Production of biodiesel from sunflower oil and ethanol by base catalyzed transesterification

MSc Thesis

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Abstract

Biodiesel is an attractive alternative fuel for diesel engines.The feedstock for biodiesel production is usually vegetable oil, pure oil or waste cooking oil, or animal fats

The most common way today to produce biodiesel is by transesterification of the oils with an alcohol in the presence of an alkaline catalyst. It is a low temperature and low-pressure reaction. It yields high conversion (96%-98%) with minimal side reactions and short reaction time. It is a direct conversion to biodiesel with no intermediate compounds.

This work provides an overview concerning biodiesel production. Likewise, this work focuses on the commercial production of biodiesel. The Valdescorriel Biodiesel plant, located in Zamora (Spain), is taken like model of reference to study the profitability and economics of a biodiesel plant.

The Valdescorriel Biodiesel plant has a nominal production capacity of 20000 biodiesel tons per year. The initial investment for the biodiesel plant construction is the 4.5 millions €. The benefits are 2 million €/year. The return of investment is calculated in less than 3 years. A biodiesel of 98% can be reached. The energy used for the biodiesel production is 30% less than the obtained energy from the produced biodiesel. Replacing petro diesel by the biodiesel produced in the plant, a significant CO_2 reduction can be reached (about 48%). It means that the CO2 emission can be reduced by 55 000 tons CO_2 per year.

The production of biodiesel from sunflower oil and ethanol using sodium hydroxide as catalyst was performed in the laboratory and the results are discussed. The results are analyzed using the statistic method of Total Quality.

The effect of the ethanol/oil ratio and the amount of used catalyst on the yield of biodiesel as well as on the properties of the produced biodiesel is studied. In the experimental part the density, viscosity and refractive index of the produced biodiesel are measured. The ethanol/oil ratio influences the biodiesel production. The yield of biodiesel increases with the ethanol/oil ratio. Regarding the influence of the amount of catalyst on biodiesel production in the studied conditions, an increase of the biodiesel yield with the amount of catalyst can be appreciated.

The study of the evolution of the transesterification during time shows that a reaction time of one hour is sufficient enough in order to reach the highest yield of biodiesel.

Sammanfattning

Biodiesel är ett attraktivt alternativt bränsle för diesel motorer. Biodiesel framställs vanligtvis ur vegetabilisk olja, avfall matolja, eller animaliska fetter.

Det vanligaste sättet idag för att producera biodiesel är genom omförestring av oljor med en alkohol i närvaro av en alkalisk katalysator. Det är en reaktion vid låg temperatur och lågt tryck. Den ger ett högt utbyte (96 % -98 %) med få sidoreaktioner vid kort reaktionstid.

Arbetet ger en översikt om produktionen av biodiesel. Likaså fokuserar detta arbete på den kommersiella produktionen av biodiesel. En ekonomisk studie ingår där lönsamhet och ekonomi för en biodieselanläggning beräknas. Valdescorriel biodieselanläggning, som ligger i Zamora (Spanien), tas som modell för studie.

Produktionskapacitet på Valdescorriel biodieselanläggning beräknas till 20 000 biodiesel ton per år. Den inledande investeringen för biodieselanläggning byggande är 4,5 miljoner €. Avkastning är 2 miljoner € / år. Investeringen kan återbetalas på mindre än 3 år. Utbyte för biodiesel kan komma upp till 98 %. Den energi som används för att producera biodiesel är 30 % mindre än den erhållna energin från den producerade biodiesel. Genom att ersätta fossil biodiesel med biodiesel som produceras i anläggningen kan CO2-utsläpp minskas med 48 %. Det innebär att utsläpp CO2 kan reduceras med 55 000 ton per år.

Framställning av biodiesel från solrosolja och ethanol med natriumhydroxid som katalysator utfördes i laboratoriet och resultaten diskuteras. Resultaten analyseras med hjälp av statistik metoden för kvalitetsstyrning (Total Quality).

Effekten av förhållande ethanol/olja och mängden använd katalysator på utbyte samt på egenskaperna hos den framställda biodieseln studeras. De egenskaper som studeras hos biodiesel är densitet, viskositet och brytningsindex. Det ethanol/olja förhållandet påverkar utbyte och egenskaper hos den framställda biodieseln. Utbyte av biodiesel ökar med förhållande ethanol/olja. Angående påverkan av mängden katalysatorer på biodiesel framställning i den studerade villkor är det inte möjligt att få en definitiv slutsats. Men det har visat sig en tendens till ökad biodiesel utbyte med mängd katalysator.

Försök syftande att studera hur omförestring utvecklas under tiden visar att det är tillräckligt med en reaktionstid på 1 timme för att uppnå högsta möjliga utbyte av biodiesel.

Acknowledgement

I sincerely thank my supervisor, Prof. Rolando Zanzi, for giving me the opportunity to do this research work, and because, he has offered me an endless number of facilities since the beginning.

I would like also thank all people in the Chemical Technology Department of KTH for their support and make the stay so pleasant. And the Chemical engineer, Mr. José Luciano González, who works in the Valdescorriel Biodiesel Plant for provide as much information.

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Contents

1. Introduction

Nowadays, majority of the worlds energy needs are supplied through petrochemicals sources. All these sources are finite and at current usage rates will be consumed shortly. The high energy demand in the industrialized world as well as the pollution problems caused due to the use of fossil fuels make it increasingly necessary to develop a new renewable energy source.

Biodiesel refers to a vegetable oil- or animal fat-based diesel fuel consisting of long-chain alkyl (methyl, propyl or ethyl) esters.

Biodiesel is an attractive alternative to fossil fuels; it is biodegradable, non-toxic and has low emission profiles as compared to petroleum fuels. Biodiesel is carbon-neutral. The amount released CO_2 by burning biodiesel is the same amount CO_2 absorbed during the formation of the raw material.

The European Union has set the target that in 2011 the biofuels will be around 6% of the transport fuel [Jos Dings, 2009].

The objective of this work is to present an overview regarding the production of biodiesel. Also is it a goal of the work to perform an economic study taking the Valdescorriel plant as reference and to estimate the reduction in the emission of CO2 when the biodiesel produced in the plan is used instead of petro-diesel.

The experimental part of this work includes the production of biodiesel from sunflower oil and ethanol using sodium hydroxide as catalyst. The objective is to study the influence of the ethanol/oil ratio and the amount of used catalyst on the yield of produced biodiesel as well as on its properties. The effects of these parameters will be studied to find optimum conditions for transesterifcation of the selected vegetable oils to ethyl ester.

1.1 Biofuels

The biofuels are produced from biomass. The biofuels may be in solid (vegetables wastes, and a fraction of the urban and industrial wastes) liquid (bioalcohols and biodiesel) or gaseous (biogas and hydrogen) form.

The first generation biofuels are produced from cereal crops (e.g. wheat, maize), oil crops (e.g. rape, palm oil) and sugar crops. Biodiesel is a first generation biofuel. Other first generation biofuels are bioethanol, biogas and straight vegetable oils.

Second generation biofuels are produced from lignocellulosic materials. The syngas produced by gasification of biomass is used as precursor of second generation biofuels like Biomass to liquid (BTL), Bio Dimethylether / Methanol, Bio_Synthetic Natural Gas and biohydrogen. Bio-oil, produced by pyrolysis of biomass, and cellulosic ethanol are also second generation biofuels.

1.2 Historical evolution

Rudolf Diesel designed a prototype of engine. The engine was showed in the Paris World Expo in 1900. The engine was planned to use vegetable oils. The first tests were done with peanuts oil.

In 1908, Henry Ford made the first design of his automobile Model T. This automobile used ethanol as fuel. From 1920 to 1924, the Standard Oil Company sold gasoline with a 25% ethanol, in the Baltimore region. The project was then abandoned because of the high prices of the corn (source of the ethanol) and the problems with storage and transport. [Reynold Millard Wik, 1963]

In the late twenties and during the thirties, Henry Ford and other experts joined their efforts trying to promote the use of ethanol. They built a fermentation plant in Atchinson (Kansas) to produce ethanol fuel. This plant produced 38000 liters ethanol per day for use as fuel. [Ove Eikeland, 2006]

During the 1930s, more than 2000 fuel stations, in the USA Midwest, sold this ethanol made from corn. This was called gasohol. Gasohol could not compete with the gasoline and the plant in Atchinson was closed in the 1940s. [Joyce Manchester, 1978].

In 1973, there was a sharp oil crisis associated to the second arab-israeli war. During this period, the fuel price was doubled in just three months. The scarcity of this non-renewable resource jeopardized the supply. This fact encouraged the search a substitute for the oil. [Joseph Coton Wright, 2010]

In Brazil, the Proalcool project began in 1975. The objective of Proalcool Project was to encourage use of ethanol as transport fuel and for industrial uses. [Carlos R. Soccol, 2005]

The fast depletion of fossil fuels and the green house gas emissions from fossil fuels are the main reason for the efforts in order to develop biofuels.

In 2003 the EU promote the use of biofuels for transport. The target was that quantity of biofuels to be placed on the market should be 2% in 2005 and 5.75% in 2010 in relation to the fossil fuel. In 2007 the EU proposed with the objective to reduce the increase in global average temperature, that 20% of the energy will come from renewable sources. In 2020, 10% of the transport fuel should come from biofuels.

1.3World trade

The “Top-10 biodiesel producers” is shown in table 1 [SAGPyA 2006]:

Table 1. Top-10 biodiesel producers

Country	Biodiesel production (mil millions of liters)
Malaysia	14.5
Indonesia	7.6
Argentina	5.3
USA	3.2
Brazil	2.5
Netherlands	2.5
Germany	2
Philippines	1.3
Belgium	1.2
Spain	1.1

The developing countries are the ones who can benefit more from this emerging business of export of raw material and biodiesel. Malaysia, Thailand, Colombia, Uruguay and Ghana are developing countries improving the biodiesel export [Matt Johnston, 2006].

1.4 Biodiesel

The biodiesel refers to methyl or ethyl esters obtained by transesterification of animal fats or vegetable oils. Biodiesel can be blended with petrodiesel. In the case of mixtures, the respective proportion of biodiesel in petrodiesel should be indicated. B20 means a mixture 20% biodiesel and 80% petroleum diesel. B100 is pure biodiesel.

Two main groups of raw materials for production of biodiesel can be distinguished: vegetable oil and waste cooking oil.

The used cooking oil is an important waste and it can be used for biodiesel production. However, the actual tendency is the utilization of pure vegetable oils cultivated for energetic use.

The main raw materials to elaborate biodiesel are:

· Conventional vegetable oils of sunflower, rapseed, soybean, coconut and palm.

The oilseeds like the sunflower and the rapseed are the main raw materials in Europe [http://www.ufop.de/downloads/ufop_brochure_06.pdf].

The soybean is the main raw material in USA and South America (Brasil and Argentina) [http://www.soystats.com/2009/page_30.htm].

The coconut is important in Philippines. Palm is the main raw material for production of vegetable oil in Malaysia and Indonesia [http://www.rimlifegreentech.com/feedstock.htm].

The rapseed (Brassica napus) is produced in the north of Europe. The sunflower (helianthus annuus) is produced in the Mediterranean countries [Gianpietro Venturi, 2000].

·Alternative vegetable oil of Brassica carinata (Ethiopian mustard), Cynara curdunculus (Cardoon), Camelina sativa usually known as camelina, Pogianus, Jathopha curcas, Crambe abyssinica.

· Seed oil genetically modified.

· Animal fats (buffalo and beef tallow).

· Waste cooking oil.

· Oil from other sources (microbial production and microalgae).

1.5 Biodiesel Production

The commercial method used for the biodiesel production is the transesterification (also called alcoholysis).

The transesterification consists on the reaction of oils or fats (triglycerides between 15 and 23 atoms, being the most common with 18) with an alcohol of low molecular weight (usually ethanol or methanol) with the presence of an alkaline catalyst (usually NaOH or KOH) to produce esters and glycerin.

Normally, the reaction takes place at atmospheric pressure and 65ºC of temperature. The process uses constant agitation, during an interval of time between one or twelve hours.

The transesterification consists of three consecutive and reversible reactions (Figure 1). The stoichiometric ratio for the transesterification reaction is three moles of alcohol and one mole of triglyceride (Figure 2). An extra amount of alcohol is added in order to move the reaction to the methyl esters formation. Glycerin is also formed in the reaction.

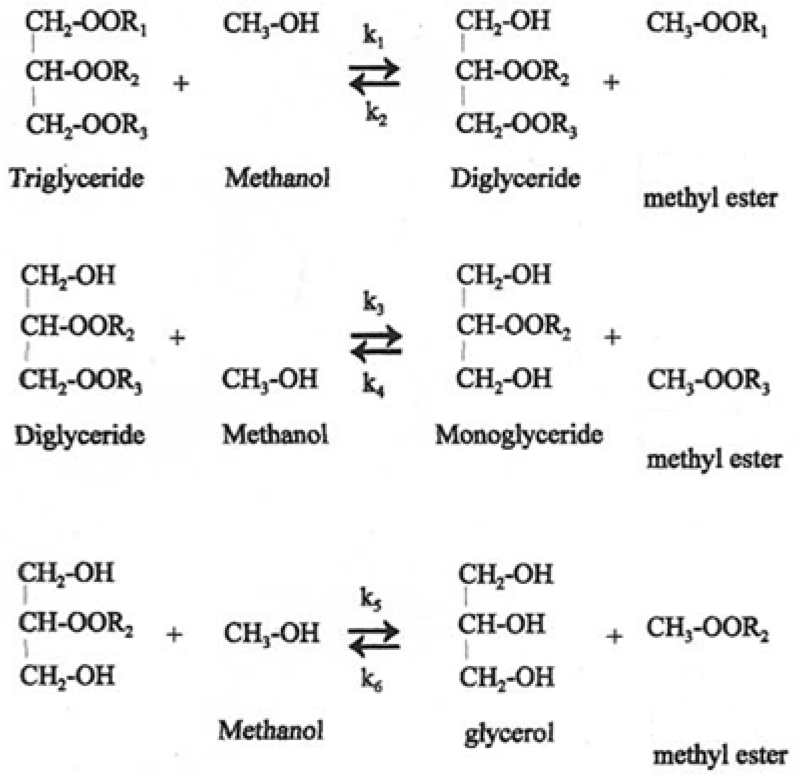


Figure 1. Transesterifcation consecutive reactions

1 oil/fat + 3 methanol ⟶ 3 methyl esters + 1 glycerin

Figure 2. Transesterification reaction

The alcohol usually used is methanol, because it is the cheapest. The process is called methanolysis, when the used alcohol is methanol. This process produces methyl esters (FAME-fatty acids methyl esters) from the fatty acids.

The by-product, glycerin, has an economical value. The glycerin can be used in manufacturing of hand cream, soap, toothpastes, and lube.

Saponification and free fatty acid neutralisation are undesirable side-reactions. These side-reactions consume the catalyst. As result, the yield of biodiesel decreases. The purification and separation steps become more complicated.

As it is showed in Figure 3, the triglyceride reacts with the basic catalyst with formation of soap and water (saponification reaction).

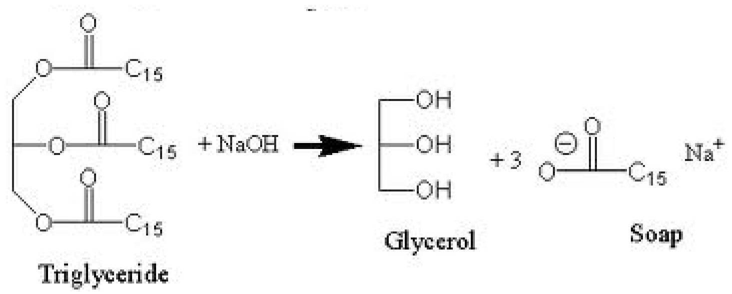


Figure 3. Saponification reaction

The saponification takes place only in the presence of hydroxide group (OH). It occurs when the catalyst is potassium or sodium hydroxide. The soap formation can be avoided by using an acid catalyst

The presence of water or free fatty acid favors the formation of soap. For this reason the oils and alcohols have to be essentially anhydrides. The water can be removed by evaporation, before the transesterification.

In order to avoid free fatty acid neutralization, vegetable oil with a low free fatty acid content can be used.

There are two ways of removal of the fatty acids from the oil. One is by neutralization, in presence of water, as it is showed in the Figure 4.

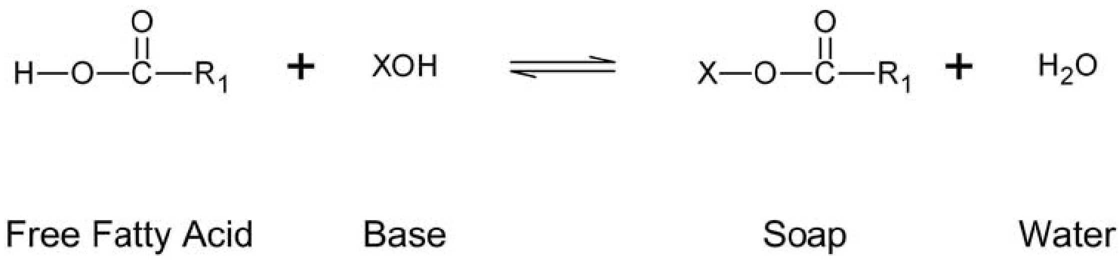


Figure 4. Neutralization reaction of fatty acids

Other way to removal the fatty acids from oil is by esterification reaction with an acid catalyst forming methyl ester, as it showed in the Figure 5.

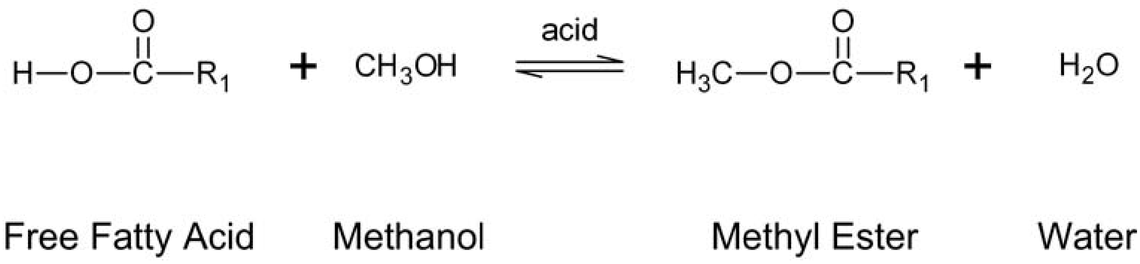


Figure 5. Esterification reaction of fatty acids

The main factors affecting to the cost of biodiesel are raw material, purification and storage [World Bank, 2008].

The use of transesterified oil sunflower oil for biodiesel production was initiated in South Africa in 1979. By 1983, this biodiesel process was completed and published internationally. An Austrian company, Gaskoks, obtained the technology from the South African Agricultural Engineers. The company built the first biodiesel pilot plant in November 1987 and the first industrial-scale plant in April 1989 [Ana Kirakosyan, 2009].

In the 90's, some plants were opened in many European countries (Czech Republic, Germany and Sweden). France also launched local production of biodiesel fuel from rapeseed oil. Renault, Peugeot and other manufacturers developed and certified truck engines for use biodiesel blends at a level of 30%. Experiments with 50% biodiesel are underway [http://www.mobiusbiofuels.com/biodiesel.htm].

Sunflower oil has good properties for production of biodiesel. In 2002, 13% of the world production of biodiesel came from sunflower oil. Sunflower oil was one the second feedstock for biodiesel production after rapeseed oil (Figure 6). But the high cost of the sunflower oil is a problem in order to obtain an economical biodiesel.

The price of sunflower seed and oil has tripled in the last 10 year since 2000/01 (Table 2, Figure 7).

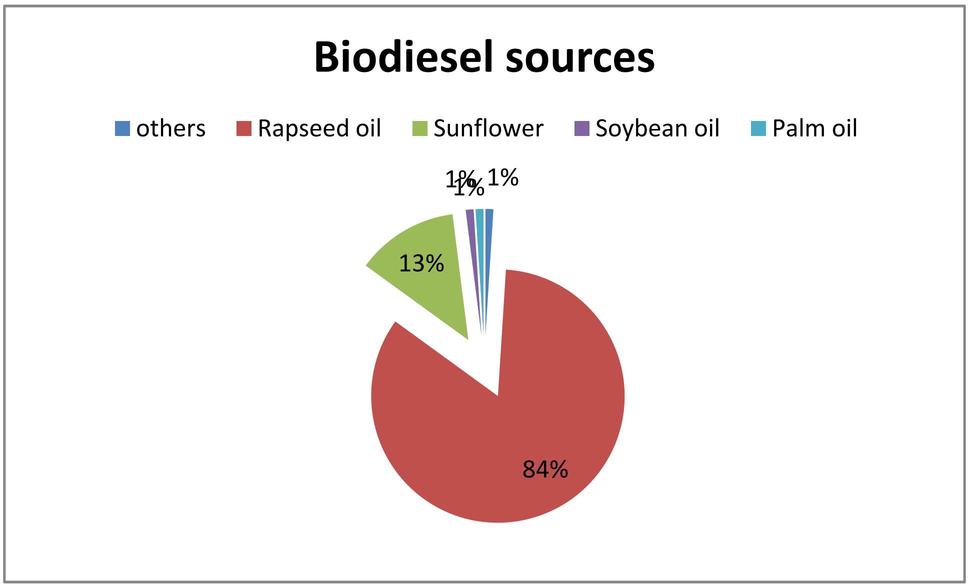


Figure 6. Biodiesel sources in 2002 [http://www.cyberlipid.org/glycer/biodiesel.htm]

Table 2. Sunflower prices [USDA and Census Bureau,2010].

YEAR	SUNFLOWER SEED ($/cwt) (1cwt = 100 lb ≈ 45,36 kg)	SUNFLOWER OIL (cents/lb) (1lb≈0,4536 kg)
1990/91	10.80	23.67
1991/92	8.69	21.63
1992/93	9.74	25.37
1993/94	12.90	31.08
1994/95	10.70	28.10
1995/96	11.50	25.40
1996/97	11.70	22.64
1997/98	11.60	27.00
1998/99	10.60	20.10
1999/00	7.53	16.68
2000/01	6.89	15.89
2001/02	9.62	23.25
2002/03	12.10	33.11
2003/04	12.10	33.41
2004/05	13.70	43.71
2005/06	12.10	40.64
2006/07	14.50	58.03
2007/08	21.70	61.15
2008/09	21.80	50.24

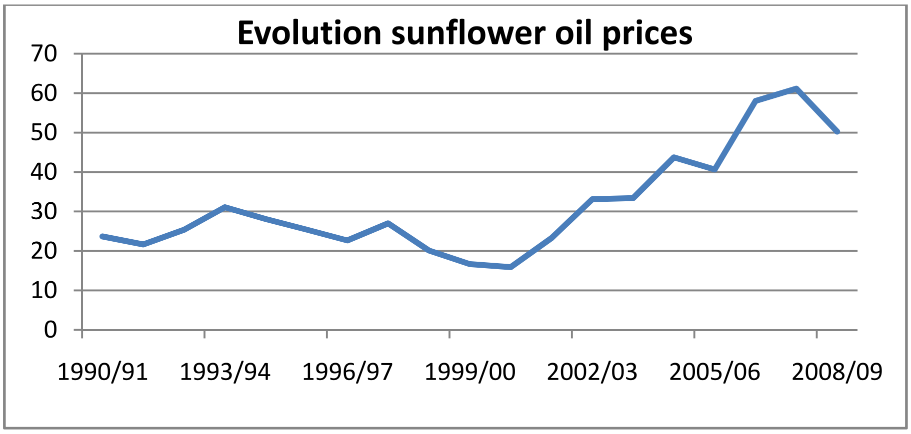


Figure 7. Evolution sunflower prices in the last 20 years.

The yields in liters oil/ha of the common crops used as feedstock for biodiesel production are shown in table 3 and figure 8. Sunflower produces about 952 liters of oil per ha.

Table 3. Liters oil per ha [Matt Johnston, 2007]

Crop	litres oil/ha	US gal/acre
avocado	2638	282
calendula	305	33
castor vean	1413	151
cocoa (cacao)	1026	110
coconut	2689	287
coffee	459	49
corn (maize)	172	18
cotton	325	35
jatropha	1892	202
jojoba	1818	194
kenaf	273	29
macadamia nut	2246	240
mustard seed	572	61
oats	217	23
oil palm	5950	635
olive	1212	129
opium poppy	1163	124
peanut	1059	113
pecan nut	1791	191
pumpkin seed	534	57
rapeseed	1190	127
rice	828	88
sesame	696	74
soybean	446	48
sunflower	952	102

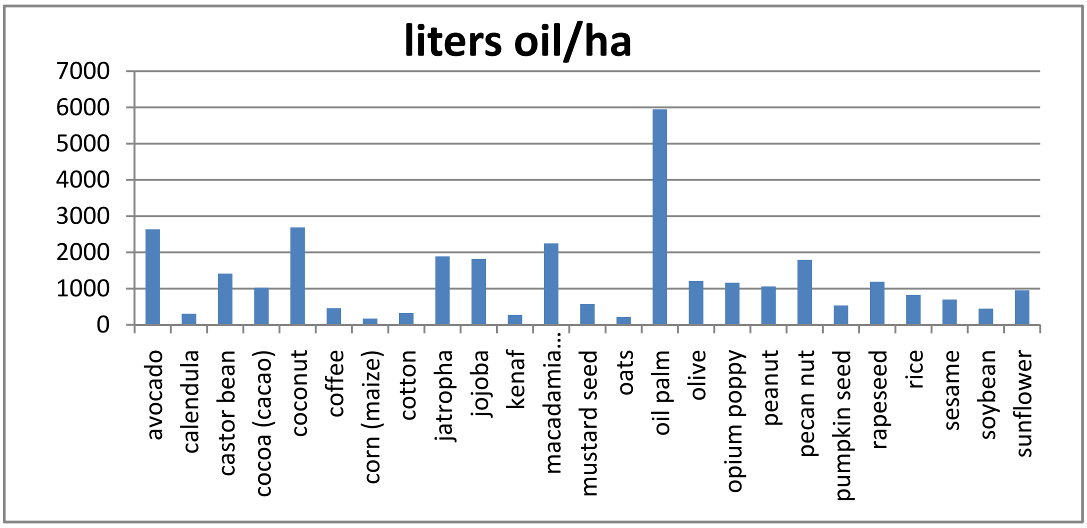


Figure 8. Yield seeds (liters oil/ha)

1.6 Biodiesel features

The biodiesel properties depend on the used feedstock (new vegetable oil, waste cooking oils, animal fats, etc).

Important properties of the biodiesel are:

- It can be used pure or blended with petrodiesel in engines
- It can be used in the diesel engine without any modifications.
- it can be storage in the same containers than petrodiesel
- It can prolong engine life due to the higher lubrication capacity
- It improves combustion process. The biodiesel contains at least 11% oxygen. Biodiesel burns better (more completely with few fuel unburned emissions) than petroleum diesel. Less smoke is produced. The use of biodiesel can reduce the emissions of unburned hydrocarbons (HI) in a 90%.
- It generates employment
- It lubricates moving engines
- It is Biodegradable
- It does not contain sulfur. No sulfur emissions are emitted during the combustion
- It is less inflammable compared with petro diesel.
- During the combustion biodiesel emits less harmful gases into the environment compared with petrodiesel. Biodiesel reduces the health risks associated with

petroleum diesel. The use of biodiesel decreases emission of PAH (identified as cancer causing). Biodiesel is non toxic.

- Greenhouse gas benefit. During the combustion of biodiesel the CO_2 cycle is closed. The CO2 produced during the combustion is the amount of CO_2 which the plants are able to metabolize through photosynthesis during growth. Moreover, this process implies low emissions of CO_2, due to the medium content carbon for plants is 77.8% and for animal fats is 76.1%. While, the content carbon for fossil diesel is 86.7%. The use of biodiesel can reduced the CO_2 emissions up to 50% in comparison to the use of petroleum diesel.
- The biodiesel transport and its storage are less dangerous than the petroleum diesel, because biodiesel has a flashpoint temperature of about 170ºC in comparison of 60 to 80 ºC for petroleum diesel.
- It is non-irritating to the skin
- It has a pleasant aroma

Moreover those advantages also other economic aspects can be taken into account:

a) Biodiesel contribute to diversification of energy sources. It is an important aspect for countries without fossil fuel sources.
b) The biodiesel contributes to agricultural and rural development.

The most important biodiesel disadvantages, in comparison with the fossil fuel, are:

1) The cost. The biodiesel production is today expensive compared with petrodiesel.
2) The biodiesel needs more additives, mainly in cold countries, due to its high cloud point.
3) Lower long-term storage stability. The biodiesel becomes rancid due to oxidation and bacterial air. This rancidity process produces aldehydes, ketones and acids, which have strong and unpleasant odors.
4) It is required 1.1 liters of biodiesel to replace one liter of petroleum diesel, because of their lower calorific power.
5) High percent blends of biodiesel can soften and degrade certain types of elastomers and natural rubbers. In this case, precautions have to be taken concerning the materials in fuelling system.
6) Biodiesel may dilute the lubricating oil of engines.
7) The biodiesel produces more NOx emissions than petrodiesel- a comparison of the emissions from biodiesel and petrodiesel is shown in table 4.

Table 4. Comparison of emissions from biodiesel and petrodiesel

Fuel	CO		TOTAL HC		NOx		Particles	
	g/Kg	Dif (%)	g/Kg	Dif(%)	g/Kg	Dif(%)	g/Kg	Dif(%)
Diesel	0.634		0.146		0.986		0.083	
B20	0.574	-12	0.128	-20	0.991	+2	0.078	-12
B100	0.497	-48	0.058	-67	1.025	+10	0.072	-47

2. Biodiesel plant profitability

An economic analysis has been done about a biodiesel plant. The Valdescorriel Zamora Biodiesel Plant (Spain) has been taken as reference.

The economic analysis has been performed for a production of 20000 tons/yr biodiesel and 2000 ton/yr glycerol. It is supposed 1500 trucks per year. In the future it is expected to increase the production up to 50000 tons per year. The plant works 8000 hours per year. Between 15 to 20 % of the biodiesel is produced from waste cooking oils, and the rest from vegetable oils.

Process description

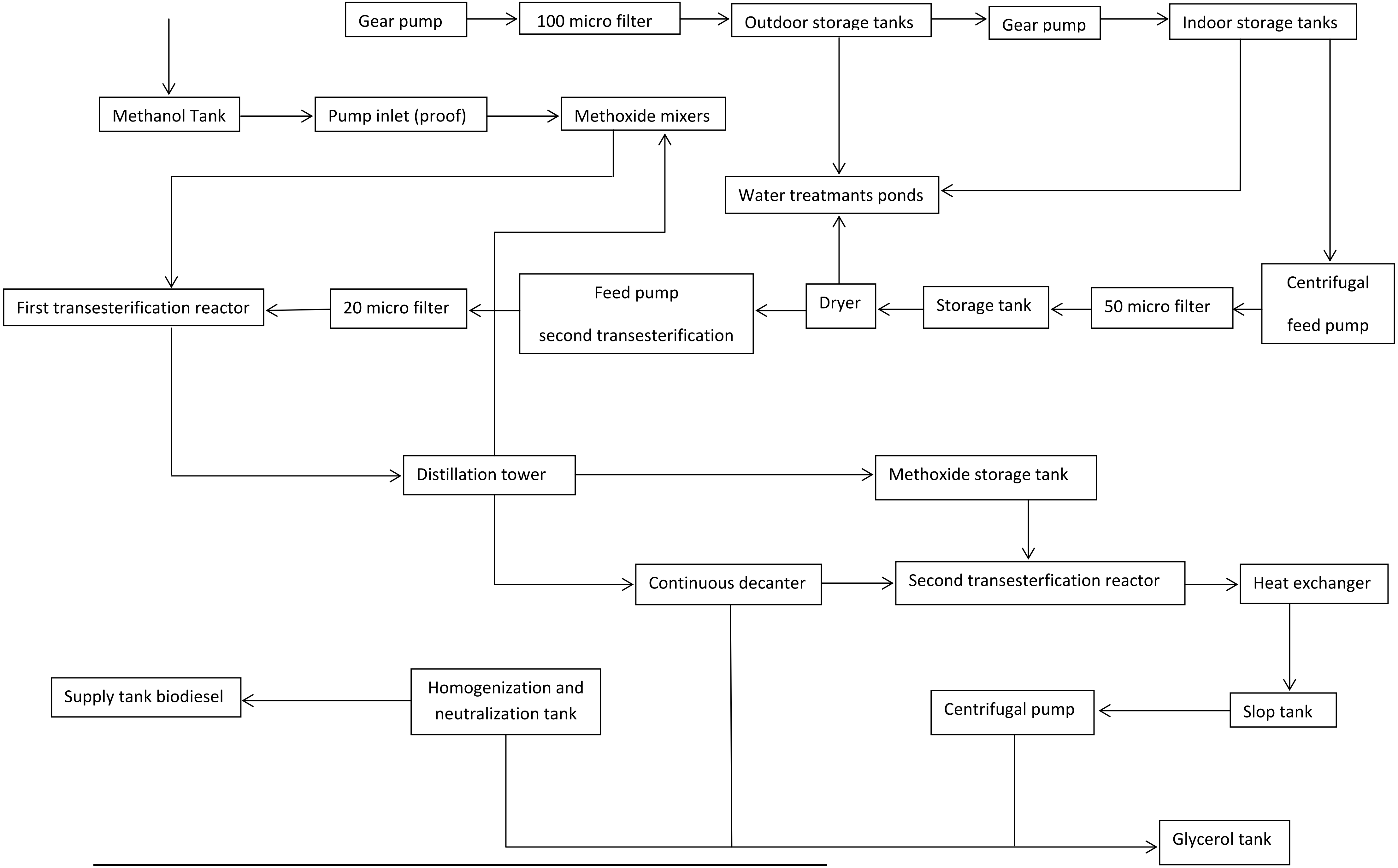
The biodiesel is produced by transesterification of oil using methanol (alcohol) and NaOH (catalyst)

The process steps are:

1) The vegetable and waste cooking oils are received. They are transported to the plant with trucks.
2) The oils are stored in outside tanks of the plant.
3) Drying and pretreatment of the oil.
4) The oil transesterification. The reactor is scheduled by 8000 hours per year, with a daily biodiesel production of 200 tons per day. The process starts with the refined oil. In the reactor, the oils are mixed with the methanol, in excess, NaOH (catalyst)

5) The reaction products are neutralized with a mineral acid. Methanol in excess is evaporated, and then condensed and stored to be reused in the next cycle.
6) The biodiesel is stored in tanks with nitrogen coverage to avoid its oxidation. The truck load is performed under nitrogen injection to avoid its degradation in transport.

Figure 9 shows the process flowchart.


Gear pump
100 micro filter
Outdoor storage tanks
Gear pump
Indoor storage tanks
Methanol Tank
Pump inlet (proof)
Methoxide mixers
Water treatmants ponds
Centrifugal feed pump
50 micro filter
Storage tank
Dryer
Feed pump second transesterification
20 micro filter
First transesterification reactor
Distillation tower
Methoxide storage tank
Continuous decanter
Second transesterfication reactor
Heat exchanger
Slop tank
Centrifugal pump
Homogenization and neutralization tank
Supply tank biodiesel
Glycerol tank

2.1 Mass flow

The oil for the biodiesel production at the Valdescorriel Zamora Plant is composed by 15-20% of waste cooking oil and 80-85% of vegetable oil

Figure 10 shows the process for production of biodiesel at the Valdescorriel Zamora Biodiesel Plant in Spain. Table 5 shows the different flows in the process.

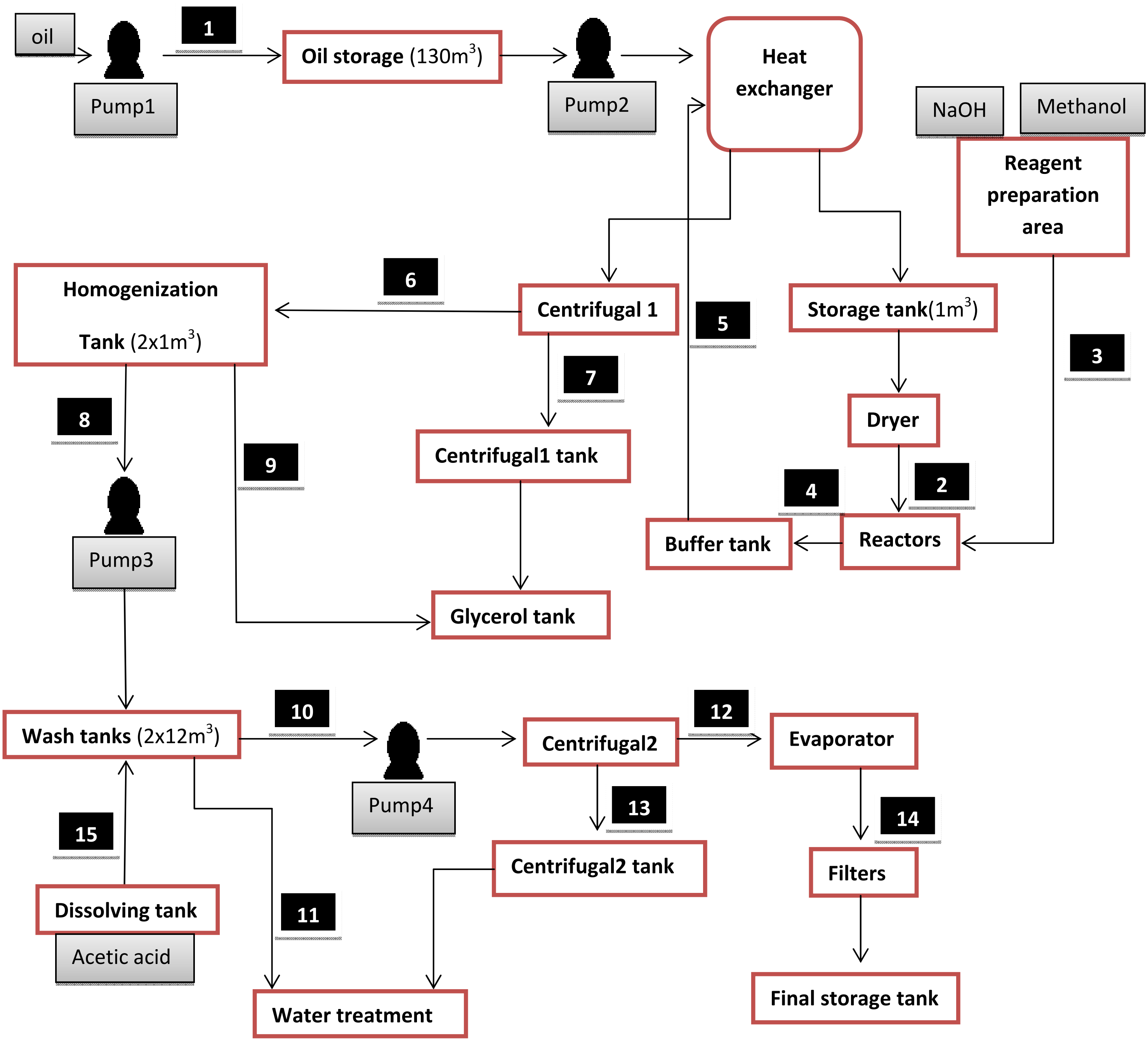


Figure 10. Biodiesel production process at the Valdescorriel Biodiesel Plant.

Table 5. Mass flow

Flow (kg)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Oil	355	355	-	12.56	12.56	12.56	-	12.56	-	12.56	-	6.28	6.28	6.28	-
Methanol	-	-	56	21.28	4.25	1.53	2.72	1.53	-	1.53	-	1.53	-	-	-
NaOH	-	-	2.8	-	-	-	-	-	-	-	-	-	-	-	-
Biodiesel	-	-	-	343.54	343.54	343.54	-	343.54	-	343.54	-	343.54	-	343.54	-
Glycerol	-	-	-	35.6	35.6	7.12	28.48	7.11	0.01	7.11	-	3.55	3.55	3.55	-
Water	-	7.12	-	7.12	7.12	7.12	-	7.12	-	87.12	4	2.62	84.5	0.08	-
Acid acetic	-	-	-	-	-	-	-	-	-	-	-	-	-	-	86

1. Flow 1: the calculation basis is for 400 liters of raw oil.
2. Flow 2: a) clean oil: 356 kg
   b) water is 2% of clean oil → 7.12 kg water
3. Flow 3: a) methanol in excess → 56 kg methanol
   b) catalyst → 2.8 kg NaOH
4. Flow 4: a) the reactor performance is 96.5% → 343.54 kg biodiesel and 12.56 kg oil
   b) about 38% of methanol excess → 21.28 kg methanol
   c) the produced glycerol is 10% of clean oil → 35.6 kg glycerol
5. Flow 5: a) methanol flow here is 20% of methanol flow in flow 4 → 4.25 kg methanol
6. Flow 6&7: a) 80% of glycerol in flow 5 is separated in flow 7 → 28.48 kg glycerol
   b) 64% of methanol in flow 5 is separated in flow 7→ 2.72 kg methanol
7. Flow 8&9: a) small amount of glycerol (0.01 kg glycerol)is separated in flow 9. The rest follows in flow 8
8. Flow 10&11: a) Flow 10: 21% water respect with the calculation basis is introduced → 80 kg water is introduced to the 7 kg water in flow 8
   Flow 11: about 4 kg waste water for cleaning
9. Flow 12&13: a) separation of 50% oil → 6.28 kg oil in flow 12
   b) separation of 50% of glycerol → 3.55 kg glycerol in flow 12
   c) separation of 97% of water → 3% of water (2.62 kg) in flow 12.
10. Flow 14: a) water elimination almost total → 0.08 kg water
11. Flow 15: a) Added acid acetic 21.5% of calculation basis → 86 kg acid acetic

2.2 Economic analysis

The analysis considered the following factors:

- Raw material costs (oils)
- Process, production and storage costs
- Distribution and marketing costs

General assumptions are:

- Biodiesel production: 20000 ton/year
- Biodiesel density (15ºC): 0.885 g/cm^3
- Sale price of biodiesel: 0.67€/l
- Glycerol production: 2000 ton/year (10% of biodiesel production)
- Sale price of glycerol: 20€/ton

The costs in order to produce 1 liter biodiesel are as follows:

Reagents

Oil: 0.503 €/l of biodiesel.

NaOH: 0.0028 €/l of biodiesel.

Water: 0.000245 €/l of biodiesel.

Acid acetic: 0.0028 €/l of biodiesel.

Energy consumption

Power: 0.00072 €/l of biodiesel.

Heat: 0.002 €/l of biodiesel.

Workpeople

20 workers: 0.017 €/l

Total cost per liter of produced biodiesel = 0.585 €/l

The calculation of the costs is shown in appendix 1.

The benefit in a typical year (selling 20000 tons of biodiesel and 2000 tons of glycerol) is:

Benefit = Income – Costs

$$\boldsymbol{Income} = \left(0.67 \frac{€}{l\ biodiesel} \cdot \frac{cm^3}{0{,}885g} \cdot \frac{10^6}{1ton} \cdot \frac{1l}{10^3} \cdot 20000\ ton\ biodiesel\ + 20 \frac{€}{ton\ glycerol} \cdot 2000\ ton\ biodiesel\right) = \mathbf{15\ 181\ 243}\ \frac{\boldsymbol{€}}{\boldsymbol{year}}$$

$$\boldsymbol{Costs} = \left(0.585 \cdot \frac{€}{l\ biodiesel} \cdot \frac{cm^3}{0{,}885g} \cdot \frac{10^6}{1ton} \cdot \frac{1l}{10^3} \cdot 20000\ ton\ biodiesel\right) = \mathbf{13\ 220\ 399} \frac{\boldsymbol{€}}{\boldsymbol{year}}$$

Benefit = Income – Costs = 1 960 904 €/year

Profitability

The variables involved in the calculation of profitability are:

- Investments: Installation and administrative costs are 4 500 000 €.
- Investments subsidies: Total amount received in form of grants. In this case, it is considered that there are no subsidies. The most unfavorable situation for recovery the investments is considered
- Operating costs: The costs involved in the management and operations of the biodiesel plant.

<u>Net present value (NPV):</u>

Net present value is the difference between the present value of the future cash flow from an investment and the amount of investment. A discounting rate is used to calculate the present value of expected cash flow. An interest rate of 5% (the usual in these projects) is used and the inflation rate does not consider. The life of the facility is 30 years. The NPV is calculated according:

$$NPV = \sum_{t=1}^{N} \frac{R_t}{(1+i)^t}$$

Where:

- R_t = Net Cash Flow (Income – Costs)
- t = time of the cash flow (30 year)
- i = Discount rate

An investment is acceptable if the NPV is positive [John Downes, 2010].

In this case, for 30 years of life of the facility the NPV is showed in the Figure 11:

NPV = 25 643 900 €

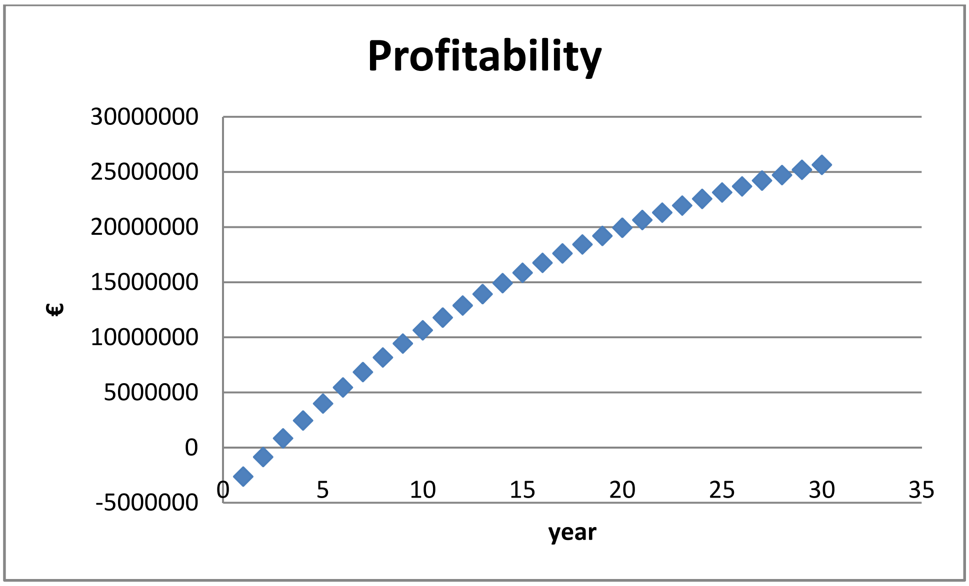


Figure 11. Profitability evolution

The investment is recovered after 3 years, in a normal market situation.

Internal Rate of Return (IRR)

The internal rate of return is the rate of return used to measure and compare the profitability of investments. It is the discount rate that make the net present valueof all cash flows from an investment equal to zero. Generally, the higher a project's internal rate of return is more desirable it is to undertake the project [http://www.investopedia.com/terms/i/irr.asp].

$$NPV = \sum_{t=1}^{N} \frac{R_t}{(1+i)^t} = 0, (i = IRR)$$

For this plant, the IRR value is: **IRR = 63%**

2.3. Calculation and comparison of greenhouse gas emissions

The decrease of gas emissions depends on the raw material. The main advantages are achieved replacing the petroleum diesel by biodiesel produced from waste cooking oils. In this case, it is possible to reduce greenhouse gas emissions in 48%.

The NO_x and particles emissions are not affected, as, it is showed in the Figure 12.

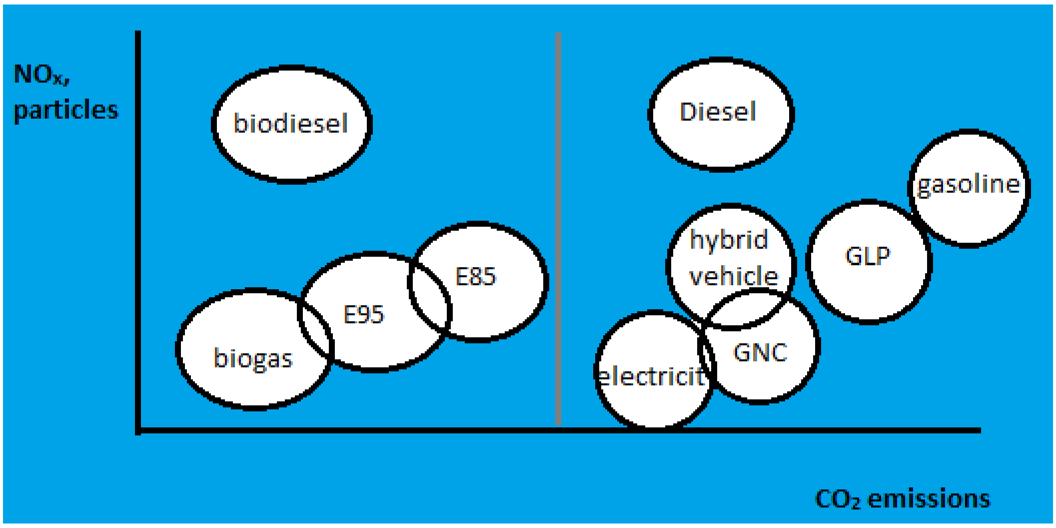


Figure 12. Biodiesel emissions

For the studied case, the plant could produce 20 000 tons per year of biodiesel, in its maximum capacity. Thus, it is possible to reduce CO_2 emissions in 55 000 tons/year.

It is considered that the biodegradability of the biodiesel is 90% after 25 days. [C.L. Peterson, 2003].

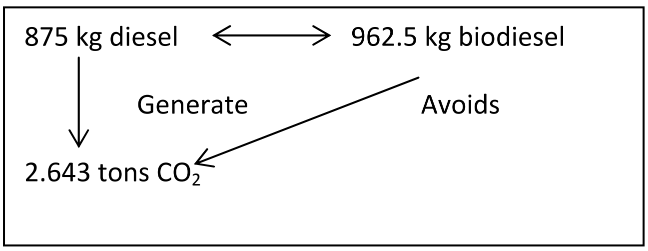
The expression used to calculate the greenhouse emissions gases:

E = C · EF · CV

E: emissions (tons of CO_2)
C: consumption
EF: Emission factor of the fuel used
CV: calorific value

➔ For the diesel:
· C = 1m^3 = 835 kg diesel
· EF = 73.52 kg CO_2/GJ
· CV = 43.46 MJ/kg
E = 2643.411 kg CO_2 = 2.643 tons CO_2

➔ For the biodiesel:
· Using relations: 1000 liters of diesel equals to 1100 liters of biodiesel



So, the CO_2 emissions could be reduced in 54 919 tons CO_2 per year, for a biodiesel production plant of 20 000 tons.

3. Experimental

The biodiesel production from sunflower oil and ethanol, with sodium hydroxide as catalyst has been studied in laboratory experiments.

The objective is to study the influence of the ratio ethanol to oil and the amount of catalyst on the yield and quality of the produced biodiesel.

The optimization of the process is also an objective of the present study.

3.1 Experimental Procedure

The raw materials involved in the reaction are sunflower oil, ethanol and the catalyst (NaOH). The reaction is made in a fume cupboard.

The different steps for the biodiesel production in laboratory are:

1. Mixing of the ethanol and the catalyst in a flask. The moisture level should be kept as low as possible. Water causes the formation of soap by saponification. It is necessary to reduce the formation of soap. Formation of soap consumes the catalyst is consumed and complicates the separation and purification process. Formation of soap also decreases the biodiesel yield.
2. The mix ethanol/NaOH is heated to 50°C (in a water bath) and stirred by a magnet at 800 rpm (constant speed), until, the catalyst is completely dissolved in the ethanol.
3. 200 ml sunflower oil is heated at 60°C.
4. The solution ethanol-catalyst and the oil are mixed in a flask. The flask is introduced in a water bath at 50°C and stirred to 500 rpm. The reaction is performed during 60 minutes.
5. The final solution is poured into a separation funnel. The top layer is the biodiesel and the bottom darker layer is the by-product, glycerol.
6. Removal the glycerol from the biodiesel, and measure the glycerol.
7. The biodiesel is washed with 5 wt% phosphoric acid (50 ml) to neutralize the catalyst residue. (Preparation of 5 wt% H_3PO_4 is described in appendix 2).
8. Measurement of the amount of produced biodiesel.
9. Analysis of the properties of the produced biodiesel: density, viscosity and refractive index.
10. The experiment is repeated a number of times varying the ratio of ethanol/oil and the catalyst weight.

Table 6 shows the amount of ethanol and catalyst used in the experiments.

Table 6. Initial conditions of the experiments (with 200 ml of sunflower oil)

Sample	Volume of ethanol	Catalyst weight
1	90	0.8
2	60	0.8
3	120	1.5
4	90	1.5
5	90	1.5
6	120	0.8
7	90	0.8
8	90	0.8
9	60	1.5
10	90	1.5
11	120	1.5
12	120	1.5

3.2 Equipments

1. Electronic scale
2. Mine-thrower
3. Test tube
4. Magnet
5. Digital magnetic stirrer
6. Flask
7. Container water bath
8. Thermometer
9. Separation funnel
10. Erlenmeyer
11. Heating device
12. Refractometer
13. Falling sphere viscometer

3.3 Chemicals & Security

Table 7. Chemicals and security

Chemical	*Hazard*	*MSDS*
Sunflower oil		
Ethanol (99.7% Solveco AB)		Appendix 3
NaOH		Appendix 4
Phosphoric acid (85%)		Appendix 5

The security required to obtain biodiesel, in the laboratory, does not request extra safety protection. The common rules in a laboratory are necessary to take into account, like use of security glasses, gloves and lab coat. Moreover, the reaction was carried out inside the extraction hood.

3.4 Methods of Data Analysis

Following properties of the produced biodiesel are analysed:

- Density: The density can be determinate with the equation: $\rho = \frac{test\ tube_{full} - test\ tube_{empty}}{biodiesel\ volume}$

- Viscosity measurement: Dynamic viscosity can be measured by the aid of a viscometer through following relation: $\eta = k \cdot t \cdot (\rho_{sphere} - \rho_{biodisel})$.

  In the equation constant value (k) is unknown and it is needed to find via another medium which has known viscosity and density. In this experiment a mixture of glycerol and water is used with volume The concentration of solution is 20% We need to find the value of k (constant); so, it is possible to use viscometer for a known fluid and measure the value of k. we use 20% glycerol solution in water.

  Following data is available for 20% glycerol solution in water

  $\rho_{Glycerol}$=1.04525 g/ml

  η=1.542 cP

  ρ_{ball}=1.32 g/ml

For this experiment the falling time is equal to 0.93 s. As a result the value of k will be equal to 6.03.

Kinematic viscosity is the ratio of dynamic viscosity to density.

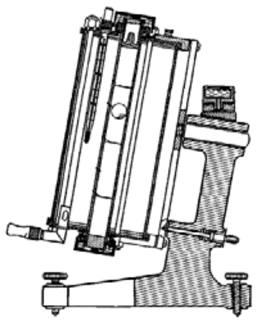


Figure 13. Falling Sphere Viscometer

- Refractive index measurement: Refractive index is a measure of the speed of light in the substance, in this case in biodiesel. It is expressed the ratio of the speed of light in vacuum relative to that in the considered medium. A refractometer (figure 14) is used to measure the refractive index.

Figure 14. Refractometer

- Refractive index measurement: Refractive index is a measure of the speed of light in the substance, in this case in biodiesel. It is expressed as the ratio of the speed of light in vacuum relative to that in the considered medium. A refractometer (figure 14) is used to measure the refractive index.

Table 8 shows yield and properties of the obtained biodiesel in the experiments

Table 8. Yield and properties of the obtained biodiesel in the experiments (used oil: 200 ml the sunflower oil).

Sample	*Volume Ethanol (ml)*	*Catalyst Weight (g)*	*Glycerin (ml)*	*Raw Biodiesel (ml)*	*Clean Biodiesel (ml)*	*Density Biodiesel (g/ml)*	*Viscosity Biodiesel (cp)*	*Refractive index*	*Yield*
1	90	0.843	29	244	216	0.82	3.16	1.4575	0.828
2	60	0.858	28	214	200	0.86	4.56	1.4580	0.804
3	120	1.508	12	288	275	0.86	4.07	1.4390	1.103
4	90	1.507	37	235	225	0.84	4.13	1.4550	0.878
5	90	1.522	30	239	229	0.84	4.60	1.4495	0.900
6	120	0.826	32	273	260	0.84	4.15	1.4555	1.017
7	90	0.823	33	240	233	0.85	4.05	1.4470	0.923
8	90	0.804	34	243	236	0.84	3.70	1.4450	0.928
9	60	1.528	47	197	194	0.85	3.83	1.4510	0.776
10	90	1.514	35	244	241	0.84	4-08	1.4440	0.955
11	120	1.537	6	297	268	0.86	4.28	1.4360	1.072
12	120	1.511	6	304	285	0.85	5.20	1.4200	1.129

The density of the sunflower oil was measured in 0.92 g/l. The viscosity of the sunflower oil was 24.317 cp and the refractive index was 1.476

- Analysis of variance:

  The lab experiments are analyzed using the statistical inference. The Anova (analysis of variance) is implemented.

  The Anova was developed around 1930 by R.A. Fisher. The Anova is the basic technique for the study of observations depends on several factors [Romero Villafranca, 2005].

  The considered variables for the statistical analysis are the ratio ethanol:oil and the amount of catalystThemolar ratio ethanol:oil takes in this analysis three different values: 4.9 (60 ml ethanol in 200 ml oil) ,7.4 (90 ml ethanol in 200 ml oil) and 10.2 (120 ml ethanol in 200 ml oil)

  The amount of Catalyst (NaOH) takes 2 values: 0.8 g and 1.5 g

The influence of the independent variables (ratio ethanol:oil and amount of catalyst) on four dependent variables (yield, density, viscosity and refractive index of the produced biodiesel) is studied.

a) Yield: The yield of biodiesel indicates the percentage of biodiesel produced, in relation to the theoretical volume calculated.

$$\%\, yield = \frac{Vreal}{Vtheo} \cdot 100$$

Where:

Vreal: Volume of biodiesel obtained in each sample.

Vtheo: Theoretical volume of produced biodiesel.

The volume of obtained biodiesel is known and measured for each sample. The theoretical volume is calculated from the molar weight (857 g/mole [A. Deligiannis, 2009]) and density (0.85 g/ml, estimated in laboratory) of the sunflower oil, and the molar weight (301 g/mole [SGAPyA]) and density (one for each sample) of biodiesel.

In the experiments, 200 ml oil was used. It corresponds to 0.198 moles:

$200ml \cdot 0.85\frac{gr}{mole} \cdot \frac{1}{857\frac{gr}{mol}} = 0.198$ moles

The theoretical amount of biodiesel formed is:

$0.198\ moles \cdot 3 = 0.594$ moles

The theoretical volume of produced biodiesel is (ρi the density of the produced biodiesel):

$$Vtheo = \frac{0.594\ moles \cdot 301\frac{g}{mol}}{\text{ρi (g/ml}}$$

The biodiesel production reaction is:

Triglycerides + Monohydric alcohol ↔ Glycerine + Monoalkyl esters

The stoichiometric reaction requires 1 mole of triglyceride and 3 moles of alcohol. The process is a sequence of three consecutive and reversible reactions. The di-glycerides and mono-glycerides are the intermediate products.

An excess of alcohol is used to shift the equilibrium to the right.

The phase of biodiesel contains some impurities, mainly, unreacted oil.

b) Density: It is defined as “the mass per unit volume of any liquid at a given temperature”. Biodiesel has a slightly higher density compared to petrodiesel.
c) Viscosity: It is an indicator of “the measure of resistance to flow of a liquid due to internal friction of one part of a fluid moving over another”.
   Biodiesel has a similar viscosity to the diesel. High viscosity values can be a result of a not efficient washing, with many remains of mono-glyceride.
d) Refractive index: It is “the relation between light speed in the vacuum and the light speed through the substance”. The refractive index of biodiesel increases with the amount of glycerol, as it can be seen in the figure 14 [Claire MacLeod,2008]

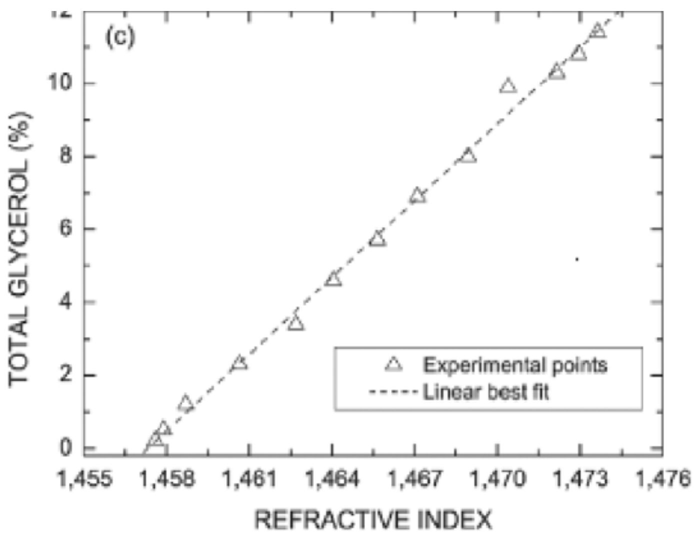


Figure 14. Relation glycerol vs. Refractive index

3.5 Results and discussion

a. Effects on Yield of produced biodiesel

In Table 9 the analysis of the variances of yield of produced biodiesel is shown.

Table 9. Analysis of Variance for Yield - Type III Sums of Squares

Source	*Sum of Squares*	*Df*	*Mean Square*	*F-Ratio*	*P-Value*
MAIN EFFECTS					
A:ratio ethanol:oil	0.0938174	2	0.0469087	25.14	0.0012
B:catalyst weight	0.00137486	1	0.00137486	0.74	0.4237
INTERACTIONS					
AB	0.00409444	2	0.00204722	1.10	0.3926
RESIDUAL	0.0111973	6	0.00186622		
TOTAL (CORRECTED)	0.149898	11			

F is the ratio of the Model Mean Square to the Error Mean Square.

When the influence of the ratio ethanol/oil on the yield of produced biodiesel is studied, the obtained p-value is lower than o.05 (table 9). It means that the ratio ethanol/oil is a significant parameter. The influence of the amount of catalyst and the interaction of both parameters (ratio alcohol:oil and amount of catalyst) has no significant influence. In these cases the obtained p-value is higher than 0.05.

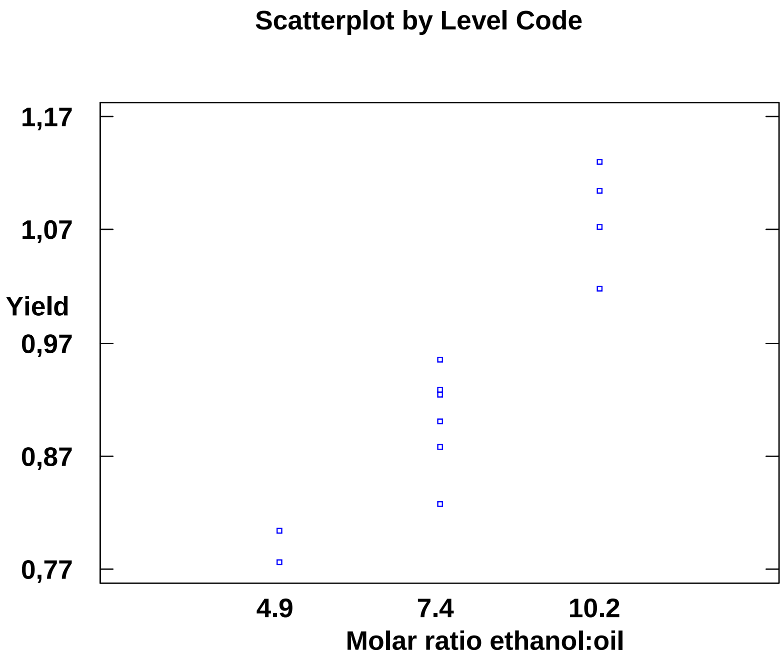


Figure 15. Scatterplot Yield vs. Ratio ethanol:oil

In figure 15 the influence of the ratio ethanol:oil on the yield of biodiesel is shown.

In table 10 the squares means of the yield of biodiesel with a confidence interval of 95% are shown.

Table 10. Least Squares Means (LSM) of Yield with 95,0% Confidence Intervals

Level	*Count*	*Mean*	*Stnd. Error*	*Lower Limit*	*Upper Limit*
GRAND MEAN	12	0.917616			
ratio ethanol:oil					
60	2	0.790506	0.0305469	0.71576	0.865251
90	6	0.90245	0.0176363	0.859296	0.945605
120	4	1.05989	0.0249414	0.998864	1.12092
catalyst weight					
0.8	5	0.905257	0.0219963	0.851434	0.95908
1.5	7	0.929976	0.0185902	0.884487	0.975465
ratio ethanol by catalyst weight					
60,0.8	1	0.804527	0.0431998	0.69882	0.910233
60,1.5	1	0.776484	0.0431998	0.670778	0.882191
90,0.8	3	0.893474	0.0249414	0.832445	0.954504
90,1.5	3	0.911426	0.0249414	0.850396	0.972456
120,0.8	1	1.01777	0.0431998	0.912063	1.12348
120,1.5	3	1.10202	0.0249414	1.04099	1.16305

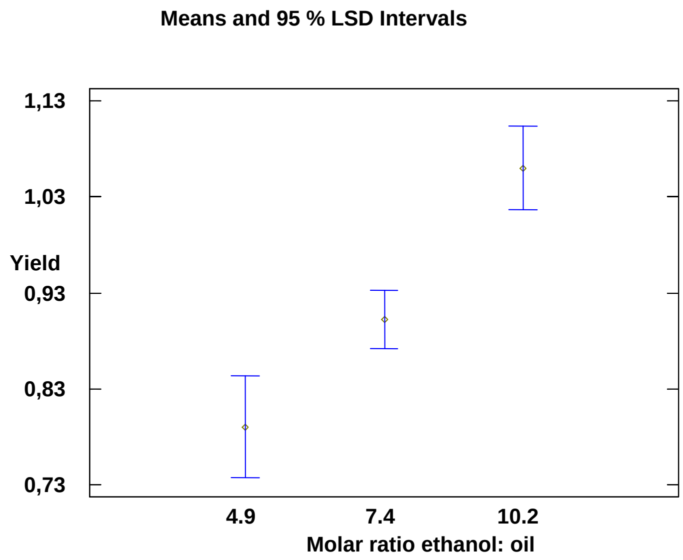


Figure 16. LSD intervals yield in relation to the ratio ethanol:oil

In figure 16 the influence of the ratio ethanol:oil on the yield of biodiesel is shown with a 95% confidence interval. No interval occurs, ratifying that the ratio ethanol:oil is a significant parameter.

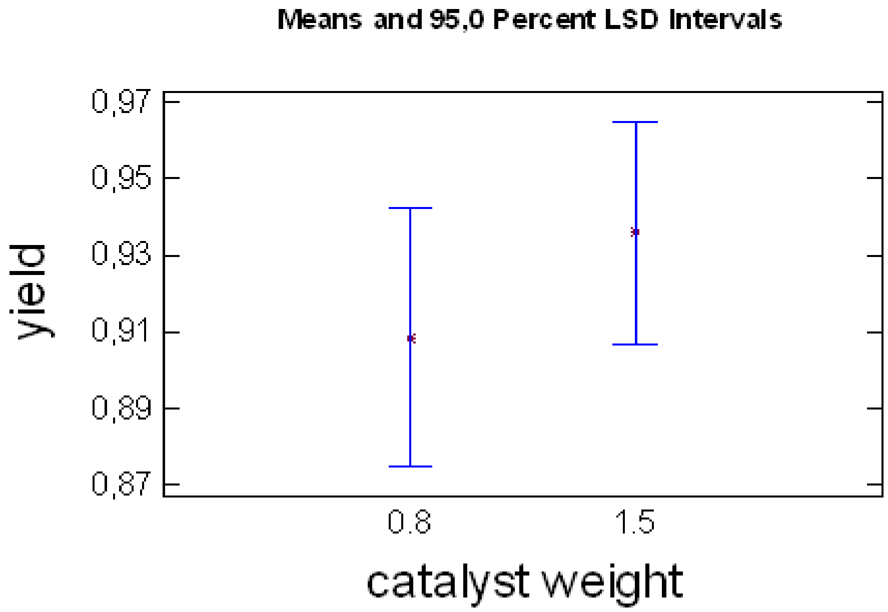


Figure 17. LSD intervals yield for catalyst weight

In figure 17 the influence of the amount catalyst on the yield of biodiesel is shown. The intervals are overlapping. The amount of catalyst is not a significant parameter.

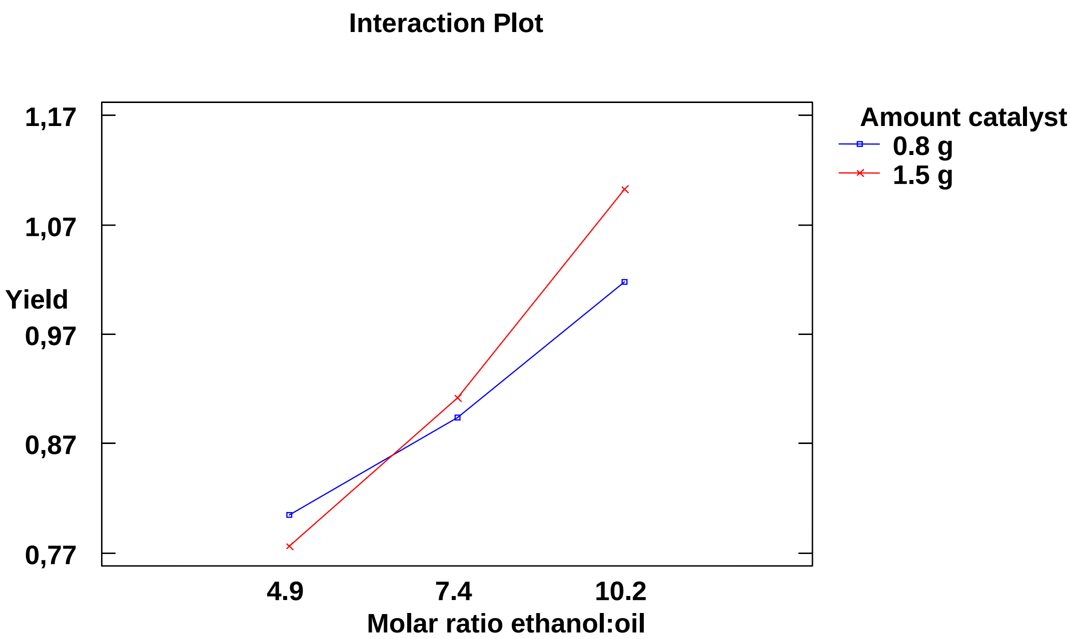


Figure 17. Interaction plot yield

Figure 18 represents the influence of the interaction of both parameters (ratio ethaol/oil and amount of catalyst) on the yield of biodiesel. The aim is to study the trend of optimal operation conditions.

The tendency for the yield is to increase with the ratio ethanol:oil and amount of catalyst.

The variance of the residuals is shown in table 11.

Table 11. Analysis of Variance for RESIDUALS - Type III Sums of Squares

Source	***Sum of Squares***	***Df***	***Mean Square***	***F-Ratio***	***P-Value***
MAIN EFFECTS					
A:ratio ethanol:oil	0.00000563537	2	0.00000281769	1.89	0.2307
B:catalyst weight	7.2565E-8	1	7.2565E-8	0.05	0.8326
INTERACTIONS					
AB	0.0000014649	2	7.32448E-7	0.49	0.6342
RESIDUAL	0.00000893805	6	0.00000148967		
TOTAL (CORRECTED)	0.0000163657	11			

F is the ratio of the Model Mean Square to the Error Mean Square.

The p-values demonstrate that there are no influent factors on the residuals.

b. Effects on the density of the produced biodiesel

In table 12 it is shown the analysis of variance of density of biodiesel affected by ratio ethanol:oil and the amount of catalyst. The p-value of the ratio etahol:oil is 0.0617, higher than 0.05. Thus the ratio ethanol:oil is considered statistically significant.

Table 12. Analysis of Variance for Density - Type III Sums of Squares

Source	***Sum of Squares***	***Df***	***Mean Square***	***F-Ratio***	***P-Value***
MAIN EFFECTS					
A:ratio ethanol:oil	0.000335284	2	0.000167642	5.12	0.0617
B:catalyst weight	0.000020108	1	0.000020108	0.61	0.4687
INTERACTIONS					
AB	0.000220656	2	0.000110328	3.37	0.1184
RESIDUAL	0.000163714	5	0.0000327428		
TOTAL (CORRECTED)	0.000767911	10			

F is the ratio of the Model Mean Square to the Error Mean Square.

In table 13 the squares means are analyzed, in order to check the information extracted from the Anova.

Table 13. Least Squares Means for Density with 95,0% Confidence Intervals

			Stnd.	***Lower***	***Upper***
Level	*Count*	*Mean*	*Error*	*Limit*	*Limit*
GRAND MEAN	11	0.851599			
ratio ethanol:oil					
4.9	2	0.86088	0.00404616	0.850479	0.871281
7.4	5	0.84563	0.00261178	0.838916	0.852344
10.2	4	0.848287	0.00330367	0.839794	0.856779
Amount catalyst					
0.8	4	0.850073	0.00301583	0.842321	0.857826
1.5	7	0.853124	0.00246241	0.846795	0.859454
ratio ethanol:oil, amount catalyst					
4.9, 0.8	1	0.86304	0.00572213	0.848331	0.877749
4.9, 1.5	1	0.85872	0.00572213	0.844011	0.873429
7.4, 0.8	2	0.84734	0.00404616	0.836939	0.857741
7.4, 1.5	3	0.84392	0.00330367	0.835428	0.852412
10.2, 0.8	1	0.83984	0.00572213	0.825131	0.854549
10.2, 1.5	3	0.856733	0.00330367	0.848241	0.865226

In figure 18, It is shown the range of the density with the 95% confidence interval in relation to the ratio ethanol:oil:

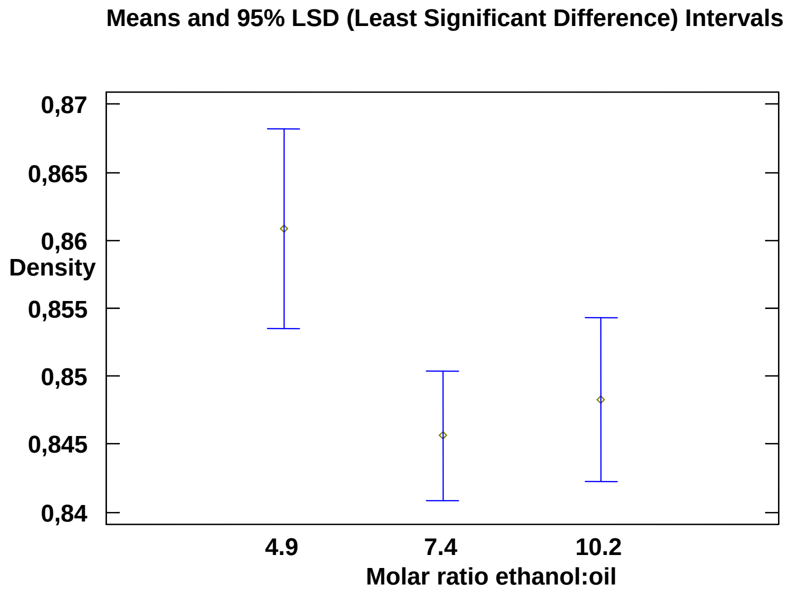


Figure 18. LSD intervals for density

The interval of the density at the ratio ethanol/oil = 4.9 is not overlapping with the interval at ratio 7.4 och 10.2. The tendency is that the density decreases with the ratio ethanol:oil.

In figure 19, the density with 95% confidence interval is shown in relation to the amount of catalyst

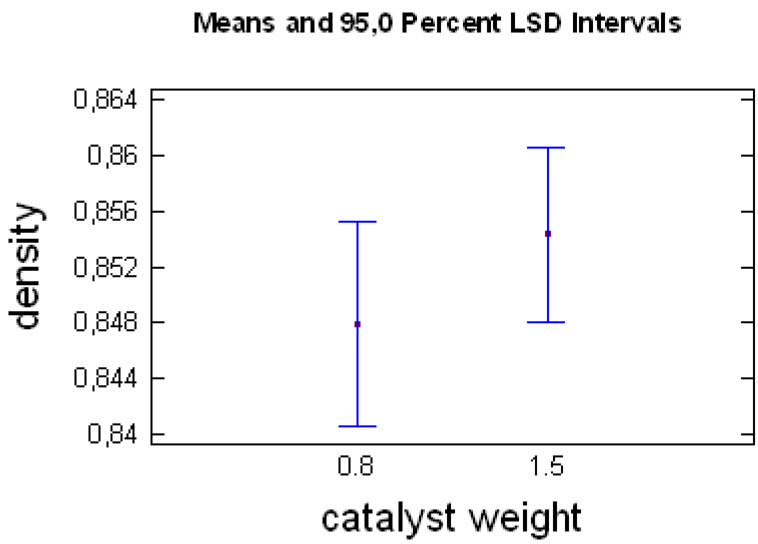


Figure 19. LSD (Least Significant Difference) intervals of the density.

In figure 20, the interaction of the ratio ethanol:oil and the amount of catalyst on the density of the produced biodiesel is shown.

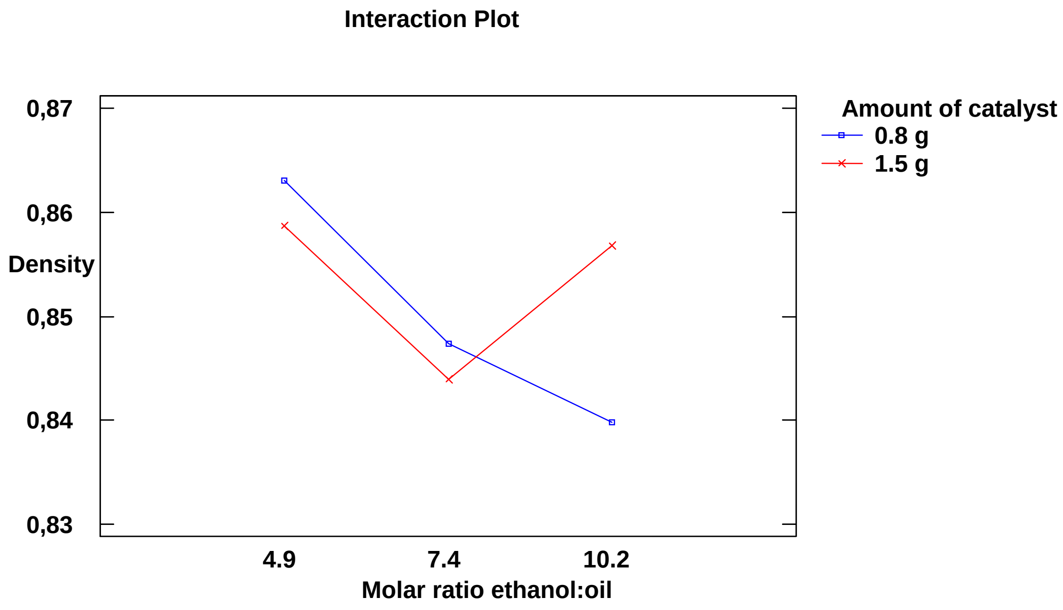


Figure 20. Interaction of the ratio ethanol:oil and the amount of catalyst on the density.

The tendency is that the density decrease with the ratio ethanol:oil.

In table 14 the analysis of variance of the residuals is shown.

Table 14. Analysis of Variance for RESIDUALS - Type III Sums of Squares

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
MAIN EFFECTS					
A:ratio ethanol:oil	5.49501E-10	2	2.7475E-10	0.80	0.5007
B:catalyst weight	3.18362E-10	1	3.18362E-10	0.92	0.3807
INTERACTIONS					
AB	1.31296E-10	2	6.56482E-11	0.19	0.8324
RESIDUAL	1.72409E-9	5	3.44817E-10		
TOTAL (CORRECTED)	2.97288E-9	10			

F is the ratio of the Model Mean Square to the Error Mean Square.

There is no significant influence of the parameters (ethanol:oil ratio and amount of catalyst)on the density according the analysis of the variances of residuals. It is not possible to conclude that the ratio ethanol and the catalyst weight are relevant factors for the density of biodiesel.

c. Effects on the viscosity of the produced biodiesel

The analysis of variance of viscosity of biodiesel is shown in table 15

Table 15. Analysis of Variance of the viscosity - Type III Sums of Squares

Source	*Sum of Squares*	*Df*	*Mean Square*	*F-Ratio*	*P-Value*
MAIN EFFECTS					
A:ratio ethanol:oil	0.131477	2	0.0657385	0.56	0.6043
B:catalyst weight	0.000973261	1	0.000973261	0.01	0.9311
INTERACTIONS					
AB	0.73693	2	0.368465	3.13	0.1315
RESIDUAL	0.589079	5	0.117816		
TOTAL (CORRECTED)	1.60434	10			

F is the ratio of the Model Mean Square to the Error Mean Square.

The parameters ratio ethanol:oil and amount of catalyst are not statistically significant. The p-value is higher than 0.05.

Table16. Least Squares Means of viscosity with 95,0% Confidence Intervals

			Stnd.	*Lower*	*Upper*
Level	*Count*	*Mean*	*Error*	*Limit*	*Limit*
GRAND MEAN	11	4.10573			
ratio ethanol:oil					
4.9	2	4.19799	0.242709	3.57409	4.8219
7.4	6	3.95566	0.140128	3.59545	4.31587
10.2	3	4.16354	0.210193	3.62322	4.70385
catalyst weight					
0.8	5	4.11634	0.174771	3.66708	4.56561
1.5	6	4.09512	0.154918	3.69689	4.49335
ratio ethanol by catalyst weight					
4.9, 0.8	1	4.56306	0.343243	3.68072	5.44539
4.9, 1.5	1	3.83293	0.343243	2.9506	4.71527
7.4, 0.8	3	3.63692	0.198171	3.1275	4.14634
7.4, 1.5	3	4.27441	0.198171	3.76499	4.78382
10.2, 0.8	1	4.14906	0.343243	3.26672	5.03139
10.2, 1.5	2	4.17801	0.242709	3.55411	4.80192

In Table 16 the squares means are analyzed, in order to check the information extracted from the Anova.

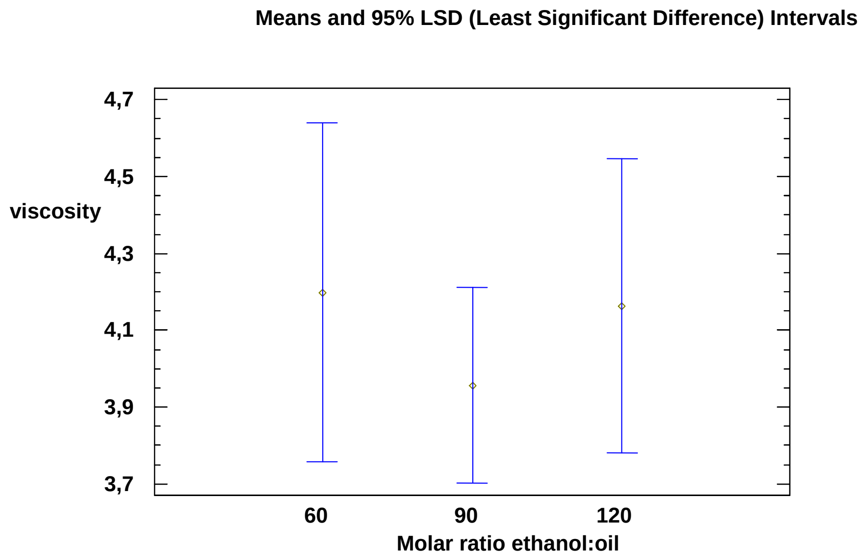


Figure 22. LSD intervals viscosity

In figure 22 the viscosity with a 95% interval is shown in relation to the ratio ethanol:oil. The ratio ethanol.oil has not a significant influence on the viscosity of the biodiesel. The intervals are overlapping. In figure 23 the viscosity is represented in relation to the amount of catalyst.

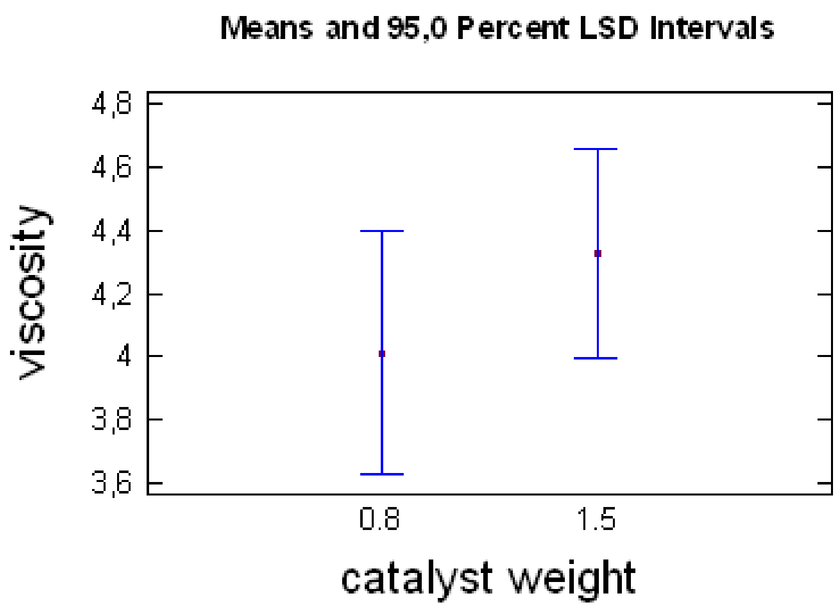


Figure 23. LSD (Least Significant Difference) intervals of viscosity

The amount of catalyst is not a significant influence on the viscosity. The intervals overlap.

In figure 24 the interaction of the ratio ethanol:oil and the amount of catalyst on the viscosity of the biodiesel is plotted. The aim is to study the optimal operation conditions. Ratio ethanol:oil and amount catalyst are not affecting the viscosity of biodiesel.

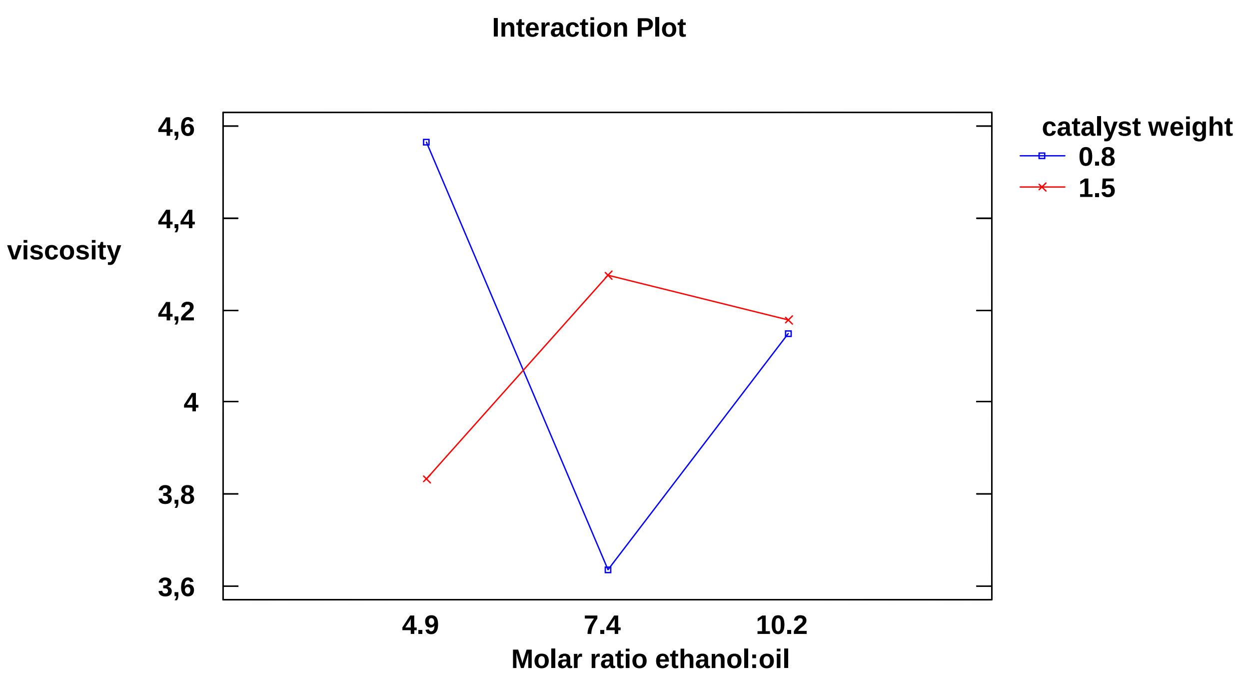


Figure 24. Interaction plot for viscosity

d. Effects on the refractive index of the produced biodiesel

The analysis of the variance (ANOVA) of the refractive index of the biodiesel is shown in table 17.

Table 17. Analysis of Variance for refractive index - Type III Sums of Squares

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
MAIN EFFECTS					
A:catalyst weight	0.000238188	1	0.000238188	3.98	0.0932
B:ratio ethanol:oil	0.000147714	2	0.000073857	1.23	0.3559
INTERACTIONS					
AB	0.000277005	2	0.000138503	2.31	0.1801
RESIDUAL	0.000359333	6	0.0000598889		
TOTAL (CORRECTED)	0.00130639	11			

F is the ratio of the Model Mean Square to the Error Mean Square.

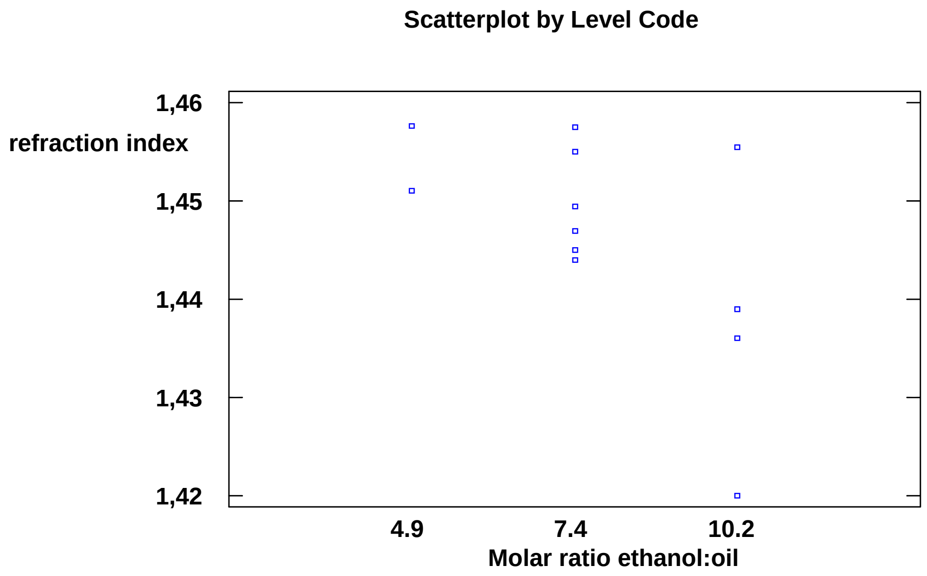


Figure 25. Scatterplot ratio ethanol vs. refractive index

In figure 25 it is plotted the refractive index of the biodiesel in relation to the ratio ethanol:oil. According to the literature, the refractive index of the biodiesel is close to 1.45 [Luis Ángel Agejas, 1996].

In table 18, the least squares means for refractive index with 95,0% confidence interval is shown.

In figure 26 the LSD (least significant difference) intervals of the refractive index are plotted in relation to the ratio ethanol:oil.

The intervals of the refractive index for the ratio ethanol:oil 4.9, 7.4 and 10.2 are overlapping 8figure 26). The appreciated tendency is that the refractive index decreases with the ratio ethanol:oil.

Table 18. Least Squares Means for refractive index with 95,0% Confidence Intervals

			Stnd.	Lower	Upper
Level	*Count*	*Mean*	*Error*	*Limit*	*Limit*
GRAND MEAN	12	1.4492			
ratio ethanol					
4.9	2	1.45435	0.00547215	1.44096	1.46774
7.4	6	1.44967	0.00315935	1.44194	1.4574
10.2	4	1.44358	0.00446799	1.43265	1.45452
catalyst weight					
0.8	5	1.45434	0.0039404	1.4447	1.46399
1.5	7	1.44406	0.00333025	1.43591	1.4522
ratio ethanol by catalyst weight					
4.9, 0.8	1	1.4577	0.00773879	1.43876	1.47664
4,9, 1.5	1	1.451	0.00773879	1.43206	1.46994
7.4, 0.8	3	1.44983	0.00446799	1.4389	1.46077
7.4, 1.5	3	1.4495	0.00446799	1.43857	1.46043
10.2, 0.8	1	1.4555	0.00773879	1.43656	1.47444
10.2, 1.5	3	1.43167	0.00446799	1.42073	1.4426

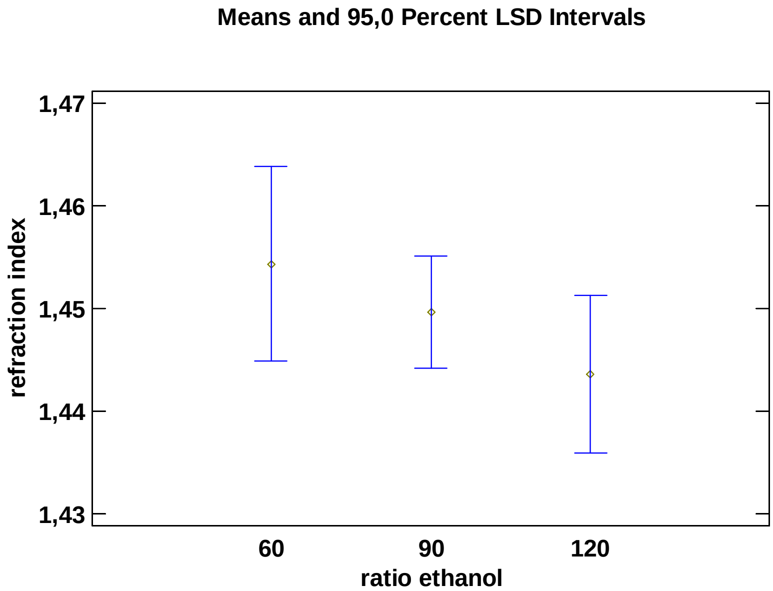


Figure 26. LSD intervals for refractive index

The refractive index values of the biodiesel are represented in figure 27, in relation to the amount of catalyst.

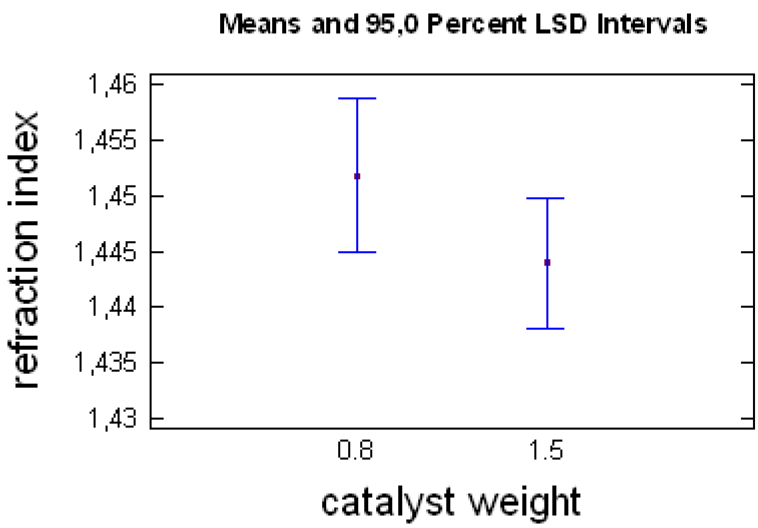


Figure 27. LSD intervals for refractive index

The amount of catalyst has not a significant influence on the refractive index. The intervals overlap.

In figure 28 it is represented the interactionof both the ratio ethanol:oil and the amount of catalyst on the refractive index.

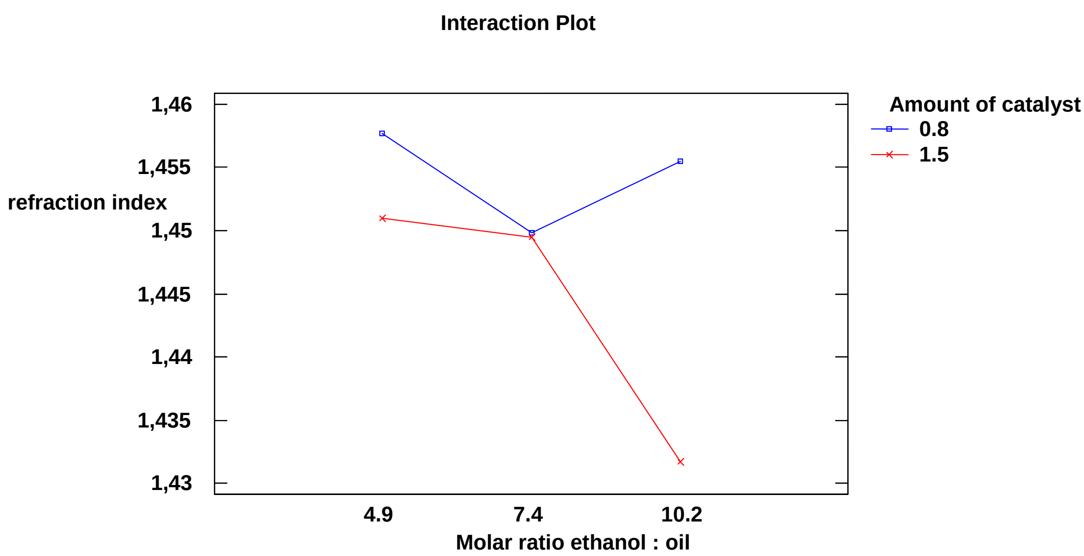


Figure 28. Interaction plot for refractive plot

When the ratio ethanol:oil increases from 4.9 to 7.4 a decrease of the refractive index is appreciated. In table 19 the variance of the residuals of the refractive index is analysed in relation to the influence of the ratio ethanol:oil and the amount of catalyst.

Table19. Analysis of Variance for residuals - Type III Sums of Squares

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
MAIN EFFECTS					
A:catalyst weight	8.90035E-10	1	8.90035E-10	0.58	0.4755
B:ratio ethanol	1.50053E-9	2	7.50267E-10	0.49	0.6362
INTERACTIONS					
AB	3.26836E-9	2	1.63418E-9	1.06	0.4025
RESIDUAL	9.22212E-9	6	1.53702E-9		
TOTAL (CORRECTED)	1.69062E-8	11			

F is the ratio of the Model Mean Square to the Error Mean Square.

There is not a significant influence of the ratio ethanol on the variance.

Prediction model

A multiple regression model is utilized in order to estimate the influence of the ratio ethanol:oil and the amount of catalyst on the yield of the biodiesel as well as on the properties of the biodiesel such as the density, viscosity and the refractive index.

Yield:

Table 20. Prediction model for the yield. Multiple regression

Dependent variable: yield

Parameter	*Estimate*	*Standard error*	*T Statistic*	*P-value*
CONSTANT	0.42519	0.0691337	6.15027	0.0002
ethanol ratio	0.0048825	0.000635587	7.68187	0.0000
catalyst weight	0.0449102	0.0379681	1.18284	0.2672

Analysis of Variance

Source	*Sum of squares*	*Df*	*Mean square*	*F-ratio*	*P-value*
Model	0.132135	2	0.0660676	33.47	0.0001
Residual	0.0177632	9	0.00197369		
Total	0.149898	11			

R-squared = 88,1498 percent

The equation which fits the data is:

yield = 0,42519 + 0,0048825*ratio ethanol + 0,0449102*catalyst weight

The p-value in the ANOVA table (table 20) is lower than 0.01. There is a statistically significant relation between the variables for a confidence level of 99%.

A simplification of the model is performed (Table 21).the p-value of the influence of the amount of catalyst on the yield of biodiesel is 0.2676 (table 20) higher than 0.10. The amount of catalyst is not a significant variable for the yield of biodiesel with a confidence interval of 90% or higher. Thus the amount of catalyst is removed from the model.

Table 21. Prediction model for the yield. Multiple regression

Dependent variable: **yield**

Parameter	*Estimate*	*Standard error*	*T Statistic*	*P-value*
CONSTANT	0.464817	0.0616692	7.53727	0.0000
ethanol ratio	0.00503661	0.000634384	7.93936	0.0000

Analysis of Variance

Source	*Sum of squares*	*Df*	*Mean square*	*F-ratio*	*P-value*
Model	0.129374	1	0.129374	63.03	0.0000
Residual	0.0205246	10	0.00205246		
Total	0.149898	11			

R-squared = 86,3076 percent

The equation which fits data is:

yield = 0.464817 + 0.00503661*ratio ethanol

The ratio ethanol:oil influences the yield of produced biodiesel. The yield increases with the ratio ethanol:oil.

Density and viscosity:

The prediction model for the density is described in the Table 22. In table 23 the prediction model for viscosity is shown.

The p-value in the analysis of variance of both the density (table 22) and the viscosity (table 25) is higher than 0.01. Thus neither the ratio ethanol:oil nor the amount of catalyst are statistically significant for the density or the viscosity of the biodiesel in a confidence interval of 90% or higher.

Table 22. Prediction Model for density

Multiple regression					
Dependent variable: **density**					
Parameter	*Estimate*		*Standard error*	*T Statistic*	*P-value*
CONSTANT	0.842742		0.0186324	45.2299	0.0000
Ratio ethanol:oil	-0.0000907018		0.000171299	-0.529494	0.6093
Amount catalyst	0.0118159		0.0102329	1.1547	0.2780
Analysis of Variance					
Source	*Sum of squares*	*Df*	*Mean square*	*F-ratio*	*P-value*
Model	0.000203981	2	0.000101991	0.71	0.5166
Residual	0.00129027	9	0.000143363		
Total	0.00149425	11			
R-squared = 13,6511 percent					

Table 23. Prediction Model for viscosity

Multiple regression					
Dependent variable: **viscosity**					
Parameter	*Estimate*		*Standard error*	*T Statistic*	*P-value*
CONSTANT	3.14106		0.782795	4.01262	0.0031
ethanol ratio	0.00418038		0.0071967	0.580874	0.5756
catalyst weight	0.509101		0.42991	1.18421	0.2667
Analysis of Variance					
Source	*Sum of squares*	*Df*	*Mean square*	*F-ratio*	*P-value*
Model	0.534031	2	0.267015	1.06	0.3875
Residual	2.27739	9	0.253044		
Total	2.81142	11			
R-squared = 18,995 percent					

The equations that fits the model expression are:

density = 0,842742 - 0,0000907018*ratio ethanol + 0,0118159*catalyst weight

viscosity = 3.14106 + 0.00418038*ratio ethanol + 0.509101*catalyst weight

Refractive index:

The prediction model for the refractive index is described in the Table 24.

Table 24. Refractive index Prediction Model

Multiple regression				
Dependent variable: **refractive index**				
Parameter	*Estimate*	*Standard error*	*T Statistic*	*P-value*
CONSTANT	1,48536	0,0132904	111,762	0,0000
ratio ethanol.oil	-0,00026	0,000122186	-2,1279	0,0622
Amount catalyst	-0,0117714	0,00729905	-1,61273	0,1413

Analysis of Variance					
Source	*Sum of squares*	*Df*	*Mean square*	*F-ratio*	*P-value*
Model	0,000649915	2	0,000324957	4,46	0,0452
Residual	0,000656472	9	0,0000729413		
Total	0,00130639	11			

R-squared = 49,749 percent

The equation that fits the model expression is:

refractive index = 1,48536 - 0,00026*ratio ethanol -0,0117714*catalyst weight

Then, the p-value in the ANOVA of the refractive index is lower than 0.05. So, there is a statistically significant relation between the variables for a confidence level of 99%.

A simplification of the model could be performed (Table 25) removing the amount of catalyst as variable affecting the refractive index. Due that the p-value of the multiple regression analysis of the refractive index in relation to the amount of catalyst is higher than 0.10 (the value is 0.1413 in table 25), it is claimed that the amount of catalyst is not statistically significant for the refractive index in a confidence interval of 90% or higher.

The ratio ethanol:oil influences the refractive index of the produced biodiesel. The refractive index of the biodiesel decreases with the ratio ethanol.oil.

Table 25. Simplificated Prediction Model for Refractive index

Multiple regression

Dependent variable: **refractive index**

Parameter	*Estimate*	*Standard error*	*T Statistic*	*P-value*
CONSTANT	1,47497	0,0125217	117,793	0,0000
ethanol ratio	-0,000300392	0,000128809	-2,33207	0,0419

Analysis of Variance

Source	*Sum of squares*	*Df*	*Mean square*	*F-ratio*	*P-value*
Model	0,000460201	1	0,000460201	5,44	0,0419
Residual	0,000846186	10	0,0000846186		
Total	0,00130639	11			

R-squared = 35,227 percent

The equation that fits the simplificated prediction model for refractive index is:

refractive index = 1,47497 - 0,000300392*ratio ethanol

Evolution of the transesterification:

The evolution of the transesterification during time has also been studied (table 26, figures 29 and 30). The experiment has been performed using 1.5 g catalyst, 120 ml ethanol and 200 ml of sunflower oil. Every 10 min a 20 ml sample of product is taken and analyzed. The aim is to study the evolution of the amount of glycerol and biodiesel present in the product. The more significant results are showed in Table 28. In appendix 6 all results of this experiment are included.

The Figure 29 shows that the amount of glycerin increases with time. So, after ten minutes of reaction the amount of glycerin is around 9%, while after one hour of reaction, the amount of glycerin reaches the 19%.

In the biodiesel phase it is included the unreacted oil. Due the oil is reacting to produce biodiesel, the raw biodiesel phase decreases during the reaction process

After the reaction finished, the phases are separated. The raw biodiesel phase is washed with 5w% phosphoric acid. The impurities are removed.

Table 26. Evolution of the reaction during time

evolution of reaction over time(1.5 gr catalyst, 120 ml ethanol, 200ml sunflower oil)						
t(min)	Glycerin(ml)	% glycerin	Biodiesel phase(ml)	% biodiesel	Clean biodiesel(ml)	% Clean biodiesel in phase[3]
10	1.6	9.09	16	90.09	14	88.23
30	2	11.11	16	88.89	15	88.75
60	3.1	19.25	13	80.75	12	92.30
90	3	18.75	13	81.25	12	92.30

3) The clean biodiesel is obtained after clean the biodiesel phase with phosphoric acid. Then, two phases are formed. And the clean biodiesel phase is measured from the top phase.

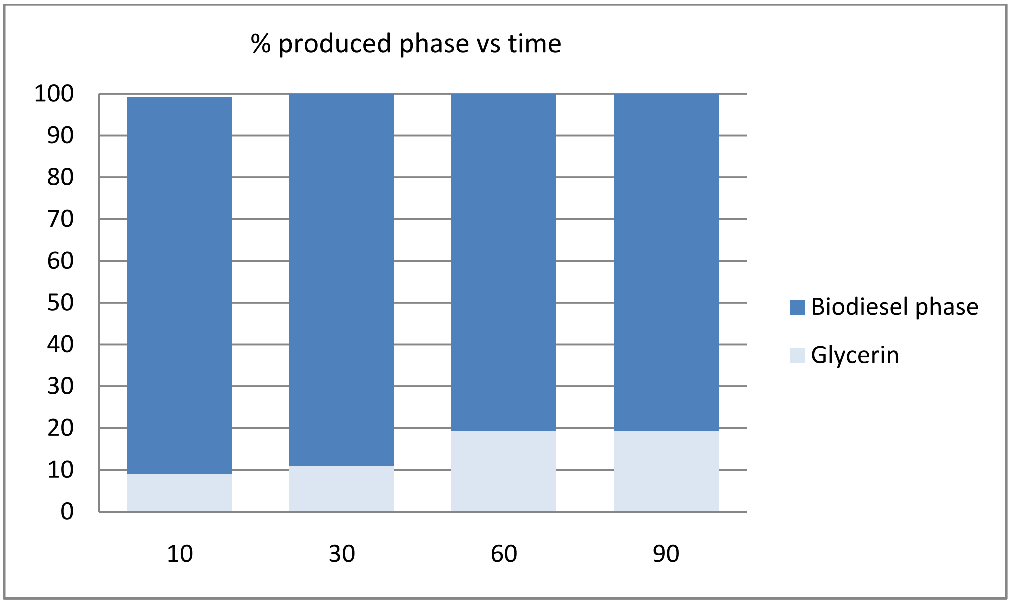


Figure 29. variation of amount produced phase with time

The amount of clean biodiesel increases during the reaction time (figure 30). After about one hour the maximum yield biodiesel is obtained (around 93-94 %). At the studied conditions with a reaction time of 1 hour it is enough to reach the highest yield of biodiesel.

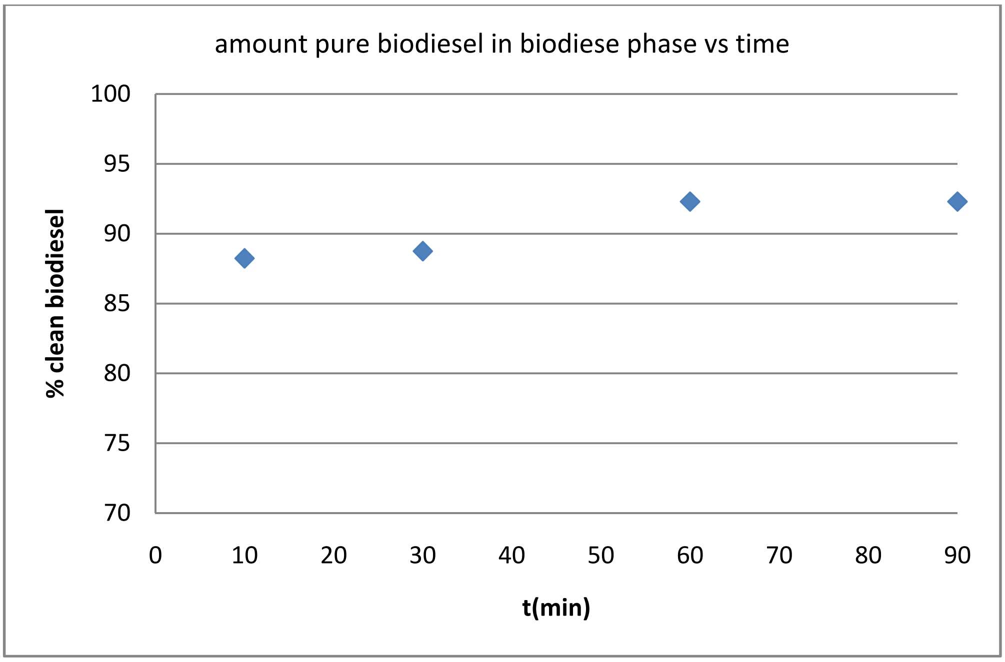


Figure 30. % clean biodiesel evolution

4. Conclusions

Biodiesel refers to methyl or ethyl esters obtained of transesterification of animal fats or vegetable oils, pure or waste cooking oils. Although, the pure biodiesel (B100) can be used in the diesel engines, currently, the biodiesel is blended with diesel. The main vehicles manufacturers have certified truck engines for use with up to 30% biodiesel in petro-diesel. Experiments with using 50% biodiesel in trucks are underway.

The Valdescorriel Biodiesel plant, located in Zamora (Spain), is taken as model of reference to study the profitability and economics of a biodiesel plant.

The Valdescorriel plant has a nominal production capacity of 20000 biodiesel tons per year and 2000 glycerol tons. The future prospects are increasing the biodiesel production until 50000 tons per year.

The biodiesel yield in the plant is 96.5%. 356 kg oil enters in the reactor, and 343.54 kg of biodiesel is produced. Recent studies have demonstrated that the biodiesel yield can reach 98%.

The initial investment for the biodiesel plant construction is the 4 500 000 €. A high initial investment is necessary. The economic analysis demonstrates that the benefits are 2 million €/year. The NPV (Net Present value) calculation shows that it is possible to recover the investment after 3 years. The IRR (Internal Return Rate) is the 63%. The life of the facility is considered 30 years.

The energy balance for the plant is positive. The energy used for the biodiesel production is 30% less than the obtained energy from the produced biodiesel.

Moreover, a significant CO_2 emissions reduction is achieved replacing petroleum diesel by biodiesel. The CO_2 reduction can reach the 48%. So, the Valdescorriel biodiesel plant can reduce the CO_2 emissions in 55 000 tons per year.

The experimental part of this work includes the production of biodiesel from sunflower oil and ethanol, with sodium hydroxide as catalyst. The aim is to study the influence of the artio ethanol:oil and the amount of catalyst on the yield as well on the properties of the produced biodiesel. The measured properties of the biodiesel are density, viscosity and refractive.

The experiments demonstrate that the ethanol/oil ratio influences on the biodiesel production. The yield of biodiesel increases with the ethanol/oil ratio.

Regarding the influence of the amount of catalyst on biodiesel production in the studied conditions is not possible to achieve a definitive conclusion. But a tendency showing an increasing of the biodiesel yield with the amount of catalyst can be appreciated. Further experiments would be necessary in this case.

Finally, a parallel experiment is performed with the aim of check the reaction evolution. The reaction reaches the maximum performance after one hour. At the studied conditions, a reaction time of 1 hour it is enough to reach the highest yield of biodiesel.

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6. Appendix

Appendix 1:

Calculation of the costs for production of 1 liter biodiesel.

Oil: 0.503 €/l of biodiesel.

400 liters oil inlet (T=65ºC, ρ=0,887 g/cm3)→ 355 kg enter the reactor

Oil price is 550 €/ton → 195.3 €/oil reactor

Reactor exit flow 343.54 kg biodiesel (T=15ºC, ρ=0,885 g/cm3) → 388 l biodiesel

Cost → 195.3€/388 l = 0.503 €/l

Methanol: 0.038 €/l of biodiesel.

56 kg methanol inlet reactor.

Around 15 liters are recovered → 41 kg methanol

Methanol price is 360€/ton → 14.76 €

Cost → 14.76€/388l =0.038 €/l

NaOH: 0.0028 €/l of biodiesel.

2.8 kg NaOH enter the reactor

NaOH price is 400 €/ton → 1.12 € NaOH reactor

Cost → 1.12€/388 l = 0.0028 €/l

Water: 0.000245 €/l of biodiesel.

Water consumption: 95 kg (ρ=1000 kg/m3) → 95 liters

Water price is 1€/m3 → 0.095 € water

Cost → 0.095€/388 l = 0.000245 €/l

Acid acetic: 0.0028 €/l of biodiesel.

Acid acetic consumption is 86 kg (ρ=1.049 g/cm3)

Acid acetic price is 12.90 €/l → 81.98 € acid acetic

Cost → 81.98 €/388 l = 0.211 €/l

Energy consumption

Power: 0.00072 €/l of biodiesel.

20kW x 2 hr reaction → 40kW·hr/388l = 0.103kW·hr/l biodiesel.

Cost → 0.103kW·hr/l x 0.007€/kW·hr = 0.00072 €/l

Heat: 0.002 €/l of biodiesel.

Boiler 106 kcal/hr x 0,7% performance = 700000 kcal/hr

Estimate annual production:

[(20000 ton/year) / (334 production days per year · 24 hr)] = 2495 kg/hr

ρ=0.885 g/cm3 → 2819.2 l/hr

[(700000 kcal/hr)/(2819.2 l/hr)] = 248.3 kcal/l = 0.28875 kW·hr/l

Cost → 0.28875 kW·hr/l x 0.007€/kW·hr = 0.002 €/l

Workpeople

20 workers: 0.017 €/l

2 engineers → Salary: 2200€ (12 payments)+social security: 880€ = 3080 €.

Total = 2 x 3080€ = 6160€/month

2 Lab technicians → Salary: 1300 € (12 payments)+ social security: 520 €=1820 €/month

Total = 2 x 1820 € = 3640 €/month

1 Administrative → Salary: 1100 € (12 payments)+ social security: 440 €= 1540 €/month

15 operators → Salary: 1000 € (12 payments)+ social security: 400€ = 1400 €
. Total = 15 x 1400 € = 21000 €/month

Cost → [6160 € +3640 € + 1540 €+ 21000 €] x 12 = 388080 €/year

20000 ton/year → 388080 € / 20000 ton = 19404 €/ton = 0.017€/l

Total cost per liter of biodiesel production = 0.585 €/l

Appendix 2: Preparation of Phosforic acid solution 5%

The available phosphoric acid is 85% concentration. The final concentration is 5%.

The amount 85% H_3PO_4 necessary to make 1 liter 5% H_3PO_4 is calculated.

$$85\% \cdot \rho \cdot V = 5\% \cdot \rho \cdot V_{total} \rightarrow 85 \cdot 1.71 \cdot V = 5 \cdot 1.04 \cdot 1000 \qquad V = 35{,}7\ ml$$

The

$$85\% \quad \rightarrow \qquad \rho = \ 1.71 \frac{g}{ml}$$

$$5\% \quad \rightarrow \quad \rho \qquad \rho = 1.04 \frac{g}{ml}$$

Thus 35,7 ml 85% H_3PO_4 is diluted with water to make 1 liter of 5% H_3PO_4

Appendix 3:

Chemical Safety Data: Ethyl alcohol

Common synonyms	Ethanol, alcohol, grain alcohol, fermentation alcohol, fermentation ethanol
Formula	C_2H_5OH
Physical properties	Form: colourless fragrant liquid Stability: Stable, but highly flammable Melting point: -144 C Boiling point: 78 C Water solubility: miscible in all proportions Specific gravity: 2.12 Explosion limits: 3.3 - 24.5%
Principal hazards	Contact with the eyes can cause considerable irritation. "One-off" consumption of small amounts of ethanol is not likely to be harmful, but consumption of large amounts can be (and has been) fatal. Chronic (long-term) ingestion of ethanol may lead to damage to a variety of organs, such as the liver, and may increase the risk of cancer. Ethanol is very flammable, so constitutes a fire risk.
Safe handling	Wear safety glasses. Ensure that no sources of ignition, such as a gas flame, hot plate or hot air gun, are present in the working area. Check that ventilation is good; use a fume cupboard if possible.
Emergency	Eye contact: Flush the eye with plenty of water. If irritation persists call for medical help. Skin contact: Wash off with water. If swallowed: If the quantity swallowed is large, call for medical help
Disposal	Small amounts of ethanol can be flushed down a sink with a large quantity of water, unless local rules prohibit this. Do not forget that this material is very flammable, so precautions must be taken to ensure that flammable vapour does not build up in the sink or drains.
Protective equipment	Safety glasses
Further information	Ethyl alcohol Chemicals in the HSci database More extensive safety data

Appendix 4:

Chemical Safety Data: Sodium Hydroxide

Common synonyms	Caustic soda, soda lye
Formula	NaOH
Physical properties	Form: White semi-transparent solid, often supplied as pellets weighing about 0.1g Stability: Stable, but hygroscopic. Absorbs carbon dioxide from the air. Melting point: 318 C Water solubility: high (dissolution is very exothermic) Specific gravity: 2.12
Principal hazards	*** Contact with the eyes can cause serious long-term damage *** The solid and its solutions are corrosive *** Significant heat is released when sodium hydroxide dissolves in water
Safe handling	Always wear safety glasses. Do not allow solid or solution to come into contact with your skin. When preparing solutions swirl the liquid constantly to prevent "hot spots" developing.
Emergency	Eye contact: Immediately flush the eye with plenty of water. Continue for at least ten minutes and call for immediate medical help. Skin contact: Wash off with plenty of water. Remove any contaminated clothing. If the skin reddens or appears damaged, call for medical aid. If swallowed: If the patient is conscious, wash out the mouth well with water. Do not try to induce vomitting. Call for immediate medical help
Disposal	Small amounts of dilute sodium hydroxide can be flushed down a sink with a large quantity of water, unless local rules prohibit this. Larger amounts should be neutralised before disposal.
Protective equipment	ALWAYS wear safety glasses when handling sodium hydroxide or its solutions. If you need gloves, neoprene, nitrile or natural rubber are suitable for handling solutions at concentrations of up to 70%
Further information	Sodium hydroxide Chemicals in the HSci database More extensive safety data

Appendix 5:

Chemical Safety Data: Phosphoric acid

Common synonyms	Ortho Phosphoric acid
Formula	H_3PO_4
Physical properties	Form: colourless liquid, typically supplied at a concentration of around 80% w/w Stability: Stable Melting point: 21 C, when pure Boiling point: 158 C, when pure Specific gravity: typically around 1.69 (depends upon concentration)
Principal hazards	*** Concentrated Phosphoric acid is a strong acid, so is capable of causing serious burns in contact with the skin, or if swallowed.
Safe handling	Wear safety glasses. Work in a well ventilated area. You will not usually be handling the concentrated acid, but if this is necessary, butyl rubber or nitrile gloves will provide good protection from spills and splashes.
Emergency	Eye contact: Immediately flush the eye with water; continue for at least five minutes. Call for medical help. Skin contact: Wash off with soap and water. If there are signs of burning or redness, call for medical help. If swallowed: Call for medical help.
Disposal	Small quantities of dilute acid can be flushed down the sink, unless this is prohibited by local rules. Large quantities or concentrated samples should be carefully neutralised before disposal.
Protective equipment	Safety glasses, rubber or nitrile gloves.
Further information	Phosphoric acid Chemicals in the HSci database More extensive safety data

Appendix 6:

Table 29. Density values for the different experiences

	sample1	*sample2*	*sample3*	*sample4*	*sample5*	*sample6*
empty cylinder	48.911	48.275	63.471	48.344	48.682	63.478
cylinder filled 25 ml	69.475	69.851	84.995	69.271	69.771	84.474
density(gr/ml)	0.823	0.863	0.861	0.837	0.843	0.839
	sample7	*sample8*	*sample9*	*sample10*	*sample11*	*sample12*
empty cylinder	63.475	63.482	63.456	48.344	63.477	48.444
cylinder filled 25ml	84.741	84.583	84.824	69.271	84.912	69.709
density(gr/ml)	0.851	0.844	0.854	0.837	0.857	0.851

Table 30. Refractive index values for the different experiences

	sample1	*sample2*	*sample3*	*sample4*	*sample5*	*sample6*
refractive index	1.4575	1.4580	1.4390	1.4550	1.4495	1.4555
	sample7	*sample8*	*sample9*	*sample10*	*sample11*	*sample12*
refractive index	1.4470	1.4450	1.4510	1.4440	1.4360	1.4200

Table 31. Viscosity values for the different experiences

sample1		***sample2***		***sample3***		***sample4***		***sample5***		***sample6***	
time	viscosity	time	Viscosity	time	viscosity	time	viscosity	time	viscosity	time	viscosity
1	1.02	1	1.69	1	1.47	1	1.36	1	1.56	1	1.35
2	1.09	2	1.63	2	1.48	2	1.42	2	1.5	2	1.42
3	1.12	3	1.65	3	1.52	3	1.37	3	1.68	3	1.58
4	1.01	4	1.63	4	1.48	4	1.40	4	1.68	4	1.38
5	0.96	5	1.68	5	1.44	5	1.37	5	1.57	5	1.42
6	1.08	6	1.69	6	1.41	6	1.39	6	1.64	6	1.40
7	1.03	7	1.67	7	1.52	7	1.41	7	1.48	7	1.36
8	1.02	8	1.63	8	1.49	8	1.34	8	1.64	8	1.44
9	1.06	9	1.64	9	1.43	9	1.38	9	1.67	9	1.45
10	1.14	10	1.65	10	1.48	10	1.41	10	1.61	10	1.53
average	1.053	average	1.656	average	1.472	average	1.385	Average	1.603	average	1.433
viscosity(cp)	**3.158**	**viscosity(cp)**	**4.563**	**viscosity(cp)**	**4.074**	**viscosity(cp)**	**4.133**	**viscosity(cp)**	**4.605**	**viscosity(cp)**	**4.149**

sample7		**sample8**		**sample9**		**sample10**		**sample11**		**sample12**	
time	viscosity	time	viscosity	time	viscosity	time	viscosity	time	viscosity	time	viscosity
1	1.39	1	1.28	1	1.36	1	1.45	1	1.58	1	1.8
2	1.5	2	1.29	2	1.39	2	1.45	2	1.52	2	1.83
3	1.41	3	1.28	3	1.34	3	1.43	3	1.45	3	1.75
4	1.42	4	1.32	4	1.33	4	1.41	4	1.59	4	1.88
5	1.50	5	1.26	5	1.38	5	1.47	5	1.50	5	1.89
6	1.43	6	1.31	6	1.41	6	1.45	6	1.56	6	1.84
7	1.43	7	1.33	7	1.38	7	1.41	7	1.58	7	1.84
8	1.41	8	1.27	8	1.40	8	1.48	8	1.53	8	1.8
9	1.41	9	1.25	9	1.39	9	1.42	9	1.54	9	1.88
10	1.40	10	1.32	10	1.40	10	1.46	10	1.54	10	1.88
average	1.43	average	1.291	average	1.378	average	1.443	average	1.539	average	1.839
viscosity(cp)	**4.047**	**viscosity(cp)**	**3.705**	**viscosity(cp)**	**3.833**	**viscosity(cp)**	**4.085**	**viscosity(cp)**	**4.282**	**viscosity(cp)**	**5.205**

Table 31. Experimental measurements of the properties of sunflower oil.

Sunflower oil		
density(gr/ml)	empty cylinder	63.468
	cylinder filled 25 ml	86.348
	density(gr/ml)	**0.9162**

viscosity(cp)	**Time**	**Result**
	1	10.27
	2	10.21
	3	10.22
	4	10.05
	5	9.51
	6	9.43
	7	9.57
	8	10.37
	9	9.98
	10	10.26
	average	9.987
	viscosity(cp)	**24.317**

refractive index	**1.476**

Table 32. Reaction evolution

evolution of reaction over time(1.5 gr catalyst, 120 ml ethanol, 200ml sunflower oil)						
t(min)	Glycerin(ml)	% glycerin	Biodiesel phase(ml)	% biodiesel	Clean biodiesel(ml)	% Clean biodiesel in phase
10	1.6	9.09	16	90.09	14	88.23
20	1.6	9.09	16	90.09	15	93.75
30	2	11.11	16	88.89	15	88.75
40	2.1	11.60	16	88.39	14	87.50
50	2.3	14.11	14	85.88	13	92.85
60	3.1	19.25	13	80.75	12	92.30
70	3	18.75	13	81.25	11	84.61
80	3.1	20.52	12	79.47	11	91.66
90	3	18.75	13	81.25	12	92.30