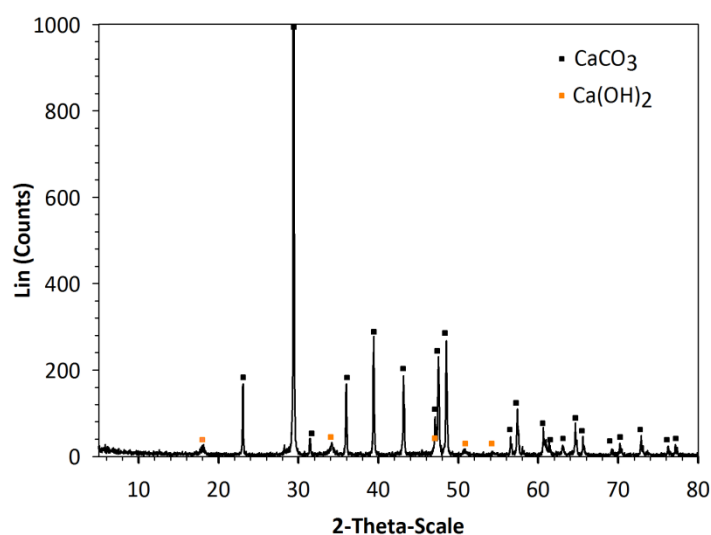


Figure 6.2. X-ray diffraction pattern for CaCO_3 prior to calcination.

Regarding calcium manganese oxide, prior to calcination was fundamentally constituted by Ca(OH)_2 presenting in smaller representation Ca_2MnO_4 and Mn_3O_4 (Figure 6.3).

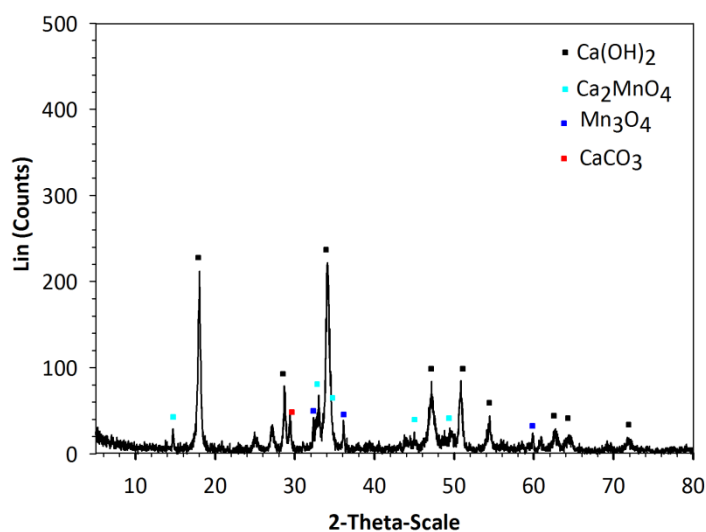


Figure 6.3. X-ray diffraction pattern for calcium manganese oxide prior to calcination.

In order to define the best suited catalyst calcination temperature, a TG analysis of CaCO_3 , the mixed oxide and Ca(OH)_2 was performed; the respective profiles are presented in Figure 6.4.

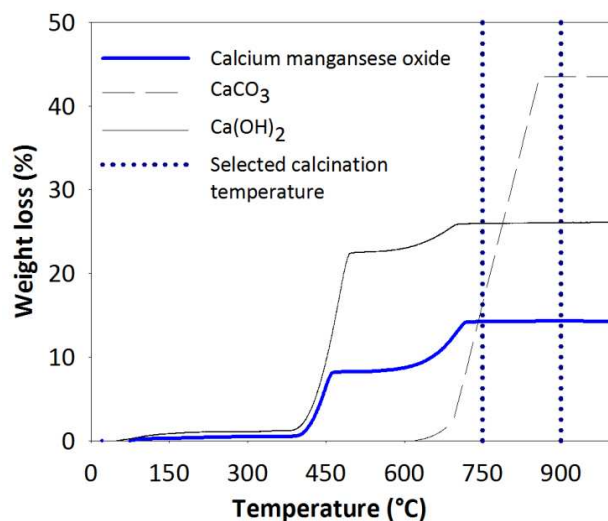


Figure 6.4. Thermogravimetric profiles of calcium carbonate, calcium manganese oxide and calcium hydroxide (heating rate: $20\text{ }^{\circ}\text{C min}^{-1}$).

By comparing the TG analysis of Ca(OH)_2 with the calcium manganese oxide one, the results show that, in fact, the calcination of the mixed oxide eliminates the presence of the calcium hydroxide specie. According to the results, the selected calcination temperatures were $900\text{ }^{\circ}\text{C}$ and $750\text{ }^{\circ}\text{C}$ for CaCO_3 and calcium manganese oxide, respectively.

After calcination of the mixed oxide at the selected temperature, the major specie present was a calcium manganese oxide presenting an empirical formula was close to $\text{Ca}_{0.9}\text{Mn}_{0.1}\text{O}$; additionally, small amounts of Ca_2MnO_4 and Mn_3O_4 were also present, as shown in Figure 6.5.

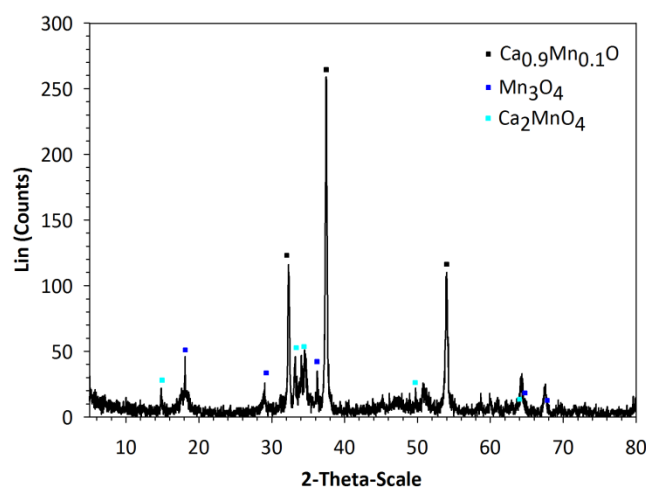


Figure 6.5. X-ray diffraction pattern for calcium manganese oxide after calcination.

6.5.3 INFLUENCE OF CALCINATION ON CATALYST PERFORMANCE

Without calcination, both catalysts (CaCO_3 and the mixed oxide) were inactive in the transesterification reaction; this fact shows that CaCO_3 and Ca(OH)_2 , which were the main species present before calcination, are non-active in the transesterification reaction; and, that the needed calcinations temperatures are related with the removal of the carbonate and hydroxide species present. Additionally, after performing the reaction, the catalyst becomes again inactive.

When using CaO as catalyst in the transesterification reaction, according to several authors (Huaping et al., 2006; Granados et al., 2007; Kouzu et al., 2008), the CO_2 is the main deactivating agent, whereas the effect of water is less important; therefore, the contact with air leads to CaCO_3 formation and consequently to catalyst deactivation.

Regarding the use of the mixed oxide catalyst, the X-ray diffraction analysis showed that inactivation after use in the reaction relates with catalyst hydration and the consequent formation of Ca(OH)_2 (Figure 6.6).

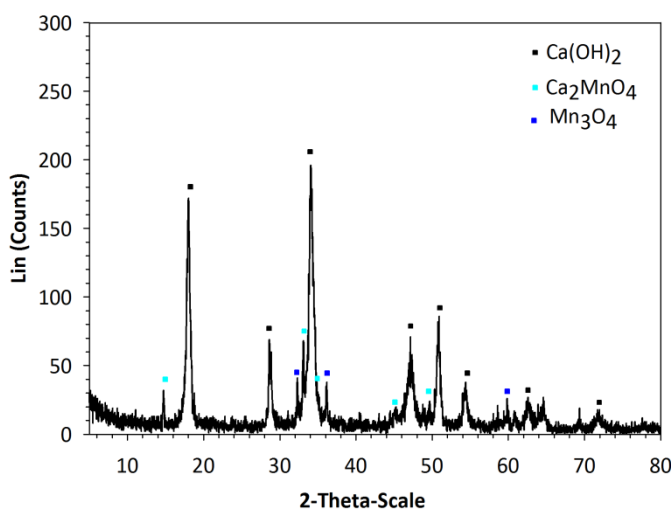


Figure 6.6. X-ray diffraction pattern for calcium manganese oxide after being used in the transesterification reaction.

Ca_2MnO_4 and Mn_3O_4 were already present before calcination, when catalyst was inactive.

Ca(OH)_2 might result from the contact with air and possibly residual water existing in the reaction media.

Therefore, the active species were CaO and $\text{Ca}_{0.9}\text{Mn}_{0.1}\text{O}$ in the case of catalysts based on calcium carbonate and calcium manganese oxide, respectively.

Since the non-active species are different when using calcium oxide (CaCO_3) compared with calcium manganese oxide (Ca(OH)_2), the last requires lower temperatures for the catalyst regeneration, 750 °C compared to 900 °C (Figure 6.4), a key step for the production process.

6.5.4 COMPARISON OF THE PERFORMANCE OF CALCIUM MANGANESE OXIDE WITH OTHER CATALYSTS

The selection of calcium manganese oxide as heterogeneous catalyst for biodiesel production was mainly based on the good results previously obtained and the lack of knowledge regarding its application; to evaluate the differences between this and other catalysts, one heterogeneous (CaO) and one homogeneous (NaOH) were selected due to their common application.

The results regarding the progression of the reaction using the three catalysts for the transesterification of lard are presented in Figure 6.7.

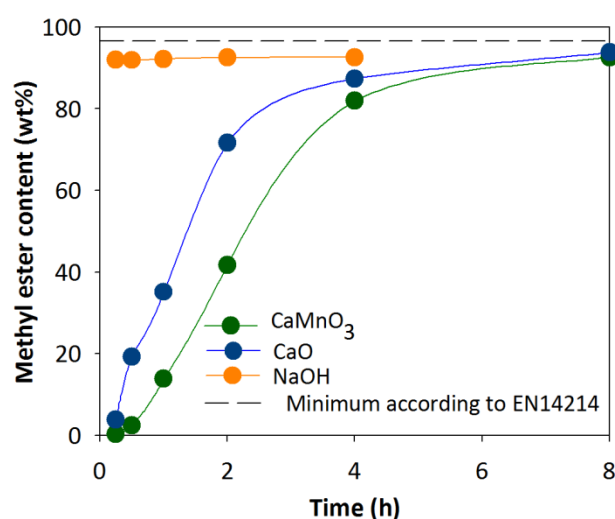


Figure 6.7. Product methyl ester content (wt.%) over time using homogeneous and heterogeneous catalysts for lard transesterification (heterogeneous transesterification: 50 °C; 18:1 methanol to lard molar ratio and 3 wt.% of catalyst; homogeneous transesterification: 60 °C, 6:1 methanol to lard molar ratio and 0.8 wt.% of catalyst).

It is clear that the reaction rate of the heterogeneous catalysis does not compete with the homogeneous one. In fact, after 15 min of reaction, the maximum methyl ester content was obtained using the homogeneous catalyst.

Regarding the use of the heterogeneous catalysts, CaO showed faster reaction rate until 4 h of reaction, showing after very similar behaviour as the calcium manganese oxide.

Considering that the same amount of the active specie existed, this fact shows that the calcium manganese oxide was less active than the CaO in the transesterification reaction; as hydration plays the main role in calcium manganese oxide deactivation, as previously reported, the use of anhydrous conditions might improve calcium manganese oxide activity in the transesterification reaction.

After 8 h, the conversion was very similar independently of the catalyst used and final methyl ester content was 92.5 wt.% using NaOH and calcium manganese oxide as catalysts and 93.8 wt.% using CaO.

It should be referred that the comparison between heterogeneous and homogeneous catalysis being made using different reaction conditions; however, such conditions were selected as being within the optimum range for both processes according to previous work (Dias et al., 2008a; Dias et al., Submitted for publication).

Higher catalyst amount (3 wt.% compared to 0.8 wt.%) and molar ratio of methanol to fat (18:1 compared to 6:1) were used in heterogeneous catalysis; however, methanol and catalyst can be reused in the transesterification process (Dias et al., Submitted for publication), which can minimize these disadvantages. On the other hand, much higher reaction times were needed to ensure reaction completion in heterogeneous catalysis (4-8 h compared to 15 min). Nevertheless, it should be considered that the introduction of an heterogeneous process reduces the need of purification steps, which are also time consuming; this means that a global evaluation of production time should be conducted in each case to conclude if in fact the higher reaction times can be compensated by the reduction of the number of purification steps.

6.5.5 LEACHING OF THE HETEROGENEOUS CATALYSTS

Catalyst leaching was evaluated by measuring the amount of calcium in the produced biodiesel using both heterogeneous catalysts.

A content of 35.4 mg of calcium per kg of biodiesel was found in biodiesel produced using the calcium manganese oxide and a content of 15.8 mg of calcium per kg of biodiesel was found in biodiesel produced using calcium oxide.

Regarding the calcium manganese oxide, considering that the mass of catalyst used was essentially constituted by $\text{Ca}_{0.9}\text{Mn}_{0.1}\text{O}$, such amount represents around 0.16 wt.% of the initial amount of catalyst used corresponding to a catalyst concentration in the raw material of around 0.005 wt.% (considering a yield of 96 wt.%, using a product loss estimate of 5 wt.% by sampling).

Regarding the calcium oxide, considering that the mass of catalyst corresponds to CaO , such amount represents around 0.06 wt.% of the initial amount of catalyst used corresponding to a catalyst concentration in the raw material of around 0.002 wt.% (considering a yield of 96 wt.%, using a product loss estimate of 5 wt.% by sampling).

The amounts of catalyst relatively to fat weight (0.005 and 0.002 wt.%), that would behave as homogeneous catalysts, are too small to be responsible for the catalytic behaviour as demonstrated from the catalyst concentration range studied in the homogeneous catalysis (from 0.2 to 1.2 wt.%).

This facts shows, together with the conclusions retained from the section 5.5.7 (catalyst maintained its activity after reuse), that the catalytic behaviour was in fact essentially heterogeneous. However, despite the small percentage relatively to the initial amount, this values exceed the standard limit imposed by the European quality standard EN 14214 (5 mg/kg biodiesel).

The results showed that when using these heterogeneous catalysts, some degree of purification (that might be considerably less than with homogeneous catalysis) should be done to ensure removal of residual catalyst that might leach into the biodiesel phase. Evaluation of catalyst leaching to the glycerine phase should also be further considered.

6.5.6 BIODIESEL PRODUCTION FROM DIFFERENT RAW MATERIALS USING CALCIUM MANGANESE OXIDE

Biodiesel production from PL, WFO and 78WFO/22PL was evaluated using calcium manganese oxide during an 8 h period, which was considered the period that ensured same purity regardless the catalyst used according to section 6.5.4.

However, to evaluate the progression of the reaction, a sample was taken after 4 h of reaction. Results regarding product methyl ester content are presented in Table 6.2.

Table 6.2: Methyl ester content of biodiesel produced from pork lard, waste frying oil and a 78/22 (w/w) mixture of waste frying oil and lard, using calcium manganese oxide as catalyst.

RAW MATERIAL	METHYL ESTER CONTENT, wt.%	
	4 h	8 h
PL	81.9	92.5
WFO	94.9	94.3
78WFO/22PL	94.8	92.1

Results showed that after 4 h of reaction when WFO and 78WFO/22PL were used as raw materials the reaction was almost completed; however, when lard was used alone, a greater reaction time was needed to ensure reaction completeness. The differences between the results probably relate with the higher viscosity of the lard which consequently retards the reaction due to more difficult contact between the three phases. As the heterogeneous catalysis is a three phase reaction system, the contact between the reactants is crucial, reason why a vigorous stirring was ensured.

The slight decrease in the methyl ester content from 4 to 8 h reaction when WFO and 78WFO/22PL were used was considered not to be significant.

After 8h of reaction, purity was similar independently of the raw material used.

6.5.7 QUALITY OF BIODIESEL

Most studies considering the use of heterogeneous catalysts for biodiesel production do not evaluate overall biodiesel quality, focusing mostly in the reaction progression as it was made on the previous sections of the present work.

Therefore, some of most relevant quality parameters, according to previously developed work (from Chapter 2 to 4), were determined in biodiesel obtained using different raw materials.

Table 6.3 presents the results and compare them with those obtained using homogeneous catalysis. The parameters which were not in agreement with the quality specifications are presented in bold.

Table 6.3: Quality parameters ^{a)} of biodiesel obtained through heterogeneous catalysis (HtC, calcium manganese oxide) and homogeneous catalysis (HmC, NaOH) ^{b)} of pork lard, waste frying oil and a 78/22 w/w mixture of waste frying oil and lard and comparison with EN 14214

PROPERTY	L		WFO		78WFO/22PL ^{c)}		EN 14214
	HtC	HmC	HtC	HmC	HtC	HmC	
Water content (wt.%)	0.04	0.11	0.04	0.10	0.04	0.06	< 0.05
Acid value (mg KOH/g)	0.25	0.04	0.28	0.08	0.17	0.07	< 0.50
Iodine value (g I ₂ /100 g)	68	67	129	117	117	108	< 120
Kinematic viscosity at 40 °C (mm ² s ⁻¹)	4.59	4.71	4.70	4.69	4.74	4.75	3.50-5.00
Methyl ester content (wt.%)	92.5	94.4	94.3	96.3	92.1	96.3	> 96.5
Linolenic methyl ester content (wt.%)	0.9	1.0	0.5	0.6	0.7	0.7	< 12.0

^{a)} The parameters which were not in agreement with the quality specifications are presented in bold.

^{b)} Dias et al. (2008b); conditions used: 60 °C, 6:1 molar ratio of methanol to raw material and 0.8 wt.% NaOH.

^{c)} A mixture of waste frying oil (80 wt.%) and lard was used.

It can be seen that the water content of biodiesel obtained using homogeneous catalysis, the iodine value of the waste frying oil methyl ester obtained through heterogeneous catalysis and the methyl ester content in all cases were the parameters that were not in agreement with the specification limits.

As expected, the fulfillment of the water content specification was more difficult when homogeneous catalysis was used due to the washing of the product and the extreme dependency upon purification methods applied afterwards.

The differences in the iodine value of the biodiesel from waste frying oil and from the mixture are obvious due to the different sources and probably different storing conditions of the frying oil used. Heterogeneous catalysis of the mixture ensured, as predicted, the agreement with the iodine value specification.

Regarding the methyl ester content, slightly higher values were obtained using homogeneous catalysis, mainly regarding the mixture; those results should be related with differences between WFO as well as the mixture ratio used in each study.

However, using different raw materials, the obtained biodiesel showed a methyl ester content varying from 92.1-96.3 wt.%, being close to the minimum required (96.5 wt.%) for a product with ensured quality.

The remaining evaluated parameters were in agreement with the product quality specifications; it should be noted that the viscosities of the products were similar (from 4.59 to 4.75 mm²s⁻¹) independently of the process and raw material used.

The acid value was higher using heterogeneous catalysis (0.17-0.25 mg KOH/g compared with 0.04-0.08 mg KOH/g) but still significantly below the upper limit (0.50 mg KOH/g). Such differences might be related with the fact that homogeneous catalysts tend to react with free fatty acids to generate soaps, therefore reducing the acid value of the final product.

6.6 CONCLUSIONS

Heterogeneous catalysis was evaluated and results showed that CaCO₃ and the mixed oxide of calcium and manganese were inactive for the transesterification reaction without calcination.

After calcination of CaCO₃, CaO formed is the active specie in the reaction. After calcination, the mixed oxide becomes mainly constituted by Ca_{0.9}Mn_{0.1}O which was the active specie in the reaction. The X-ray diffraction analysis showed that by contact with air (prior to calcination) and after being used in the reaction (air contact and other sources of humidity) the mixed oxide probably releases CaO that becomes hydrated; therefore, in this case the main non-active specie was Ca(OH)₂.

Results regarding biodiesel purity after 8 h reaction were similar independently of the catalyst used (Ca_{0.9}Mn_{0.1}O, CaO and NaOH). Comparing both heterogeneous catalysts, CaO showed higher reaction rates than Ca_{0.9}Mn_{0.1}O. The mixed oxide catalyst needed, however, lower activation temperature.

Leaching results showed that catalytic behaviour could be classified as essentially heterogeneous; however, purification might be needed to ensure product complying with European quality standards regarding calcium content.

Regardless the raw material used, after 8 h of reaction, calcium manganese oxide catalysis led to similar results regarding reaction completeness and better results regarding product quality compared to NaOH catalysis.

However, heterogeneous process used higher catalyst amount and molar ratio of methanol to fat and also much higher reaction times than the homogeneous catalysis.

Methanol and catalyst might be recycled in the process; regarding the impact of a higher reaction time, it should be considered that the introduction of an heterogeneous process might reduce the need of purification steps, which are also time consuming.

Therefore, a global evaluation of the production process time should be conducted in each case to conclude if in fact the higher reaction times can be compensated by the reduction of the number of purification steps and associated product losses and environmental impacts.

Heterogeneous catalysis needs further optimization; however, results demonstrated that it might in fact bring benefits in biodiesel production, namely by improving product quality as well as reducing purification steps and associated wastes.

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CHAPTER 7 CONCLUSIONS AND FUTURE WORK

CONCLUSIONS

The main conclusions of the work were divided in the homogeneous and heterogeneous biodiesel production process and will be presented from now on.

Homogeneous biodiesel production process

By studying the commonly used biodiesel production process, using sunflower oil, soybean oil and waste frying oil as raw materials and NaOH, CH₃ONa and KOH as catalysts, it was possible to conclude that:

- Biodiesel production using virgin oils results in higher yields (reaching 97 wt.%) compared to the production using waste frying oils (reaching 92 wt.%);
- Most biodiesel properties were in agreement with the quality standard EN 14214; however, soybean oil methyl ester presents an iodine value higher than the limit and maximum water content can be difficult to achieve (evaporation at reduced pressure was selected as an efficient dehydration method);
- Biodiesel kinematic viscosity and purity were important quality properties to select catalytic conditions to be used; using KOH as catalyst, minimum purity was not obtained;
- Using KOH as catalyst, selected catalytic conditions for ensuring a proper viscosity were:
 - 0.6 wt.% for virgin oils and 0.8 wt.% for waste frying oils.
- Using the sodium based catalysts, selected catalytic conditions were:
 - 0.6 wt.% CH₃ONa using both virgin oils; 0.6 wt.% NaOH using sunflower oil and 0.8 wt.% using soybean oil; and 0.8 wt.% using both catalysts for waste frying oils.

By evaluating the incorporation of animal fat (pork lard) in vegetable oil (soybean oil and waste frying oil) for biodiesel production, it was possible to conclude that:

- The product yields using raw material mixtures varied from 81.7 to 88.8 (wt.%);
- The use of mixtures as raw materials allowed biodiesel production according to EN 14214 except for the purity, which was, however, close to the minimum limit;
- It was postulated and confirmed by a linear model that:
 - For the main methyl esters, the composition of biodiesel corresponded to the weighted average of the composition of each component of the mixture;
 - The quality parameter of biodiesel obtained from the mixture corresponded to the weighted average of the parameters of biodiesel resulting from each component (for some parameters and mixtures).

By studying a two-step process including acid esterification followed by basic transesterification of acid waste lard, it was possible to conclude that:

- Homogeneous basic transesterification of lard presenting an acid value of $14.57 \text{ mg KOH g}^{-1}$ could not be performed;
- The use of acid esterification pre-treatment allowed the reduction of the acid value of the raw material to 3 mg KOH g^{-1} (20% of the initial value) enabling further basic transesterification; however, low yields were obtained (65 wt.%);
- Catalyst amount and temperature during acid esterification mostly affected biodiesel quality and the selected esterification conditions were 65°C , 2.0 wt.% H_2SO_4 and 5 h, which led to a product viscosity of $4.81 \text{ mm}^2 \text{ s}^{-1}$ and a purity of 99.6 wt.%;
- Basic transesterification of a mixture of acid waste lard and soybean oil showed that blending might be an interesting alternative to enable homogeneous transesterification of acid wastes with higher yields (purity of 99.8 wt.% and yield of 77.8 wt.%).

Heterogeneous biodiesel production process

By studying heterogeneous catalysts for biodiesel production using mostly pork lard as raw material, it was possible to conclude that:

- The basicity of the catalyst plays an important role in its activity regarding the transesterification reaction and only calcium oxide and mixed oxide catalysts with pHpzc higher than 12 presented activity;
- From the studied catalysts, calcium oxide, mixed oxide of calcium and manganese and mixed oxide of calcium and barium were active in the transesterification reaction (after calcination), but CaO and calcium manganese oxide showed the best results;

- Calcination of the materials was essential; in fact, CaCO_3 and the mixed oxide of calcium and manganese were inactive for the transesterification reaction without calcination;
- The active specie of the calcium manganese oxide catalyst was $\text{Ca}_{0.9}\text{Mn}_{0.1}\text{O}$;
- Carbonation was probably responsible for the deactivation of CaO catalyst whereas hydration was responsible for the deactivation of calcium manganese oxide;
- Using response surface methodology it was possible to conclude that the temperature and the interaction between temperature and catalyst concentration mostly influenced product purity obtained from lard using calcium manganese oxide as catalyst;
- Calcium manganese oxide was reused without loss of activity;
- There were evidences of residual catalyst leaching to biodiesel; however, catalytic behaviour could be classified as essentially heterogeneous.

By comparing the use of different catalysts (homogeneous and heterogeneous) and different raw materials in heterogeneous catalysis using calcium manganese oxide, it was possible to conclude that:

- Independently of the catalyst studied, $\text{Ca}_{0.9}\text{Mn}_{0.1}\text{O}$, CaO or NaOH , biodiesel purity after 8 h reaction was similar (92.1-94.3 wt.%);
- CaO showed higher reaction rates than $\text{Ca}_{0.9}\text{Mn}_{0.1}\text{O}$; however, the mixed oxide catalyst needed lower activation temperature;
- Independently of the raw material used, after 8 h of reaction, calcium manganese oxide catalysis led to similar results regarding the reaction progression and better results regarding product quality compared to NaOH catalysis;
- A global evaluation of biodiesel production time will indicate if the higher reaction times can be compensated by the reduction of the purification steps and associated product losses and environmental impacts;
- Heterogeneous catalysis might in fact bring benefits in biodiesel production, namely by improving product quality as well as by reducing purification steps, but further research work needs to be conducted.

There is no doubt that biodiesel production is a subject of great interest to the society as proven by the press releases presented in Appendix E, which relate with the development of the present work. Research can play, in fact, an important role on the promotion and future effective implementation of alternative processes to sustain future biofuels production.

FUTURE WORK

Due to the large spectrum of subjects covered by the present work, many research lines for future work were opened. The main subjects which were considered to be important developing in the future regarding homogeneous and heterogeneous process are presented from now on.

Homogeneous biodiesel production process

To study the developed homogeneous biodiesel production process considering:

- The use of other raw materials: non edible oils (e.g. castor oil and *Jatropha curcas* oil), algae oils, other wastes (e.g. fish oil and wastewaters with high lipid content), and mixtures (including three or more components);
- The improvement of homogeneous transesterification using a two step basic transesterification process (with glycerol removal) and alternative processes for catalyst extraction from biodiesel phase (namely by using glycerol);
- The identification of yield losses and possible improvements regarding biodiesel production using acid esterification followed by basic transesterification.

Heterogeneous biodiesel production process

To study the developed heterogeneous biodiesel production process considering:

- The use of other raw materials (namely acid) and the application of anhydrous conditions;
- The characterisation of the catalysts, including the quantification of the active species;
- The preparation of the mixed oxide catalysts considering different proportions of the oxides and also different supports;
- The evaluation of the catalyst activity after several experiment cycles and the catalyst characterization before and after being used through X-ray diffraction;
- The determination of the amount of catalyst leached to the products using different catalysts and evaluation of purification methods to remove residual leached catalyst from biodiesel, including washing and extraction with glycerol amongst others;
- The evaluation of the impact of increased reaction time in heterogeneous process in the overall production process, compared with the homogeneous one (at an industrial scale) and; the determination of biodiesel production costs using heterogeneous catalysis, including the costs of catalyst preparation and re-activation.

APPENDIX A EQUIPMENT AND APPARATUS USED IN ANALYTICAL METHODS

ACID VALUE

The acid value of raw materials and biodiesel was determined according to NP EN ISO 660 (2002) and EN 14104 (2003) by volumetric titration using the apparatus presented in Figure A.1.



Figure A.1. Apparatus^{***} used for measuring acid value.

VISCOSITY

Biodiesel viscosity was measured according to the standard ISO 3104 (1994) at 40 °C using a viscometer precision bath VB-1423 (JP Selecta) and Cannon-Fenske glass capillary viscometers as presented in Figure A.2.



Figure A.2. Viscometer bath for biodiesel viscosity determination.

^{***} Note that the iodine value of the raw materials was also determined by volumetric titration, according to the standard ISO 3961 (1996), using a similar apparatus.

DENSITY

Biodiesel density was measured using a VWR brand hydrometer, M50 (0.850-0.900 g mL⁻¹) according to the standard EN ISO 3675 (1998) (Figure A.3.).



Figure A.3. Biodiesel density measurement using a hydrometer.

FLASH POINT

Biodiesel flash point was measured using the rapid equilibrium closed cup method according to the standard ISO 3679 (2004). The equipment used was a Stanhope-Seta, model 30000-0 Setaflash 3 (Figure A.4).

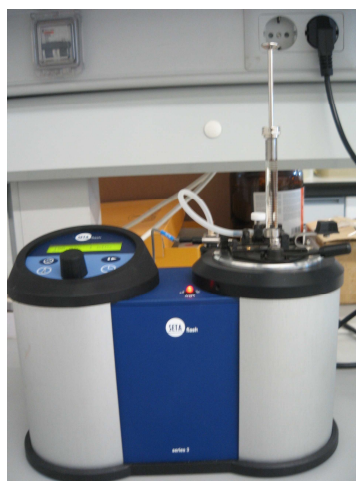


Figure A.4. Flash point closed cup tester.

COPPER CORROSION

Biodiesel copper corrosion was determined using a copper strip test according to the standard ISO 2160 (1998). The determination was made in a SETA copper corrosion bath model 11300-0, presented in Figure A.5, at 50 °C.

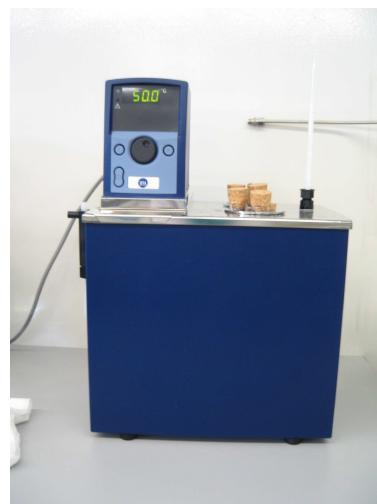
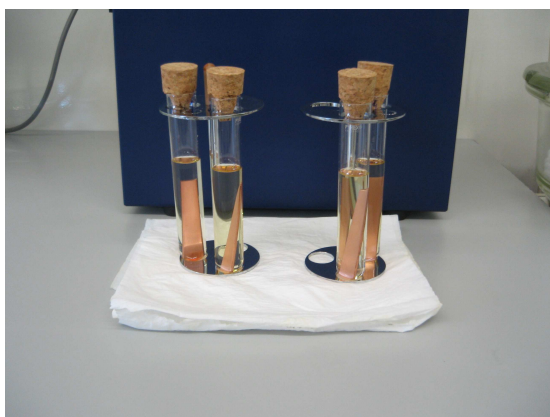


Figure A.5. Copper corrosion equipment.

WATER CONTENT DETERMINATION

For the water content determination in oils and animal fats the standard ISO 8534 (1996) was used whereas for the determination in biodiesel samples the standard NP EN ISO 12937 (2003) was used. The equipment used was a coulometric Karl Fischer titrator, KEM – Model MKC-501, presented in Figure A.6.



Figure A.6. Karl Fisher coulometric titrator.

METHYL ESTER AND LINOLENIC METHYL ESTER CONTENT/ IODINE VALUE

The biodiesel ester and linolenic acid methyl ester contents were determined by GC according to the standard EN 14103 (2003); GC analysis were also made to analyse biodiesel composition according to EN 14103 (2003) and NP EN ISO 5508 and for determination of biodiesel iodine value from ester content according to annex B of EN 14214 (2003). The equipment used was a Dani GC 1000 DPC gas chromatograph (DANI Instruments S.p.A.) presented in Figure A.7.



Figure A.7. Gas chromatograph and computer for data acquisition.

APPENDIX B DETERMINATION OF THE MEAN MOLECULAR WEIGHT OF TRIGLYCERIDES

Biodiesel is constituted by a mixture of fatty acid methyl esters. The ester composition varies in agreement with the fatty acids present in the triglyceride used for production.

Through the chromatographic analysis it is possible to know the methyl ester composition of the produced biodiesel and therefore its mean molecular weight.

Table B-1 presents an example of the methyl ester composition, obtained through GC, of a soybean oil methyl ester sample.

Table B-1: Methyl ester profile (wt.%) obtained from the transesterification of soybean oil and molecular weight (MW) of each ester.

METHYL ESTER	MOLECULAR FORMULA	CONTENT P_{ME} (wt.) ^{a)}	MW ^{b)} (g mol ⁻¹)
C16:0	CH ₃ COO - (CH ₂) ₁₄ -CH ₃	11.0	270.4
C18:0	CH ₃ COO - (CH ₂) ₁₆ -CH ₃	3.3	298.5
C18:1	CH ₃ COO - (CH ₂) ₇ CH=CH-(CH ₂) ₇ CH ₃	25.4	296.5
C18:2	CH ₃ COO - (CH ₂) ₇ CH=CH-CH ₂ - CH=CH(CH ₂) ₄ CH ₃	53.6	294.5
C18:3	CH ₃ COO - (CH ₂) ₇ CH=CH-CH ₂ -CH=CH- CH ₂ -CH=CH-CH ₂ -CH ₃	5.3	292.5
C20:0	CH ₃ COO - (CH ₂) ₁₈ -CH ₃	0.4	326.6
C20:1	CH ₃ COO - (CH ₂) ₇ CH=CH-(CH ₂) ₉ CH ₃	0.3	324.5
C22:0	CH ₃ COO - (CH ₂) ₂₀ -CH ₃	0.4	354.6
C22:2	CH ₃ COO - (CH ₂) ₇ CH=CH-CH ₂ - CH=CH(CH ₂) ₈ CH ₃	0.2	350.6
C24:0	CH ₃ COO - (CH ₂) ₂₂ -CH ₃	0.1	394.7

^{a)} P_{ME} – percentage of methyl ester; ^{b)} Considering the following molecular weights - C: 12.01 g mol⁻¹; H: 1.008 g mol⁻¹; O: 16.00 g mol⁻¹.

The mean molecular weight of methyl esters (MMW_{ME}) can be obtained using Equation B-1 deduced in the following way:

$$MMW_{ME} = \frac{w_{ME}}{\sum_{i=1}^n n_{ME_i}} = \frac{1}{n_{ME_1}/w_{ME} + n_{ME_2}/w_{ME} + n_{ME_3}/w_{ME} + \dots + n_{ME_n}/w_{ME}}$$

$$MMW_{ME} = \frac{1}{(w_{ME_1}/MW_{ME_1})/w_{ME} + (w_{ME_2}/MW_{ME_2})/w_{ME} + (w_{ME_3}/MW_{ME_3})/w_{ME} + \dots + (w_{ME_n}/MW_{ME_n})/w_{ME}}$$

$$MMW_{ME} = \frac{1}{A} \times 100; A = \frac{P_{ME_1}}{MW_{E1}} + \frac{P_{ME_2}}{MW_{E2}} + \frac{P_{ME_3}}{MW_{E3}} + \dots + \frac{P_{ME_n}}{MW_{En}} \quad (\text{Equation B-1})$$

Where:

MMW_{ME} – mean molecular weight of the methyl ester ($g\ mol^{-1}$);

W_{ME} – weight of the methyl ester (g);

n_{ME} – moles of methyl ester;

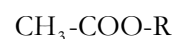
P_{ME} – percentage of methyl ester, by weight.

Applying Equation B-1 to the presented example (Table B-1), we have:

$$A = \frac{11.0}{270.4} + \frac{3.3}{298.5} + \frac{25.4}{296.5} + \frac{53.6}{294.5} + \frac{5.3}{292.5} + \frac{0.4}{326.6} + \frac{0.3}{324.5} + \frac{0.4}{354.6} + \frac{0.2}{350.6} + \frac{0.1}{394.7}$$

$$MMW_{ME} = 292.7\ g\ mol^{-1}$$

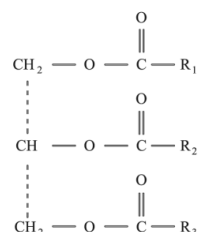
On the other hand, the methyl ester molecule can be generically represented by:



In the molecule, R represents the fatty acid radical that varies according to composition of the triglyceride. The molecular weight of the radical (MW_R) can be determined according to the following equation:

$$MW_R = MW_{ME} - MW_{C_2H_3O_2} = (MW_{ME} - 59.04)\ g\ mol^{-1} \quad (\text{Equation B-2})$$

On the other hand, the triglyceride molecule can be generically represented by:



Considering that $MW_{R1} = MW_{R2} = MW_{R3} = MMW_R$ (mean molecular weight of the radical); knowing the mean molecular weight of the radical we can then calculate the mean molecular weight of the triglyceride (MMW_{TG}). The MMW_{TG} can, therefore, be determined according to Equation B-3 which results from combining this assumption with Equation B-2.

$$MMW_{TG} = 3 \times MMW_R + MM_{C_6H_5O_6} = 3 \times MMW_R + 173 = 3 \times (MMW_{ME} - 59.04) + 173.1 = 3 \times MMW_{ME} - 4$$

$$MMW_{TG} = 3 \times MMW_{ME} - 4 \quad (\text{Equation B-3})$$

In the case of the present example we have:

$MMW_{TG} = 3 \times 292.7 - 4$; $MMW_{TG} = 874.1\ g\ mol^{-1}$; note that the slight difference between this result and the one presented in Table 2.1 ($874\ g\ mol^{-1}$), relates with rounding.

APPENDIX C USING CORRECTION FACTORS IN CHROMATOGRAPHIC ANALYSIS

The determination of the ester and linolenic methyl ester was made according to the European Standard EN 14103 (2003). This standard specifies the use of gas chromatography (GC) to obtain the peak area percentage of all FAME present in the sample using an internal standard and considering that the result calculation based on relative peak areas represents a percentage by mass. Therefore, the ester content (C), expressed as a mass fraction in percentage, is calculated according to Equation C-1.

$$C = \frac{(\sum_{i=1}^n A_i) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{w} \times 100 \quad (\text{Equation C-1})$$

Where,

$\sum_{i=1}^n A_i$ – total peak area from the methyl ester C_{14} to that in $C_{24:1}$;

A_{EI} – peak area corresponding to the internal standard - methyl heptadecanoate;

C_{EI} – concentration, in milligrams per millilitre, of the methyl heptadecanoate solution being used;

V_{EI} – volume, in millilitres, of the methyl heptadecanoate solution being used;

w – weight, in milligrams, of the sample.

Correction factors are used when: i) methyl esters with less than 8 carbon atoms, or methyl esters with secondary functions are present; ii) using thermal conductivity detectors and iii) less uncertainty is needed.

Therefore, with the objective of increasing the accuracy of the results, because the other cases do not apply to the produced biodiesel samples, the use of correction factors was evaluated according to the European Standard EN ISO 5508 (1996).

The correction factors were determined using a reference chromatogram, which resulted from analysing a reference mixture of fatty acid methyl esters, of known composition, under similar conditions as the samples.

Initially, one reference mixture was ordered (standard 1); however, due to the fact that difference between area percentage and mass percentage for the internal standard was higher than for the other FAME, another standard was ordered (standard 2) and results were afterwards compared. FAME mixtures from Supelco (Supelco 37 component fame mix) were used.

This standard consisted on a mixture of 37 FAME, in CH_2Cl_2 , with a concentration of 10 mg mL^{-1} . Regarding to GC analysis, a Dani GC 1000 DPC gas chromatograph (DANI Instruments S.p.A.), with an AT-WAX (Heliflex capillary, Alltech) column (30 m, 0.32 mm internal diameter and $0.25 \mu\text{m}$ film thickness) was used. The injector temperature was set at 250°C , while the detector (FID) temperature was set at 255°C . The carrier gas used was the N_2 with a flow of 2 mL min^{-1} . Injection was made in a split mode, using a split flow rate of 50 mL min^{-1} , the volume injected was $1 \mu\text{L}$ and the standard solution was injected without any dilution or treatment. The following temperature program was used: 120°C , heating at a rate of 4°C min^{-1} until 220°C and holding at that temperature for 10 min.

To determine the correction factors, the following procedure was used:

It is known, for a reference mixture, the mass percentage of each component (methyl ester)⁺⁺⁺; for component i , it is given by Equation C-2:

$$\left[\frac{w_i}{\sum_{i=1}^n w_i} \right] \times 100 \quad (\text{Equation C-2})$$

where,

w_i – weight of component i ;

$\sum w$ – sum of weights of all components of the reference mixture;

From the GC analysis it is then possible to calculate the relative percentage of the areas given by each component. For component i , it is given by:

$$\left[\frac{A_i}{\sum_{i=1}^n A_i} \right] \times 100 \quad (\text{Equation C-3})$$

where,

A_i – peak area corresponding to component i ;

$\sum_{i=1}^n A_i$ – sum of areas corresponding to all components of the reference mixture.

The correction factor could then be calculated using Equation C-4.

⁺⁺⁺ The standard has a composition certificate presenting the mass percentage for each FAME.

$$K_i = \frac{w_i}{\sum_{i=1}^n w_i} \times \frac{\sum_{i=1}^n A_i}{A_i} \quad (\text{Equation C-4})$$

Usually, correction factors are presented as standardised to K_{C16} . Therefore, correction factors are usually given by:

$$K'_i = \frac{K_i}{K_{C16}} \quad (\text{Equation C-5})$$

Because the determination method comprises the use of an internal standard, the correction factor should also be determined for the internal standard, being after designated as K'_s .

The weight percentage of component i might finally be obtained by applying the calculated correction factor, according to Equation C-6.

$$P\left(\frac{w_i}{w_t}\right) = \frac{w_s \times K'_i \times A_i}{w \times K'_s \times A_s} \times 100 \quad (\text{Equation C-6})$$

Where,

w_s – weight of the internal standard;

A_s – peak area corresponding to the internal standard;

w – weight of the sample.

The total mass percentage can finally be obtained from the sum of the mass percentage of each component present in the sample according to Equation C-7.

$$P(\text{FAME}) = P\left(\frac{m_i}{m_t}\right) + P\left(\frac{m_j}{m_t}\right) + P\left(\frac{m_k}{m_t}\right) + \dots \quad (\text{Equation C-7})$$

Figure C.1 shows the chromatogram obtained using the standard 1 and Figure C.2 shows the chromatogram obtained using the standard 2.

It can be seen that the first peaks have greater areas than the others of the same weight percentage (examples of the standard composition are further given in Table C-1 and Table C-2). These differences are mainly due to the temperature program used that is adjusted to determine from C14:0 to C24:1 (according to the EN 14103), but can also be attributed to retention mechanisms and the detector response.

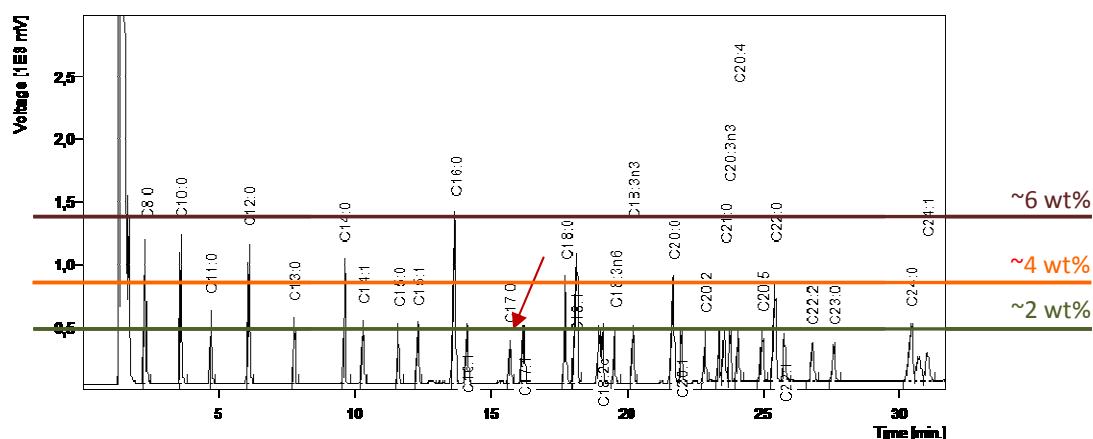


Figure C.1. Chromatogram resulting from analysing a reference mixture -standard 1- Supelco 31 FAME Mix; arrow indicates internal standard; lines show as indication approximately height levels for peaks concerning the wt.% of the FAMES in the mixture.

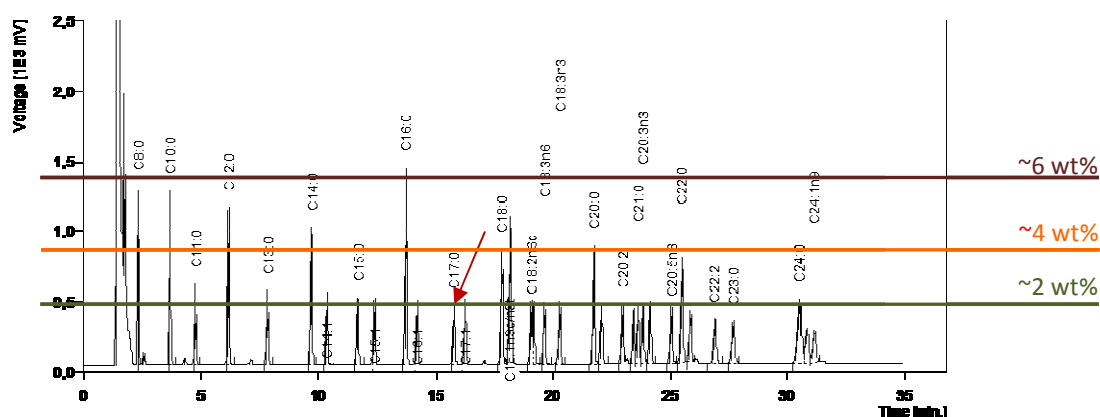


Figure C.2. Chromatogram resulting from analysing a reference mixture - standard 2 - Supelco 31 FAME Mix; arrow indicates internal standard, lines show as indication approximately height levels for peaks concerning the wt.% of the FAMES in the mixture.

For instance, if we compare with a chromatogram obtained from an initial temperature program of 50 °C (Figure C.3), it can be seen that there is apparently no such difference regarding the areas for these FAME (from C10:0 to C14:0).

Comparing the chromatograms in Figure C.1 and Figure C.2, it seems that the internal standard C17:0 peak is smaller than the ones showing similar weight percentage, specially regarding standard 1. However to confirm this fact, the correction factors were calculated, for FAME normally found in biodiesel samples used in this work (C16:0-C24:0) (Table C-1, Table C-2).

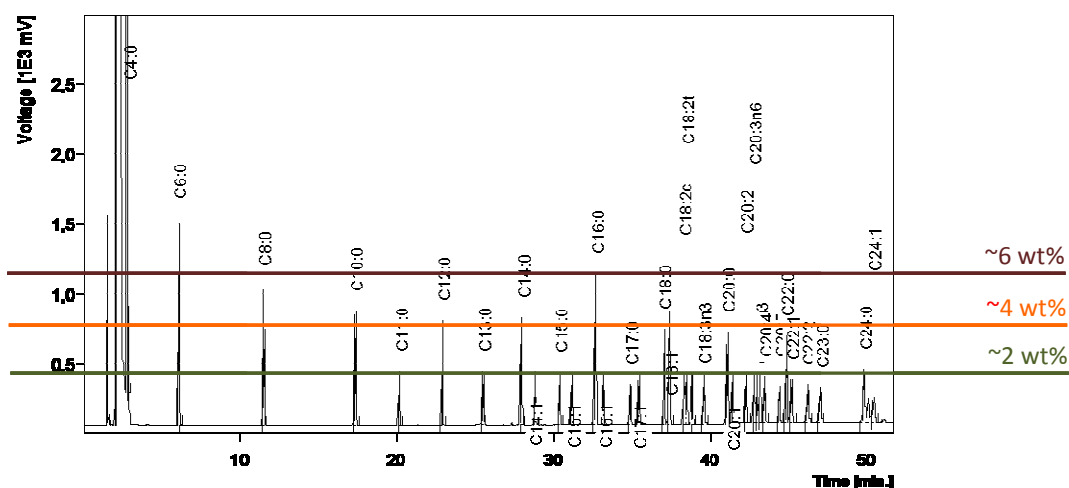


Figure C.3. Chromatogram resulting from analysing a reference mixture – standard 1 (Supelco 37 Component Fame Mix); Temperature program: 50 °C, holding for 2 min, heating at a rate of 4 °C min⁻¹ until 220 °C and holding at that temperature for 15 min.

Table C-1: Correction factors for reference mixture 1

FAME	AREA (mv.s)	CV (%) ^{a)}	Sup-37 (wt.%) ^{b)}	K _i	K'	K's
C16:0	7195.34	2.1	5.922	0.98	1.00	
C16:1	2313.22	2.1	1.977	1.02	1.04	
C17:0	1815.62	2.6	1.974	1.29		1.32
C18:0	4749.67	2.8	3.952	0.99	1.01	
C18:1	7238.36	2.5	6.152	1.01	1.03	
C18:2c	2333.53	1.8	1.995	1.02	1.04	
C18:3n6	2320.51	1.7	1.979	1.01	1.04	
C18:3n3	2329.89	2.1	1.980	1.01	1.03	
C20:0	4885.45	3.4	3.978	0.97	0.99	
C20:1	2391.90	3.1	1.978	0.98	1.00	
C20:2	2388.23	3.2	1.988	0.99	1.01	
C22:0	4882.63	3.6	3.985	0.97	0.99	
C22:2	2345.11	3.2	1.997	1.01	1.03	
C24:0	5033.11	3.9	4.069	0.96	0.98	
SUM	52222.58		43.93			

^{a)} CV –coefficient of variation; ^{b)} Sup-37 – percentages according to the standard certificate.

Table C-2: Correction factors for reference mixture 2

FAME	AREA (mv.s)	CV (%) ^{a)}	Sup-37 (wt.%) ^{b)}	K _i	K'	K's
C16:0	7067.382	0.9	5.989	1.01	1.03	
C16:1	2279.759	0.8	1.996	1.04	1.06	
C17:0	2188.637	0.6	2.003	1.09		1.11
C18:0	4694.492	0.8	4.015	1.02	1.04	
C18:1	7319.714	2.8	6.005	0.97	1.00	
C18:2c	2317.503	1.5	2.007	1.03	1.05	
C18:3n6	2306.576	0.6	2.012	1.04	1.06	
C18:3n3	2417.042	4.4	1.999	0.98	1.00	
C20:0	4840.09	1.1	4.001	0.98	1.00	
C20:1	2393.302	1.7	1.998	0.99	1.01	
C20:2	2296.145	1.5	1.997	1.03	1.05	
C22:0	4767.925	0.3	3.995	0.99	1.02	
C22:2	2325.725	1.6	2.001	1.02	1.04	
C24:0	5025.623	2.5	3.999	0.94	0.97	
SUM	52239.92		44.02			

^{a)} CV –coefficient of variation; ^{b)} Sup-37 – percentages according to the standard certificate.

The calculation was made using an average area resulting from three injections with results showing a coefficient of variation (CV) smaller than 5%. From these Tables, it can be observed that K' values are the highest for the internal standard, and different for both standards.

To be sure that the problem was not related with the method or the operator, reference standard 1 was also analysed in other lab, using different equipment and operator.

These analysis were made at the Bromatology Laboratory (Faculty of Pharmaceutical Sciences of Oporto University), in a GC-FID, with a CP-Sil 88 column, 50 m, using the following temperature program: 140 °C, holding for 5 min, heating at a rate of 4 °C min⁻¹ until 220 °C and holding at that temperature for 12 min. Results are presented in Table C-3.

These analysis were made to confirm if the results for C17:0 were different than for the other FAME; however, because a different temperature program was used, comparison between each K' was not made. It can be however verified that for C17:0 K' was very high.

Afterwards, in order to evaluate the difference between using both standards and considering that differences between wt.% according to the certificate of composition of both standards were less than 0.1%, the mean peak areas of each FAME considering both samples were calculated (Table C-4).

Table C-3: Results for the analysis of the reference mixture 1 at an external laboratory

Fame	Area	Sup-37 (wt.%)^{a)}	K_i	K'	K's
C16:0	297039	5.922	1.06	1.00	
C16:1	93838.5	1.977	1.13	1.06	
C17:0	77686	1.974	1.36		1.27
C18:0	215475	3.952	0.98	0.92	
C18:1	325522.5	6.152	1.01	0.95	
C18:2c	104884.5	1.995	1.02	0.95	
C18:3n6	103007.5	1.979	1.03	0.96	
C18:3n3	100956.5	1.980	1.05	0.98	
C20:0	228828	3.978	0.93	0.87	
C20:1	107609.5	1.978	0.98	0.92	
C20:2	111988.5	1.988	0.95	0.89	
C22:0	232142	3.985	0.92	0.86	
C22:2	111988.5	1.997	0.95	0.89	
C24:0	233840.5	4.069	0.93	0.87	

^{a)} Sup-37 – percentages according to the standard certificate.

Table C-4: Mean area of FAME using both standards

FAME	MEAN AREA (mv.s)	CV (%)^{a)}
C16:0	7131.36	1.8
C16:1	2296.49	1.6
C17:0	2002.13	10.3
C18:0	4722.08	2.0
C18:1	7279.04	2.5
C18:2c	2325.52	1.5
C18:3n6	2313.54	1.2
C18:3n3	2373.47	3.7
C20:0	4862.77	2.3
C20:1	2392.60	2.3
C20:2	2342.19	3.1
C22:0	4825.28	2.7
C22:2	2335.42	2.3
C24:0	5029.37	3.0

^{a)} CV –coefficient of variation

The CV was calculated for each FAME and it was verified that it was always below 3.7%, except for the FAME C17:0, which was 10.3%. This shows that similar results were obtained for all FAME using both standards, except for C17:0.

Such difference could probably be related with error during preparation of the first standard used, considering C17:0.

However, taking into account that $K=1$ is obtained when there is no difference between the results (%) considering area or weight, the biggest difference is still found for C17:0, and even for standard 2 is high; such difference should be reflected in the final results.

To see how much such corrections would affect the results, the ester content of one biodiesel sample was calculated. Biodiesel sample was obtained from the transesterification of soybean oil and the sample preparation consisted of weighting approximately 250 mg of sample and then adding 5 mL of a methyl heptadecanoate solution (10 mg mL^{-1} in heptane); 1 μL of a diluted sample (8:1) was injected. Table C-5 shows the mean areas of the FAME identified in the sample as well as the coefficient of variation.

Table C-5: Mean area for FAME of one biodiesel sample

FAME	MEAN AREA (mv.s)	cv (%) ^{a)}
C16:0	2897.65	2.16
C17:0	10585.17	0.34
C18:0	2059.91	1.00
C18:1	17844.66	1.34
C18:2	26921.77	1.64
C18:3n3	59.75	2.61
C20:0	137.78	0.23
C20:1	90.51	0.73
C22:0	357.14	0.83
C24:0	106.08	2.73

^{a)} CV –coefficient of variation

The ester content was after calculated using Equation C-7 and considering the correction made with standard 1 and 2, with standard 1 and 2 but excluding C17:0 correction and with no calibration. Table C-6 shows the results.

Table C-6: FAME content (wt.%) of one biodiesel sample considering no calibration, calibration using both standards with and without internal standard correction

CALIBRATION	ESTER CONTENT (wt.%) ^{a)}
No calibration	95.6
Calibration using standard 1	74.8
Calibration using standard 1 excluding C17:0 correction	96.1
Calibration using standard 2	88.6
Calibration using standard 2 excluding C17:0 correction	95.7

^{a)} Coefficient of variation 1.4% in all cases

From the results it is clear a great difference between calibrating using standard 1 or 2 when considering the internal standard peak (C17:0).

Because there is no reasonable explanation for this difference only for this FAME, a defect in the standard considering the C17:0 was considered and calibration excluding C17:0 correction was evaluated. Using this calibration, results obtained using both standards and without calibration were similar. For this reason, no correction was considered throughout the studies.

APPENDIX D LITERATURE REVIEW CONCERNING BIODIESEL PRODUCTION THROUGH HETEROGENEOUS CATALYSIS

Table D-1: Calcium derived heterogeneous catalysts for biodiesel production

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
CaO ^{a)}	Commercial CaO dipped into an ammonium carbonate solution, stirred, dried, milled and calcined at high temperature for 1.5 h.	0.5 – 2.5 wt.% catalyst 6:1-15:1 methanol/oil molar ratio 70 °C 2.5 h	- Conversion from 80 to 93 wt.%; - Maximum conversion was obtained using 70 °C, 2.5 h, 1.5 wt.% catalyst and 9:1 molar ratio.	- The dosage of catalyst was the most notable factor; >6:1 molar ratio little effect was noticed.
CaO ^{b)}	- CaO (up to 99.9 purity) without treatment; - Activation made by pre-treatment with methanol: 1.5 h activation time at room temperature.	0.7 wt.% catalyst 26 wt.% methanol 60 °C 3 h	90 wt.% yield; - By activation CaO was converted into Ca(OCH₃)₂ which acted as an initiating reaction reagent; - Glycerine is produced and so is a calcium–glycerin complex, by reaction of CaO with glycerine), which functions as the main catalyst.	CaO activated with methanol was an efficient catalyst for a high-yield transesterification reaction.
CaO Ca(OH) ₂ CaCO ₃ ^{c)}	- CaO: Calcination of pulverized CaCO₃ at 900 °C, 1.5 h in a helium gas flow - MgO and SrO were used as reference	14 mmol catalyst: 0.78 g CaO in 100 mL 12:1 methanol/oil molar ratio - N₂ gas flow 2-4 h	Biodiesel yields were 93 wt.% using CaO, 12 wt % using Ca(OH)₂ and no conversion was observed using CaCO₃ in 1 h reaction.	- MgO was not active; - Using CaO: transesterification of WFO (5.1 mg KOH/g) showed yield above 99% in 2 h; - Some catalyst changed into calcium soap by reaction with free fatty acids.

^{a)} Huaping, Z., Zongbin, W., Yuanxiong, C., Ping, Z., Shijie, D., Xiaohua, L. and Zongqiang, M. (2006). *Preparation of Biodiesel Catalyzed by Solid Super Base of Calcium Oxide and Its Refining*; ^{b)} Kawashima, A., Matsubara, K. and Honda, K. (2009). *Acceleration of catalytic activity of calcium oxide for biodiesel production*. *Bioresource Technology* **100** (2): 696-700. *Process. Chinese Journal of Catalysis* **27** (5): 391-396; ^{c)} Kouzu, M., Kasuno, T., Tajika, M., Sugimoto, Y., Yamanaka, S. and Hidaka, J. (2008). *Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production*. *Fuel* **87** (12): 2798-2806.

Table D-1: Calcium derived heterogeneous catalysts for biodiesel production (*continued*)

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
$\text{Ca}(\text{OCH}_3)_2$ ^{d)}	- Direct reaction of calcium with methanol in a slurry reactor at 65 °C for 4 h; - Dried at 105 °C (1 h) and removal of most methanol by filtration.	0.5 – 4 wt.% catalyst 1:1 vol.% methanol to oil - Catalyst first dispersed in methanol and after the SBO was added 900 rpm 40-65 °C 3 h	98 wt.% yield within 2 h when using 4 wt.% catalyst.	- Calcium methoxide had excellent catalytic activity and stability; - Optimal conditions: 1:1 vol.% methanol to oil, 2 wt.% $\text{Ca}(\text{OCH}_3)_2$, 65 °C and 2 h.
CaO ^{e)}	Commercial	- Catalyst was first dispersed in methanol and after the SBO was added 800 rpm 3:1-18:1 methanol/oil molar ratio 50-80 °C 3 h	- Optimum conditions: 12:1 methanol/oil molar ratio, 8 wt.% CaO, 65 °C and 2.03% water content in methanol - Biodiesel yield exceeded 95% at 3 h.	CaO maintained sustained activity for 20 cycles and biodiesel yield at 1.5 h was not affected.
$\text{Ca}(\text{OCH}_2\text{CH}_3)_2$ ^{f)}	- Calcium was dispersed in ethanol under magnetic stirring, and heated to 65 °C; - After 8 h of reaction, ethanol was distilled at reduced pressure and the catalyst was dried at 105 °C for 1 h.	0.25-4.0% catalyst 3:1-15:1 methanol/oil molar ratio 800 rpm 30-65 °C 3 h	- Optimum conditions: 3 wt.% catalyst, 12:1 methanol/oil molar ratio and 65 °C; 95.0 wt.% biodiesel yield within 1.5 h.	91.8% yield obtained using SBO and ethanol; - Biodiesel yield increased with increasing catalyst amount and a 95.0% biodiesel yield was obtained by using 4.0 wt.% catalyst.

^{d)} Liu, X., Piao, X., Wang, Y., Zhu, S. and He, H. (2008). *Calcium methoxide as a solid base catalyst for the transesterification of soybean oil to biodiesel with methanol*. Fuel **87** (7): 1076-1082.; ^{e)} Liu, X. J., He, H. Y., Wang, Y. J., Zhu, S. L. and Piao, X. L. (2008). *Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst*. Fuel **87** (2): 216-221.; ^{f)} Liu, X. J., Piao, X. L., Wang, Y. J. and Zhu, S. F. (2008). *Calcium ethoxide as a solid base catalyst for the transesterification of soybean oil to biodiesel*. Energy & Fuels **22** (2): 1313-1317.

Table D-1: Calcium derived heterogeneous catalysts for biodiesel production (*continued*)

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
CaO supported on porous silica ^{g)}	▪ Siliceous supports: fumed silica and two mesoporous silica-based materials, SBA-15 and MCM-41 which presented high specific surface areas: SBA-15: 5 g of Pluronic 123 polymer was dissolved in 200 mL of a 0.4 M H₂SO₄ stirred at ambient temperature during 1 day; 0.2 g NaOH, 197.3 mL sodium silicate aqueous solution were added stirred and aged at room temperature for 5 days. Product was filtered, washed, dried and calcined at 823 K for 6 h; MCM-41 silica: according to Fuentes-Perujo et al. (2006) ^{h)}; Fumed silica: commercial. ▪ Different supports were impregnated using the incipient wetness method with solutions of calcium acetate. The amount of calcium oxide incorporated ranged between 4 -20 wt.%; ▪ Activation of catalysts at 1073 K.	▪ 0.4 – 1.6 wt.% catalyst ▪ 2:1 – 11:1 methanol/oil molar ratio ▪ 1250 rpm ▪ 25-60 °C ▪ 1 h ▪ Inert atmosphere (N₂) ▪ Transesterification of ethyl butyrate and after of vegetable oils	▪ Methanol/oil molar ratio was the main factor; ▪ A sample containing 14 wt.% of CaO supported on SBA-15 was the most active; ▪ Transesterification activity of vegetable oils confirmed the results obtained with ethyl butyrate; ▪ SFO conversion was 95% after 5 h and for castor oil was 65% after 1 h of reaction.	▪ Without activation all catalysts were inactive in the transesterification of ethyl butyrate with methanol; ▪ Maximum conversion was attained after activation at 1073 K; ▪ Unlike commercial CaO, no lixiviation of the active phase was detected in the reaction medium.

^{g)} Albuquerque, M. C. G., Jiménez-Urbistondo, I., Santamaría-González, J., Mérida-Robles, J. M., Moreno-Tost, R., Rodríguez-Castellón, E., Jiménez-López, A., Azevedo, D. C. S., Cavalcante Jr, C. L. and Maireles-Torres, P. (2008). *CaO supported on mesoporous silicas as basic catalysts for transesterification reactions*. Applied Catalysis A: General **334** (1-2): 35-43.; ^{h)} D. Fuentes-Perujo, J. Santamaría-González, J. Mérida-Robles, E. Rodríguez-Castellón, A. Jiménez-López, P. Maireles-Torres, R. Moreno-Tost and R. Mariscal, *J. Solid State Chem.* **179** (2006), p. 2182.

Table D-1: Calcium derived heterogeneous catalysts for biodiesel production (*continued*)

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
Activated CaO ¹⁾	- CaO: supplied as a fine powder (Aldrich, 99.9% of the metallic atoms are Ca), 10% of the weight was lost by calcination at 1000 °C (previously partially carbonated and hydrated); - CaO was stored under vacuum in a desiccator with silica gel and KOH pellets, to remove the H₂O and CO₂ of the residual desiccator atmosphere; - Activation: outgassing at temperatures > 973 K.	- Approximately 1% catalyst 13:1 methanol/oil molar ratio 1000 rpm 60 °C	- CaO was rapidly hydrated and carbonated by contact with room air (few minutes); - CO₂ was the main deactivating agent; - The surface of the activated catalyst was an inner core of CaO particles covered by very few layers of Ca(OH)₂; - Activation was required to revert the CO₂ poisoning; - The catalyst could be reused for several runs; - The catalytic reaction had heterogeneous and homogeneous contributions; 94 wt.% yield for the first run (CaO outgassed at 973 K), other runs 80 wt.%.	Part of the reaction takes place on basic sites at the surface of the catalyst, the rest is due to the dissolution of the activated CaO in methanol that creates homogeneous leached active species.

¹⁾ Granados, M. L., Poves, M. D. Z., Alonso, D. M., Mariscal, R., Galisteo, F. C., Moreno-Tost, R., Santamaría, J. and Fierro, J. L. G. (2007). *Biodiesel from sunflower oil by using activate calcium oxide*. Applied Catalysis B: Environmental **73** (3-4): 317-326.

Table D-1: Calcium derived heterogeneous catalysts for biodiesel production (*continued*)

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
CaO and Mg supported on Al ₂ O ₃ ^{j)}	▪ MgO and CaO supported on Al₂O₃ were synthesized using a modified single step sol-gel method: To prepare 80 wt.% CaO on Al₂O₃: aluminum isopropoxide water and HNO₃ were mixed at 85 °C under total reflux for 1 h and calcium nitrate tetrahydrate was added. Excess water was removed to obtain the mixed oxide gel; Gels were dried at 120 °C, 18 h and then calcined at 500 °C for 6 h. Catalysts were finally ground and sieved, then stored in desiccators. To synthesize MgO on Al₂O₃ catalyst, magnesium nitrate hexahydrate was used as the precursor for MgO: Pure MgO was prepared by precipitating magnesium nitrate (pH 9) with NH₄OH and washed with deionized water for several times, before applying the same heat treatment procedure used for the gels. ▪ CaO: commercial.	▪ 2 wt.% catalyst ▪ 6:1 - 30:1 methanol/oil molar ratio ▪ 50 °C ▪ 4 h ▪ 1100 rpm	▪ Pure CaO and MgO were not active and CaO/ Al₂O₃ catalyst showed the highest activity; ▪ Not only the basic site density but also the basic strength was important to achieved high biodiesel yield; ▪ Biodiesel yield over 80 wt.% CaO/Al₂O₃ catalyst increased to 97.5% from 23% when methanol/oil molar ratio was 30:1.	▪ Transesterification of green microalgae <i>Nannochloropsis oculata</i>; ▪ Microalgae extraction: The wet paste collected by centrifuging was dried at 60 °C under vacuum of 100 mbar for 12 h; Microalgae lipid was extracted with hexane in a Soxhlet extractor at 80 °C for 10 h.

^{j)} Umdu, E. S., Tuncer, M. and Seker, E. (2009). *Transesterification of Nannochloropsis oculata microalgae's lipid to biodiesel on Al₂O₃ supported CaO and MgO catalysts*. Bioresource Technology **100** (11): 2828-2831.

Table D-1: Calcium derived heterogeneous catalysts for biodiesel production (*continued*)

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
Waste eggshell ^{k)}	Eggshell was rinsed with deionised water, dried at 100 °C for 24 h, crushed and calcined (200 - 1000 °C) for 2 h under static air.	3 wt.% catalyst 9:1 methanol/oil molar ratio 65 °C 3h (maximum yield) - vigorous stirring	- Highly active, reusable solid catalyst was obtained; - Yield increased with increasing methanol/oil molar ratio being higher above 9:1; - When a small amount of catalyst (<1 wt.%) was used, the maximum product yield could not be reached. Yield increased when catalyst concentration increased up to 3 wt.%; - More than 10 wt.% catalyst led to slurry (mixture of catalyst and reactants); - Optimum conditions (yield exceeded 95 wt.%): 9:1 methanol/oil molar ratio , 3 wt.% catalyst (calcined at 1000 °C), 65 °C, 3 h.	- CaO was the active phase of the eggshell derived catalysts; - Calcinations below 600 °C did not lead to the formation of CaO; - Best catalytic performance was obtained for calcination > 800 °C (crystalline CaO); - Samples calcined at 700 °C for 2 h contain CaCO₃ as the major phase and CaO as a minor phase, hence middle yield was obtained.

^{k)} Wei, Z., Xu, C. and Li, B. (2009). *Application of waste eggshell as low-cost solid catalyst for biodiesel production*. Bioresource Technology **100** (11): 2883-2885.

Table D-1: Calcium derived heterogeneous catalysts for biodiesel production (*continued*)

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
Ca(OCH ₃) ₂ MgOx(OCH ₃) _{2-2x} ¹⁾	▪ Powder of MgO_x(OCH₃)_{2-2x} was prepared from magnesium methoxide solution in methanol by vacuum evaporation in a rotary evaporator for 2 h at 60 °C; ▪ Commercial Ca(OCH₃)₂.	▪ Approximately 17:1 molar ratios of tributyrin to magnesium or calcium catalysts ▪ 6:1 molar ratio of methanol to tributyrin ▪ 60 °C	▪ Pre-dissolved in methanol, magnesium methoxide was a powerful homogeneous catalyst for tributyrin transesterification; ▪ The reaction started as a heterogeneous but interaction of Ca(OCH₃)₂ with reaction products such as glycerol gave rise to catalytically active homogeneous species; ▪ The formation of glycerin renders homogeneous magnesium methoxide and led to a precipitate of complex composition containing derivatives of glycerol, mono-, dibutyrin and butyric acid.	▪ Transesterification of tributyrin with methanol; ▪ Formed in a side reaction, calcium butyric acid derivatives contributed to Ca(OCH₃)₂ dissolution, but do not deactivate the surface of the catalyst.

¹⁾ Martyanov, I. N. and Sayari, A. (2008). *Comparative study of triglyceride transesterification in the presence of catalytic amounts of sodium, magnesium, and calcium methoxides*. Applied Catalysis A: General **339** (1): 45-52.

Table D-2: Heterogeneous catalysts containing NaOH/KOH for biodiesel production

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
NaOH supported on alumina ^{m)}	- Preparation by incipient wetness impregnation of the 212–300 µm size fraction of commercial alumina : Aqueous NaOH solutions were slowly added to the support; The catalytic carrier was previously calcined in a muffle for 12 h at 773 K. - After impregnation the catalysts were dried for 12 h at 393 K under reduced pressure (10 kPa); - A part of the dried catalysts was treated in a muffle at 673 K for 12 h.	0.1 or 0.05 wt.% catalyst using 6:1 methanol/oil molar ratio 0.1 or 0.2 wt.% catalyst using 12:1 methanol/oil molar ratio 50 °C - Up to 24 h - Inert atmosphere (N₂)	- Transesterification rate depended on the catalyst/methanol ratio, whereas reaction selectivity was governed by the methanol/oil molar ratio; - Calcination of the NaOH/Al₂O₃ catalysts had a negative effect on their activity; - Performance of NaOH/alumina catalysts just dried at 393 K was not far of that of homogeneous NaOH.	Measurements of sodium leached during the progress have evidenced some lack of chemical stability of the supported NaOH catalysts under the reaction conditions studied.
NaX zeolites loaded with KOH ⁿ⁾	- Commercial NaX zeolite was oven dried at 383 K for 2 h; - Modified NaX catalysts with different KOH loadings; NaX zeolite was impregnated with an aqueous solution of KOH. Samples with various KOH loadings were impregnated for 24 h; The pretreated samples were dried via rotary evaporation and then heated in an oven at 393 K for 3 h before use.	1 - 6 wt.% catalyst 4:1-16:1 methanol/oil molar ratio 2-8 h 200 and 800 rpm	- At lower stirring speed, the oil conversion reached 68.7% after 8 h, whereas at 800 rpm the oil conversion reached 85.6% at the identical conditions; - Increased catalyst amount from 1% to 3% resulted increased conversion of methyl esters from 33.4% to 85.6%; however, with further increase in the catalyst amount, the conversion was decreased, possibly due to a mixing problem of reactants, products and solid catalyst; - For methanol/oil molar ratio close to 10:1 the conversion reached the maximum (85.6%); - The loading of KOH on the NaX zeolite resulted in an increase in the basic strength over the parent NaX zeolite.	An efficient mixing of the reagents was essential to reach high conversion.

^{m)} Arzamendi, G., Campo, I., Arguiñarena, E., Sánchez, M., Montes, M. and Gandía, L. M. (2007). *Synthesis of biodiesel with heterogeneous NaOH/alumina catalysts: Comparison with homogeneous NaOH*. Chemical Engineering Journal **134** (1-3): 123-130. ⁿ⁾ Xie, W., Huang, X. and Li, H. (2007). *Soybean oil methyl esters preparation using NaX zeolites loaded with KOH as a heterogeneous catalyst*. Bioresource Technology **98** (4): 936-939.

Table D-2: Heterogeneous catalysts containing NaOH/KOH for biodiesel production (*continued*)

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
Metal catalysts supported on NaX faujasite zeolite and ETS-10 zeolite ^{a)}	- Zeolites were exchanged with potassium, cesium, NaX containing occluded sodium oxide and occluded sodium azide. The catalysts were calcined at 500 °C prior to use in order to increase activity; (Note: ETS10: new microporous inorganic titanium containing zeolite) - Immediately prior to use, the zeolites were placed in small stainless steel pans and were heated in air from room temperature to 500 °C at 1 °C/min in the Fisher Isotemp® muffle furnace and held at that temperature for 4 h. - NaO_x/NaX catalysts were pre-treated at similar conditions in a thermogravimetric analyzer operated under inert nitrogen atmosphere; - While still warm, approximately 0.03 g of freshly calcined catalyst was immediately transferred into the glass vials and filled with reactants.	0.03 g catalyst/0.3 mL SBO 6:1 methanol/oil molar ratio 60, 120 and 150 °C 24 h	- Increased conversions were attributed to the higher basicity of ETS-10 zeolites and larger pore structures that improved intra-particle diffusion; - Methyl ester yield increased with an increase in temperature from 60 to 150 °C; - Due to low conversions without pre-treatment at 500 °C, prior to use the reactions were repeated with the catalysts pre-treated at 500 °C for 4 h, the conversions were after much higher; - Nickel presented the highest activity amongst the metals evaluated and potentially could be configured to promote commercial reactions.	The catalyst was reused without observed loss of activity.

^{a)} Suppes, G. J., Dasari, M. A., Doscocil, E. J., Mankidy, P. J. and Goff, M. J. (2004). *Transesterification of soybean oil with zeolite and metal catalysts*. Applied Catalysis A: General **257** (2): 213-223.

Table D-2: Heterogeneous catalysts containing NaOH/KOH for biodiesel production (*continued*)

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
KOH loaded on Al ₂ O ₃ and NaY zeolite supports ^{b)}	▪ KOH/ Al₂O₃ catalyst: Prepared with varying KOH loadings (10, 15, 20, 25, 30, and 35 wt.%); Impregnation of Al₂O₃ support with aqueous solution of KOH, dried in a oven at 110 °C for 24 h and calcined at 500 °C for 3 h. ▪ KOH/NaY zeolite catalyst: Zeolite was dried in a oven at 110 °C for 2 h to remove the absorbed water on the surface; NaY zeolite was impregnated with an aqueous solution of KOH with various loadings (8, 9, 10, 13, 15 wt.%) for 24 h; finally, it was dried in air at 110 °C for 24 h.	▪ Reference conditions 3 and 6 wt.% of the catalyst (20 wt.% KOH/ Al₂O₃, 10 wt.% KOH/NaY) 15:1 methanol/oil molar ratio 60 °C 1-6 h 300 rpm	▪ Optimum conditions: KOH/ Al₂O₃: 2 h reaction time, 25 wt.% KOH/ Al₂O₃, 15:1 methanol/oil molar ratio, 300 rpm stirrer speed, and 60 °C, yield of 91.07% was obtained; KOH/NaY: 3 h reaction time, 10 wt.% KOH/NaY, 15:1 methanol to oil molar ratio, 300 rpm stirrer speed, and 60 °C, yield of 91.07% was obtained. ▪ Using the optimum conditions, about 51.26 and 3.18% of the K was leached from 25 wt.% KOH/Al₂O₃ and 10 wt.% KOH/NaY, respectively; ▪ The 10 wt.% KOH/NaY should be proper for the transesterification reaction since the amount of K in the fresh catalyst was about the same as in the used catalyst.	▪ Palm oil was used; ▪ The type of support strongly affects the activity and leaching of the active species of the catalyst.

^{b)} Noiroj, K., Intarapong, P., Luengnaruemitchai, A. and Jai-In, S. (2009). *A comparative study of KOH/Al₂O₃ and KOH/NaY catalysts for biodiesel production via transesterification from palm oil*. Renewable Energy **34** (4): 1145-1150.

Table D-3: Heterogeneous catalysts containing zirconia (ZrO₂) for biodiesel production

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
Sulfated Zirconia ^{a)}	- Conventional zirconia (ZrO₂): Calcination of zirconium oxychloride hydrate for 5 h at 600 °C. - Solvent-free preparation according to the procedure by Sun et al. (2005) ^{b)}: ZrOCl₂·8H₂O and (NH₄)₂SO₄, in a molar ratio of 1:6, were ground in an agate mortar for 20 min at room temperature (25 °C); After standing for 18 h at room temperature in air, the sample was calcined for 5 h at 600 °C. - Standard sulfated zirconia: Precipitation of zirconium oxychloride hydrate ZrOCl₂·8H₂O with ammonium hydroxide at pH 8.5. The resulting ZrO₂·xH₂O was thoroughly washed with water to remove chloride salts, dried for 24 h at 100 °C, and ground to a powder. The powder was then sulfated by impregnation with 15 mL of 0.5 mol/L H₂SO₄ per gram of powder for 24 h, followed by drying for 24 h at 100 °C and calcination in air at 650 °C for 4 h to produce SO₄/ZrO₂.	1, 2.5, 5, 10 wt.% catalyst 1:20 methanol/oil molar ratio 85, 100, 120, 150 °C 0.5, 1 and 2 h	- Sulfated zirconia, synthesized by a solvent-free method (S-ZrO₂), was very active in the transesterification of SBO and the esterification of fatty acids; - Under optimized conditions (120 °C, 1 h, 5 wt.% catalyst) conversions were 98.6% (methanolysis) and 92% (ethanolysis) with an immediate separation of the glycerine; - However, S-ZrO₂ is rapidly deactivated and this aspect must be further evaluated.	Zirconia sulphated by standard methods had low activity (conversion of 8.5%) and conventional zirconia was inactive.

^{a)} Garcia, C. M., Teixeira, S., Marciniuk, L. L. and Schuchardt, U. (2008). *Transesterification of soybean oil catalyzed by sulfated zirconia*. Bioresource Technology **99** (14): 6608-6613.;

^{b)} Sun et al., 2005 Y. Sun, S. Ma, Y. Du, L. Yuan, S. Wang, J. Yang, F. Deng and F.-S. Xiao. (2005). Solvent-free preparation of nanosized sulfated zirconia with Brønsted acidic sites from a simple calcination. Journal of Physical Chemistry B **109**: 2567–2572.

Table D-3: Heterogeneous catalysts containing zirconia (ZrO₂) for biodiesel production (*continued*)

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
Modified Zirconia ^{c)}	- Commercially available amorphous precursors were used: sulfated zirconia (XZO1249) (SZ), tungstated zirconia (XZO1251) (WZ) and titanium zirconia (TiZ); - The amorphous samples were dehydrated at 120 °C for 1 h and then calcined in a furnace at different temperatures (400–900 °C) using flowing air.	0.09-0.1 g/mL catalyst 7.1-9.1 mol/L ethanol 75-120 °C	- SZ catalyst was found to be the most active for esterification and transesterification but its activity was not easily regenerated; - TiZ showed greater activity than WZ for transesterification, the opposite result was found for esterification; - The higher activity of TiZ towards transesterification was suggested to be due to its basic sites, which are likely poisoned in the presence of the carboxylic acid during esterification; - WZ was found to be the most suitable of these catalysts for carrying the reactions, being more active than TiZ for esterification and more easily regenerated than SZ by simple re-calcination in air; - For reaction of oleic acid and a triglyceride (tricaprylin) mixture on WZ, conversion of both reactants occurred simultaneously. The conversion of tricaprylin proceeds not only by transesterification but also by hydrolysis (due to the by-product water from esterification of oleic acid) followed by esterification.	Catalysts were evaluated for both esterification and transesterification reactions.

^{c)} López, D. E., Goodwin Jr, J. G., Bruce, D. A. and Furuta, S. (2008). *Esterification and transesterification using modified-zirconia catalysts*. Applied Catalysis A: General **339** (1): 76-83.

Table D-3: Heterogeneous catalysts containing zirconia (ZrO₂) for biodiesel production (*continued*)

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
Tungstated zirconia ^{d)}	- Amorphous tungstated zirconia hydroxide precursor was used: XZO1251 (16 wt% WO₃); - To activate the catalyst, samples were dehydrated at 120 °C for 1 h and pre-treated for 3 h under an air atmosphere in a furnace at calcination temperatures between 400 and 900 °C.	2 wt.% catalyst 100% excess methanol 60, 120 °C 2 h 1790 rpm	- Transesterification of triacetin with methanol at 60 °C and esterification of acetic acid with methanol at 60 °C and 120 °C (gas phase) were investigated; a strong influence of calcination temperature on the activity for both reactions was found; - Optimum calcination temperature was 800 °C.	For the catalyst that exhibited the optimum catalytic activity, selective poisoning of the potential catalytic centers revealed that Brønsted sites play the major role in carrying out these reactions.
Mg/Zr catalysts ^{e)}	- Catalysts with different Mg/Zr ratios (1:1, 2:1, 3:1 wt.%) were prepared by co-precipitation method - Required amounts of Mg(NO₃)₂ and ZrO (NO₃)₃ were dissolved in deionised water; - Two precursor solutions were mixed homogeneously and allowed to precipitate using a basic solution of 1 M KOH and 0.25 M K₂CO₃ at a pH of 10; - After precipitation, the precipitate was filtered and washed with water - The resultant catalyst was oven dried at 120 °C for 12 h and calcined at 650 °C for 4 h.	2.5 - 10 wt.% catalyst 25:1-55:1 methanol/oil molar ratio 65 °C	- The transesterification activity depended upon the number and strength of basic sites in the catalysts; - High activity of Mg/Zr catalyst with 2:1 ratio was due to the presence of strong basic sites generated by the strong interaction of zirconia with magnesia; - The catalyst tolerates the presence of free fatty acid and water during transesterification to produce biodiesel; - The rate of transesterification reaction increases with the decrease in the weight of the catalyst from 10 wt.% to 2.5 wt.%, showing that at lower catalyst amounts the catalyst was very active.	- Room temperature transesterification of edible and non-edible oils; - Progress of the reaction was monitored by thin layer chromatography.

^{d)} López, D. E., Suwannakarn, K., Bruce, D. A. and Goodwin Jr, J. G. (2007). *Esterification and transesterification on tungstated zirconia: Effect of calcination temperature*. Journal of Catalysis **247** (1): 43-50.; ^{e)} Sree, R., Seshu Babu, N., Sai Prasad, P. S. and Lingaiah, N. (2009). *Transesterification of edible and non-edible oils over basic solid Mg/Zr catalysts*. Fuel Processing Technology **90** (1): 152-157.

Table D-3: Heterogeneous catalysts containing zirconia (ZrO₂) for biodiesel production (*continued*)

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
Zirconia-supported isopoly and heteropoly tungstates ^{f)}	The isopoly and heteropoly tungstate catalysts were prepared by suspending zirconium oxyhydroxide in water/methanol solution of ammonium metatungstate/silicotungstic acid and phosphotungstic acid followed by drying and calcination at 750 °C.	- Reference conditions in Parr autoclave (50 ml) 3 wt.% catalyst 10–20 times excess methanol 160–200 °C 5h	- Zirconia-supported isopoly tungstate showed superior catalytic performance than zirconia-supported heteropoly tungstate catalysts; - Under the reaction conditions of 200 °C and methanol/oil molar ratio 15, 15% WO₃/ZrO₂ calcined at 750 °C gave 97% conversion of SFO; - This catalyst also efficiently catalyzed methanolysis of other vegetable oils like mustard and sesame oil.	The deactivated catalyst could be regenerated by calcination without appreciable loss in activity.

^{f)} Sunita, G., Devassy, B. M., Vinu, A., Sawant, D. P., Balasubramanian, V. V. and Halligudi, S. B. (2008). *Synthesis of biodiesel over zirconia-supported isopoly and heteropoly tungstate catalysts*. Catalysis Communications **9** (5): 696-702.;

Table D-4: Heterogeneous catalysts containing hydrotalcite ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$) for biodiesel production

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
KF/hydrotalcite ^{a)}	▪ Coprecipitation 80 mL of two solutions, one containing $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.06 mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.02 mol) and other containing NaOH (0.16 mol) and Na_2CO_3 (0.04 mol) were synchronously dropped into 50 mL of 338 K water and stirred maintaining the pH between 9 and 10; The resulting mixture was held at 338 K while being stirred vigorously for 24 or 48 h and then filtered and washed with water until the filtrate pH was near 7; The precipitate was dried at 373-398 K overnight and calcined at 723 K for 3 h. ▪ The mixed Mg-Al oxides was grinded with KF by the ratio of 20 -100 wt.% hydrotalcite, while dropping some water; the paste was dried at 338 K overnight.	▪ 1-5 wt.% catalyst ▪ 3:1-24:1 methanol/oil molar ratio ▪ 45-75 °C ▪ 1-5 h	▪ When the reaction was carried out at 65 °C, with 12:1 methanol/palm oil, 3 h and 3 wt.% catalyst, the yield of FAME reached 85%; ▪ When the reaction time prolonged to 5 h, the yield become 92%.	▪ Considering the multiformity of hydrotalcite itself, the activity of the catalyst could be improved.

^{a)} Gao, L. J., Xu, B., Xiao, G. M. and Lv, J. H. (2008). *Transesterification of palm oil with methanol to biodiesel over a KF/hydrotalcite solid catalyst*. Energy & Fuels **22** (5): 3531-3535.

Table D-4: Heterogeneous catalysts containing hydrotalcite ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$) for biodiesel production (*continued*)

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
Mg–Al Hydrotalcite ^{b)}	- Hydrotalcite samples were activated at different temperatures (400–800 °C); - Hydration: Catalysts were hydrated for 12 h at room temperature under a flow of He saturated with water vapour; this process resulted in a water gain of 26 ± 2 wt.% regardless of the original calcination temperature.	10, 20 wt.% catalyst - Anhydrous methanol (99.9 wt.%) 30:1 molar ratio of methanol to poultry fat 1417 rpm	- In the absence of calcination, the crystalline layered double hydroxide intercalate precursor, hydrotalcite, showed no catalytic activity; - Calcination at optimum temperature was key in obtaining the highest catalyst activities; - Hydration of the calcined catalyst before reaction using wet nitrogen decreased catalytic activity; - Methanol had to be contacted with the catalyst before reaction; otherwise, catalyst activity was seriously impaired by strong adsorption of triglycerides on the active sites; - Temperature (60–120 °C) and methanol-to-lipid molar ratio (6:1–60:1) affected the reaction rate in a positive manner.	- Poultry fat transesterification; - No signs of catalyst leaching; - The catalyst underwent significant deactivation during the first reaction cycle probably due to deactivation of the strongest base sites. Subsequent reaction cycles showed stable activity; - By re-calcination in air, complete catalyst regeneration was achieved.

^{b)} Liu, Y., Lotero, E., Goodwin Jr, J. G. and Mo, X. (2007). *Transesterification of poultry fat with methanol using Mg-Al hydrotalcite derived catalysts*. Applied Catalysis A: General **331**: 138-148.

Table D-4: Heterogeneous catalysts containing hydrotalcite ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$) for biodiesel production (*continued*)

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
Hydrotalcite ^{c)}	- Two aqueous solutions were prepared: $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, (NaOH 50% in water), Na_2CO_3 in 100 ml distilled water; - The final product had an Mg to Al atomic ratio equal to 2 :1. - The first solution was put into the flask where the second one was added during 4 h. The mixture was vigorous agitated and kept at $27 \pm 1^\circ\text{C}$; - The Mg-Al-CO_3 hydrotalcite catalyst was formed and mixed while heated at 65°C for 20 h; - Product was filtered, cleaned and dried (at $100\text{--}120^\circ\text{C}$) yielding a fine white powder; - Calcination was made for comparison at 350°C for 6 h.	1 wt.% catalyst 6:1 methanol/oil molar ratio $180\text{--}210^\circ\text{C}$ - Up to 15 h - Initial pressure was from 2200 to 2900 kPa - For avoiding oxidation of the reactants N_2 atmosphere was used	- The basic Mg-Al-CO_3 hydrotalcite catalyst used showed a high activity for methanolysis and esterification reactions of refined and acidic cottonseed oil as well as in a representative high water content animal fat feed; - Non-calcined and calcined forms of the catalyst were tested and the activity of the calcined catalyst was lower than the initial activity of the non-calcined catalytic system but it appeared the same with the reused non-calcined system; - Better yields were achieved by a second glycerol phase removal stage (1st removal at 9 h, and 2nd at 12 h).	Free fatty acids appear to enhance the reaction rates acting as catalysts, but they are also consumed through esterification.

^{c)} Barakos, N., Pasias, S. and Papayannakos, N. (2008). *Transesterification of triglycerides in high and low quality oil feeds over an HT2 hydrotalcite catalyst*. Bioresource Technology **99** (11): 5037-5042.

Table D-5: Heterogeneous catalysts based on dolomite ($\text{CaMg}(\text{CO}_3)_2$) for biodiesel production

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
Modified dolomite ^{a)}	▪ $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were used as received to prepare modified dolomites by precipitation; ▪ The amount of metal loaded was fixed at 2 mmol metal per g of dolomite; ▪ Dolomite was calcined between 600 and 800 °C and dispersed in deionised water under vigorous stirring at 60 °C; An aqueous solution of a metal nitrate was then added dropwise into the slurry and the mixture was stirred for 4 h; The precipitated product was recovered by filtration, washed with deionised water and dried overnight at 120 °C; ▪ Before being used, parent and modified dolomites were calcined at 800 °C for 2 h.	▪ 5 – 13 wt.% catalyst ▪ 15:1-50:1 methanol/oil molar ratio ▪ 60 °C ▪ Up to 5 h	▪ The catalyst modified from dolomite calcined at 600 and 700 °C, followed by the precipitation from $\text{Ca}(\text{NO}_3)_2$ and the subsequent calcination at 800 °C, exhibited the most active catalytic activity, giving the methyl ester content of 99.9% using 15:1 methanol/oil molar ratio, 10 wt.% catalyst for 3 h; ▪ The high activity of the catalyst should be due to the presence of two active CaO sites generated from the precipitated $\text{Ca}(\text{OH})_2$ located in the crystalline phase of dolomite, and from CaCO_3 remaining after the calcination of the parent dolomite at 600–700 °C.	▪ Palm kernel oil transesterification.

^{a)} Ngamcharussrivichai, C., Wiwatnimit, W. and Wangnoi, S. (2007). *Modified dolomites as catalysts for palm kernel oil transesterification*. Journal of Molecular Catalysis A: Chemical **276** (1-2): 24-33.

Table D-5: Heterogeneous catalysts based on dolomite ($\text{CaMg}(\text{CO}_3)_2$) for biodiesel production (*continued*)

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
Calcined dolomitic rock ^{b)}	- Natural dolomitic rock was ground and sieved to particles between 149–250 μm; - Calcination at 900 °C for 3 h in a static muffle furnace and cooling in air to 100 °C was performed; - Catalysts were after transferred to a vacuum desiccator.	0.05 g of catalyst, 0.01 mol of glyceryl tributyrate or glyceryl trioctanoate, 0.0025 mol of hexyl ether as internal standard, and 0.3036 mol of methanol - Olive oil transesterification was performed as above except that 0.16 g extra virgin olive oil was used; equating to 0.2 mmol of triglyceride based on the majority glyceryltrioleate component, only 25 mg of calcined dolomite was added 60 °C 3 h	- Material which was uncalcined, or only heated to 600 °C, was inactive for transesterification; - High temperature calcination reveals Mg surface segregation as MgO nanocrystals dispersed over $\text{CaO}/(\text{OH})_2$ particles. CO_2 evolved during calcination increases both the surface area and basicity of natural dolomite; - Calcined dolomite was an effective catalyst for the transesterification with methanol of C4, C8 and even long-chain C16–18 triglyceride mixtures; - Catalytic transesterification rates were slower for more bulky triglycerides and may reflect mass transport limitations in accessing base sites.	Calcined dolomitic rock exhibited high activity towards transesterification of glyceryl tributyrate, trioctanoate and even olive oil.

^{b)} Wilson, K., Hardacre, C., Lee, A. F., Montero, J. M. and Shellard, L. (2008). *The application of calcined natural dolomitic rock as a solid base catalyst in triglyceride transesterification for biodiesel synthesis*. Green Chemistry **10** (6): 654-659.

Table D-6: Heterogeneous catalysts based on other oxides for biodiesel production

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
Mixed oxide of Zn and Al ^{a)}	Info is not provided	Higher temperature and pressure than homogeneous catalysis processes	Two successive stages of reaction and glycerol separation in order to shift the equilibrium of methanolysis	–
ZnO-La ₂ O ₃ ^{b)}	- Homogeneous-coprecipitation: 2 M Zn(NO₃)₂ and 1 M La(NO₃)₃ were prepared with distilled water solutions with varying ratios of Zn–La (1:0, 1:1, 3:1, 9:1, 0:1) mixed with a 2 M urea solution; - The mixture was boiled for 4 h, and dried at 150 °C for 8 h, followed by step-rising calcination at 250 °C, 300 °C, 350 °C, 400 °C and finally at 450 °C for 8 h. - Catalysts were noted as Zn₁₀La₀, Zn₁La₁, Zn₃La₁, Zn₉La₁, Zn₀La₁₀ according to their compositions.	2.4 wt.% catalyst 6:1-42:1methanol/oil molar ratio 180-210 °C	- There was a strong interaction between zinc and lanthanum species, and the catalyst with 3:1 of zinc to lanthanum ratio showed higher activity than pure metal oxides; - At 200 °C, Zn₃La₁ was highly tolerant to free fatty acids and water, being active in both transesterification and esterification reactions, and no hydrolysis activity was observed; - Within 3 h, 96% yield of FAME was obtained even using crude palm oil, crude SBO, WFO, food-grade SBO with 3% water and 5% oleic acid addition; - Reaction temperature should be from 170 °C and 220 °C to change unrefined and waste oils into FAME based on Zn₃La₁ catalyst; - Lanthanum promoted ZnO dispersion, increased the surface amounts of acid and base sites, thus enhanced the catalyst ability in both transesterification and esterification reaction.	The zinc and lanthanum mixed oxide allowed the direct use of unrefined and waste oils for biodiesel production.

^{a)} Bournay, L., Casanave, D., Delfort, B., Hillion, G. and Chodorge, J. A. (2005). *New heterogeneous process for biodiesel production: A way to improve the quality and the value of the crude glycerin produced by biodiesel plants*. *Catalysis Today* **106** (1-4): 190-192; ^{b)} Yan, S., Salley, S. O. and Simon Ng, K. Y. (2009). *Simultaneous transesterification and esterification of unrefined or waste oils over ZnO-La₂O₃ catalysts*. *Applied Catalysis A: General* **353** (2): 203-212.

Table D-6. Heterogeneous catalysts based on other oxides for biodiesel production (*continued*)

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
ZnO modified with alkali earth metals ^{c)}	▪ Zinc oxide was pre-treated at 873 K for 3 h; ▪ Catalysts were prepared by an impregnation method with an aqueous solution of an alkaline earth metal nitrate; Equivalent amounts of the corresponding nitrates, prepared as 0.1 mol/L aqueous solutions, were stirred with 15 g of support at room temperature for 2 h; ▪ The resulting slurry was evaporated to dryness and heated at 393 K overnight; ▪ Before carrying out the catalytic reaction, the as-prepared catalysts were calcined at desired temperatures in air for 5 h.	▪ 1.9 wt.% catalyst ▪ 6:1 – 18:1 methanol/oil molar ratio ▪ Anhydrous methanol ▪ 65 °C ▪ 1-6 h	▪ The highest catalytic activity was obtained with ZnO loaded with 2.5 mmol Sr(NO₃)₂/g, followed by calcination at 873 K for 5 h; ▪ When the transesterification reaction was carried out at reflux of methanol (338 K), with a 12:1 methanol/oil molar ratio and 5 wt.% catalyst, the conversion of SBO was 94.7%; ▪ Tetrahydrofuran used as a co-solvent increased the conversion up to 96.8%; ▪ Best conditions: 12:1 methanol/oil molar ratio, 5 wt.% catalyst and 4 h reaction time.	▪ The recovered catalyst exhibited lower catalytic activity with a conversion of SBO of 15.4%.

^{c)} Yang, Z. and Xie, W. (2007). *Soybean oil transesterification over zinc oxide modified with alkali earth metals*. Fuel Processing Technology **88** (6): 631-638.

Table D-6: Heterogeneous catalysts based on other oxides for biodiesel production (*continued*)

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
CaTiO ₃ CaMnO ₃ Ca ₂ Fe ₂ O ₅ CaZrO ₃ CaO-CeO ₂ ^{d)}	▪ Metal oxides (up to 99.9% purity) were dried in an oven at 300 °C for 4 h before use; ▪ Conventional solid-state reaction was performed: CaTiO₃ preparation: an equimolar mixture of TiO₂ and CaCO₃ was milled in an agate mortar and the mixed powder was calcined in air to 500 °C at a rate of 2 °C/min and then at 1050 °C for 2 h in an alumina crucible; Ca₂Fe₂O₅ preparation: a mixture containing a 1:2 molar ratio of Fe₂O₃ and CaCO₃ was milled and calcined in air to 900 °C at a rate of 2 °C/min and then at 1050 °C for 4 h. ▪ The other catalysts were prepared in the same manner; ▪ The obtained substances were stored in dry boxes.	▪ 10 wt.% catalyst ▪ Approximately 6:1 methanol/oil molar ratio (26 wt.% methanol) ▪ 60 °C ▪ 10 h	▪ CaTiO₃ had a base strength in the range of 6.8–7.2. CaMnO₃, Ca₂Fe₂O₅, CaZrO₃ and CaO-CeO₂ had the highest base strengths, in the range from 7.2 to 9.3; ▪ The Ca series catalysts showed a high yield of methyl ester. CaMnO₃, Ca₂Fe₂O₅, CaZrO₃, and CaO-CeO₂, whose catalytic basicities were the highest, showed 92%, 92%, 88%, and 89% yields of the ester, respectively; ▪ CaTiO₃, whose basicity was also high, provided a yield of 79%; ▪ For the catalysts with low basicities: BaTiO₃, BaZrO₃, BaCeO₃, MgTiO₃, MgZrO₃, MgCeO₃, LaZrO₃ and LaCeO₃, ester yields were 1% or less and little activity as a basic catalyst was observed.	▪ Rapeseed oil transesterification; ▪ The base strengths of the catalysts were determined using the Hammet indicators; ▪ High durability of catalytic activity was found for the catalyst samples of CaZrO₃ and CaO-CeO₂, which were able to provide methyl ester yields greater than 80% after being used 5 times and 7 times, respectively.

^{d)} Kawashima, A., Matsubara, K. and Honda, K. (2008). *Development of heterogeneous base catalysts for biodiesel production*. Bioresource Technology **99** (9): 3439-3443.

Table D-6: Heterogeneous catalysts based on other oxides for biodiesel production (*continued*)

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
Sn complex incorporated in ionic liquid and ion-exchange resin SnO ^{a)}	▪ Incorporation of Sn complex in ionic liquid (Catalyst 1): The Sn (3-hydroxy-2-methyl-4-pyrone)₂(H₂O)₂ (0.036 g) prepared according to De Oliveira et. al (2000)^{b)} was mixed at room temperature in BMI(PF6) prepared according to Suarez et al. (1998)^{c)} (2 mL) until its complete dissolution. ▪ Supporting the Sn complex in ion-exchange resin (Catalyst 2): The Sn(3-hydroxy-2-methyl-4pyrone)2(H₂O)₂ (0.200 g) was dissolved in DMSO (9 mL) and then impregnated in an acid ion-exchange resin (4 g) at 60 °C for 72 h; The resulting product (Catalyst 2) was isolated by filtration, washed with distilled water, and dried in a vacuum desiccator over silica gel. ▪ SnO (Catalyst 3) A water solution containing acetylacetone and sodium hydroxide was slowly added, under magnetic stirring, to a water solution (20 mL) of Sn (II) chloride (0.551 g, 2 mmol); The mixture was left under stirring at 40 °C for 30 min and then kept in a refrigerator overnight; The resulting precipitate was isolated by filtration, washed several times with distilled water and dried in a vacuum desiccator over silica gel; The resulting complex was calcined at 500 °C for 24 h.	▪ 10 g of vegetable oil and 2 mL of catalyst ▪ 1 or 0.5 g of catalyst ▪ 2 or 3 (5 wt.%) ▪ 15 wt.% methanol ▪ 60 °C	▪ The use of BMI(PF6) to anchor the tin complex for the methanolysis of SBO; ▪ The tin complex lost its catalytic activity when supported in the organic resin; ▪ Tin oxide was active for SBO methanolysis (conversion yields up to 93% in 3 h were achieved); it was also possible to reuse it without activity loss.	▪ SBO; ▪ Previously, good results were obtained using the complex Sn (3-hydroxy-2-methyl-4pyrone)2(H₂O)₂ alone as catalyst for vegetable oil alcoholysis.

^{a)} Abreu, F. R., Alves, M. B., Macêdo, C. C. S., Zara, L. F. and Suarez, P. A. Z. (2005). *New multi-phase catalytic systems based on tin compounds active for vegetable oil transesterification reaction*. Journal of Molecular Catalysis A: Chemical **227** (1-2): 263-267; ^{b)} De Oliveira, A. B., Jorge, I. F., Suarez, P. A. Z., De S. Basso, N. R. and Einloft, S. (2000). *Synthesis and characterization of new bivalent tin chelate of 3-hydroxy-2-methyl-4-pyrone and its use as catalyst for polyesterification*. Polymer Bulletin **45** (4): 341-344; ^{c)} Suarez, P. A. Z., Einloft, S., Dullius, J. E. L., De Souza, R. F. and Dupont, J. (1998). *Synthesis and physical-chemical properties of ionic liquids based on 1- n-butyl-3-methylimidazolium cation*. Journal de Chimie Physique et de Physico-Chimie Biologique **95** (7): 1626-1639.

Table D-6: Heterogeneous catalysts based on other oxides for biodiesel production (*continued*)

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
KF/ZnO ^{d)}	▪ KF/ZnO catalyst was prepared by impregnation of the ZnO support with aqueous solution of KF·2H₂O; ▪ After impregnation, the sample was dried at 110 °C overnight and calcined at 873 K for 5 h in a muffle furnace.	▪ Around 2-6 wt.% catalyst ▪ Around 7-13 methanol/oil molar ratio ▪ 65 °C ▪ Around 7-11 h	▪ Catalyst amount had the greatest effect on biodiesel yield, while methanol/oil molar ratio and reaction time were insignificant; ▪ Optimum conditions for biodiesel production were: catalyst amount of 5.52 wt.%, methanol/oil molar ratio of 11.43 and reaction time of 9.72 h; ▪ The optimum biodiesel yield was 89.23%.	▪ Palm oil; ▪ It was observed that the experimental value obtained was in good agreement with the value predicted from the models.

^{d)} Hameed, B. H., Lai, L. F. and Chin, L. H. (2009). *Production of biodiesel from palm oil (Elaeis guineensis) using heterogeneous catalyst: An optimized process*. Fuel Processing Technology **90** (4): 606-610.

Table D-6: Heterogeneous catalysts based on other oxides for biodiesel production (*continued*)

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
ZrO ₂ , ZnO, SO ₄ ²⁻ /SnO ₂ , SO ₄ ²⁻ /ZrO ₂ , KNO ₃ /KL zeolite ^{e)}	▪ KNO₃, ZnO, SnCl₂ and ZrO₂ were used; ▪ SO₄²⁻/SnO₂ preparation: SnCl₂ was dissolved in distilled water and aqueous ammonium hydroxide was gradually added into this solution until the pH reached 8; The yellowish solid precipitated was collected by filtration, washed with distilled water, and dried at 110 °C for 12 h; The hydroxide was equilibrated with H₂SO₄ for 2 h, dried and calcined at 500 °C for 4 h. ▪ SO₄²⁻/ZrO₂ preparation: zirconia powder was immersed in a H₂SO₄ solution for 30 min, filtered and dried at 110 °C for 24 h yielding the sulphate salt (SO₄²⁻/SnO) and after calcined at 500 °C for 2 h. ▪ KNO₃/KL zeolite preparation: the KL zeolite was impregnated with KNO₃ solution, dried at 100 °C and then calcined at 600 °C for 2 h. ▪ KNO₃/ZrO₂ preparation: grinding of 40 g of ZrO₂ with 8 g of KNO₃, followed by the addition of 24 ml of distilled water; the paste was dried at 110 °C for 12 h and after calcined at 600 °C for 2 h.	▪ 3 wt.% catalyst ▪ 6:1 methanol/oil molar ratio ▪ 200 °C ▪ 50 bar ▪ N₂ atmosphere ▪ 350 rpm	▪ Results show that ZnO and SO₄²⁻/ZrO₂ exhibited the highest activity for oil transesterification; ▪ Only 1 wt.% of SO₄²⁻/ZrO₂ was needed to catalyze the reaction, resulting in fatty acid methyl esters content higher than 90%; ▪ A study of the catalyst recyclability indicated that the spent SO₄²⁻/ZrO₂ could not be directly reused for the transesterification; ▪ The spent catalyst could be easily regenerated and the same activity could be obtained.	▪ Crude Palm oil and crude coconut oil were used.

^{e)} Jitputti, J., Kitiyanan, B., Rangsunvigit, P., Bunyakiat, K., Attanatho, L. and Jenvanitpanjakul, P. (2006). *Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts*. Chemical Engineering Journal **116** (1): 61-66.

Table D-6: Heterogeneous catalysts based on other oxides for biodiesel production (*continued*)

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
Mixed oxides derived from Mg–Co–Al–La layered double hydroxide (LDH) [†]	- The mixed oxide catalysts denoted as Mg_xCoAl_yLa_z (x = 2 or 3 and y + z = 1) were prepared by calcining their precursors Mg_xCoAl_yLa_z–LDHs - LDH materials were synthesized by a co-precipitation method: 50 mL of mixed salt solution containing 0.2x M Mg(NO₃)₂·6H₂O, 0.2 M Co(NO₃)₂, 0.2y M Al(NO₃)₃·9H₂O and 0.2z M La(NO₃)₃ were added into 200 mL of a mixed base solution containing 0.4 M NaOH and 0.026 M Na₂CO₃. - A precipitate was formed and the mixture was aged to 353 K under continuous stirring for 6 h. The mixed suspension was then cooled down, and the LDH precipitate was separated and washed with deionised water via centrifugation. - The collected LDH was dried at 373 K overnight and calcined at 873 K for 4 h at a heating rate of 10 K/min. All calcined catalysts were ground to powder (mean particle size less than 100 nm) prior to use; - The Mg₃Al–LDH used in the preliminary test was prepared in a similar way as described above, except that no Co or La was added and the formed LDH calcination was done at 773 K; - The resulting catalyst was in a powder form where no additional grinding was required.	16:1 ethanol/oil molar ratio 200 °C 5 h - Parr 4560 mini bench top reactor was used 25 atm	- The catalytic activity of the Mg₂CoAl was demonstrated and catalyst was stable and reusable, maintaining its activity after 7 cycles; - The kinetics of the transesterification of canola oil catalyzed by Mg₂CoAl could be modelled as a first-order reaction; - All four Mg–Co–Al–La mixed oxide catalysts maintained their morphology, while exhibiting high yields of 96–97% when the transesterification was conducted at 473 K with an ethanol-to-oil ratio of 16:1 and a catalyst loading of 2 wt.%.	- Canola oil; - Variations of several experimental parameters with Mg₂CoAl showed that the reaction temperature had a dominant effect on the catalytic performance.

[†] Li, E., Xu, Z. P. and Rudolph, V. (2009). *MgCoAl-LDH derived heterogeneous catalysts for the ethanol transesterification of canola oil to biodiesel*. Applied Catalysis B: Environmental **88** (1-2): 42-49.

Table D-7: Heterogeneous catalysts supported in alumina for biodiesel production

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
$\text{KNO}_3/\text{Al}_2\text{O}_3$ ^{a)}	- The catalyst was prepared by impregnation of alumina with an aqueous solution of potassium nitrate; 30 ml of potassium nitrate was loaded on 10 g of alumina followed by atmospheric drying; - Prior to each reaction, catalysts were calcined at the desired temperature (typically at 773 K) in air during 4 h.	1.0–9.0 wt.% catalyst 3:1 – 15:1 methanol/oil molar ratio - Anhydrous methanol 50 – 70 °C 1–7 h	- Maximum conversion was obtained when the molar ratio was very close to 12:1, further increase in the molar ratio caused a little improvement in the conversion; - The conversion increased with the increase of catalyst amount from 1 to 6 wt.%, but with further increase the conversion decreased; - The nearly equilibrium conversion was found to be about 87% at 7 h of reaction; - When the reaction was carried out at 70 °C, with a 12:1 methanol to <i>Jatropha</i> oil molar ratio, 6 h, 6 wt.% catalyst and a agitation speed of 600 rpm, conversion reached 84%.	- An efficient mixing of the reagents was essential to reach a high conversion of the oil; - The catalyst was recycled to study the reusability; it may be used at least for three times.

^{a)} Vyas, A. P., Subrahmanyam, N. and Patel, P. A. (2009). *Production of biodiesel through transesterification of Jatropha oil using KNO₃/Al₂O₃ solid catalyst*. Fuel **88** (4): 625–628.

Table D-7: Heterogeneous catalysts supported in alumina for biodiesel production (*continued*)

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
Alumina loaded with KI ^{b)}	- Impregnation of alumina with a KI aqueous solution; 10 g of the support was impregnated with 30 mL of the potassium compounds solution; water was further removed in a rotary evaporator at 353 K; - This impregnate was dried in a oven at 393 K overnight and calcined in a muffle furnace at designated temperatures for 3 h before use.	1-3.5 wt.% catalyst 9:1 – 25:1 methanol/oil molar ratio - Anhydrous methanol - Methanol reflux temperature 4-10 h	- Methyl esters conversion was gradually increased with the rise of the calcination temperature from 473 to 773 K; at higher than 773 K the conversion dropped considerably due to lower basicity; - Optimal calcination temperature was 773 K, giving a maximum conversion of 87.4%; - Increasing methanol/oil molar ratio, the conversion increased considerably, optimum ratio was 15:1; - When the catalyst amount increased from 1 to 2.5 wt.%, the conversion increased but with further increase in the catalyst amount the conversion was decreased due to a mixing problem involving reactants, products and solid catalyst; - At about 2.5% catalyst amount (15:1, 8 h), a high conversion of up to 96% was obtained; - Optimum catalyst: 35 wt.% KI loading on Al₂O₃ calcined at 773 K for 3 h.	- SBO was used; - The main reasons for the catalytic activity towards the reaction were attributed to the K₂O species formed by the thermal decomposition of loaded KI, and the surface Al–O–K groups formed by salt-support interactions; - The catalysts activities were correlated with their corresponding basic properties.
Na/NaOH/ γ -Al ₂ O ₃ ^{c)}	- To eliminate chemical species adsorbed on the surface, γ-Al₂O₃ was pretreated at 550 °C for 12 h; - Successive treatment of γ-Al₂O₃ with sodium hydroxide and sodium at 320 °C under nitrogen was made.	2 wt.% catalyst 9:1 methanol/oil molar ratio 60 °C 2 h 300 rpm - N₂ atmosphere 20 vol.% hexane as co-solvent	- The Na/NaOH/γ-Al₂O₃ heterogeneous base catalyst showed almost the same activity under the optimized reaction conditions compared to conventional homogeneous NaOH catalyst; - The basic strength of Na/NaOH/γ-Al₂O₃ catalyst was estimated and the correlation with the activity towards transesterification was proposed.	- The use of a co-solvent was found to be inevitable for the transesterification; - Among the co-solvents tested, n-hexane was the most effective.

^{b)} Xie, W., Huang, X. and Li, H. (2007). *Soybean oil methyl esters preparation using NaX zeolites loaded with KOH as a heterogeneous catalyst*. Bioresource Technology **98** (4): 936-939;

^{c)} Kim, H.-J., Kang, B.-S., Kim, M.-J., Park, Y. M., Kim, D.-K., Lee, J.-S. and Lee, K.-Y. (2004). *Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst*. Catalysis Today **93-95**: 315-320.

Table D-8: Zeolites as heterogeneous catalysts for biodiesel production

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
Zeolites ^{a)}	▪ MFI zeolites: synthesized with different Si/Al molar ratios through hydrothermal reaction of a synthetic mixture composed of colloidal silica, aluminium hydroxide, potassium hydroxide and deionized water; The synthetic mixture was aged for 72 h and heated at 190 °C for 48 h. ▪ Na-type MFI zeolites: treated with ammonium nitrate of 0.5 N at 60 °C to exchange its cations to ammonium ions; H-type MFI zeolites: obtained by calcining them at 550 °C for 6 h in air. ▪ Dealuminated MOR zeolite: MOR zeolite (Si/Al = 10) was purchased from Tosoh Co. and used as a starting material for dealumination, acetic acid of 6 N was employed in the preparation to obtain the MOR zeolites with different Si/Al molar ratio. The parent MOR zeolite was treated with acetic acid solution for 5 h. Refluxing time was 12 h to allow more efficient removal of aluminium atoms from the zeolite framework; The acid-treated MOR zeolites were carefully washed with deionized water and dried at 100 °C followed by calcining at 500 °C in air stream for 12 h. H-type MOR zeolites were obtained by the ion exchange according to the method mentioned above. ▪ H-beta (HBEA) and H-faujasite (HFAU) zeolites: prepared from Na-BEA zeolite and Na-FAU zeolite exchange with a 2 M solution of NH_4NO_3 at 80 °C; Samples were filtered, washed and dried overnight at 100 °C.	▪ 10 wt.% catalyst ▪ 30:1 methanol/oil molar ratio ▪ 60 °C ▪ 3 h ▪ 600 rpm ▪ Oleic acid was added as an excess free fatty acid reagent 10 vol.% of oil	▪ The zeolite catalysts were active on the esterification reaction of free fatty acids with methanol; ▪ Conversions of free fatty acids of around 80% were obtained using HMFI (25 Si/Al molar ratio) zeolite and HMOR zeolite at 60 °C; ▪ The catalytic activity for free fatty acids removal lowered with decreasing acidity of HMFI zeolites. On the contrary, the HMOR zeolites exhibited similar free fatty acid conversion using different Si/Al molar ratio, although the acidity decreased; ▪ Acid strength and pore mouth size of the zeolites affected the catalytic activity of free fatty acids removal.	▪ WFO was used.

^{a)} Chung, K.-H., Chang, D.-R. and Park, B.-G. (2008). *Removal of free fatty acid in waste frying oil by esterification with methanol on zeolite catalysts*. *Bioresource Technology* **99** (16): 7438-7443.

Table D-9: Other heterogeneous catalysts for biodiesel production

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
Heteropolyacid $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ ^{a)}	The heteropolyacid was pre-treated at 300–400 °C to acquire super acid sites.	0.05 – 1.5 g catalyst (in 20 mL oil) 3:1 – 9:1 methanol/oil molar ratio 20, 25, 40 and 60 °C 1 h	- The solid acid was shown to be an efficient catalyst for the production of biodiesel with high yields (99%) using a low catalyst concentration (1.85.10-3:1 wt. ratio), a 5.3:1 methanol/ oil molar ratio and the co-solvent tetrahydrofuran in a relatively short reaction time (45 min) and not very high temperature (55 °C); - Increase in the conversion of vegetable oil from 47% to 94% was noticed when the amount of catalyst increased from 0.05 to 1.5 g and the acid-catalyst process attains a maximum conversion at 0.1 g of the catalyst; - The increase in the conversion with increasing catalyst weight was attributed to an increase in the availability and number of catalytically active sites; - The catalyst was easily separated from the production mixture and could be reused a minimum of six times.	- The vegetable oil used in this study was Eruca sativa Gars oil; - At 60 °C, free fatty acid present did not decrease the catalytic activity of heteropolyacid because they reacted with methanol to generate the fatty acid methyl ester; - With water content below 0.5%, conversion was slightly reduced to 80% but a significant reduction (to 4%) was achieved when 1% of water was added.

^{a)} Chai, F., Cao, F. H., Zhai, F. Y., Chen, Y., Wang, X. H. and Su, Z. M. (2007). *Transesterification of vegetable oil to biodiesel using a heteropolyacid solid catalyst*. Advanced Synthesis & Catalysis **349** (7): 1057-1065.

Table D-9: Other heterogeneous catalysts for biodiesel production (*continued*)

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
Tri-potassium phosphate; Tri-sodium phosphate ^{b)}	- CaO was prepared by calcination of CaCO₃ powders (average particle diameter of 45 µm, surface area of 2900 cm²/g), in N₂ gas flow at 1000 °C for 5 h; - Tri-potassium phosphate (K₃PO₄) and tri-sodium phosphate (Na₃PO₄) were obtained from Wako Pure Chemistry Industry.	1-4 wt.% catalyst 6:1 methanol/oil molar ratio 30, 45, 60 °C	- Tri-potassium phosphate shows high catalytic properties for the transesterification reaction compared to CaO and tri-sodium phosphate; - Transesterification of WFO required approximately two times more solid catalyst than transesterification of SFO; - The FAME yield reached 97.3% (tri-potassium phosphate) using a catalyst concentration of 4 wt.% at 60 °C for 120 min; - After regeneration of the used catalyst with aqueous KOH solution, the FAME yield recovered to 88%.	- SFO and WFO transesterification; - Co-solvent changed the reaction to two-phase, but reduced the FAME yield; - Catalyst particles were easily agglomerated by the glycerol drops derived from the homogeneous liquid in the presence of co-solvents, reducing the catalytic activity.

^{b)} Guan, G., Kusakabe, K. and Yamasaki, S. (2009). *Tri-potassium phosphate as a solid catalyst for biodiesel production from waste cooking oil*. Fuel Processing Technology **90** (4): 520-524.

Table D-9: Other heterogeneous catalysts for biodiesel production (*continued*)

CATALYST	PREPARATION	REACTION CONDITIONS	RESULTS	OBSERVATION
Montmorillonite KSF ^{c)}	Commercial, used as received.	1-5 wt.% catalyst 1:4-1:12 methanol/oil molar ratio 50-190 °C 60-300 min 190-200 rpm	- The yield of oil to biodiesel was found to be lower at 4% catalyst as compared to 2% catalyst when reaction temperature was lower than 95 °C, suggesting real interactions between the reaction temperature and the active site on the catalyst itself; - At a shorter reaction period, 2% catalyst showed a significant lower yield compared to that of 4% catalyst. However, the yield by 2% catalyst continues to steadily increase until it subsequently exceeds to that of 4% catalyst after 210 min of reaction; - The 4% catalyst showed a fairly constant yield and slightly dropped when the reaction period is beyond 210 min. From this behavior, it was inferred that the equilibrium of the reactions is reached rapidly with 4% catalyst, and after reaching the equilibrium, the transesterification reactions may become stagnant or start to reverse; - The equilibrium of transesterification reactions by 2% catalyst may only be reached after longer reaction time because of smaller active site availability; - Montmorillonite KSF could be used as an effective catalyst for the conversion of palm oil to FAME.	- The ability of montmorillonite KSF to catalyze the transesterification reactions, at any rate, was due to the acidic properties of the catalyst itself; - Future research on this catalyst is important to investigate wider range of the parameters, such as the mixing intensity and reaction pressure.

^{c)} Kansedo, J., Lee, K. T. and Bhatia, S. (2009). *Biodiesel production from palm oil via heterogeneous transesterification*. Biomass and Bioenergy **33** (2): 271-276.

APPENDIX E PRESS RELEASES

Table E-1 presents several of the published news related with the developed work as well as links to follow some online (consult CD file).

Table E-1: Press releases related with the developed work, including source and date released as well as page and link.

<i>Title</i>	SOURCE	DATE	PAGE/HOUR	LINK
<i>Programa Biosfera - Investigadores portugueses transformam gordura em Biodiesel</i>	RTP2	25-07-2010	13.30h	
<i>Instituições de ensino inovam nos resíduos</i>	Água & Ambiente	01-06-2010	53	-
<i>Gordura de carne gera biocombustível</i>	Renováveis magazine.pt	05-04-2010	-	
<i>Conversa com Doutor Fernando Castro</i>	Notícias de Guimarães	26-03-2010	10/11	-
<i>FEUP valoriza resíduos de animais para produção de biocombustível</i>	Água & Ambiente	01-03-2010	56	-
<i>Biocombustível da gordura da carne</i>	Diário Notícias	28-02-2010	18	-
<i>Transformar a gordura da carne em biocombustível</i>	Vida Económica	26-02-2010	2	-
<i>Transformar a gordura da carne em biocombustível</i>	O Mirante	25-02-2010	2	-
<i>Gordura animal serve para combustível</i>	SIC Notícias	24-02-2010	12:32	
<i>Projecto 'FatValue'</i>	Porto Canal	18-02-2010	19:30	
<i>Empresa parceira em projecto de valorização de resíduos animais</i>	Diário de Aveiro	07-02-2010	7	-
<i>Gordura animal transformada em biocombustível</i>	Diário Notícias	06-02-2010	34/35	-
<i>Gordura animal transformada em biocombustível</i>	dn.pt	06-02-2010	-	
<i>Courato para biodiesel</i>	SOL	05-02-2010	38	-
<i>Gordura da carne transformada em biocombustível</i>	Ambiente Online	02-02-2010	-	
<i>FEUP transforma gordura da carne em biocombustível</i>	Ciência pt	02-02-2010	-	
<i>Fazer biodiesel com gordura animal</i>	dn.pt	02-02-2010	-	
<i>Gordura de carne amiga do planeta</i>	Metro	02-02-2010	7	-
<i>Gordura de carne gera biocombustível</i>	Expresso OnLine	01-02-2010	-	
<i>Da pré-graduação à investigação Avançada</i>	Boletim Informativo, n.º 37 FEUP	2006	12	-