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Conversion of Waste cooking Oil into Biofuel as alternative and renewable energy

Sékou Magassouba [(1)] ; Mohamed A. Camara [(2)] ; Kissi Traoré [(3)], Sékou Traoré [(3)]

(1) Faculty of Natural Sciences University of Conakry; UGANC; Conakry, Guinea

(2) Polytechnic Institute, University of Conakry UGANC, Department of Electrical Engineering; Conakry, Guinea;

(3) Polytechnic Institute, University of Conakry UGANC, Department of Chemical Engineering; Conakry, Guinea;

Corresponding Author: Sékou Traoré: sktraore@gmail.com

Abstract

Food supply services such use a large amount of oil for frying. After use, the cooking oil constitutes a waste whose management become an environmental issue. Huge quantities of waste cooking oil WCO are poured into the environment and contaminate water resources with severe consequences. There is a growing interest in its use in producing renewable energy to achieve potential benefits. WCO can be processed into biodiesel, an alternative to fossil oil. In fact, the continuous depletion of fossil fuel and petroleum products, their limited resources and environment concerns are a matter of concern. Nowadays waste cooking oil is used as feedstock in the preparation of biodiesel. Indeed, huge quantities of waste cooking oil WCO are produced in restaurants and hotels with a very limited reuse value and posing environmental issues, Biodiesel was synthesized from diverse local sources such waste cooking oil by alkali-catalyzed transesterification with methanol. Prior to transesterification WCO was subjected to filtration and dehydration. The composition and properties of the raw WCO and the resulting biodiesel were characterized by Gas chromatography Mass Spectrometry (GC-MS), Fourier transform infrared spectroscopy (FT-IR). From the tests, composition and properties met the ASTM criteria for fuel standard.

Key words: *Waste cooking oil, fatty acid, alcohol, transesterification, biodiesel.*

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I. INTRODUCTION

Human civilization predominantly depends on the utilization of energy, it plays a big role in socio-economic development by improving the standard of living, Energy is vital for the economic development of every country. Every sector of the economy such as agriculture, industry, transport, commercial and domestic sectors require energy. A huge amount of the total energy output worldwide is produced from fossil fuels unanimously conceded as finite resource, The world is no longer endowed with new sources of cheap fossil fuels and experts have warned about the depletion of the present sources in the near future **[1].**

Conventional Petrodiesel is considered to be one of the largest contributors to environmental pollution problems worldwide; turning to more environmentally friendly and sustainable fuels has today become a necessity in combating increased Greenhouse Gas (GHG) levels and climate change. Over the past two decades, biofuels have gained continuous interest due to the renewable feedstock and their short life cycle **[2]**. Substitute energy sources are required because of the high price of petroleum products, decrease in fossil fuel reserves, and atmospheric pollution caused by petroleum-based fuels, **[3]**. Biodiesel, derived from a renewable, domestic resource, and thereby relieving reliance on petroleum fuel imports, is an innovative solution to the rapidly evolving energy crisis, **[4]**. Biodiesel fuels also emit lower levels of carbon monoxide, particulate matter, and unburned hydrocarbons compared to petroleum-based diesel **[5]**.

Any substance containing fatty acid may suitable to produce biodiesel. Hence any lipid from biomass represents substrate for the manufacture of biofuel. However, the use of comestible fats and vegetable oils for biodiesel poses the issue of fuel versus food disagreement. Biodiesel is renewable and does not contribute to global warming due to its closed carbon cycle. A life cycle analysis of biodiesel showed that overall CO2 emissions were reduced by 78% compared with petroleum-based diesel fuel **[6]**. The foremost technical challenge of converting WCO is its collection, mainly due to the high costs in the logistics. Even if numerous solutions exist which can be competently adapted to different contexts, they still are not applied on a large scale. For this reason, the RecOil project records and make available best practices and suggestions for newcomers who would like to implement a WCO collection project **[7]**. This study aims to encourage the shift from WCO unsuitable disposal to sustainable recycling.

I. Concept of renewability of biomass and energy

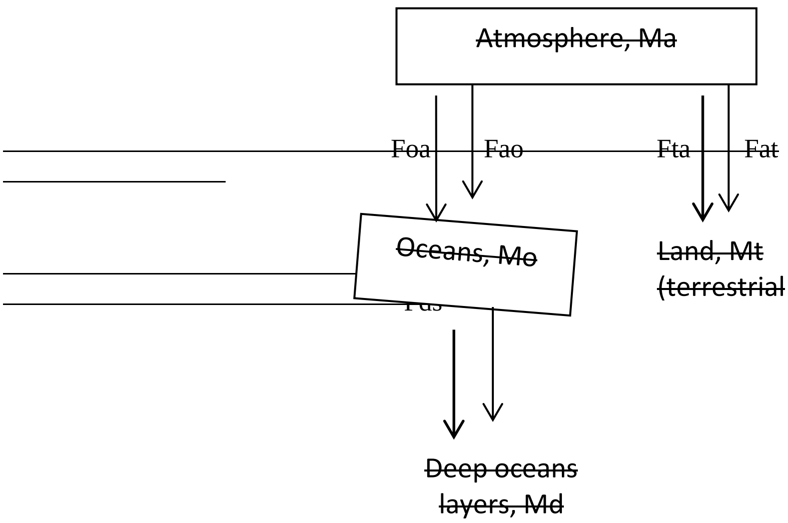
Biomass is the largest and most important renewable energy option at present and can be used to produce different forms of energy. As a result, it is capable of providing all the energy services required in a modern society **[8]**. The advantage of biodiesel is related to the renewable nature which itself resides in the cyclic character of the carbon entering into the composition. Indeed, the carbon constituting the molecular chain of oils and fats undergoes a double cycle: global and metabolic.

Renewability and versatility are among many other important advantages of biomass as an energy source. Human-induced changes to the cycling of nutrients in terrestrial ecosystems significantly affect the sustainability of raw material and feedstock production, the state of the natural resource base, and the equilibrium of the environment **[9]**.

The study of cycles has always been of interest for scientists. On one hand it allows a better control of the flow of matter and energy through reduction of losses resulting with an increment of biomass in terms of volume and quality; especially in food and biofuel production. The chemical energy is stored in the form of biomolecules in plants, which are harvested by the organisms that eat them forming food chains. The basic equation of photosynthesis is relatively simple, Water and carbon dioxide combine to form carbohydrates and molecular oxygen,

The cycle of the elements is the combination of many different physical, chemical, and biological processes that transfer them between the major storage pools: the atmosphere, plants, soils, freshwater systems, oceans, and geological sediments. It is a set of phenomena that assure the continuous flow of single mineral elements in the form of ions to more complex organic substances and inversely the return of the organic state in the mineral state. The major bio-essential elements, including carbon and the nutrient elements N, P, S, K and Ca are efficiently recycled within terrestrial and marine ecosystems,

The transport of elements and substances in biogeochemical systems explains the renewability as shows Figure I **[10]**. The symbol *M* (with units of mass or moles) stands for matter; *Ma* matter in atmosphere; *Mt* in earth; *Mo*; that in oceans; *Md* matter in deep oceans; *F* (the exchange rates or flows *F's* have units of mass or moles per unit of time) stands for flux; *Fta*: flux from earth to atmosphere; *Fat*: that of atmosphere to to earth; *Foa*: flux from ocean to atmosphere; and *Fao*: that of atmosphere to oceans. A quantitative description would give numerical values of the amounts and fluxes for the *F's* in terms of the *M's*,



~~Figure I **[10]**: Schema of pools representation of global carbon cycle~~

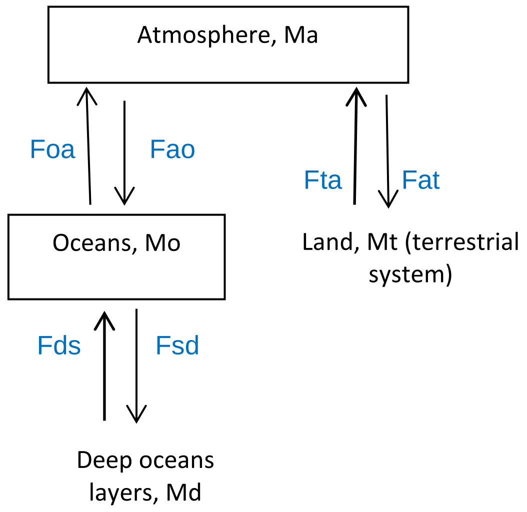


Figure I **[10]**: Schema of pools representation of global carbon cycle
Please pay attention to the orientation of arrows

II. Food waste recovery

The Food and Agriculture Organization of the United Nations estimated that approximately one-third of all food produced for human consumption worldwide is lost or wasted. Taking simple steps in everyday life can make a difference in addressing this issue. Reducing wasted food is a triple win; it's good for the economy, for communities, and for the environment **[11]**. Diverting food waste from landfills can also protect water quality. When waste decomposes in landfills, it creates leachate, a liquid composed primarily of dissolved organic matter, inorganic ions such as ammonia, phosphate, and sulfate, and heavy metals **[12]**. Diverting food waste from landfills reduces the volume of organic matter, correspondingly reducing not only the amount of leachate but also the concentration of dissolved organic matter in the leachate, Leachate leaks from landfills without adequate liners, percolating into soils and groundwater, potentially increasing biological oxygen demand and nutrient loads in adjacent water bodies **[13]**. By diverting food waste, landfills are less likely to contribute eutrophic and hypoxic events and hence can help protect water quality.

The Food recovery hierarchy prioritizes actions organizations can take to prevent and divert wasted food. Each tier of the Food Recovery Hierarchy focuses on different management strategies for your wasted food. The top levels of the hierarchy are the best ways to prevent and divert wasted food because they create the most benefits for the environment, society and the economy.

II.1. Waste Cooking Oil

WCO enters in the category of biomass consisting mainly of a mixture of organic substances; its conversion and/or recycling come in the food recovery chain as shows Figure 2 below. As shows the figure biofuel production from WCO as industrial process, comes at the fourth stage of food recovery pecking order.

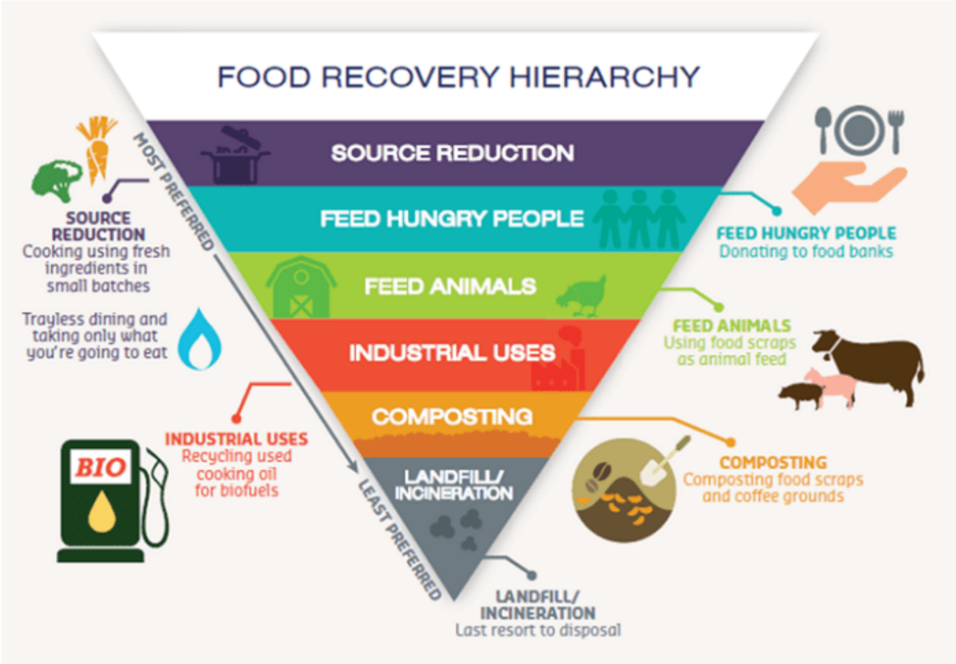


Figure 2: Source: United States Environmental Protection Agency

Waste cooking oil refers to the used vegetable oil resulting from cooking food. Recurrent frying for preparation of food makes the comestible plant oil no longer appropriate for consumption due to high free fatty acid (FFA) content [10]. Waste oil has many disposal problems like water and soil pollution, human health concern and disturbance to the aquatic ecosystem so rather than disposing it and harming the environment, it can be used as an effective and cost-efficient feedstock for Biodiesel production as it is readily available **[12]**, **[14]**.

Inappropriate WCO disposal rises the operating cost of wastewater treatment, the risk of groundwater contamination, as well as the greenhouse gas emissions that are associated with its degradation, Converting WCO to biodiesel offers a sustainable solution in the exploitation of a problematic waste and its transformation into an energy resource, hence contributing to the reduction of environmental pollution and Petrodiesel dependence.

Since times, the search for a sustainable and efficient raw material for biofuel production has widely outshined, WCO is found to be one of the best raw materials for biodiesel due to its availability, renewability, In fact, enormous amounts of waste cooking oils are existing throughout the world, particularly in the industrialized regions, The amount of cooking oil produced every year is immense, over 15 million of tons, which, if converted, can satisfy to a large extent the world demand of biodiesel. The manufacture of biofuel from WCO permits for a 21% in crude oil saving and 96% in fossil energy saving **[15]**. Managing of WCO represents a substantial challenge because of their storage problems and probable pollution of the water and land resources.

II.2. Biodiesel technology

Biodiesel is prepared from biomass or bio waste, which can be replenished year after year through sustainable farming practices, Biomass and biofuel are renewable while fossil fuels require millions of years to form.
After filtration and drying of WCO, the stages and processes leading to the obtention of biodiesel are defined in Fig.2. Prior to transesterification, esterification is required only in the case when the amount of FFA is over 2%.

II.2.1. Transesterification

Transesterification is a stepwise process and excess alcohol is used to drive the reaction to the forward direction, Biodiesel is a clear amber-yellow liquid with a viscosity similar to that of Petrodiesel and is generally synthesized via liquid base catalyzed transesterification of C14-C20 triacylglyceride (TAG) components of lipids with C1-C2 alcohols into Fatty Acid Methyl Esters (FAMEs) which constitute biodiesel, alongside glycerol as a potentially valuable by-product as shows the reaction below.

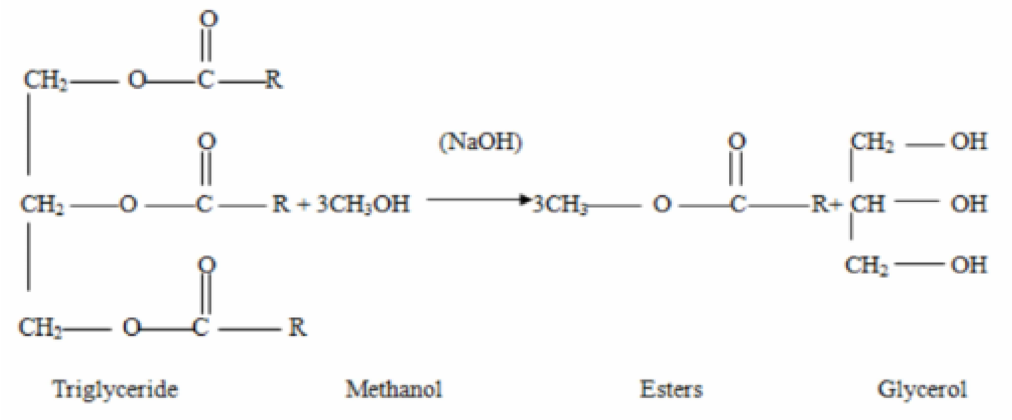


Figure 3: Transesterification reaction of WCO

The majority of biodiesel today is produced through homogeneous alkali-catalysed transesterification of edible vegetable oils **[16]**, Homogeneous catalysts are those which are soluble during the reaction, they may be liquid or gaseous. They are of two types: acidic and alkaline. Acidic catalysts like H2SO4 are used widely for Esterification while Alkaline catalysts like NaOH and KOH are used for Transesterification **[17]**. The advantages of homogenous catalysts are: ability to catalyze reaction at lower reaction temperature and atmospheric pressure; high conversion can be achieved in less time, (iii) availability and it is economical **[18]**. This process enables a good product quality and a relatively shorter reaction time. The effective use of Alkaline homogenous catalyst is limited only for refined vegetable oil with less than 0,5 wt. % FFA or acid value less than 1 mg KOH/g, [3]. Moreover, the separation of these catalysts after the reaction is completed, requires the washing of biodiesel with water which might result in loss of Fatty acid alkyl esters, energy consumption and H2SO4,

II. MATERIALS AND METHODS

Waste cooking oil WCO was obtained from hotels, restaurants, households and several food sellers in Conakry, the capital City of Guinea. Chemicals used in the transesterification are methyl alcohol (99.8%, Merck); sodium hydroxide (99%, Merck) and deionized water. In order to remove suspended solid particles and other inorganic residues, WCO samples were settled during five days at ambient temperature and filtered by sieves of hole size 100 nm. Prior to the synthesis the raw materials of WCO collected are mixed into one. The mixture is then precipitated for 24 hours. After precipitation WCO is subjected filtration and heating to 100ºC to ensure an anhydrous medium for 20 min with continuous stirring. After pretreatment, a preliminary analysis of used cooking oil was carried out. The effect of conversion reaction variables such as alcohol to oil molar ratio, catalyst concentration and reaction time was investigated. Transesterification was carried out using 1 to 10 (wt.%) of catalyst concentration.

The oil was then weighed and taken in a 500 ml three-necked round flask. A water condenser system and a thermometer were connected to the flask. As catalyst the NaOH pellets was dissolved in methanol with 1:1 to 8:1 ratio. The WCO was warmed by placing the flask in a 65°C water bath. After the temperature is reached, the sodium methoxide solution was gradually added into the WCO while stirring during 1 hour. The resulting product was taken into a separating funnel and stand 24 hours. Two phases were distinct: a golden yellow liquid representing the biodiesel on top and the glycerol at the bottom. Biodiesel purification was carried out by washing using hot water at 80°C twice as much washing, Ratio between volume of biodiesel and water for washing are 1:1. Biodiesel is then heated at 110ºC for 10 minutes using a hot plate to remove moisture. Gas Chromatography and Mass Spectroscopy GC-MS and Fourier transform Infrared spectroscopy FT-IR were used to determine the physicochemical properties and the fatty acid composition of the parent WCO and the resulting biodiesel. The properties of biodiesel were compared with conventional Petrodiesel. From the tests, the flash point, water and sediment, total acid number, viscosity at 40ºC and density met the ASTM criteria for fuel standard.

III. RESULTS

Fig.4 shows the decantation and washing of the transesterified WCO. After complete drying the resulting product exhibits following parameters.

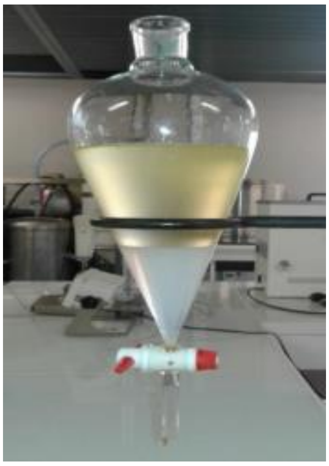


Figure 4: a) Decantation after transesterification b) Washing the WCO-biofuel

Effect of transesterification parameters

The key parameters influencing the alkali catalyzed transesterification reaction are:
alcohol/oil molar ratio, catalyst formulation and concentration, reaction temperature, reaction time.

- methanol to oil molar ratio: The furthermost operative variable that affects the methyl ester production yield during the transesterification reaction is the molar ratio of alcohol to WCO. Since transesterification is an equilibrium reaction, a large excess of alcohol is required for the reaction to move forward and avoid the reversible reaction.

Figure 5 shows that the optimum FFA conversion rate to biodiesel was 97% at 6:1 molar ratio. Over this ratio the conversion rate declines.

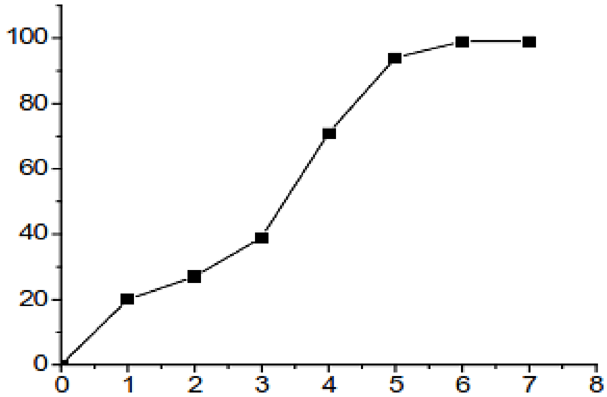


Figure 5 Effect of Methanol to FFA molar ratio on FFA conversion

- Catalyst concentration is a key factor for the conversion of FFA to methyl ester. Sodium hydroxide was used in a range from 1 to 10 wt.%. The highest biodiesel yield of 96%was achieved using catalyst 6 wt.% concentrations.

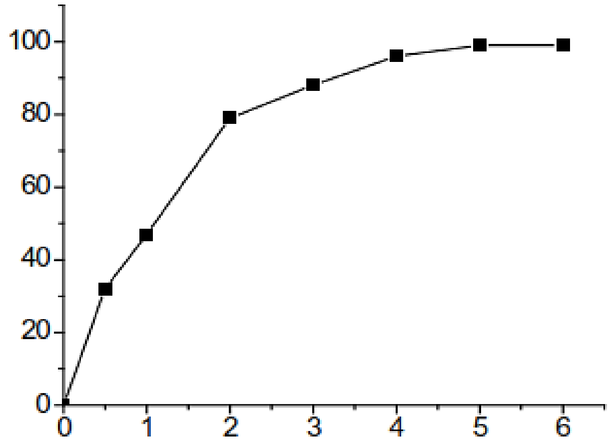


Figure 6: Effect of catalyst concentration on esterification reaction

- Temperature plays a weighty effect on conversion of WCO to methyl ester. Increasing temperature during the transesterification process results with a corresponding increasing conversion rate. Fig.7 shows that the conversion was 98% at 60°C temperature.

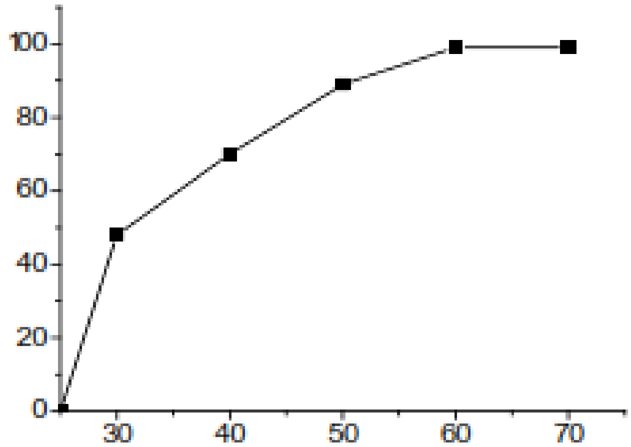


Figure 7**:** Effect of Temperature on esterification reaction

Composition of WCO-biofuel

The chemical composition of WCOs is quite similar to one of the parent comestible oils, and differs from the former in terms of decomposition and leaching products. Through the frying progression, a portion of triglycerides, of the ester moiety, break down. The degree of such degradation depends on the number of frying cycles, frying time, temperature, and the specific vegetable oil. As shows figure 8, the GC-MS analysis of biodiesel, four main characteristics peaks of fatty acid methyl esters (FAMEs) appear by the retention time and the fragmentation pattern data. Namely C18 fatty acids are the major fatty acid constituents of the synthesized biodiesel. The identified FAMEs are methyl oleate, methyl linoleate, methyl palmitate, and methyl stearate. These results are consistent with previous studies. Nearly 60% of the fatty acids were found to be C18:1 while C18:2, C18:3 fatty acids were found to be approximately 26%. Palmitic acid and stearic acid were the major saturated fatty acids found in our WCO ethyl ester. The quantity and nature of fatty acid content are the major factors that determine the viscosity of biodiesel. The above qualitative and quantitative values are similar with a previous study for waste cooking oils.

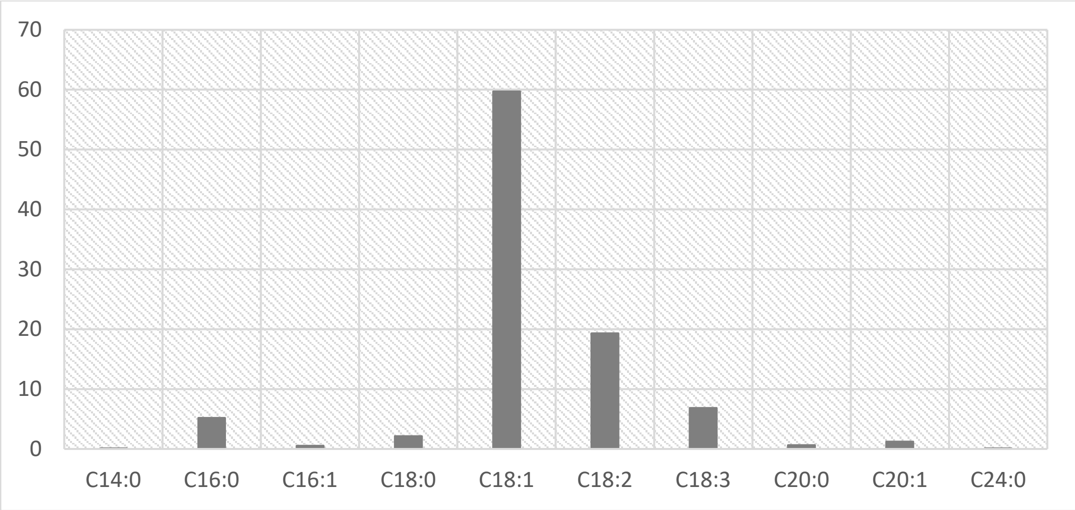


Figure 8: Fatty acid composition of WCO- biodiesel.

FT-IR spectrometry is a fast and precise method for determination of FAME. It identifies the key functional groups presence at the optimum produced biodiesel sample. Figure 9 shows the produced biofuel absorption peaks at 1434 cm-1 which is the methyl ester group (CO-O-CH3) and the characterization peak at 1195 cm-1 corresponding to (C-O) ester peak. It was apparent the decrease of CH2-O- groups in oil and the appearance of CH-O- vibrations in biodiesel.

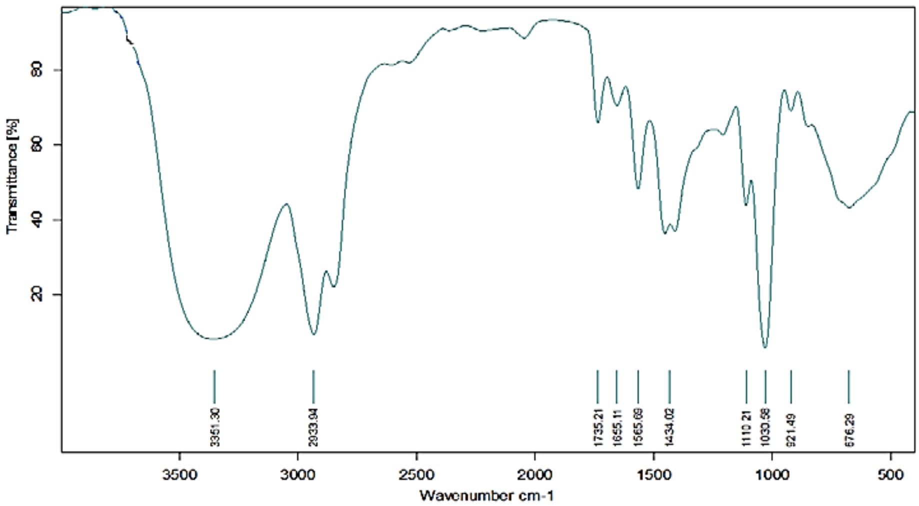


Figure 9: FT-IR spectrum for biodiesel produced at optimum conditions.

Fuel properties of WCO and of Biodiesel

The GC test shows that all the parameters of the resulting biofuel were within the limits of ASTM standards as shows the table below.

Table1: Compared Physic and chemical ASTM properties of WCO, biodiesel synthetized from WCO and conventional Diesel.

Item	Density	Viscosity@40°C	Flash point °C	Cloud point °C
WCO	O,917	31,7	197	-11
Biodiesel from WCO	0,887	4,4		-13
Conventional Diesel	0,850	3,07		-16

The viscosity of WCO 31,7 at 40°C is very high and it is not suitable as a fuel, whereas biodiesel has lower viscosity 4,4 is suitable to be used as a fuel. One of the foremost drives of the transesterification reaction was to decrease the viscosity of WCO in order to obtain the properties that are suitable for using it as a fuel. Table

1 shows that the viscosity of biodiesel produced is 4,4 mm2/s; which lies within the ASTM D6751-12. But it higher than that of conventional Diesel 3,07.

Density is an important parameter for combustion system, since it impacts the efficacy of the fuel atomization. Density is the mass of biodiesel per unit volume at a certain temperature. Hence the lower the density value the better the biodiesel. The results show that the density of the biodiesel produced was within the ASTM D6751-12 standards limits; it is slightly higher than that of the conventional Diesel.

IV. DISCUSSION

With the increasing amount of waste generation from different processes, there has been a rising interest in the use of waste in producing sustainable substances to achieve potential benefits. Waste resources resulting from different industrial processes requires proper management to safeguard a cleaner environment. The use of recycled foodstuffs in valuable products is quite attractive due to the low-cost related to the waste management in addition to saving required space for landfill purposes.

Biofuel production from WCO is commonly carried out through the process of transesterification reaction. The reaction is expedited with a suitable catalyst either homogeneous or heterogeneous. Biofuel has been confirmed to have an advantage over its conventional fuel counterpart because of the renewability of its parent WCO. The present study shows the possibility of manufacturing biodiesel from WCO. The preparation of biodiesel in this paper involved a one-step transesterification process **[19].** The highest yield of the conversion process was 97% at 6:1 methanol/alkali molar ratio. The yield compares favorably with results from previous literatures **[20]** whose yields were between 80-98% under similar reaction conditions. Such a high yield may be attributable to the nature and concentration of the NaOH catalyst used for the reaction process. It is well known that alkaline catalyst such as NaOH and KOH produce quicker reaction time and better yield compared to acid catalyst. Some studies reported 85% biodiesel yields from WCO which is similar to our results **[21]**. Comparable investigations obtained 92.76% of biodiesel from WCO at temperature 66.5 °C **[22]**.

Most of the physicochemical properties of the produced biodiesel fall within the range stipulated by American Society for Testing and Materials (ASTM) for biodiesels. Namely C18 fatty acids are the major fatty acid constituents of the synthesized biodiesel. The identified FAMEs are methyl oleate, methyl linoleate, methyl palmitate, and methyl stearate. These results are consistent with previous studies. **[23]**. Nearly 60% of the fatty acids were found to be C18:1 while C18:2, C18:3 fatty acids were found to be approximately 26%. This implies oil of high stability as monounsaturated/unsaturated fatty acids are less prone to oxidation and rancidity [22].

The viscosity of biodiesel from waste cooking oil was found to be higher than that of conventional Diesel. Since various properties of obtained biodiesel resemble the conventional Diesel, it could be used directly in existing engines with slight modifications like blending with Petrodiesel **[24]**

From an economic point of view; the production of biodiesel is very feedstock sensitive. Many investigations lead to the finding that feedstock cost represents a very significant percentage of total biodiesel cost. For instance, to produce biodiesel from soybean oil, the cost of the raw oil accounted for 88 % of total estimated production costs **[25]**.

Regarded from a waste management perspective, producing biodiesel from WCO is environmentally beneficial, since it provides a cleaner way for disposing these products; meanwhile, it can yield valuable cuts in CO2 as well as significant tail-pipe pollution gains.

V. CONCLUSION

Owing to their residue-nature and to a huge availability, WCO represents a valuable raw material for the production of biofuel as renewable energy. The conversion of WCO into Biofuel through catalyzed transesterification reaction was successful. The optimal reaction parameters were: 6:1 alcohol/WCO molar ratio; catalyst 6 wt.% NaOH concentration at 60°C. With regard to the chemical composition almost 60% of the fatty acids were found to be C18:1 while C18:2, C18:3 fatty acids were found to be approximately 26%. Properties such as density, viscosity, flash and cloud points of the resulting biodiesel were in conformity with the American fuel standards (ASTM D 6571).

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