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CHARACTERIZATION OF BIODIESEL PRODUCTION POTENTIAL FROM WASTE COOKING OIL IN SAN PEDRO SULA, HONDURAS IN 2022

PRIOR TO OBTAINING THE DEGREE OF

ENERGY ENGINEER

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DEDICATION

I dedicate this work to my parents, Omar Enamorado and Dilcia Jerezano. I love you!

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Abstract

Climate change effects are increasing in magnitude and frequency. The global surface mean temperature has increased 1.1°C since 1800. This is mainly due to the greenhouse gasses produced by the usage of fossil fuels as energy resource. It is known that biofuels emit less greenhouse gases than fossil fuels and can decelerate climate change. For example, biodiesel, an alternative biofuel for diesel, produces 74% less greenhouse gasses emissions than diesel. Biodiesel can be produced from vegetable oils, animal fats and even restaurants waste cooking oils. The objective of this research is the characterization of biodiesel production potential from Waste Cooking Oils (WCO) of restaurants in San Pedro Sula, Honduras. This is a step forward for the exploitation of this alternative fuel, and for a transition to cleaner fuels. To characterize this production potential, restaurants were surveyed and asked for samples of their WCO, to which their properties and quality for biodiesel production were analyzed. These oil samples were pretreated, converted into biodiesel, and purified to measure their yields. From the restaurants, data like oil consumption, oil type, and oil disposal were obtained. From the WCO samples, measurements of density, viscosity, water content, acid value, and Free Fatty Acids (FFA) content were made. From the produced biodiesel, measurements of density and viscosity were made. From the production processes, measurements of crude glycerol yield, consumption factors of methanol, potassium hydroxide, sulfuric acid, water, and energy per processed WCO mass were made. These results are to be used to better understand this primary energy resource in the city, help in future prefeasibility and feasibility studies for a biodiesel refinery using WCO from this city restaurants. Also, these results can be used as a base for characterization of biodiesel production potential from WCO in other cities around the world.

Keywords: Renewable energy, Biofuels, characterization, waste cooking oil, biodiesel, production potential, Honduras.

RESUMEN

Los efectos del cambio climático están aumentando en magnitud y frecuencia. La temperatura media de la superficie global ha aumentado 1.1°C desde 1800. Esto se debe principalmente a los gases de efecto invernadero producidos por el uso de combustibles fósiles como recurso energético. Se sabe que los biocombustibles emiten menos gases de efecto invernadero que los combustibles fósiles y pueden frenar el cambio climático. Por ejemplo, el biodiésel, un biocombustible alternativo al diésel, produce un 74% menos de emisiones de gases de efecto invernadero que el diésel. El biodiésel se puede producir a partir de aceites vegetales, grasas animales e incluso aceites de cocina usados. El objetivo de esta investigación es la caracterización del potencial de producción de biodiésel a partir de Residuos de Aceites de Cocina (RAC) de restaurantes en San Pedro Sula, Honduras. Este es un avance para la explotación de este combustible alternativo y para una transición hacia combustibles más limpios. Para caracterizar este potencial de producción se encuestó a restaurantes y se les solicitó muestras de sus RAC, a los cuales se les analizó sus propiedades y calidad para la producción de biodiésel. Estas muestras de aceite fueron pretratadas, convertidas en biodiésel y purificadas para medir sus rendimientos. De los restaurantes se obtuvieron datos como consumo de aceite, tipo de aceite y desecho de aceite. A partir de las muestras de RAC, se realizaron mediciones de densidad, viscosidad, contenido de agua, índice de acidez y contenido de Ácidos Grasos Libres (AGL). A partir del biodiésel producido se realizaron mediciones de densidad y viscosidad. A partir de los procesos de producción se realizaron mediciones de rendimiento de glicerol crudo, factores de consumo de metanol, hidróxido de potasio, ácido sulfúrico, agua y energía por masa de RAC procesada. Estos resultados se utilizarán para comprender mejor este recurso energético primario en la ciudad, ayudar en futuros estudios de prefactibilidad y factibilidad para una refinería de biodiésel que utilice RAC de los restaurantes de esta ciudad. Además, estos resultados pueden utilizarse como base para la caracterización del potencial de producción de biodiésel a partir de los RAC en otras ciudades del mundo.

Palabras clave: Energías renovables, biocombustibles, caracterización, aceite de cocina usado, biodiésel, potencial de producción, Honduras.

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I. INTRODUCTION

Climate change is the increase, in frequency and magnitude, of severe droughts, forest fires, floods, hurricanes, colder winters, hotter summers, polar ice melting, and global warming. The principal cause of climate change is the increase of atmospheric concentration of Greenhouse Gases (GHGs), which intensifies the greenhouse effect. The increase of GHGs is mainly due to the high consumption of fossil fuels, which releases GHG when produced and burned as an energy source for transportation or electricity production.

If fossil fuels are substituted by less contaminant fuels, like biofuels, the climate change can be decelerated. Some biofuels are bioethanol, biogas, and biodiesel. Bioethanol is ethanol that comes from sugar-rich plants and can substitute gasoline. Biogas is methane that comes from decomposition of organic matter, like organic residues or animal stools, and can substitute natural gas. Biodiesel is fatty acid alkyl ester that can be produced from vegetable oils, animal fats and even restaurants waste cooking oils. Biodiesel can substitute petrol diesel, while releasing 74% less GHG than diesel. Even though this last biofuel is known, there are no studies of characterization of biodiesel from restaurants waste cooking oils in big cities of Honduras.

Some studies had evaluated waste cooking oil as feedstock for biodiesel production. Alfonso Alvarez (2013) evaluated the production of biodiesel from waste cooking oil from a neighborhood in Tijuana, Mexico finding that this feedstock has low free fatty acid content making it a great biodiesel feedstock. Putri Primandari & Arafat (2021) evaluated the feasibility of using waste cooking oils from chicken fast foods in Padang, Indonesia, as biodiesel feedstock, finding that these oils exceed free fatty acid and water content requirements and only by an intensive pre-treatment they can be used for biodiesel production. Not all biodiesel production and commercialization from animal fats in Jutiapa, Honduras was economically non-viable because of the low demand and high initial investment. Díaz & Zepeda (2012) made a biofuels diagnostic in Central America with special interest in Honduras concluding that biodiesel produced from straight vegetable oil cannot economically compete with petrol diesel without government incentives in the country. Waste cooking oil quality for biodiesel

production has been analyzed by different methods like near infrared spectroscopy by García Martín & al (2019). they studied the determination of the acidity of waste cooking oils by near infrared spectroscopy, finding that this method can predict its acidity with a R² of 0.970. Sugiarto & al (2021) Analyzed the water content on biodiesel from crude palm oil and biodiesel from virgin coconut oil as diesel engine fuel, finding that biodiesel from crude palm oil absorbs less humidity than biodiesel from virgin coconut oil. For oils with high free fatty acid content, Citra Dewi & Slamet (2019) researched a novel approach of esterification process using heterogeneous photo-catalyst TiO₂ in biodiesel synthesis from waste cooking oil. They conclude that this esterification can reduce up to 45.2% the free fatty acid content in waste cooking oil. For biodiesel production enhancement, Nurul Moulita & al (2019) evaluated the conversion of waste cooking oil into biodiesel using microwaves and high voltage technology obtaining a biodiesel yield of 88.88% within 10 minutes.

In contrast with the past research projects, the actual research is based on a big city of Honduras, which has not been studied and may have an interesting biodiesel production from Waste Cooking Oil (WCO). This Research characterize WCO as a primary energy resource for biodiesel production. Properties, quantity, and quality for biodiesel production were measured from samples of WCO from different city restaurants. Biodiesel was made with each sample and some biodiesel properties, yield, and feedstock consumption were measured to characterize the biodiesel production potential from WCO of the city restaurants.

Restaurants of different types were surveyed to know their oil consumption and disposal. Samples of their WCO were collected. These samples were individually filtered and analyzed. Their density, viscosity, water content, and Free Fatty Acid (FFA) content were measured using, respectively, a U tube densimeter, an experimental viscometer, an oven, a balance, and by titration. Depending on the FFA and water content of each sample, they were pretreated differently to prepare them for biodiesel production. Biodiesel was produced by a base catalyzed transesterification with methanol. Feedstocks and reagents consumption during all the pretreatment, production, and purification processes were measured. Biodiesel yield was measured for each sample. Weighted Arithmetic Mean (WAM) were calculated for the consumption and yield variables from the samples to estimate a biodiesel production potential of the city restaurants.

This research is structured as follows: Chapter II identifies the problem and its context. Chapter III presents the theoretical framework that supports this research. Chapter IV explains the methodology used to obtain the results. Chapter V shows the obtained results. Chapter VI presents the conclusions. Chapter VII gives recommendations for future projects or research. Finally, Chapter VIII explains the applicability of the conclusions.

II. PROBLEM IDENTIFICATION

In this chapter is stablished the thesis' problem to solve, its historical background of how the problem arises and its importance to society.

2.1 PRECEDENTS OF THE PROBLEM

According to the United Nations (2020), climate change is a long-term change in climatological properties and patterns of a region or the entire world. Climate change is a reality, every year we experience more severe droughts, forest fires, floods, hurricanes, colder winters, hotter summers, and polar ice melting. Since the 1800's we have experienced a continuously global mean temperature rise of about 1.1°C, this increase is called global warming. Studies estimate a 1.5°C rise in the global mean temperature will cause an unreturnable point for human existence.



Figure 1: "Change in global surface temperature (annual average) as observed and simulated using human & natural and only natural factors (both 1850–2020)" (IPCC, 2021, pg 6)

Source: IPCC (2021)

This global warming is due to a phenomenon called greenhouse effect. This effect is related to the working principle of a greenhouse where, thanks to the glass roof and walls, the inside is warmer than the outside. The high frequency light coming from the sun has no problem passing through the glass, but once it is absorbed by the plants a part of it is remitted back as low frequency light, and it cannot escape to the outside through the glass. The glass reflects this low frequency light back to the inside making itself a heat trap. (University of California Museum of Paleontology, 2022)

Joseph Fourier, French mathematician and physicist, proposed in 1820 that the Earth, due to its temperature, irradiates energy as low frequency light to space. And maybe some of that energy is kept inside the atmosphere due to the air acting as the glass of a greenhouse. Later in 1850 Eunice Newton Foote experimented with glass cylinders containing different gasses exposed to sunlight. She detected that air containing high water vapor concentration was hotter than dry air, and even hotter with CO₂. She concluded that some gasses act as the glass wall of a greenhouse and now these are called greenhouse gasses (GHGs). Since the industrial revolution, the climatological negative effects of burned fuels emissions from the contemporary economy and industry were more notorious over time. In 1989 the United Nations established the IPCC, Intergovernmental Panel on Climate Change, to study the causes and effects over climate change and global warming (History.com Editors, 2022).

The United Nations, (2020) states that gasses like water vapor, CO₂, CH₄, and NO₂ are greenhouse gasses. These greenhouse gasses are emitted by the combustion of any fuel like coal, wood, gasoline, diesel, natural gas, and many others. Humans need to consume these fuels as energy sources to keep their lifestyle and economic growth.

The University Corporation for Atmospheric Research, (2022) declares that Atmospheric CO₂ concentration in the 1800s were around 270 parts per million (ppm) at the beginning of the industrial revolution. In 2015 the concentration of CO₂ was about 400 ppm.



Figure 2: How a greater concentration of CO₂ prevents low frequency light from escaping Earth's atmosphere Source: University Corporation for Atmospheric Research (2022)

A solution to global warming is to change our energy sources from fossil fuels to low GHG emission energy sources, green energy sources. Biofuels, from plants or organic matter, are an alternative for fossil fuels. Biofuels are renewable if their sources (plants) are planted at the same or higher rate that the biofuel is consumed. Biofuels are green, low GHG emissions, because their carbon emissions are consumed by plant photosynthesis making a cycle where the same CO₂ they emit is recycled by the plant that originates them at first. In the other hand fossil fuels' emissions come from carbon deposits that were underground for millions of years. (Dahiya, 2020)

Life Cycle Emissions (LCE) are the emissions emitted during all stages of the production and consumption of a product. LCE from biodiesel are 74% less than that of petrol diesel (U.S.A. Department of Energy, 2008).

According to Dahiya (2020) one of the many biofuels is biodiesel. Biodiesel may substitute petroleum diesel in the same applications. Biodiesel can be produced from vegetable oils or animal fats. Even used cooking oil is a valid feedstock to produce biodiesel.

In a big city most restaurants use vegetable oils to cook, and once it is used, they throw it away. There is a big potential for producing biodiesel from restaurants' waste cooking oil and help the actual global warming crisis.

2.2 DEFINITION OF THE PROBLEM

A valuable renewable fuel potential from cities' wastes is being ignored and wasted in big cities of Honduras. In all restaurants, where cooking oil or animal fats are used, exist the potential of producing a fuel from those waste. Biodiesel, an organic and renewable fuel that can substitute petroleum diesel, can be produced from waste cooking oils and animal fats but nowadays this opportunity is being ignored in San Pedro Sula, Honduras, which is one of the biggest and most economically productive cities in the country. In addition, in this city, many restaurants have troubles managing their waste cooking oil and there is no municipal system to especially collect and treat this residue. Clearly there is a big economic opportunity of producing a valuable product. But how big is the biodiesel production potential that is being wasted in San Pedro Sula, Honduras by 2022?

2.3 JUSTIFICATION

The unsustainable use of fossil fuels is threatening humans' existence by emitting GHGs which accelerates global warming. A low GHGs emitting alternative to fossil fuels are biofuels, such as biodiesel. Biodiesel, by coming from plants that absorb CO₂, is considered a renewable low

emission fuel. Biodiesel may substitute petroleum diesel and emit less GHGs than it. Biodiesel is mainly produced from vegetable oils, but humans need these oils for other purposes, mainly for cooking. Studies have shown that biodiesel may also be produced from used cooking oil. In San Pedro Sula, Honduras many restaurants have troubles managing their waste cooking oil and there is no municipal system to especially collect and treat the waste cooking oil. All this used cooking oil is being wasted, instead of being converted into a valuable renewable fuel like biodiesel; and by this increasing the city economic growth while helping the actual climate crisis.

2.4 RESEARCH QUESTIONS

- How many kilograms of each type of cooking oil are consumed per month by the studied restaurants?
- How many kilograms of each reagent are needed to convert one kilogram of each sample of waste cooking oil into biodiesel?
- How many kilograms of biodiesel are produced per kilogram of each sample of waste cooking oil?
- How many kilograms of biodiesel per month could be produced from all the waste cooking oil of these restaurants in San Pedro Sula, Honduras?
- How many kilograms of GHGs emissions per month could be avoided if this biodiesel substitute its equivalent in petroleum diesel?
- What are the Honduran government incentives for producing biodiesel from waste cooking oil?
- How economically viable is to produce biodiesel from the waste cooking oil of these restaurants in San Pedro Sula, Honduras?

2.5 OBJECTIVES

2.5.1 GENERAL OBJECTIVES

Characterize the biodiesel production potential from waste cooking oil of restaurants in San Pedro Sula, Honduras to help with the city waste management and with the transition to low carbon emissions fuels.

2.5.2 Specific Objectives

- Select a group of restaurants to study in San Pedro Sula, Honduras, based on availability and willingness to participate on the study.
- Characterize quantitative and qualitative the vegetable oil consumption from these restaurants in San Pedro Sula, Honduras, by interviewing restaurant managers.
- Recollect samples of waste cooking oil from restaurants in San Pedro Sula.
- Analize the waste cooking oil quality, by titration, for biodiesel production.
- Produce biodiesel, by transesterification, from collected oil samples.
- Analize the biodiesel yield from the transesterified samples.
- Characterize quantitative and qualitative the biodiesel production potential from the waste cooking oil of these restaurant in San Pedro Sula, Honduras.

2.6 RESEARCH CONCEPTUAL DIAGRAM





Figure 3: Conceptual diagram of the actual scenario of restaurants' waste cooking oil management.

Source: Own Elaboration

2.6.2 PROPOSED SITUATION



Figure 4: Conceptual diagram of the proposed scenario for restaurants' waste cooking oil management.

Source: Own Elaboration

2.6.3 PROCESSES DIAGRAM OF A BIODIESEL BIOREFINERY



Figure 5: Production processes diagram of biodiesel biorefineries. The orange box represents the biorefinery limits to show its inputs and outputs.

Source: Own Elaboration

III. THEORETICAL FRAMEWORK

In this chapter is explained all the fundamental concepts, theory, and proven experiments to understand fuels, organic chemistry for oils, biodiesel, biodiesel properties, analysis, and production.

3.1 THERMAL MOTORS AND DIESEL ENGINES

There exist many types of thermal motors which convert thermal energy into mechanical energy. Some thermal motors are gas turbines, vapor turbines, gasoline engines, diesel engines, and Stirling engines. Motors can be divided by their movement as rotatory or alternative, by the working fluid as gaseous fluid or gas-liquid fluid, by their fuel combustion system as external or internal combustion, and by their thermodynamic cycle as Otto, Diesel, Rankine, Ericsson, Stirling, Brayton, and Carnot cycle. The Diesel motor was initially proposed and created by Rudolph Diesel, a German engineer. This motor is an alternative, gaseous working fluid, internal combustion, and runs in a diesel thermodynamic cycle. What makes this motor unique is the diesel cycle from which it gets its name. Diesel cycle is like the Otto cycle with the difference that the fuel in the Diesel cycle is ignited by the high pressure and high temperature of the air in the cylinder instead of a high energy spark as in the Otto cycle. Diesel cycle allows greater compression ratios which increase the efficiency (Çengel, Boles, & Kanoğlu, 2019).



Figure 6: Main difference between gasoline and diesel engine ignition system. Source: (Çengel, Boles, & Kanoğlu, 2019).



Figure 7: Comparison between Otto cycle and Diesel cycle. TDC is Top Dead Center. BDC is Bottom Dead Center. Source: (Çengel, Boles, & Kanoğlu, 2019)



Figure 8: Comparison between Otto cycle and Diesel cycle Efficiency. r^{*c*} *is called the cutoff ratio, and it is the ratio of the cylinder volumes after and before the combustion process in a diesel engine.*

Source: (Çengel, Boles, & Kanoğlu, 2019)

The first Diesel engine made by Rudolph Diesel in 1900 was presented in a Paris scientific exposition and operated with peanut oil as fuel. Nowadays it operates with petrol diesel as fuel due to its lower price. Petroleum diesel and vegetable oils have similar combustion properties but different physical and chemical properties which need to be considered for the tank, pump, and engine construction. (Knothe, History of Vegetable Oil-Based Diesel Fuels, 2010)

3.1.1 REQUIREMENTS OF DIESEL MOTOR'S FUELS

Diesel motors are designed to work by highly compressing air to reach pressures and temperatures where the fuel will ignite, initiate combustion, by itself. Some important combustion properties for diesel fuels are flash point, cetane number and heat of combustion. Flash point is the temperature at which the fuel ignites. Most vegetable oils have greater flash points than petrol diesel. Cetane number is a value that determines the delay time from fuel injection to fuel combustion. The greater the cetane number, the less delay time. Most vegetable oils have lower cetane number than petrol diesel. The heat of combustion is the energy produced by each combusted kilogram of fuel (Demirbas, 2008).

•		•
Combustion Property	Vegetable Oils	Petrol Diesel
Flash point [°C]	226 ~ 275	52 ~ 77
Cetane Number [-]	27.6 ~ 52.9	46 ~ 55
Heat of Combustion [MJ/kg]	39.3 ~ 39.8	45.3 ~ 46.7

Table 1: important combustion properties of vegetables oils and petrol diesel

Source: (Demirbas, 2008)

Using vegetable oils as diesel engines fuel will decrease engine life by producing an excess of carbon deposits buildup (coking) and buildup of vegetable oils in the engine lubricant. This happens mainly because of vegetable oil high viscosity, which is more than 10 times higher than petrol diesel (Department of Energy, USA, 2020). This high viscosity force the injectors to do more work, the fuel is poorly atomizated and the combustion is incomplete. (Knothe, 2010)



Figure 9: viscosity of diesel and sunflower oil at different temperatures. Source: (Department of Energy, USA, 2020)

There exist many methods to reduce the viscosity of vegetable oils, some of which are blending, esterification, transesterification, micro-emulsification, and pyrolysis. The most used method is transesterification of vegetable oils to produce a less viscous fuel named biodiesel (Caetano, Ribeiro, Ribeiro, Baptista, & Monteiro, 2019).

3.2 FUELS

Fuels are any material (solid, liquid or gas) that can be combusted (burned) to produce thermal energy (heat). Chemically speaking, a fuel is mostly composed of carbon and hydrogen that when exposed to oxygen, certain temperature, and pressure, will chemically react with oxygen to finally produce CO₂, H₂O, and a net excess of energy as heat (Çengel, Boles, & Kanoğlu, 2019).

3.2.1 FOSSIL FUELS

Fossil fuels were produced by decomposition of organic matter under high temperatures and pressures during millions of years. Chemically, fossil fuels are mostly

composed by hydrocarbons like alkanes, alkenes, and aromatics among other hydrocarbons. The most common fossil fuels are coal, gasoline, diesel, liquified petroleum gas (LPG), and natural gas. Coal is a solid fossil fuel composed mainly of pure carbon molecules and is found in underground mines. Gasoline and diesel are liquid fuels with different boiling points and densities. Both are extracted from crude petroleum buried underground. Natural gas is a gas trapped in underground deposits and is mainly methane (CH₄) with other hydrocarbons (Dahiya, 2020).

3.2.2 BIOMASS AND BIOFUELS

Biomass is any organic material that comes from a recent living organism. This includes but is not limited to plants, wood, fruits, vegetables, oils, fats, lipids, sugar, animal flesh, organic residues, and dung. Biofuels are any fuels that its origin can be traced back from biomass. This includes but is not limited to wood, charcoal, vegetable oil, bioethanol, biodiesel, and biogas (Dahiya, 2020).

3.2.3 VEGETABLE OILS AND ANIMAL FATS

Vegetable oils are lipids that comes from vegetables, oilseeds, and other plants. Some examples are canola oil, corn oil, soybean oil, cocoa butter, sunflower oil, olive oil, palm oil and peanut oil. Vegetable oils are used in the food industry to cook at higher temperatures as they have high flash point, and their boiling point is higher than that of water. Animal fats, like animal tallow, are lipids that comes from animals. Vegetable oils, as written before, can be used as fuels, especially as diesel engine fuel (Demirbas, 2008). The use of these lipids as energy sources date back to around 15,000 years, when were used as lamp fuel for lighting (Bryant & Love, 2017).

3.2.4 BIODIESEL

Biodiesel is a sustainable, renewable, and biodegradable alternative fuel for petroleum diesel. Biodiesel comes from lipids, like vegetable oils and animal fats, by a process called transesterification. It is made to solve the problems of vegetable oils high viscosity, by being almost ten times less viscous than vegetable oils, but still a little more viscous than petrol diesel (Caetano, Ribeiro, Ribeiro, Baptista, & Monteiro, 2019).

Table 2: viscosity comparison between diesel engine fuels.

Physical Property	Vegetable Oils	Biodiesel	Petrol Diesel
Viscosity at 40°C [mm ² /s]	39.2 ~ 65	3.5 ~ 5	2 ~ 4.5

Source: (Caetano, Ribeiro, Ribeiro, Baptista, & Monteiro, 2019)

3.3 ORGANIC CHEMISTRY FOR BIODIESEL

Organic chemistry is the area of chemistry that studies the properties and behavior of organic matter, the composition of living beings. That is, matter composed mainly by carbon molecules and to a lesser extent by other atoms like hydrogen, oxygen, nitrogen, sulfur, and phosphorus (McMurry, 2012).

To understand biodiesel production and chemical properties it is indispensable to have some background in its organic chemistry.

3.3.1 Organic Functional Groups

It exists millions of different organic compounds, but they can be categorized in groups according to their chemical composition. This groups are called functional groups. Most members of a functional group will have similar properties and will undergo same reactions in similar conditions. Some common functional groups are:

- Alkanes
- Alkenes
- Alkynes
- Alcohols
- Ethers
- Aldehydes
- Ketones
- Carboxylic Acids
- Esthers

(Burns, 2011).

Below are explained the important functional groups involved in biodiesel production.

3.3.2 Alkanes

Alkanes are carbon chains with only simple bonds between them. Their chemical composition

is C_nH_{2n+2}. Alkanes are non-polar compounds, so they are insoluble in water but very miscible

in each other and other non-polar solvents (Silberberg, 2013).



Figure 10: Formulas, molar masses (in g/mol), structures, and boiling points (in $^{\circ}$ C at one atm pressure) of the first 10 unbranched alkanes.

Source: (Silberberg, 2013)

3.3.3 Alcohols

Alcohols are carbon structures that have one or more OH group bonded to it. Some examples of alcohols are methanol (CH₃OH), ethanol (CH₃CH₂OH) and glycerol (glycerin) (Burns, 2011).



alcohol group

Figure 11: Alcohol group Source: (Silberberg, 2013)

In biodiesel production, methanol and ethanol are used as feedstock to make biodiesel, and glycerol is a byproduct of the process (Demirbas, 2008).

3.3.4 CARBOXYLIC ACIDS

Carboxylic acids are polar carbon structures with a carboxylic group bonded to it, they are also weak acids (Holum, 1999).



carboxylic acid group

Figure 12: Carboxylic acid group

Source: (Silberberg, 2013)

These compounds have many important reactions for biodiesel production. In a process called esterification, carboxylic acids react with alcohols to form esters, which will become biodiesel. Vegetable oils and animal fats are composed, besides others, by long chain carboxylic acids called fatty acids (Holum, 1999).

3.3.5 Esters

Esters are compounds formed by the union of carboxylic acids and alcohols. This reaction is called esterification (McMurry, 2012).



ester group

Figure 13: Ester group

Source: (Silberberg, 2013)

Vegetable oils, animal fats and biodiesel are mainly esters, but with different alcohols and carboxylic acids (Dahiya, 2020).

3.3.6 DIRECT ESTERIFICATION

Direct esterification, also known as Fischer esterification, is the production of an ester by reacting a carboxylic acid with an alcohol in presence of an acid catalyst like for example hydrochloric acid (HCl) (McMurry, 2012).



Source: (Silberberg, 2013)

Direct esterification is an equilibrium reaction. The opposite reaction of esterification is hydrolysis, where an ester and a water molecule produce an alcohol and a carboxylic acid. To

determine which process will occur an excess of one group of reagents must be introduce o removed and the Le Châtelier principle governs the reaction (Holum, 1999).

3.3.7 TRANSESTERIFICATION

Transesterification, also known as alcoholysis, is the process of changing the alcohol of an ester for another alcohol and by this producing a different ester. Transesterification is an equilibrium reaction, so according to the Le Châtelier principle, to produce more reagents from one side, an excess of reagents from the other side should be introduced (McCarthy, Melman, Reffell, & Gordon-Wylie, 2020).



Figure 15: General reaction for transesterification. Both the forward and backward reactions can be catalyzed by acid or base. The equilibrium is generally shifted by increasing the desired esters' alcohol concentration.

Source: (McCarthy, Melman, Reffell, & Gordon-Wylie, 2020)

3.3.8 BIOMOLECULES

Biomolecules are molecules present in living organisms. Biomolecules are divided into families with different properties and functions in living organisms. The most common biomolecules are carbohydrates, lipids, proteins, vitamins amino acids, and nucleic acids (Burns, 2011).

3.3.9 LIPIDS

Lipids are hydrophobic biomolecules, that means insoluble in water. This is because of their nonpolar structure that makes them only soluble in nonpolar solvents. The main purpose of lipids in living organisms is to store energy. Some lipids are fatty acids, triglycerides, diglycerides, monoglycerides, and phospholipids. These lipids constitute oils and fats (Burns, 2011).

3.3.10 FATTY ACIDS

Are long chain carboxylic acids. They can be saturated, monounsaturated, or polyunsaturated. When saturated, all the carbons in the carbon chain have as much hydrogen bonds as they can have, the fatty acids are saturated of hydrogen, and there are no double bonds between carbons in the carbons chain. When monounsaturated there exist one doble bond between two carbons in the carbon chain and the fatty acid does not have as much hydrogens as its structure allows it to have. When polyunsaturated there exist two or more double bonds between carbons in the carbon chain, and the fatty acid does not have as much hydrogens as its structure allows it to have. When polyunsaturated there exist two or more double bonds between carbons in the carbon chain, and the fatty acid does not have as much hydrogens as its structure allows it to have. Fatty acids may also have "cis" and "trans" bonds, which is a geometrical characteristic of bonds. This bond's property is important in humans' diet and health. Many studies show that high consumption of fatty acids with high content of trans bonds produce cardiovascular diseases (Burns, 2011).

3.3.11 TRIGLYCERIDES

Triglycerides, also known as triglycerols or triacylglycerols, are triesters formed by one molecule of glycerol (glycerin), which is an alcohol, and three fatty acid molecules, which are long carbon chain carboxylic acids, these can be the same or different fatty acids. Triglycerides are the main molecules of oils and fats (McMurry, 2012).


Figure 16: General structure of a triglyceride.

Source: (McMurry, 2012)



Figure 17: A hypothetical triglyceride containing oleic (monounsaturated), linoleic (diunsaturated), and linolenic (triunsaturated) chains.

Source: (McCarthy, Melman, Reffell, & Gordon-Wylie, 2020)

3.3.12 CHEMISTRY OF OILS AND FATS

Oils and Fats are triglycerides. Popularly oils come from vegetable, seeds, and plants; and fats come from animals. Chemically, the main difference between them is that animal fats have more saturated fatty acids in their triglycerides and vegetable oils have more mono and polyunsaturated fatty acids in theirs. Vegetable oils tend to be more liquid and less viscous than fats. Animal fats tend to solidify at higher temperatures than vegetable oils. The more saturated fatty acids have a triglyceride, the more solid will it be, as it happens with animal tallow and coconut oil (Burns, 2011).

Species	16:0	18:0	18:1	18:2	18:3	Others
Peanut	11	2	48	32	0	7
Soybean	11	4	24	54	7	0
Oil-seed rape/Canola	4	2	60	22	10	2
Flax/Linseed	3	7	21	16	53	0
Sunflower	7	5	19	68	1	0
Oil palm kernel	8	3	15	2	0	72*
Oil palm mesocarp	45	4	40	10	0	1
Jatropha	14	7	45	33	0	1

Table 3: Percentage distribution of fatty acids in different oils and fats

*Palm kernel oil is rich in short-chain saturated fatty acids: 4% 10:0, 48% 12:0, 16% 14:0

Source: (Bryant, Fatty Acids, Triacylglycerols and Biodiesel, 2017)

Sample	16:0	16:1	18:0	18:1	18:2	18:3	Others
Cottonseed	28.7	0.0	0.9	13.0	57.4	0.0	0.0
Poppyseed	12.6	0.1	4.0	22.3	60.2	0.5	0.0
Rapeseed	3.8	0.0	2.0	62.2	22.0	9.0	0.0
Safflowerseed	7.3	0.0	1.9	13.6	77.2	0.0	0.0
Sunflowerseed	6.4	0.1	2.9	17.7	72.9	0.0	0.0
Sesameseed	13.1	0.0	3.9	52.8	30.2	0.0	0.0
Linseed	5.1	0.3	2.5	18.9	18.1	55.1	0.0
Wheat grain	20.6	1.0	1.1	16.6	56.0	2.9	1.8
Palm	42.6	0.3	4.4	40.5	10.1	0.2	1.1
Corn marrow	11.8	0.0	2.0	24.8	61.3	0.0	0.3
Castor	1.1	0.0	3.1	4.9	1.3	0.0	89.6
Tallow	23.3	0.1	19.3	42.4	2.9	0.9	2.9
Soybean	11.9	0.3	4.1	23.2	54.2	6.3	0.0
Bay laurel leaf	25.9	0.3	3.1	10.8	11.3	17.6	31.0
Peanut kernel	11.4	0.0	2.4	48.3	32.0	0.9	4.0
Hazelnut kernel	4.9	0.2	2.6	83.6	8.5	0.2	0.0
Walnut kernel	7.2	0.2	1.9	18.5	56.0	16.2	0.0
Almond kernel	6.5	0.5	1.4	70.7	20.0	0.0	0.9
Olive kernel	5.0	0.3	1.6	74.7	17.6	0.0	0.8
Coconut	7.8	0.1	3.0	4.4	0.8	0.0	65.7

Table 4: Percentage distribution of fatty acids in different oils and fats

Castor oil contains 89.6% ricinoleic acid.

Bay laurel oil contains 26.5% of 12:0 and 4.5% of 14:0 fatty acids.

Peanut kernel oil contains 2.7% of 22:0 and 1.3% of 24:0 fatty acids.

Coconut oil contains 8.9% of 8:0, 6.2% of 10:0, 48.8% of 12:0, and 19.9% of 14:0 fatty acids.

Source: (Demirbas, 2008)

3.3.13 TRANSESTERIFICATION OF TRIGLYCERIDES (OILS AND FATS) INTO FATTY ACIDS METHYL ESTERS (FAME-BIODIESEL)

If the three fatty acids molecules bonded to the glycerol molecule undergoes a transesterification with methanol or ethanol, three molecules of fatty acids methyl esters (FAME), or ethyl esters (FAEE), will be formed. FAMEs and FAEEs are the chemical composition of biodiesel. FAMEs and FAEEs have similar combustion and chemical properties. When to use methanol or ethanol to produce biodiesel depends on the alcohol price and availability. Around the world, FAME is the most common biodiesel produced (McCarthy, Melman, Reffell, & Gordon-Wylie, 2020).



Figure 18: General transesterification of triglycerides to biodiesel

Source: (Knothe, 2010)



Figure 19: Examples of fatty acids methyl esters (Biodiesel), methyl oleate (top), methyl linoleate (middle), and methyl linolenate (bottom).

Source: (Dahiya, 2020)



Figure 20: Acid- or base-catalyzed transesterification reaction mechanism

Source: (Dahiya, 2020)

The transesterification process can be analyzed and quantified by methods like Gas Chromatography (GC), High Performance Liquid Chromatography (HPLC), Nuclear Magnetic Resonance (NMR) spectroscopy, Near Infrared (NIR) spectroscopy, and Fourier-Transform Infrared (FTIR) spectroscopy (Knothe, 2010).

3.3.14 BIODIESEL AND PETROL DIESEL CHEMICAL STRUCTURE COMPARISON

The figures below show how similar are the structures of diesel and biodiesel. The oxygen atoms in the biodiesel make it a better combustible having a cleaner and faster combustion (McCarthy, Melman, Reffell, & Gordon-Wylie, 2020).



Figure 21: Hexadecane (C₁₆H₃₄), also known as cetane, is a common petrol diesel molecule. Source: (National Library of Medicine, 2022)



Source: (Röttig, 2010)

3.3.15 SAPONIFICATION OF FREE FATTY ACIDS AND TRIGLYCERIDES

Saponification is the process of producing soaps from fatty acids in presence of a strong base like NaOH or KOH (Holum, 1999).



Figure 23: General Saponification Reaction. In this reaction the carboxylate ion is a soap.

Source: (Carey & Giuliano, 2017)

Saponification can also occur with the fatty acids of a triglyceride in presence of a strong

base like NaOH or KOH (McMurry, 2012).



Triglycerid

Figure 24: Saponification of triglycerides

Source: (McMurry, 2012)

3.3.16 SOAPS

Soaps are organic compounds made from fatty acids and an alkaline metal like sodium (Na) or potassium (K). Soap main characteristic is that it is a good polar solvent and a good non-polar solvent at the same time. This occurs because the alkaline end is an ionic and polar structure, and the hydrocarbon end is a non-polar structure. So, soaps can mix well with both types of solvents (Holum, 1999).



Sodium stearate [CH₃(CH₂)₁₆CO₂Na]

Figure 25: A soap structure with its electrostatic distribution.

Source: (Carey & Giuliano, 2017)



Figure 26: soaps capturing fats and other non-polar compounds with their carbon chain. This "capsules" then can be dragged by water pulling from the polar end of soaps.

Source: (Holum, 1999)

Soaps formation can be a problem if the vegetable oils or animal fats have too much free fatty acid or water concentration and a basic catalyst is used during transesterification. This will produce too much soap that will highly reduce the biodiesel yield (Demirbas, 2008).

3.4 BIODIESEL PRODUCTION PROCESSES

In this section are discussed all the methods, considerations, and procedures used to produce biodiesel at a low scale.

3.4.1 FEEDSTOCK SELECTION

Biodiesel production feedstock includes vegetable oils or animal fats. Some examples are animal tallow, animal fats, palm, canola, corn, olive, soybean, avocado, peanut, and fish oil. When selecting a feedstock, economic factors like the price and availability, and technical factors like free fatty acids (FFAs) and Water content, must be considered. In some countries, there could be a greater production of certain oil among others, or some residues may be highly abundant and available, like waste cooking oil, animals' tallow or fats, making these a cheap and suitable feedstock (Clarke, 2017). Biodiesel feedstock can represent up to 70% or 80% of total production costs. Production costs may be reduced by up to 50% to 70% by using waste cooking oil or animal fats (Caetano, Ribeiro, Ribeiro, Baptista, & Monteiro, 2019).

Feedstock water and FFAs content are important for biodiesel production. During the transesterification process another reaction is taking place at the same time which is saponification. As explained in section 3.3.15, if FFAs are mixed with a base catalyst, like the one used in the transesterification process, soaps will be produced. Soaps will stick to biodiesel and will drag biodiesel away during decantation and water washing, reducing the biodiesel total yield. Also, the greater the water content present in the transesterification, the more saponification reactions will occur. When cooking oils are used in restaurants and are heated

to very high temperatures, the oils tend to degrade, and many fatty acids are released from the glycerol producing "free fatty acids". Waste cooking oils and animal fats have high content of FFAs, greater than 5% m/m. Also cooking oils are used with food, that contaminates the oil with water, salts, and other species. Feedstocks with high water and FFAs content must undergo a pretreatment to reduce these impurities. These pretreatments increase energy and reagents consumption. Therefore, feedstocks with low water and FFAs content, like unused refined oils, are preferable, having greater biodiesel yield and less energy and reagents consumption (Caetano, Ribeiro, Ribeiro, Baptista, & Monteiro, 2019).

Feedstock	FFAs content [% m/m]
Refined vegetable oils	<0.05%
Crude vegetable oil	0.3% ~ 0.7%
Restaurant waste grease	2% ~ 7%
Animal fat	5% ~ 30%
Trap grease	40% ~ 100%

Table 5: FFAs mass concentration in different biodiesel feedstocks

Source: (Dahiya, 2020)

3.4.2 FEEDSTOCK ANALYSIS

As mentioned before, vegetable oils and animal fats, depending on their origin, may have too much FFAs and water content. Feedstocks FFAs and water content must be analyzed before transesterification to conclude if it is feasible to transesterify having a low soap production. FFAs content can be analyzed by a potentiometer or a titration method in a feedstock sample. Water content can be analyzed using methods like evaporation, distillation, xylene method, and Coulometric Karl-Fischer Titration. If none of these complex machines or methods are available, water content can be estimated by drying a feedstock sample and calculating its weight loss. This method is not so precise but it is helpful enough (Demirbas, 2008).

In FFAs titration, the objective is to determine how many milligrams of a base catalyst, like NaOH or KOH, is needed to neutralize the FFA in the oil. As these bases have the same equivalent of a fatty acid, one mol of base neutralizes one mol of FFA in the oil. If a basic water solution of NaOH or KOH with a known molarity is poured slowly into the oil, at some point the oil will be neutralized and then became basic. A pH indicator should be poured in the oil solution to show when the oil became basic. Phenolphthalein is the indicator used for this method, which change to a pink color when the pH become 8.5. oil is insoluble in water so to mix the basic water solution with oil, a solvent like isopropyl alcohol is needed. The volume of basic water needed, to change the color of the oil solution to pink for more than 30 seconds, is used to determine the amount of moles of KOH or NaOH needed to neutralize the moles of FFA in the tested oil.

For biodiesel production, some authors establish FFAs content must be less than 0.5%(m/m) (Caetano, Ribeiro, Ribeiro, Baptista, & Monteiro, 2019), others less than 2%(m/m) (Pruszko, 2020), others less than 3%(m/m) (Clarke, 2017), and in the worst case FFAs content must be less than 5%(m/m) but in this case, due to the catalyst loss, additional base catalyst must be added to keep the reaction and soap formation must be expected during transesterification (Gerpen & Knothe, 2010).

Water content must be below 0.5% m/m of oil (Caetano, Ribeiro, Ribeiro, Baptista, & Monteiro, 2019).

3.4.3 ALCOHOL SELECTION

The alcohol must be a short carbon chain alcohol like methanol, ethanol, propanol, isopropyl alcohol, butanol, and isobutyl alcohol (Demirbas, 2008). A short carbon chain alcohol is recommended for the transesterification reaction to be faster and for the biodiesel to have good combustion properties. Methanol is preferred for being the shortest chain alcohol achieving the fastest reactions (Caetano, Ribeiro, Ribeiro, Baptista, & Monteiro, 2019). When selecting an alcohol, price and availability must be considered. In some countries, like Brazil, bioethanol production and commercialization has been incentivized by its government and the prices and availability for ethanol are respectively lower and easier than in other countries. Many fatty acid alkyl esters have been produced with the mentioned alcohols having acceptable physical, chemical, and combustion properties (Demirbas, 2008).

3.4.4 CATALYSTS SELECTION

The catalysts needed depend on the process. In biodiesel production from waste cooking oils there are two processes where a catalyst is needed, FFA direct esterification and triglycerides transesterification. The first is a pretreatment process and the second is the main production process. For esterification an acid catalyst, like sulfuric acid (H₂SO₄) or phosphoric acid (H₃PO₄), is needed (Pruszko, 2020). For transesterification an acid catalyst may also be used, but base catalysts like Sodium hydroxide (NaOH) or Potassium Hydroxide (KOH) are more recommended as the speed of reaction increases with base catalysts. NaOH tends to be cheaper and easier to find, but if KOH is used in transesterification, phosphoric acid can be used in water washing to neutralize the KOH producing potassium phosphate, a valuable byproduct for fertilization (Gerpen & Knothe, 2010).

3.4.5 FEEDSTOCK PRETREATMENT

- Filtration: Every biodiesel feedstock must be filtered using a mesh of 100µm before any other process. Especially those feedstocks from waste cooking oil (Dahiya, 2020).
- FFAs esterification: If the FFA content is too high, they must be directly transformed into biodiesel through esterification with the selected alcohol and an acid catalyst, normally sulfuric acid. It is recommended 2.25g of methanol and 0.05g of sulfuric acid to esterify 1g of FFA. First the sulfuric acid must be dissolved in the alcohol and then mixed with the feedstock. This should be mildly mixed for one hour at a Temperature of 60°C. After esterification a water washing, and a second esterification are recommended (University of Idaho, 2018).
- Water washing: This must be done after esterification to remove the acid catalyst residue.
- Water drying: If the water content is too high, the feedstock must be dried by heating it at 110°C for 10 to 30 minutes before the transesterification process to avoid soap formation.

3.4.6 TRANSESTERIFICATION PROCESS

Transesterification may occur by acid or base catalyst. A base catalyzed is preferred as it is faster. When base catalysts are used transesterification takes from five minutes up to one hour. Acid catalyst may take from 10 minutes up to two hours (Pruszko, 2020).

Before starting the transesterification process, the feedstock water content should be less than 0.5% m/m, FFAs content should be at least less than 5% m/m, and it must be filtered using a mesh of 100 μ m. If it does not satisfy one of these conditions, it is recommended to be pretreated as shown in the past section (Caetano, Ribeiro, Ribeiro, Baptista, & Monteiro, 2019). For transesterification to happen the alcohol must be in its alkoxide form, that is, its OH group must be ionized as a O⁻ group. This is accomplished by dissolving the base in the alcohol. Examples of alkoxides are methoxide (CH_3O^-) and ethoxide ($CH_3CH_2O^-$).

If the feedstock has less than 0.5% FFA, the amount of catalyst needed is around 1% of the oil mass. If the feedstock has more than 0.5% FFA an additional amount of catalyst is needed. This extra catalyst is calculated as the acid value by titration (Pruszko, 2020).

Once the catalyst has been dissolved in the alcohol, these can be mixed with the feedstock to undergo transesterification. This mixture should be mildly mixed for one hour at a Temperature of 60°C to accelerate the reaction while avoiding the evaporation of methanol. Biodiesel and glycerol will be produced in this process.

Transesterification reaction can be enhanced and speed up by ultrasounds, microwave, membranes, and supercritical conditions (Caetano, Ribeiro, Ribeiro, Baptista, & Monteiro, 2019).

3.4.7 BIODIESEL PURIFICATION PROCESSES

Once transesterification has ended, a mixture of biodiesel, glycerol, excess methanol, and catalyst will remain. A purification process must be applied to obtain a pure biodiesel that satisfy international quality standards.

• Glycerol decantation: once the transesterification has ended, two phases with different colors will be noticeable. The light-yellow phase is the biodiesel, and the dark orange phase is the glycerol. Because of their different densities, the glycerol will remain in the bottom and the biodiesel in the top. This mixture should be transferred into a funnel type vessel with a valve at its bottom. After waiting approximately 8 hours for the phase separation, the valve is opened until all the glycerol is retrieved and stored in a separate

deposit. A faster method to separate the glycerol is centrifugation. The biodiesel phase must undergo other purification processes to be purified.

- Alcohol distillation: if it is wanted to reduce cost, the excess alcohol can be retrieved from the mixture to recycle it in the next transesterification process. This is recommended to be done after decantation to avoid reverse reaction of transesterification. The mixture should be heated at a temperature slightly above the alcohol boiling temperature. The vapors of the alcohol must be guided into a condenser and then to another deposit to be stored.
- Acid water washing: To eliminate the catalyst leftovers and soap emulsions an acid water solution is slowly poured to neutralize them and form salts. A very slight mixing is recommended to avoid unnecessary emulsions and more acid consumption. the water is drained out with all the formed salts. hydrochloric acid (HCl) is a common choice, but if phosphoric acid (H₃PO₄) is used the resulting salt can be a fertilizer byproduct when KOH was used in transesterification (Demirbas, 2008).
- Water washing: Distilled water is then poured to collect all other polar residues like alcohol, soaps, glycerol, acids, bases, and salts. A very slight mixing is recommended to avoid unnecessary emulsions. After waiting for the water-biodiesel phase separation, the water is drained out with all the impurities. Three cycles of water washing are recommended to eliminate all residues (Caetano, Ribeiro, Ribeiro, Baptista, & Monteiro, 2019).
- Water drying: Biodiesel can absorb up to 550ppm of water in it. to eliminate all the water left in the biodiesel, the biodiesel must be heated above the water boiling temperature of 100°C, 110°C is commonly used. This takes around one hour.

 Filtration: at last, the biodiesel must be filtered with a 5µm stainless steel mesh to remove any solid impurities (Dahiya, 2020).

3.5 BIODIESEL PROPERTIES AND QUALITY

Biodiesel must satisfy some physical, chemical, and combustion properties to work well in diesel motors. Biodiesel properties depend on the nature of the feedstock fatty acids. The fatty acids chain length and saturations will strongly determine the biodiesel properties (Clarke, 2017).

3.5.1 VISCOSITY

Viscosity represents the fluids resistance to deformation, movement, or "flow". Viscosity is also the ratio between a liquid deformation and the force applied to deform it. In liquids, the higher its temperature the lower its viscosity (Cengel & Cimbala, 2006). Fuels low viscosity makes them easier to be pumped, injected, and atomized to have a better combustion (Demirbas, 2008). For oils and biodiesel, the larger the carbon chain length, the more saturated, and the more trans bonds are in the fatty acids, the greater the viscosity (Knothe, 2010). Viscosity can be measured with a cylindrical torque viscometer or an Ostwald viscometer. When measuring the viscosity, the liquid temperature must be mentioned with its viscosity value. According to the standard ASTM D6751, biodiesel kinematic viscosity must be between 1.9 to 6 mm²/s at 40°C (Clarke, 2017).

3.5.2 DENSITY

Density is an object mass divided by its volume. A fuel density is important as the injection system works with a specific volume amount instead of a mass amount (Demirbas, 2008). Biodiesel (FAME) density depends on their feedstock origin. According to the European

standard EN 14214 the density of biodiesel must be between 860~900 kg/m³ at 15°C. Biodiesel density is lower than its oil form but greater than petrol diesel.

3.5.3 CETANE NUMBER

This is an empirical value to evaluate fuels performance in diesel engines. Cetane number is, in some way, an equivalent to the octane number for gasoline engines. Although they do not measure the same physical properties of fuels during combustion, both try to measure how good will a fuel operate in a diesel or gasoline engine. For example, octane number represents the fuel resistance to autoignition at high pressures, an important parameter to prevent knocking and secure a gasoline engine life (Clarke, 2017). The octane number is calculated by measuring the concentrations of two compounds, isooctane, and n-heptane, that, when mixed, will perform the same way in a gasoline engine as the evaluated fuel. Isooctane has an octane number of 100, n-heptane has an octane number of 0, gasoline has an octane number between 87~94 (Knothe, 2010).

Cetane number represents the delay time a fuel takes from the injection until the combustion in a diesel engine. Cetane number is calculated by measuring the concentrations of two compounds, hexadecane (cetane) and 2,2,4,4,6,8,8-heptamethylnonane, a highly branched compound, that, when mixed, will perform with the same delay in a diesel engine as the evaluated fuel. Cetane number for cetane is 100, for 2,2,4,4,6,8,8-heptamethylnonane is 15, for diesel is between 46~55, for vegetable oils is between 27~53, and, according to the standard ASTM D6751, for biodiesel it must be between 48~60 (Knothe, 2010).

Cetane number increases with a larger carbon chain length, less branches, and more saturated fatty acids (Clarke, 2017). Cetane number is experimentally measured using a cetane engine (Knothe, 2010).

3.5.4 HIGH HEATING VALUE (HHV)

The High Heating Value (HHV) is the maximum thermal energy that can be produced by the combustion of a fuel. biodiesel HHV is around 39.2 to 40.6 MJ/kg. Even thou biodiesel HHV is lower than that of diesel, biodiesel is denser and have oxygen atoms that enhance combustion. The HHV is measured in a bomb calorimeter (Demirbas, 2008).

3.5.5 FLASH POINT

It is the temperature at which the fuel ignites when it is in presence of a flame. This property is important for storage and handling precautions. According to the standard ASTM D6751 biodiesel flash point should be greater than 93°C. By this, biodiesel is safer to storage and handle than diesel, gasoline, ethanol, and methanol (Dahiya, 2020).

3.5.6 CLOUD POINT

The cloud point is the temperature at which crystals first appear (Dahiya, 2020). The more saturated and larger carbon chain length has the feedstock fatty acids, the greater the cloud point and the worse will the biodiesel operate in cold weathers (Clarke, 2017). Biodiesel cloud point requirements depends on the geographic place where it will be used and the season when it will be used in order to prevent engine malfunctioning.

3.5.7 POUR POINT

The pour point is the lowest temperature at which the fuel is observed to flow (Dahiya, 2020). The more saturated and larger chain length has the feedstock fatty acids, the greater the pour point and the worse will the biodiesel operate in cold weathers (Clarke, 2017). Biodiesel pour point requirements depends on the geographic place where it will be used and the season when it will be used in order to prevent engine malfunctioning.

3.5.8 DISTILLATION RANGE

Fuels are mixtures of different compounds; each compound has different boiling temperature. When the fuel is heated each compound evaporates in its boiling temperatures leaving the fuel with less mass. The Distillation range measures the temperature at which 90% of the fuel mass has been boiled. According to the standard ASTM D6751 biodiesel distillation range should be greater than 360°C (Bateni, Saraeian, Able, & Karimi, 2019). A more graphical method to show this behavior is the distillation curve. This curve determines the boiling ranges distribution of the fuel compounds. (Demirbas, 2008).



Figure 27: Distillation curve for petrol diesel, Cotton Seed Oil Methyl Ester (CSOME) and Cotton Seed Oil Ethyl Ester (CSOEE)

Source: (Demirbas, 2008)

These and other requirements of biodiesel properties are stablished by the American standard ASTM D6751 and the European standard EN 14214.

IV. METHODOLOGY

The purpose of this chapter is to establish the approaches, procedures, instruments, and methods used to obtain the research results.

4.1 APPROACH

The research will have a mixed approach. The study will collect qualitative results like the type of cooking oils used and how do restaurants treat their waste cooking oil. It will also have quantitative results like the amount of oil used in each restaurant, the free fatty acids content and water content of each sample, among others.

4.2 RESEARCH VARIABLES

In this research, variables can be divided into three categories:

- 1. Restaurants consumption behavior
- 2. Waste cooking oil samples properties
- 3. Biodiesel yield from oil samples

4.2.1 RESTAURANTS CONSUMPTION BEHAVIOR

These variables show how much and which cooking oils are used in restaurants and how they manage these residues. These variables will be measured per each restaurant. For the population sample, statistical values, like mean, mode, median, and standard deviation, will be calculated for each quantitative variable. A projection will be made to estimate the total population behavior.

- a) Main food type
 - This qualitative variable says what kind of food is which the restaurant serves the most. Some examples are chicken, steak, Mexican food, Asian food, pizzas, burgers, and soups.
 - i. Method or instrument needed: Survey.
- b) Usage of cooking oils or animal fats
 - This qualitative variable says if they use cooking oils, animal fats, both, or neither.

- i. Method or instrument needed: Survey.
- c) Type of Cooking oil used
 - This qualitative variable says which cooking oil is consumed by a restaurant.
 Some examples are vegetable, canola, sunflower, soybean, corn, olive, and avocado oil.
 - i. Method or instrument needed: Survey.
- d) Cooking oil monthly consumption
 - This quantitative variable approximates how many liters of cooking oil are consumed per month in a restaurant. Its unit is liters per month [l/month].
 - i. Method or instrument needed: Survey.
- e) Waste cooking oil disposal
 - This qualitative variable says what does the restaurant do with the waste cooking oil. Some examples are to sell it, donate it, or throw it away.
 - i. Method or instrument needed: Survey.

4.2.2 WASTE COOKING OIL SAMPLES PROPERTIES

These variables show waste cooking oil samples physical properties, chemical properties, impurities, and how feasible it is to convert these feedstocks into biodiesel. These variables will be measured for each restaurant. For the population sample, statistical values, like mean, mode, median, and standard deviation, will be calculated for each quantitative variable. A projection will be made to estimate the total population behavior.

- a) Feedstock density
 - This quantitative variable measures how much mass is in a defined volume of an object. Its unit is kilograms per cubic meter [kg/m³]
 - i. Method or instrument needed: liquid densimeter and a graduated U tube.
- b) Feedstock kinematic viscosity
 - This quantitative variable measures a liquid resistance to flow. Its unit is square millimeters per second [mm²/s]. This is calculated by dividing its dynamic

viscosity by its density. Dynamic viscosity also measures a liquid resistance to flow by measuring how a liquid deforms when a shear stress is applied.

- i. Method or instrument needed: Viscometer.
- c) Feedstock water content
 - This quantitative variable measures how much water mass is diluted in the oil mass. Its unit is mass percentage [%(m/m)].
 - i. Method or instrument needed: Balance, thermometer, and boiling station.
- d) Feedstock acid value
 - This quantitative variable measures how much KOH mass is needed to neutralize the FFAs in a unit mass of feedstock. Its unit is mg KOH/g oil. This is a practical way to measure how good is a feedstock (oil or fat) to produce biodiesel through basic transesterification reaction. the amount of KOH needed to neutralize the feedstock FFAs will tell us how much NaOH or KOH will be lost during transesterification, and how much soap will be formed if we try to transesterify this feedstock without pretreating its FFAs.

i. Method or instrument needed: Titration.

- e) Feedstock FFAs percentage
 - This quantitative variable measures how much mass of FFAs is in a unit mass of 0 feedstock. Its unit is mass percentage [%(m/m)]. It is measured by complex like physical-chemical methods nuclear magnetic resonance, gas chromatography, spectroscopy, spectrometry and FTIR. An approximate method is to find the moles of FFAs from titration and multiplying it by the mean of the fatty acids' molar mass, this method is easier, cheaper, alternative, but not so exact. The molar mass of the oleic acid is a recommended value to use due to its predominance in the most used oils. The most common fatty acids in oils, shown in section 3.3.12, are palmitic (256g/mol), oleic (282g/mol), linoleic (280g/mol), linolenic (278g/mol). Using oleic molar mass also gives a conservative result, supposing the greater FFA mass possible. Then this mass is divided by the oil total mass.
 - i. Method or instrument needed: Titration.
- f) KOH needed to transesterify the feedstock

- This quantitative variable measures the total amount of KOH needed to transesterify the feedstock, including the KOH to neutralize the FFAs. Its unit is mg KOH/g oil.
 - i. Method or instrument needed: Titration.
- g) NaOH needed to transesterify the feedstock
 - This quantitative variable measures the total amount of NaOH needed to transesterify the feedstock, including the NaOH to neutralize the FFAs. Its unit is mg NaOH/g oil.
 - i. Method or instrument needed: Titration.

4.2.3 BIODIESEL YIELD FROM OIL SAMPLES

These variables show what was the biodiesel production yield and the quality of it. These variables will be measured for each restaurant. For the population sample, statistical values, like mean, mode, median, and standard deviation, will be calculated for each quantitative variable. A projection will be made to estimate the total population behavior.

- a) Produced biodiesel density
 - This quantitative variable measures how much mass is in a defined volume of an object. Its unit is kilograms per cubic meter [kg/m³]
 - i. Method or instrument needed: liquid densimeter and a graduated U tube.
- b) Produced biodiesel kinematic viscosity
 - This quantitative variable measures a liquid resistance to flow. Its unit is square millimeters per second [mm²/s].
 - i. Method or instrument needed: Viscometer.
- c) Biodiesel production
 - This quantitative variable measures how much biodiesel mass was produced for each unit mass of feedstock. Its unit is mass percentage [%(m/m)].
 - i. Method or instrument needed: Balance.
- d) Biodiesel production yield

- This quantitative variable measures how much biodiesel mass was produced contrasted with the theoretical prediction of biodiesel production. Its unit is mass percentage [%(m/m)].
 - i. Method or instrument needed: Balance.
- e) Crude glycerol production
 - This quantitative variable measures how much crude glycerol mass was produced for each unit mass of feedstock. Its unit is mass percentage [%(m/m)].
 - i. Method or instrument needed: Balance.
- f) Net sulfuric acid used
 - This quantitative variable measures how much H₂SO₄ mass was used during all the production processes for each unit mass of feedstock. Its unit is mass percentage [%(m/m)].
 - i. Method or instrument needed: Balance.
- g) Net Potassium hydroxide used
 - This quantitative variable measures how much KOH mass was used during all the production processes for each unit mass of feedstock. Its unit is mass percentage [%(m/m)].
 - i. Method or instrument needed: Balance.
- h) Net water used
 - This quantitative variable measures how much water mass was used during all the production processes for each unit mass of feedstock. Its unit is mass percentage [%(m/m)].
 - i. Method or instrument needed: Balance.
- i) Net methanol used
 - This quantitative variable measures how much methanol mass was used during all the production processes for each unit mass of feedstock. Its unit is mass percentage [%(m/m)].
 - i. Method or instrument needed: Balance.
- j) Net energy used
 - This quantitative variable measures how much energy was used during all the production processes for each unit mass of feedstock. Its unit is mass percentage [%(m/m)].

i. Method or instrument needed: Wattmeter.

4.3 APPLIED TECHNIQUES AND INSTRUMENTS

4.3.1 SAMPLE SIZE DETERMINATION OF THE POPULATION

When it is needed to calculate a variable's mean value from a population, and there is only a sample of that population available, the mean value of the sample may be close to the population mean value. The bigger the sample the closer its mean value is from the population's mean value. To determine the sample size of a population when the population size is known, a statistical formula (equation 1) is used which depends on:

- Population size
- standard deviation of the variable distribution
- Error range accepted for the mean value prediction
- Result reliability

(Lohr, 2022)

This formula supposes that the population's variable has a normal distribution.

$$n = \frac{N \cdot \sigma^2 \cdot Z^2}{e^2 \cdot N + \sigma^2 \cdot Z^2}$$

Equation 1: Sample size formula

n = Sample Size

N = Total Population Size

Z = Normal Distribution *Z* value to determine reliability

 σ = Standard Deviation

e = *Error Range*

(Lohr, 2022)

The *e* and *Z* are chosen by the user. *e* values are chosen as a +- error range for the mean value prediction, examples are 1%, 2%, 5%, or in the units of the variable, like 1ml, or 2kg. *Z* values are related to reliability percentages that the prediction is correct, like 99%, 95%, or 80% (Lohr, 2022).

Z values are related as follows:

Reliability	Z value
99%	2.58
98%	2.33
95%	1.96
90%	1.65
85%	1.44
80%	1.28

Table 6: Normal distribution Z values according to its reliability

Source: (WALPOLE, MYERS, MYERS, & YE, 2012)

The σ is calculated from preliminary distribution studies of the same variable to the same population. Values for σ must be in the same units as the *e* values (Lohr, 2022).

4.3.2 SURVEYS

Surveys are a research method where people of a determined population are questioned about their studied variables, to obtain and order that information. They are used to obtain oil consumption data from restaurants.

4.3.3 FILTRATION AND FILTERS

Filtration is a process where mixtures of compounds with different sizes or states of matter are separated. Like solids from solids, or solids from liquids. This is achieved by making the mixture pass through a filter with pores of a specific diameter that only allows some of the compounds to pass. It is used to separate biodiesel and biodiesel feedstocks from their solid impurities.

4.3.4 BALANCE

It is an instrument used to measure the weight of an object depending on the force applied by the object to its mechanism. It is used to measure the mass quantity used of each reagent in the biodiesel production. For this study, a balance with 0.01g precision was used.

4.3.5 LIQUID DENSIMETER

It is a graduated instrument that floats in liquids and according to its submerged volume, the liquid's density can be calculated. It is used to measure the density of the water used for oil density measurement.

4.3.6 U TUBE

It a tube in U shape. It is used to measure the density of a liquid insoluble in water by measuring the heights' ratio of the measured liquid and water. The density of the used water must be measured with another density calculation method.

4.3.7 EXPERIMENTAL VISCOMETER

It consists of an open graduated volumetric container with a long thin pipe at its bottom in which the liquid will be discharged. A 50ml syringe connected to a thin straw will be used as the viscometer for this research. The viscosity of the liquid is proportional to the time it takes to discharge the liquid from an specific volume to another specific volume, for example from

30ml to 10ml. the working principle of this viscometer is explained more in depth in section 4.7.3.

4.3.8 OVEN

It is an instrument used to heat objects or substances. It is used to evaporate the water content from oil.

4.3.9 BOIL

It is a process of changing a compound state of matter from liquid to gas by increasing its temperature up to its boiling temperature. It is used to dry the biodiesel and biodiesel feedstock.

4.3.10 WATER CONTENT APPROXIMATION

It is a method to approximate a solution's water content by measuring its change in mass before and after increasing the solution's temperature above the water boiling temperature. It is used to approximate water content in biodiesel feedstock.

4.3.11 PH DIGITAL METER

It is an instrument used to measure the concentration of H_3O^+ ions in a solution to see how acid or alkaline is it. It is used to measure the pH of wash water.

4.3.12 PH NEUTRALIZATION

It is the process of neutralizing a solution's pH by using acids, water or bases until its pH reaches a value of seven. It is used to purify biodiesel.

4.3.13 TITRATION

It is the process of measuring the concentration of a specific acid or base in a solution by reaching a known pH when adding a known quantity of a standard acid or base. It is used to know the FFAs concentration in biodiesel feedstock. Oils' acid content cannot be measured directly with a pH meter because it is a nonpolar molecule and does not have enough water to produce OH⁻ or H⁺. To titrate oils, a nonpolar solvent like isopropyl alcohol is needed to dilute base water in the oil.

4.3.14 MAGNETIC MIXER

It is a machine that has a platform to place a flask with liquid compounds and where a rotating magnetic field is induced in order to place a magnet inside the flask to mix the compounds. It is used to mix the compounds in esterification, transesterification, pH neutralization, methoxide elaboration and water washing.

4.3.15 ESTERIFICATION

It is the process of producing an ester by the synthesis of an alcohol and a carboxylic acid in presence of a strong acid as catalyst. It is used to produce methyl esters (biodiesel) from free fatty acids and methanol.

4.3.16 ALKOXIDE SYNTHESIS

Consist in dissolving a certain amount of a base, like sodium hydroxide (NaOH) or potassium hydroxide (KOH), into an alcohol, like methanol (CH₃OH) or ethanol (CH₃CH₂OH), to form an alkoxide, like methoxide (CH₃O⁻) or ethoxide (CH₃CH₂O⁻), water (H₂O) and alkaline metal ions (Na⁺, K⁺). Alkoxides are used in the transesterification of biodiesel.

4.3.17 TRANSESTERIFICATION

It is a substitution reaction where an ester substitutes its alcohol by another alcohol to form a different ester. For this reaction to take place, one of the alcohols must be as an alkoxide to attack the ester with the other alcohol. It is used to transform glycerol tri-esters (lipids) to methyl esters (biodiesel).

4.3.18 DECANTATION AND DECANTATION FUNNEL

It is the process of separating compounds with different densities and that are insoluble between them. This is achieved using a decantation funnel, which is a graduated funnel with a precision valve in its bottom. This process is used to separate water from oil, water from biodiesel, and glycerin from biodiesel.

4.3.19 DISTILLATION

It is the process of separating mixtures of compounds with different boiling temperatures. This is achieved by heating the mixture up to the lowest boiling temperature of either compound,

guiding the new gaseous compound to another deposit and cooling it back into its liquid state. This is used to recover unreacted methanol from the produced crude biodiesel.

4.3.20 WATER WASHING

It consists in pouring water in a mixture of polar and non-polar substances, like oil or biodiesel, to extract the polar and ionic impurities from the oil or biodiesel. It is used to clean the biodiesel from the remaining alcohol, catalyst, soap and glycerol. These are polar molecules and ionic compounds.

4.3.21 OTHER CHEMICAL INSTRUMENTS

- thermometer
- Beakers
- Erlenmeyer flasks
- Graduated cylinder

- Burette
- Pipette
- Spatula
- Syringe

4.4 MATERIALS

- Plastic bottles (>500 ml)
- Plastic funnels
- Laboratory coat
- Surgical mask
- Nitrile gloves
- Isopropyl Alcohol

- Potassium hydroxide
- Sodium hydroxide
- Phenolphthalein
- Anhydrous methanol
- Hydrochloric acid (37% m/m)
- Sulfuric acid

4.5 SOFTWARES

- 1) Excel
- 2) Google Forms

4.6 POPULATION AND SAMPLE

4.6.1 POPULATION

The studied population are the restaurants in San Pedro Sula, Honduras.



Figure 28: Location of San Pedro Sula city Source: Own Elaboration

The number of this population was initially going to be determined by consulting the city municipality. Unfortunately, the municipality was not willing to give us this information.

The closest information of the number of restaurants in San Pedro Sula, Honduras, was obtained from the National Institute of Statistics, INE for its acronym in Spanish. This institute has recorded a value of the number of restaurants, bars, and canteens.

The value of the number of restaurants, bars and canteens in San Pedro Sula is 2,829 (Instituto Nacional de Estadística, 2022).

Unfortunately, this value also considers locals that does not use vegetable oils like bars, canteens, coffee shops, and bakeries. But considering the unwillingness of the city municipality, this is the best approximation for the city number of restaurants.

4.6.2 SAMPLE

Initially the studied sample was going to be the 28 restaurants, in San Pedro Sula, affiliated to the Commerce and Industry Chamber of Cortes, CCIC for its acronym in Spanish. The CCIC is

a public association of businesses and industries that promotes the economy growth of Cortés department by enterprise development. Unfortunately, the CCIC did not collaborate in linking us with their affiliated restaurants.

After looking for restaurants managers willing to participate in this research, we selected the restaurants in the Gran Central Metropolitana, which is the biggest and most important bus station of San Pedro Sula, as the population sample. In this station there are 23 restaurants of different food types.



Figure 29: Gran Central Metropolitana bus station.

Source: (La Prensa, 2020)



Figure 30: Bus Station food court Source: Own Elaboration

This place and restaurants were chosen because of time, accessibility and because we had contacts who knew some restaurants managers, making it easier to have reliable answers and more oil samples.

The method stablished in section 4.3.1, to determine the sample size, was omitted due to time, accessibility, availability, and resources limitation. Using this method, a study for the whole city was unreachable, as the population size was too big to be studied considering the past factors.

4.7 RESEARCH METHODOLOGY

To obtain the results for the studied variables, the following processes were followed step by step.





Figure 31: A step by step diagram of the research methodology

Source: Own Elaboration

4.7.1 SURVEYS

A survey was made to each restaurant in the bus station. The questions of the survey can be found in annexes section 10.1.

4.7.2 SAMPLES COLLECTION

 After asking to the restaurants' managers, in the survey, if they would let us collect a sample of their waste cooking oil, we proceeded to collect, with a filter and funnel, a sample (of around 500 ml) in a plastic bottle. We labeled each bottle with a number to link it with its restaurant.

4.7.3 SAMPLES ANALYSIS

- Filtration:
 - \circ Before studying the oils' property, a filtration process is needed. It is recommended to use a filter of <100 μ m (Dahiya, 2020) (Caetano, Ribeiro, Ribeiro, Baptista, & Monteiro, 2019).
 - $\circ~$ A paper filter of 10 μm was used to filter all the oil samples.
- Oil Density Calculation
 - The density was calculated using a tube with U form, where distilled water, with a known density, and the oil will be poured as the following image:



Figure 32: oil density determination using a U form tube

Source: (Gerbyl, 2018)

o The oil density was calculated by the following physical analysis:

$$P_A = P_B$$

$$\rho_1 g y_L = \rho_2 g y_R$$

$$\rho_1 y_L = \rho_2 y_R$$

$$\rho_2 = \rho_1 \frac{y_L}{y_R}$$

Equation 2: Oil density formula

 $P_A = Pressure in point A$ $P_B = Pressure in point B$ $\rho_1 = Water density$ $\rho_2 = Oil densuty$ g = Gravity

 $y_L = Height of the water from point A$

 $y_R = Height of the oil from point B$

- The water used was distilled water and its density was measured submerging a liquid densimeter into a large, graduated cylinder with the distilled water.
- Viscosity Measurement
 - Viscosity was measured using an experimental viscometer consisting of a thin long straw connected to a large syringe as shown in the following figure:



Figure 33: Proposed experimental viscometer

• This setup can be analyzed as a laminar flow passing by a cylindrical tube. The inner laminar flow in the thin and long straw is determined by the Poiseuille equation. Poiseuille equation expresses the volumetric flow in function of the liquid dynamic viscosity, pressure difference between the ends of the tube, and geometrical dimensions of the tube. Considering that the hydrostatic pressure at the top of the straw can be expressed as a function of the volume in the syringe, and this volume changes in time due to the flow at the bottom of the straw, a differential equation can be stated and solved. By this, it can be demonstrated, as it is in annex 10.3, that the time it takes for the volume in the

Source: Own Elaboration

syringe to change, for example from 30ml to 10ml, is proportional to the kinematic viscosity of the flowing liquid as follows:

$\nu = K \cdot \Delta t$

Equation 3: Kinematic viscosity depending on time in the experimental viscometer

 $v = Kinematic viscosity [mm^2/s]$

K = Constant which depends on constant geometrical dimensions $[mm^2/s^2]$

 $\Delta t = Time \ it \ takes \ for \ the \ volume \ in \ the \ syringe \ to \ be \ reduced$ from 30ml to 10ml [s]

- The value of *K* was calculated experimentally by measuring the time it takes using distilled water at 20°C, which viscosity has been precisely calculated by other authors. This measurement was repeated 10 times to obtain a better approximation in the mean value of *K*.
- For this viscometer setup the calculated K was 0.36454 mm²/s².
- Titration of FFAs
 - 1) Prepare a base solution of one g/L of NaOH or KOH in a volumetric flask.
 - 2) In a conical flask pour 20 milliliters of anhydrous isopropyl alcohol.
 - 3) In that flask, mix a sample of two milliliters of the oil to be tested.
 - 4) Add three to four drops of phenolphthalein to the oil solution.
 - 5) fill a graduated burette with the base solution.
 - 6) slowly pour the base solution from the burette to the conical flask while stirring it. Do this until the oil-alcohol solution turns pink and stop pouring the base solution. The color must remain for at least 30 seconds, if it does not keep pouring until it does.
 - When this happens all the FFAs have been neutralized by the same amount of base moles.
 - Measure, from the burette, the volume of base solution used to neutralize the FFAs.
 - Calculate the number of grams and moles of base needed per liter of oil. The base solution was one g/L, molar mass of NaOH is 39.997 g/mol and for KOH is 56.1056 g/mol.

 $M_{NaOH} = V_{NaOH} * (1g/l)$ Equation 4: Calculation of NaOH mass needed per liter of oil
$$n_{NaOH} = \frac{M_{NaOH}}{39.997 g/mol}$$

Equation 5: Calculation of NaOH moles needed per liter of oil

 $M_{NaOH} = mass of NaOH needed per liter of oil [g/l]$ $V_{NaOH} = volume of NaOH consumed in titration [l]$ $n_{NaOH} = moles of NaOH needed per liter of oil [mol/l]$

- 10) With the values of step nine and the density of the oil, calculated in other methods, calculate the acid value in mg_{KOH}/g_{oil} . KOH is used as a standard.
- 11) If the titration was made with NaOH, the amount of KOH of step 10 can be calculated considering that one mol of FFA is neutralized with one mol of NaOH or one mol of KOH, so the moles of NaOH used are the same moles of KOH that would have been used.
- 12) Calculate the FFAs percentage in the oil. For this, the amount of equivalentgrams of base needed per liter of oil, obtained in step 9, is also the amount of equivalent-grams of FFA per liter of oil. Multiply these moles by the molar mass of oleic acid, which is 282.47g/mol, to estimate the FFAs grams in a liter of oil. With the density of the oil calculate the grams of FFAs per gram of oil. Multiplying this by 100 we obtain the percentage of FFAs in the oil.
- Water Content Estimation
 - 1) Measure a beaker mass with a balance.
 - 2) Measure the mass of an oil sample poured in the beaker with a balance.
 - 3) Measure the mass of the beaker with the oil with a balance.
 - 4) Introduce the beaker with oil into an oven.
 - 5) Heat the oil up to 110°C for 30 minutes.
 - 6) Measure the mass of the beaker and the oil again with a balance.
 - 7) Calculate the difference of mass before and after the heating.
 - 8) That mass is the water content.
 - Divide that water mass by the oil mass, and multiply by 100, to obtain the percentage of water content.

4.7.4 SAMPLE PRETREATMENT

• Esterification of FFAs

- If the feedstock has more than 2% of FFA, 2.25g of methanol are mixed with 0.05g of sulfuric acid per each gram of FFA. First the sulfuric acid must be dissolved in the alcohol and then mixed with the feedstock. This should be mildly mixed for one hour at a Temperature of 60°C.
- Acid Neutralization
 - The remaining solution of the esterification is acid and must be neutralized. This was achieved by pouring a NaOH solution 0.01M until the water exiting has a pH a little greater than seven. The remaining water was taken away by decantation.
- Water washing
 - The feedstock is washed until the exiting water has a neutral pH. The remaining water was taken away by decantation.
- Feedstock Drying
 - The feedstock was heated up to 110°C for 30 minutes to evaporate the excess of water before the transesterification process to reduce the soap production.

4.7.5 TRANSESTERIFICATION

- Methoxide Elaboration
 - The amount of methanol and base to elaborate the methoxide depends on the amount of oil to be transesterify and its acid value.
 - A 6:1 molar ratio of methanol to oil is recommended. If the molar mass of the oil is unknown, like when the origin of the oil is unknown, or when a fatty acids' profile test is not available, assuming it to be 876g/mol is an acceptable average for many vegetables cooking oils, according to the Idaho University. Considering methanol molar mass to be 32.04g/mol, the kilograms of methanol needed per kilogram of oil will be as follows:

$$\frac{N_{Methanol}}{N_{oil}} = 6$$

$$N_{Methanol} = 6 \cdot N_{oil}$$

$$\frac{M_{Methanol}}{m_{Methanol}} = 6 \cdot \frac{M_{oil}}{m_{oil}}$$

$$\frac{M_{Methanol}}{M_{oil}} = 6 \cdot \frac{m_{Methanol}}{m_{oil}}$$

$$\frac{M_{Methanol}}{M_{oil}} = 6 \cdot \frac{32.04g/mol}{876g/mol}$$
$$\frac{M_{Methanol}}{M_{oil}} = 0.219$$

Equation 6: Mass relation between methanol and oil

 $N_{Methanol} = moles of methanol [mol]$ $N_{oil} = moles of oil [mol]$ $M_{Methanol} = mass of methanol [g]$ $M_{oil} = mass of oil [g]$ $m_{Methanol} = molar mass of methanol [g/mol]$ $m_{oil} = molar mass of oil [g/mol]$

- So, 219 grams of methanol per kilogram of oil are needed.
- The amount of base mass is 1% of the oil mass to be transesterified, this is only when the FFAs percentage is less than 0.5%. if the FFA percentage is between 0.5% and 5% an excess of base must be added to neutralize these FFAs. This extra amount is determined by calculating the acid value in titration. The acid value tells how many milligrams of KOH is needed to neutralize the FFA of one gram of oil, this value is also in grams of KOH per kilogram of oil. So, the total mass of KOH needed per kilogram of oil is as follows:

$$M_{KOH} = 1\% \cdot 1kg\left(\frac{1000g}{1kg}\right) + AV_{KOH}$$

Equation 7: Mass of KOH needed per mass of oil

 $M_{KOH} = mass of KOH$ to be used in transesterification [g/kg] $AV_{KOH} = acid value in KOH [g_{KOH}/kg_{oil}]$

The same can be calculated when using NaOH, but the acid value must be expressed in grams of NaOH per kg of oil. Acid value can be converted from KOH to NaOH by considering that the same amount of moles must be consumed in either case.

$$M_{NaOH} = 1\% \cdot 1kg\left(\frac{1000g}{1kg}\right) + AV_{NaOH}$$

Equation 8: Mass of NaOH needed per mass of oil

 $M_{NaOH} = mass of NaOH to be used in transesterification [mg/kg]$ $AV_{NaOH} = acid value in NaOH [g_{NaOH}/kg_{oil}]$

- Methoxide is elaborated by pouring the base in methanol and stirring it until all the base has been dissolved.
- Transesterification
 - The methoxide solution is mixed with the oil according to the relations determined before. The temperature should be around 60°C and the mixture should be slightly stirred for around one hour. The color of the mixture will change and become a little darker. Biodiesel and glycerol are being produced. Also, the FFAs are reacting with the excess base to produce soaps.
 - 4.7.6 BIODIESEL PURIFICATION
- Glycerol Decantation
 - Using a decantation funnel, the glycerol is removed by opening the downstream valve and falling by gravity. The valve is closed when all the glycerol phase is removed and once a stream of biodiesel is visible in the valve exit. The amount of crude glycerol produced was measured using a balance.
- Methanol Distillation
 - After the transesterification, the excess methanol in the biodiesel and crude glycerol may be retrieved by distillation, heating the mixture up to 70°C and condensing the methanol vapors in another vessel, to reuse it in the next transesterification. The boiling temperature of methanol is 64.7°C. Due to time, resources, and the low amount of alcohol used for this research, methanol distillation was omitted.
- Base Neutralization
 - The remaining catalyst in the biodiesel is neutralized with acid water. The used acid was sulfuric acid due to its availability. A solution of 0.01M of sulfuric acid is used until the pH of the wash water exiting the vessel is around six. The use of acid is sometimes needed when high amount of soap or emulsions were formed during transesterification. Acids neutralize the soaps producing salts.

This water was removed by decantation. The amount of acid was measured using a pipette.

- Water Washing
 - The remaining biodiesel was washed with water to finish neutralizing any acid or base remaining, and to clean the biodiesel from alcohol, glycerol, soaps, and catalyst remaining. This water was removed by decantation. The amount of water was measured using a graduated cylinder.
- Water Drying
 - The biodiesel is heated up to 110°C to evaporate all the excess of water dissolved in it. This process takes around 30 minutes until no more bubbles of water are seen and the cracking sound of boiling has stopped. After drying, the biodiesel must look clear. The amount of energy was recorded using a wattmeter.
- Biodiesel Filtration
 - Biodiesel was filtered with a filter of $<5 \mu m$ to remove any impurity.

4.7.7 BIODIESEL ANALYSIS

Each sample of produced biodiesel is analyzed. Their density and viscosity are to be measured using the same methods used for the oil analysis.

4.7.8 RESULTS ANALYSIS

During each production process the amount of resources and reagents used must be measured and recorded to know their consumption depending on the processed oil mass.

When the results of the 12 samples were completely recorded, statistical parameter like mean, median, minimum, maximum, range, standard deviation, and weighted arithmetic mean were calculated for each result variable.

4.8 ACTIVITIES SCHEDULE

Activities for the Development of the Research		Weeks								
		2	3	4	5	6	7	8	9	10
Problem identification and setting of objectives										
Development of the theoretical framework to support the research										
Development of the methodology of the research										
Realization of surveys and collection of oil samples										
Analysis of oil samples										
Oil pretreatment, biodiesel production, and purification										
Analysis and elaboration of result										
Elaboration of introduction and abstract										
Conclusions and Recommendations Elaboration										
Final Review Elaboration										
Scientific Article Elaboration										
Pre-Defense										

Table 7: Activities schedule

V. RESULTS

In this chapters are shown the research results after applying all the steps stablished in the research methodology.

5.1 RESULTS OF RESTAURANTS' CONSUMPTION BEHAVIOR

When trying to survey the restaurants we find that some of them were unavailable, or not wanted to answer. The surveys were as follows:



5.1.1 Types of Studied Restaurants



In the studied sample were restaurants of different food types:

Figure 35: Pie chart of types of studied restaurants (18 restaurants in total).

Source: Own Elaboration

Most of the restaurants are traditional food and chicken food, being these a 61% of all restaurants.

5.1.2 OILS AND FATS USAGE

Most of the restaurants use only oils as shown in the following graph:



Figure 36: Distribution of oils' and fats' usage in restaurants of different types.

5.1.3 Type of Oils Used in the Restaurants

None of the restaurants, which say to use cooking oils, knew what type of cooking oil use, they only have an idea that is a vegetable oil and consider it as a generic vegetable oil.

5.1.4 Amount of Oil Consumption

The following table presents the results of the oil consumption of each restaurant:

Restaurant #	Gal/week		
1	7		
2	4		
3	0.5		
4	7		
5	6		
6	20		
7	0.4		
8	9		
9	15		
10	5		
11	3		
12	10		
total	86.9		
Mean	7.24		

Table 8:	Restaurants	weekly oil	consumption
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These results, when converted to liters of oil per year, and calculating the mean and median value, can be graphed as follows:



Figure 37: Oil consumption, in liters per year, of surveyed restaurants

Source: Own Elaboration





Figure 38: Oil consumption, in liters per year, of surveyed restaurants, ordered from highest to lowest



A frequency distribution of these oil consumption can be made as follows.



Source: Own Elaboration

If we order and add the oil consumption by the types of restaurants, we obtain the following graph.



Figure 40: Bar graph of the total oil consumption by restaurant type

Dividing each amount by the number of restaurants in each type we can calculate a mean value of oil consumption for each type of restaurant as follows:





Source: Own Elaboration

Chicken restaurants are the ones with more oil consumption from all types of restaurants.

5.1.5 MANAGEMENT OF OIL RESIDUES

The following pie chart shows the restaurants' behavior with the oil residues:





Most restaurants use to throw the oils away. But when we relate the amount of oil in each restaurant with their behavior, we observe that more oil is been sold than throwed away.



Figure 43: Pie chart of the oil residues management by oil consumption [L/year].

Source: Own Elaboration

5.1.6 COLLECTION OF WASTE COOKING OIL SAMPLES

After the survey, the samples were collected. There were 12 samples collected, each from a different restaurant.



Figure 44: Samples collected from 12 studied restaurants.

5.2 RESULTS OF WASTE COOKING OIL SAMPLES PROPERTIES

After realizing the tests stablished in the methodology, results for the oils were obtained. All the measurements were recorded and tabulated in Annex 10.4.

In San Pedro Sula, Honduras, Restaurants Waste Cooking Oil (WCO) characterization has the following statistical values:

Parameters	Restaurant Consumption	Density at 20°C	Viscosity at 20°C	Acid Value	%FFA	Max Humidity
[-]	[L/year·Rest.]	[kg/m³]	[mm²/s]	[mgKOH/gOil]	[% m/m]	[% m/m]
Min	78.7	895	24.09	1.01	0.51%	0.21%
Мах	3,936	916	35.77	8.39	4.21%	1.05%
Mean	1,425	909	29.10	2.65	1.33%	0.29%
Median	1,279	910	29.57	1.77	0.89%	0.21%
Std. Dev.	1,127	5.46	3.31	2.18	1.09%	0.00%
WAM	-	910	28.39	3.14	1.58%	0.28%

Table 9: Statistical values of the WCO characterization in San Pedro Sula

Rest. = Restaurant

Std. Dev = Standard deviation

WAM = Weighted Arithmetic Mean (weighted with oil consumption) These results were obtained by analyzing 12 different WCOs.

Source: Own Elaboration

By comparing the oils properties with a sample of petrol diesel from a commercial gas station, the following results were found.

At 20°C, oil density is greater than diesel density by an average factor of 1.08.

At 20°C, oil viscosity is greater than diesel viscosity by an average factor of 16.96.

Some clarifications must be done for the water content measurement and the Free Fatty Acids (FFA) content before stating the oil quality.

Oil Samples Water Content

When measuring the water content, no mass difference was detected with the balance after the boiling of water. Considering that the balance precision was not exact enough to detect the mass difference, the water content was considered to be less than the minimum detectable mass difference of the balance which is 0.1g. By this, a "maximum possible water content" is measured by the balance precision. Because different oil masses were used for each sample, different maximum possible water content were measured.



Figure 45: Maximum possible water content of each oil sample

Source: Own Elaboration

The high "maximum possible water content" of sample #4 is due to the low amount of sample oil that the restaurant gave us. So, the amount of oil tested in this method was not enough for a better measurement.

Except for one sample, most oils have less than the 0.5% of water content, which is recommended for direct transesterification of the oils. These are good results for biodiesel feedstocks.

Oil Samples Acid Value

Since it was observed that all the samples have less than 5% FFAs, they can be direct transesterified, but with an extra catalyst addition, expecting soap formation, and biodiesel yield loss.

Almost 84% of the oil samples have less than 2% FFAs, which for some authors these oils would be considered good feedstocks, in which pretreatment may be avoided. For the other oil samples an acid esterification is recommended to avoid a high biodiesel yield loss.

5.3 RESULTS OF PRODUCED BIODIESEL FROM OIL SAMPLES

The biodiesel was produced, and its properties, production and consumption factors were measured as explained in the methodology. All the measurements were recorded and tabulated in Annex 10.4.

Characterization of biodiesel produced from Restaurants WCO in San Pedro Sula, Honduras, has the following statistical values:

Sample	Restaurant Consumption	Biodiesel yield factor	Biodiesel Production Potential	Density at 20°C	Viscosity at 20°C
[-]	[kg/year·Rest.]	[% m/m]	[kg/year·Rest.]	[kg/m³]	[mm²/s]
Min 70		70.9%	52	842	2.2
Max	3,580	92.7%	2,654	866	4.5
Mean 1,297		81.7%	1,054	851	2.6
Median	1,156	84.0%	896	851	2.3
Std. Dev.	1,028	7.5%	816	6.8	0.7
WAM	-	81.2%	_	851	2.7

Table 10: Statistical values of the biodiesel characterization from WCO in San Pedro Sula

Rest. = Restaurant

Std. Dev = Standard deviation

WAM = Weighted Arithmetic Mean (Biodiesel yield factor was weighted with oil consumption. Density and viscosity were weighted with biodiesel production potential) These results were obtained by analyzing 12 different WCOs.

Source: Own Elaboration

By comparing the biodiesel properties with a sample of petrol diesel from a commercial gas station, the following results were found.

At 20°C, Biodiesel density is greater than diesel density by an average factor of 1.016.

At 20°C, Biodiesel viscosity is greater than diesel viscosity by an average factor of 1.509.

5.3.1 DENSITY COMPARISON BETWEEN OIL AND BIODIESEL.

If we compare the oil density and biodiesel density for each sample, we get the following graph:



Figure 46: Comparison between water, diesel, oil, and biodiesel densities for each sample

Source: Own Elaboration

The last graph shows that all biodiesel samples from waste cooking oil are denser than petrol diesel but less dense than its oil form.

At 20°C, Biodiesel density shows an average reduction of 6.29% from its oil form density.

5.3.2 VISCOSITY COMPARISON BETWEEN OIL AND BIODIESEL.

If we compare the oil viscosity and biodiesel viscosity for each sample, we get the following graph:



Figure 47: Comparison between oil and biodiesel viscosities at 20°C for each sample

Source: Own Elaboration

The last graph shows that all biodiesel samples from waste cooking oil are more viscous than petrol diesel but less viscous than its oil form.

At 20°C, Biodiesel viscosities show an average reduction of 90.90% from their oil form viscosities.

5.4 BIODIESEL PRODUCTION FACTORS

After all the pretreatment, production, and purification processes, biodiesel production results were obtained. All the measurements were recorded and tabulated in Annex 10.4.

Note: Only sample #6 and #10 were pretreated with esterification due to their high FFAs content (>2%).

The byproducts yield and resources consumption for biodiesel production from restaurants WCO in San Pedro Sula, Honduras, has the following statistical values:

Davamatara	Byproducts yield	Resources consumption factors							
T drameters	Crude Glycerol	Methanol	Potassium Hydroxide	Sulfuric Acid	Distilled Water	Energy			
[-]	[% m/m]	[% m/m]	[g/kg]	[g/kg]	[% m/m]	[kWh/kg]			
Min	16.6%	21.9%	11.01	0.02	79%	1.78			
Мах	34.5%	31.4%	12.62	2.17	212%	5.67			
Mean	22.5%	23.2%	11.86	0.39	144%	2.87			
Median	20.0%	21.9%	11.77	0.12	150%	2.44			
Std. Dev.	5.5%	3.2%	0.50	0.69	39%	1.30			
WAM	23.5%	23.9%	11.98	0.53	149%	3.20			

Table 11: Statistical values of the byproducts yield and resources consumption factorsfor biodiesel production from WCO in San Pedro Sula

These values are given by mass of processed oil.

Std. Dev = Standard deviation

WAM = Weighted Arithmetic Mean (Weighted with oil consumption) These results were obtained by analyzing 12 different WCOs.

The following clarifications must be done for the crude glycerol yield measurements and the energy consumption factor.

The crude glycerol produced was measured by weighing the decanted glycerol. This glycerol was not subjected to any purification process due to time and resources limitations. It must be considered as a mixture of methanol, catalyst, soaps, water, and glycerol, where glycerol is the predominant compound of it.

Energy consumption has been measured in kilowatts-hour per mass of processed oil. Energy was used to stir, heat and dry using a magnetic stirrer and electric heater. Because of these used instruments, these measurements are not a good approximation to a real biodiesel refinery energy consumption, where different machines, processes, and controls are used. These consumption results are just to be considered as a low-cost first approximation attempt.

As said before, sample six and 10 needed an acid esterification pretreatment where more energy was required to heat, stir, and dry. Sample four has a greater energy consumption per oil mas due to the low sample mass and the base electric energy consumption needed to heat the electric heater at the desired temperature. This is another factor that affects the usability of these results, no distinguishment was done between the starting base energy consumption and the steady state energy consumption.

Clarification of the importance and usability of the Weight Arithmetic Mean (WAM):

The WAM is a better approximation of the overall yield or consumption factor of a random sample of restaurants in the city than the mean value of them. As it is composed of different type of restaurants considering their own oil consumption and oil quality for biodiesel production.

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5.5 CITY PRODUCTION POTENTIAL OF BIODIESEL FROM WCO

A preliminary biodiesel production potential can be approximated by multiplying the number of restaurants in the city times the mean restaurant oil consumption times the WAM of the biodiesel yield factor

 $BDPP = NR_{SPS} \cdot ROC_M \cdot BDYF_{WAM}$

Equation 9: Preliminary estimation of biodiesel production potential

 $BDPP = Biodiesel \ Production \ Potential \ [kg/year]$ $NR_{SPS} = Number \ of \ Restaurants \ in \ San \ Pedro \ Sula \ [-]$ $ROC_{M} = Restaurants \ Oil \ Consumption \ Mean \ Value \ [kg/year]$ $BDYF_{WAM} = Biodiesel \ Yield \ Factor \ Weight \ Arithmetic \ Mean \ Value \ [\% \ m/m]$ This equation gives the following:

 $BDPP = 2,829 \cdot 1297 kg/year \cdot 81.2\%$ BDPP = 2,979,400 kg/year

The preliminary biodiesel production potential from WCO of restaurants in San Pedro Sula, Honduras is of 2,979 Tons of biodiesel per year. This value is very optimistic as it considers locals that does not consume oils, like bars, canteens, coffee shops and bakeries, in the number of restaurants in the city. The real amount of oil consumer restaurants in the city is unknown.

VI. CONCLUSIONS

In this research, it has been characterized the Waste Cooking Oil (WCO) quantity and quality for biodiesel production from restaurants in San Pedro Sula, Honduras. 12 samples of WCO, from 12 different restaurants located in the biggest bus station of the city, were collected, analyzed, pretreated, processed, and purified into biodiesel. These restaurants were surveyed about their oil consumption and disposal. Density, viscosity, water content, Free Fatty Acids (FFAs) content, and acid value of the oil samples were measured using a U-tube liquid densimeter, experimental viscometer, oven, balance, and titration. Depending on these quality variables of WCO, each sample was pretreated. Then these samples were transesterified with methanol and KOH as catalyst considering their acid values. The biodiesel was purified. Properties of these produced biodiesel samples, like density and viscosity, were measured to be compared with their oil form and a diesel sample. Biodiesel yield and consumption factors were calculated for each sample. Biodiesel production potential was calculated for each restaurant. A Weighted Arithmetic Mean (WAM) was calculated for the biodiesel production potential of the studied restaurants in the city. Finally, a biodiesel production potential of the whole city was estimated.

This research obtained the following conclusions:

- 12 restaurants of different types of food were able and willing to participate in this research. Time and resources were other variables that limited the number of restaurants.
- 2. Different types of restaurants consume different amount of oil. In average, a chicken food restaurant consumes 1,811 liters of oil per year, a traditional food restaurant consumes 1,132 liter of oil per year, a Chinese food restaurant consumes 1,181 liters of oil per year, and a soup food restaurant consumes 79 liters of oil per year. None of the interviewed restaurants know what type of oil they consume.
- 3. In average the oil consumption of a restaurant in the city is 1,425 liters of oil per year.
- 4. 12 WCO samples from different restaurants were successfully collected, filtered, and analyzed.
- 5. Restaurants WCO in San Pedro Sula are technically viable biodiesel feedstock considering their water content, free fatty acids (FFAs) content, and acid value determined in table 9, section 5.2.

- 6. All WCO samples were successfully transesterified with methanol and KOH catalyst. Two of the 12 samples were pretreated by acid esterification due to their high FFAs content (>2% m/m). Nevertheless, considering that the weighted arithmetic mean (WAM) of the FFA content in the WCOs is less than 2%, no acid esterification pretreatment will be needed for a combination of restaurants WCOs.
- Measurements of biodiesel mass yield per mass of WCO had a mean value of 81.66% m/m, and a WAM of 81.24% m/m.
- 8. Viscosity of biodiesel produced from restaurants WCO in San Pedro Sula satisfy the range of viscosity from ASTM D6751
- 9. The byproducts yield and resources consumption per WCO mass in biodiesel production were measured and summarized in table 11, section 5.4.
- 10. A preliminary biodiesel production potential from WCO of restaurants in San Pedro Sula, Honduras is of 2,979 Tons of biodiesel per year. This value is very optimistic as it considers locals that does not consume oils, like bars, canteens, coffee shops and bakeries, in the number of restaurants in the city when calculated. The real amount of oil consumer restaurants in the city is unknown.

After finishing this research, it has been noticed that the main limitations of this research were 1) the low size of the studied sample of restaurants, and 2) the general approach of working with different types of restaurants. A more precise research project should center itself in studying more restaurants and only of one type of food restaurant, like chicken food restaurants in the city.

These results can be used to better understand this primary energy resource in the city, help in future decision making, prefeasibility, and feasibility studies for a biodiesel refinery using WCO from this city restaurants. These results can also be used as a base for characterization of biodiesel production potential from WCO in other cities around the world.

VII. RECOMMENDATIONS

Considering the mentioned conclusions, the following recommendations are presented.

- A biodiesel production project can initially center its efforts working with chicken food restaurants, as they are the ones with highest oil consumption and will produce the most feedstock amount for the biodiesel project, lowering the oil collection costs.
- For a biodiesel production project that will work with a random group of different types of restaurants, a good approximation of the expected oil feedstock of that random group will be 1,425 L/year per restaurant.
- 3. A biodiesel plant that works with a combination of oils, of random different restaurants in the city, can avoid water drying pretreatment and the costly acid esterification pretreatment to reduce soap formation. Even if too much soap is formed, adding sulfuric acid after transesterification will neutralize the soaps making it a good alternative for the pretreatment.
- 4. A biodiesel yield of 81.24% m/m per oil mass, is an acceptable value to use in prefeasibility and feasibility studies for biodiesel plants.
- 5. The byproducts yield and resources consumption per WCO mass in biodiesel production summarized in table 11, section 5.4 can be used in prefeasibility and feasibility studies for batch biodiesel reactor plants using the WCO of San Pedro Sula's restaurants.
- Studies of prefeasibility and feasibility for biodiesel production plant using the WCO of San Pedro Sula's restaurants should limit their size to produce no more than 2,979 Tons of biodiesel per year to avoid oversizing issues.
- 7. It is recommended to do a bigger research, that considers more restaurants in San Pedro Sula, to improve and make more precise the city biodiesel production potential characterization. This bigger research, if done, should use the method stablished in section 4.3.1 to improve its reliability.

VIII. APPLICABILITY

These results can be used to better understand this primary energy resource in the city, help in future decision making, prefeasibility, and feasibility studies for a biodiesel refinery using WCO from this city restaurants.

These results can also be used as a base for characterization of biodiesel production potential from WCO in other cities around the world.

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X. ANNEXES

10.1 SURVEY QUESTIONS

The survey consists of the following questions (some are multiple choice, and others are short answer questions):

- 1) What is your main food type?
- 2) Do you use cooking oil and/or animal fats in your restaurant?
 - a. Only cooking oils
 - b. Both, cooking oils and animal fats
 - c. Only animal fats
 - d. Use neither
- 3) What type of cooking oil you use?
 - a. Generic Vegetable Oil
 - b. Palm Oil
 - c. Canola Oil
 - d. Corn Oil
 - e. Soybean Oil
 - f. Sunflower Oil
 - g. Other: _____
- 4) Approximately, how many gallons per week do you use in cooking oil?
- 5) What do you do with the residues of your cooking oil?
 - a. Throw them away
 - b. Donate them
 - c. Sell them

d. Other:_____

- 6) Would you let us collect a sample of your waste cooking oil?
 - a. Yes
 - b. No

The names of the restaurants are treated anonymously.

10.2 SURVEY ANSWERS

No.	What is your main food type?	Do you use cooking oil and/or animal fats in your restaurant?	What type of cooking oil you use?	Approximately, how many gallons per week do you use in cooking oil?	What do you do with the residues of your cooking oil?
1	chicken	only oils	generic vegetable oil	7	throw them away
2	chicken	only oils	generic vegetable oil	4	sell them
3	traditional food	only oils	generic vegetable oil	0.5	throw them away
4	Chinese food	only oils	generic vegetable oil	6	throw them away
5	soups	only oils	generic vegetable oil	0.4	throw them away
6	traditional food	only oils	generic vegetable oil	9	sell them
7	chicken	only oils	generic vegetable oil	5	sell them
8	chicken	only oils	generic vegetable oil	10	sell them
9	chicken	only oils	generic vegetable oil	20	sell them
10	traditional food	only oils	*Did not answer*	*Did not answer*	throw them away
11	hamburgers	only oils	generic vegetable oil	*Did not answer*	sell them
12	traditional food	both	generic vegetable oil	3	throw them away
13	traditional food	both	generic vegetable oil	7	throw them away
14	traditional food	both	generic vegetable oil	15	reuse them

15	traditional food	only fats	*Not applicable*	*Not applicable*	*Not applicable*
16	coffee & bakery	neither	*Not applicable*	*Not applicable*	*Not applicable*
17	coffee & bakery	neither	*Not applicable*	*Not applicable*	*Not applicable*
18	coffee & bakery	neither	*Not applicable*	*Not applicable*	*Not applicable*
19	natural juices	neither	*Not applicable*	*Not applicable*	*Not applicable*
20	coffee & bakery	neither	*Not applicable*	*Not applicable*	*Not applicable*
21	pizza	*Not available*	*Not available*	*Not available*	*Not available*
22	pizza	*Not available*	*Not available*	*Not available*	*Not available*
23	*unknown*	*Not available*	*Not available*	*Not available*	*Not available*

10.3 DEMONSTRATION OF VISCOSITY PROPORTIONAL DEPENDENCY TO TIME IN THE

PROPOSED EXPERIMENTAL VISCOMETER

The proposed experimental viscometer looks as follows:



This is analyzed as follows:



This setup consists of a thin long straw connected to a large syringe. This can be analyzed as a laminar flow passing by a cylindrical tube. The inner flow in the thin and long straw is laminar due to its low Reynolds Number (<2300). This inner laminar flow is determined by the

Poiseuille equation. Poiseuille equation expresses the volumetric flow in function of the liquid dynamic viscosity, pressure difference between the ends of the tube, and geometrical dimensions of the tube.

the Poiseuille equation for a vertical tube is the following:

$$Q = \frac{\pi \cdot R^4 \cdot (\Delta P + \rho gL)}{8 \cdot L \cdot \mu}$$

 $Q = Liquid volumetric flow [m^3/s]$

 $\pi = Pi [3.1415 \dots]$

R = Cylindrical tube radius [m]

 $\Delta P = Pressure \ difference \ in \ the \ tube \ [N/m^2]$

 $\rho = Liquid \ density \ [kg/m^3]$

- $g = Gravity \ aceleration \ [9.81m/s^2]$
- $L = Tube \ length \ [m]$
- $\mu = Dynamic \ viscosity \ [kg/m \cdot s]$

The pressure difference between the edges of the straw is:

$$\Delta P = P_1 - P_2$$
$$P_2 = P_0 = 0$$
$$\Delta P = P_1$$

 $\Delta P = Pressure \ difference \ in \ the \ tube \ [N/m^2]$

- $P_1 = Pressure at the top of the straw [N/m^2]$
- P_2 = Pressure at the bottom exit of the straw $[N/m^2]$
- $P_0 = Atmospheric Pressure [0N/m^2]$

The hydrostatic pressure at the top of the straw can be expressed as a function of the liquid volume in the syringe as follows:

$$P_{1} = \rho \cdot g \cdot h$$
$$V = h \cdot A_{1}$$
$$h = \frac{V}{A_{1}}$$
$$P_1 = \frac{\rho \cdot g}{A_1} \cdot V$$

 $P_1 = Pressure at the top of the straw [N/m^2]$

- $\rho = Liquid \ density \ [kg/m^3]$
- $g = Gravity \ aceleration \ [9.81m/s^2]$

$$h = liquid height [m]$$

- $A_1 = Transversal area of the syringe [m^2]$
- V = Actual volume of the liquid in the syringe [m³]

By substituting the pressure difference, in the Poiseuille equation, by the hydrostatic pressure in function of the volume, we obtain the following:

$$Q = \frac{\pi \cdot R^4}{8 \cdot L \cdot \mu} \cdot \left(\frac{\rho \cdot g}{A_1} \cdot V + \rho \cdot g \cdot L \right)$$

This can be rearranged as follows:

$$Q = \frac{\pi \cdot R^4 \cdot g}{8 \cdot L \cdot A_1} \cdot \frac{\rho}{\mu} \cdot (V + L \cdot A_1)$$

The kinematic viscosity can be introduced in the equation as follows:

$$\nu = \frac{\mu}{\rho}$$
$$Q = \frac{\pi \cdot R^4 \cdot g}{8 \cdot L \cdot A_1} \cdot \frac{1}{\nu} \cdot (V + L \cdot A_1)$$

v = Liquid kinematic viscosity $[m^2/s]$

To make the equation easier to operate, all the geometrical constants can be substituted by new constants as follows:

$$K_1 = \frac{\pi \cdot R^4 \cdot g}{8 \cdot L \cdot A_1}$$
$$K_2 = L \cdot A_1$$

Now we have an equation that relates the volumetric flow to the liquid volume in the syringe, and the kinematic viscosity of the liquid as follows.

$$Q = K_1 \cdot \frac{1}{\nu} \cdot (V + K_2)$$

As the liquid in the syringe is drained in the straw, the liquid volume in the syringe will be changing depending on time and the volumetric flow as the following differential equation.

$$dV = -Qdt$$

By substituting the volumetric flow obtained from the Poiseuille equation in this differential equation, we obtain the following:

$$dV = -K_1 \cdot \frac{1}{\nu} \cdot (V + K_2) dt$$

This can be solved and integrated as follows:

$$\nu \cdot \frac{1}{(V+K_2)} dV = -K_1 dt$$
$$\nu \cdot \int_{V_1}^{V_2} \frac{1}{(V+K_2)} dV = -K_1 \int_{t_1}^{t_2} dt$$
$$\nu \cdot \ln\left(\frac{V_2 + K_2}{V_1 + K_2}\right) = -K_1(t_2 - t_1)$$

When reordering the equation, we get the following:

$$\nu = \frac{K_1}{ln\left(\frac{V_1 + K_2}{V_2 + K_2}\right)}\Delta t$$

Now we have an equation that relates the kinematic viscosity only to the time it takes for the liquid volume, in the syringe, to pass from V_1 to V_2 . If we set constant V_1 and V_2 in all the experiments, then the equation can be simplified to a proportional relation with only one constant as follows:

$$K_3 = \frac{K_1}{ln\left(\frac{V_1 + K_2}{V_2 + K_2}\right)}$$
$$v = K_3 \Delta t$$

In this research $V_1 = 30ml$ and $V_2 = 10ml$. The value of K_3 was obtained by experimental measurements with liquids of known viscosity like distilled water.

10.4 OBTAINED RESULTS DATA

Sample	Restaurant Consumption	Restaurant Consumption	Density	Restaurant Consumption	Viscosity	Acid Value	%FFA	Humidity
	[gal/sem]	[l/year]	[kg/m³]	[kg/year]	[mm²/s]	[mgKOH/gOil]	[% m/m]	[% m/m]
1	7	1378	902	1243	30	1.71	0.86%	0.21%
2	4	787	910	717	26	1.23	0.62%	0.21%
3	0.5	98	909	89	26	1.77	0.89%	0.22%
4	7	1378	911	1256	N/A	2.31	1.16%	1.05%
5	6	1181	906	1070	30	1.01	0.51%	0.25%
6	20	3937	909	3580	24	5.71	2.87%	0.21%
7	0.4	79	895	70	36	1.57	0.79%	0.22%
8	9	1772	911	1614	31	2.23	1.12%	0.21%
9	15	2953	916	2703	32	1.76	0.89%	0.22%
10	5	984	912	897	28	8.39	4.21%	0.21%
11	3	591	912	538	31	1.54	0.77%	0.21%
12	10	1968	910	1792	28	2.54	1.28%	0.21%
Total	86.9	17106	10903	15570	320	31.77	15.97%	3.43%
Mean	7.2	1425	909	1298	29.10	2.65	1.33%	0.29%
Median	6.5	1279	910	1157	29.57	1.77	0.89%	0.21%
Min	0.4	79	895	70	24.09	1.01	0.51%	0.21%
Max	20.0	3937	916	3580	35.77	8.39	4.21%	1.05%
Est. Dev.	5.7	1128	5.46	1028.17	3.31	2.18	1.09%	0.24%

Table 12: Measurements of oil samples quality

Source: Own Elaboration

Sample	Restaurant Consumption	Density	Viscosity	Biodiesel yield factor	Biodiesel Production Potential
[-]	[kg/year]	[kg/m ³]	[mm ² /s]	[% m/m]	[kg/year]
1	1243	853	2.31	83.7%	1041
2	717	849	2.28	79.7%	571
3	89	851	2.28	91.0%	81
4	1256	842	N/A	70.9%	891
5	1070	842	2.19	84.3%	902
6	3580	856	4.53	74.1%	2654
7	70	867	2.85	73.9%	52
8	1614	844	2.48	92.7%	1496
9	2703	856	2.39	85.4%	2310
10	897	850	2.24	71.5%	641
11	538	854	2.23	86.3%	464
12	1792	851	2.70	86.2%	1544
Total	15570	10216	28	980%	12649
Mean	1297.5	851	2.59	81.7%	1054
Median	1156.5	851	2.31	84.0%	896
Min	70.4	842	2.19	70.9%	52
Max	3580.5	867	4.53	92.7%	2654
Est. Dev.	1028.2	6.83	0.68	7.5%	816
WAM				81.2%	

Table 13: Measurements of biodiesel samples quality

Source: Own Elaboration

Sample	Glycerol Yield	methanol Consum. %	KOH Consum. Fact.	Sulfuric Acid Consum. Fact.	Water Consum. %	Energy Consum. Fact.
[-]	[% m/m]	[% m/m]	[g/kg]	[g/kg]	[% m/m]	[kWh/kg]
1	19.0%	21.9%	11.71	0.11	113.6%	1.90
2	18.2%	21.9%	11.23	0.02	138.8%	2.53
3	19.0%	21.9%	11.77	0.18	148.8%	2.39
4	22.7%	21.9%	12.31	0.14	212.1%	5.67
5	16.6%	21.9%	11.01	0.03	165.7%	2.49
6	30.7%	28.4%	12.08	1.47	171.9%	4.83
7	26.8%	21.9%	11.57	0.19	165.2%	1.93
8	19.9%	21.9%	12.23	0.06	103.5%	1.78
9	20.1%	21.9%	11.76	0.20	185.2%	2.57
10	34.5%	31.4%	12.62	2.17	152.0%	4.27
11	18.7%	21.9%	11.54	0.02	100.6%	2.27
12	23.5%	21.9%	12.54	0.05	79.5%	1.86
Total	269.7%	278.74%	142.37	4.63	1737.05%	34.499
Mean	22.5%	23.23%	11.86	0.39	144.75%	2.875
Median	20.0%	21.90%	11.77	0.12	150.39%	2.441
Min	16.6%	21.90%	11.01	0.02	79.55%	1.780
Max	34.5%	31.38%	12.62	2.17	212.13%	5.674
desv. Est.	5.5%	3.17%	0.50	0.69	39.01%	1.301
WAM	23.5%	23.9%	11.98	0.53	149.4%	3.20

Table 14: Measurements of byproducts yield and resources consumption factors during the biodiesel production

Source: Own Elaboration