SCHOOL OF SCIENCE AND ENGINEERING

Valorization of Olive Oil Water Effluents and Olive Pomace into Biodiesel

Capstone Design - Final Report

Spring 2016

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Supervised by: Dr. Samir EL HAJJAJI
# Table of Contents

Acknowledgments.......................................................................................................................... ii
Abbreviations.................................................................................................................................. iii
List of figures...................................................................................................................................... v
List of tables....................................................................................................................................... vii
Abstract ........................................................................................................................................... viii

I. Introduction ................................................................................................................................. 1
  1.1 Renewable energy ..................................................................................................................... 1
  1.2 Wastes generated by the olive oil industry .............................................................................. 1
  1.2 One solution: biodiesel ........................................................................................................... 6
  1 STEEPLE analysis ..................................................................................................................... 9

2 Experimental results .................................................................................................................... 10
  2.2 Chemicals and equipment used .............................................................................................. 10
  2.3 Olive oil extraction from pomace .......................................................................................... 11
      3.3.1 Optimization of the extraction time ................................................................................. 13
      3.3.2 Large-scale extraction of oil from pomace ..................................................................... 16
  3.3 Olive oil extraction from oil water effluents ........................................................................... 18
  3.4 Biodiesel production .............................................................................................................. 21
  3.5 Qualitative Analysis ................................................................................................................ 29
      3.5.1 Thin Layer Chromatography (TLC) .................................................................................. 29
      3.5.2 Comparison of the properties of biodiesel, diesel, and oil .............................................. 32
      3.5.2.1 Density .......................................................................................................................... 32
      3.5.2.2 Heat Content ............................................................................................................... 33

Conclusion ........................................................................................................................................ 40
References .......................................................................................................................................... 42
Appendix ........................................................................................................................................... 44
Acknowledgments

First of all, I would like to express my genuine gratitude to Dr. Samir El HAJJAJI for his excellent supervision, precious time, and patience. Throughout all the tasks and experiments carried out, he provided me with the necessary guidance to successfully reach the goal of my capstone project. I also want to thank the lab technician Mr. Abdellatif OUDDACH for his help and availability.

Most importantly, I would like to express my sincere gratefulness to my parents and closest friends who gave me constant support and encouraged me in the hardest times.

Last but not least, I would like to express my appreciation to the School of Science and Engineering (SSE) for all the knowledge, skills, and abilities I have been able to acquire throughout the four years I spent at Al Akhawayn University.

SAMIR EL HAJJAJI
MAY 3, 2016
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>b.p</td>
<td>Boiling point</td>
</tr>
<tr>
<td>rpm</td>
<td>Revolutions per minute</td>
</tr>
<tr>
<td>Equ.</td>
<td>Equivalence</td>
</tr>
<tr>
<td>Owe.</td>
<td>Oil water effluents</td>
</tr>
<tr>
<td>Exp.</td>
<td>Experiment</td>
</tr>
<tr>
<td>Temp.</td>
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<tr>
<td>Adv.</td>
<td>Advantages</td>
</tr>
<tr>
<td>Disadv.</td>
<td>Disadvantages</td>
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<tr>
<td>Sol.</td>
<td>Solution</td>
</tr>
<tr>
<td>w.</td>
<td>By weight</td>
</tr>
<tr>
<td>TDS</td>
<td>Total dissolved solids</td>
</tr>
<tr>
<td>B20</td>
<td>20% biodiesel blend with diesel</td>
</tr>
<tr>
<td>B100</td>
<td>100% biodiesel</td>
</tr>
<tr>
<td>C₆H₁₄</td>
<td>Hexane</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>Symbol</td>
<td>Name</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>MeONa</td>
<td>Sodium methoxide</td>
</tr>
<tr>
<td>KOH</td>
<td>Potassium hydroxyde</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>Phosphoric acid</td>
</tr>
<tr>
<td>KMnO₄</td>
<td>Potassium Permanganate</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin layer chromatography</td>
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<tr>
<td>OBC</td>
<td>Oxygen bomb calorimeter</td>
</tr>
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</table>
List of figures

Figure 1: Geographic location of Ain Taoujdate. ................................................................. 3
Figure 2: Disks of olive paste .................................................................................................. 4
Figure 3: Canal system and decantation wells used in the semi-traditional mill .................. 4
Figure 3: Functioning of an olive decantation well ............................................................... 4
Figure 5: Pool containing olive oil water effluents in Ain Taoujdate. February 2016 .......... 5
Graph 1: Reductions in pollutant emission obtained when using B100 and B20 fuels instead of petro diesel ......................................................................................................................... 7
Figure 6: Extraction of oil from pomace with hexane ........................................................... 12
Figure 7: Evaporation of the extracted oil solution in hexane ............................................. 13
Figure 8: Pomace sample ...................................................................................................... 14
Graph 2: Extraction yields obtained at different extraction times based on Table 1 .......... 15
Figure 9: Setup used in the large-scale extraction of oil from pomace ............................... 16
Figure 10: New setup used in the large-scale extraction of oil from pomace ....................... 17
Figure 11: Homogenizing the sample of oil water effluents collected during the olive oil production season ................................................................................................................. 18
Graph 3: Composition of the first sample of oil water effluents collected in Feb.2016 .... 20
Graph 4: Composition of the second sample of oil water effluents collected in Nov.2015 .... 20
Figure 12: Collecting olive oil from water effluents ............................................................. 21
Figure 13: General equation of the transesterification reaction of a triglyceride ............... 22
Figure 14: Heating the mixture to produce biodiesel ............................................................ 23
Figure 15: Layers of biodiesel and glycerin in a separatory funnel ...................................... 25
Figure 16: Centrifuged test tube containing biodiesel, soap, and an aqueous solution ....... 26
Figure 17: Filtration of the mixture of biodiesel and sodium sulfate over coton under vacuum. 27

Figure 18: Thin layer chromatography in progress................................................................. 30

Figure 19: TLC performed on biodiesel and oil sample .......................................................... 31

Figure 20: Calorimeter ............................................................................................................. 33

Figure 21: Bomb inside the calorimeter .................................................................................... 34

Graph 5: Heating curve of Benzoic acid .................................................................................... 35

Graph 6: Heating curve of Oil .................................................................................................. 36

Graph 7: Heating curve of Diesel ............................................................................................... 37

Graph 8: Heating curve of Biodiesel ........................................................................................ 38
List of tables

Table 1: Results of the oil extraction time optimization with pomace ................................................. 14
Table 2: Composition of oil water effluents ......................................................................................... 19
Table 3: Advantages and Disadvantages of MeONa and KOH as catalysts ........................................ 22
Table 4: Oil, MeOH, and MeONA properties and quantities ................................................................. 24
Table 5: Quantities used for the transesterification reaction when scaling up ..................................... 25
Table 6: Oil, MeOH, and KOH properties and quantities ....................................................................... 27
Table 7: Summary of the biodiesel experiments .................................................................................... 28
Table 8: Density of oil, biodiesel, and oil ............................................................................................. 32
Table 9: Summary of the properties of oil, biodiesel, and diesel ......................................................... 39
Abstract

During the olive oil production process, two types of by-products are generated by olive mills in Morocco: olive oil water effluents and olive pomace. The olive oil water effluents is a sort of dark liquid highly concentrated with organic compounds and the olive pomace represents the solid residue which contains leaves, olive pits, olive skin, and branches. These wastes are evacuated in the environment and cause a serious harm due to the toxic chemicals they contain.

My capstone project deals with the valorization of these wastes. The purpose of this project is to turn the residual oil contained in olive oil water effluents and olive pomace into a green fuel which could be used in our everyday life: biodiesel. Biodiesel is in fact an ecological and environmentally friendly fuel that can replace diesel fuel in any diesel-powered vehicle or engine.

To carry out this project, I collaborated with the owner of a semi-traditional olive mill situated in Ain Taoujdate, to work on samples of olive oil water effluents and samples of pomace.

By performing the adequate laboratory experiments, characterization of these wastes and extraction of their residual oil was successfully made. This oil subsequently, served as a starting material to produce biodiesel.
I. Introduction

1.1 Renewable energy

Renewable energy is defined as the energy resultant from the use of natural resources. These include solar, wind, and hydroelectric power, in addition to biomass and geothermal energy. Over time, these resources reload themselves in such a way that the Earth’s resources are never reduced or drained. The most significant benefits to note regarding these resources is their abundance and availability.¹

Using this kind of energy has indeed a great deal of advantages compared to the conventional energy thanks to its low to inexistent environmental impact. In fact, conventional energy usually results in serious repercussions on the environment by polluting the air, land, and water. Thus, resorting to renewable energy is a must to guarantee a sustainable future for our planet and to ensure the coming generations can enjoy what the Earth has to offer.

1.2 Wastes generated by the olive oil industry

With an annual production of 140 000 tons of olive oil in 2014-2015, Morocco is ranked the 5th biggest producer of olive oil in the world after Spain, Tunisia, Italy and Greece.¹ Unfortunately, like in nearly all industries, the production of this good is accompanied by the production of wastes that represent a major environmental issue and must be dealt with. During the olive oil production process, two kinds of residues are generated: the pomace and the
oil water effluents. The olive pomace is a solid mixture which contains the skin, pulp pit, and stem of the olives.³

On the other hand, the oil water effluents are dark liquid effluents characterized by high concentrations of organic compounds, including organic acids, sugars, tannins, pectins and phenolic substances that make them phytotoxic and inhibit bacterial activity.⁴

When these wastes are released in the environment, they cause a serious negative impact. Indeed, when they are discharged in rivers for example, the water becomes heavily concentrated with organic matter and pollutants thus it is no longer able to self-purify. In addition, these wastes can lead to other threats such as the destruction of the bacterial microflora of the soil, the pollution of groundwater and water dams, and infecting the roots of the plants and trees. A study conducted a few years ago by the Moroccan Ministry of Environment estimated that Morocco produced around 250,000 m³ of olive oil water effluents annually.⁵

Consequently, the production of olive oil generates several solid and liquid wastes and olive mills are considered to be an alarming source of pollution. As a matter of fact, the same Ministry of Environment has allocated 86 million dirhams in 2014 and 2015, to fight against the olive mills’ wastes and other kinds of pollutions.⁶

In the framework of my capstone project, I collaborated with the owner of a semi-traditional olive mill situated in Ain Taoujdate, a small agricultural town located 68 km to the north of Ifrane, 25 km southwest of Fez (Figure 1) to work on samples of olive oil water effluents and olive pomace.
After the olive harvest, olives are crushed, forming a sort of paste. In a powerful hydraulic press, the paste is piled up in the form of disks which are pressed to produce olive oil (Figure 2). However, when pressing the disks, a juice made of a mixture of olive oil and oil water effluents is produced and transferred into indoor decantation wells via a canal system (Figure 3). Because the density of olive oil is lower than the density of the oil water effluents, the olive
oil floats on the top of the wells and the oil water effluents are sent to an outdoor pool as depicted in Figure 4.

Figure 2: Disks of crushed olive paste under hydraulic

Figure 4: Functioning of an olive decantation well

Figure 3: Canal system and decantation wells used in the semi-traditional olive mill
In fact, like every mill in Morocco, this mill is also required to dispose of its water effluents in an outdoor pool in which the waste is dumped during the olive oil production season.

The size of this particular pool was measured on site to be exactly 13.80m x 9.30m x 0.92m (length x width x depth), which corresponds to a working volume of 118.07m$^3$ (Figure 5).

![Figure 5: Pool containing olive oil water effluents in Ain Taoujdate. February 2016](image)

According to the mill’s owner, this pool is filled with effluents 1.5 times every year during the olive oil production season; in other words, the amount of effluents released by this particular mill is 177.1m$^3$/year (1.5x118.07). In spite of being stored in this pool to undergo evaporation and decomposition, these effluents still represent a real environmental concern since they contain toxic chemicals which ultimately affect the roots of surrounding trees and plants, groundwater, and the air (foul-smelling).

However, these wastes can be taken care of. In fact, the oil water effluents usually contain a type of antioxidants called polyphenols that have an important value in the market. Their prices...
can reach about 2000 €/g and they have diverse applications in cosmetics, pharmaceutical, and food industry. Moreover, the oil water effluents still contain a quantity of olive oil that can be extracted and used for the production of biodiesel as the very goal of the capstone project described herein.

1.2 One solution: biodiesel

The capstone project described herein deals with the valorization of two types of by-products generated by olive mills in Morocco: olive oil water effluents and olive pomace. More specifically, the purpose of this project is to turn the residual oil contained in these wastes into a green fuel: biodiesel. In other words, the goal is to convert wastes into a higher-value product that can be used in our everyday life.

Biodiesel is considered as an ecological and environmentally friendly fuel which can replace diesel fuel in any diesel-powered engine. It can be used either on its own in its pure form or blended with petroleum diesel at any ratio. As soon as biodiesel is used, as B20 or B100, a significant reduction in the pollutants normally emitted during the combustion of diesel is observed (Graph 1).
Biodiesel can be made from animal fats, vegetable oil, or recycled cooking oils and greases. Its use counts numerous benefits which include the following:\(^9,10\)

- It produces less greenhouse emissions and it is less pollutant than other fuels, notably diesel.
- It releases less toxic chemicals in the air.
- It is biodegradable and does not contain sulfur or aromatics.
- It can reduce the production of CO\(_2\) by more than 52\% and up to 78\% in comparison with diesel.
- It results in a considerable decrease of carbon monoxide, unburned hydrocarbons and particulate matter.

**Graph 1: Reduction in pollutant emissions obtained when using B100 and B20 fuels instead of petro diesel**\(^8\)
• It also has a positive energy balance. In other terms, 4.5 units of energy are gained from every unit of energy needed to produce a liter of biodiesel.
• It is a cost efficient option.
• It decreases the dependence on foreign suppliers in terms of oil and strengthens the economy.
• It is safe to handle, store, and transport.
• It has lubricating properties which may extend the lifetime of engines.
• Its cetane number is higher than petroleum diesel fuel’s so it yields a great level of combustion quality during compression ignition.
1 STEEPLE analysis

This project has many societal and ethical implications which include the following:

- **S** Societal: The project can help farmers who produce olive oil to raise their revenues by utilizing biodiesel in their own vehicles and machinery for instance.

- **E** Economical: It has the potential to develop a new technology to better valorize olive oil water effluents and reduce their toxicity in the environment.

- **T** Technological: It can reduce the amount of toxic waste generated during the olive oil production process and promote the use of an unexploited renewable energy source.

- **E** Environmental: If this project is applied in all the olive mills in Morocco, it will help enhance the environmental-friendly image of our country in the world. This is particularly important now given that Morocco will be hosting the 22nd session of the Conference of the Parties (COP 22)

- **P** Political: The project can be extended to all the olive mills in Morocco providing there are no legal constraints.

- **L** Legal: This project does not pose any problem in terms of ethics.

2 Experimental results

2.2 Chemicals and equipment used

- Pomace was ground with a 500W *Bosch* grinder, model MMB11R2.
- Oil samples were centrifuged in a 5500 rpm *Hettich zentrifugen* centrifuge, model EBA 30.
- Biodiesel samples were centrifuged in a *BECTON DICKINSON* centrifuge, model Compact II 420227.
- To mix small samples of biodiesel with water, a *VELP SCIENTIFICA* vortex shaker, model Zx3 was used.
- All reactions were heated and stirred by using a digital stirring hotplate with external platinum probe. Either a *VWR* VMS-C7 advanced series, or a *DLab* MS-H280-pro.
- Weights were measured either with a readability of 0.01g with an *AND* balance, model EK610i, or with a readability of 0.05g with a *KERN* balance, model KB10K0.05N, or with a readability of 0.0001g with an *OHAUS* balance.
- Vacuum distillations were performed by means of piston-powered vacuum pump capable of generating a pressure of 0.85 atm and an air flow of 38 l/min.
- Conductivity of water effluents samples was measured with a *YSI* conductivity meter, model 33.
- pH of water effluents samples and temperature measurements in the bomb calorimeter were recorded with a *Hanna instruments* pH meter, model HI 9318.
- Water content and total dissolved matter contents in filtered water effluents were determined accurately at 80°C with of a VWR oven, model 1300U.
• A Parr plain jacket oxygen bomb calorimeter, model 1341 was used to determine the heat content.

• Potassium hydroxide, KOH, with a purity of 86% was supplied by Fluka, Switzerland.

• Hexane, C₆H₁₄, used in the oil extraction was supplied by Sigma-Aldrich, USA, (> 99% pure).

• Methanol, MeOH, used for the transesterification reaction had a purity of 99.5% and was supplied by VWR.

• Sodium methoxide, MeONa, used as a catalyst, a 5.4M (30% w.) in MeOH was provided by Acros Organics, USA.

• The phosphoric acid solution, used for washing biodiesel was made from 85% H₃PO₄, it was supplied by Fluka, Switzerland.

• Potassium permanganate, KMnO₄, used in the TLC staining bath, was supplied by Sargent-Welch, USA.

• Ethyle Acetate, C₄H₈O₂ was supplied by Sigma Aldrich, USA.

• Sodium sulfate, Na₂SO₄ used to dry biodiesel was supplied by J.T.Baker, USA.

• TLC plates made of silica gel matrix supported on plastic (polyethylene terephthalate) were supplied by Fluka, Germany.

2.3 Olive oil extraction from pomace

The residual olive oil contained in olive pomace cannot be extracted mechanically even by using a mill’s powerful hydraulic press. However, it can be extracted chemically by using a suitable solvent; this solvent should be non-polar (like the oil), have a low boiling point and be relatively inexpensive. Hexane, C₆H₁₄, turned out to be one of the best solvents which can meet
all these criteria (b.p.: 69°C at sea level/60°C in Ifrane, price: 182 dhs/L\textsuperscript{11}), therefore it was used as the extraction solvent in this project.

The typical experimental procedure used to extract olive oil from pomace is indicated below.

In a round-bottom flask fitted with a water condenser (Figure 6), a certain amount of ground pomace (e.g. 20g) was introduced; then, a specific amount of hexane (e.g. 50mL) was added and the suspension was refluxed at 70°C for a certain amount of time (e.g. 10min), without stirring. Afterwards, the mixture was filtered over cotton and washed with another portion of hexane (e.g. 50mL) to extract as much oil as possible, before proceeding to the evaporation (Figure 7) in order to afford a solvent-free olive oil. Finally, the extraction yield was calculated according to the following formula:

\[
\text{extraction yield} = \frac{m_{\text{oil extracted}}}{m_{\text{pomace sample}}} \times 100
\]
To optimize the extraction step, different extraction times were tested by using 20.00g of pomace and a total of 100mL of hexane (50mL used for the extraction, 50mL for washing). Once the extractions completed and the oil samples collected, two major problems were observed; the oil samples were differing in colour and had an odour of hexane. The difference in colour was probably due to the fact that the pomace samples used were not homogeneous, some containing more yellow crushed pits or greenish solids than others (Figure 8). As for the hexane odor, it can be simply explained by the evaporation time which was apparently too short to allow full removal of hexane.
Figure 8: Pomace sample

To rule out any doubt regarding the results, it was decided to repeat the experiments again, following the same procedures but by using a more homogeneous sample of pomace this time, and increasing the time and temperature of the evaporation step.

Table 1 and Graph 2 summarize the results obtained in the optimization step.

<table>
<thead>
<tr>
<th></th>
<th>Exp. 1</th>
<th>Exp. 2</th>
<th>Exp. 3</th>
<th>Exp. 4</th>
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</thead>
<tbody>
<tr>
<td>Extraction time (min)</td>
<td>10</td>
<td>40</td>
<td>60</td>
<td>95</td>
</tr>
<tr>
<td>Mass of pomace used (g)</td>
<td>20.01</td>
<td>20.01</td>
<td>20.01</td>
<td>20.02</td>
</tr>
<tr>
<td>Mass of oil extracted (g)</td>
<td>1.27</td>
<td>1.46</td>
<td>1.66</td>
<td>1.50</td>
</tr>
<tr>
<td>Extraction yield (%w.)</td>
<td>6.35</td>
<td>7.29</td>
<td>8.29</td>
<td>7.49</td>
</tr>
</tbody>
</table>

Table 1: Results of the oil extraction time optimization with pomace.  
Conditions: extraction temperature: 70°C, quantity of hexane used for the extraction: 50.0mL, quantity of hexane used for washing: 50.0mL.
Graph 2: Extraction yields obtained at different extraction times based on Table 1

As expected, Graph 2 shows a steady increase of the yield from 10 to 60 minutes; however, it unexpectedly shows a slight decrease of the yield between 60 and 95 min. This decrease can be again explained by the fact that the pomace samples employed were not perfectly homogeneous. Getting them perfectly homogeneous would certainly prevent such irregularities; nevertheless, it would entail a tedious and lengthy operation of sieving to eliminate non-oily particles such as debris and crushed pits. Due to time constraints, it was decided not to perform such an operation in this project. For the same reason, although the best extraction time was found to be 60 min (8.29 g oil extracted per 100g of pomace), it was decided to perform future extractions for only 40 min (7.29 g oil extracted per 100g of pomace) in order to save precious time during the lab sessions which are already very limited in time.
3.3.2 Large-scale extraction of oil from pomace

The next experiment aimed at increasing the quantity of pomace used to get a bigger quantity of oil to be used as a starting material in biodiesel production.

To conduct the latter, all the quantities reported in Table 1 were scaled up by a factor of 15. Therefore, the quantity of pomace used was increased from 20g to 300g, and the quantity of hexane used for the extraction was increased from 50mL to 750mL. Given the large quantities, the 100mL round-bottom flask used as the initial reaction vessel had to be replaced by a 5L Erlenmeyer flask. The setup used for this extraction is shown in Figure 9.
Unfortunately, the 5L Erlenmeyer flask could not be fitted with a condenser because it did not feature a ground glass joint. Consequently, it had to be sealed tightly with a cork stopper to prevent loss of hexane vapours and could not be kept at atmospheric pressure when heating was turned on. This setup quickly proved to be unsuitable and unsafe as it could not withstand the pressure build-up caused by hexane vapours. This was illustrated by the brutal ejection of the cork stopper along with most of the reaction mixture when heating was turned on.

The extraction was repeated by using a more suitable flask, a 1L two-neck round-bottom flask fitted with two condensers, one of the condensers being just optional (Figure 10). This time, quantities were scaled up by a factor of 10 instead of 15. About 200g of pomace was used with 500mL of hexane. This experimental setup turned out to be much safer since it was at atmospheric pressure.
Once the extraction completed, the suspension was filtered over cotton, washed with a small portion of hexane, transferred into another 1L two-neck round-bottom flask and distilled under vacuum to recover the hexane used. This protocol eventually afforded a total of 28.42g of oil.

3.3 Olive oil extraction from oil water effluents

To analyze a sample of oil water effluents collected personally in February 2016 from an olive mill in *Ain Taoujdate*, it was first tried to filter the sample by means of cotton wool first and a sintered funnel next. However, both attempts failed because of the presence of mud within the sample, which clogged the filters. To solve this problem, it was decided to centrifuge the sample first, for 5 minutes, at the highest speed, in order to remove fine particles of mud before proceeding to the filtration of the sample over cotton wool.

It turned out that the sample contained only a negligible amount of oil; therefore, it was agreed to work with a sample of olive oil water effluents that was collected a few months ago from the inside of the same olive mill during the olive oil production season. Since it had been settling for several months, this sample was first homogenized by stirring it vigorously with a drill-powered paint mixer (Figure 11).

![Figure 11: Homogenizing the sample of oil water effluents collected during the olive oil production season in November 2015](image-url)
Table 2 summarizes the results found after the analysis of the two samples. Graph 3 and Graph 4 give a visual representation of the composition of the water effluents 'samples.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sample collected in Feb.2016 (a)</th>
<th>Sample collected in Nov.2015 (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity of olive oil water effluents analyzed</td>
<td>730.50 g</td>
<td>315.20 g</td>
</tr>
<tr>
<td>pH of the filtered sample</td>
<td>4.95</td>
<td>Not determined</td>
</tr>
<tr>
<td>Conductivity of the filtered sample</td>
<td>7000 µS/cm</td>
<td>7000 µs/cm</td>
</tr>
<tr>
<td>%w. H₂O</td>
<td>91.9 %</td>
<td>80.3 %</td>
</tr>
<tr>
<td>%w. Total dissolved solids</td>
<td>6.3 %</td>
<td>5.0 %</td>
</tr>
<tr>
<td>%w. large sediments</td>
<td>0.3 %</td>
<td>4.4 %</td>
</tr>
<tr>
<td>%w. mud</td>
<td>1.4 %</td>
<td>10.3 %</td>
</tr>
<tr>
<td>%w. oil</td>
<td>≈ 0 %</td>
<td></td>
</tr>
</tbody>
</table>

Sample (a): Oil water effluents collected from the surface of the mill’s outdoor pool in Feb.2016.
Sample (b): Oil water effluents collected from the surface of the mill's outdoor pool during the olive oil production season (Nov. 2015).

Table 2: Composition of oil water effluents
Graph 3: Composition of the first sample of oil water effluents collected in Feb.2016

Graph 4: Composition of the second sample of oil water effluents collected in Nov.2015
3.4 Biodiesel production

In order to produce biodiesel, greater quantities of olive oil were needed to perform the experiments. Consequently, oil was collected manually with a beaker from the top of 30L drums of effluents which were left to settle for several months (Figure 12). This oil was filtered to get rid of the solid sediments it contained. Afterwards, it was heated to ensure it did not contain water.

![Figure 12: Collecting olive oil from water effluents](image)

Once the collection of a sufficient amount of olive oil from the olive oil water effluents’ samples completed, it was subjected to a transesterification reaction by using MeONa as a catalyst to convert it into biodiesel. The overall reaction is shown in Figure 13.
The transesterification reaction of a triglyceride can use either sodium methoxide, MeONa, or potassium hydroxide, KOH, as a catalyst. The use of either one counts some advantages and disadvantages (Table 3), so both of them were used in experiments to compare their yield in the production of biodiesel.

| Triglyceride + Methanol $\xrightarrow{\text{catalyst}}$ Glycerin + Biodiesel + Impurities (Free fatty acids) |
|---------------------------------------------------|---------------------------------------------------|---------------------------------------------------|---------------------------------------------------|---------------------------------------------------|
| $R_1\text{COOCH}_2$ | $R_2\text{COOCH}$ | $R_3\text{COOCH}_2$ | $3\text{CH}_3\text{OH}$ | $\text{HOCH}_2$ | $\text{HOCH}$ | $\text{HOCH}_2$ | $R_1\text{COOCH}_3$ | $R_2\text{COOCH}_3$ | $R_3\text{COOCH}_3$ | $R_1\text{COOCH}$ | $R_2\text{COOCH}$ | $R_3\text{COOCH}$ |

**Figure 13: General equation of the transesterification reaction of a triglyceride**

The transesterification reaction of a triglyceride can use either sodium methoxide, MeONa, or potassium hydroxide, KOH, as a catalyst. The use of either one counts some advantages and disadvantages (Table 3), so both of them were used in experiments to compare their yield in the production of biodiesel.

<table>
<thead>
<tr>
<th>Adv.</th>
<th>Sodium methoxide MeONa</th>
<th>Potassium hydroxide KOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adv.</td>
<td>It is water-free since it has been made commercially according to the reaction: $\text{Na}<em>\text{(s)} + \text{MeOH}</em>\text{(l)} \rightarrow \text{MeONa}_{\text{(in MeOH)}} + \frac{1}{2} \text{H}<em>2\text{O}</em>\text{(g)}$</td>
<td>It does not jellify the glycerin upon cooling.</td>
</tr>
<tr>
<td>Adv.</td>
<td>It is completely soluble in methanol</td>
<td></td>
</tr>
</tbody>
</table>

| Disadv. | Because it is a sodium containing catalyst, the glycerin jellifies in its presence upon cooling | It is not completely soluble in methanol |
| Disadv. | When mixed with methanol, water is formed according to the reaction: $\text{MeOH}_\text{(l)} + \text{KOH}_\text{(s)} \rightarrow \text{H}_2\text{O}_\text{(l)} + \text{MeOK}_{\text{(in MeOH)}}$ | |

**Table 3: Advantages and Disadvantages of MeONa and KOH as catalysts**
As a first attempt, oil was mixed with methanol and a commercial 30% sodium methoxide solution. The reaction mixture was heated in a round-bottom flask for 1 hour at 60°C (Figure 14). Since oil and methanol are not miscible, a vigorous stirring was needed for the reaction to be successful. Table 4 shows the quantities of the reactants and catalyst needed to perform this experiment.

Figure 14: Heating the mixture to produce biodiesel
<table>
<thead>
<tr>
<th></th>
<th>Molecular weight (g/mol)</th>
<th>Density (g/ml)</th>
<th>Equ.</th>
<th>Quantity (g)</th>
<th>Number of moles (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>920 (a)</td>
<td>______</td>
<td>1</td>
<td>21.26</td>
<td>23.1</td>
</tr>
<tr>
<td>MeOH</td>
<td>32.04</td>
<td>0.7918</td>
<td>6</td>
<td>4.44</td>
<td>138.6</td>
</tr>
<tr>
<td>MeONA (30% Sol.)</td>
<td>______</td>
<td>0.960</td>
<td>2.5 %</td>
<td>1.77</td>
<td>______</td>
</tr>
</tbody>
</table>

(a): Estimate based on the molecular weight of soybean oil

Table 4: Oil, MeOH, and MeONA properties and quantities

At the end of the reaction, two distinct layers could be observed upon standing and cooling: biodiesel and glycerin (Figure 15).

Figure 15: Layers of biodiesel and glycerin in a separatory funnel
The experiment was performed again. But this time the quantities of oil, sodium methoxide and methanol were scaled up as showed in Table 5:

<table>
<thead>
<tr>
<th></th>
<th>Molecular weight (g/mol)</th>
<th>Density (g/ml)</th>
<th>Equ.</th>
<th>Quantity (g)</th>
<th>Number of moles (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>920 (a)</td>
<td>_______</td>
<td>1</td>
<td>100.13</td>
<td>108.8</td>
</tr>
<tr>
<td>MeOH</td>
<td>32.04</td>
<td>0.7918</td>
<td>6</td>
<td>20.91</td>
<td>652.6</td>
</tr>
<tr>
<td>MeONa (30% Sol.)</td>
<td>_______</td>
<td>0.960</td>
<td>2.5 %</td>
<td>8.33</td>
<td>_______</td>
</tr>
</tbody>
</table>

(a) Estimate based on the molecular weight of soybean oil

Table 5: Quantities used for the transesterification reaction when scaling up

The previously obtained biodiesel had jellified due to the glycerin it contained, so it had to be heated in the oven in order to make it liquid again. It was afterwards washed with 25ml of a 10% phosphoric acid solution (H₃PO₄) two times in order to neutralize the basic catalyst (MeONa). Next, it was washed with warm water to get rid of the excess of acid and keep the pH of biodiesel neutral. The top layer obtained in the separatory funnel was transferred into test tubes and centrifuged. When the centrifugation was complete, three distinct layers were noticeable: biodiesel, soap, and an aqueous solution (Figure 16).
The biodiesel collected from this procedure was put back into the separatory funnel to remove the small amount of aqueous solution (water and phosphoric acid) it still contained. Then, it was dried over sodium sulfate and filtered over cotton (Figure 17). Afterwards, it was heated at 150°C under vacuum to remove any traces of methanol and water present in the biodiesel. This experiment subsequently resulted in the production of 71.18 g of biodiesel, which represents a yield of 71.08%.

Figure 16: Centrifuged test tube containing biodiesel, soap, and an aqueous solution
Another experiment aimed at making biodiesel by using the second catalyst: KOH. **Table 6** shows the quantities used for this experiment.

![Figure 17: Filtration the mixture of biodiesel and sodium sulfate over cotton under vacuum](image)

<table>
<thead>
<tr>
<th>Molecular weight (g/mol)</th>
<th>Density (g/ml)</th>
<th>Equ.</th>
<th>Quantity (g)</th>
<th>Number of moles (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>920 (a)</td>
<td>1</td>
<td>148.89</td>
<td>161.8</td>
</tr>
<tr>
<td>MeOH</td>
<td>32.04</td>
<td>6</td>
<td>31.11</td>
<td>970.97</td>
</tr>
<tr>
<td>KOH (86% Sol.)</td>
<td></td>
<td>2.5%</td>
<td>4.32</td>
<td></td>
</tr>
</tbody>
</table>

*(a) Estimate based on the molecular weight of soybean oil*

**Table 6**: Oil, MeOH, and KOH properties and quantities
After adding up the solution of methanol and potassium hydroxide (KOH) to the oil, the mixture was heated at 60°C for 1 hour, as in the previous experiment, with a vigorous stirring.

Again, upon completion of the reaction, when transferring the reaction mixture into the separatory funnel, two layers were noticeable: biodiesel at the top and glycerin at the bottom. Glycerin was drained and the biodiesel layer was washed with 25ml of hydrochloric acid (HCl) two times in order to neutralize the basic catalyst, KOH in this case, and washed with warm water. It was later centrifuged, dried over sodium sulfate, and filtered over cotton as previously done. Then, it was heated for 13 hours at 150°C to evaporate the excess methanol and residual water. Surprisingly, even though the starting quantity of olive oil (148.89g) was greater than the one used in the previous experiment, the mass of biodiesel made was only 69.82g, which corresponds to a yield of 46.89%. This is probably caused by the change of catalyst and/or the loss of some biodiesel during the washing step.

The Table 7 summarizes the three experiments performed to produce biodiesel.

<table>
<thead>
<tr>
<th></th>
<th>Temp. (°C)</th>
<th>Heating time</th>
<th>Oil (g)</th>
<th>MeOH (g)(6equ.)</th>
<th>MeONa (2.5%w.)(g)</th>
<th>KOH (2.5%w.)(g)</th>
<th>Biodiesel (g)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp.1</td>
<td>60</td>
<td>1h</td>
<td>21.26</td>
<td>4.44</td>
<td>1.77</td>
<td>_____</td>
<td>_____</td>
<td>_____</td>
</tr>
<tr>
<td>Exp.2</td>
<td>60</td>
<td>1h</td>
<td>100.13</td>
<td>20.91</td>
<td>8.33</td>
<td>_____</td>
<td>71.18</td>
<td>71.08%</td>
</tr>
<tr>
<td>Exp.3</td>
<td>60</td>
<td>1h</td>
<td>148.89</td>
<td>31.11</td>
<td>_____</td>
<td>4.32</td>
<td>69.82</td>
<td>46.89%</td>
</tr>
</tbody>
</table>

Table 7: Summary of the biodiesel experiments
3.5 Qualitative Analysis

3.5.1 Thin Layer Chromatography (TLC)

Thin layer chromatography (TLC) is a chromatographic technique used to separate the components of a mixture by using a thin stationary phase supported by an inert backing. This procedure can be performed either on the analytical scale in order to observe the completion or the progress of a reaction, or on the preparative scale to purify small amounts of a given sample. This tool is broadly utilized because of its advantages. TLC is in fact simple, relatively inexpensive, is very sensitive, and has a quick speed of separation. As all chromatography, this is how the principle of TLC: a compound will have different affinities for the mobile and stationary phases, and this has an impact on the speed at which this compound migrates. The goal of TLC technique is to obtain well defined and well separated spots.\(^\text{12}\)

The thin layer chromatography (TLC) was consequently run to check the completion of the reaction and to know how pure the products earlier obtained are. For this experiment, silica gel TLC plates on plastic support were used.

Oil and biodiesel samples obtained were diluted in hexane before being loaded on a 10x5cm silica plate. Then, the plate was placed into a 250ml beaker containing a mixture of ethyl acetate (4ml) with hexane (25ml), at a respective ratio of 15% and 85% (Figure 18).
When the solvent reached the top of the plate, the plate was subjected to a brief drying before immersing it into a beaker of distilled water in order to saturate the silica with water. Next, it was stained in a 1% potassium permanganate solution in NaOH. It was afterwards extensively washed in another beaker of distilled water and dried on an even surface to prevent cracking of the gel.\textsuperscript{13}

By performing the thin layer chromatography on a biodiesel sample, clear spots of biodiesel, oil, and some impurities appeared on the silica plate and Figure 19 shows the results obtained. The biodiesel produced does not contain any trace of oil. However, biodiesel and oil both contain some monoglyceride, diglyceride, and free fatty acids. In addition, some spots are noticeable at the top of the plate; these are maybe some impurities created during the transesterification reaction.
After the separation is complete, individual compounds appear as spots separated vertically. Each spot has a retention factor (Rf) which is equal to the distance migrated over the total distance covered by the solvent. The Rf formula is:

$$Rf = \frac{\text{distance traveled by the sample}}{\text{distance traveled by the solvent}}$$

The Rf value can be used to identify compounds due to their uniqueness to each compound under given elution conditions.\(^\text{12}\)
Rf\textsubscript{oil} = 0.42 - 0.51 and Rf\textsubscript{biodiesel} = 0.54 - 0.76.

3.5.2 Comparison of the properties of biodiesel, diesel, and oil

3.5.2.1 Density

To measure the density of a specific liquid, the hydrometer is the best tool to use. It is usually made of glass, and consists of a cylindrical stem and a bulb weighted, usually with mercury or lead in order to float. To determine the density of the liquid, it has to be poured in into a tall container, this could be a graduated cylinder with a minimum volume of 250ml for example, and the hydrometer is gently lowered into the liquid until it floats by itself. Then, the level at which the liquid is in contact with the stem determines the density of the liquid.

However, in this case, the relatively small quantities of biodiesel produced did not enable the use of that technique. Consequently, in order to measure the density of the biodiesel and compare it with the densities of oil and diesel, a 5ml volumetric pipette and a high precision analytical balance to measure the mass to the nearest 0.1mg were used. Table 8 shows the densities found for the oil, biodiesel and diesel.

<table>
<thead>
<tr>
<th></th>
<th>Oil</th>
<th>Biodiesel</th>
<th>Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (g)</td>
<td>4.412</td>
<td>4.294</td>
<td>4.105</td>
</tr>
<tr>
<td>Volume (ml)</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
</tr>
<tr>
<td>Density (g/ml) at 15°C</td>
<td>0.882</td>
<td>0.858</td>
<td>0.821</td>
</tr>
</tbody>
</table>

**Table 8: Density of oil, biodiesel, and oil**
As expected, the density of biodiesel is found between the density of oil and the one of diesel, which means that quality of the biodiesel produced is relatively good and would be later evaluated with respect to the European and American quality standards of biodiesel.

3.5.2.2 Heat Content

A calorimeter is a device which measures and quantifies the heat transferred from or to an object. (Figure 20).

When opening the device, there is a bomb. It is a thick-walled explosion-proof metal container (Figure 21). In a small metal pan, the sample to be burned is placed, and a very thin nickel-chromium or iron ignition wire is in contact or very close to the sample. Electric current passes which heats the wire and initiates the combustion once a voltage is applied. ¹⁴

![Figure 20: Calorimeter](image)
In order to determine the heat content of the biodiesel, diesel, and oil, it was first needed to calculate $C_{cal}$, the heat capacity of the calorimeter used.

For that purpose, the following equation of enthalpy was used:

$$
\Delta H = \frac{-C_{cal} \times \Delta T}{m_{sample}}
$$

So:

$$
C_{cal} = \frac{\Delta H \times m_{sample}}{\Delta T}
$$

In order to determine this value, the bomb calorimeter was used by performing the experiment on 0.99g of benzoic acid. It was placed inside the bomb along within oxygen, and the temperature was recorded periodically before and after the ignition. Graph 5 shows the heating curve obtained plotting.
Then $C_{\text{cal}}$ has been calculated, such that:

$$C_{\text{cal}} = \frac{\Delta H \times m_{\text{sample}}}{\Delta T}$$

$$C_{\text{cal}} = \frac{-26.485 \times 0.99}{3.0}$$

$$C_{\text{cal}} = 8.729 \text{ kJ/°C}$$

The experiment was repeated with oil, diesel, and biodiesel samples to determine their heat content. **Graph 6**, **Graph 7**, and **Graph 8**, show their respective heating curves.
Graph 6: Heating curve of Oil

Calculation of the heat content of oil:

\[
\Delta H = \frac{-C_{cal} \times \Delta T}{m_{sample}}
\]

\[
\Delta H = \frac{-8.729 \times 3.7}{1.01}
\]

\[
\Delta H = -31.97 \text{ kJ/g}
\]
Graph 7: Heating curve of Diesel

Calculation of the heat content of diesel:

\[ \Delta H = \frac{-C_{cal} \times \Delta T}{m_{sample}} \]

\[ \Delta H = \frac{-8.729 \times 4.4}{1.00} \]

\[ \Delta H = -38.40 \text{ kJ} / \text{g} \]
Graph 8: Heating curve of Biodiesel

Calculation of the heat content in biodiesel:

$$\Delta H = - \frac{C_{cal} \times \Delta T}{m_{sample}}$$

$$\Delta H = \frac{-8.729 \times 4.2}{1.00}$$

$$\Delta H = -36.66 \text{ kJ} / \text{g}$$
As expected, the heat content of biodiesel is slightly lower than the heat content of diesel (-4.5%); which means that the biodiesel produced would be nearly as efficient as diesel when burnt in an engine.

Table 9 gives a summary of the properties previously determined for oil, biodiesel, and diesel.

<table>
<thead>
<tr>
<th></th>
<th>Density (g/ml)</th>
<th>Δ H (kJ/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>0.882</td>
<td>-31.97</td>
</tr>
<tr>
<td>Biodiesel</td>
<td>0.856</td>
<td>-36.66</td>
</tr>
<tr>
<td>Diesel</td>
<td>0.821</td>
<td>-38.40</td>
</tr>
</tbody>
</table>

Table 9: Summary of the properties of oil, biodiesel, and diesel

When comparing the value of the density measured for biodiesel (856kg/m$^3$) to the European quality standards (EN14214, see Appendix), one can see that it is not compliant (860-900 kg/m$^3$); this is actually understandable since the source of biodiesel is not the same. In fact, Europe generally produced its biodiesel from grape seed oil which leads to a greater density than olive oil biodiesel.

Nevertheless, the U.S quality standards for biodiesel (ASTM D6751, see Appendix) do not mention anything about the density. Thus, if made in considerable quantities, the density would not prevent biodiesel from being exported to the U.S.
Conclusion

To guarantee a sustainable future for our planet, it is compulsory to resort to renewable energies. My capstone project revolves around the valorization of olive oil water effluents and olive oil pomace to generate one of these renewable energies: biodiesel.

I have come to realize that this project is for me an occasion to develop hands-on skills through very interesting laboratory experiments and a chance to acquire new knowledge about biodiesel. In fact, experiments were conducted to first extract olive oil from olive pomace then from olive oil water effluents. The oil from the latter was then converted into biodiesel through a transesterification reaction. It was afterwards characterized through a qualitative analysis using TLC. Some properties such as the density and heat content were also determined. Unfortunately, due to time constraints, I was not been able to carry out experiments to decontaminate the deoiled olive oil water effluents as well as converting oil extracted from pomace into biodiesel.

If this project is implemented in the olive mill of Ain Taoujdate, almost 755,648L (118,070L x 9% x 71.08%) of biodiesel could be produced each year. In other words, farmers could save money by using the biodiesel produced from the waste they generate during the olive oil production season, i.e olive oil water effluents, to run their engines and vehicles instead of buying the costly and polluting diesel fuel.

In addition, if this project is to be performed on a very large scale, with the adequate technology, significant quantities of biodiesel could be produced. In fact, as mentioned previously, Morocco produces around 250,000m³ of olive oil water effluents annually; from
these wastes around 9% of olive oil could be extracted. Afterwards, 71.08% of this oil can be converted into biodiesel. In other terms, 6.4% of olive oil water effluents can be transformed into biodiesel. Putting that into numbers, 16,000,000 L of biodiesel could be produced each year. This significant quantity could be comparable to the quantity used to fill a 40m$^3$ tank truck 400 times. It is also equivalent to saving 14,550,000 L of diesel per year$^{15}$ and saving 39,727 tons of CO$_2$ each year.$^{16}$
References

8. Cincinatti Office of Environmental Management & US Department of Energy NREL studies
11. Source: quote received by Somaprol in March 2013. One bottle of 2.5L = 456 dhs, VAT included.
Based on a 10% reduction in biodiesel’s fuel economy

Estimate calculated on: www.icbe.com/carbondatabase/volumeconverter.asp
Appendix

Olive Mill in Ain Taoujdate
Transfer of olives in the stone mill

Stone crushing of a mixture olives/added water
Olive paste spread on fiber disks, stacked on top of each other
Disks containing olive paste are pressed, and olive oil along with water effluents are extracted.

**Pomace:** Still contains $\approx 8\%$ of olive oil

**OWE:** Still contain some olive oil
### EN14214 quality standards for biodiesel

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
<th>Limits</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester content</td>
<td>DIN EN 14103</td>
<td>≥ 96.5</td>
<td>% w.</td>
</tr>
<tr>
<td>Density at 15°C</td>
<td>DIN EN ISO 12185</td>
<td>860-900</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Viscosity at 40°C</td>
<td>DIN EN ISO 3104</td>
<td>3.5-5.0</td>
<td>mm²/s</td>
</tr>
<tr>
<td>Flash point</td>
<td>DIN EN ISO 3679</td>
<td>≥ 120</td>
<td>°C</td>
</tr>
<tr>
<td>Cold Filter Plugging Point</td>
<td>DIN EN 116</td>
<td>-</td>
<td>°C</td>
</tr>
<tr>
<td>Sulfur</td>
<td>DIN EN ISO 20884</td>
<td>≤ 10</td>
<td>ppm</td>
</tr>
<tr>
<td>Organic matter (10%)</td>
<td>DIN EN ISO 10370</td>
<td>≤ 0.3</td>
<td>% w.</td>
</tr>
<tr>
<td>Octane</td>
<td>IP 498</td>
<td>≥ 51.0</td>
<td>-</td>
</tr>
<tr>
<td>Sulfur ash</td>
<td>ISO 3987</td>
<td>≤ 0.02</td>
<td>% w.</td>
</tr>
<tr>
<td>Water</td>
<td>DIN EN ISO 12937</td>
<td>≤ 500</td>
<td>ppm</td>
</tr>
<tr>
<td>Total contamination</td>
<td>DIN EN 12662</td>
<td>≤ 24</td>
<td>ppm</td>
</tr>
<tr>
<td>Copper corrosion</td>
<td>DIN EN ISO 2160</td>
<td>n° 1</td>
<td>grad corrosion</td>
</tr>
<tr>
<td>Oxidation stability (110 °C)</td>
<td>DIN EN 14112</td>
<td>≥ 6</td>
<td>hours</td>
</tr>
<tr>
<td>Acid number</td>
<td>DIN EN 14104</td>
<td>≤ 0.5</td>
<td>mg KOH/g</td>
</tr>
<tr>
<td>Iodine number</td>
<td>DIN EN 14111</td>
<td>≤ 120</td>
<td>g iodine / 100 g</td>
</tr>
<tr>
<td>Linolenic acid methyl ester</td>
<td>DIN EN 14103</td>
<td>≤ 12.0</td>
<td>% w.</td>
</tr>
<tr>
<td>Methanol</td>
<td>DIN EN 14110</td>
<td>≤ 0.20</td>
<td>% w.</td>
</tr>
<tr>
<td>Free glycerol</td>
<td></td>
<td>≤ 0.020</td>
<td>% w.</td>
</tr>
<tr>
<td>Mono – glycerides</td>
<td></td>
<td>≤ 0.80</td>
<td>% w.</td>
</tr>
<tr>
<td>Di – glycerides</td>
<td>DIN EN 14105</td>
<td>≤ 0.20</td>
<td>% w.</td>
</tr>
<tr>
<td>Triglycerides</td>
<td></td>
<td>≤ 0.20</td>
<td>% w.</td>
</tr>
<tr>
<td>Total glycerol</td>
<td></td>
<td>≤ 0.25</td>
<td>% w.</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>DIN EN 14107</td>
<td>≤ 10.0</td>
<td>ppm</td>
</tr>
<tr>
<td>Metals I (Na + K)</td>
<td></td>
<td>≤ 5.0</td>
<td>ppm</td>
</tr>
<tr>
<td>Metals II (Ca + Mg)</td>
<td>DIN EN 14538</td>
<td>≤ 5.0</td>
<td>ppm</td>
</tr>
</tbody>
</table>
## ASTM D6751 quality standards for biodiesel

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
<th>Limits</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flash point, closed cup</td>
<td>ASTM D93</td>
<td>≥ 93</td>
<td>°C</td>
</tr>
<tr>
<td>Water and sediment</td>
<td>ASTM D2709</td>
<td>≤ 0.05</td>
<td>% v.</td>
</tr>
<tr>
<td>Kinematic viscosity at 40°C</td>
<td>ASTM D445</td>
<td>1.9 - 6.0</td>
<td>mm²/s</td>
</tr>
<tr>
<td>Sulfated ash</td>
<td>ASTM D874</td>
<td>≤ 0.02</td>
<td>% w.</td>
</tr>
<tr>
<td>Sulfur</td>
<td>ASTM D5453</td>
<td>S15 grade : ≤ 0.0015</td>
<td>% w.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S500 grade : ≤ 0.0500</td>
<td>% w.</td>
</tr>
<tr>
<td>Copper strip corrosion</td>
<td>ASTM D130</td>
<td>n° 3 max</td>
<td>-</td>
</tr>
<tr>
<td>Alcohol content</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(one of the following must be met)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol Content</td>
<td>EN 14110</td>
<td>≤ 0.20</td>
<td>% v.</td>
</tr>
<tr>
<td>Flash Point, Closed Cup</td>
<td>D93</td>
<td>≥ 130</td>
<td>°C</td>
</tr>
<tr>
<td>Cetane number</td>
<td>ASTM D613</td>
<td>≥ 47</td>
<td>-</td>
</tr>
<tr>
<td>Cloud Point</td>
<td>ASTM D2500</td>
<td>-a</td>
<td>°C</td>
</tr>
<tr>
<td>Carbon residue</td>
<td>ASTM D4530</td>
<td>≤ 0.05</td>
<td>% w.</td>
</tr>
<tr>
<td>Acid number</td>
<td>ASTM D664</td>
<td>≤ 0.50</td>
<td>mg KOH/g</td>
</tr>
<tr>
<td>Free glycerin</td>
<td>ASTM D6584</td>
<td>0.02</td>
<td>% w.</td>
</tr>
<tr>
<td>Total glycerin</td>
<td>ASTM D6584</td>
<td>0.24</td>
<td>% w.</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>ASTM D4951</td>
<td>≤ 10</td>
<td>ppm</td>
</tr>
<tr>
<td>Vacuum distillation end point</td>
<td>ASTM D1160</td>
<td>360</td>
<td>°C</td>
</tr>
<tr>
<td>Oxidation stability</td>
<td>EN 14112</td>
<td>≥ 3</td>
<td>hours</td>
</tr>
<tr>
<td>Calcium &amp; Magnesium (combined)</td>
<td>EN 14538</td>
<td>≤ 5</td>
<td>ppm</td>
</tr>
</tbody>
</table>

(a) Must be reported to customer