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Synthesis and Characterization of Biodiesel from Non-Edible Castor Seed Oil

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Abstract: ***Concerns on the ever increasing cost of fossil fuel, fast depletion of world reserves and the impact on environmental pollution has necessitated the search for alternative energy sources. Consequently, bio-fuels (biodiesel, bio-alcohol and biogas) have been identified as sustainable substitutes. The use of food crops for biodiesel production has been very much criticized as they affect food supply. As a result, scientists are now focusing on the utilization of non-edible feedstock for biodiesel production. It is on this background that castor bean seeds (Ricinuscommunis)have been investigated as possible feedstock for the production of biodiesel. The objective of this work was to extract oil from castor bean seeds, and use it to synthesis biodegradable biodiesel. The oil content of the castor bean seeds was extracted with n-hexane using soxhlet extraction method. Extracted castor oil was upgraded by trans-esterification using sodium methoxide as catalyst. The castor oil and biodiesel were characterized by FT-IR spectrophotometer .The peaks at 1720-1760 cm^{-1} in biodiesel correspond to methyl ester group (C=O) and 1400-1500cm^{-1} correspond to C-H bending mode this confirms successful trans-esterification of castor oil to biodiesel. An optimal biodiesel yield of 70% was obtained within 60min at 60^{o}C by using 6:1 molar ratio (methanol: oil) and 0.7% w/v catalyst concentration. The obtained fuel properties of castor biodiesel were density 0.88kg/L, flash point of 96 ^{o}C, kinetic viscosity of 5.67 mm^{2}/s, pour point of -9^{o}C, cetane number of 54 and calorific value of 3870kJ/kg. The overall results compared with those of commercial available diesel show that castoroil can serve as a veritable feedstock for the production of biodiesel that can effectively be utilized in diesel engines.***

Keywords: Surfactant, Fatty Methyl Ester, Castor Oil Fatty Acid Methyl Ester, Free fattyacid, Castor Oil

1. Introduction

1.1 Background

The Biofuels have assumed significant importance globally as the world addresses changing patterns in energy supply and demand. In the few years the world is projected to experience net deficits of petroleum supplies as new oil discoveries are offset by depletions. Further, as the world focuses on global climate change, biofuels have assumed importance as the most practical alternative to petroleum fuels in efforts to reduce carbon emissions in the transport sector. While biofuels comprise biodiesel, bioethanol and other biomass based fuels; this project addresses biodiesel as the area that requires immediate prioritization. Bioethanol and other biomass based fuels will be addressed in different project that might be undertaken.

Several feed stocks from vegetable source such as soybean, rapeseed, canola, palm, corn, Japtropha and castor seeds have been studied as an alternative to oil candidate. Among these sources, castor seeds are a potentially promising feed stock since among vegetable oils, castor oils distinguished by its high content (over85%) of ricinoleic acid. There is no other vegetable oil contains so high proportion of fatty hydroxyl acids and castor oil is the most stable viscosity of any vegetable oil (Ogunniyi, 2006).

Petroleum fuels have remained almost entirely unchallenged since the motor vehicle was invented. However, their reserves are not uniformly distributed and their increased use contributes to a variety of local and regional air pollution problems and potential climatic change (Poulton, 1974). Although studies indicate the existing oil reserves can meet the world‘s oil requirements for the next few years (Eastop*et al.*, 1995; Hansen *et al.*, 1989), concerns have been raised on the impact of the use of fossil fuels on the environment. The recent witnessed fuel crises and the world oil price fluctuations have generated the desirability to develop renewable fuels to decrease the dependence on fossil fuels. The need to reduce the growth of the consumption of fossil fuels, for economic and environmental reasons can best be accomplished by using renewable substitutes (Guibet, 1997; Pramanik, 2002). Kenya which does rely on fossil fuel imports is feeling the environmental effects and the oil price fluctuations.

Biodiesel is renewable and does not contribute to global warming due to its closed carbon cycle. Climate change due to global warming has its links with the effects of environmental degradation (for example, CO_2 emissions from fossil fuels). Being a signatory to the Kyoto Protocol; by reducing carbon emissions through large afforestation programs (biofuels) it provides the opportunity to trade in carbon credits with the countries that immediately require them under the Kyoto Protocol. Biofuel commands crucial advantages such as technical feasibility of blending, superiority from the environment and emission reduction angle, its capacity to provide energy security to remote and rural areas and employment generation. Moreover, biofuel will also provide rich biomass and nutrients to the soil and check degradation of land. The consumption and demand for the petroleum products are increasing every year due to increase in population, standard of living and urbanization. The increase in crude oil import affects the country‘s economy and its development. The acid rain, global warming and health hazards are the results of ill effects of increased polluted gases like SO_x, CO_x and particulate matter in atmosphere.

Biodiesel is most commonly made by trans-esterification process of the oil through the use of a catalyst and an alcohol, typically methanol. The chemical reaction that occurs through this process breaks down the oil molecules and replaces the glycerine portion of the molecule with an alcohol molecule. The glycerine separates to the bottom and is drained off resulting in biodiesel. The biodiesel is then typically washed, to remove any extra impurities and is then used as a fuel in a diesel engine without making any modifications to the engine.

There are variety processes or the combination of the processes to obtain the oils from the castor seeds. The hydrate presses, continuous screw presses and also solventextractionarethecommonmethodstoobtaintheoilsfromthecastorseeds. However, the most satisfactory approach to get the oil is hot pressing the castor seeds by using a hydraulic press and then followed by solvent extraction. This proposal is however focused at extraction of castor oils using solvent. The castor seed firstly face the separation process of the shell from the nibs and then byusing them or tar and pestle, the seeds were crushed into the paste (cake) to release the castor fat for the extraction process(Ogunniyi, 2006).

1.1.1 Vegetable oils

Conventional vegetable oils such as linseed, cotton seed, soybean, sunflower, castor, peanut, coconut, palm and others have emerged as prime candidates of alternative fuels used in diesel engines. Currently the larger portion of these conventional vegetable oils produced locally are used in production of human and animal food, cooking oil, soap and other industrial chemicals. Kenya imports about 80% of the vegetable oil and other associate foods in its requirements. Munavu & Odhiambo (1984) identified several indigenous and non-conventional sources of vegetable oils and further established that their properties are similar to those of conventional vegetable oils.

Most vegetable oils can be substituted directly for diesel fuel but may create problems mostly resulting from incomplete combustion which result to injector nozzle coking and even failure due to polymerization of the oil (Fuels *et al.*, 1984). Other than operational factors such as cold starting unreliable ignition, misfire and reduced thermal efficiency have added to the general advance of unmodified vegetable oils as long term diesel fuel replacement in Direct Injection engines and small capacity Indirect Injection diesel engines where the detrimental effects have been greatest.

A more satisfactory fuel is obtained by chemically changing the vegetable oil into a form whose characteristics resemble that of the diesel fuel it is designed to substitute. Used vegetable oil is increasingly being processed into biodiesel, or (more rarely) cleaned of water and particulates and used as a fuel (Zhang *et al.*, 2003). To ensure that the fuel injectors atomize the fuel in the correct pattern for efficient combustion, vegetable oil fuel must be heated to reduce its viscosity to that of diesel, either by electric coils or heat exchangers.

1.1.2 Biodiesel

Biodiesel is defined as mono alkyl esters of long fatty acids obtained from renewable lipid feed stock such as vegetable oils or animal fats (Zhang *et al.*,2003; Demirbas, 2000; Kinney & Clemente, 2005). Biodiesel has physical properties very similar to petroleum-derived diesel fuel, but its emission properties are superior. Biodiesel has more advantages compared to diesel fuel, such as: it is renewable; energy efficient; biodegradable; non-flammable and nontoxic; offers the same performance and engine durability as petroleum diesel fuel; reduces global warming; tail pipe and particulates emissions and its life expectancy is thinner than regular diese land serves as a better lubricant thus, increasing engine life (Meher*etal.*,2006; Srivastava & Prasad, 2000). Biodiesel is usually produced by the transesterification of vegetable oils or animal fats with methanol or ethanol (Knothe & Steidley2005). A complete understanding of the physical and chemical properties of biodiesel raw materialis important to the development of biodiesel. The properties of the various individual fatty esters that make biodiesel determine the overall fuel properties. Structural features that influence the physical and fuel properties of a fatty ester molecule include: chain length, degree of unsaturation and branching of the chain. These affects cetane number and exhaust emissions, heat of combustion, cold flow, oxidative stability, viscosity, and lubricity (Anand*etal.*,2011; Garnica *et al.*, 2009; Knothe, 2005). Factors such as geography, climate, and economics determine which vegetable oil is of greatest interest for potential use in biodiesel fuels (Knothe *et al.*, 2005**).** This work will show the influence of raw material composition in the biodiesel properties. The biodiesel raw material will be Castror oil. A comparative study will be carried out on properties of Castror biodiesel and those of other biodiesel and diesel fuel in literature.

Important disadvantages of biodiesel include high feedstock cost, inferior storage and oxidative stability, lower volumetric energy content, inferior low-temperature operability versus petrodiesel, and in some cases, higher NO_x exhaust emissions (DeOliveira*et al.*, 2006; Knothe, 2008). Many of these deficiencies can be mitigated through cold flow improver (Sern *et al.*, 2007; Hancsok *et al.*, 2008; Moser, 2008a,); additives, blending with petrodiesel (Benjumea*et al.*, 2008; Moser, 2008b), and/or reducing storage time (Bondiol*et al.*, 2003).

Additional methods to enhance the low-temperature performance of biodiesel include crystallization fractionation (Dunn *et al.*, 1997; Kerschbaum *et al.*, 2008) and trans-esterification with long- or branched-chain alcohols (Lee *et al.*, 1995; Foglia *et al.*, 1997; Wu *et al.*, 1998). Strategies to improve the exhaust emissions of biodiesel, petrodiesel, and blends of biodiesel in petrodiesel include various engine or after-treatment technologies such as selective catalytic reduction (SCR), exhaust gas recirculation (EGR), diesel oxidation catalysts, and NO_x or particulate traps (McGeehan, 2004; Knothe, 2006). However, feedstock acquisition currently accounts for over 80% of biodiesel production expenses, which is a serious threat to the economic viability of the biodiesel industry (Paulson and Ginder, 2007; Retka-Schill, 2008). One potential solution to this problem is employment of alternative feedstocks of varying type, quality, and cost. These feedstocks may include soapstocks, acid oils, tall oils, used cooking oils, and waste restaurant greases, various animal fats, non-food vegetable oils, and oils obtained from trees and microorganisms such as algae. However, many of these alternative feedstocks may contain high levels of free fatty acids (FFA), water, or insoluble matter, which affect biodiesel production.

The main advantages of using biodiesel fuels as 100 % mono alkyl esters of vegetable oil and animal fat or biodiesel blends (up to 20 % blend to the diesel fuel) are producing less smoke and particulates and having higher cetane numbers (Antolin*et al.*, 2002; Encinar*et al.,* 2007). In addition, the production of biodiesel should be encouraged especially in developing countries because of the following considerations; Biodiesel is produced from sustainable/ renewable biological sources. Ecofriendly and oxygenated fuel. It provides a market for excess production of vegetable oils and animal fats. It decreases the country's dependence on imported petroleum and thus enhances energy security and also reduces expenditure on imports. Biodiesel is renewable and does not contribute to global warming due to its closed carbon cycle. The exhaust emissions from biodiesel are lower than with regular diesel fuel (sulfur free, less Carbon monoxide, Hydrocarbons, Particulate matter and aromatic compounds emissions). Biodiesel has excellent lubricating properties and its fuel properties are the same as those of conventional fuel and can be used in existing unmodified diesel engines. Jobs creation and diversification of rural economies. It will conserve our forests and reduce deforestation where more will be planted to get seeds for biodiesel processing hence encourage Afforestation. The production of biodiesel will increase carbon trading opportunities. Non-toxic, biodegradable and safe to handle.

1.2 Problem statement

Environmental pollution and diminishing supply of fossil fuels are the key factors leading to search for the alternative sources of energy. Today, 86% of the world energy consumption and almost 100% of the energy needed in the transportation sector is met by fossil fuels (Dorianetal.,2006). Since the world's accessible oil reservoirs are gradually depleting, it is important to develop suitable long-term strategies based on utilization of renewable fuel that would gradually substitute the declining fossil fuel production. In addition, the production and consumption of fossil fuels have caused the environmental damage by increasing the CO2 concentration in the atmosphere (Westermannetal.,2007).

Since more than 95% of the biodiesel is synthesized from edible oil, there are many claims that a lot of problems may arise. By converting edible oils into biodiesel, food resources are actually being converted into automotive fuels. It is believed that large-scale production of biodiesel from edible oils may bring global imbalance to the food supply and demand market. Recently, environmentalists have started to debate on the negative impact of biodiesel production from edible oil (Butler, 2006). They claimed that the expansion of oil crop plantations for biodiesel production on a large scale may increase deforestation in countries like Malaysia, Indonesia and Brazil. Further more, the line between food and fuel economies is blurred as both of the fields are competing for the same oil resources. In other words, biodiesel is competing limited land availability with food industry for plantation of oil crops. Arablel and that would otherwise have been used to grow food would instead be used to grow fuel (Anonymous, 2004). In fact, this trend is already being observed in certain part of this world. There has been significant expansion in the plantation of oil crops for biodiesel in the past few years in order to fulfill the continuous increasing demand of biodiesel.

1.3 Objectives of the study

1.3.1General Objective

To extract the castor oil by using solvent extraction method, characterize the castor oil that is modified for synthesis of biodegradable biodiesel.

1.3.2 Specific objectives

1) To extract the castor oil from castor seed by using solvent extraction method.
2) To assess physicochemical properties of castor oil suitable for Biodiesel synthesis.
3) To determine physicochemical properties of Castor biodiesel and compare it with those of commercial petroleum diesel and biodiesel available in literature.

2. Methodology

2.1 Introduction

This chapter gives the instrumentation, materials, methods, and procedures of analysis used in the study. Castor oil was the main raw material used in the synthesis of the eco-friendly COFAMEs biodiesel the procedures used to evaluate the physicochemical, nutrition value and fuel properties of castor oil and COFAMEs have been stated in this chapter.

2.2 Cleaning of glassware and testing of apparatus

All glassware's were cleaned using plenty of water and rinsed by distilled water before being dried in oven. Measuring apparatus were calibrated before being used and were tested.

2.3 Castor seeds sampling and process

Local castor (*RicinusCumunis* L.) seeds were harvested by cutting from local area in Eldoret. The castor seeds were cleaned to remove extraneous material. The cleaned castor seeds were then placed in open area for sun drying until the casing splits and sheds the seeds. The seeds were then dried inside an oven at 60°C for 7 hour to reduce its moisture content which normally castor bean contain about 3 to 7% of moisture. After that, the shell was separated from the nibs (cotyledon) by using the tray that blows away the cover inorder to achieve high yield. By using the grinding machine, the castor beans were crushed into a paste which is called 'cake' to weaken the cell wall to release castor fat during the extraction.

2.4 Moisture content of the seeds

The cleaned castor seeds were weighed and then dried inside an oven at 80°C for 7 hours and the weight of the seed was taken after every 2hours. The step was repeated until the weight of the seed was constant. During the 2 hours interval, the seeds were removed from the oven and then cooled inside the desiccators for 30minutes. The cooled seeds were then remove from the desiccators and re-weighed. The percentage of the moisture inside the castor seeds was calculated.

2.5 Oil Extraction

Castor oil was extracted from castor seed using solvent extraction method. Solvent extraction was chosen since this method recovers almost all the oils and leaves behind only 0.5 – 0.7% residual oil in the raw materials (Liauw*et al.*, 2008). In this study, hexane solvent was used to extract oil from castor seeds, since it is highly efficient and highly volatile hence easily removed through evaporation.

To carry out castor oil extraction, 300g of castor seeds were ground and put in a 2.5 L glass bottle and 1.5L of hexane solvent was added and then corked for three days. After three days, the mixture was filtered and the filtrate concentrated using rotary evaporator at (40 – 60^0C). The extracted seed oil was then stored in freezer at -2^0C for further use.

2.6 Determination of the Percentage of Castor Oil Extracted (Oil Yield)

A sample of 30g of castor seed were crushed and placed inside the thimble and 300mL of the hexane was poured into the round bottom flask. The soxhlet was heated at 60°C and the extraction was allowed for 3 hours continuously extraction. The procedure was repeated by using the different weights of the castor cake. The final step was the solvent which was hexane, was removed by distillation process and the percentage of extracted oil was determined.

2.7 Physical and Chemical Analysis of castor Oil

Prior to the synthesis of castor biodiesel calculation of oil yield, and analysis of physiochemical properties castor oil was carried out. These physicochemical properties include density and specific gravity, free fatty or acid value, saponification value, iodine value, specific gravity, viscosity, refractive index and peroxide value.

2.7.1 Determination of Acid Value/ Free Fatty Acid (FFA)

A sample of 2g of the oil was measured and poured in a beaker. A neutral solvent (a mixture of petroleum ether and ethanol) was prepared and 50ml of it was taken and poured into the beaker containing the oil sample. The mixture was stirred vigorously for 30minutes. 0.56g of potassium hydroxide (KOH) pellet was measured and placed in a separate beaker and 0.1M KOH was prepared, 3drops of phenolphthalein indicator was added to the sample and was titrated against 0.1M KOH till the color change observed turned pink and persisted for 15minutes.

2.7.2 Determination of Saponification Value

Indicator method was use as specified by ISO 3657 (1988). A sample of 2g of castor oil was weighed into a conical flask; 25mL of 0.1N ethanolic potassium hydroxide was then added. The content which was constantly stirred was allowed to boil gently for 60 minutes. A reflux condenser was placed on the flask containing the mixture. Few drops of phenolphthalein indicator was then added to the warm solution and then titrated with 0.5M HCl to the end point until the pink colour of the indicator just disappeared. The same procedure was used for other samples and blank.

2.7.3 Determination of Iodine Value

The oil was poured into a small beaker, a small rod was added to it.2g of the oil was weighed and poured into a glass-stopper bottle of about 250 ml capacity. 10ml of carbon tetrachloride was added to the oil to dissolve. 20ml of Wij's solution was added and a stopper was inserted and allowed to stay in the dark for 30minutes. 15ml of potassium iodide solution (10%) and 100ml of water was introduced and the mixture was thoroughly mixed and titrated with 0.1M sodium thiosulphate solution using starch as indicator (titration = 'A'ml). A blank was carried out at the same time starting with 10ml of carbon tetrachloride (titration = 'B'ml)

2.7.4 Determination of Specific Gravity

Density bottle was used to determining the density of the oil. A clean and dry bottle of 25mL capacity was weighed (W_0) and then filled with the oil, stopper inserted and reweighed to give (W_1). The oil was substituted with water after washing and drying the bottle and weighed to give (W_2).

2.7.5 Determination of Viscosity

A clean, dried viscometer with a flow time above 200 seconds for the fluid to be tested was elected. The oil sample was filtered through a sintered glass (fine mesh screen) to eliminate dust and other solid material in the liquid sample. The viscosity meter was charged with the sample by inverting the tube's thinner arm into the liquid sample and suction force was drawn up to the upper timing mark of the viscometer, after which the instrument was turned to its normal vertical position. The viscometer was placed into a holder and inserted to a constant temperature bath set at 29°C and allowed approximately 10 minutes for the sample to come to the bath temperature at. The suction force was then applied to the thinner arm to draw the sample slightly above the upper timing mark. The afflux time by timing the flow of the sample as it flow freely from the upper timing mark to the lower timing mark was recorded.

2.7.6 Determination of Refractive Index

Refractometer was used in this determination. Few drops of the oil sample were transferred into the glass slide of the refractometer. Water at 30°C was circulated round the glass slide to keep its temperature uniform. Through the eyepiece of the refractometer, the dark portion viewed was adjusted to be in line with the intersection of the cross. At no parallax error, the pointer on the scale pointed to the refractive index. This was repeated and the mean value noted and recorded as the refractive index.

2.7.7 Determination of pH Value

A sample of 2g was weighed and poured into a clean dry 25mL beaker and 13mL of hot distilled water was added to the oil sample in the beaker and stirred slowly. It was then cooled in a cold-water bath to 25°C. The pH electrode was standardized with buffer solution and the electrode immersed into the sample and the pH value was read and recorded.

2.7.8 Unsaponifiable Matter Content
The percentage of unsapponifiable matter, was determined by saponifying oil sample using alcoholic KOH. A sample of 5g of castor oil was measured into 250 mL round bottomed conical flask and 30mL of 0.5M ethanolic KOH was added and boiled in a water bath under reflux condenser for 1 hour. The mixture was put in a separating funnel, 50mL of diethyl ether and 50 mL of distilled water contained 5% $NaHCO_3$ added and shaken vigorously and left to stand to 1 hour. The dissolved soap and water was drained, more distilled water was periodically added to wash the mixture until all the soap and impurities were completely removed. After washing, the sample was dried under vacuum.

2.7.9 Determination of peroxide value
A sample of 1g of castor oil was weighed into a clean drying boiling tube, 1g of powdered potassium iodide and 20ml of solvent mixture (2volume of glacial acetic acid + 1volume of chloroform) was added, the tube was placed in boiling water so that the liquid boils within 30seconds and was also allowed to boil vigorously for not more than 30seconds. The content was quickly poured into a flask containing 20ml of potassium iodide solution; the tube was washed out with 25ml of distilled water and was titrated with 0.002M sodium thiosulphate solution using starch as indicator. A blank was also carried out at the same time.

2.7.10 Determination of refractive index
Abbe's refractometer was used to determine the moisture content of the oil sample,

2.8 Synthesis of castor oil (COFAMEs) biodiesel

The single step base trans-esterification catalysis was carried out, prior to trans-esterificaiton process, 500mL of castor oil was preheated at the temperature of 120^{0}C for 90 minutes in a flat bottom flask with constant stirring at 250 rmp by means of magnetic flux heater. The heating was stopped and the oil was made to cool down to 60^{0}C. In a separate closed glass bottle, 4g of NaOH was dissolved in 50mL methanol with constant stirring for 15 minutes in a rotary shaker to produce a highly reactive sodium methoxide protonic species.

To synthesise biodiesel, 500mL of castor oil was poured into a 1L three – necked round bottom flask, then 50 mL sodium methoxide was gently added into the flask. A magnetic rod was placed inside the flask. The flask was placed in water bath on a hot magnetic flux heater setup. The flask openings were fitted into a condenser, thermometer, and a cork. The temperatures of the setup were maintained at the range of 60-70^{0}C and magnetic revolutions at 250 rmp. The mixture was stirred vigorously and refluxed for 3 hours. The solution was then cooled, and poured into a separating funnel, it was left to stand for 12 hours. The mixture separated into two layers, with the top layer consisting of methyl esters and bottom layer glycerol. Glycerol was removed and castor methyl esters remained in the separating funnel.

To remove any remaining methanol, glycerin, catalyst, soaps and other impurities, castor methyl esters was washed. The initial washings was done using warm distilled water containing 10% phosphoric acid. This was repeated 5 times, thereafter, washing was done using 100% warm distilled water. This was repeated until the washing water become clear, that is when the pH of the biodiesel becomes relatively neutral. The remove water/moisture, the obtained COFAMEs was dried by heating at 100^{0}C for 1 hour on a hot magnetic stirrer plate. The COFAMEs obtained was then stored in a clean bottle and kept in the freezer at -2^{0}C for further use.

3. Results and Discussion

3.1 Physicochemical properties of the extracted castor oil and AOCS castor oil standard

Ricinuscommunis oils that was utilised as a feedstock in the production of biodiesel was characterized to determine the physiochemical properties such as density, pH, viscosity, acid value, iodine value etc. The results obtained on the properties of oils were compared with that of American Oil Chemists' Society (AOCS) standard values and the results obtained are presented in Table 4.1.

Table 4.1 Physicochemical properties of the extracted castor oil and AOCS castor oil standard

Property	Present study	AOCS standard value	Jumat*et al*.2010
Oil yield %	33.2	-	48.32
Moisture content (%)	0.4	0.355	0.3
Acid value(mg NaOH/g of Oil)	0.869	2max	1.48
Refractive index	1.4674	1.467-1.470	1.792
Density (kg M^{-3}) at 25^o*C*	0.961	0.913-0.970	0.948
PH	6.34		5.8
Specific gravity	0.9587	0.88-0.915	-
Viscosity at 28^{o}C (st)	0.64842	6.3-8.9	0.425
Free fatty acid value (mg/g of KOH)	5.6	≤3	7.4
Iodine value (g/l_2/100g of oil	84.8	83-88	58.64
Saponification value (mg of KOH/g of oil	181.55	176-184	180.77
Unsaponification Matter content (%)	0.7	0.7(Max %)	-
Peroxide Value (meq O_2/kg of Oil	183	150-240	158.64
Solubility in alcohol	Complete	Complete	Complete

Source of AOCS STD values: (Ali *et al* ,2005**).**

Table 4.1 presents the result of the yield and the physicochemical parameters of castor seed oil. . The results obtained on the properties of oils were compared with that of American Oil Chemists' Society (AOCS) standard values. The oil content was 33.2 %. This yield may be as a result of environmental factor which enhance the growth and productivity of the seed. This value falls within the range value of 30-55% reported by Aldrich, (2003). This yield makes the industrial practice of the oil recovery a profitable venture. The moisture content of the crude oil was 0.40%, which was within the range specified by AOCS as shown in the Table 4.1 indicating low moisture or volatile content might be as a result of effectiveness of the distillation apparatus used for oil recovery. Again, the low moisture or volatile content is an indication of good shelf life characteristic. The specific gravity was 0.9587. This was in line with 0.9587 reported by (Salunke, 1992) and also fall within the range specified by AOCS as indicated in Table 4.1. The density was determined to be 0.961, this density can further be reduced by esterification to 0.85 so as to meet the biodiesel energy application (Bello &Makanju, 2011). The refractive index was determined to be 1.4674 also within the range specified by AOCS in Table 4.1.This value is an indication of the level of saturation of the oil. The fire, flash and smoke points of the oil have linear relationship with the content of the free fatty acid present in the oil because these are parameter indicative of combustion (AOAC, 1990). The viscosity was determined at 28^{o}C using viscometer. The value obtained was 0.64842 cps, showing that the oil was light and so probably highly unsaturated; the high value might be as a result of suspended particles still present in the crude oil sample. The colour was determined using lovibund tintometer and the value was 2.00TU. The high value was as a result of the presence of high number of red pigment. The PH of the sample was 6.34; the low level was an indicative of the presence of reasonable quantity of free fatty acid in the oil, which is a good indicator of the advantageous utilization of the oil in soap making. All these physical parameters are indications that the oil to be used for industrial purposes. The free fatty acid and acid values was determined to be 5.6 % oleic acid and 8.69 % oleic acid respectively. This can be used to check the level of oxidative deterioration of the oil by enzymatic or chemical oxidation. These values fall within the range specified by AOCS standards for free fatty acid of oil which is expected to range between 0.00 -9.00% before it finds application in corking, but on the contrary the value is high for the oil under study. However, the free fatty acid can be modified to edible oil by subjecting it to refining and this will also improve its quality for industrial usage. The saponification value of the oil was 181.55 mg KOH/g oil, which is within the range of values 156 to 185 mg KOH/g oil as reported by other scholars (Weisis, 1971; Jumat *et al*, 2010) and also AOCS standards. The iodine value is a measure of the degree of unsaturation and it an identity characteristic of seed oils, making it an excellent raw material for soaps cosmetics industries (Hamilton, 1999). Research has shown that oils with high saponification value are valuable raw materials for soaps and cosmetics (Abayeh*et al*, 1998). The Iodine value determined for the castor seed oil was 84.8 wijs. This value could be used to quantify the amount of double bond present in the oil which reflects the susceptibility of oil to oxidation. Also, it enables us to classify the oil in the non-drying groups, since I V obtained is < 100, which are useful in the manufacture of soaps (Kochhar, 1998) and can be regarded as liquid oil. Thus, the oil may find its application in the manufacturing of lubricants, hydraulic fluids and coating (Ibiyemi et al, 1992). The peroxide value was found to be 183.00 Meq/kg. The high peroxide value of the oil sample shows that the oil is prone to rancidity and thus less stable.

3.2 Physicochemical properties of COFAMEs Biodiesel

The physicochemical properties of the biodiesel produced from Castor beanwere determined as presented in Table 4.2. The results obtained from this study with respect to density and specific gravity, PH, kinematic viscosity, Specific gravity, flash point, saponification value, peroxide value and iodine value.

Table 4.2: Physicochemical properties of COFAMEs biodiesel and ASTM biodiesel standard

Property	Present study	ASTM Standard value
Biodiesel yield %	70	-
Acid value	6	-
Density (kg/L) at 15^{o}C	0.88	0.83-0.86
PH	6.0	-
Specific gravity	0.96	0.913-0929
Kinetic viscosity at 25^{o}C (mm2/s)	5.67	1.3-4.1
Iodine value (g/l_2/100g of oil	95	-
Saponification value (mg of KOH/g of oil	165	-
Peroxide Value (meq O_2/kg of Oil	0.34	-

Source of ASTM Biodiesel STD values: (Singh & Singh, 2010;Herskowitz*et al*.,2012)

To achieve optimum yield of biodiesel from non-edible oil seeds, alkali based trans-esterification was carried out. The PH of the synthesized COFAMEs biodiesel was 6.0 this implied that it was relatively acidic. Its density was 0.88Kg/L which was within the range specified by ASTM biodiesel standard shown in Table 4.2.

Kinetic viscosity of COFAMEs was 5.67 mm^2/s which was higher than the ASTM biodiesel standard. Therefore, the density and viscosity of COFAMEs biodiesel implies that COFAMEs could not be applied as fuel in diesel engines.

Saponification value of COFAMEs was 165 mg of KOH/g of biodiesel which was slightly lower than that of the extracted Castor oil which was 176 this shows that the COFAMEs biodiesel could be applied in detergent industries.

Peroxide values of COFAMES was 0.34 meq O_2/Kg. This show that castor biodiesel could be rancid because of oxygen absorption during storage or processing.

The iodine value of COFAMEs obtained was 94gl_2/100g of biodiesel which was significant high. This show that COFAMES contains more unsaturated bonds in their carbon chains hence can undergo a lot of reactions because of their existence of reactive double bonds. Although this is limitation as being applied as fuel. Since higher iodine values of biodiesel influences the oxidation and formation of deposits in the diesel engines (Knothe and Steidley, 2005)

3.3 Fuel properties of COFAMEs Biodiesel

The fuel characteristics of the synthesized COFAMEs biodiesel were evaluated to the ASTM standard methods. The evaluated physicochemical properties of the biodiesel produced from Castor beanwere determined and compared with ASTM specifications for petroleum diesel (Table 4.3). The results obtained from this study with respect to density, kinetic viscosity, Specific gravity, flash point, cloud and pour points, sulphur, Cetane number as well as gross heat of combustion or Calorific value.

Table 4.3: Fuel properties of COFAMEs biodiesel and ASTM biodiesel standard

Property	Present study values	ASTM standard value for biodiesel	ASTM standard for petrol diesel
Biodiesel yield %	70	-	-
Density (Kg/L) at 15^{o}C	0.88	0.86-0.869	0.95max
Kinetic viscosity at 40^{o}C (mm^2/s)	5.67	1.3-4.1	1.9-4.1
Flash point (^{o}C)	96	93.0min	150min
Sulfur % weight	0.0008	0.05	0.005
Colour comparison	2.0	2.0	2.0
Pour point (^{o}C)	-9	-35-15	15max
Cloud Point (^{o}C)	-6	-15-6	40max
Cetane number	54	40-55	40min
Calorific value (kJ/kg)	3870	≥4200	≥4200

4.5 ASTM Standard Source :(Singh &singh, 2010; Herskowitz*et al.*, 2012)

3.3.1 Viscosity

Kinematic viscosity is a measure of resistance to flow of a liquid due to internal friction of one part of the fluid moving over another. High viscosity affects the atomization of a fuel upon injection into the combustion chamber and thus leads to the formation of engine deposits. High viscosity is the major problem preventing the use of vegetable oils and animal fats directly in diesel engines as it affects the flow of fuel and spray characteristics (Hossain & Davies, 2010). High Speed Diesel (HSD) has viscosity of 1.3-4.1 mm^2/s at 40 ^{o}C whereas the viscosities of COFAMEs biodiesel was 5.67 which was slightly higher than the ASTM standard. although,it falls within the acceptable limit of fossil diesel (ASTM) as presented in Table 4.3. It can be therefore said that the COFAMEs has a higher tendency of forming deposits in engines It shows that viscosities of COFAMEs biodiesel are comparable to ASTM biodiesel standard.

3.3.2 Density

The density of COFAMEs at 15 °C was found to be 0.88 kg/L, which is closer to the density of diesel (0.83) 0.86 kg/L can be used as an alternative fuel.

3.3.3 Flash point

The flash point is the lowest temperature at which an applied ignition source will cause the vapours of the fuel to ignite. It is therefore a measure of tendency of a sample to form a flammable mixture with air.Higher flash points make for safe handling and storage of biodiesel (Hossainand Davis 2010). The Flash Points of COFAMEs biodiesel was 96 ^{o}C which is higher than that of ASTM biodiesel standard (60-80 ^{o}C).

3.3.4 Sulphur contents

The most valuable result is the reduction and absence of percentage of total sulphur contents in COFAMEs biodiesel that will result in reduction of Sox in exhaust gases which is one of the reasons of acid rain. Sulfur content of COFAMEs biodiesel was 0.0008 lower compared to ASTM biodiesel standard of 0.05.

3.3.5 Cloud point and pour point

Cloud point is the temperature at which a cloud of wax crystals first appear in the oil when it is cooled. The pour point is the lowest temperature at which the oil sample can still be moved. These properties are related to the use of biodiesel in colder region (Arjun *et al.*, 2008). The cloud points of COFAMEs biodiesel was -6^{o}C and the pour point was -9^{o}C. Pour point and cloud point of COFAMEs was almost within the specified range by ASTM as shown in Table 4.3. Lee *et al* (1995) argued that the cloud points were affected by the presence of monoglycerides while the pour points were not affected.

3.3.6 Calorific value

TheCalorific value of COFAMEs was 3870 kJ/kg this was within the ASTM standard range of biodiesel and petro-diesel. Results obtained in this study indicates a density value for castorbiodiesel that is within recommended limits for biodiesel fuels by ASTM.

3.3.7 Viscosity

Viscosity, being a measure of the internal flow of resistance of a liquid would obviously affect injection lubrication and fuel atomisation. High viscosity will increase engine deposits. Thus, the 5.67 mm^2/s viscosity recorded for castoroil compared to the 4.1 ASTM value makes it a better alternative to petroleum diesel. In addition, a highly viscous oil would also help in lubricating the engine. The pour, cloud and flash points are also important parameters in fuel performance. While, the pour point is the lowest temperature at which fuel can still be moved before it gels, the cloud point is the temperature at which small solid crystals are first visually observed as the fuel cools down. The flash point on the other hand, is the lowest temperature at which the vapour above the fuel becomes flammable. These three parameters therefore, describe the different temperatures at which fuel can be moved or safely stored. The pour, cloud and flash points reported for castorbiodiesel (table 3) are generally higher than those of ASTM petroleum diesel but still in agreement. It therefore, follows that castor biodiesel is safer to use.

3.4 Fourier Transform Infrared Spectrophotometric Analysis of COFAMEs

Fourier transform infrared spectrometry (FTIR) was used to evaluate the possible functional groups present in biodiesel. It was an easy way to identify the presence of functional groups in the sample and its structure based on the energies associated with the molecular vibration when irradiated. Castor oils and COFAMEs were run through FTIR, the bonds as well as functional groups present were found to respond differently to the incoming radiation, due to variation in their molecular vibration of stretching and bending. The response of the functional groups were characterized by observing the transmission of infrared radiations and comparing it with known standards in order to identify the type and the nature of functional groups present in the samples. The presence and the nature of functional groups among other factors provided information on the stability of the biodiesel fuel. The research was done to design and evaluate the functional groups and structure so us to establish the reactivity of the fuels as a function of possible degradation.

The FT-IR analysis of functional groups of castor biodiesel was presented in Table 4.6. It was observed from the table that = C-H groups were the most abundant in castor oil and castor biodiesel, and they all possess bending type of vibrations appearing at low peak of the spectrum and are all double bonded. Though the remaining functional group is quite different in terms of structure, wave number and vibration, they all possess single bonds as a unifying factor. The Fourier Transform Infra-Red and Infra Red analysis shows that the functional groups present in the fuel sample are: ester stretch, C-H aliphatic, both functional groups present in *Ricinuscommunis* oil and methyl esters.

Table 4.6: FT-IR and IR functional group frequencies of Castor Biodiesel

Peak (1/cm)	*Characteristics*
3300	Presence of –OH
2900	C-H aliphatic stretch
1720	C=O ester group
1400-1500	C-H bending
1140	C-O presence
700-850	C-H out of plane

The FT-IR and IR analysis of all the samples (shown in the figures 4.1 and 4.2 below) obtained indicates the presence of: ester stretch and C-H aliphatic, both which are the expected functional groups thus confirming the presence of methyl esters. Figure 4.2 shows strong peaks at 1720 and 2900 which were due to C=O ester group and C-H aliphatic stretch. The absence of a peak at 1720 cm^{-1} in figure 4.3 and its presence in figure 4.1 and 4.2 it shows that the oil was converted to methyl esters. The peak at 1480 cm^{-1} is considered to be the $–CH_3$ asymmetric bending vibrations (Al-Alawi, 2006). In the mid IR spectra region the conversion of TAGs to FAMEs involves the loss of glycerol resulting in decrease in peak height at 1480 cm^{-1}. The peak at 1480cm^{-1}, which is attributed to the terminal CH_3 group in TAG, DAG, MAG, FFA and FAME and to the OCH_2 group in the glycerol of TG, DG and MG has also been monitored using IR (Zheng et al., 2004).

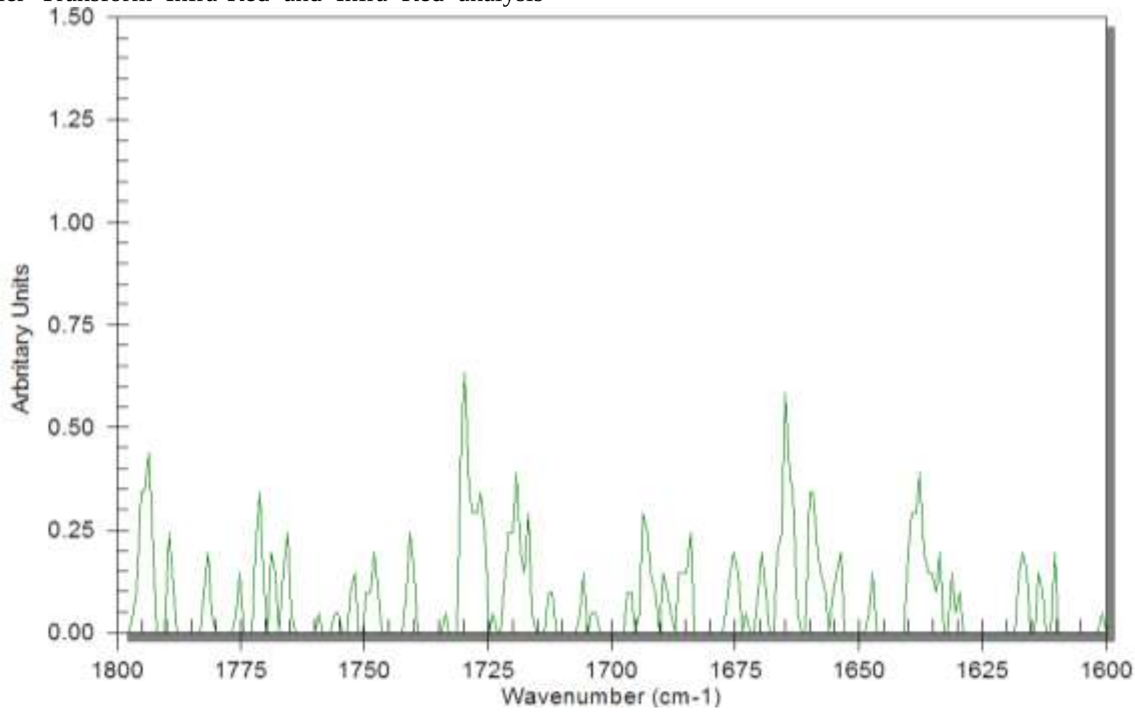

Figure 4.1: FTIR for castor biodiesel

Figure 4.1 shows a strong peak at 1720 cm^{-1} and indicates the presence of an ester hence the conversion of fatty acid to methyl esters. The peak from 2785 cm^{-1} to 2850 cm^{-1} shows the presence of $–CH_2$ asymmetric stretch Figure 4.2. The absence of the peak at 3500 cm^{-1} for OH shows that the methanol that was used was completely converted to $–CH_3$ and the peak at 1500 cm^{-1} shows the $–CH_2$ scissor stretch. Figure 4.5 show that the fossil diesel has a peak at 1720 and 2850 for ester carbonyl group and $–CH_2$ respectively. These peaks are comparable to that obtained on the methyl ester of castor biodiesel. Trans-esterification process can be monitored by comparing the peaks of the methyl esters and that of the oil.

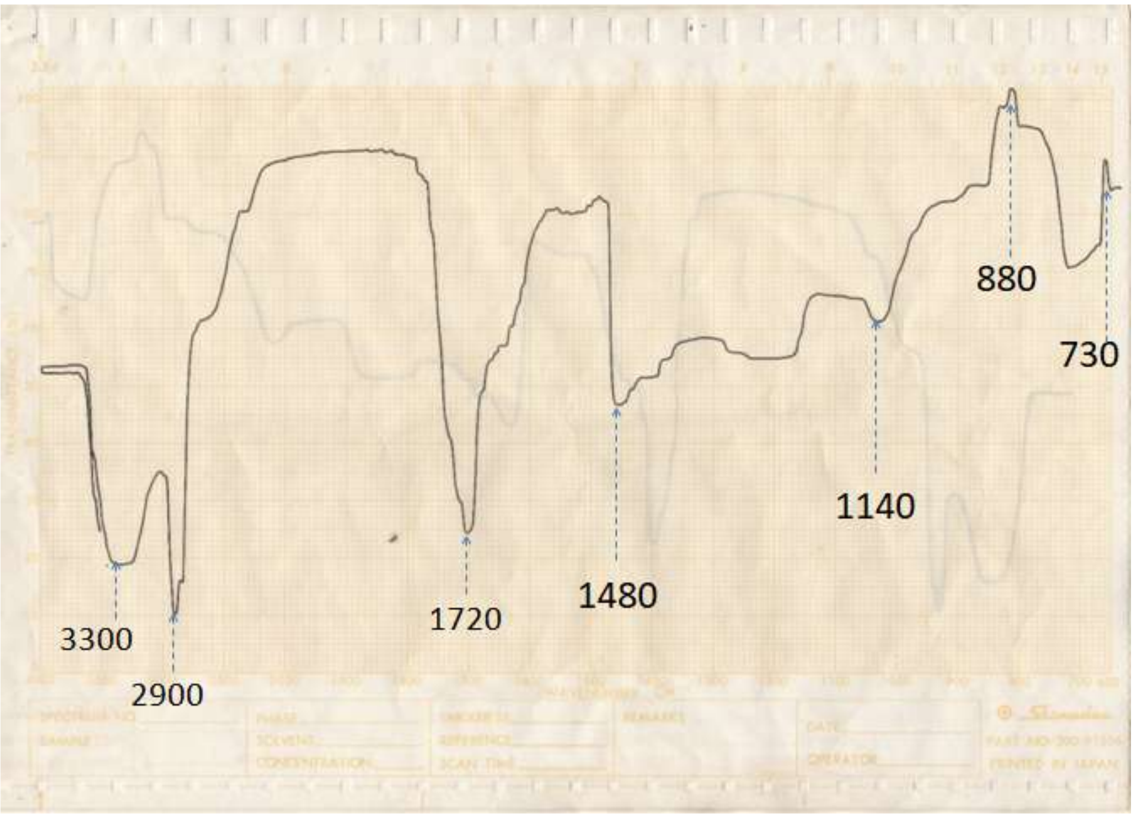

Figure 4.2: IR for castor biodiesel

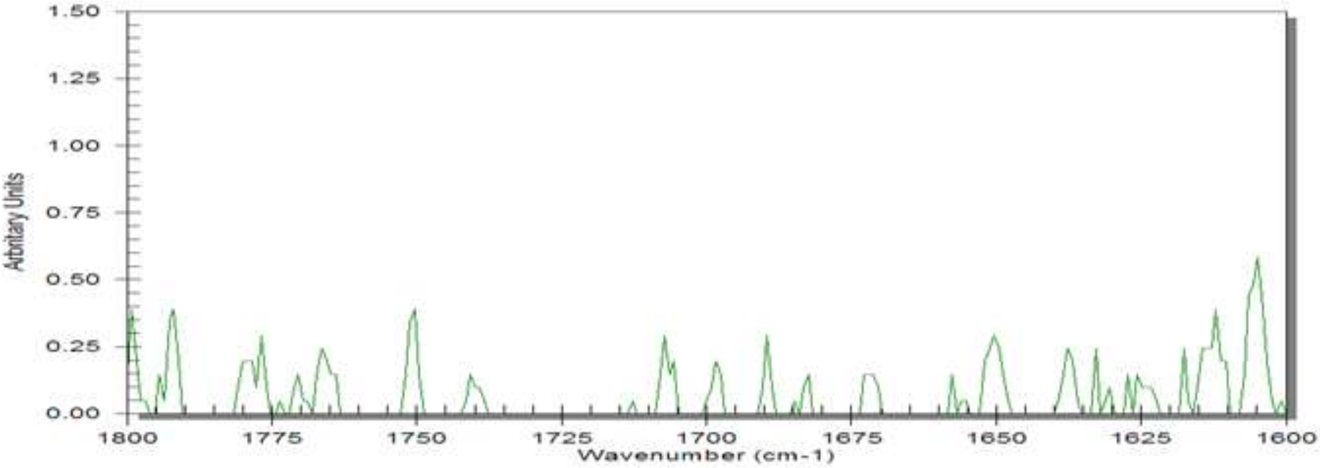

Figure 4.3: FTIR for Casto

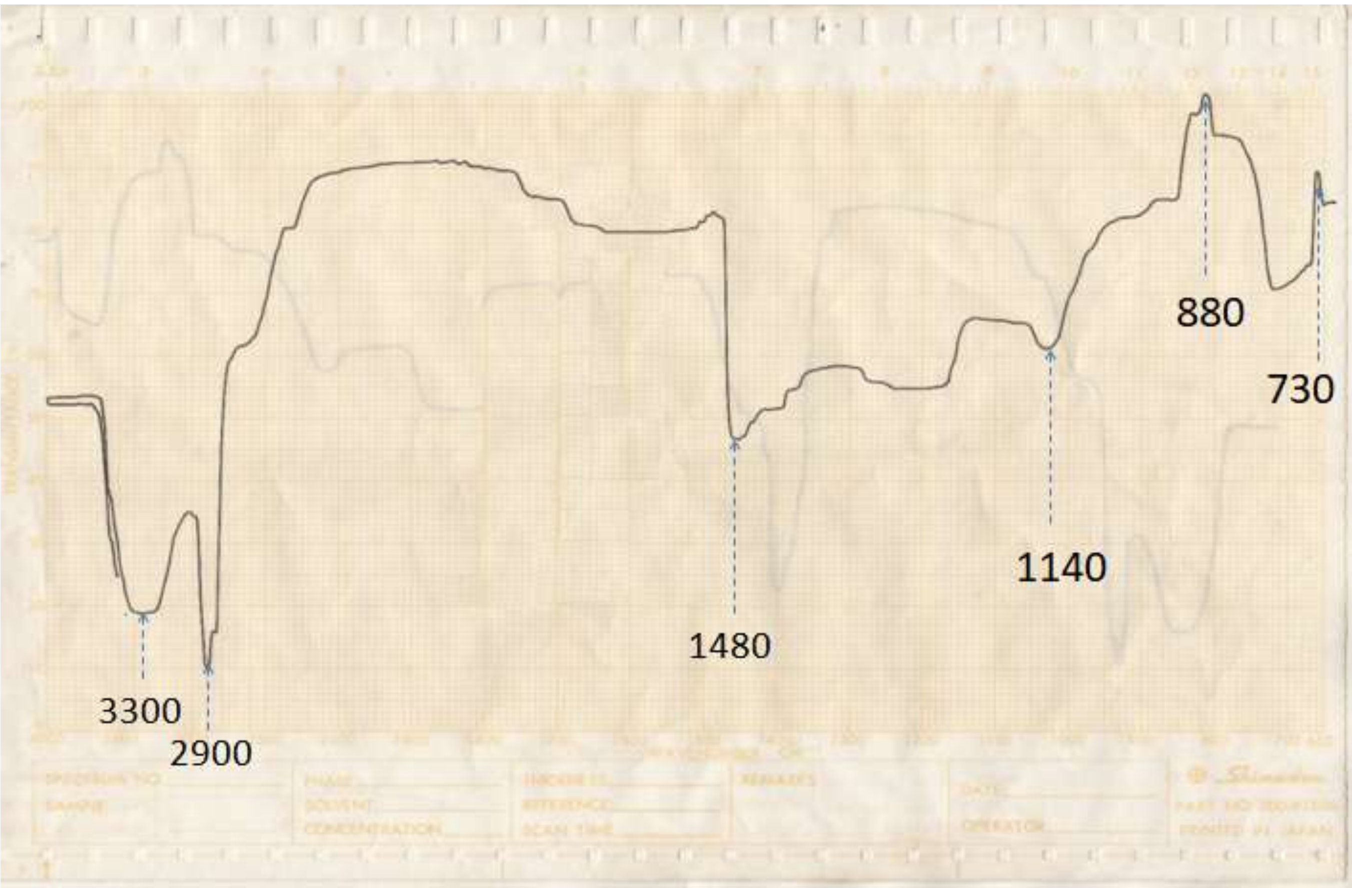

Figure 4.4: IR for Castor oil

Figure 4.4 shows negative absorbance at 1500 to 1700 cm^{-1} and 1800 to 2500 cm^{-1} due to the difference in the amount of light being absorbed by a functional group in a compound that particular wavelength. The peak at 720cm^{-1} it shows the -CH group out of plane. The peak at 1400 to 1500 cm^{-1} shows the -CH bending. The IR spectrum for the castor oil (figure 4.4) at 2850 to 3000 cm^{-1} it shows a shoulder as compared to that of the methyl ester which showed peaks. This enables one to monitor the trans-esterification process.

4. Conclusion

The primary objective of this research project was to extract oil from castor bean seeds, and use it to synthesis biodegradable biodiesel. The oil content of the castor bean seeds was extracted with n-hexane using soxhlet extraction method. The vegetable oils were converted to biodiesel through trans-esterification using sodium methoxide as a catalyst. The physicochemical properties of these castor oil and castor biodiesel were characterized by specific gravity, kinematic viscosity, acid value, calorific value and iodine value and compared to those of ASTM standard values. Castor oil had a high acid value of 8.69 mg KOH/g oil as compared to AOCS standard value of 3 mg KOH/g oil. Castor oil had an iodine value of 84.8 mgI_2/g oil compared to that of AOCS standard value of 83 to 87 mg I_2/g oil. These values however increased after trans-esterification to 95.. The flash point of castor biodiesell was with a value of 96 ^{0}C as compared to that of ASTM standard value of 60-80 $^{\circ}$C

Higher specific gravity values as well as kinematic viscosity values were observed in the case of castor oil and biodiesel as compared to ASTM standard value. Specific gravity was 0.9587, 0.96 and at 15°C and kinematic viscosity was 0.6484,5. at 40 $^{\circ}$C respectively. Specific gravity were within the ASTM standard value unlike the kinetic viscosity which much higher as per the ASTM standard value of 1.3-1.4. The (calorific value) of 3870 and cetane number were within the ASTM standard value of ≥4200 and 40-50 respectively. The proximate analysis of castor oil seeds revealed the following composition in (%): dry matter 96.52, crude protein 24.01, crude fat 35.61, crude fibre 5.98, total ash 3.42 and Nitrogen Free Extract 27.50. The seeds were also rich in calcium 1.538, potassium 1.333, phosphorous 3.033, sodium 1.632, zinc 2.742, iron 0.042 manganese 0.005 and magnesium 2.525 and copper 0.001

Based on the findings of this study the following conclusion can be made:

To the need to move away from oil as a major source of energy is growing every year, due to the price instability and environmental pollution which are the consequence of over dependence on the fossil fuel. The current research and development on alternative energy that will replace fossil fuel is now focusing on the biofuel. Renewable biofuel will reduce the dependence on oil and also reduce the trade deficit of nations, especially the developing nations. However, for biofuel to compete with the fossil fuel and possibility replacing it as the energy source, needs to be easy, cheap and fast to produce. Production of biofuel from vegetable oil is however not economical due to the fact that production of biodiesel from vegetable will lead to food crisis while trying to solve energy crisis. It is therefore much more desirable to use non-edible oils as a feedstock in the production of biodiesel, which is the focus of this study. This study report the production of biodiesel from non-edible oils *RicinusCommunis*as alternative to petrol diesel. Based on the results of experimental analysis, it can be concluded that oils from both feed stocks are suitable for the production of biodiesel.

The result also shows that the oil can be classified as drying oil which can be hydrated by sulphonation to give semi-drying or drying oil which can be used extensively in paint and vanishes. Considering the high percentage yield of the castor seed oil (33.2%), farming castor plant should be encouraged to boost the commercialization of castor seed to enhance the economic growth of individual and the country at large particularly in this era of biotechnology and industrialization to feed these industries.

4.1 Recommendations

The following work is recommended for further study;

1) Quantification of fatty acid methyl esters using the GC and HPLC in castor biodiesel.
2) More investigations should be carried out in studying the emission and performance of diesel engine using the castor biodiesel and its blend with diesel from 0% to 40% by volume.
3) Research to obtain further methods of efficient processing and detoxification to enable full utilization of the castor seeds and cake as alternatives to conventional feedstuffs is being given consideration.
4) More investigation should be carried out on the physical–chemical of properties of castor biodiesel and bioethanol in ethanol blends and present an option to decrease the castor oil biodiesel viscosity specification.
5) Research to obtain further methods of efficient processing and detoxification to enable fullutilization of the castor seeds and cake as alternatives to conventional feed stuffs is being given consideration.

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