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Pilot-scale Unit for Biodiesel Production
Impact of UCO quality and properties on process yield

MASTER DISSERTATION

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MASTER IN APPLIED BIOCHEMISTRY

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Abstract

Several alternative feedstocks have been tested for biodiesel production. As feedstock can represent up to 80% of the operation costs, used cooking oil (UCO) has been widely chosen. The UCO's price is not the only advantage. Using waste as a raw material is also environmental friendly.

In Madeira Island, there is only one pilot unit dedicated to biodiesel production, and it is located at the company Grupo Sousa / Metal Lobos Lda. in Industrial Free Zone of Madeira. This unit is designed to process two 1000L sets every three days through homogeneous alkaline transesterification in the batch regime, using methanol as a reactant, sodium methoxide as a catalyst, and UCO as feedstock. This raw material is collected in several commercial establishments such as hotels and restaurants. Its proper functionality could bring economic and environmental value to the company and Madeira Island by lowering exhaust emissions and fuel costs.

The purpose of the present work is: (i) Test the pilot unit for possible operational failures and optimization possibilities, (ii) test the establishment of biodiesel production using UCO collected in the region, (iii) analyze how feedstock properties can influence transesterification yields

Several laboratory tests (transesterifications) were performed to acquire a deeper understanding of the reaction behavior and variables before starting the pilot unit tests. On the pilot unit, four tests were performed using a minimum feedstock volume of 500L of UCO.

Biodiesel production yields in the pilot unit varied from 78.52 to 90.37% (w/w). The lowest yields were the ones obtained using UCO with higher acidity values and lower alcohol to oil molar ratio in the reaction (biodiesel with purity of 96.3% (w/w) was obtained with UCO with 9.8% free fatty acids (w/w) and alcohol to oil molar ratio of 7:1). From the evaluation of the transesterification yields, it was possible to conclude that in this pilot unit the influence of the feedstock's acidity is not so significant, but, it is of utmost importance to further analyze the impact of the impurities on the glycerol quality, as this may determine the economic viability of the whole process.

It was concluded that the pilot unit was functional for biodiesel production, but, due to the feedstock properties variability, optimization should be taken into consideration. Improving both process and procedures such as UCO collection and storage could raise the unit's yield.

Keywords: Biodiesel; Used cooking oils; Homogeneous alkaline transesterification; Methanol; Sodium methoxide.

Resumo

Várias matérias-primas têm sido testadas para a produção de biodiesel. Como a matéria-prima pode representar ate 80% do custo operacional, os óleos alimentares usados (OAU) têm sido uma escolha frequente. O preço dos OAU não é a única vantagem. O facto de usarmos um resíduo como matéria-prima é também uma boa escolha do ponto de vista ambiental.

Na Ilha da Madeira existe apenas uma unidade piloto dedicada à produção de biodiesel e está situada na empresa Grupo Sousa / Metal Lobos Lda. da zona franca da Madeira. Esta unidade está desenhada para processar dois sets de 1000L em cada três dias através de transesterificação alcalina homogénea em regime de lotes, usando metanol como reagente, metóxido de sódio como catalisador e OAU como matéria prima. Os óleos são recolhidos em vários estabelecimentos comercias da região tal como hotéis e restaurantes. O seu bom funcionamento poderá trazer valor ambiental e económico tanto para a empresa como para a Ilha da Madeira, baixando o nível de emissões de escape e os custos com combustíveis.

Os objetivos deste trabalho são: (i) testar a unidade piloto para possíveis falhas de operação assim como para oportunidades de otimização, (ii) testar a implementação de produção de biodiesel utilizando OAU recolhidos na região da Ilha da Madeira, (iii) analisar de que modo as propriedades da matéria-prima influenciam o rendimento da reação de transesterificação.

Foram realizados vários ensaios laboratoriais (transesterificações) de forma a adquirir um conhecimento mais aprofundado do comportamento e varáveis da reação antes de passar aos testes na unidade piloto. Nesta última foram realizados 4 testes processando sempre mais de 500L de OAU.

Os rendimentos de produção de biodiesel na instalação variaram entre 78,52 e 90,37% (w/w), sendo que o rendimento menor foi obtido como OAU de maior valor de acidez e com uma menor razão molar álcool/óleo na reação (foi obtido biodiesel com pureza de 96,3% (w/w) usando OAU de valor de acidez 9,8% ácidos gordos livres (w/w) e razão molar álcool/óleo de 7:1). Avaliando os rendimentos de transesterificação, foi possível concluir que a influência da acidez da matéria-prima para este parâmetro não é significativa. No entanto, é importante avaliar o impacto das impurezas e propriedades da matéria prima na qualidade do glicerol produzido pois esta poderá determinar a viabilidade económica do processo.

Conclui-se que a unidade piloto é funcional para a produção de biodiesel, no entanto, devido essencialmente à variabilidade da matéria prima, sugere-se uma otimização. Melhorando o processo e alguns procedimentos tais como a recolha e conservação dos OAU, talvez se possa alcançar um aumento do rendimento da unidade.

Palavras chave: Biodiesel; Óleos alimentares usados; Transesterificação homogénea alcalina; Metanol; Metóxido de Sódio

Índex

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Equations

Abbreviations

ASTM - American Section of the International Association for Testing Materials

BX – B100 (X=100) 100% Biodiesel; B10 (X=10) 10%; B20 (X=20) 20%

CFPP – Cold filter plugging point

C – Catalyst concentration

CN – Cetane number

CP – Cloud point

DG – Diglyceride

EN – European standard

EtOH – Ethanol

FA – Fatty acid

FAAE – Fatty acid alkyl esters

FAME – Fatty acid methyl esters

FFA – Free fatty acids

FER – Fossil energy ratio

GC – Gas chromatography

HPLC – High-performance liquid chromatography

IV – Iodine value

M – methanol to oil molar ratio

MeOH – Methanol

MG – Monoglyceride

MW – Microwave

$NaOCH_3$ – Sodium methoxide

PP – Pouring point

PV – Peroxide value

PVO – Pure vegetable oil

TG – Triglyceride

TX – Test X (x= 1-4)

UCO – Used cooking oil

1 Scope and goals

1.1 The economic and environmental framework

Nowadays in RAM, (Região Autónoma da Madeira – Autonomous Region of Madeira) the fossil fuel with more consumption is petrodiesel. In 2016, 96 million liters of diesel were consumed comparing with 41million liters of gasoline[1]. Therefore, it makes sense to try and replace petrodiesel with biodiesel to accomplish community directives. The lack of available areas for vegetable oils production renders biodiesel production from this raw material, impossible. Another possibility is to use available feedstock in the region such as used cooking oil. This usage will provide a biofuel that is sustainable, biodegradable and less polluting, resulting in an environmental improvement by avoiding disposal on domestic sewage and water treatment plants. According to the MIRR (Mapa Integrado de Registo de Resíduos – Integrated Waste Registration Chart), in 2015 and 2016, 375 and 432 ton of UCO were collected in the region, respectively. Assuming a 90% reaction yield, this would generate c.a. 337.5 and 388.8 ton of biodiesel respectively for 2015 and 2016. Adding to this, the PAESI-M (Plano de ação para a energia sustentável na Ilha da Madeira – Action plan for renewable energy on Madeira Island)[2] has a goal for 2020 of a 20% increase in the contribution of renewable energy sources in the demand for primary energy and a 20% decrease in CO_2 emissions, when comparing to 2005.

Adding to the above-mentioned actions, small islands such as Madeira Island should also have proper waste management. Some residues can be burned, such as garbage and tires, but there are other wastes that should be recycled instead. Used cooking oil is one of them, and the lack of facilities to do so has given the opportunity for some companies to collect, transport, and sell the UCO on the mainland. This transport is achieved by sea, and therefore it contributes to marine and atmospheric pollution. Having this in mind, Grupo Sousa / Metal Lobos Lda. invested in a pilot unit capable of recycling the UCO inside the RAM.

1.2 Goals

(i) Test the pilot unit for possible operational failures and optimization possibilities
(ii) Test the establishment of biodiesel production using UCO collected in the region
(iii) Analyze how feedstock properties can influence transesterification yields
(iv) Build a comprehensive Operation Manual (there was no existing manual)

2 Introduction

2.1 Biodiesel

2.1.1 History and description

Biodiesel, known as a renewable fuel that consists of Fatty acid alkyl esters (FAAE), or when using methanol (MeOH), Fatty acid methyl esters (FAME), is produced all over the world using as feedstock vegetable oils, animal fats, and fatty acid triglycerides [3].

When Rudolph Diesel (1858-1913) invented and developed the diesel engine, not only he tested his invention with conventional diesel but also with peanut oil. Following the peanut oil, several other were tested such as palm oil, soybean oil, cottonseed oil and castor oil.[4] The demand for biodiesel comes to a halt because petroleum, in the 1920s, was substantially cheaper and that led to the optimization of the diesel engine using petrodiesel fuel. The 1970s oil-crisis did kick-start the interest in alternative fuels and investigations with vegetable oils restarted, giving an advantage to their market[5]. A Brazilian scientist, Expedito Parente, was the first person to get a patent for the industrial process of producing biodiesel in 1977[6]. A further boost for the interest in this renewable fuel is the environmental challenges that are surfacing alongside with an increasing demand for energy and the decrease of easily obtainable, and cost-efficient fossil fuels. The impending dangers and the environmental implications of fossil fuels have been reviewed widely in the literature[7]. Data from 2008 reports that non-renewable fossil fuels provide 86% of the energy consumed worldwide and nearly 100% of energy desired in the transportation sector[8]. More recently, reviewing the production of renewable and sustainable energy, it was stated that biofuels are a great alternative to meet the increasing energy demand[9].

Because biodiesel production may come from vegetable oils, animal fats and microalgae, it is a renewable and clean fuel. Operations with some of these feedstocks can be defined as the indirect use of solar energy, considering the way plants produce their biomass energy. When comparing biodiesel properties with those of petrodiesel, many similarities can be found but, containing no sulfur, no toxicity and being biodegradable are attributes that all add to the advantages of this renewable fuel over the petrodiesel fuel[6]. It diminishes the greenhouse effect since biodiesel does not contribute to the increase in carbon dioxide levels in the atmosphere. Most modern engines can operate with biodiesel without significant modifications. Biodiesel is not only used for transportation, but it is also used in manufacturing, construction machinery and generators for firing boilers purpose[10]. In 2011,

a 5.54 fossil energy ratio (FER) of biodiesel was reported[11]. This means that when using one unit of fossil energy to produce biodiesel, the energy output is 5.54 times bigger. This FER shows a larger energy return that other fuels cannot accomplish[12]. This indicator is expected to rise even more in the next years due to better farming technologies, energy-saving farm practices, and continuous eve more development on energy-efficiency procedures and technologies.

Many factors contribute to the cost of biodiesel such as feedstock cost, processing the feedstock and other reactants, purification technology, transportation, storage, and working capital. However, the primary factor influencing the cost of biodiesel production is the feedstock price, which can be up to 80% of the operating cost[13]. Therefore, using waste fats and UCO as a raw material in comparison with vegetable oils, is preferable, due to cost decrease and environmental impact. An advantage of UCO over edible vegetable oils and animal fats used as feedstock to produce biodiesel is the fact that these compete with the food market, thus raising their price and consequently the biodiesel production cost. Without biodiesel production, UCO would be a waste to dispose of, as it has no further value for the food market.

Many studies on technologies and different methods to evaluate optimal conditions of biodiesel production technically and economically have been carried out. Four primary ways to make biodiesel are: 1) neat use or blending of vegetable oils; 2) microemulsions; 3) thermal cracking (pyrolysis) and 4) transesterification[14]. Transesterification is one of the most used techniques in biodiesel production industry, and it takes place between fatty feedstock, and alcohol (MeOH, ethanol, butanol) in the presence of an acid or alkaline catalyst, or without application of the catalyst[15].

Vegetable oils and animal fats are mainly made of triacylglycerols (TAG; usually called triglycerides; TG). Chemically, TG are esters of fatty acids (FA) with glycerol (1,2,3-propanotriol; glycerol is also commercially known as glycerine. The TG of vegetable oils and animal fats contain several different FA. Thus, different FA can be linked to the glycerol backbone. The different FA that are attached in the TG are the FA profile (or FA composition). FA have different chemical and physical properties depending on their structure parameters such as chain length and unsaturation degree. Therefore, the FA profile of vegetable oil or animal fat determines some of its properties. The triglyceride, diglyceride (DG) and monoglyceride (MG) structures are represented in Figure 1.

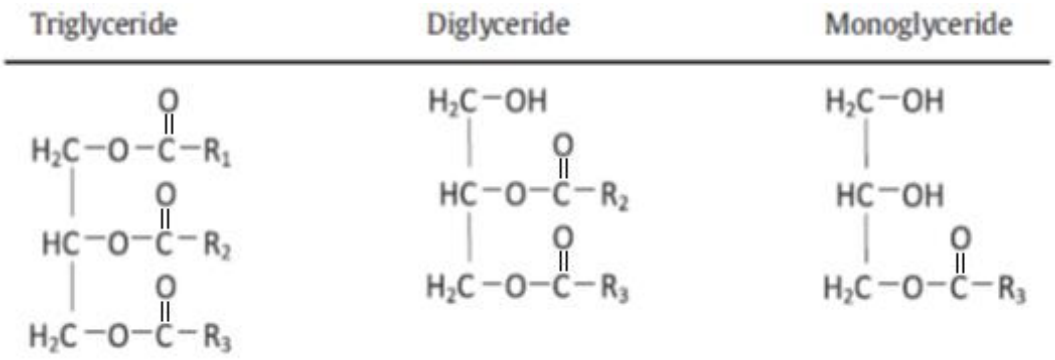

FIGURE 1 - MOLECULAR STRUCTURE OF A TRIGLYCERIDE, DIGLYCERIDE, AND MONO-GLYCERIDE[4]

Transesterification results in the corresponding alkyl esters (for MeOH, methyl esters) of the FA mixture that the vegetable oil or animal fat consists. Thus, biodiesel refers to the mixture of monoalkyl esters of fatty acids that derived from triglycerides.

MeOH is preferable for biodiesel production because it is the least expensive and has higher reaction rates. Although other alcohols can be employed, existing commercial regulation standards such as EN 14214:2012+A1:2014 and ASTM D6751-11a (Table 1) are designed to evaluate only methyl esters as biodiesel.

Biodiesel can be mixed with petrodiesel to obtain a fuel with some improved properties over petrodiesel. In many countries, biodiesel blends with petrodiesel are used instead of pure biodiesel. Biodiesel blends are often called B20 or B30, which means there is a mixture of 20% or 30% biodiesel in petrodiesel, respectively.

2.1.2 Properties and standard requirements

For biodiesel to be used as transportation fuel, it must meet standard requirements (EN 14214:2012 and ASTM D6751-11a). Replacing petrodiesel for low-quality biodiesel, due to incomplete reaction or impurities, in a diesel engine could result in many problems such as cold start problems, lower engine speed and power and injector coking[13]. Fuel standards have been adopted to control performance, emissions, quality and to prevent consumers from buying low-quality fuel. Two of the most important international standards are tabulated in Table 1. Excellent antifoaming properties, cetane number (combustion speed indicator) higher than petrodiesel, and polarity are important properties to justify the biodiesel use. [16] Biodiesel improved polarity over petrodiesel helps to enhance many properties such as solvency, detergency, wet-ability and conductivity.

TABLE 1 - DIFFERENT STANDARD SPECIFICATION FOR BIODIESEL FUEL[4]

Property	Units	Limits	
		EN14214	ASTM D6751
FAME content	% (w/w)	>96.5	-
Density, 15°C	kg/m^3	860-900	-
Viscosity, 40°C	mm^2/s	3.5-5.0	1.9-6.0
Flash point, closed cup	°C	>101	>93
Carbon residue (on 10% distil resid)	% (w/w)	<0.03	<0.05
Cetane number	-	>51	>47
Sulphated ash	% (w/w)	<0.02	<0.02
Water content		<500 (mg/kg)	<0.05 (%vol)
Total contamination	mg/kg	<24.0	-
Copper corrosion strip (3h at 50°C)	Rating	1	<3
Oxidation stability, 110°C	h	>8.0	>3.0
Acid value	mg KOH/g	<0.50	<0.50
Iodine value	g I_2/100g	<120	-
Linolenic acid methyl ester	% (w/w)	<12.0	-
Polyunsaturated (≥ 4 double bonds) methyl esters	% (w/w)	<1	-
Methanol content	% (w/w)	<0.20	<0.2
MG content	% (w/w)	<0.70	-
DG content	% (w/w)	<0.20	-
TG content	% (w/w)	<0.20	-
Free glycerol	% (w/w)	<0.020	<0.02
Total glycerol	% (w/w)	<0.250	<0.24
Group I metals (Na+K)	mg/kg	<5.0	<5.0
Group II metals (Ca+Mg)	mg/kg	<5.0	<5.0
Phosphorus content		<4.0 (mg/kg)	<0.001 (% w/w)
Cold soak filterability	seconds	-	<360
Distillation temp (90% recovered)	°C	-	<360

Specifications presented in Table 1 also push biodiesel's exhaust emissions to lower levels than petrodiesel, except for nitrogen oxides (NO_x)[17]. Table 2 shows the emissions percentage from different reports on this matter. Biodiesel's emissions were compared with 100% of exhaust emissions from petrodiesel engines. This means that if biodiesel has a 50% value for compound X, petrodiesel emits double the amount of X than biodiesel. Consequently, if compound Y has a 200% value for biodiesel, it means that biodiesel emits double the amount of Y than petrodiesel. The emission of NO_x increases due to the oxygen content in the biodiesel. Lower CO emissions probably indicates better combustion. SO_2 levels are absent as biodiesel has no sulfur in its composition. Hydrocarbons, particulate matter, and polycyclic aromatic hydrocarbons present lower values than petrodiesel too. The variations in each study usually rely on the feedstock properties as well as the type of transesterification employed.

TABLE 2 - PERCENTAGE OF EXHAUST EMISSION FROM BIODIESEL ENGINES[18]

Fuel type	Carbon monoxide (%)	Hydrocarbon (%)	Nitric oxide (%)	Sulphur dioxide (%)	Particulate matter (%)	Polycyclic aromatic hydrocarbons (%)	References
B100 (AcidCat)	52	33	110	-	53	-	Lotero et al. (2005)[19]
B100	90	90	115	-	67	-	Chincholkar et al. (2005)[20]
B100 (Palm)	67	23	75	0	33	-	Wirawan et al. (2008)[21]
B100 (mAlgae)	50	-	113	0	70	20	Khan et al. (2009)[22]
B100 (2stepC)	60	50	105	0	35	-	Bouaid et al. (2012)[17]
B100	87	-	111	-	-	-	Tomic et al. (2013)[23]
B100 (UCO)	56	32	-	0	60	25	Talebian-Kiakalaieh et al. (2013)[5]

A critical property of biodiesel is its flash point. Biodiesel must have a flash point above 101°C (EN14214), exceeding that of petrodiesel or gasoline, making it safer and easier to use, store and handle. Studies also report that biodiesel can be mixed in a small ratio with petrodiesel without changing fuel properties in a critical way[13]. The low-temperature flow properties of the blended fuel with lower than 30% biodiesel (B30) are very similar from petrodiesel. If certified biodiesel is correctly blended into petrofuels and handled by standard techniques, the results are acceptable, and the fuel is of high-quality and performance.

Some biodiesel users stated that issues with deposits on the walls of fuel tanks appeared when changing from petrodiesel. This is due to the improved solvent properties of biodiesel. Loose sediments can cause filter plugging during this transition[19].

2.1.2.1 Burning properties

The highest heating value of biodiesel is about 10% smaller than that of petrodiesel fuel on a mass basis (40.1-45.0 MJ/kg)[24].

Higher biodiesel viscosity reduces the amount of fuel leaking from the injection pump. Ignition delay is also an important fuel burning characteristic. The ignition delay is the time between injection of fuel into the cylinder and ignition start, and it is characterized by cetane number (CN). A smaller time gap between injection and ignition indicates a higher CN and vice versa. Cetane (hexadecane; $C_{16}H_{34}$) is a long straight-chain hydrocarbon and has a CN of 100. Most biodiesels have CN higher than 51 while the CN of petrofuels usually ranges from 40 to 52[25]. The higher CN of biodiesel comes from its linear structure. Linear chain molecules have a beneficial influence on CN while petrodiesel and their mixture of hydrocarbons have not.

2.1.2.2 Flow properties

One of the main reasons that the direct use of vegetable oils as diesel fuel has been unsatisfactory is its high viscosity[13]. The glycerol backbone of TG is stripped off to reduce viscosity. Thus, the viscosity is a good indicator of a proper transesterification reaction[26]. Since low temperatures normally means higher viscosity, operating engines in cold climate regions offer a more significant challenge. Low-temperature properties depend on indicators such as cloud point (CP), pour point (PP), and cold filter plugging point (CFPP), and should be monitored closely. Cloud point is the temperature at which it is possible to easily see a

cloud of crystals appearing in the fuel when temperature drops. The lowest temperature at which the fluid pours is the pour point. The CFPP is the minimum temperature at which a given volume of biodiesel flows under vacuum conditions through a standardized wire mesh filter screen within a specific period.

The properties of biodiesel at low temperatures depends mainly on its feedstock fatty acid composition. Saturated fatty acids turn into saturated FAME after transesterification. Saturated FAME crystallize at a higher temperature that unsaturated FAME due to their different structure and configuration. Branched molecules have weaker intermolecular forces and therefore withstand a much lower temperature before crystalizing. Transesterification with branched alcohols and isomerization were the techniques used to enhance low-temperature properties by introducing branched structure in biodiesel.[27] In addition to FA composition, transesterification intermediates such as monoglycerides and diglycerides when present in FAME can significantly diminish low-temperature properties of biodiesel.

2.1.2.3 Stability

Biodiesel is susceptible to changes during storage, such as oxidation, leading to fuel degradation. Oxidation stability is an important parameter as it determines the fuels resilience to chemical changes. Oxidation stability of biodiesel depends greatly on water content[28], FA compositions and degree of unsaturated FA. Saturated FAME are less prone to oxidize than unsaturated ones, while polyunsaturated FAME are at least twice as reactive than monounsaturated FAME [29]. In addition to the degree of unsaturation, the position of it is also an important factor to determine the stability of biodiesel. It is reported that η-3 fatty acids oxidize faster than η-6 fatty acids[30].

Many vegetable oils have antioxidant compounds in their composition, i.e., tocopherol or Vitamin E, slowing the rate of the oxidation reaction. When they are depleted, the rate of oxidation reaction increases. Some fuel properties such as viscosity, density, and CFPP, are not affected by the addition of antioxidants. However, the addition of high amounts can change the acid value of biodiesel to levels out of standard limits[31].

Oxidation stability is often determined by the rancimat method as per EN 14112 or AOCS Cd 12b-92. Alternatively, oxidation stability of biodiesel can be evaluated by peroxide value (PV) and iodine value (IV).

2.2 First, second, third, and fourth-generation biofuels

Biofuels are solid, liquid, or gaseous fuels from biological sources and can be used as a substitute for petrofuels[32]. Biofuels are a renewable and sustainable alternative energy source to comply with three important rules of world-energy: security, economic development, and environmental protection[33].

Biofuels can be classified according to several points. Among those are, their nature, source, development stage and production technique[34]. Regarding the development stage in the production technology, biofuels classify as first, second, third and fourth-generation.

First-generation biofuels are produced from food crops with accessible starch, sugar or oils. Bioethanol as it is produced from the starch present in many cereals and other plants by fermentation, and biodiesel, produced by transesterification of vegetable oils or animal fats, both belong in this category.

The second-generation for the biofuel production development stage are lignocellulosic raw materials resulting from different biomass wastes such as agriculture, forestry solid remnants, and efluents from food and paper industry[35]. As this crystal-like structure requires pre-treatment and hydrolysis before fermentative steps, most microorganisms cannot use this lignocellulosic complex as their carbon source to produce biofuel making it harder to obtain than first generation biofuels. Further developments in this production technologies could possible render these biofuels commercially viable at large scale.[9]

Algae and aquatic biomass have the potential to emerge as a new range of third-generation biofuels. Cell walls and their carbohydrates could be used for fermentation in bioethanol production and accumulated lipids can also be transesterified to produce biodiesel. Many advantages favour the use of these feedstocks in biofuel production such as availability, no competition with land and food market, high quality of by-products and the effectiveness at capturing CO_2.[9]

The metabolic engineering of algae or other microbes constitutes the fourth-generation biofuels. Recombinant DNA and bioengineering techniques can be used to modify cellular metabolism and properties to enhance biofuel production and, at the same time, find a way to capture CO_2[36]. Some stresses, such as lack of nitrogen, can be applied to

microalgae that usually do not produce many storage nutrients resulting in slow proliferation and accumulation of lipids and starch[9].

Efforts are still needed for the improvement of both thermochemical and biological routes. To optimize the thermochemical ways, investments in process and catalyst development should be taken into consideration. On the other hand, research to develop biochemical routes includes initial pretreatment steps as well as hydrolysis and fermentation procedures.

The first-generation biofuels, concerning the product development stage, are the best choice to succeed in the coming years. Production techniques and equipment are well established, and a lot of information is available for research.

2.3 Biodiesel production techniques

There are many reports on biodiesel production using edible oils as feedstocks. However, implementing a sustainable production chain based on a food competitor raises ecological and ethical issues. Adding to this, competition on the food market influences the vegetable oils price turning them too expensive for biodiesel production. Consequently, employing used and non-edible oils in biodiesel production eliminates that matter[37].

For the purpose of biodiesel production, several accepted technologies have been well established such as micro-emulsification, pyrolysis, and transesterification.

Micro-emulsification appeared as a possible technique to solve the high viscosity issue of the vegetable oil. Formed with MEOH, EtOH or 1-butanol, these three components fluids: an oil phase, an aqueous phase, and a surfactant, are stable and clear[16]. Microemulsion of vegetable oils would not solve all the biodiesel problems. Viscosity can be lower than the oil but engine issues such as irregular injector needle sticking, heavy carbon deposits and incomplete combustion may appear.[38]

Pyrolysis is another unusual technique for biodiesel production where heat is applied to convert one organic substance into another with or without using a catalyst[39]. Although the liquid product fractions of the thermally decomposed oil present similar properties as diesel fuels, equipment and pyrolysis procedures costs can only be devalued for large scale productions. One disadvantage of this procedure is the production of some low-value materials and, sometimes, more gasoline than biodiesel as well[40]. To Grupo Sousa / Metal Lobos Lda. this process is highly undesired due to environmental concerns. Adding to that, the production of such low-value materials could withdraw the economic advantage.

The most common technology for biodiesel production is transesterification of TG with alcohol resulting in biodiesel as main product and glycerol as a by-product. This procedure started in 1938, when the glycerol fraction present in vegetable oils was described as having no calorific value and likely to cause carbon deposits on the engine, hindering its best performance. It was concluded that the engine should run only on the residue fatty acid, biodiesel[41].

2.4 Transesterification

TG transesterification for biodiesel production is accomplished using a monohydric aliphatic alcohol, with or without a catalyst. The basic three steps transesterification reaction mechanism using MeOH as the alcohol is illustrated in Figure 2. To push the reaction equilibrium towards the products and maximize FAME production, an excess of MeOH is used. MeOH is mainly employed because of its low cost and physical and chemical advantages (polar and shortest chain alcohol) [42]. Due to its hydrophobic and hydrophilic nature, TG and alcohols cannot be easily mixed together to form a single phase. Thus, this absence of surface contact between the two reactants decreases the reation rate. To overcome this issue, catalyst were introduced in the reaction to solve the two-phase problem of the mixture. During the transesterification, the solubility between both phases increases. This is due to biodiesel molecules formation as they have higher polarity than TG[43]. Production of transesterification intermediates such as MG and DG, as well as soaps, also boosts the mixture solubility. However, further ahead on the reaction, two considerable immiscible phases are formed. The polar phase containing glycerol and the nonpolar containing biodiesel. Separation of these products is, therefore, easily obtained in a settling tank, favoured by this limited solubility[44].

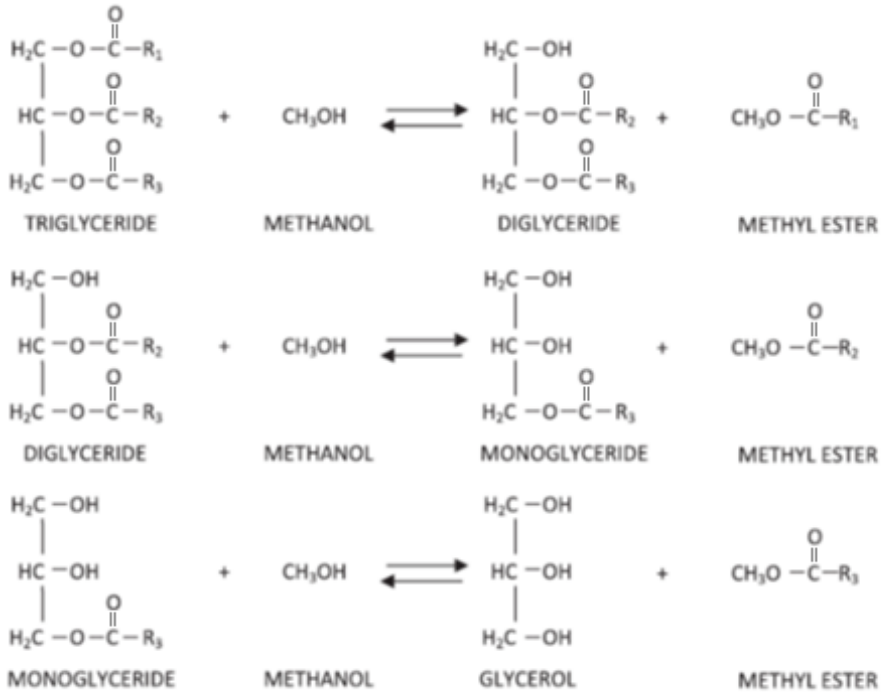

FIGURE 2 - SCHEME FOR STEP-WISE TRANSESTERIFICATION REACTION WITH METHANOL[4]

Many parameters have impact on the transesterification reaction rate. Some are more important than others, nevertheless, optimization of all conditions is a critical step in biodiesel production. Conditions such as reaction temperature, concentration of catalyst, alcohol to oil molar ratio, reaction time are the ones that can be monitored closely. Water content and FFA values of the feed oil are harder to control therefore a careful choice of the feedstock is advised[45].

2.4.1 Catalysed transesterification

Transesterification reactions can be accomplished using alkali, acid or enzyme as catalyst. However, enzyme-catalized tranesterification has not been a first choice as it reaction time is much longer and production costs are higher too. Chemical catalyzed procedures are also much simpler. TG transesterification with alkali catalysts can achieve great yields of biodiesel product in a short time (30–60 min)[46].

There are two types of catalysed transesterification for biodiesel production: homogeneous and heterogeneous. Selecting the perfect catalyst for the specific production scale and process is a crucial step to lower the costs. Feedstock properties must also be taken into consideration when choosing the correct catalyst. For lower values of FFA (<3% w/w) alkali-catalyzed reaction gives a better conversion in a relatively short time, while for higher FFA acid-catalyzed esterification followed by transesterification is preferable[47].

Acid transesterification is very water sensitive as its presence can greatly affect production yields, with the reaction stopping completely with 5% (w/w) water content[48]. Using an acid catalyst has more disadvantages such as slower reaction rate, higher operation costs (higher temperature and longer reaction time), and moreover, acid wastes must be disposed of, adding yet another cost.[48]

Nowadays, homogenous transesterification is the most commonly applied technique and alkali catalysts, such as metal alkoxides[49], hydroxides, and sodium or potassium carbonates[50] are the most common. Critical for an effective alkali transesterification reaction is the production of nucleophilic alkoxides from the alcohol to attack the electrophilic part of the carbonyl group of the TG[51].

The general layout of homogeneous catalytic transesterification process is shown in Figure 3.

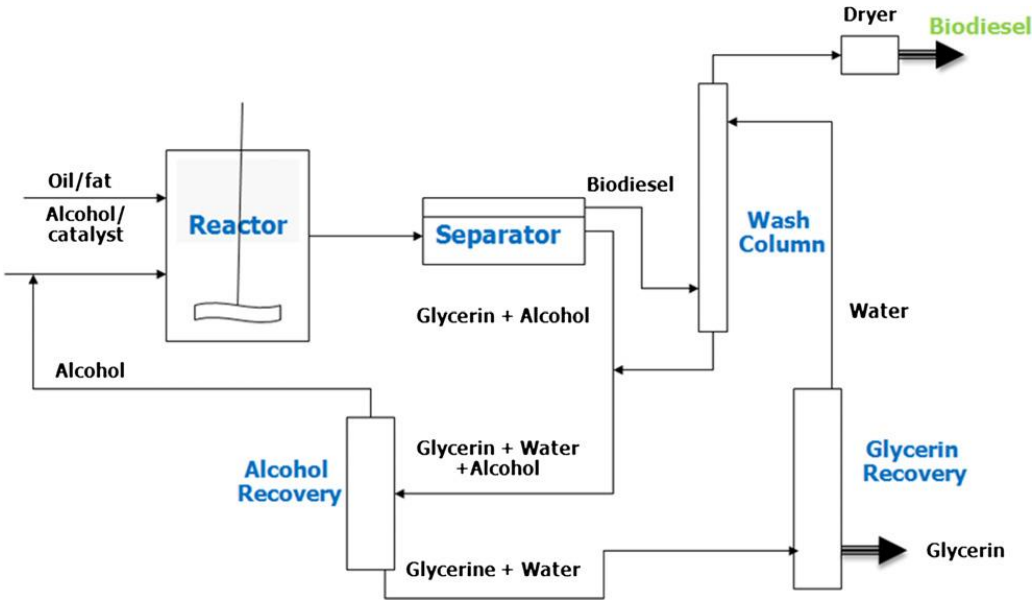

FIGURE 3 - THE PROCESS FLOWCHART OF HOMOGENEOUS CATALYTIC TRANSESTERIFICATION PROCESS[48]

When catalysts such as metal alkoxides and hydroxides are used for biodiesel production with methanol (transesterification/methanolysis), the active catalytic species are the same, i.e., methoxide ion (CH_3O^-) thus, equally effective[24]. Transesterification using of 0.5% (w/w) sodium methoxide ($NaOCH_3$) as a catalyst was reported as effective as when using 1.0% (w/w) sodium hydroxide (NaOH) for a 6:1 alcohol to oil molar ratio[52]. Adding to this, alkoxides in solution with the corresponding alcohol have a great advantage over hydroxides since the water-forming reaction showed in Equation 1 cannot occur with alkoxides, thus ensuring that the transesterification system remains as water-free as possible.[53]

$$R'OH + XOH \rightleftarrows R'OX + H_2O \quad (R' = alkyl; X = Na \text{ or } K)$$

EQUATION 1 – WATER-FORMING REACTION BETWEEN HYDROXIDES AND ALCOHOL[54]

Biodiesel production from TG is accomplished with three consecutive and reversible steps: 1) creation of a tetrahedral intermediate; 2) cleavage of the intermediate into DG ion and one fatty acid ester, and 3) recovery of the catalyst by proton transfer. These three steps repeat themselves to produce each fatty acid ester as well as one glycerol molecule[55]. Methanolysis of TG to glycerol by homogeneous alkali consumes three molecules of MeOH, produces three molecules of FAME and several reactions can also co-occur. The most

undesirable side reaction is the hydrolysis of ester compounds in the reaction system[56]. This hydrolysis is called saponification and it consumes the catalyst producing alkali salts of FA known as soaps[57]. The soap presence in the reaction mixture, due to its structure and corresponding polarity, will render a harder biodiesel and glycerol separation.

Homogeneous alkali catalysts are usually used mostly due to these facts: (i) modest operation conditions; (ii) high reaction yields in less time (97% or more in 10 min to 2 hours); (iii) high catalytic activity; (iv) widely available and economical[58]. However, in this type of transesterification many of the reactant's impurities such as FFA and water, as well as excess catalyst from the reaction, tend to attach to the glycerol phase. This renders this by-product very low on quality, making it harder to sell. Adding to this, disposal of this residue adds not only costs but an environmental concern as well.[38]

Alkali catalytic transesterification is usually carried out at low temperatures (60-65°C) with low catalyst concentrations (0.5-2.0% w/w)[59]. Limitations could be found in this process if the reactants have purity issues, high FFA content on the feedstock, as well as traces of water in all starting materials. The absence of moisture in the transesterification process is important as shown in Equation 2. If the oils contain FFA, they will not be converted to biodiesel but to much soap instead[48], as shown in Equation 3.

$$R - COOCH_3 + H_2O \rightleftarrows R - COOH + CH_3OH \ (R = alkyl)$$

EQUATION 2 - HYDROLYSIS OF ALKYL ESTERS TO FREE FATTY ACIDS[48]

$$RCOOH + NaOH\ (or\ KOH) \rightarrow RCOONa^+\ (or\ RCOOK^+) + H_2O$$

EQUATION 3 - SIDE REACTION IN BIODIESEL PRODUCTION: SAPONIFICATION TO CREATE SOAPS[48]

2.4.2 Two-step transesterification

Some authors state that alkaline catalysts are not the best choice to transesterify an oil containing high FFA. When using feedstock with a high FFA value, it is preferable to esterifiy the FFA to FAME first, using a acid catalyst[49], then, a second step, transesterification with an alkali catalyst. It is not advised to use a feedstock with FFA higher than 3% w/w, especially when no pretreatment is applied. However, used coking oils can present higher values. A two-step process using alkaline catalysis in both steps accomplished an increase of 10% on the global yield for a feedstock containing 4.0% (w/w) FFA.[60]

2.5 Industrial biodiesel production procedure by transesterification

2.5.1 Feedstock

Commonly used feedstock for biodiesel production also known as lipid feedstock include vegetable oils, animal fats, and other plant-like organisms such as microalgae and cyanobacteria. As different plants and animals have different optimum climates, the feedstock type highly depends on where the production plant is established. For example, coconut oil is a lipid feedstock used for the synthesis of biodiesel in coastal areas and potential non-edible oils used as raw material in India include Jatropha oil *(Jatropha curcas)* and Karanja oil *(Pongamia pinnata)*[61].

The common fatty acids found in vegetable oils are present in Table 3 . The different configurations (isomers) of the chains have great influence on the "stacking" of TG molecules, the proximity between molecules, and intermolecular forces between molecules. All these factors are important when determining the vegetable oils properties such as viscosity, crystallization, and melting temperature.

TABLE 3 – STRUCTURES OF COMMON FATTY ACIDS FOUND IN VEGETABLE OILS[4]

System name	Common name	Symbol	Formula	Double bond position [a]
Saturated				
Decanoic	Capric	C10:0	$C_{10}H_{20}O_2$	-
Dodecanoic	Lauric	C12:0	$C_{12}H_{24}O_2$	-
Tetradecanoic	Myristic	C14:0	$C_{14}H_{28}O_2$	-
Hexadecanoic	Palmitic	C16:0	$C_{16}H_{32}O_2$	-
Octadecanoic	Stearic	C18:0	$C_{18}H_{36}O_2$	-
Eicosanoic	Arachidic	C20:0	$C_{20}H_{40}O_2$	-
Docosanoic	Behenic	C22:0	$C_{22}H_{44}O_2$	-
Tetracosanoic	Lignoceric	C24:0	$C_{24}H_{48}O_2$	-
Monounsaturated				
Hexadecenoic	Palmitoleic	C16:1	$C_{16}H_{30}O_2$	9c
Octadecenoic	Petroselinic	C18:1	$C_{18}H_{34}O_2$	6c
Octadecenoic	Oleic	C18:1	$C_{18}H_{34}O_2$	9c
Octadecenoic	Elaidic	C18:1	$C_{18}H_{34}O_2$	9t
Octadecenoic	Vaccenin	C18:1	$C_{18}H_{34}O_2$	11c
Eicosenoic		C20:1	$C_{20}H_{38}O_2$	5c
Eicosenoic	Gadoleic	C20:1	$C_{20}H_{38}O_2$	9c
Eicosenoic	Gondoic	C20:1	$C_{20}H_{38}O_2$	11c
Docosenoic	Erucic	C20:1	$C_{20}H_{38}O_2$	13c
Polyunsaturated				
Hexadecadienoic		C16:2	$C_{16}H_{28}O_2$	
Octadecadienoic	Linoleic	C18:2	$C_{18}H_{32}O_2$	9c12c
Octadecatrienoic	α-Linolenic	C18:3	$C_{18}H_{30}O_2$	9c12c15c
Octadecatrienoic	ɣ-Linolenic	C18:3	$C_{18}H_{30}O_2$	6c9c12c
Octadecatrienoic	Eleostearic	C18:3	$C_{18}H_{30}O_2$	9c11c13t
Octadecatrienoic	Calendic	C18:3	$C_{18}H_{30}O_2$	8t10t12c

[a] c=*cis* formation; t=*trans* formation

2.5.2 Used cooking oil

Several important properties of UCO should be evaluated before starting biodiesel production. Two different UCO provenances could mean two completely different feedstocks. Origin of UCO determines the FA compositions while handling when cooking affects chemical and physical properties such as viscosity, water content and FFA content.[4]

Three different reactions can take place when cooking with vegetable oils at high temperatures: thermolytic, oxidative and hydrolytic reactions. Thermolytic reactions occur in the absence of oxygen in which saturated FA are decomposed into smaller compounds such as alkanes, ketones, esters, and diacylglycerides. Alternatively, in the presence of oxygen, oxidative and nonoxidative reactions will co-exist. Oxidative reactions will occur as shown in Figure 4.[4]

$$Initiation: RH \rightarrow R^{\cdot} + H^{+}$$

$$Propagation: R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$$

$$ROO^{\cdot} + H^{+} \rightarrow ROOH$$

$$ROOH \rightarrow RO^{\cdot} + OH^{\cdot}$$

$$Termination: RO^{\cdot} + H^{+} \rightarrow ROH$$

$$OH^{\cdot} + H^{+} \rightarrow H_2O$$

FIGURE 4 – SCHEME OF THE OXIDATIVE REACTION MECHANISM[4]

Also, when water is present, hydrolytic reactions take place during food preparation forming DG, MG, FFA, and glycerol.[62] This increases the feedstock acidity.

Joining together all these reactions and their respective formed derivatives, the polar content of the oil increases. At catering companies, it is mandatory that UCO should no longer be used for culinary purposes when the polar content exceeds 25%[63].

As attractive as using UCO as a raw material can be, in most cases, it contains high amounts of FFA and water due incorrect handling, exposure to heat and moisture from food, especially frozen foods. Therefore, the acid value of feedstock depends highly on its history. Direct alkali-catalyzed transesterification of “acid” oils is not recommended, but pre-treatment to remove FFA and water can be applied.

2.5.3 Transesterification elements and parameters

2.5.3.1 Effects of alcohol used in the transesterification

Usually a 6:1 alcohol to oil ratio is used in alkali-catalysed transesterification, achieving a 98% conversion. It is also reported that changing this ratio to higher values does not improve the conversion rate[49]. When too much alcohol is used in transesterification, the polarity of the reaction mixture rises, thus increasing the solubility of the glycerol back into the ester phase and promoting the reverse reaction, thereby reducing the conversion yield.

One of the first steps while setting a transesterification process is the reactants choice, alcohol included. Mainly due to a lower cost, methanol is usually the first option to be taken into consideration. The most common disadvantage reported for the usage of MeOH for transesterificaation is its low solubility with TG. Some methods are used to overcome this issue such as the use of rigorous mechanical stirring[64], a co-solvent[65], supercritical conditions[51], and the use of other techniques such as microwave[66] and ultrasonic stirring[67]. Experimenting with EtOH, propanol, and butanol was attempted. Some challenges may appear when using EtOH or even longer alcohols rather than MeOH. Longer carbon chains lead to a decrease in nucleophilicity and reactivity of the corresponding alkoxides[68].

2.5.3.2 Effects of catalyst type

Homogeneous catalyst are usually the type of catalysts employed in tranesterifictaion but heterogeneous catalyst were also reported for this process as it can simplify the biodiesel purification process, eliminate wastewater efluents, and render continuous production into a possible process.[49] To enable biodiesel production without catalyst as well as much shorter reaction times, transesterification under supercritical conditions were also tested[51]. However, extreme conditions such as high pressures and temperatures, and possible consequent polymerization is a significant disadvantage to this procedure. The final purification step is very challenging[69].

In this work, Sodium methoxide was used as an alkali catalyst. Sodium methoxide ($NaOCH_3$) is an alkali chemical that has various uses in industry. Its basic strength makes it ideal as a catalyst and condensation and reduction agent in organic synthesis[70]. $NaOCH_3$ diluted to 25−30% w/w in MeOH has been increasingly employed as a transesterification catalyst in biodiesel production[71].

2.5.3.3 Effects of reaction conditions

Before the transesterification reaction started only alcohol and oil phases are present. After that, product, by-product as well as intermediates are present. Those intermediates (MG and DG) act as surfactants to improve the mass transfer of TG into MeOH. The by-product (glycerol) separates as an additional phase and, in homogenous transesterification, the catalyst dissolves in the glycerol phase lowering catalyst concentration available for the reaction, therefore slowing its rate.

As temperature rises, so does the reaction rate for transesterification. Higher temperature has influence on the energy state forcing reacting molecules to move and vibrate faster, thus, having more chance to collide with one another. However, to prevent the reverse reaction, the reaction temperature should be kept just below the boiling point of the corresponding reacting alcohol that is 65°C for MeOH and 78°C for EtOH.

According to Hamze et al.[72], who have studied the interaction effects of the operating parameters, at catalyst (KOH) concentrations levels (C) (range 0.5-1.5% w/w), the MeOH/oil molar ratio (M) near the medium value is preferred (range 3:1-9:1). The temperature range was from 25°C to 65°C. At low levels of C, the yield increased with the temperature. At low M values, biodiesel yield decreased gradually with the temperature rising, while at high M values the biodiesel yield change in opposite direction. Also, at low to medium temperature, biodiesel yield initially increased with M and then declined near the medium M value. At high temperature, increasing the biodiesel yield can be observed with an increase in the M values, while the maximum yield was obtained approximately near the maximum M value. Finally, using numerical optimization, the study concluded that the optimum conditions to achieve maximum yield were the temperature of 65°C, MeOH to oil molar ratio of 7.5:1 and catalyst concentration of 1.4% (w/w). The predicted yield was evaluated as 99.5% at this point.

2.5.3.4 Effects of ultrasound irradiation and other options

Ultrasonic irradiation is one of the techniques successful at surpassing the immiscible nature of TG and alcohol in transesterification. This technique allows for a reduction in process time as well as catalyst consumption[73]. On chemical reactions this technique has a great influence as it raises the mechanical energy needed to boost the transesterification reaction, replacing mechanical agitation and heating required to establish close contact between the two immiscible phases[74].

One of the biggest barriers to biodiesel process is when moving to a large scale. Even though many techniques have proven to be successful at lab-scale, economical efforts and an appropriate engineering approach is needed to accomplish continuous and profitable biodiesel production. Choedkiatsakul[75] has employed a commercial available professional microwave (MW) reactor in a continuous process instead of conventional batch MW units, hoping to provide the guideline for the development of a large-scale process for biodiesel production, but with no success. Other studies state that MW heating has proven to enhance heat transfer in the transesterification process[76].

2.5.4 Separation and "washing"

After the reaction, product and by-product must be separated. As mentioned before, due to low solubility as well as high density, glycerol separation is accomplished easily on a settling tank. The excess MeOH used to deslocate the reaction equilibrium to the desirable products side also acts as a solubilizer slowing down the separation. However, MeOH should be kept in the mixture until the glycerol is fully separated to prevent the inverse reaction to occur. After separation, biodiesel goes through a washing step to remove impurities and MeOH. Flash destillation or an evaporator are usually used to recover MeOH from both biodiesel and glycerol streams.

2.5.4.1 Biodiesel washing

Removing, MeOH, free glycerol, excess catalyst, reaction intermediates, water and other impurities are of utmost importance to generate only high-quality biodiesel meeting international standard specifications[77]. At this step, soaps, free glycerol, water, alcohol, catalyst and FFA are the impurities that should be withdrawn from the process to avoid

decreasing the biodiesel quality[18]. Engine problems can also be prevented when biodiesel is properly washed[78]. The washing is commonly done by two techniques: wet and dry washing.

2.5.4.1.1 Wet washing process

In the wet washing process, distilled warm water is used to remove glycerol, MeOH, and soaps. This step is accomplished spraying the water over the biodiesel and then letting it settle and water drained. After repeating this procedure, if colourless water is obtained meaning that no more impurities are being washed, the removal of impurities is complete. The fact that MeOH and glycerol are both soluble in water helps turn this process effective at removing these impurities[79]. However, the long separation time and loss of yield through the rinsing waters turn this step undesirable and pollutant[80].

2.5.4.1.2 Dry washing process

Dry washing biodiesel usually involves using an ion exchange resin or magnesium silicate powder[81]. Replacing water and avoiding wastewater production is a great advantage for this procedure. This step is usually added in the final stage increasing the process efficiency[78].

In our work, we used RESIN R, a polishing media with sulfonic acid as its functional group that was formulated especially to remove by-products after transesterification to produce biodiesel. This medium replaces magnesium silicate “wash” and improves plant productivity lowering operation costs while trying to achieve ASTM or EN specifications for B100. This product has an extended life before exhaustion. However, its lifetime is much dependent upon the point of installation in the biodiesel production stream and on the number of impurities in the untreated biodiesel. [82] It functions both as a desiccant medium and as an ion exchange polishing medium. As a desiccant, it has a high loading capacity to absorb free glycerol which results in media swelling. Traces of MeOH and water, although being absorbed to a limited degree, should be then removed by stripping in the destillation step. Additionally, the ionic exchange capacity removes residual catalyst and salts that remain after phase separation, i.e., by exchanging primarily sodium (Na+) or potassium (K+) of the catalyst for hydrogen (H+) on the resin. This exchange neutralizes sodium (potassium) methoxide catalyst reverting it to MeOH, and soaps will be converted to FA[83].

The resin can be washed with MeOH on site several times to maintain its ability to remove glycerol. However, it must be ionically regenerated to keep the capacity to remove traces of catalyst and soaps. This regeneration can only be accomplished on the supplier.

2.5.5 Methanol stripper

When dry washing procedures are adopted in biodiesel production, MeOH is not retained by the resins. Thus, to meet specification standards, it must be removed afterwards. MeOH remaining in the final biodiesel is highly undiserable due to environmental and safety concerns. MeOH is toxic and too much MeOH present in the biodiesel will make the fuel flammable and, therefore, dangerous. To prevent this, most conventional biodiesel manufacturers waste much MeOH by "wet washing" the final product[84].

MeOH recovery can make the biodiesel production process more efficient from both economic and environmental point of view. Therefore. in designing a cost-effective MeOH recovery unit, the energy requirement is a critical parameter, as it may increase the cost of biodiesel compared to conventional petrodiesel.

Recovered MeOH can and should be re-inserted in the process but, as it might be not as pure as the original, a larger amount could be needed.

2.5.6 Glycerol recovery and purification

Biodiesel produce large amounts of glycerol. To try and diminish the low-quality glycerol produced, many researchers have converted it into glycerol carbonate (GC) using many different techniques[85, 86, 87].

To improve the glycerol's quality, usually, acid is added to split the soaps into FFA and salt. After acidulation and separation of the FFA, the MeOH present in the glycerol is withdrawn by vacuum flash distillation or another type of evaporator. After this steps, the glycerol should have a purity of about 85.0% and is typically sold to a glycerol refiner. The glycerol refining process can be improved even further taking the purity up to 99.5–99.7% using ion exchange procedures.

2.6 Techniques for biodiesel characterization

Some of the key properties that demonstrate good quality biodiesel are density, flash point, viscosity, calorific value, cetane number, oxidation stability and cloud point[88]. Some parameters such as water content, methanol content, FAME content, and iodine value will influence these properties. Traces of MG, DG, unreacted TG, unseparated glycerol, FFA, and catalyst can remain and contaminate the final product. The determination of product quality is, therefore, very important to the successful biodiesel production and final commercialization.

Various techniques have been developed to monitor the reaction, and acquisition of more detailed information requires more sophisticated, expensive, and time-consuming techniques and vice-versa. Chromatography techniques are most commonly used because they offer the comprehensive perception of transesterification progress and detailed information required for quality control of the product. Biodiesel is mainly characterized by gas chromatography (GC).

2.6.1 Gas chromatography

Most chromatographic analyses have been applied only to methyl esters and not higher esters such as ethyl or isopropyl. Most methods would need modifications for proper analysis of the higher esters. For example, changes in the temperature programs or other parameters may be necessary. Gas chromatography (GC) higher accuracy in quantifying minor components is a huge advantage as well. The first work reported on the use of capillary GC within biodiesel discussed the quantitation of esters as well as MG, DG and TG[89].

Developments have been made to allow TG and ester simultaneous determination using Gas chromatography technique on a single run. In principle, TG, DG, MG, and glycerol can be analyzed without derivatization[84]. Derivatization, when needed, is due to free hydroxyl groups present in MG and DG, which cause difficulty in quantifying these materials. To improve peak properties such as separation and shape, and allow for a better identification step, free hydroxyl groups are eliminated from MG, DG, and glycerol thus changing its structure and polarity. To correctly identify the peaks present in the sample, their retention times are compared with those of internal standards and identified through relative retention time. An example of a gas chromatogram is represented in Figure 9. In this

chromatogram, methyl esters are represented by the thickest peak with approximately 10 minutes retention time

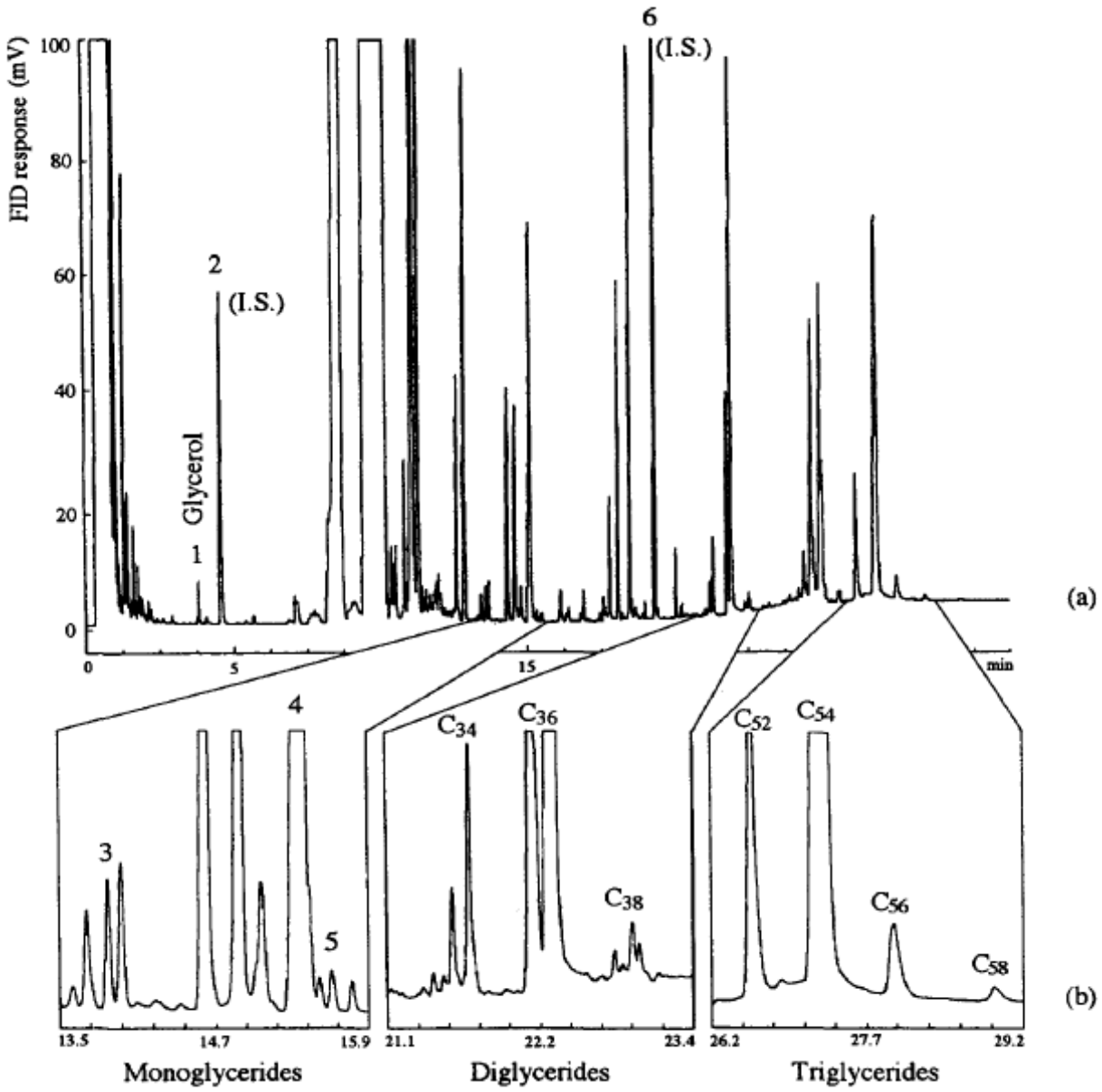

FIGURE 5 - (A) GAS CHROMATOGRAM OF SILYLATED RAPESEED OIL METHYL ESTER WITH 1,2,4-BUTANETRIOL AND TRICAPRIN AS INTERNAL STANDARDS. (B) ENLARGEMENTS OF THE REGIONS, WHERE THE SIGNALS OF MONO-, DI- AND TRIGLYCERIDES APPEAR IN THE UPPER GAS CHROMATOGRAM. PEAK ASSIGNMENT: 1 = GLYCEROL; 2= 1,2,4-BUTANETRIOL, I.S.; 3 =MONOPALMITIN; 4=MONOOLEIN, MONOLINOLEIN, MONOLINOLENIN; 5 = MONOSTEARIN, 6 = TRICAPRIN, I.S.; C_{34-C38} = DIGLYCERIDES WITH CARBON NUMBERS OF 34, 36 AND 38; C_{52-C58} = TRIGLYCERIDES WITH CARBON NUMBERS OF 52, 54, 56 AND 58.[90]

2.7 Guidelines for the future of Biodiesel

Even using the cheapest refined oil as feedstock, biodiesel struggles while competing economically with petrodiesel. Many published calculations concluded that biodiesel produced from edible grade vegetable oils is not economically competitive with petrofuels[91]. The main reason is the high price of vegetable oils present in the food market. Their results in an overall production cost that exceeds the price of the petrofuels that the biodiesel is designed to replace. This price gap can be even more significant when petroleum prices are low. Sentiment among commercial fleet operators and individual consumers in favor of renewable, domestically produced, low-pollution fuels is not strong enough to support the use of alternative fuels at these prices. In Europe, tax rates on petroleum are used to shorten the gap between fossil and renewable fuels and promote more biodiesel usage. Legislative approaches, such as cuts in taxes and supportive payments to producers, were made to push biodiesel forward. In Portugal, part of the National energy action plan is to achieve a "20-20-20" goal in 2020, consisting in: i) reach a 20% decrease in hazardous emissions in comparison with 1990; ii) 20% of energy income from renewable sources; iii) 20% decrease in primary energy consumption in comparison with the forecast for 2020. To pursue this goal, the Portuguese Government has tax benefits to companies who help achieve it.[92]

Production-oriented approaches to improve the economics of biodiesel can include the investigation of lower-cost lipids as feedstock. The composition of these alternate feedstocks, however, can require modification of existing technologies for their conversion into acceptable biodiesel fuels. Also, a desire to reduce the waste streams of spent catalyst and other byproducts resulting from the traditional alkali-catalyzed transesterification reaction has stimulated investigations into alternative means of conducting and catalyzing biodiesel synthesis.

3 Laboratory tests

3.1 Feedstock samples and other reactants

Several feedstock samples (Sample 1 to Sample 4) were collected from a gathering company responsible for gathering UCO at restaurants, hotels and other producers around the Madeira Island region. The company collects the UCO in 50L storage barrels and then pours them through a couple of meshes to retain most of the impurities, ending in the final storage tank. Another UCO sample (Sample 5) was collected from a local bar without interference from the gathering company. A pure vegetable oil (PVO) sample was also bought for tests and blending. All samples used for the lab tests had their acidity determined by volumetric titration according to standard EN 14104:2003. The sample is dissolved in a suitable solvent mixture (ethanol and diethyl ether, 1:1), and the acids present are titrated with a methanolic solution of potassium hydroxide. The acid value, wAV, expressed as a mass fraction, is equal to wAV=56.1*c*V/m, where c is the exact concentration, in moles per liter, of the standard volumetric potassium hydroxide solution used. V is the exact volume of potassium hydroxide solution needed to titrate de sample, in mililiters, m is the exact mass of sample used, in grams and 56.1 is the molar mass of potassium hhydroxide. In addition to these calculations, the approximate free fatty acid content (acidity) is calculated from wFFA = 0.5 × wAV. The acidity values are shown in Table 4.

The folowing reactants were used in the aboved mentioned procedures:

- Methanol (>99.8%, Chem-Lab NV, Belgium)
- Ethanol (96%, Chem-Lab NV, Belgium)
- Diethyl ether (>99.8%, Chem-Lab NV, Belgium)
- Potassium Hydroxide (85% pellets PA, Panreac, European Union)
- Sodium methoxide ($NaOCH_3$ 30% in methanol adquired by Grupo Sousa / Metal Lobos Lda in 2013 from Quimitécnica.)

3.2 Laboratory production tests

With the goal of trying to obtain our starting conditions for the pilot-unit tests, several experiments were carried at lab-scale in Universidade da Madeira (UMa). These experiments were performed using UCO (neat and blended with pure vegetable oil) as feedstock (220-230g), MeOH (6:1 molar ratio), and the catalyst, sodium methoxide. Reaction conditions were chosen from the common values among the literature. These conditions included ultrasonic agitation and temperature of 323°K ±5. The amount of catalyst added is set accordingly to the feedstocks acidity. After titration, the feedstock poured into a 500ml beaker and heated to the desired temperature. MeOH and the catalyst are mixed and added to the feedstock when it reaches 323°K, starting the reaction. The reaction time is 120 min, except for the reaction time tests. After this, the resulting mixture was stored for sedimentation for about 16-18 hours. Finally, the phases are separated, their volume and weight measured, and the reaction yield calculated.

With this procedure, three different sets of tests were carried including acidity, catalyst concentration and temperature tests. Initially, different blends were made to achieve several feedstocks with different acid values, ranging from 0 to 5.6% FFA, and the reaction proceeded with varying amounts of catalyst added, accordingly. The acid values range was chosen to cross the maximum 3% theoretical value for the feedstock. The second set of tests consisted of using UCO2 (acidity 4.2% FFA) and varying the catalyst amount added ranging from 3.7 to 5.0% w/w). Since the amount of catalyst should be enough to neutralize the FFA and transesterify the TG, the catalyst concentration values range was chosen to cross the 4.2% acid value of the sample. The third set was carried maintaining the same feedstock (UCO2) and maintaining the catalyst amount (4.0% w/w) but varying the reaction time ranging from 60 to 150 minutes. The temperature range was chosen to cross the optimum theoretical of 120 minutes. Figure 6 shows one of the tests carried at the laboratory of Universidade da Madeira. At the top is the lower density biodiesel and the bottom the “heavy” glycerol along with the soaps formed.

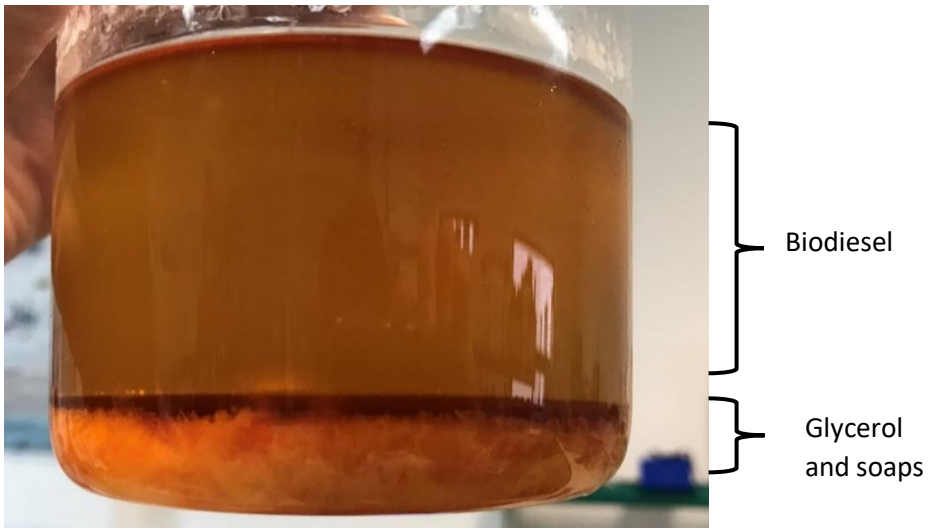

FIGURE 6 - TRANSESTERIFICATION TEST WITHOUT PRE-TREATMENT

3.3 Pre-treatment tests (Neutralization)

As our collected samples showed high acidity, pre-treatment tests were carried to lower this parameter. These tests consist in neutralizing the FFA present in the feedstock by mixing it with different amounts of compound A ([A]), ranging from 0.5 to 0.0625% (w/w). The feedstock (UCO4) is poured into a 300ml beaker and heated to 65°C ±5. Compound A is diluted in water and then mixed with the feedstock for 60 minutes. A saponification reaction will occur as shown in equation 3 and the resulting soaps precipitate making them ready for removal. The resulting treated UCO is then titrated, and its volume and weight measured to calculate the neutralization yield. After this, the neutralized UCO follows the mentioned biodiesel synthesis procedure. In the end, combining both neutralization and biodiesel production yields, we obtain a global yield of both procedures together.

3.4 Results and discussion

As the main objective of this work is to determine the influence of the feedstock properties in biodiesel production, it is essential to know the variability of such an important parameter as the acidity. As it is shown in table 4, the feedstocks acidity varies, ranging from 5.12% to 9.07% FFA (w/w), higher than the theoretical 3% maximum value. All yields are calculated on a mass basis according to equation 4.

$$Yield = \frac{mass\ of\ biodiesel}{mass\ of\ feedstock} * 100$$

EQUATION 4 – MASS YIELD CALCULATION FORMULA

TABLE 4 – INFORMATION REGARDING USED COOKING OIL SAMPLES FOR LABORATORY TESTS

Sample number	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Origin	Company	Company	Company	Company	Local bar
Date of collection	out/13	27/01/2017	27/02/2017	24/04/2017	11/05/2017
Acidity (% FFA)	5.12	4.20	9.07	5.37	0.77

The first set of tests consisted in varying the acidity of the feedstock by blending UCO samples with neat vegetable oil. As shown in table 5 and figure 7, as the feedstock's

acidity rises, the reaction yield is lower. The FFA present in the feedstock are saponified by the catalyst, forming soaps. In addition to this, these soaps can also emulsify the mixture making harder to separate and recover the methyl esters. Also, the amount of catalyst needed to neutralize the feedstocks acidity increases resulting in TG saponification.

TABLE 5 - ACIDITY TESTS

Sample	Blending (% vegetable oil)	Acidity (%FFA)	FAME yield (%) w/w
PVO	100	0.04	95.99
Sample 2+PVO	50	2.08	74.60
Sample 1+PVO	55	2.30	73.98
Sample 1+PVO	40	2.60	68.47
Sample 1+PVO	35	2.85	69.58
Sample 1+PVO	20	3.10	53.57
Sample 2	0	4.20	44.74
Sample 4	0	5.6	28.45

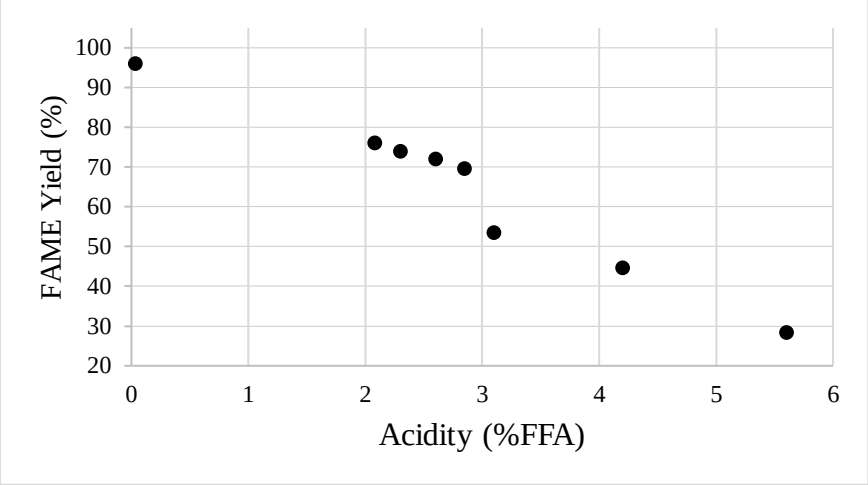

FIGURE 7 - ACIDITY VS. FAME YIELD PROFILE

The second set of tests consisted of varying the amount of catalyst added, maintaining a constant acidity level on the feedstock. This constant value was achieved by always using the same sample as raw material (Sample 2 – 4.2% FFA). As shown in table 6 and figure 8,

for 4.2% acidity value, adding 4.0% of catalyst achieved the best yield. For values lower than 4.0%, the amount of catalyst remaining after FFA neutralization, probably wasn't enough to fully transesterify the TG, resulting in a lower biodiesel production yield. When values higher than 4.0% catalyst were added, the yield is also decreasing, that could be due to saponification of TG by the excess catalyst.

TABLE 6 - CATALYST CONCENTRATION TESTS

Sample	Acidity (%FFA w/w)	Cat (% w/w)	FAME yield (% w/w)
Sample 2	4.2	3.7	24.31
Sample 2	4.2	4.0	44.74
Sample 2	4.2	4.5	39.55
Sample 2	4.2	5.0	13.54

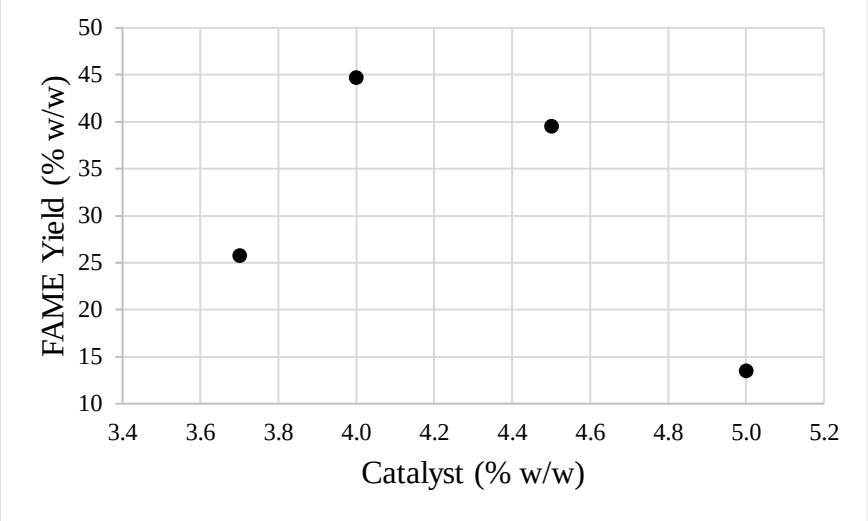

FIGURE 8 – CATALYST CONCENTRATION VS. FAME YIELD PROFILE

The third set of tests were carried maintaining the feedstock's acidity (UCO2 – 4.2% FFA) and the amount of catalyst (4.0%), constant, but varying the reaction time, ranging from 60 to 150 minutes. As shown in table 7 and figure 9, the best yield value was obtained when the reaction was maintained for 120 minutes. For shorter reaction times than that, probably the transesterification was not complete, lowering the biodiesel production yield.

When the reaction endured for 150 minutes, the yield decreased probably due to some procedure failure such as MeOH evaporation and, thus, reverse reaction.

TABLE 7 - REACTION TIME TESTS

Sample	Reaction time (min)	Acidity (%FFA)	FAME yield (% w/w)
Sample 2	60	4.2	24.27
Sample 2	90	4.2	41.21
Sample 2	120	4.2	44.74
Sample 2	150	4.2	20.56

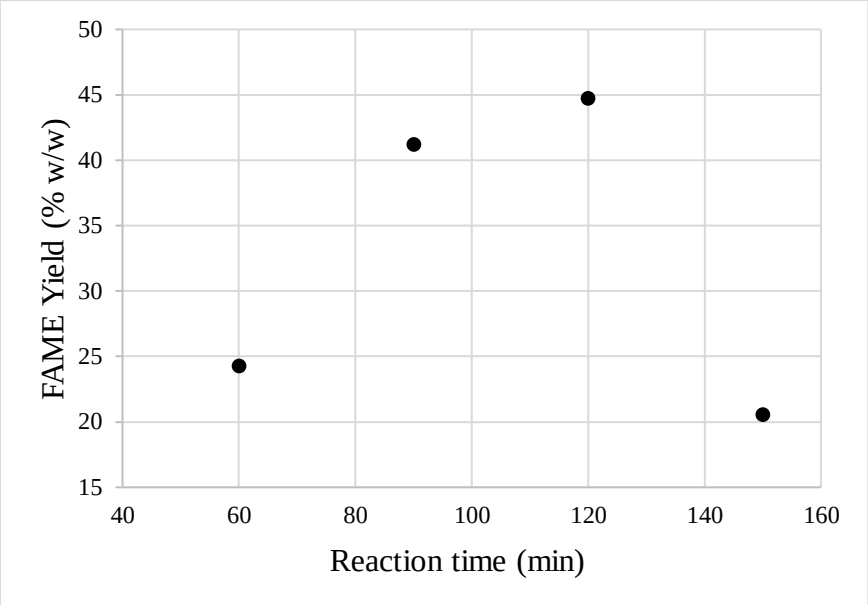

FIGURE 9 – REACTION TIME VS. FAME YIELD PROFILE

Regarding the neutralization tests, in figure 10 is shown a test carried using UCO and compound A. It is possible to observe the lower part containing the fatty acids salts from saponification and in the upper part, the neutralized UCO.

Figure 11 shows a transesterification reaction using the neutralized UCO as feedstock. As it can be observed, without any FFA presence, there is no soap formation, thus, achieving a perfect separation between biodiesel and glycerol, and a better product, from a visual point of view.

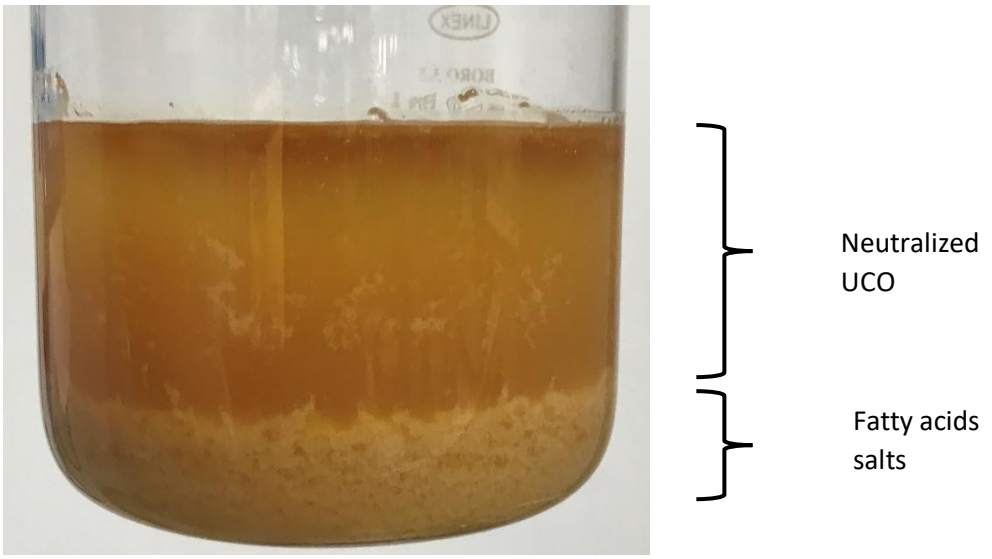

FIGURE 10 – UCO NEUTRALIZATION TEST

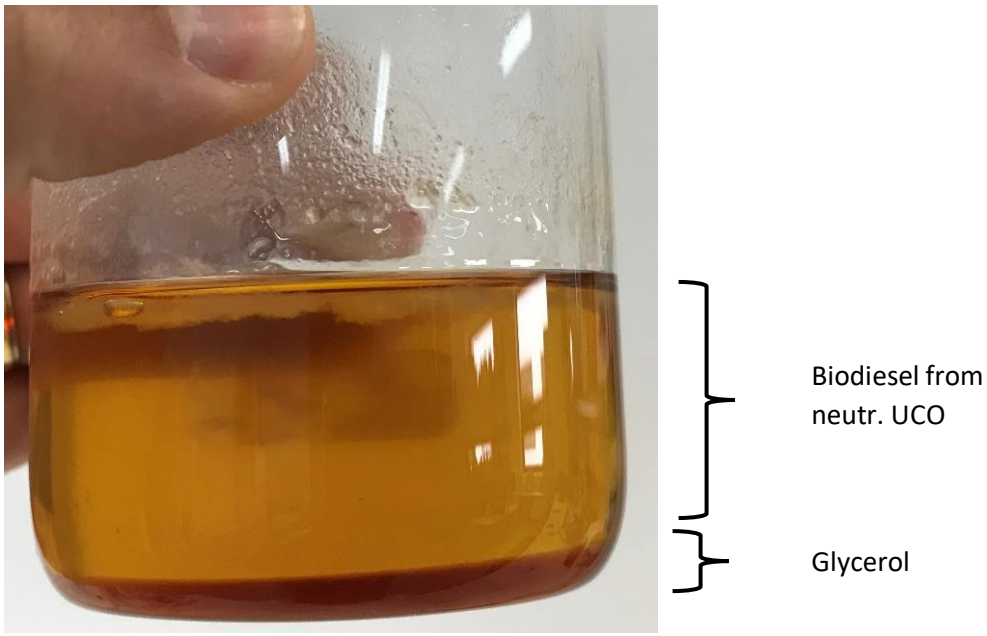

FIGURE 11 – TRANSESTERIFICATION WITH NEUTRALIZED UCO

Table 8 and Figure 12 show that adding less A results in an incomplete neutralization, thus, higher acidity of the neutralized oil. Naturally, as we add less A, less FFAs are neutralized and, consequently, the weight loss should lower accordingly. Nevertheless, the results show otherwise. When changing from 0.50% to 0.25% of added A, the weight loss is lower but, when the added amount drops even more, the results demonstrate an increase in the weight loss. This is due to the poor separation between the neutralized oil and the few saponified FFA. To ensure complete extraction of saponified FFA, some emulsified oil is

extracted too. One way to prevent this from happening is by using a centrifuge, improving the saponified FFA precipitation. The concentration of A that achieved a better balance between weight loss and the neutralized oil's acidity was 0.25%. That value resulted in acidity of 0.08% FFA and a 21.48% weight loss. This was supposed to be the concentration value for the neutralization test in the pilot unit. This test, represented in figures 15 and 16, resulted in both products with the best visual aspect and a yield of 92.67% (w/w). The global yield (calculated with the initial amount of feedstock added and the resulting biodiesel produced from the neutralized oil) was 72.76% (w/w).

TABLE 8 – NEUTRALIZATION TESTS

Sample	% A (w/w)	Resulting acid value (%FFA)	% weight loss
Sample 4	0.50000	0.06	33.0%
Sample 4	0.25000	0.08	21.5%
Sample 4	0.12500	0.10	30.6%
Sample 4	0.09375	0.30	38.8%
Sample 4	0.06250	1.46	37.7%
Sample 4	0.00000	5.2	-

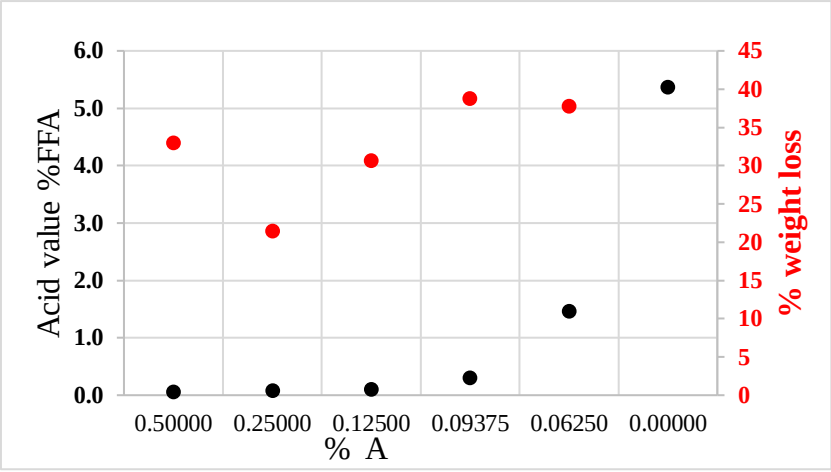

FIGURE 12 - %A ADDED VS. ACID VALUE AND WEIGHT LOSS PROFILE

To prevent excessive weight loss when less than 0.25% A was added, a centrifuge was used, testing the solution mentioned before. The results are represented in table 9 and figure 13 and show a decreasing weight loss as expected.

TABLE 9 – WEIGHT LOSS TESTS

Sample	% A (w/w)	Resulting acid value (%FFA)	% weight loss
Sample 4	0.12500	0.10	15.57%
Sample 4	0.09375	0.30	17.34%
Sample 4	0.06250	1.46	13.65%

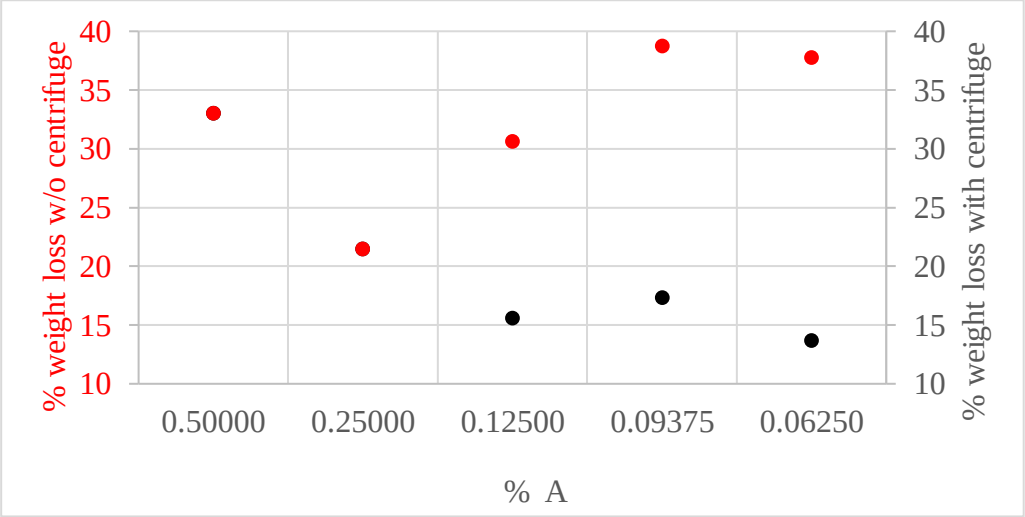

FIGURE 13 - % WEIGHT LOSS W/O CENTRIFUGE VS. WITH CENTRIFUGE

4 Pilot-unit tests

4.1 Methods and materials

4.1.1 Pilot unit

The pilot-unit transesterification tests took place in a batch pilot unit built in 2013 at Grupo Sousa / Metal Lobos Lda. Piping and instruments diagram is presented in Appendix A. The pilot plant tests were separated in two different purposes: testing the unit; and biodiesel production.

At first, a full-scale comprehensive check-up was needed to uncover possible operation issues and optimization opportunities. The whole unit was checked with biodiesel streaming through all tanks and instruments. At this point a couple of critical challenges were found. The most relevant for the work was the fact that the thermocouples were installed too high up in the tanks, preventing tests with less than 600L of feedstock. Below this limit, as the thermocouples were not in contact with the fluids, no temperature was measured, and the electrical heating would not shut down at the selected pre-set temperature. Further issues regarding the vacuum system, ionic resins, glycerin tank and methanol recovery tank were found and solved. To prevent or attenuate these issues, pipes and tanks needed some changes before starting the tests. Selected tanks and pipes were isolated to prevent heat loss while operating, saving power and time. Level indicators were added where needed, valves and instruments were correctly identified to allow easy and fast identification. Also, an extra tank was added downstream of the condenser, allowing to take MeOH samples from the recovery.

The biodiesel production tests at the pilot unit consisted in four (4) batches using three (3) different samples. The last two tests (T3+T4) were accomplished using the exact same feedstock and parameters but test 4 was subjected to pre-treatment before transesterification.

FIGURE 14 - PILOT PLANT AT GRUPO SOUSA / METAL LOBOS LDA.

4.1.2 Feedstock

The feedstock samples (Sample 2, 6 and 7), were collected at an identified company, the same as in the laboratory tests. There, at first, samples are poured through a set of meshes retaining most of the big contaminators such as food pieces and even plastic bottles from vegetable oils. Then, is transferred to a settling tank waiting for transport to its destination. When collecting the feedstock from this company, it was noticed that the barrels used to transport the oil from the restaurants were washed with water that also runs to the settling tank along with the oil. As the oil remains in the settling tank for two to three weeks before transport, water presence, and consequent hydrolysis, deteriorates the oil rising its acidity to levels higher than desired for alkali-transesterification. The feedstock reaches our facility in 1000L cubes that are directly attached to the installation. Different properties of the samples were determined: i) acidity, by volumetric titration according to standard EN 14104:2003; ii) fatty acid composition (using gas chromatography according to EN 14103 (2003) and ISO 5508 (1996); iii) iodine value according to standard ISO 3961 (2013); iv) water content, using coulometric Karl Fisher titration. Titration was accomplished in UMa laboratory using the same methodology as the laboratory tests. The other determinations were accomplished in a certified outsourced laboratory.

4.1.3 Methoxide dissolution

After measuring the feedstock acidity (same titration method and reactants as in the laboratory tests), MeOH (99.9%, acquired in 2013 from RNM produtos químicos) and sodium methoxide ($NaOCH_3$ 30% solution in methanol acquired in 2013 from QimiTécnica) are pumped into the methoxide production tank according to the titration result. Recirculation is then used to mix the reactants. The tank has a 250L capacity and mixing (recirculation) takes about 5 minutes.

4.1.4 Ultrasonic transesterification

The oil is transferred to a holding tank until the level reaches 1000L and then into the reactor to reach 55°C. Recirculation and mechanical stirring inside the reactor help to achieve an uniform temperature.

The ultrasonic reactor is an essential component of the process, allowing to maximize the reaction rate. Integrated into the recirculation system, it provokes molecular cavitation ensuring a high yield of methyl esters at the end of the reaction. The low power consumption

and efficiency of this reactor make it a huge advantage. The reaction tank has a 1300L capacity, processing about 1000L of UCO per batch. Reaction time is 120 minutes. Heating is supplied by an internal power heater. Methoxide is added to start the reaction.

4.1.5 Separation

When the reaction is complete, the separation step takes place in a settling tank with a 1300L capacity. Settling time should be at least 12 hours. The tank should be kept at a minimum temperature of 30°C to promote settling. After settling, glycerol and most of the feedstock impurities such as FFA, salts as well as much dissolved methanol, are pumped from the tank's bottom to the glycerol purification reactor. When only biodiesel is left in the settling tank, it is pumped through the ionic resins into the drying buffer tank.

4.1.6 Biodiesel purification

Biodiesel's purification first step is realized through two ionic exchange resin columns. Biodiesel passes through those columns at a constant speed and stripped of traces of glycerol and catalyst. The columns hold 150kg of RESIN R allowing purification of 150.000L of biodiesel. This ionic resin is specially crafted to be used after transesterification and glycerol separation, before drying. Excess catalyst, salts, and residues of glycerol are removed to allow drying without risking the reverse reaction to occur.

4.1.7 Methanol recovery

To ensure that the produced biodiesel meets the EN 14214 requirements for flash point, and to reduce biodiesel production operation cost, a MeOH recovery system is used. As a 6:1 oil to alcohol molar ratio is used to improve reaction rate (approximately double the amount consumed in the reaction), almost 50% excess MeOH remains. In this study, the MeOH stripping system is composed of a preheating tank and a vacuum flash distillation column (-500mbarg), therefore providing a fast and cheap operation. In flash distillation, the most volatile component of the mixture, which is methanol, is quickly vaporized while entering an environment where a much lower pressure is present. Some of the advantages of using vacuum flashing are that both water and MeOH are removed, low levels of MeOH and water remain in esters, both ASTM and EN standards are met, it minimizes the necessary energy input and allows better control of MeOH emissions.

Buffer tank heating is switched on as well as the flash control unit. The buffer tank provides pre-heating and a continuous distillation step. Biodiesel is poured inside the flash, and the vacuum provides a complete and efficient step without excessive power waste. The control unit works in an ON-OFF sequence pumping the MeOH-free biodiesel when the flash column reaches a specific volume, maintaining the column free for more biodiesel.

As most of the MeOH left over will be found in the glycerol by-product, separating the MeOH out of the glycerol is very important too. The procedure for MeOH recovery from glycerol is similar to the used for biodiesel.

MeOH needs to have a purity of 95% or higher to avoid problems caused by having too much water in the next batch. Thus, it is important to take samples of the recovered MeOH to evaluate the water content.

4.1.8 Filtering / Storage

At the process's final stage, Biodiesel is filtered through a 1-micron nylon bag filter to ensure the absence of particles. Before being transferred to the final tank, several parameters are checked such as water content, methanol content and flash point.

4.1.9 Glycerol purification

After being pumped from the settling tank, the glycerol is highly impure. Therefore, impurities such as MeOH, catalyst residues, and other contaminants must be withdrawn from the by-product. Distillation, refining with active carbon and sometimes ion exchange could be done to eliminate these impurities, but, previously to any other operation, because MeOH and water removal below thresholds improves solidification, glycerol must be heated to decrease its viscosity, allowing for better handling. In this work glycerol is subjected to a 500mbar vacuum, working as a MeOH and water stripper. When the glycerol is purified, it can be stored for selling or used to make soap.

4.1.10 Pre-treatment

Test 4 consisted in a pre-treatment prior to transesterification to prevent the negative influence that high acidity values have on transesterification rates. This pre-treatment consisted of adding compound A, forcing a saponification reaction on the FFA present in the feedstock. 0,19% w/w of compound A was used to perform this step. This value was chosen to reach a complete neutralization while preventing excessive mass loss. The compound A

pure powder was diluted in water and then added to the acid UCO. Between test 3 and test 4, this was the only difference in the process. Therefore, the feedstock was the same, maintaining all its properties such as acidity value and FA profile. The saponification reaction took place in the transesterification reactor at a 60°C temperature for 60 minutes. As the reaction period ended, the mixture was transferred to a cubic meter cube for sedimentation, this way preventing clogging the reactor. The mixture was left for settling for about 16 hours. As the soaps have a higher density than the neutralized UCO, these settled at the bottom of the cube. Then the lighter UCO was transferred back into the reactor with the help of a pneumatic pump making it ready for transesterification with the same amount of reactants as test 3. All separation and biodiesel purification steps had the same procedure as in test 3.

4.1.11 Biodiesel characterization

The biodiesel characterization was to be performed according to the European biodiesel standard EN 14214 (2008). The following parameters were determined: i) density, determined using a hydrometer method according to the standard EN ISO 12185 (1996); ii) flash point, using a rapid equilibrium closed cup method, according to the standard ISO 2719 (2002); iii) water content, by Karl Fischer coulometric titration according to the standard NP EN ISO 12937 (2000); iv) ester and linolenic acid methyl ester contents, by GC according to the standard EN 14103 (2011); v) free and total glycerol and MG, DG, and TG content according to the standard EN 14105 (2003); vi) iodine value, determined from ester content according to the standard EN 16300 (2012); vii) methanol content according to the standard EN 14110 (2003); and viii) group I metals (Na+K) content according to the standard 14538 (2006). Some of these parameters were chosen for analysis to determine the procedures effectiveness and the proper functioning of the pilot unit, such as methanol and water content from distillation, ester content from the reaction, and sodium and glycerol content from exchange resins. Other useful parameters were not available for determination.

4.2 Results and discussion

Some properties the feedstock samples were determined and are shown in table 10. Once again, the variability of the feedstock acidity is well present.

TABLE 10 – INFORMATION REGARDING FEEDSTOCK SAMPLES FOR PILOT UNIT TESTS

Tests	T1	T2	T3	T4
Feedstock	Sample 2	Sample 6	Sample 7	Sample 7
Date of test	27/07/2017	23/08/2017	26/09/2017	29/10/2017
Acidity (% FFA w/w)	4.20	5.88	9.82	9.82
Iodine value ($gI_2/100g$)	106	-	-	-
Water content (% w/w)	0.22	-	-	-

Biodiesel production yields are presented in table 11. They varied from 78.52 to 90.37 (% w/w). When comparing the first and second tests, we notice a descent in yield that could be due to several parameters, but, as shown in the lab tests, higher acidity has a negative influence on yield. When comparing T1 with T3, both having the same 7.1 alcohol to oil molar ratio, the decrease in the yield was not so significant as when comparing T1 with T2. In our pilot unit, the molar ratio may have a greater influence in yield than acidity but further tests should be done in the future to evaluate this assumption. That would allow us to use more MeOH in the reaction but only if we can manage to recover the excess successfully. However, it is important to remember that adding too much MeOH will increase the energy input needed for the following recovery and purification and increase solubility between the glycerol and biodiesel.

T4 was subjected to a pre-treatment with compound A to lower the high acidity of the UCO. The feedstock was the same as used in T3 being the pre-treatment the only variable influencing the yield. As shown in table 11, the pre-treatment was very effective lowering the feedstock acidity from 9.82% to 0.13% FFA (w/w). The difference between transesterification yields is not significant and, as this saponification resulted in a mass loss of 29%, the global yield (calculated with the initial amount of feedstock added in and the resulting biodiesel produced from the neutralized oil) of 62.37% makes the pre-treatment undesirable. As demonstrated in the lab tests, mass loss (29%) could be diminished using a

better method such as centrifugation. This way all the heavy soaps would be withdrawn from the neutralized UCO.

TABLE 11 - BIODIESEL PRODUCTION PARAMETERS

Test	Molar ratio MeOH/UCO	Pre-treatment	Catalyst (% w/w)	Acidity (%FFA w/w)	FAME Yield (% w/w)
T1	7.1	No	2.07	4.20	90.37
T2	6.0	No	2.07	5.88	78.52
T3	7.1	No	2.07	9.82	88.24
T4	7.1	Yes	2.07/0.19	9.82-0.13	87.41-62.37

As it can be observed in table 12, all produced samples fulfilled the European standard limits regarding density, iodine value, linolenic methyl ester content, total glycerol as well as all the reaction intermediates. This shows a complete conversion, therefore, good reaction effectiveness. Low flash points indicate non-effective MeOH recovery, which is also reflected in high MeOH contents. Among the measured parameters, free glycerol and sodium were not compliant by all samples showing a possible issue with the exchange resins (that could be improved performing a regeneration with MeOH), or the separation process, or both.

Adding to the glycerol traces in the biodiesel, shown by the analyses, considerable amounts of biodiesel were detected in the glycerol storage tanks too. As high amounts of MeOH in the reaction can improve glycerol solubility in biodiesel, this allows the biodiesel to pour easily with the glycerol when fully opening the separation valve. Perhaps lowering MeOH to oil ratio to 6:1 and optimizing the separation procedure could help improve FAME content and free glycerol values. It was verified that the purity (FAME content) obtained ranged from 93.7 to 94.0 (% w/w).

The water content in T1 was high as expected due to a very ineffective distillation in this test, a step that was improved in the later tests. That water presence explains the high flash point presented by T1 when comparing to the other tests.

TABLE 12 - BIODIESEL CHARACTERIZATION

Property	Unit	**T1**	**T2**	**T3**	**T4**	Limits	Test method
FAME content	% (w/w)	---	---	**94.0**	**93.4**	>96.5	EN 14103
Density at 15°C	Kg/m^3	895.3	886.5	885.8	885.7	860-900	EN ISO 12185
Flash point	°C	113.0	**43.5**	**65.5**	**54.0**	>101.0	EN ISO 2719
Water content	mg/kg	**1741**	456	435	379	<500	EN ISO 12937
Iodine value	$gI_2/100g$	---	---	96.2	99.1	<120.0	EN 16300
Linolenic acid methyl ester	% (w/w)	---	---	1.4	1.2	<12.0	EN 14103
Methanol	% (w/w)	---	---	**0.37**	**0.52**	<0.20	EN 14110
Monoglyceride	% (w/w)	---	---	0.52	0.64	<0.70	EN 14105
Diglyceride	% (w/w)	---	---	<0.10	<0.10	<0.20	EN 14105
Triglyceride	% (w/w)	---	---	<0.10	<0.10	<0.20	EN 14105
Free glycerol	% (w/w)	---	---	**0.032**	**0.093**	<0.020	EN 14105
Total glycerol	% (w/w)	---	---	0.189	0.282	<0.250	EN 14105
Na+K	mg/kg	---	---	**5.9**	**6.5**	<5.0	EN 14538

At the end of all the tests and analysis, a step by step operation manual was constructed in a very comprehensive way. This manual is of utmost importance and value for the company as no previous manual existed before and this was one of the work's goals. This manual has detailed and engineered tips to allow a correct unit operation without production issues, enabling an efficient and effective work.

5 Conclusions and future works

5.1 Conclusions

Biodiesel will be in use in the coming years as a mandatory petrodiesel additive. The use of UCO as feedstock play a major role supplying biodiesel to various sectors such as those of agriculture and transportation. However, using this type of raw material affects production processes and costs as well as the resulting biodiesel characteristics. UCO has high acidity due to degradation caused by heat and food moisture from cooking. Thus, a proper procedure should be applied to operate with this kind of feedstock. The significant variability of the supplied feedstock acidity (4.2-9.82% w/w) must be minimized. Washing the UCO containers from the restaurants with water and pouring it along with the UCO to the storage tank at the supplier plant is a procedure that must be avoided. Permanent contact with water for long periods of time raises the acidity to higher values.

Alkali homogeneous transesterification of TG with MeOH is widely applied at industrial scale. Alkaline homogeneous transesterification using MeOH as reactant and sodium methoxide as the catalyst, has proven to be effective when producing biodiesel from UCO collected in Madeira Island at laboratory tests in Universidade da Madeira and in a pilot plant situated in Grupo Sousa / Metal Lobos Lda. at Madeira Island. The laboratory tests showed the optimum conditions for transesterification for small-scale, thus allowing to start the pilot tests with robust parameters.

We concluded in the laboratory tests that the acidity of the feedstock has high influence in the transesterification yield. High acid values represent FFA present in the feedstock, thus resulting in a saponification reaction when the alkaline catalyst is added. Using pure vegetable oil with low acidity brought, as expected, the higher yield but this would increase the cost of the feedstock to undesired values. It was observed an optimum region of catalyst concentration to be added in the reaction, close to the sample's acid value. For higher amounts, the catalyst remaining will saponify the methyl esters resulted from transesterification. For lesser quantities, the catalyst is not enough to transesterify all the TG.

An effective way to neutralize the high feedstock acidity when using UCO is by adding compound A. This saponification reaction has proven to be effective, lowering the acidity to minimum values, therefore, raising the yields of the remaining neutralized oil. The mass loss related to this reaction is 21.5% (w/w) when 0.25% (w/w) of A is added. This mass

loss values were successfully lowered when a centrifuge was used, and that results in a better global yield.

On the pilot plant tests, the yields were better than on the laboratory tests, considering the feedstock acidity. We concluded that the plant is perfectly functional and fit to achieve good reaction yields. This could be probably due to the capability of the ultrasonic reactor, and the ionic-exchange resins. The main issue is related with by-product glycerol, as its solubility with soaps and other impurities lowers this by-product's commercial value.

The pre-treatment was not so beneficial in the pilot unit test as in the laboratory test. The yields obtained in the pilot plant with high acidity feedstock turned the pre-treatment undesirable. When saponifying the FFA, the mass loss was so high (29% w/w) that the remaining neutralized oil, even if completely transesterified, would not obtain better results than with no pre-treatment.

The analysis on the biodiesel produced showed that even with the feedstock properties being so irregular, some of the parameters present in the EN 14214 were accomplished, therefore pushing for future works in order to improve these values. Further optimization of the procedures and some improvements on the pilot plant could easily turn this plant into a more efficient biodiesel production plant.

5.2 Proposal for future works

The capability of this pilot unit to produce biodiesel has been proven, but, this production procedure is not fully optimized. Here are some key points and suggestions for future works:

- The feedstock received was not adequately prepared for this type of process. Issues like high acidity as well as water and impurities content should be improved. With better filtration and handling this could be easily achieved.
- The flash distillation procedure also needs improvements. At the moment, it is not achieving its full benefit for the pilot unit. Some pimping and instruments changes should be done to enhance this step of the process.
- Glycerol is also an essential part of biodiesel production. Glycerol can be an earning if sold, or an expense if needed to be disposed of. Procedures to improve the glycerol's purity such as fatty acids separation should be taken into consideration.

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6. Appendix

(As the piping and instruments diagram as well as the operation manual are for exclusive use of the company Grupo Sousa / Metal Lobos Lda. both of these parts are written in Portuguese language.)

A. Unidade piloto – Tubagem e Instrumentação

A.1 Lista de instrumentação

- **UCO –** Tanque de óleos alimentares usados (OAU-alimentação)
- **UCO pump –** Bomba de OAU
- **F-0002 –** Filtro de OAU
- **T-0101 –** Tanque de receção de OAU
- **R-0102 –** Reistências de aquecimento eletricas
- **TT-0103 –** Transmissor de temperatura
- **V-0104 –** Válvula manual
- **V-0105 –** Válvula manual
- **V-0106 –** Válvula manual
- **LI-0107 –** Indicador de nível

- **MeOH –** Tanque de metanol
- **$NaOCH_3$ –** Tanque de metiláto de sódio
- **V-0003 –** Válvula manual
- **V-0004 –** Válvula manual
- **T-0201 –** Tanque de mistura de reagentes
- **LI-0202 –** Indicador de nível
- **V-0203 –** Válvula manual
- **V-0204 –** Válvula manual
- **V-0205 –**Válvula manual
- **FI-0206 –** Indicador de fluxo
- **V-0207 –** Válvula manual
- **V-0208 –** Válvula manual

- **T-0209 –** Tanque de recuperação de metanol
- **P-0210 –** Bomba elétrica
- **V-0211 –** Válvula manual
- **V-0212 –** Válvula manual
- **V-0213 –** Válvula manual
- **SG-0214 –** Visor de vidro
- **V-0215 –** Válvula manual
- **LI-0216 –** Indicador de nível

- **T-0301 –** Reator de transesterificação
- **R-0302 –** Resistências de aquecimeto elétricas
- **AG-0303 –** Agitador
- **TT-0304 –** Transmissor de temperatura
- **V-0305 –** Válvula manual
- **V-0306 –** Válvula manual
- **V-0307 –** Válvula manual
- **LI-0308 –** Indicador de nível
- **V-0309 –** Válvula manual
- **P-0310 –** Bomba elétrica
- **V-0311 –** Válvula manual
- **M-0312 –** Pre-misturador
- **X-0313 –** Reator ultrasónico
- **PI-0314 –** Indicador de pressão
- **V-0315 –** Válvula manual
- **V-0316 –** Válvula manual
- **V-0317 –** Válvula manual
- **PP-0320 –** Bomba pneumática

- **T-0401 –** Tanque de sedimentação
- **V-0402 –** Válvula manual
- **V-0403 –** Válvula manual
- **LI-0404 –** Idicador de nível
- **V-0405 –** Válvula manual
- **P-0410 –** Bomba elétrica

- **T-0501 –** Coluna de resinas nº1
- **V-0502 –** Válvula manual
- **V-0503 –** Válvula manual
- **V-0504 –** Válvula manual
- **T-0511 –** Coluna de resinas nº2
- **V-0512 –** Válvula manual
- **V-0513 –** Válvula manual
- **V-0514 –** Válvula manual
- **V-0515 –** Válvula manual
- **SG-0516 –** Visor de vidro

- **T-0601 –** Tanque de destilação de Biodiesel
- **R-0602 –** Resistências de aquecimento elétricas
- **TT-0603 –** Transmissor de temperatura
- **V-0604 –** Válvula manual
- **P-0610 –** Bomba elétrica
- **V-0611 –** Válvula manual
- **V-0611 –** Válvula manual
- **V-0612 –** Válvula manual
- **SG-0613 –** Visor de vidro

- **T-0701 –** Coluna de destilação por flash - Biodiesel
- **LA-0702 –** Atuador de nível
- **PI-0703 –** Indicador de pressão
- **V-0704 –** Válvula manual
- **V-0705 –** Válvula manual
- **P-0710 –** Bomba elétrica
- **SG-0711 –** Visor de vidro
- **F-0720 –** Filtro
- **V-0721 –** Válvula manual
- **V-0722 –** Válvula manual
- **C-0723 –** Contador
- **V-0724 –** Válvula manual
- **V-0725 –** Válvula manual
- **V-0726 –** Válvula manual

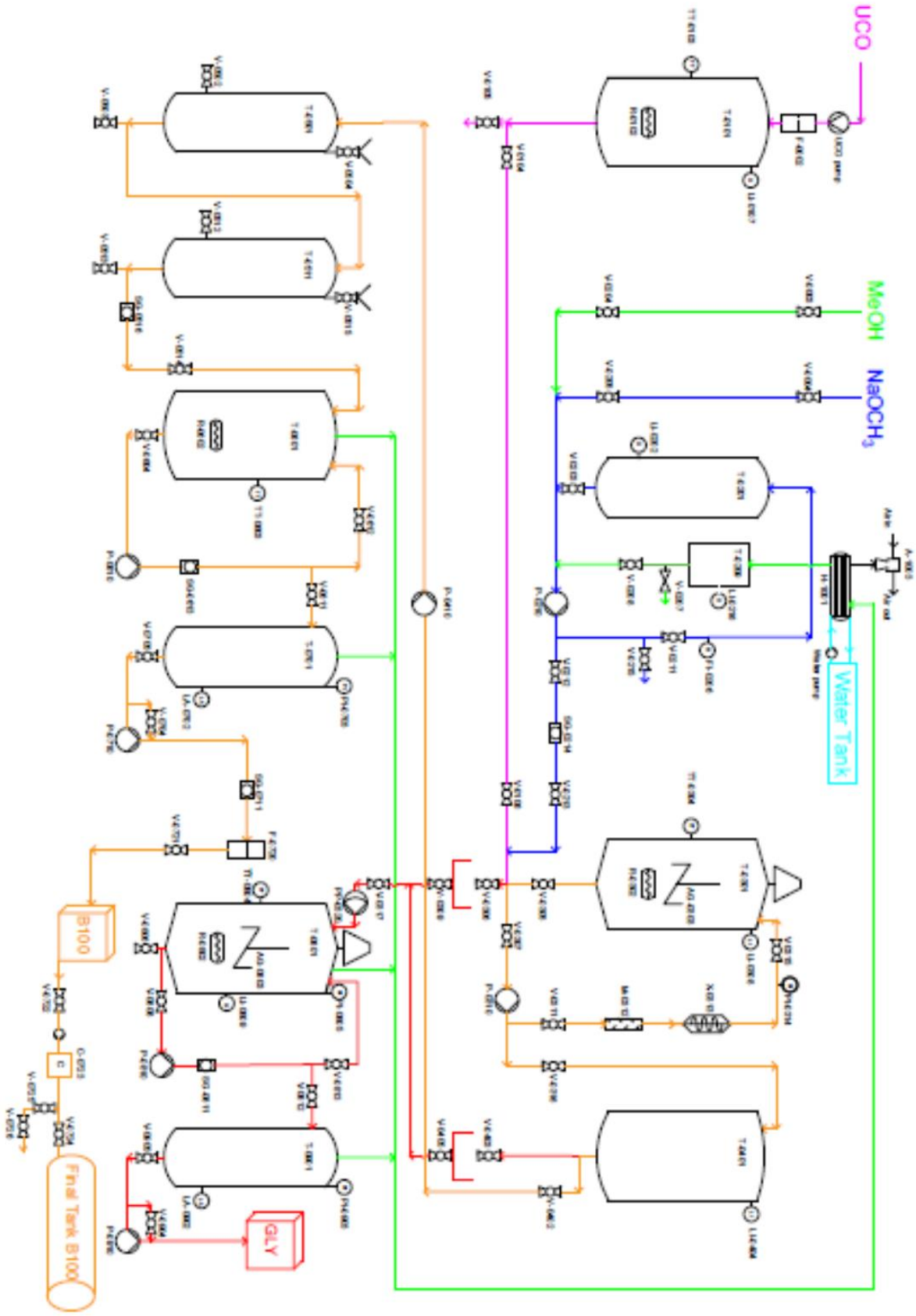
- **B100 –** Tanque de receção de Biodiesel
- **Tanque final de Biodiesel**

- **T-0801 –** Tanque de purificação de glicerol
- **R-0802 –** Resistências de aquecimento elétricas
- **AG-0803 –** Agitador
- **TT-0804 –** Trasmissor de temperatura
- **PI-0805 –** Indicador de pressão
- **V-0806 –** Válvula manual
- **V-0808 –** Válvula manual
- **LI-0809 –** Indicador de nível
- **P-810 –** Bomba elétrica
- **SG-0811 –** Visor de vidro
- **V-0812 –** Válvula manual
- **V-0813 –** Válvula manual

- **T-0901 –** Coluna de destilação por flash - Glicerol
- **LA-0902 –** Atuador de nível
- **PI-0903 –** Indicador de pressão
- **V-0904 –** Válvula manual
- **V-0905 –** Válvula manual
- **P-0910 –** Bomba elétrica
- **GLY –** Tanque final de glicerol

- **H-1001 –** Condensador
- **A-1003 –** Bomba de vácuo Venturi
- **Bomba de água**

A.2 Diagrama



B. Manual de operação da unidade piloto

0. Procedimentos de preparação

Antes de iniciar o processo de produção de biodiesel, várias etapas de preparação / segurança devem ser realizadas:

- Coloque todos os EPI necessários (equipamento de proteção individual, luvas, óculos, roupas, botas ...)
- Ligue todas as luzes
- Feche a porta para o exterior
- Coloque o sinal "Em produção" na porta
- Certifique-se a instalação está limpa e livre de obstáculos
- **Acoplar o tanque de matéria-prima à bomba OAU com a válvula fechada**
- Posicionar a mesa de apoio com as ferramentas necessárias e folhas de registro
- O peso do tanque de matéria-prima deve ser registrado

Nota 1: alguns trapos devem ser mantidos por perto para limpar pequenas fugas imediatamente.

Nota 2: Todas as bombas, agitadores, resistências de aquecimento e reator de ultrassons são elétricos, e ligam-se e desligam-se no quadro elétrico da unidade piloto. (Exceção, bomba P-320 que é pneumática e liga-se e desliga-se ao lado do quadro elétrico da luz)

Nota 3: Todas as válvulas são manuais, e no início da operação todas as válvulas estão fechadas (exceção V-315, sempre aberta)

Nota 4: O vácuo é ligado e desligado manualmente ao lado do quadro elétrico da luz

Nota 5: Este procedimento está preparado para ser seguido passo a passo, segundo a ordem descrita

1. Trasfega para o tanque de receção (T-101) e pré-aquecimento (R-102)

Nota 1: O tanque de receção T-101 tem uma capacidade 2000Lt permitindo armazenar 2 lotes, poupando tempo na produção seguinte.

i. **Ligue o interruptor de alimentação principal** no quadro elétrico da unidade piloto
ii. **Abrir a tampa superior e a válvula de fundo** do tanque OAU
iii. **LIGAR a bomba OAU** e iniciar a trasfega para T-101
iv. Quando todo o OAU estiver no T-101, **desligar a bomba OAU, e fechar a tampa superior e a válvula de fundo do tanque e ligar o aquecimento (R-102, 40 ° C)**.

Nota 2: O tanque de matéria-prima deve ser pesado quando a trasfega termina.
Nota 3: é essencial observar o indicador de nível antes de ligar o aquecimento (R-102), porque se o nível de OAU não atingir o nível da posição das resistências poderá criar um aumento perigoso da pressão no interior do tanque.

2. Trasfega de OAU para o reator (T-301)

Nota 1: quando o tanque de receção é abastecido com 2000Lt, após a trasfega do primeiro lote, o aquecimento deve permanecer ligado mantendo o segundo lote, a 40 ° C, poupando assim tempo para produção seguinte.

i. **ABRIR V-104, V-106, V-307, V-311**
ii. **DESLIGAR as resistências R-102**
iii. **LIGAR a bomba P-310**
iv. Quando 1000Lt de OAU forem trasfegados, **LIGAR o aquecimento (R-302, 55 ° C)**
v. **FECHAR V-106 e V-104**
vi. **ABRIR V-305** para iniciar a recirculação no T-310

3. Mistura de reagentes

Nota 1: Este procedimento pode ser iniciada enquanto o OAU está a ser trasfegado para o T-301

Nota 2: A quantidade de metanol e metilato de sódio, a serem misturados, é calculado previamente de acordo com o peso de matéria-prima e acidez.

Nota 3: É essencial que o metanol seja o último reagente que passa através dos tubos e instrumentos (P & I) porque o metóxido de sódio é muito reactivo e não deve permanecer em contacto com a tubagem por um período prolongado (entre produções).

i. **Abrir a tampa superior e a válvula no fundo** do tanque de metilato de sódio
ii. **ABRIR V-004, V-205, e V-211**
iii. **LIGAR a bomba P-210**
iv. Quando todo o metilato de sódio é trasfegado, **DESLIGAR bomba P-210, FECHAR V-004, V-0205**, **tampa superior e válvula de fundo** do tanque de metilato de sódio.
v. **Abrir a tampa superior e a válvula de fundo** do tanque de metanol
vi. **ABRIR V-003, V-204**
vii. LIGAR bomba P-210
viii. Quando todo o metanol é trasfegado, **DESLIGAR bomba P-210**, **fechar a tampa superior e a válvula de fundo** do tanque de metanol e **FECHAR V-003 e V-204.**
ix. Para iniciar a mistura reagentes, **ABRIR V-203 e LIGAR bomba P-210.**
x. Após 5 minutos de mistura **DESLIGAR bomba P-210 e FECHAR V-203 e V-211**

4. Reação de transesterificação

Nota 1: quando o OAU atinge 55°C no reator R-301, os procedimentos para iniciar a reação podem começar

i. **FECHAR V-305 e DESLIGAR bomba P-310**
ii. **ABRIR V-203, V-212, V-213 e LIGAR bomba P-210** para iniciar a trasfega dos reagentes para o reator R-301
iii. Quando todos os reagentes são trasfegados, **FECHAR V-213, V-212, V-203 e desligar a bomba P-210**
iv. **ABRIR V-305 e LIGAR bomba P-310 para iniciar a recirculação em R-301.**
v. **LIGAR agitador AG-303, e o reator de ultrassons X-313 (50% de potência)**
vi. A reação de transesterificação leva 120 minutos
vii. **Quando a reação está terminada, DESLIGAR agitador AG-303, X-313 e R-302.**
viii. **FECHAR V-311, ABRIR V-316 para iniciar a trasfega da mistura para T-401**
ix. Quando toda a mistura foi trasfegada, **as FECHAR V-316, V-307, V-305 e DESLIGAR bomba P-310.**

Nota 2: é essencial observar o indicador de nível antes de ligar o aquecimento (R-302), porque se o nível de mistura não alcançar o nível de aquecimento, isso irá criar um aumento perigoso da pressão no interior do tanque.

5. Separação

Nota 1: nesta etapa, a mistura divide-se em duas partes, a parte superior é o biodiesel, e a parte inferior é o glicerol. Esta sedimentação deve durar pelo menos 15 horas

i. Para começar a transferir o glicerol para T-801, **ABRIR V-403, V-405, V-317 e LIGAR a bomba P-320**

Nota 2: A válvula V-403 não pode ser aberta completamente, porque demasiado fluxo irá fazer com que algum biodiesel para fluir, juntamente com o glicerol

Nota 3: observe atentamente o indicador de nível LI-809 perto do T-801 para evitar encher completamente o tanque.

Nota 4: prestar muita atenção à cor do líquido que vai escorrendo através da válvula V-403 e fecha-la imediatamente quando o fluido se tornar mais claro. (O fluido inicial, o glicerol é muito mais escuro do que o biodiesel)

ii. Quando todo o glicerol é transferido para T-801, **FECHAR V-317, V-405, V-403 e DESLIGAR P-320**

6. Purificação de biodiesel através de resinas de permuta iónica

i. Para começar a passar o biodiesel pelas colunas de resina, **ABRIR V-402, V-514 e LIGAR bomba P-410**

ii. Quando todo o biodiesel estiver transferido para o tanque T-601, **FECHAR V-514, V-402 e desligar a bomba P-410**

Nota 1: é fundamental observar o indicador de nível antes de ligar o aquecimento (R-602), porque se o nível de biodiesel não atingir o nível de posição da resistência, poderá criar um aumento de pressão perigoso dentro do tanque

7. Destilação de metanol

i. Para iniciar o aquecimento no tanque T-601, **LIGAR aquecimento R-602 (set-point de 110 ° C)**

ii. **ABRIR V-604, V-612 e LIGAR bomba P-610 / P-710**

Nota 1: é fundamental observar o indicador de nível antes de ligar o aquecimento (R-602), porque se o nível de biodiesel não atingir o nível de posição das resistências, poderá criar um aumento de pressão perigoso no interior do tanque.

Nota 2: embora o set-point para R-602 seja de 110 ° C, a temperatura irá subir parando perto de 65 ° C (ponto de ebulição do metanol)

iii. Quando a temperatura de biodiesel parar de subir, **ligar o vácuo e a bomba de água**

Nota 2: quando o vácuo estiver **ON, certifique-se todas as válvulas estão fechadas para evitar a perda de pressão**

Nota 3: A temperatura irá cair à medida que o vácuo aumenta, diminuindo o ponto de ebulição do metanol

Nota 4: deve ser possível escutar o metanol verter para o tanque de recuperação metanol T-209, e depois de algum tempo, será possível ver o nível de metanol a subir (LI-216)

iv. A destilação de metanol deve decorrer durante cerca de duas horas, mas confirmar sempre, observando e escutado o tanque de receção.

Nota 5: Antes de começar a transferir o biodiesel para o tanque de recolha, certifique-se a mangueira depois da válvula V-721 é inserido na tampa superior do tanque

v. Quando o nível de metanol LI-216 parar de subir, **FECHAR V-612, ABRIR V-611, V-705, V-721 e DESLIGAR aquecimento R-602**

Nota 6: as bombas P-610 e P-710 vão ligar e desligar automaticamente assegurando que o biodiesel não ultrapassa o atuador de nível LA-702

Nota 7: quando não há mais biodiesel no tanque T-601, a bomba P-610 vai ficar sempre ON

vi. Quando não há mais Biodiesel no tanque T-601, **DESLIGAR a bomba P-610 / P-710 e Mudar a bomba P-710 de auto para manual**

Nota 8: ao transferir o biodiesel para o seu tanque de recolha, o vácuo pode precisar de ser temporariamente desligado para evitar que o ar que flua a partir do exterior para dentro da tubagem.

vii. Quando não há mais biodiesel no tanque T-701, **FECHAR V-604, V-611, V-705, V-721 e MUDAR a bomba P-710 de manual para AUTO**

viii. Se a qualidade do biodiesel for aprovada, **ABRIR V-722, V-724 e LIGAR a bomba de biodiesel**

ix. Quando todo o biodiesel está no tanque final, **DESLIGAR bomba Biodiesel, FECHAR V-722, e V-724**

8. Purificação do glicerol

Nota 1: purificação de glicerol consiste em destilar o metanol

Nota 2: Este passo pode ser iniciado quando todo o glicerol estiver dentro do tanque T-801

i. Para iniciar o aquecimento no tanque T-801, **LIGAR aquecimento R-802 (valor nominal de 110 ° C)**

ii. **ABRIR V-808, V-813 e LIGAR P-810 / P-910 e agitador AG-803**

Nota 1: é essencial observar o indicador de nível antes de ligar o aquecimento (R-802), porque se o nível de glicerol não atingir o nível de posição das resistências, poderá criar um aumento perigoso da pressão no interior do tanque.

Nota 2: embora o set-point para o R-802 seja de 110 ° C, a temperatura irá subir e depois parar perto de 65 ° C (ponto de ebulição do metanol)

iii. Quando a temperatura de glicerol parar de subir, **LIGAR o vácuo e a bomba de água**

Nota 2: quando o vácuo está ON, certifique-se que todas as válvulas estão fechadas para evitar a perda de pressão

Nota 3: a temperatura irá cair à medida que o vácuo aumenta, diminuindo o ponto de ebulição do metanol

Nota 4: deve ser possível ouvir o metanol a verter para o tanque de recuperação de metanol T-209, e depois de algum tempo, deve ser possível ver o nível de metanol (LI-216) a subir.

iv. A destilação de metanol deve decorrer durante cerca de duas horas, mas confirmar sempre, observando e escutado o tanque de receção.

Nota 5: antes de começar a transferir o glicerol para o seu tanque de recolha, certifique-se que a mangueira depois da bomba P-910 é inserida na tampa superior do tanque

v. Quando o nível de metanol LI-216 parar de subir**, FECHAR V-813, DESLIGAR R-802 e agitador AG-803, ABRIR V-812 e V-905**

Nota 6: as bombas P-810 e P-910 vai ligar e desligar automaticamente assegurar o glicerol não ultrapasse o nível do atuador LA-902

Nota 7: quando não há mais glicerol no tanque T-801, a bomba P-810 irá permanecer sempre ligada

Nota 9: ao transferir o glicerol ao seu tanque de retenção, o vácuo pode precisar de ser temporariamente desligado para evitar o ar que flui a partir do exterior para dentro da tubagem.

vi. Quando não há mais glicerol no tanque T-801, **DESLIGAR bomba-810 P / P-910 e MUDAR P-910 de auto para manual**

vii. Quando não há mais Glicerol o tanque T-901, **FECHAR V-905, V-812, V-808 e MUDAR bomba P-910 de manual para AUTO**

viii. DESLIGAR o vácuo