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MASTER'S THESIS

Title: Development of an additive for diesel fuel based on vegetable oil production wastes.

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ABSTRACT

With an average carbon numbers ranging from 10 to 22, diesel fuel is a combination of hydrocarbons [1].

During cold temperatures, large wax crystal lattices begin to solidify, leading to a phenomenon named as diesel fuel gelling [2]. This may lead to several problems. The lower the temperature, the harder the vaporization of the diesel oil and the longer the start delay of the engine [3]. This problem needs to be solved through cold flow additive improvers.

This experimental analysis has for fundamental goal to find out how the sunflower oil waste can be utilized as a bio-additive to implement the cold temperature properties of the Petro-diesel. This is achieved through the treatment of sunflower oil waste with acetone, before extracting the acid present through distillation. The Free Fatty Acid (FFA) was determined using a pipette. Using KOH as a catalyst and ethanol as an alcohol, biodiesel was obtained through transesterification with a temperature ranging between 50 to 60 degrees Celsius.

The ester obtain was later mixed with the Petro-diesel. The CFPP, CPP and lubrication ability of this mixture was analyzed and compared with the initial Petro-diesel. Also, some IR-spectra of the mixture were determined.

From the result received it can be said that the mixture of additives and diesel fuel obtained has a good lubrication and filtration ability.

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INTRODUCTION

During winter time, some properties of petro-diesel are affected. Formation of wax (paraffin) can be observed. This may have led to problem such as diesel tank clogging. Russian oil production is nearly solely and stressed from the problem of paraffin formation [4].Thermal, chemical or mechanical method can be useful for paraffin moderation.

Due to its higher cetane number, biodiesel (mono-alkyl esters) improves the ignition quality even if it is blended with mineral diesel. It has better lubricant properties than diesel fuel. It can be used as an additive in petro-diesel.

This proposed study strives to improve the cold properties of petro-diesel with additives based on vegetable oil production waste such as sunflower. Through transesterification, the esters would be obtained and later mixed with the initial petro-diesel to improve its cold properties. An Infra-Red spectroscopy would be run to endorse the chemical quality of some samples.

1.1 Historical evolution of diesel and biodiesel

The diesel engine was invented in the 1890s by the German engineer Rudolf Diesel [5]. From the outset the diesel engine had one advantage over its petrol counterpart in that it had the capacity to run on fuels derived from a variety of sources, including vegetable oil. Indeed, at the Paris Exposition of 1900 a diesel engine running on peanut oil was exhibited [5].

Modern biodiesel fuel is an outcome of research conducted in 1930s in Belgium, which is made by converting vegetable oils into compounds called fatty acid methyl esters [6].

The European biodiesel industry was launched around the late 1980s [5].

Pacific Biodiesel became one of the first biodiesel plants in the United States in 1996, establishing a biodiesel production operation to recycle used cooking oil into biodiesel on the island Maui in Hawaii [6].

1.2 Aims and objectives

The main aim of the present study is to produce biodiesel(as an additive) through transesterification process using low-value triglyceride resources such as waste edible oils like sunflower in the presence of KOH as the alkali catalyst and ethanol as the alcohol reagent.

It also has for objectives to assess the yield and purity performance from waste sunflower with KOH during transesterification process. Mixing the additive obtained with the initial diesel to improved its cold properties.

1.3 Scope

-Extracting the acid present in the sunflower waste through vacuum distillation

-Determining the rate of the fatty present

-Determining the amount of catalyst (KOH) needed during each experiment

-Analyzing the influence of catalyst concentration on yield and purity of biodiesel using batch transesterification process

-Observing the effect of molar ratio

Analyzing the effect of the flow rate and residence time

-Observing the effect of reaction temperature in biodiesel

-Determining the cold properties of the additive blended with diesel oil

-Comparing the results obtained with the initial petro-diesel.

2.0 Literature review

2.1.1 Wax in diesel fuel

Wax seems brown in color and cloudy in appearance during low temperature. It is less dense than oil. Wax gel and aging gel are 2 main steps in wax formation[7]. When wax gel seems more mature in size and its hardness has risen in term of quality, it is mentioned as aging. There are more than 15 atoms of carbon number of paraffinic molecules in wax[4].

Nuclei are unstable clusters and may be obtained by the dissolution of the clusters when its expected size has not been reached. Gravity settling is one of the mechanism used in wax formation .Molecular diffusion, shear dispersion, Brownian diffusion are additional kinds of mechanism[8].

Some parameters influencing wax formation are listed as follow:

-Melting point

-Pour point

-Wax Appearance Temperature (WAT) or Cloud Point

-Pressure

-Oil composition

-Water oil ratio

-Flow rate

2.1.2 Cold flow properties of diesel fuel

Cloud Point (CP) is the temperature at which wax crystal is observed. Diesel fuel has usually a CP falling in the interval of 10 to 20 $^{\circ}$ C [9]. Below Cloud Point, it can be noticed that wax may be damageable [10]. Some of ASTM Standards used to determine the CP are:

-ASTM D5771-02 -ASTM D5772-02 -ASTM D5773-02 -ASTM D2500 Pour Point (PP) is the lowest temperature at which fuel becomes fluid. The diesel fuel viscosity is linked to its Pour Point. A low viscosity has for result a high Pour Point. However, a sudden rise up of the oil viscosity can be justify by the presence of asphaltenes in the oil, formed as a result of cracking process. Asphaltenes have the capacity to retain wax crystals in suspension, which may later lead to a lesser PP. In the case of PP, ASTM standards method such as ASTM D5949-02, ASTM D97 can be used to determine the pour point.

Cold filter plugging point (CFPP) is the temperature at which fuel filters plug.ASTM standard test method such as ASTM D6371, can be used to find the CFPP of diesel fuel.

Low temperature flow test (LTFT) is an indicative of low temperature flow performance of test diesel oil.ASTM Standard such as ASTM D4539-03 can be used to find the LTFT.

2.1.3 Types of additives used for diesel oil

Additive [11] is the term use to describe a material that has the ability to influence the properties of the fuel. Additives [11] are generally used to develop the fuel properties. They do not form naturally and a low quantity of it are blended with diesel fuel [12].

Cold flow improvers are mostly vinyl ester co-polymers like ethylene vinyl acetate (EVA) [13]. A percentage falling between 20 to 30 percent of Ethylene Vinyl Acetate is the quantity frequently use [9]. Studies showed that the higher the EVA in the fuel, the lower the WAT. This will prevent the wax of being crystallized [14]. It is the type of cold flow improver mostly use, especially in Alaska. Olefinester copolymers can also be combined with EVA [14]. Cold flow improver is frequently use during pre-combustion.

This additive has for aims to :

-Prevent the settlement of big steady lattice

-Modifying the size and shapes from plate-like to needle-like as an antisettling.

However, it has a limitation such as the settlement of precipitated crystal growth at the lowest part of the tank.

Cetane improvers are principally alkyl nitrates such as 2-Ethyl Hexyl Nitrate (2-EHN) [15] .Peroxides like tertiary butyl peroxide can also be used but it is less cost effective than alkyl nitrates. By adding a cetane improver to the oil, the cetane number can be boost from 5 to 10 marks. These types of additives are use during combustion.

The objectives of this type of additives are :

-To provide a cost-effective increase in diesel cetane quality which will result in reducing ignition delay.

- To improve cold start

- To minimize engine noise

- To minimize oil consumption

Cetane improvers may have some negative aspects such as the presence of nitrogen in its composition that can lead to an increase of nitrogen in diesel fuel [16].Polyethers and di-t-butyl peroxide are types of nitrogen-free cetane improvers. Since the engine of the diesel power plant has been maintain inside, it is not advice to use a cetane improver for diesel power plant because of the low probability of cold start [3].

Ethylene Glycol Mono Methyl Ether (EGME) [17]or Diethylene Glycol Mono Methyl Ether (DIEGME) [15] are types of Glycol ethers use in diesel fuel as deicers. It has for objectives to:

-Lower the gelling point of the water below the cold filter plug point (CFPP) of diesel oil

-Prevent ice crystals from plugging the fuel filter

Stabilizers: Cyclic amines are frequently used as diesel fuel. Stabilizes Antioxidants are found in several stabilizers. As a remedial to initiation of unwanted reactions, it forms a bond with free radical in fuel. It may be difficult to establish the necessity of stabilizers [4] in diesel fuel due to the fact that it stability may diverge from one fuel to another.

Stabilizer [4] have for objectives to:

- Diminish plugging and filter deposit

- Diminish the ability for injection and pumping system component sticking.

Demulsifiers and dehazers: with low temperature, water can be formed in diesel fuel which may lead to the establishment of some contaminants in the fuel. It can influence the performance of the engine. Demulsifiers [2] aim to prevent the formation of water based emulsion [16]. They favor the settlement and the removal of water at the lowest part of the tank.

They are complex mixtures of a wide variety of alkoxylate (Hancsok, S.P.Srivastara Jeno, 2014) chemistries comprising phenolic resins, esters, polyamines, sulphonates or alcohols (methanol may have some side effect on diesel fuel) which have a reaction with ethylene or propylene oxide.

Lubricity improvers : they are surface active compounds, consisting of an active polar head group Oleic acid, linoleic acid, α linolenic acid are examples of lubricity improvers [2]. Those types of additives have for role the restoration lubricity lost.

Corrosion inhibitors : Alkyl-succinates, carboxylic acids salts, dimer acids and amines salts are varieties of corrosion inhibitors.It prevents corrosive effects of water on fuel handling systems and components.

2.2.0 Properties of biodiesel

This fuel has similar properties to fossil diesel but it is much better than the latter [6]. Biodiesel poses fewer actual dangers than diesel. This plant or animal-based fuel burns very clean and is biodegradable and non-toxic. Furthermore, it does not pose any danger when it evaporates. When biodiesel burns, it releases fewer pollutants. Also, the combustion outlet does not contain aromatic and Sulphur compounds.

2.2.1 Pour point

It is the temperature at which biodiesel solidifies [18] and can no longer be pumped. Fuel with lower pour point limit the use in cold environment.

2.2.2 Flash point

It is the minimum temperature at which biodiesel gives off sufficient vapors which can be mixed with air and will ignite [[20],[18]]. Biodiesel has an average flash point of 150°C [20]. It is used as a directive for safety precautions in fuel handling and storage.

2.2.3 Viscosity

Biodiesel has its viscosity often by a factor of two higher than petro-diesel [21]. The percentage of biodiesel is linked to its viscosity. The viscosity of biodiesel can increase due to the chain length of the alcohol or the fatty acid.

2.2.4 Acid number

The acid number is a parameter that informs the quantity of free fatty acids and of acids originating from degradation reactions of biodiesel. The ASTM D 6751 biodiesel acid-number limit was synchronized with the European biodiesel value of 0.50, in 2006 [22]. ASTM D 664 is the standard reference method for measuring the acid number of both ASTM biodiesel and petroleum-derived diesel [[4],[20],[22]].

2.2.5 Calorific value

The calorific value of biodiesel is about 37.27 MJ/kg. It plays a major role in the fuel consumption, exhaust emission and thermal efficiency.

2.2.6 Cetane number

It is the measures of ignition delay [3]. A high increase of cetane number leads to a short ignition delay [3]. Cetane numbers can be measured method by the Cooperative Fuel Research (CFR) Committee which is a scheme acquired in 1930s, and later standardized as ASTM D613 [20].Biodiesel has its cetane number usually greater than diesel fuel [17]. The cetane number of biodiesels is generally varying between 45 and 70, as compared to 40 and 52 for typical petroleum diesel fuels [17].

2.2.7 Density

Density is the mass per unit volume of a substance [23]. It can influence the mass flow rate of biodiesel.

2.3 Types of feedstocks use in biodiesel production

Oils and fats, known as lipids, are hydrophobic substances insoluble in water and are of animal or vegetal origin [[24],[20]]. They differ in their physical states at room temperature. From a chemical viewpoint, lipids are fatty glycerol esters known as triglycerides [[25],[10]].

The biodiesel is classified as first, second and third generation depending on the material, its properties, the free fatty acids content [26]. The first-generation biodiesel is mainly obtained from edible oils like corn, rice, sorghum, canola, peanut, jatropha, mahua, Karanja, tobacco and sunflower oil [[26],[24]]. In the developing countries where food security is one of the major concern, instead of edible oils, biodiesel production can be done with other low cost feed stock [26]. The vegetable oil has advantages that is that it can be mixed with Petro-diesel and used for ignition engines and causes less pollution.

It has also benefitted that it is portable, easily available, and renewable has high energy content. But it is highly viscous in nature, costly and less volatile [[26],[21]]. The second-generation biodiesel is produced with the help of non-edible oils and used cooking oils and waste animal fats such as beef tallow, pork lard, fish oil and poultry fat [27].Non edible oil crops are grown in waste lands and have low cultivation cost and can grow in adverse climatic conditions [[28],[10],[29]]. The non-edible crops solve the problem of competition for food resources, results in lot of valuable byproducts and considerably economical [29]. These sources have drawback that they have higher acidity and high fatty acids content. The biodiesel produced from sources waste oil from refineries, waste grease oil forms the third-generation biodiesel [29]. By depending on these resources, addresses the issue of disposing the waste and improving the environmental impact.

2.4 Alcohol use in biodiesel production

Alcohols that can be used in biodiesel production are those with short chains, including methanol, ethanol, butanol, and amylic alcohol [[12],[30]]. The alcohol used for biodiesel production is until now almost entirely methanol. Methanol is a large-scale synthetic intermediate obtained from methane processing and available at 100–300 Euro/t. It is also possible to use anhydrous ethanol, which is commonly used as a gasoline additive with environmental advantages.

However, a comparison of both alcohols in the biodiesel production has shown that the use of ethanol instead of methanol is 3-4 times more expensive [29]. This effect is coming from the actual price as well as the molar weight differences. Moreover, ethanol forms an azeotrope with water, which makes its recovery and recycling after transesterification even more expensive [31].

2.5 Catalysts use in biodiesel production

A catalyst is a substance that increases the chemical reaction rate without being consumed by the reaction itself [24]. Theoretically, the catalyst is practically consumed in one stage and regenerated at a later stage, and this operation is continuously repeated without imposing a permanent change on the catalyst. Accordingly, the catalyst in a given reaction can be recycled unchanged at the end of the reaction [24]. Catalysts change the speed of a chemical reaction that can be thermodynamically carried out [20]. Therefore, they cannot perform reactions that are not thermodynamically feasible. Basically, a catalyst is considered a chemical compound capable of applying an accelerating effect on the reaction rate and a directional effect on the reaction progression which is thermodynamic in nature [[24],[12]].

In a reversible reaction, the catalyst evenly affects the rate of forward and backward reactions. Therefore, the equilibrium constant of the reaction is the same whether in the presence of a catalyst or without it. When there are several mechanisms available for the reaction, the catalyst must be selected. In principle, the catalyst should increase the ratio of the desired material to the unwanted material [[24],[31]]. Although ideally catalysts remain unchanged during the reaction, this is inaccurate in practice, since the catalyst itself is a reactive substance that undergoes irreversible physical and chemical changes during the reaction, reducing its ability to function [24]. Over time, this reality may be vividly observed since the catalyst enters into billions of reactions. In general, the catalysts used in the transesterification of vegetable oils and animal fats can be classified into three groups – homogeneous, heterogeneous and enzymes [24].

The homogeneous catalysts can be divided into two categories, alkalis and acids [24]. The most common alkali catalysts are potassium hydroxide, potassium methoxide, sodium hydroxide and sodium methoxide. Alternately, the acid catalysts include products like sulphuric acid, hydrochloric acid and sulphonic acid [24].

The other group is formed by heterogeneous catalysts. It includes enzymes, titanium silicates, alkaline-earth metal compounds, anion exchange resins and guanadines heterogeneisated on organic polymers [24].

A third option is also available, it is using supercritical methanol [24]. In this case, no catalyst is needed, but, on the other hand, high temperature and high-pressure conditions.

2.6 Types of biodiesel production

Although there are many standard methods for biodiesel production, it seems that the most common way to produce biodiesel is through transesterification [[27],[23]]. This process involves a catalyzed chemical reaction including vegetable or animal oil and an alcohol for the production of fatty acid alkyl esters (biodiesel) and glycerin [10].

2.6.1 Pyrolysis

It is the decomposition of biomass (organic matter) at a higher temperature in the inert atmosphere to produce liquid oil, gas products and bio-char [[23],[32]]. It is one of the commonly used method for converting the waste materials into useful products. The fuel produced has the properties it can be stored and transported economically. The biodiesel has almost the similar properties when compared with diesel fuel. It can be used for combustion process or can be modified into liquid transport fuels. The pyrolysis process has the following drawbacks [23].

The bio-oil has properties like lower heating value, less volatility, instability that does not satisfy the properties of standard petroleum fuel properties. These are due to the presence of some unwanted chemical compounds. The elimination of oxygen is required to improve the properties of bio-oil and can be done using hydrotreating and catalytic cracking [[20],[24]]. Hydrotreating employs hydrogen for removing oxygen in the water form, while

catalytic cracking uses catalyst to remove oxygen [28]. It is difficult to find out the main product from the pyrolysis because the process is dependent on the experimental conditions such as vapor residence time, temperature of the reaction and the heating rates.

The process has main three products liquid oil, solid residue and incondensable gases.

Therefore, these experimental conditions have to be optimized to obtain the desired product.

2.6.2 Reactive Distillation

It is a process in which the chemical reaction and the product separation occur together in the same unit [30]. It is beneficial for the reactions where one of the reactants is present in excess or when one of the products has to be removed for the completion of the reaction. The process does not require any post-processing separation and purification steps. It reduces the number of process units and thus decreasing the cost of the process.

2.6.3 Reactive Extraction

The conventional methods for biodiesel production involve various steps such as extracting oil, purification of the oil and the transesterification process [[25],[20]]. These steps form a major part of the biodiesel production cost. Thus, there is a requirement for a method which extracts the oil and also the oil is subjected to transesterification process.

In this method oil-containing material is treated with alcohol, so that extraction and transesterification steps are carried out together.

Depending on the type of catalyst, the reaction extraction can be chemical or enzymatic type transesterification [24]. Thus, the process reduces the number of steps and the cost of the process.

2.6.4 Microwave process

Microwave is a type of electromagnetic irradiation with wavelength varying from 0.01 to 1 m and frequency in the range of 0.3 to 300 GHz [24]. These are non-ionizing radiations having lower energy content that does not ionize the atoms, but instead affects the molecular motion without changing the structure. It accelerates the chemical reactions and delivers the required energy to the reactants present in the system [24]. The reactants present such as feed oil, alcohol and the catalyst contain polar as well as ionic components and these components absorb the microwave energy. Thus, the heat transfer is more efficient when compared to the conventional methods.

Because in conventional methods transfer of energy is dependent on convection and thermal conductivity of the system. It results in friction between the molecules and heat energy is produced. The process does not require samples free of water. The reaction is carried out in a short period of time.

The process requires internal mixing of the components because the microwaves may not reach to the higher depth and uniform mixing may not possible [[24],[30]]. Thus, the system has to be modified and modification in the experimental setup has to be done for reaching the target of biodiesel yield. It has also mass transfer limitations and the localized superheating has to be minimized.

2.6.5 Supercritical Method

A pure substance has a critical point between the gas and liquid [24]. There is formation of high-density fluid (supercritical fluid) above the critical point and cannot be subjected to condensation even after increasing temperature or pressure [[25],[31]]. In the supercritical state, the various properties such as dissociation constant, dielectric constant, specific gravity, polarity and viscosity changes drastically with respect to temperature and pressure [24].

These properties are beneficial for the reactions involved in biodiesel production. The supercritical technique uses the solvent in the supercritical condition i.e., at the critical temperature and pressure.

The drawbacks found in the catalytic transesterification process like by-products formed, wastewater generated, high enzyme cost can be eliminated. The separation and purification of the product is simpler and it requires no catalyst [24]. By using the components in supercritical state, homogeneous phase is formed which accelerates the transesterification reaction without using any catalyst [33]. In the homogeneous phase, his gas-liquid interface can be eliminated and the diffusivity of the components can be increased. The reaction happens at relatively higher temperature and pressure. Therefore, co-solvent which has critical point lesser than the solvent in the reaction mixture and the co-solvent decreases the critical point of the solution [33].

Thus, the reaction can be conducted at a moderate condition and the solubility of the oil and alcohol can be increased. The reaction can be completed faster in shorter because of the operating conditions. Because of the high temperature and pressure maintained in the process, the cost of the process increases and the energy required is more. Safety is one of the important issues with the supercritical method, since the process vessel is operated at higher pressure.

2.6.6 Ultrasound process

Ultrasound cavitation is advantageous over conventional mixing and forms effective contact between the two immiscible phases [33]. It increases the mass transfer between the feed oil and the reactants during transesterification process.

It is considered as cost-efficient process compared to the mechanical agitation and provides the activation energy to the transesterification process [24]. The process produces cavitation bubbles which passes through the solution and exerts varying pressure. The bubble collapses suddenly and releases the required amount of energy. The process improves the overall reaction rate, increases the biodiesel yield and decreases the reaction time.

The effect of ultrasound depends on two technical factors such as selecting the energy intensity and population of active cavitation. These two parameters are used for finding the efficiency. A large number of experiments are conducted to measure these key factors. Thus, some theoretical approach has to be developed to measure these parameters. The process has technical limitations and thus has to be studied thoroughly and research has to be carried out.

2.6.7 Transesterification process

The most common technology of biodiesel production is transesterification of oils (triglycerides) with alcohol which gives biodiesel (fatty acid alkyl esters, FAAE) as main product and glycerin as by product.

The first step is the conversion of triglycerides to diglycerides, which is followed by the conversion of diglycerides to monoglycerides and of monoglycerides to glycerol, yielding one methyl ester molecule from each glyceride at each step. Transesterification, also called alcoholysis, is exchanging of alcohol from an ester by another alcohol in a process similar to hydrolysis, except that an alcohol is used instead of water.

3.0 Methodology

3.1 Transesterification

3.1.1 Description

It is the most usual way of producing biodiesel [23]. The reaction begins when an alcohol, such as ethanol, is catalyzed, usually by potassium hydroxide (KOH) [33]. The mixture is later added to the acid that has been extracted from the sunflower waste (triglyceride).



3.1.2 Reagents

-Sunflower waste (It was the sample used in the production of biodiesel)

-Acetone -Ethanol (alcohol) -Potassium hydroxide (catalyst)

3.1.3 Equipment

-Speed controller -Hot plate -Thermometer -Magnetic stirrer -Condenser -Three -neck flask



Figure 2 - Transesterification process set

3.1.4 Procedure

Based on calculation, potassium hydroxide (KOH) has been weighted and added to the require amount of alcohol. This mixture was later shaken to allow the KOH to dissolve in the methanol before pouring it in a three-neck flask and placing it on the electrical stove with a temperature ranging between 50 to 60 degrees Celsius. A condenser has been connected to one neck of the flask for cooling. A thermometer calibrated from 0 to 100 degree Celsius was placed in the middle neck of the flask. A separating funnel containing a measured amount of fatty acid is then connected to the last neck of the flask. The fatty acid is added drop by drop to the alcohol and stirred up with the help of a magnet for a duration of 1 hour.

The mixture obtained at the end of that period had to be cooled down totally before proceeding to the collect of the ether yield, using a separator funnel. The bottom layer is considered as waste and need to be removed first. Later 100ml of water is added to the top layer to wash out some remaining waste. After the removal of water, the final ether yield needs to be weighted and stock in a bottle. A small amount of salt is also added to favor the dry out of any remaining amount of water present in the ether. This experiment is repeated up to 3 times with different mass weight percent of KOH, Weight of methanol used and mass of fatty acid used during the experiment. A part of the samples will be later analyzed before mixing it to diesel.

Weight percent of KOH (wt. %) = (mass of KOH)/(mass of ethanol) x 100

3.2. Acid extraction from waste sunflower

3.2.1. Reagents

-Waste from sunflower was used as feedstock in this experiment

-Acetone had been used as a solvent to treat the raw material and extract the acid present in the sample

3.2.2 Equipment

-Weight balance -Separatory funnel of 500ml -Conical flask -Funnel -Vacuum dryer



Figure 3 – Acid extraction through vacuum dryer.

3.2.3 Procedure

-1 portion of phospholipid requires 4 portions of acetone

-150.15g of waste sunflower was weighted and put in a cylinder

-500 ml of acetone was later mixed with the measured sample -The blend had to be shaken for 1 minute before being put to rest for 5 minutes. This practice had been repeated 5 times.

-The solution had been put to rest for not less than 72 hours

-The 2 layers of mixture obtained, had to be separated using a separator funnel of 500 ml.

-276g of a solvent had been yield (It is a liquid with acetone)

-A rotational vacuum dryer is later used to remove water from the acid at a temperature located between 60 to 70 degrees Celsius (acetone has a temperature around 50 degrees Celsius)

-The filtrated solvent yields

3.3 Alcohol- catalyst mixing

3.3.1 Reagents

-100ml of ethyl alcohol -8g of KOH (catalyst)

3.3.2 Equipment

-Heater -Condenser -Round bottom flask -Thermometer

3.3.3 Procedure

-Some amount of KOH (KOH is used as a catalyst) was added to measure the titration

-The KOH solution is later poured in the ethyl alcohol(ethanol)

-100 ml of ethyl alcohol was later mixed with 8g of KOH (solid state)

-The mixture is stirred until the catalyst is completely dissolved in the alcohol and later taken to heat until it reaches its boiling point

-The duration of boiling was set to 1 hour

-Flask and cooler were used

-KOH was removed from that solution after the time reached

-The remaining liquid had to be distillate and that alcohol was put in a place for not less than 3 days

-The top part of the layer (transparent, colorless or clear) for preparation solution of titration

3.4 Fatty acid

3.4.1 Chemical titration method

Fatty acid concentrations equal or higher than 1 mm may be easily determined by titrimetry even in the presence of other lipids. Titrimetry was classically used to determine the acid value (free fatty content) of vegetable oils and fats. This acid value is defined as the number of mg of KOH required to neutralize the fatty acids contained in 1 g of the fat. It is very easy to express the results in other units as mg fatty acids per g of sample or mmoles per Kg.

3.4.2 Procedure

-Weigh 0.1 to 10 g of oil or fat (according to the expected acid value) in glass vial and dissolve in at least 50 ml of the solvent mixture (if necessary, by gentle heating).

-Titrate, with shaking, with the KOH solution (in a 25 ml burette graduated in 0.1 ml) to the end point of the indicator (5 drops of indicator), the pink color persisting for at least 10 s.

3.5 Filtration ability (CFPP)

The test method used was ASTM D-6371. It grants the assessment of the lowest temperature at which diesel fuel may encounter difficulty to flow. A 45ml of the mixture was measure with a cylindrical glass and introduce into the test jar and closed with a stopper. A thermometer introduced into the device had for role to the temperature of the liquid throughout its period of filtration. When the fluid has reached its lowest level, the device automatically gives a signal through a particular noise. The filtration ability of the fluid is then recorded.

The image bellows is a device used to determine the filtration ability of a liquid.



Figure 4 – CFPP device.

3.6 Cloud Point (CP)

The petroleum industry used ASTM 2500-02 for CP test method.45ml of the mixture was measured and introduce to the device. After naming the sample and correcting the setting, the device begins to run its analysis. At the end of the experiment, the result has been recorded on the screen.

The image bellows is a cloud point device



Figure 5 – Cloud point device

3.7 Lubrication ability

The method used in this experiment is the ISO 12156:1. The equipment is firstly clean with toluene (for 10mn) and later with acetone (5 to 10mn). This is primordial for the removal of any sediment or particle. The kit is transfer to an ultrasonic bath. Through ultrasound contaminants are removed from the surface with the help of an aqueous solution.

A desiccator cabinet has a dry inert environment which can be used to stock volatile products such as biodiesel. The right humidity and temperature had to be fixed. The right condition was established at 60°C. 2ml of the mixture was placed on the plate. 200g of load had to establish contact with the plate and ball for 1 hour and 15 minutes. The next step was to estimate the area of roughness through microscope and deduct the lubrication ability using the points obtained on Y and X axes.

The image bellows is a device used to determine the lubrication ability of a liquid.



Figure 6 – Lubrication ability device.

4.0 Result and discussion

The table below is a summary of the initial products used and the final ether received during the transesterification process.

Table 1 – Summary of initial product used and final ester yield during transesterification

Experiments	1	2	3	
Duration	1 hour	1 hour	1 hour	
Temperature	50-60	50-60	50-60	
(Celsius)				
Amount of alcohol	60ml	80 ml	80 ml	
used (ml)				
Weight percent of	1.5	3	0.75	
KOH (Wt. %)				
Mass of initial acid	10.35 g	30 g	30 g	
Mass of final ether	2.9 g	14.73g	17.87g	
yield				

The following results below represent the effects of additives on cold temperature of diesel realized on Sample 1.Some of the cold flow properties analyze were filtration ability (CFPP), Cloud Point (CP) and lubrication ability.

4.1 Filtration ability (CFPP)

The table below is a result of filtration ability obtained from the mixture (additives +diesel).

Percentage of additives	0.57	0.13	0.06	0.02
blended (%)				
Mass of additives blended	0.2386	0.0529	0.024	0.008
(g)				
Mass of diesel used	41.68	41.68	1.68	41.68
CFPP (filtration ability) of	-51	-50	-49	-48
mixture				
CFPP of initial diesel (°C)	-40	-40	-40	-40

Table 2 – Filtration ability of the blended liquids

The CFPP test done on 4 different samples proved that the additives mixed with diesel fuel has improved its filtration ability. Indeed, the initial diesel had a CFPP of -40°C and the 4 samples mixed with additives had a filtration ability o -51°C,-50°C,-49°C and -48°C respectively. The additives do not really affect the cold properties of diesel.

4.2 Cloud Point (CP)

The table below are results of Cloud Point obtained from the mixture (additives +diesel).

Percentage of additives	0.57	0.13	0.06	0.02
blended (%)				
Mass of additives	0.2386	0.0529	0.024	0.008
blended (g)				
Mass of diesel used	41.68	41.68	41.68	41.68
Cloud Point (CPP) of	-33.0	-34.0	-35.0	-35.0
mixture (°C)				
Cloud point (CPP) of	-34	-34	-34	-34
initial diesel (°C)				

Table 3 – Cloud Point of the mixture

The cloud point test done on 4 different samples has shown that the additives used do not really affect the cold flow properties of diesel.

4.3 Lubrication ability

The table below are results of lubrication ability obtained from the mixture (additives +diesel).

Percentage of esters blended (%) to	0.13	0.06
initial diesel		
Mass of biodiesel blended (g)	0.0529	0.024
Mass of initial diesel used (g)	41.68	41.68
Lubrication ability	340(<460)	411(<460)
	good	good
Lubrication ability of initial diesel	478	478
used		

Table 4 - Lubrication ability of the esters blended

Lubrication ability was tested on 2 different samples mixed with additives of 0.13% and 0.06% respectively. The results obtained for each of them were 340 and 411. The initial diesel fuel used in this research had a lubrication ability of 478. Mixtures having a lubrication ability of 340 and 411 are both lesser than 460. Therefore, they both have a good lubrication ability.

4.4 Infra-Red Spectra

The graph below is an Infra-Red spectra obtained from RS sample 1.



Graph 1 – RS sample 1 IR spectra

The graph below is an Infra-Red spectra obtained from RS sample 2.



RS Sample 2

Graph 2 - RS sample 2 IR spectra

The graph below is an Infra-Red spectrum obtained from RS sample 3.

Graph 3-RS sample 3 IR spectra

Peaks at 1376 and 1463 refer to deformation vibrations of – CH3 and -CH2 groups in aliphatic compounds (1463 refer to -CH2 and 1376 to -CH3 + -CH2). The same groups produce stretching vibrations at wave numbers of 2852, 2923, 2954 (2954 refers to – CH3 and 2852, 2920 refers to -CH2). All this bands indicate vibrations between carbon and hydrogen in C-H groups. Absorption at 723 or 721 refers to pendulum vibrations of -CH2 groups when the amount of these groups more than 4 like -CH2-CH2-CH2-CH2-CH2-CH2. This proves that using material consisted of long-chain carboxylic acids. Bands at 1741 refer to C=O group (carbonyl group). These bands present at all the spectra. It is possible to say that some of components from using fraction have double bonds (CH2=CH2). It can be seen from bands at 3008. But amount of such structures is not high because intensity of the band is not high. We can observe actual intensities in the second column of the table located on each the spectroscopy.

Carboxylic acids, which were obtained from plants, have bands at 1238, 1160 and 1097 cm⁻¹. But for esters these bands have position of 1241, 1176 and 1166. Moreover, the band at 1176 must have high intensity. As it can be seen such construction of the spectra was observed for RS Sample 1 only. According to this, we had success with the Sample 1 only. Other samples consist of acids.

The first reaction gave esters probably because all acetone has not been removed after extraction. Acetone can act as a catalyst in this case.

CONCLUSION

Transesterification process was used to obtain esters which were used as additives to increase the quality of diesel. Several conclusions can be deducted from the diverse tests done on the additives mixed with diesel.

From the results and analysis obtained, it can be said that the additives obtained do not affect greatly the Cloud Point. The mixture has a good lubrication ability. The additives are suitable for diesel fuel. From Infra-Red spectroscopy, it can be noticed that acetone can act as a catalyst when it is not fully removes from the sample. This may justify the reason why the research gives a positive feedback only with the first sample.

ABBREVIATION LIST

ASTM: American Society for Testing and Materials CFPP: Cold Filter Plugging Point CP: Cloud Point DIEGME: Glycol Mono Methyl Ether EGME: Ethylene Glycol Mono Methyl Ether EVA: Ethyl Vinyl Acetate FAAE: Fatty Acid Alkyl Esters FFA: Free Fatty Acid IR-spectra: Infra-Red spectroscopy KOH: Potassium hydroxide LTFT: Low Temperature Flow Test NAOH: Sodium hydroxide 2-EHN: 2-Ethyl Hexyl Nitrate

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MASTER'S THESIS

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04.04.01 Chemistry 04.04.01/05 Petroleum Chemistry and Refining

Research supervisor

Candidate of Chemical Sciences, Associate Professor

Vladimir Safin

Graduate

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