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OPTIMIZATION OF BIODIESEL PRODUCTION FROM WASTE LARD BY A TWO-STEP PROCESS

MASTER THESIS

Of

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Dedicated to my
2F's

Foreword – Acknowledgements

The present study signifies the end of my graduate studies at the Department of Environmental Engineering of the Technical University of Crete, studies which were accompanied by creative experiences, significant academic progress and unique and unforgettable memories. Especially in the present global circumstances, where environmental and economic indicators are under stress and efficiency is a matter of increasing interest, I honestly regard that the background I obtained all these years at the Department will greatly assist me in addressing successfully future challenges that will rise in my professional career.

At this point, I wish to express my sincere acknowledgements to Associate Professor Theocharis Tsoutsos for the guidance and the creative collaboration we had all these years, with the hope of forming new collaboration ventures in the future. In addition, I would like to acknowledge Professor Nikolaos Kalogerakis and Associate Professor Nikolaos Pasadakis for their suggestions and input for the successful completion of the present study as members of the Defending Committee.

Last, but not the least, it would be unfair not to mention the most important ex-departmental critical factors for the successful completion of this study:

- Martha, for the encouragement, unending tolerance and unintended inspiration that she generously offers me…

- The Sailing Team of TU Crete and all fellow crew mates, for the unforgettable trips so far (shall be continued anyway!)…

- "Heavy melons" team, for the points they collected last season…

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Abstract

Alternative fuels and biodiesel in particular are facing major challenges in order to be considered as sustainable fuels and to gain significant market share over their primary competitor, crude oil. Waste lard is a by-product of hog industry with limited other uses and low market price. Local availability is already high and if proper waste management schemes will be implemented, an additional increase in the production is expected.

In this study, this potential sustainable biodiesel feedstock is assessed in terms of feedstock characterization, pretreatment and transformation optimization and key fuel property determination. The concept and the aim of the study is to present a comprehensive solution for the transformation of waste lard to biodiesel under mild conditions. Besides, the study was the incentive to develop and evaluate analytical methods for key biodiesel measurements and to create relative experimental know-how.

Results are showing that despite some quality characteristics of waste lard biodiesel were not met the respective limits, waste lard biodiesel can be addressed as a alternative fuel and produced under mild conditions. Effects of production parameters on the reaction performances are also indicated and evaluated. Among others, it is suggested that further quality properties of lard biodiesel should be measured so as to determine whether they are below or above the limits and to improve fuel properties by combining more local sustainable feedstocks (e.g. olive pomace oil).

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1. INTRODUCTION

1.1 Purpose of this section

The first section of this document presents the aim and the scope of this study and reviews the current available processes and the state of the art regarding biodiesel production, the existing situation regarding biofuel policies and outlook regarding biodiesel production. It also provides a holistic review of the scientific sources regarding biodiesel production from waste animal fat, details process strategies and compares the pros and cons of each one. The Introduction ends with a sort reference on the sustainability advantages of biodiesel production from waste raw materials and potential other sources of sustainable raw materials.

1.2 Aim and objectives

The aim of this study is to provide a comprehensive overview of the potential of waste lard as raw material for biodiesel production in the island of Crete. The document will analyze why and how biodiesel can be a feasible energy option for the partial coverage of current demand and will present experimental results from laboratory tests regarding the optimization of a two step production process under mild conditions. It is worth mentioning that the present project was one of the first of its kind exclusively conducted in the Technical University of Crete and one of its added values was the acquisition of relative experimental know-how.

1.3 Sustainability and biodiesel

Over the last decades, the economic growth has been mainly based on the radical technological achievements on the assumption that resources and energy flows would be stable, adequate and indiscriminate. However, due to the exhaustion of natural resources as a result to the overloading of their capacity, the constraints in availability due to geopolitical reasons and the need for improvement of the life quality for the developing societies, the humanity has realized that a turn to an advanced developing model shall be adopted.

The concept of sustainable development has been released by the United Nations in 1987 through the Brundtland Report (1), which defines sustainable development as 'development which meets the needs of the present without compromising the ability of future generations to meet their own needs. An alternative to this definition could be that "sustainable development is the concept of development where environmental, social and economical efficiency is equally maximized for the long-term benefit and viability and with responsibility against the humanity and the planet".

Biofuels and especially biodiesel have been heavily criticized lately regarding their environmental performance and their social impacts (2), (3), (4). Policy makers and other stakeholders are struggling to find answers to if and how sustainability can be realized, and how to encourage sustainable practices through policy guidelines and norms. Regarding environmental performance, major drawbacks of biodiesel are the impacts of cultivations on soil quality, land-use change, water consumption, overall carbon balance and biodiversity (5), (6), (7), (8), (9). On the social context, biodiesel production can be controversial in terms of food shortage and security, poverty reduction, commodity market prices, labor equality and relations.

In order to overhaul the biodiesel status, address and enhance the production of sustainable biofuels European Union adopted in its policy special provisions regarding sustainability criteria for biofuels (10). In short, the sustainability provisions are:

- The greenhouse gas emission saving from the use of biofuel shall be at least 35 %

- Biofuels shall not be made from raw material obtained from land with high biodiversity value

- Biofuels shall not be made from raw material obtained from land with high carbon stock (e.g. wetlands, continuously forested areas, land spanning more than one hectare with trees higher than five meters and a canopy cover of between 10 % and 30 %, or trees able to reach those thresholds in situ)

- Biofuels shall not be made from raw material obtained from land that was peat land

- Agricultural raw materials cultivated in the Community and used for the production of biofuels shall be obtained in accordance with certain requirements and standards establishing common rules for direct support schemes for farmers under the common agricultural policy and establishing certain support schemes for farmers in accordance with the minimum requirements for good agricultural and environmental condition.

According to the same directive, various common raw materials for biodiesel production have been ranked depending on their respective carbon saving potential and, as expected, the use of waste raw materials is advantageous over the other alternatives.

Table 1: Typical and default values for biofuels if produced with no net carbon emissions from land-use change (10)

Biofuel production pathway	Typical greenhouse gas emission saving	Default greenhouse gas emission saving
Rape seed biodiesel	45%	38%
Sunflower biodiesel	58%	51%
Soybean biodiesel	40%	31%
Palm oil biodiesel (process not specified)	36%	19%
Palm oil biodiesel (methane capture)	62%	56%
Waste vegetable or animal oil biodiesel	88%	83%

In addition to the European policy, scientific bibliography indicates that utilization of waste or by-product raw material can achieve higher environmental and financial performance compared to conventional biomass raw materials.

1.4 The basics of biodiesel production

Biodiesel is an alternative to fossil petroleum-based fuel, derived from oily biomass, suitable for pure use in internal combustion diesel engines (11). Chemically is defined as the methyl esters of vegetable or animal oils and fats which are meeting certain quality standards so as to be used as pure or blended fuel in diesel engines. It is obtained by transesterifying vegetable or animal oils and fats with methanol toward the production of their respective methyl esters and glycerol.

Biodiesel can be produced from a great variety of feedstocks. Usually in industrial level, the most common feedstocks include common vegetable oils (e.g. palm oil, rapeseed oil, soybean oil and sunflower oil), animal fats (tallow or lard) and recovered frying oils (12). The choice and the selection of the feedstocks is mainly depends on local availability, costs and physicochemical properties (13).

As mentioned, biodiesel is produced by a reaction called transesterification, which is the process of exchanging the organic group R_1 of an ester with the organic group R_2 of an alcohol (CH_3 in the case of biodiesel) (14). These reactions are often catalyzed by the addition of an acid or base catalyst, depending on the properties of the reactants. In biodiesel production, methanol is used as the alcohol and potassium or sodium hydroxide as base catalyst. According to the reaction stoichiometry, 1 molecule of triglycerides reacts with 3 molecules of methanol to produce 3 molecules or methyl esters (biodiesel) and 1 molecule of glycerin (Figure 1).

Figure 1: The transesterification reaction
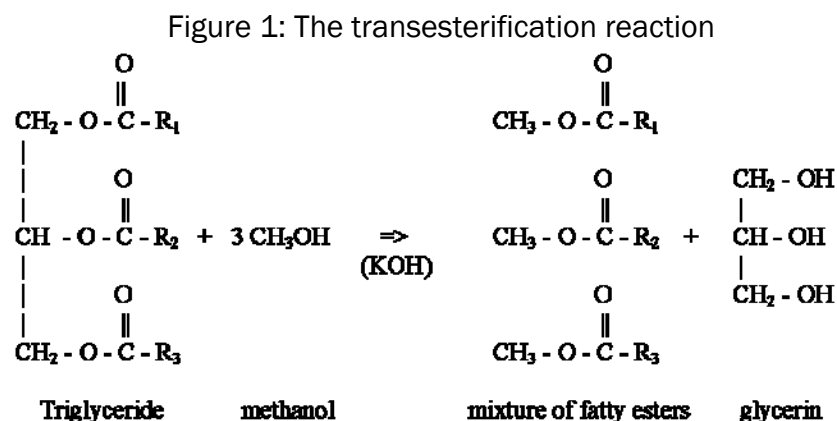
The concept of utilizing vegetable oils as fuel for diesel engines is new. It is known that back at the end of 19th century, Rudolf Diesel, the inventor of the

diesel engine, considered the use of unmodified vegetable oils as primary fuel for diesel engines. It is also documented the use of pure peanut oil in Diesel's engine during the Paris Exposition in 1900.

However the use of pure oils as fuels for internal combustion engines has not expanded as vegetable oils due to their high kinematic viscosity in comparison to the fossil diesel fuel and the operational problems associated with this. On the other hand, transesterified oils and fats have a molecule structure similar to the structure of hexadecetane. Hexadecane ignites very easily under compression and for this reason, it is assigned a cetane number of 100, and serves as a reference for other fuel mixtures.

Figure 2: Molar structure of hexadecatane (left) and a common methyl ester (right)
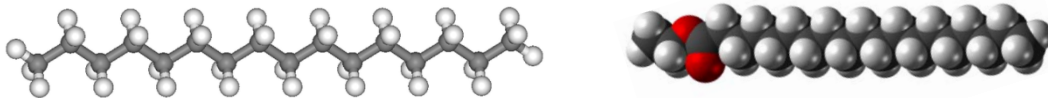
1.4.1 Transesterification reaction

During the reaction of transesterification, triglycerides of the oil are converted to their respective methyl ester through a chain of reaction. As intermediate products are formed di and mono glycerides during the

Figure 3: Triglyceride conversion to methyl esters (11)
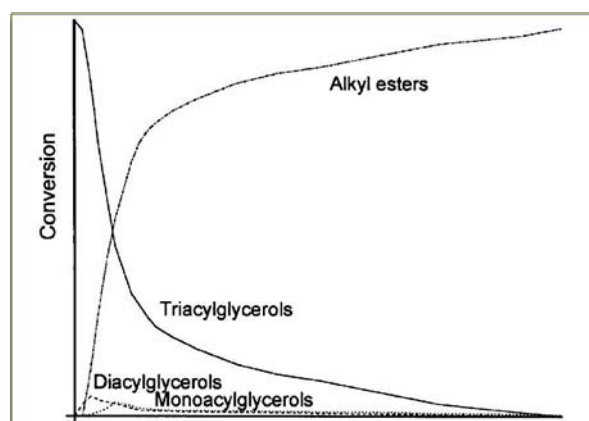
transesterification reaction. A qualitative plot of the conversion of triglycerides to methyl esters is given in Figure 3 (**11**).

Usually, basic catalysts are used however in certain cases acid or enzyme catalysis can be utilized. Each catalysis pathway has several advantages and disadvantages which are listed in Table 1.

Table 2: Advantages and disadvantages of each catalysis pathway (**12**)

Catalysis	Advantages	Disadvantages
Basic	+ Higher conversion + Shorter reaction time + Less corrosive to equipment + Less excess of alcohol for the reaction	- Sensitive to free fatty acids - Need for product purification - Sensitive to water content of the feedstock
Acid	+ Esterification of free fatty acids	- Slower reaction rate - Sensitive to water content of the feedstock - Unwanted secondary products - High corrosiveness - Intensive reaction conditions
Enzymatic	+ No need for product purification + Esterification of free fatty acids + Mild reaction conditions	- Lower conversion - High costs - Methanol toxicity

1.4.2 Critical properties of the feedstocks

The chemistry described above forms the basic concept of industrial biodiesel production. However, the final biodiesel properties, the cost and method of production are closely related to the feedstock utilized each time for the process. The critical physicochemical properties of each feedstock   which assessed for biodiesel production suitability are described briefly below.

1. Acidity

Acidity expresses the content of oil in free fatty acids and is either expressed as acid value (the mg of KOH required to neutralize 1 g of oil) or as percent acidity (the per cent content of free fatty acids with the assumption that all free fatty acids are from a certain compound, usually oleic acid). In the case of basic catalyzed process, free fatty acids are converted to soaps, as shown in Figure 4. The higher the acidity in a specific feedstock, the less favorable is the biodiesel production, as free fatty acids should either be removed prior to processing or transformed to esters by applying a pretreatment step.

Figure 4: Soap formation reaction for oleic acid
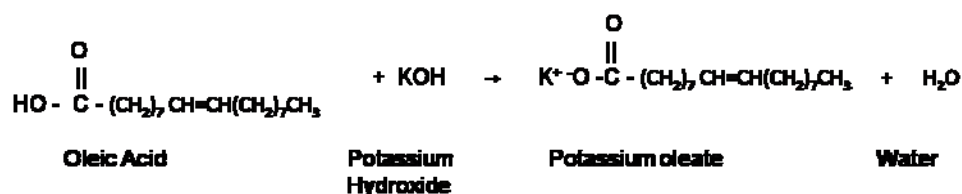
Acidity in fresh oils depends on multiple factors but usually is associated with the quality of the raw material from which the oil is extracted. In cases of long storage periods of the raw materials prior to processing acidity is higher due to biological decomposition of triglycerides to free fatty acids. Also, decomposition of triglycerides can be accelerated by the presence of moisture, salts, heat and radiation.

2. Fatty acid profile

Oils and fats are defined as a mixture of monoglycerides, diglycerides and triglycerides (MDT's). MDT's are defined as the ester derived from glycerol and one, two or three fatty acids respectively. Fatty acid is a carboxylic acid with a long unbranched aliphatic tail (chain), which is either saturated or

unsaturated. Most naturally occurring fatty acids have a chain of an even number of carbon atoms, from 4 to 28. When they are not attached to any other molecule fatty acids are called "free" fatty acids and their concentration defines the acidity of the oil and when they react with alkaline solutions they are transformed to soaps.

Fatty acid profile affects many properties of the biofuel. Most important property of the fatty acid profile is the chain length and the degree of the saturation. According to Knothe, "while in many respects biodiesel possesses advantages or is competitive with petroleum-derived diesel fuel, virtually all biodiesel fuels, typically the methyl esters, produced from these oils have performance problems such as poor low-temperature properties or insufficient oxidative stability. Considerable research has focused on solving or alleviating these problems and five approaches have been developed. Besides the approach of using additives, changing the fatty ester composition by either varying the alcohol or the fatty acid profile of the oil have been studied. Changing the fatty acid profile can be achieved by physical means, genetic modification of the feedstock or use of alternative feedstocks with different fatty acid profiles. In some cases approaches may overlap."

3. <u>Moisture, insoluble impurities and unsaponifiable matter</u>

According to Gerpen et al. (1), "moisture, insoluble impurities and unsaponifiable matter is a combined measure of the percentage of moisture (M), insoluble materials (I) and unsaponifiable matter (U) present in oils. The I and U components indicate the presence of various possible non-triglyceride materials that serve as contaminants for the biodiesel product and reduce product yields. The moisture value is particularly important, because moisture

can lead to the production of free fatty acids and soaps instead of esters in the reaction system."

The reaction of water hydrolysis of a triglyceride toward the formation of a diglyceride and a free fatty acid is shown in Figure 5.

Figure 5: Triglyceride hydrolysis reaction

$$
\begin{array}{lcccc}
 & O & & & \\
 & \| & & & \\
CH_2 - O - C - R_1 & & CH_3 - OH & & \\
| & & | & & \\
| \quad O & & | \quad O & & O \\
| \quad \| & & | \quad \| & & \| \\
CH - O - C - R_2 \; + \; H_2O & >>> & CH_3 - O - C - R_2 \; + \; HO - C\text{-}R_1 \\
| & & | & & \\
| \quad O & & | \quad O & & \\
| \quad \| & & | \quad \| & & \\
CH_2 - O - C - R_3 & & CH_3 - O - C - R_3 & &
\end{array}
$$

Triglyceride   **Water**   **Diglyceride**   **Fatty acid**
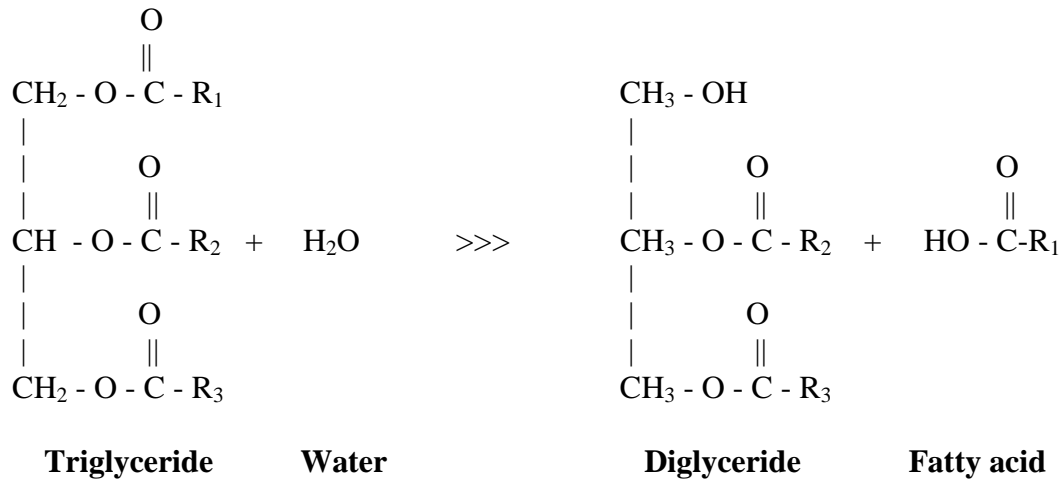
1.4.3 Post-reaction processing

Since the transesterification reaction has been finalized, the ester product should be treated and refined so as to meet certain quality criteria and properties. These steps are including glycerol/ester separation, residual alcohol recovery, catalyst and soap removal, drying and filtering. Each of these steps has detrimental effect in critical fuel properties, therefore, it is important to ensure the appropriate treatment.

1.5 Biodiesel quality standards

The development of biodiesel's industrial production was triggered by extensive field tests of biodiesel use in running engines and vehicles so as to determine the limits of various fuel properties. In Europe, the quality of biodiesel is assessed under the provisions and the requirements of quality

standard EN 14214. The standard provided in Table 3, contains 25 different quality parameters that should be met from each biodiesel sample so as to be suitable for use in vehicles as substitute for diesel fuel in transport sector.

In the US, the basis for biodiesel fuel quality is ASTM D 6751, indicated in Table 4. The standard set specific limits so as a fatty acid ester to carry the designation "biodiesel fuel" or "B100" and to perform properly as a compression ignition fuel either pure 100 % or blended with petroleum-derived diesel fuel.

Each quality standard includes certain testing methods to perform the property measurements. Methods explain in detail the process of measurement, from reagent quality requirements, sample preparation, testing procedure and results calculation and reporting. The goal of the methods is to create a common way of identical testing and reporting procedure in various laboratories.

Table 3: The European biodiesel quality standard EN 14214

Property	Units	lower limit	upper limit	Test-Method
FAME content	% (m/m)	96,5	-	EN 14103
Density at 15°C	kg/m³	860	900	EN ISO 3675 / EN ISO 12185.
Viscosity at 40°C	mm²/s	3,5	5,0	EN ISO 3104
Flash point	°C	> 101	-	EN ISO 2719 / EN ISO 3679.
Sulfur content	mg/kg	-	10	- EN ISO 20846 / EN ISO 20884.
Carbon residue remnant (at 10% distillation remnant)	% (m/m)	-	0,3	EN ISO 10370
Cetane number	-	51,0	-	EN ISO 5165

Sulfated ash content	% (m/m)	-	0,02	ISO 3987
Water content	mg/kg	-	500	EN ISO 12937
Total contamination	mg/kg	-	24	EN 12662
Copper band corrosion (3 hours at 50 °C)	rating	Class 1	Class 1	EN ISO 2160
Oxidation stability, 110°C	hours	6	-	prEN 15751 / EN 14112
Acid value	mg KOH/g	-	0,5	EN 14104
Iodine value	-	-	120	EN 14111
Linolenic Acid Methylester	% (m/m)	-	12	EN 14103
Polyunsaturated (>= 4 Double bonds) Methyl ester	% (m/m)	-	1	EN 14103
Methanol content	% (m/m)	-	0,2	EN 14110I
Monoglyceride content	% (m/m)	-	0,8	EN 14105
Diglyceride content	% (m/m)	-	0,2	EN 14105
Triglyceride content	% (m/m)	-	0,2	EN 14105
Free Glycerin	% (m/m)	-	0,02	EN 14105 / EN 14106
Total Glycerin	% (m/m)	-	0,25	EN 14105
Group I metals (Na+K)	mg/kg	-	5	EN 14108 / EN 14109 / EN 14538
Group II metals (Ca+Mg)	mg/kg	-	5	EN 14538
Phosphorus content	mg/kg	-	4	EN14107

Table 4: The American Biodiesel standard ASTM D6751

Property	Method	Limits	Units
Flash point, closed cup	D 93	130 min	° C
Water and sediment	D 2709	0,050 max	% volume
Kinematic viscosity, 40 ° C	D 445	1,9 – 6,0	mm^2/s
Sulfated ash	D 874	0,020 max	wt. %
Total Sulfur	D 5453	0,05 max	wt. %
Copper strip corrosion	D 130	No. 3 max	
Cetane number	D 613	47 min	
Cloud point	D 2500	Report to customer	° C
Carbon residue	D 4530	0,050 max	wt. %
Acid number	D 664	0,80 max	mg KOH/g
Free glycerin	D 6584	0,020	wt. %
Total glycerin	D 6584	0,240	wt. %
Phosphorus	D 4951	0,0010	wt. %
Vacuum distillation end point	D 1160	360 °C max, at T-90	% distilled

2. METHODOLOGY

2.1 Purpose of this section

In this section, the reader will get familiarized with the aim and the process of the experimental procedure followed in the project. The Methodology section contains the experimental design followed in the laboratory tests, the description of the laboratory devices and the steps of the experimental process. The purpose of the section is to provide information and data in such detail so as to be possible to replicate and extend the experimental work in the future and to be easily understandable the way that experimental work was conducted.

2.2 Raw material

Waste lard was supplied by the Creta Farm pork-meat company (Rethymno, Crete, Greece), one of the largest pork meat producers in Greece. Waste lard in mainly produced as a by-product of the pork meat production and is mainly used as feedstock to the animal feed industry. However, the risk of animal disease expansion had a detrimental effect on the use and the prices of these animal origin raw materials. Therefore, nowadays biodiesel industry can provide a stable and secure alternative market for these raw materials which can contribute also to the sustainability of the biodiesel fuel use.

2.3 Tasks

The methodology of the project was based on similar studies in the scientific bibliography for evaluating biodiesel potential and suitability of various raw materials. The steps of the study and the tasks of each step are presented in Figure 6.

Figure 6: Steps and tasks for project execution

Literature review
- Scientific database search
- Paper benchmarking

Raw material characterization
- Raw material acquisition
- Analytical measurements

Process design
- Experimental conditions for pretreatment and transformation stages
- Laboratory preparations (reagents, glassware, equipment)

Experiments
- Tests and measurements

Statistical processing
- Statistical methods
- Results processing with Minitab

Results and conclusions
- Results and findings
- Report preparation

2.4 Instruments and equipment

The acid esterification and base transesterification experiments were conducted in a 500 mL three-neck flask, inserted in a glass filled with water placed on a heating magnetic stirrer model C-MAG HS 7 by Ikamag®. Constant temperature conditions were applied by continuous controlling of the water bath temperature and assuming temperature equilibrium between water and sample volumes. Methanol loss prevention under atmospheric temperature was achieved by refluxing methanol vapor with a water condenser.

Total and free glycerol and mono-, di- and triglyceride content were measured by gas chromatography according to EN 14105 analytical standard. Analysis was performed in GC-FID SRI 8610C instrument mounted with Restek MXT 500 biodiesel gas chromatography column with an internal diameter of 0,53mm, a film thickness of 0,15µm and a length of 15m, with helium as carrier gas.

Ester content, linolenic acid methylester and polyunsaturated (>= 4 double bonds) methyl ester contents were measured according to EN 14103 analytical standard procedure. Analysis was performed in a Shimadzu GC-FID 17A gas chromatograph, mounted with gas chromatography column Mega Biodiesel 103 with an internal diameter of 0,32mm, a film thickness of 0,25 µm and a length of 30m.

The acid value is expressed in mg KOH required to neutralize the free fatty acids present 1 g of oil. The analysis was performed according to EN ISO 660 for the determination of acid value and acidity in animal and vegetable fats and oils. The analytical procedure involves titration of an oil sample with ethanolic potassium hydroxide solution until the color change of the phenolphthalein indicator.

The acid value of biodiesel is also expressed in mg KOH required to neutralize 1 g of biodiesel. Acidity in biodiesel is due to the presence of free fatty acids and mineral

acids residues from the various treatments stages. The acid value of a fuel sample is also linked with the fuel's age and oxidation, so generally is used as a fuel aging indicator. The acid value of biodiesel was measured in accordance with EN 14104 testing method which is similar to the EN ISO 660 testing method, described earlier in detail.

The density at 15 ^{o}C was measured in a density meter instrument Anton Paar DMA 38, calibrated and performed according to ASTM D4052.

The kinematic viscosity was measured with a capillary viscometer employing Cannon-Fenske viscometers immersed in water bath, according to ASTM D445.

Water removal from the final biodiesel product was performed in rotary evaporator Heidolph Laboretta 4011-digital under vacuum and in elevated temperature.

2.5 Experimental design

The purpose of the design was to evaluate the significance of process parameters and to optimize the biodiesel production process of waste lard employing a two step process under mild conditions. The first step was to esterify the free fatty acids present in the fat under acid homogeneous catalyst and the second step was to transesterify the glycerides to their respective methyl esters under basic homogeneous catalyst. Therefore, a 2^3 experimental design for each step was performed and tests were run in duplicate so as to minimize experimental error and increase model accuracy.

The method of factorial design has been developed by Box (15) and is widely used by experimenters for a number of reasons. According to the authors, some of these reasons are:

1. It requires a relatively few runs per factor studied; and although it is unable to explore fully a wide region in the factor space, it can indicate major trends and so determine a promising direction for further experimentation

2. When a more thorough local exploration is needed, it can be suitably augmented to form composite designs

3. The interpretation of the observations produced by the designs can proceed largerly by using common sense and elementary arithmetic

The selection of the experimental conditions was made after comparing typical values of process parameters from the relevant existing scientific literature (16), (17), (18), (19), (20), (21). The 3 selected parameters for exploration in the pretreatment stage were process duration (time), methanol-to-oil ratio and catalyst-to- oil ratio and the response was the transformation yield (%). In the transesterification reaction process variables under investigation were methanol-to-oil ration, process duration and catalyst –to-oil ration. In Table 5 variables under investigation and their respective high and low values are presented in detail.

Table 5: Process variables under investigation for each stage

Stage	Variable	Low value	High value
Pretreatment	Methanol-FFA ratio (mole/mole FFA)	15:1	23:1
	Catalyst-FFA ratio (% wt FFA)	20	40
	Time (min)	60	120
Transesterification	Methanol-oil ratio (mole/mole oil)	6:1	9:1
	Catalyst-oil ratio (% wt oil)	1	2
	Time (min)	30	60

For the calculation of the methanol to free fatty acids ratio and the methanol to glycerides ratio, the average molecular weight (MW) of the lard was estimated according to its fatty acid profile. The methodology of average lard molecular weight is based on estimating the molecular weight of the triglycerides and the molecular weight of the present free fatty acids and then, adding them in order to calculate the molecular weight of the lard. The estimation is based on the assumption that no diglycerides and monoglycerides are present in the oil.

Below, in Figure 7 is depicted a typical molecule of a triglyceride. The calculation equations are shown below the figure.

Figure 7: Structure of triglyceride
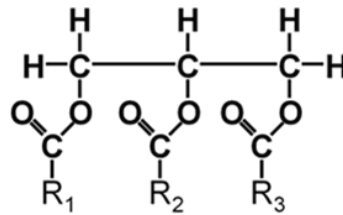
$$MW_{oil} = MW_{TG} + MW_{FFA}$$

$$MW_{TG} = 3(\overline{R}) + 173$$

$$\overline{R} = \Sigma\left(\frac{\% FA_n}{100} \times MW_n\right)$$

Where:

MW_{oil} = molecular weight of the oil

MW_{TG} = molecular weight of triglyceride

MW_{FFA} = molecular weight of free fatty acid

$\% FA_n$ = wt% of fatty acid

MW_n = molecular weight of fatty acid <u>minus</u> molecular weight of COOH

(- 45.02)

Therefore,

$$\overline{R} = \sum \left(\frac{(1.0 \times 183.36) + (21.1 \times 211.41) + (1.5 \times 209.4) + (11.5 \times 239.46) + (40.1 \times 237.45) + (21.7 \times 235.43) + (1.5 \times 233.42)}{100} \right) \rightarrow$$

$$\rightarrow \overline{R} = 226,92$$

$$MW_{TG} = 3*(226,92) + 173 = 853,78$$

$$MW_{oil} = MW_{TG} + MW_{FFA} = (0,9344 \times 853,78) + (0,0656 \times 271,94) = 815,61 \text{ g/mol}$$

2.6 Materials and methods

2.6.1 Characterization of the feedstock

Dehydrated lard was provided by CretaFarm S.A., a meat industry company located in Rethymnon, Crete, Greece. As it was when supplied, the feedstock was not subjected to any further refining process prior to the experimental process.

The fatty acid composition of the oil was analyzed using gas chromatography (GC) (Shimadzu, model GC-17A). The chromatograph was equipped with flame ionization detector (FID) and mounted with a Mega Biodiesel 103 0,2mm x 0,25μm x 30m column. Helium was used as carrier gas at suitable flow rate. Injector and detector temperatures were constant for the whole analysis at 300 °C. Temperature program of the column oven started at 200 °C, then to 240 °C at a rate of 5 °C/min, hold at 240 °C for 5 min, to 260 at a rate of 5 °C/min and finally, hold at 260 °C for 5 min.

The acid value of the lard was obtained according to the official method for the determination of acid value and acidity in vegetable and animal oils and fats of the

European Committee for Standardization (EN 660:1999), adopted by the Hellenic Organization for Standardization SA . The method's principle is that a test portion is dissolved in a mixed solvent and titrated with an ethanolic solution of potassium hydroxide till it reaches the endpoint. The known quantity of potassium hydroxide contained in the ethanolic solution is needed to fully neutralize the present FFA in the test portion. Acid value is expressed as mg of KOH needed to neutralize 1 g of the oil whereas acidity is calculated and expressed conventionally as percentage of a certain fatty acid present in the oil.

2.6.2 Pretreatment method

According to scientific literature (22), (23), feedstock with acidity above 1% cannot be converted efficiently to biodiesel with the conventional alkaline process. If FFA content is above this limit, soap formation decreases catalyst activity and inhibits the reaction rate and time for completion. Moreover, water formation is causing more soap formation by hydrolyzing the triglycerides to free fatty acids. Increased soap content in reaction mixtures also decelerates glycerol separation and increases settling time for adequate glycerol removal.

Picture 1: Testing equipment for esterification step

Esterification catalyzed by homogeneous acid catalyst is a common way for converting FFA to esters. After this pretreatment step, the reaction mixture has a low acidity and can be followed by a common alkaline transesterification so as to convert triglycerides to the desired final product. Esterification conditions varied according to Table 1. For the tests, 50,0 g of raw material was weighted and added to a 500 mL spherical reaction flask (Picture 1). The reaction flask with the lard was immersed in hot water

bath in the desired temperature (50±1 °C) to heat the lard and tapped with a water-cooled condenser for refluxing methanol vapors. Predefined sulfuric acid and methanol quantities were mixed in a 250 mL Erlenmeyer flask and added to the heated oil after the oil reached the reaction temperature. After placing the reaction flask back inside the water bath, the magnetic stirrer was turned on. At this point the reaction started (t=0). As soon as the reaction started, samples of 5 mL were obtained from the reaction mixture at certain times (1h and 2h) so as to determine total acidity reduction. Results were expressed as final acidity and acidity reduction (%).

After all the tests were completed, a larger batch was produced with adequate oil quantity for the experimental tests of the transesterification step (Picture 2).

Picture 2: Larger batch production for the transesterification experiments

2.6.3 Transesterification method

Transesterification reaction is the most significant step during the biodiesel production process as its completion signifies the transformation of the oil to the desired esters. In the present study, it was evaluated the transformation of acid pretreated lard to ester by applying basic homogeneous transesterification under mild conditions. Similarly to the pretreatment stage, experimental conditions were indicated by scientific bibliography (24), (25), (26), (27).

Transesterification tests were conducted in a three-neck 500 mL spherical flask immersed in a heated water bath at the desired temperature (50±1 °C) and tapped with a methanol vapor condenser. In each test, 50,0 g of pretreated lard were inserted

in the flask and heated up to the desired temperature. At that time, predefined amounts of premixed KOH and methanol were dissolved in the oil. Immediately after this, the magnetic stirrer was turned on and the reaction started (t=0). Periodically (at 30 and 60 min) samples of 5 mL were collected so as to measure ester content. Samples were subjected to hot de-ionized water washing so as to remove catalyst and methanol content and drying prior to the analysis.

2.6.4 Biodiesel quality determination

Final biodiesel production was prepared after finalizing both stages and selecting optimum condition for each stage. An adequate amount of lard (300 g) was treated under selected conditions so as to produce enough quantity of biodiesel for quality testing procedure. After the transesterification step, the biodiesel was further purified so as to achieve highest quality characteristics. During the purification, the

Picture 3: Biodiesel - wash water separation

final processed liquid was centrifuged so as to separate glycerol from crude biodiesel. Centrifugation was performed at 4.000 rpm for 5 min. After glycerol removal, crude biodiesel was submitted to wet washing with warm (~50°C), softened water for catalyst, methanol and soap removal. Wet washing was continued until crystal clear water was obtained after vigorous mixing of water with biodiesel (Picture 3). Next to wet washing, biodiesel was further purified with a commercial dry washing process with magnesium silicate as solid absorbent. An amount of 2% wt ratio of magnesium silicate to biodiesel was stirred with the biodiesel under elevated temperature (60°C) for 15 min. Finally, biodiesel was filtered through 1

µm filters to remove magnesium silicate remnants and other solid impurities present in the fuel. Analytical procedure and methods for determining biodiesel quality have been described in detail earlier in chapter 2.3.

2.6.5 Reagents and chemicals

The reagents used during the characterization of the feedstock, the pretreatment and the transesterification reaction, purification and characterization of the biodiesel and their respective supplier and analytical grade are listed in Table 6.

Table 6: Reagents supplier and analytical grade

Reagents	Supplier
Methanol 99,8%	Fluka
Sulfuric acid 95-97%	Fluka
Potassium Hydroxide 85%, pellet	Panreac Quimica Sau
Ethanol absolute 99,9%	Fisher Scientific, P.A.
Diethyl ether 99,5%	Panreac Quimica Sau
Potassium hydroxide standard solution 0.1M	Sigma-Aldrich Fluka, denatured ethanol with toluene
Magnesium silicate	Magnesol D-Sol, Dallas Group
Phenolphthalein 98-100%	Riedel-de Haën
Sodium Sulfate anhydrous	Fluka, Ph Eur, anhydrous
n-Heptane	Fluka, PESTANAL®, solvent for residue analysis
Analytical standards	
Methyl heptadecanoate	Fluka analytical standard (≥99%)
N-methyl-N-trimethylsilytrifluoroacetamide (MSTFA)	Restek Inc., USA

Stock Solution Monopalmitin Std, in Pyridine	Restek Inc., USA
Stock Solution (s)-(-)1,2,4,-butanetriol Std	Restek Inc., USA

3. RESULTS

3.1 Purpose of this section

The Results section is to present in a comprehensive way the results of the experimental procedure; statistically analyze and evaluate the effect of each parameter in the process output and graphically present important findings of the experimental procedure.

3.2 Feedstock quality characterization results

Lard quality characterization results are related with the suitability of the feedstock to be used as raw material for biodiesel production. In the present study, fatty acid profile, acidity and acid value were determined. Results are presented in Table 7.

Table 7: Methyl ester profile of waste lard raw material

Lard methyl ester profile	
Methyl ester group	Concentration (wt%)
Myristate (C14:0)	1,0
Palmitate (C16:0)	21,1
Palmitoleate (C16:1)	1,5
Stearate (C18:0)	11,5
Oleate (C18:1)	40,1
Linoleate (C18:2)	21,7
Linolenate (C18:3)	1,5
Others	2,3
Acid value and acidity	
Acid Value (mg KOH/g lard)	13,06

Acidity (%)	6,56

3.3 Pretreatment optimization results

Pretreatment experiments were conducted according to the conditions specified earlier in chapter 2.4. Interaction effects of two and three factors were also considered in the statistical analysis. Table 8 contains the process variable values in original and coded units and acidity reduction results. In the table, process parameters are coded as X_1 for process time, X_2 for catalyst amount and X_3 for methanol quantity. Interactions are symbolized as X_1X_2, X_1X_3, X_2X_3 and $X_1X_2X_3$ respectively. Acidity reduction (Y) is calculated by applying the following equation:

$$Y = \frac{AV_{in} - AV_f}{AV_{in}} \times 100\%$$

where:

AV$_{in}$: the initial acidity of the lard (13,06mg KOH/g lard)

AV$_f$: the final mixture acidity at the end of each experiment

Table 8: Physical and coded values of process parameters and respective acidity reduction

	No.	Initial test No.	Time (h)	Catalyst (wt % FFA)	Methanol (Molar ratio FFA)	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	$X_1X_2X_3$	Y(%)
Initial runs	1		1	20	15:1	-1	-1	-1	1	1	1	-1	72,47
	2		1	20	23:1	-1	-1	1	1	-1	-1	1	84,43
	3		1	40	15:1	-1	1	-1	-1	1	-1	1	77,84
	4		1	40	23:1	-1	1	1	-1	-1	1	-1	88,96
	5		2	20	15:1	1	-1	-1	-1	-1	1	1	86,27
	6		2	20	23:1	1	-1	1	-1	1	-1	-1	92,41
	7		2	40	15:1	1	1	-1	1	-1	-1	-1	88,57
	8		2	40	23:1	1	1	1	1	1	1	1	92,33
Star point	9	0	1,5	30	19:1	0	0	0	0	0	0	0	89,11
	10	0	1,5	30	19:1	0	0	0	0	0	0	0	89,42
Replicated runs	11	4	1	40	23:1	-1	1	1	-1	-1	1	-1	89,88
	12	8	2	40	23:1	1	1	1	1	1	1	1	94,20
	13	1	1	20	15:1	-1	-1	-1	1	1	1	-1	71,70
	14	5	2	20	15:1	1	-1	-1	-1	-1	1	1	86,43
	15	2	1	20	23:1	-1	-1	1	1	-1	-1	1	83,74
	16	6	2	20	23:1	1	-1	1	-1	1	-1	-1	93,63
	17	3	1	40	15:1	-1	1	-1	-1	1	-1	1	75,23
	18	7	2	40	15:1	1	1	-1	1	-1	-1	-1	88,50

3.4 Transesterification optimization results

Transesterification optimization experimental procedure was also conducted under the same experimental design. Parameters under evaluation were process time (X_1), catalyst concentration (X_2) and methanol to triglyceride ratio (X_3). Second (X_1X_2, X_1X_3, X_2X_3) and third ($X_1X_2X_3$) order interactions were also taken into consideration for process optimization. Response vector contains total ester content of test samples determined by gas chromatography after sample purification. Physical and coded values as well as experimental results are indicated in Table 9.

Table 9: Physical and coded values of transesterification process parameters and optimization results

	No.	Initial test No.	Time (h)	Catalyst (wt % oil)	Methanol (Molar ratio triglyceride)	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	$X_1X_2X_3$	Y(%)
Initial runs	1		1	2	9:1	1	1	1	1	1	1	1	97,2
	2		0,5	1	9:1	-1	-1	1	1	-1	-1	1	84,3
	3		0,5	2	6:1	-1	1	-1	-1	-1	-1	1	83,2
	4		1	1	9:1	1	-1	1	-1	-1	-1	-1	91,4
	5		1	1	6:1	1	-1	-1	-1	1	1	1	86,2
	6		1	2	6:1	1	1	-1	1	-1	-1	-1	90,8
	7		0,5	2	9:1	-1	1	1	-1	1	1	-1	93,9
	8		0,5	1	6:1	-1	-1	-1	1	1	1	-1	76,4
Replicated runs	9	1	1	2	9:1	1	1	1	1	1	1	1	96,8
	10	8	0,5	1	6:1	-1	-1	-1	1	1	1	-1	77,2
	11	6	1	2	6:1	1	1	-1	1	-1	-1	-1	91,0
	12	7	0,5	2	9:1	-1	1	1	-1	1	1	-1	93,9
	13	3	0,5	2	6:1	-1	1	-1	-1	-1	-1	1	85,3
	14	4	1	1	9:1	1	-1	1	-1	-1	-1	-1	91,2
	15	2	0,5	1	9:1	-1	-1	1	1	-1	-1	1	84,1
	16	5	1	1	6:1	1	-1	-1	-1	1	1	1	86,9

3.5 Transesterification vs. reaction time

The reaction completion can be monitored by taking samples during the reaction and measuring ester content over time. In a test run, we studied the formation of esters over the process duration to trace how the process rate is decreasing and where is the endpoint of the reaction. As shown in Figure 6, the biggest part of ester formation is completes at the first 30 min of the reaction time. After then, only 3-5% of the oil is converted to biodiesel for the rest 30 min.

From Figure 8, it can be also observed that a better approach of biodiesel reaction could be the separation in two distinct steps. Step 1 could last 15-20 min so as to transform around 70-80% of the feedstock to biodiesel and then, after removing produced glycerol, in step 2 to complete the reaction in shorter time and with greater efficiency.

Figure 8: Ester content over reaction time for a test run
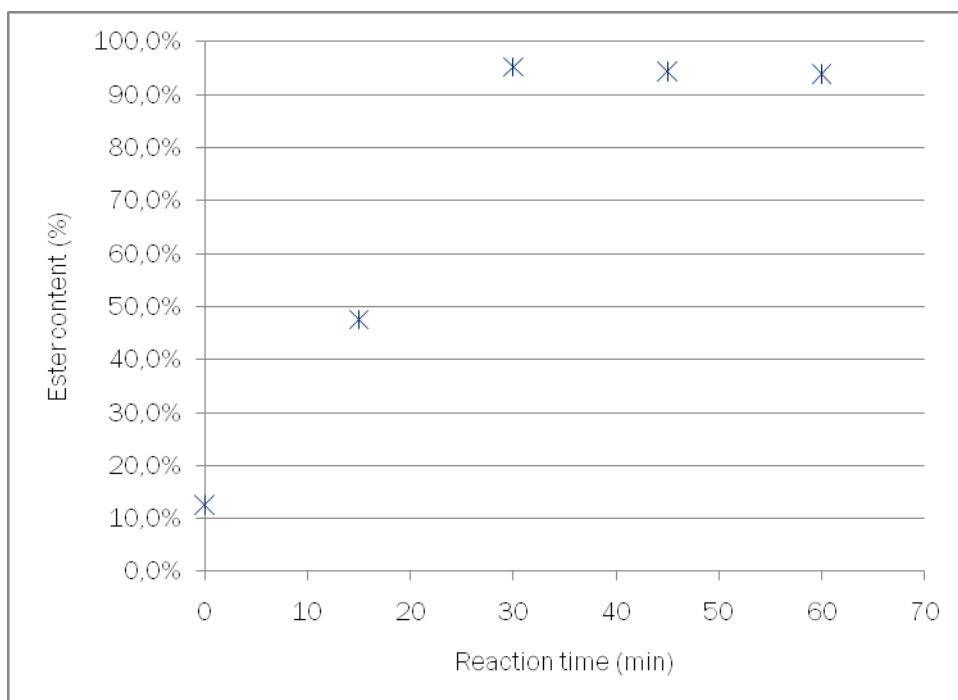
3.6 Biodiesel quality determination results

This section contains the results of biodiesel quality determination. The sample was prepared under the optimum process conditions specified in the previous stages. The scope is to compare fuel properties with property limits according to official biodiesel standards. Besides, some of the biodiesel fuel properties can be improved by blending different feedstock prior to transesterification. These properties are feedstock dependant and usually are related with the fatty acid profile of the raw material. Table 10 indicates the observed value of each quality parameter as well as the respective standard limits in Europe and in the USA.

Table 10: Properties of lard methyl esters and respective standard limits

Property	Observed value	Limits	
		EN 14214	ASTM D6751
Ester content (%)	99,4	96,5	-
Density at 15°C (kg/m³)	877	860-900	900
Viscosity at 40°C (mm²/s)	10,87	3,5-5,0	1,9 – 6,0
Monoglyceride content (%)	0,0156	<0,8	-
Diglyceride content (%)	0,0005	<0,2	-
Triglyceride content (%)	0,0040	<0,2	-
Free Glycerine (%)	0,0031	<0,02	<0,020
Total Glycerine (%)	0,0075	<0,25	<0,240
Acid value (mgKOH/g biodiesel)	0,42	0,5	0,8

4. STATISTICAL ANALYSIS OF EXPERIMENTAL RESULTS

4.1 Scope

The scope of the chapter is to statistically process the experimental results and to quantify the importance of each experimental parameter so as to indicate the most critical process factors. It is worth mentioning that statistical analysis covers only the region where each parameter was examined, therefore importance of each parameter is concluded for this certain region. Confidence level for all stages has been considered at 95%.

4.2 Analysis of variance for the pretreatment stage

Effect estimation and analysis of variance were calculated using the software Minitab Release 14 which supports the development and the processing of full factorial designs. Experiments were conducted in random order so as to minimize experimental error due to possibly biased experimenter. Tables 11 and 12 are presenting the ANOVA results and factor's effects.

The behavior of the reaction under evaluation is described by the linear model presented in Equation (1).

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_1 x_2 + \beta_5 x_1 x_3 + \beta_6 x_2 x_3 + \beta_7 x_1 x_2 x_3 \tag{1}$$

Table 11: Effects and coefficients for the linear model of the esterification reaction

Estimated Effects and Coefficients						
Term	Coefficient	Effect	Coef. value	SE Coef	T	P
Constant	β_0		85,599	0,2545	336,35	0,000
Time	β_1	9,388	4,694	0,2545	18,44	0,000
Catalyst	β_2	2,68	1,34	0,2545	5,27	0,001
Methanol	β_3	9,445	4,722	0,2545	18,56	0,000
Time*Catalyst	β_4	-1,465	-0,732	0,2545	-2,88	0,018
Time*Methanol	β_5	-3,745	-1,872	0,2545	-7,36	0,000
Catalyst*Methanol	β_6	-0,638	-0,319	0,2545	-1,25	0,242

Time*Catalyst*Methanol	β_7	-0,332	-0,166	0,2545	-0,65	0,530
Ct Pt			3,666	0,7635	4,80	0,001
S = 1,01799	R^2 =	98,89%				

Table 12: ANOVA results for the esterification linear model

Analysis of Variance					
Source	Degrees of Freedom	Sum of Squares	Mean Square	F	P
Main Effects	3	738,062	246,021	237,4	0,000
2-Way Interactions	3	66,311	22,104	21,33	0,000
3-Way Interactions	1	0,442	0,442	0,43	0,530
Curvature	1	23,896	23,896	23,06	0,001
Residual Error	9	9,327	1,036		
Total	17	838,038			

The model fit is checked with the correlation factor R^2, which equals to 98.89%, thus indicating adequate correlation performance. Model significance is indicated true by the F value, as it is much higher than the upper 5% point of F distribution for $F_{(8,9)}$, which equals to 3,23.

The Pareto chart presented in Figure 9 indicates that most significant effects for the pretreatment process are methanol to oil ratio, reaction time and the interaction between the two of them. Catalyst concentration seems to affect process yield but not so much as the other factors. All effects except from interaction between catalyst and methanol ratio and third order interaction are statistically significant.

Except from main effects, second and third order interactions, the curvature and its statistical significance have been estimated, as shown in Table 12, and resulted to be statistically significant. Although there is a high correlation factor, it is indicated that a further non linear, quadratic model can be developed and evaluated.

Figure 9: Pareto chart for the full factorial design for the pretreatment stage including factors, second and third order interactions

Pareto Chart of the Standardized Effects
(response is C8, Alpha = ,05)

2,26

Factor	Name
A	Time
B	Catalyst
C	Methanol

Term (C, A, AC, B, AB, BC, ABC)

Standardized Effect
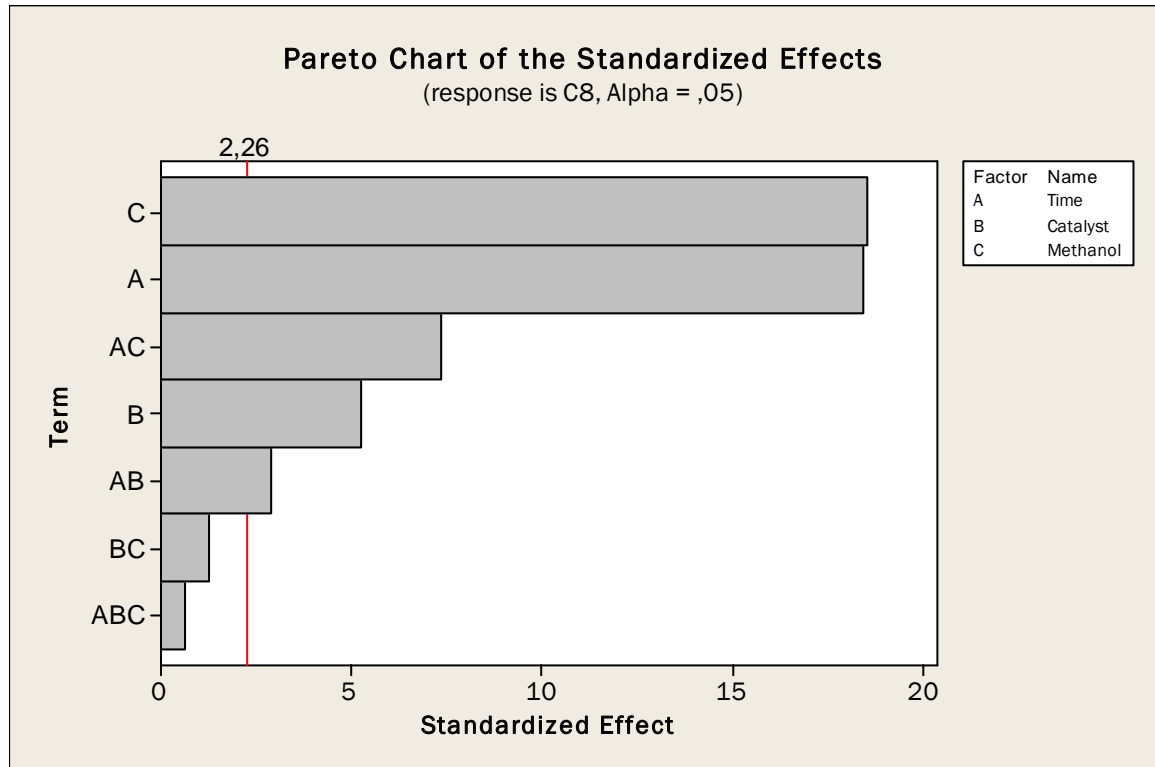
4.3 Analysis of variance for the transesterification stage

Once more, for the transesterification stage, the simplest linear model of Equation 2 was employed so as to describe the effect of the various process parameters on the reaction yield.

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_1 x_2 + \beta_5 x_1 x_3 + \beta_6 x_2 x_3 + \beta_7 x_1 x_2 x_3 \qquad (2)$$

Calculated values for model coefficients and effects as well as correlation factor R^2 are presented in Table 13.

Table 13: Effects and coefficients for the linear transesterification model

Estimated Effects and Coefficients						
Term	Coefficient	Effect	Coef. value	SE Coef	T	P
Constant	β_0		88,1125	0,1508	584,38	0,000
Time	β_1	6,65	3,325	0,1508	22,05	0,000
Catalyst	β_2	6,8	3,4	0,1508	22,55	0,000
Methanol	β_3	6,975	3,4875	0,1508	23,13	0,000
Time*Catalyst	β_4	-1,775	-0,8875	0,1508	-5,89	0,000
Time*Methanol	β_5	-1,55	-0,775	0,1508	-5,14	0,001
Catalyst*Methanol	β_6	0,9	0,45	0,1508	2,98	0,017
Time*Catalyst*Methanol	β_7	-0,225	-0,1125	0,1508	-0,75	0,477
S = 0,603117		R^2 =	99,50%			

From Table 13, it is observed that only the third order interaction is not statistically significant (p value over than 0,05), however also second order interactions show low effect. For the time factor, second order interactions with methanol and catalyst have a negative effect on the process yield. Correlation of the model to the observed values is very high (99,50%), indicating that model can successfully describe the process progress.

Table 14 presents the results of the analysis of variance for the model of Equation 2.

Table 14: ANOVA results for the transesterification linear model

Analysis of Variance					
Source	Degrees of Freedom	Sum of Squares	Mean Square	F	P
Main Effects	3	556,453	185,484	509,9	0,000
2-Way Interactions	3	25,453	8,484	23,32	0,000
3-Way Interactions	1	0,203	0,203	0,56	0,477
Residual Error	8	2,91	0,364		
Pure Error	8	2,91	0,364		
Total	15	585,018			

From a statistical standpoint, linear equation can be considered significant due to high F (Table 14) value and satisfactorily describes the progress of the reaction in the area of experiments. Curvature has not been calculated as in the transesterification stage, no central points were tested. From the Pareto chart in Figure 10, it can be observed from the length of each bar that main effects affect by far more than second order interaction with reaction time to have the greatest influence.

Figure 10: Pareto chart for the full factorial design for the transesterification stage including factors, second and third order interactions
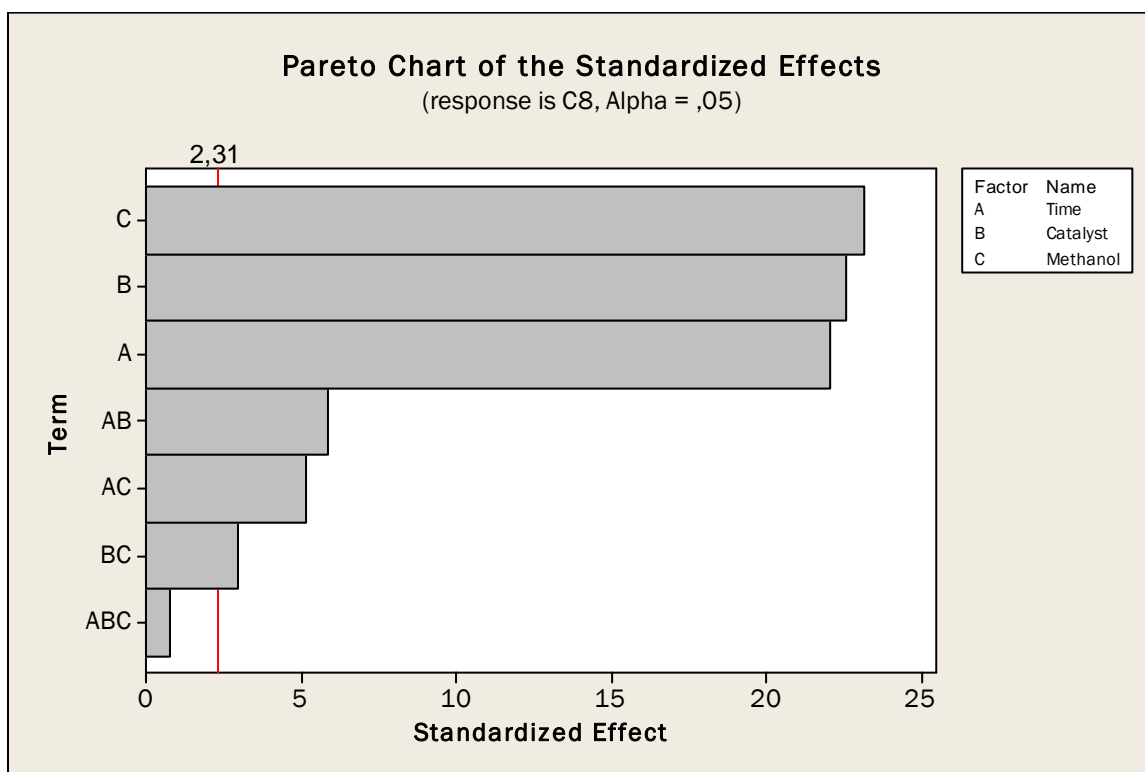
4.4 Conclusions

Since biodiesel production has became an industrial activity, understanding the influence of production parameters in the performance of the reaction is extremely important so as to optimize the process. This coordinated approach considered only three production parameters for each production stage, since they are considered among the most important and in order to be completed in a timely manner.

This study identified the statistical significance and the influence of each parameter as well as the influence of the two and three way interactions. In the case of two way interactions, we considered them as the combined effect of the two parameters. Albeit the fact that the study focused only in a certain region of parameters values, it is clearly indicated which are the most significant process parameters for each stage and which are negligible or, at least, not so important for the process outcome.

The statistical analysis has shown that:

❖ For the pretreatment stage the most significant process factors are methanol to FFA ratio and duration of the process (process time). Also, second order interactions between process time and methanol to FFA ratio have also high significance. On the contrary, catalyst concentration had limited influence on the pretreatment performance, nor the two stage interactions with the other parameters.

❖ The performance of biodiesel transforming process (transesterification) is highly dependent on the main examined process factors (namely methanol to oil ratio, catalyst concentration and process duration). Second order interactions have also a limited influence that can be also ignored. Third order interaction is statistically unimportant and can be ignored.

❖   The model equations describing the reaction performances according to the examined process parameters and

the two and three way interactions have a satisfying correlation with the experimental results (98,9% & 99,5%).

❖ The obtained equation for the performance of the esterification stage (pretreatment) if only statistically significant factors are considered is:

$$Y=85,59+4,69T+1,34C+4,72M-0,79T*C-1,87T*M$$

- T: reaction time in minutes

- C: catalyst concentration (wt % FFA)

- M: Methanol molar ratio to FFA

❖ The obtained equation for the performance of the transesterification stage if only statistically significant factors are considered is:

$$Y=88,11+3,32T+3,4C+3,48M-0,88T*C-0,77T*M+0,45C*M+3,666*CtPt$$

- T: reaction time in minutes

- C: catalyst concentration (wt % oil)

- M: Methanol molar ratio to triglycerides

- CtPt: If it is Center point equals to1, else equals to 0

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Outcomes and added value of the study

Biodiesel production from waste acid lard was effectively produced through a two step homogeneous catalyzed process. Experimental results show that in order to effectively pre-treat the feedstock and to transform it to biodiesel that conforms with the biodiesel quality standard, much attention should be given to certain process parameters as indicated by the statistical analysis of the results. However, it is remarkable to point out that in the case of transesterification stage, only two experiments were resulted to adequate conversion of the feedstock to biodiesel.

Waste lard can represent a major feedstock source for sustainable biodiesel production in the short term as it can be obtained from existing companies in the hog sector. One advantage of the feedstock is that the production process is distinctly different from the other livestock segments as usually most of the animals are raised in certain farms and therefore the dispersion of collection point is relatively low. From this standpoint, it is relatively easy and financially more profitable to create and integrate a collection system for this particular feedstock towards the production of biodiesel.

This particular study was the first comprehensive effort so as to explore a new unconventional but promising feedstock for sustainable biodiesel production in the Region of Crete. Despite the absence of relevant laboratory experience from past projects, the final results can clearly present some interesting outcomes and underline some points for further research and exploration.

General conclusions of the study are:

- ❖ Waste lard is a very promising feedstock source that is readily available from certain industrial sites. If it is also considered the current situation of animal waste processing in the island of Crete and in Greece, it is easily understood that available quantities could be higher, acquisition price lower and therefore biodiesel potential much more promising

- ❖ The exploitation of waste lard toward the production of biodiesel can include environmental and social benefits beyond the economic viability. Indicatively value added benefits could be:

  - ▪ Mitigation of climate change

  - ▪ Reduction of crude oil pollution

  - ▪ Proper waste management

  - ▪ Energy independency

  - ▪ Job creation

  - ▪ Renewable energy awareness

  - ▪ Reduction of air emissions and dangerous pollutants

- ❖ Biodiesel from waste lard meet all the process dependant quality properties (e.g. glyceride content, glycerin content) limits. That fact underlines that process development and production conditions are proper so as to produce biodiesel from lard with adequate quality to be used in vehicles

- ❖ Biodiesel from waste lard does not meet certain feedstock dependant properties (e.g. viscosity). Feedstock dependant properties cannot be modified by any processing.

- ❖ Statistical analysis showed a clear significance image of the production parameters. At the certain region of process conditions, most important process parameters were indicated and should be considered if further process optimization will be requested

❖ There are also other process factors that should be accounted for and examined so as to achieve optimum process result, such as rate of stirring, process temperature and number of step on a multi-step transesterification process

5.2 Difficulties and obstacles

Difficulties and obstacles faced during the study were due to lack of infrastructure and lack of relevant laboratory experience. To overcome those, more time and effort as well as development of collaborations with other laboratories and professors were essential. Major hindrances were:

❖ Absence of scientific equipment for accurate and precise process conditions (temperature, stirring and pressure) and sampling

❖ Lack of analytical scientific equipment designated to the determination of critical quality properties of biodiesel (cloud point, water content, methanol content etc)

❖ Limited laboratory space for experimental runs and tests and limited availability of certain laboratory devices and equipment (magnetic stirrers, centrifuge)

❖ Time, chemicals and glassware constraints

As an added value of the study, it can be considered the development of relevant know-how and acquisition of experience that can be used for further research efforts and initiatives. In short, in the framework of the study the following tasks were completed:

❖ Acquisition and collection of all the official analytical standards for feedstock characterization and biodiesel quality determination

- ❖ Restoration and activation of a non-operational gas chromatography instrument. The device was specifically configured so as to operate according to European analytical standard EN 14105 for the determination of ester content in biodiesel samples. To learn more about the analysis method, detailed information can be found in Appendix 1 – Analytical standard EN 14105

- ❖ Acquisition and set up of a new gas chromatograph specially configured to analyze and measure concentrations of monoglycerides, diglycerides, triglycerides, total and free glycerol according to official analytical standard EN 14108

- ❖ Instrumentation acquisition and configuration for the measurement of acid value and acidity in vegetal oil and biodiesel samples

- ❖ Acquisition of essential glassware and laboratory devices for the experimental procedures of the pretreatment and transesterification stages

5.3   Recommendations for further research and actions

Waste lard is an unexplored biodiesel feedstock source with limited exploitation so far. According to the findings of the present study and the available scientific bibliography, there are recommendations for further research at experimental in terms of process optimization, fuel properties determination and improvement and end use testing.

Experimental efforts should focus on:

1. Further process optimization taking into consideration also other process parameters (temperature, agitation, pressure), process techniques (e.g. multiple step transesterification, glycerolysis of free fatty acids), reactor

systems (e.g. supercritical reactors, ultrasound assisted reactors), total energy investment, energy payback and cost

2. Further fuel properties determination (e.g. pure point, cetane number, methanol content, cloud point) so as to conclude in which property limits the fuel fails to meet and how that properties can be improved. Commonly, a mixture of many different feedstocks can be the solution for property improvement. Therefore, it is also strongly suggested to combine waste lard with other locally available, sustainable raw materials (waste frying oil, olive pomace oil) so as to produce biodiesel that will fulfill all the fuel property requirements. It is also advisable to examine whether the viscosity measurement is realistic as there are evidences that the viscometer measurements are not accurate

3. Further biodiesel penetration in the fuel market. As a major step towards the adoption of wide use of sustainable biodiesel as transport fuel, it is suggested the pilot development of a small scale production system for the generation of biofuel in adequate quantities for pure or high-ratio blended use in a monitored fleet of vehicles, so as to determine impacts of biodiesel fuel in engine parts and fuel supply system. The aim will be the positive impact on potential end users and the decrease of reluctance and unwillingness for the adoption of alternative biofuels.

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