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Production and Evaluation of Biodiesel from Palm Oil and Ghee (Clarified Butter)

Padmarag Deshpande[1] *, Kavita Kulkarni[2]
1. M.Tech Student, Department of Chemical Engineering, BVDU, Pune, India
2. Associate Professor, BVDU College of Engineering, Pune, India
Bharati Vidyapeeth Deemed University, College of Engineering, Pune, 411043, India
* E-mail- padmarag_26@yahoo.co.in
E-mail- kskulkarni@bvucoep.edu.in

Abstract
The scarcity of conventional fossil fuels, growing emissions of combustion-generated pollutants, and their increasing costs will make biomass sources more attractive. Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources. The finite nature of fossil fuels necessitates consideration of alternative fuels from renewable sources. This article reports experimental work on the production of biodiesel by Transesterification from two biofeeds, having less Iodine Value; *Palm oil and Ghee (known as Clarified Butter)* using alkaline catalyst. The variables affecting the yield and characteristics of the biodiesel produced from these biofeed were studied. The biodiesel samples were physiochemically characterized according to ASTM standards. From results it was clear that the biodiesel fuel produced from Palm oil and Ghee (Clarified Butter) was within the recommended standards of biodiesel fuel and shows promising alternative.

Keywords: Biodiesel, Transesterification, Palm oil, Ghee (Clarified Butter), Optimum condition

1. Introduction

Biodiesel is a notable alternative to the widely used petroleum-derived diesel fuel since it can be generated by domestic natural sources such as soybeans, palm, coconuts, and even recycled cooking oil and thus reduces dependence on diminishing petroleum fuel from foreign sources. The injection and atomization characteristics of the vegetable oils are significantly different than those of petroleum derived diesel fuels, mainly as the result of their high viscosities. Modern diesel engines have fuel-injection system that is sensitive to viscosity change. One way to avoid these problems is to reduce fuel viscosity of vegetable oil in order to improve its performance. The conversion of vegetable oils into biodiesel is an effective way to overcome all the problems associated with the vegetable oils. Dilution, micro-emulsification, pyrolysis, and transesterification are the four techniques applied to solve the problems encountered with the high fuel viscosity [1, 2]. Transesterification is the most common method and leads to monoalkyl esters of vegetable oils and fats, now called biodiesel when used for fuel purposes. The methyl ester produced by transesterification of vegetable oil has a high cetane number, low viscosity and improved heating value compared to those of pure vegetable oil which results in shorter ignition delay and longer combustion duration and hence low particulate emissions. [3, 4].

Biodiesel is a cleaner burning alternative to petroleum-based diesel fuel. Just like petroleum-based diesel fuel, biodiesel operates in the compression ignition (diesel) engines. The successful introduction and commercialization of biodiesel in many countries around the world has been accompanied by the development of standards to ensure high product quality and user confidence [5]. Some biodiesel standards are ASTM D6751 (ASTM = American Society for Testing and Materials) and the European standard EN 14214. The biodiesel is characterized by determining its physical and fuel properties including density, viscosity, iodine value, acid value, cloud point, pure point, gross heat of combustion and volatility. In general, biodiesel compares well to petroleum-based diesel [6, 7].

Elemental composition and relative amounts of compounds present in biodiesel and diesel fuel are given in Tables 1 and 2. Due to presence of electronegative element oxygen, biodiesel is slightly more polar than diesel fuel as a result viscosity of biodiesel is higher than diesel fuel. Presence of elemental oxygen lowers the heating value of biodiesel when compared the diesel fuel. The lower heating value (LHV) is the most common value used for engine applications [8].

Table. 1. Elemental analysis of biodiesel and diesel fuels [8]

Elements	**Composition (%)**	
	Biodiesel	**Diesel fuel**
Carbon (C)	79.6	86.4
Hydrogen (H)	10.5	13.6
Oxygen (O)	8.6	-
Nitrogen (N)	1.3	-
C/H	7.6	6.5

Table. 2. Composition of biodiesel and diesel fuels [8]

Type of compounds	**Biodiesel**	**Diesel fuel**
n-Aliphatic	15.2	67.4
olefinic	84.7	3.4
Aromatics	-	20.1
Naphthenes	-	9.1

Transesterification:

Transesterification is a most common [9] and well established chemical reaction in which a primary alcohol reacts with the triglycerides of fatty acids (vegetable oil) in presence of a catalyst to form glycerol and esters [10, 11-13].

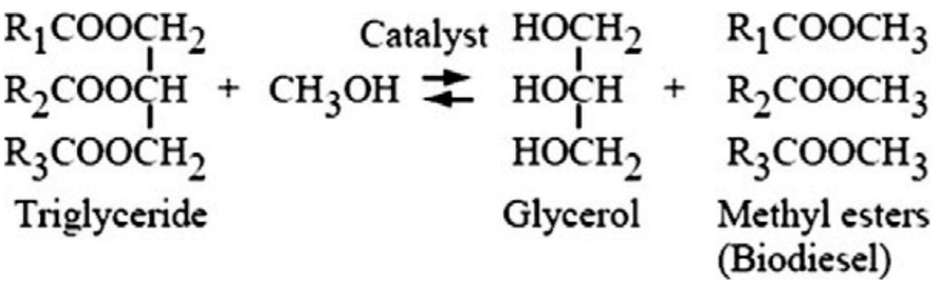

Fig.1. Transesterification of Triglycerides with alcohol

Where R1, R2, R3 are long-chain hydrocarbons, sometimes called fatty acid chains [11]. For an alkali catalyzed transesterification, the triglycerides should have lower free fatty acid (FFA) content, and the alcohol must be anhydrous to render soap formation. Soap formation lowers the yield of esters and renders the separation of esters and glycerol [14, 15, 16]. Up to about 5% FFA, the reaction can be catalyzed using an alkali catalyst [17]. The extent of transesterification and side reactions depends upon the type of feedstock, catalyst formulation, catalyst concentration, alcohol-to-oil ratio, reaction temperature and reaction time [18, 19].

Table 3. Biodiesel, B100, specifications (ASTM D 6751 – 02 requirements)

Properties	Limits	Units
Flash point	130 min.	^{0}C
Kinematic viscosity at 40^{0}C	1.9 – 6.0	mm^2/s
Water and sediment	0.050 max	% volume
Specific gravity	0.86-0.89	-
Cloud point	report	^{0}C
Pour point	-10 to 12	^{0}C
Acid value	0.80 max	mg KOH/g
Distillation temperature,90% recovered	327 max.	^{0}C

This experimental work was focused on the production of biodiesel from ***Palm oil*** and ***Ghee (Clarified Butter)*** using transesterification with sodium hydroxide as alkaline catalyst and methanol as alcohol to react with Triglyceride. The reason for taking this as a Bio-Feedstock is these biofeed shows low iodine number and less degree of unsaturation [20]. High Iodine value of any vegetable oil sample shows high degree of unsaturation. When heating unsaturated fatty acids, polymerization of glycerides occur, this may lead to the gum formation. Some physical properties of the vegetable oils are shown in Table 4. [21, 22, 23].

Table 4. Some physical properties of the biofeed

Properties	Palm oil	Ghee(Clarified butter)[24]
Specific gravity	0.9072	0.9390
Kinematic viscosity, at 40^{0}C	42.5 mm^2/sec	54.6 mm^2/sec
Acid value,mg KOH/g	0.437	0.374
Iodine value	40	36.7
Pour point,^{0}C	22	35

2. Materials and methods

2.1. Materials

In this study two commercially biofeeds: ***Palm oil and Ghee (Clarified Butter)*** were used in the methyl ester production. Pure sodium hydroxide as alkaline catalyst and methyl alcohol (Methanol) of 99.5% purity (density: 0.791–0.792 kg/l) were used in the transesterification process.

2.2. Experimental procedures

The transesterification was carried out in 2 *l* reaction flask equipped with stirrer, thermometer and heating mantle. The transesterification process was studied at three catalyst loadings (0.15%, 0.5% and 1.5% NaOH wt/wt), and three alcohol-to-oil ratios (0.15, 0.25 and 0.45 v/v) at a reaction time (0.5–3 h) at 60 ± 2 ^{O}C. Also, transesterification reaction was studied at different operating temperature in the range (40-70 ^{O}C) keeping other parameter constant. Care was taken to make biofeed free from water, as any water or moisture in the system will consume some of catalyst and slowdown the transesterification reaction. Hence; Feed (Palm oil) was preheated at 110 ^{0}C in order to ensure complete removal of water; if present.

The catalyst was dissolved into methanol by stirring. 1000 ml of the oil was introduced into the reaction flask. After the appropriate temperature was reached, NaOH previously dissolved in methanol was added and the mixture was continuously stirred at 400-600 rpm by means of a stirrer. After the preestablished the mixture was carefully transferred to a separating funnel and allowed to stand there overnight. Lower value of the specific gravity of the final product is an indication of completion of reaction and removal of heavy glycerin [25].The lower layer (mainly glycerol, some methanol and catalyst) was drained out. The upper layer (methyl esters, some methanol and traces of the catalyst) was then cleaned thoroughly by washing with warm (50^0C) distilled water in order to remove the impurities like uncreated methanol, uncreated oil and catalyst and again mixture was settled to give methyl ester as top layer; water phase from bottom was drained out. Once the phases had been separated, the excess alcohol and water traces were removed and biodiesel was dried with flash evaporation.

Same procedure as mentioned above was repeated using *Ghee (Clarified Butter)* as a biofeed for the production of Biodiesel (Methyl ester) and studied at different operating variables such as catalyst loading in the range (0.15-2% NaOH wt/wt) and methanol to oil ratio v/v in the range (0.15- 0.55v/v) at operating temperature $60 \pm 2\ ^OC$.The effect of reaction time was also studied on methyl ester yield.

3. Result and Discussion

Alkaline catalyst transesterification of Palm oil and Ghee (Clarified Butter) was carried out taking consideration to achieve maximum yield of biodiesel methyl ester, so factors affecting the yield of the methyl ester were studied.

3.1 Factors affecting the yield of methyl ester

3.1.1 Effect of alcohol

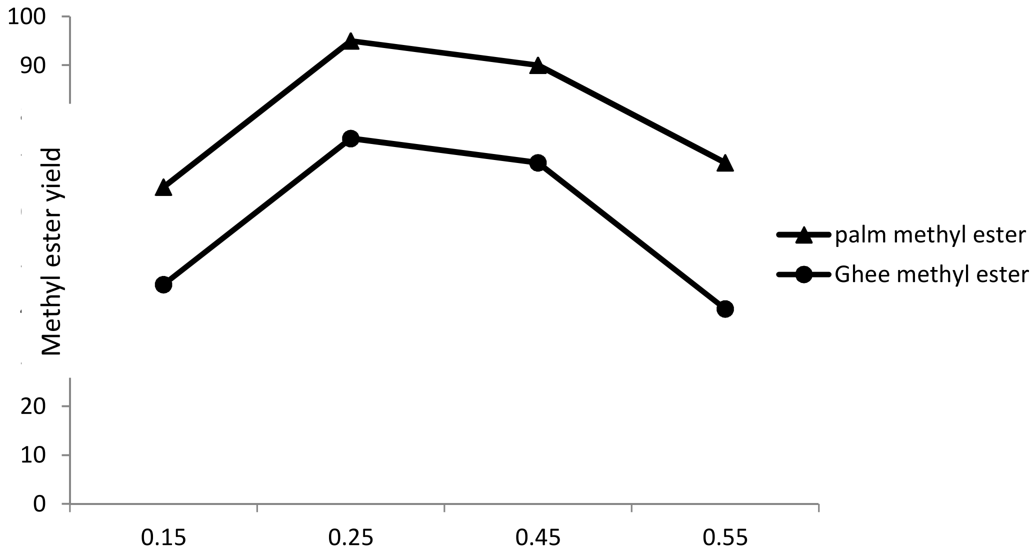

Fig.2. Effect of methanol to oil ratio on me %, temperature 60^0C, reaction time 1.5 h)

The important parameter affecting the yield of methyl ester is ratio of methanol to oil (biofeed) (v/v) basis. The above graph shows that the yield increases with increase in methanol/oil(biofeed) ratio in reaction,whereas,for ghee, the yield is comparatively low with same amount of methanol/ghee ratio[Fig.2].

Most researchers found that excess alcohol was required to drive the reaction close to completion. Higher molar ratios result in greater ester production in a shorter time [25].

In the present research, methanol was used. The effect of methanol in the range of 0.25 to 0.55 (v/v ratio) at $60 \pm 1\ ^0C$ was investigated, keeping other process parameters fixed. Presence of sufficient amount of methanol during transesterification is essential to break glycerin, fatty acid linkages. But when the ratio increased to 0.45, high methanol amounts interfere with the separation of glycerin because of an increase in solubility; the glycerin remaining in the solution drives the equilibrium back to the left side of reaction, resulting in the lower yield of esters. This means that the maximum conversion (optimum condition) to the methyl ester is achieved at a ratio (methanol/biofeed) of 0.25(v/v).

3.1.2. Effect of catalyst concentration

The effect of catalyst loading (NaOH) on methyl ester conversion was studied for two different biofeed i.e. ,Palm oil and Ghee(Clarified Butter) in the range of 0.15-1.5 wt/wt % at 60 ± 2 ^{O}C and 0.25 v/v ratio [Fig.3].

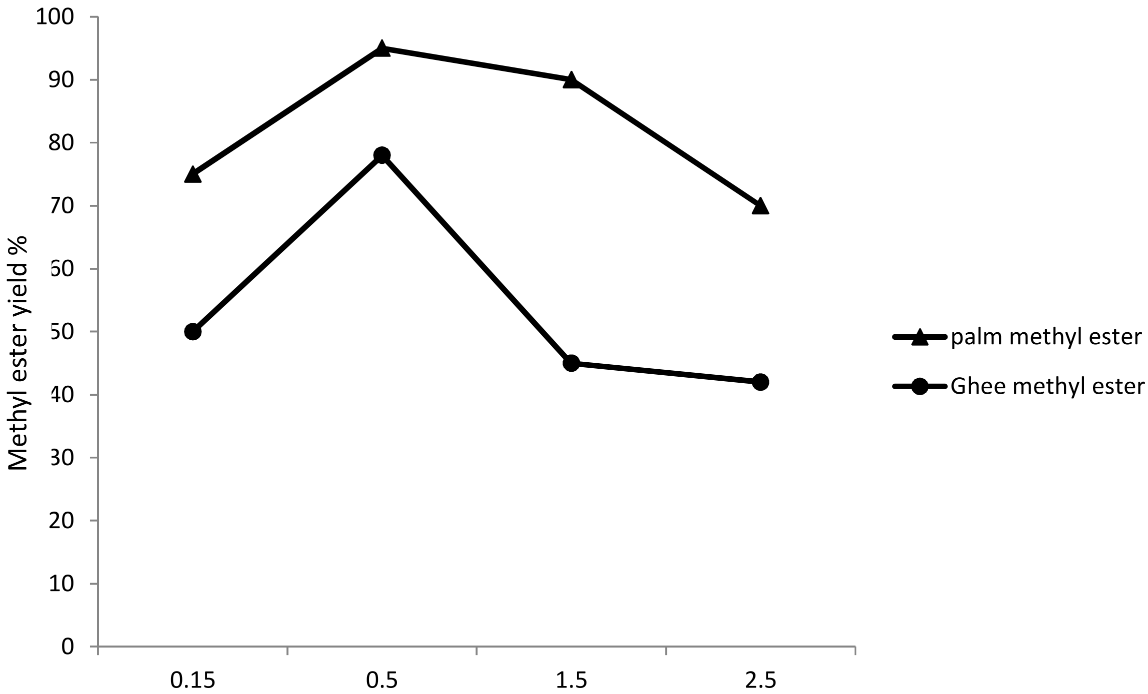

Fig.3. Effect of catalyst cor hanol/oil 0.25, temperature 60^{0}C, reaction time 1.5 h)

It was observed that the yield of the methyl esters was small at lower catalyst concentration due to incomplete reaction, and then increased as the catalyst concentration was increased. The optimal yield was observed at 0.5 wt%. However, using higher catalyst concentrations than 0.5 wt%, the yield decreased and resulted in no clear separation during settling, while during washing with warm de-ionized water more soap was observed, due to the excess catalyst favoring the process of saponification.

Therefore the optimum catalyst concentration was found to be 0.5 wt/wt% for sufficient methyl ester production. Also, it was observed that the yield of Palm oil methyl ester is comparatively high (more than 90%) than Ghee methyl ester.

3.1.3 Effect of Operating Temperature

The effect of operating temperature was observed at 40, 60, and 70 ^{0}C keeping other parameters fixed. [Fig.4]. It was found that near boiling point of methanol (methanol B.P:64.2 ^{0}C)[26] at 60 ^{0}C,methyl ester yield is maximum with shorter reaction time time(1 hr),whereas at 40 ^{0}C yield was low and reaction time was more.

It was observed that increase in temperature favors the influence on methyl ester conversion, but the operating temperature higher than boiling point of methanol, will evaporate the alcohol and thus resulted in less yield.

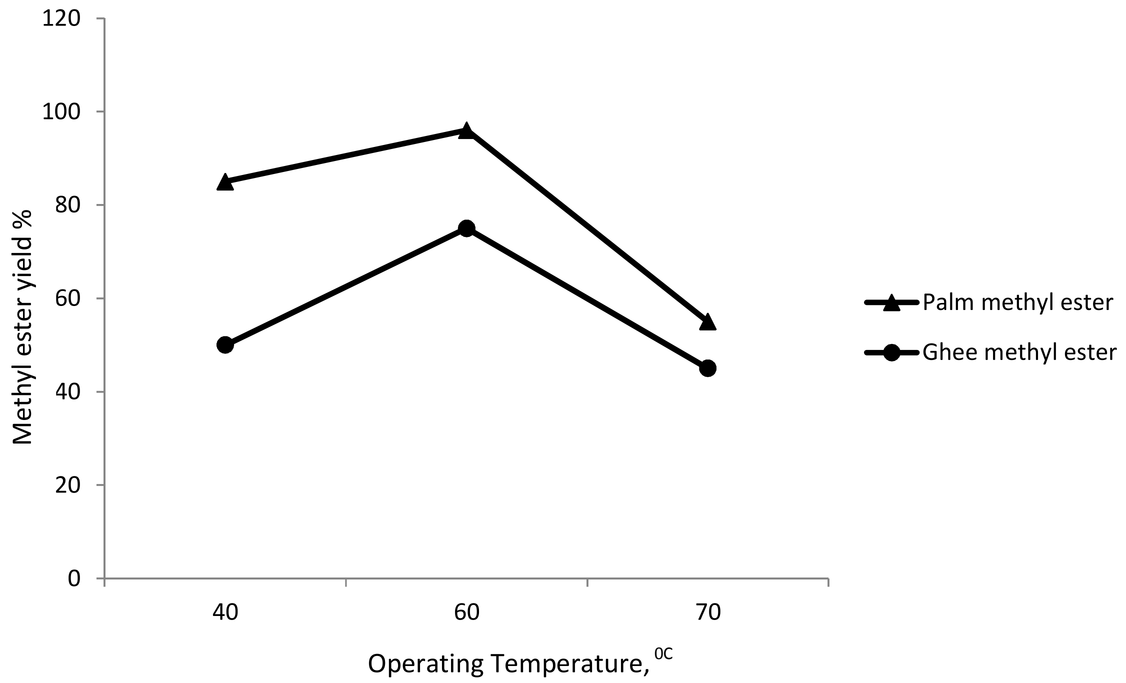

Fig.4. Effect of operating temperature on methyl ester yield (catalyst concentration 0.5 wt%, methanol/oil 0.25v/v)

3.1.4 Effect of Reaction time

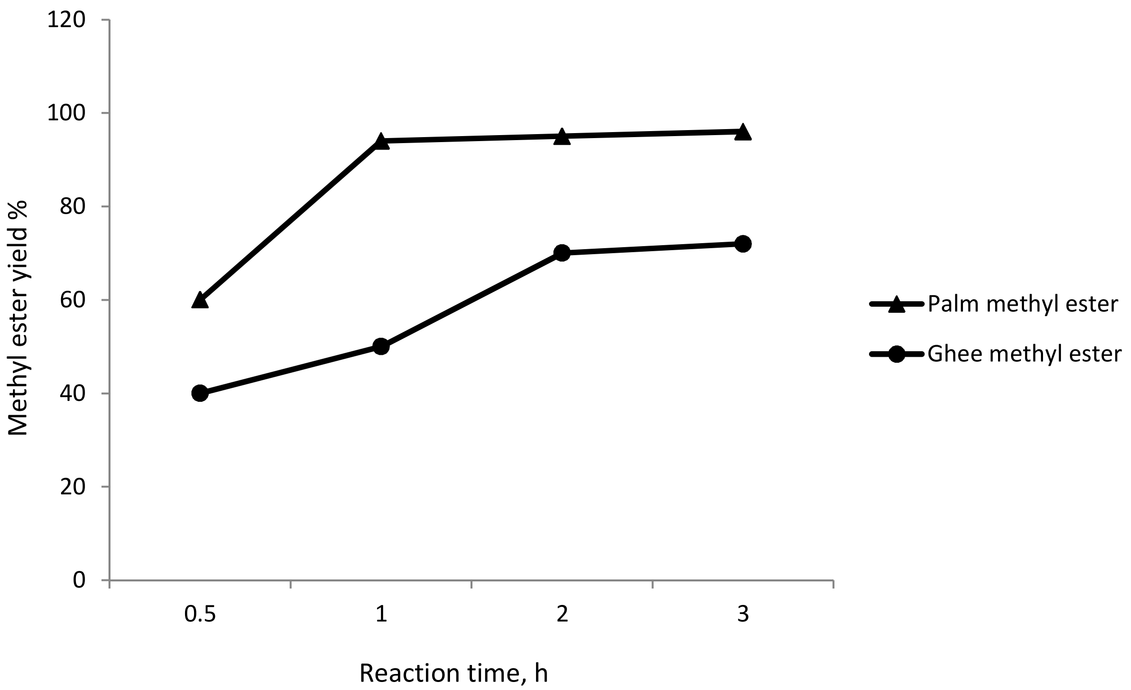

Fig.5. Effect of reaction time on methyl ester yield (methanol/oil, 0.25 v/v, catalyst concentration 0.5 wt%, temperature 60^{0}C)

Reaction time in this study was investigated using the optimal parameters obtained in the experimental work. Several investigators found that the transesterification reaction starts very fast and almost 80% of the conversion takes place in the first 30 min and after 1 h, almost 93–98% conversion of the triglycerides into ester takes place [27, 28].

In the present work, the effect of reaction time from 0.5–3 h on the reaction yield was investigated [Fig. 5]. It was clear that the conversion was lower for shorter times and increased as the time was increased to 1 h. Increasing the reaction time to beyond 1 h no noticeable change in the yield was detected, the ester yield change slightly. But for Ghee methyl ester yield was lower than palm oil methyl ester and reaction time was much higher than palm oil methyl ester conversion.

3.2 Properties of fatty acid methyl ester (Biodiesel)

The physical properties of biodiesel derived from Palm oil and Ghee (Clarified Butter) were evaluated in laboratory using specific gravity, API Gravity, Kinematic viscosity, Flash point, Pour point, Heat of combustion, ASTM Distillation, Refractive Index [29,30]. The physical properties of methyl ester (biodiesel) were similar to those of diesel fuel. The results are tabulated below:

Table.5. Results

Properties	**Biodiesel**		**Standard Diesel Fuel**
	Palm methyl ester	**Ghee methyl ester**	
Specific gravity	0.866	0.876	0.858
API gravity	31.9	28.20	34.97
Kinematic Viscosity at 40 ^{0}C,cSt	4.1	5.2	3.4
Flash Point,^{0}C	140	164	55
Pour Point, ^{0}C	9	2	-6
Cloud point, ^{0}C	12	5	-3
Heating Value, MJ/Kg	40.01	37.06	43.8
Distillation temperature, at 90% recovery, ^{0}C	320 max	312 max	327 max
Acid value, mg KOH/g	0.27	0.32	0.12
Refractive index, at 30 ^{0}C	1.430	1.431	1.425

3.2.1. Specific Gravity, API Gravity and Diesel Index

Specific gravity represents the ratio of weight of experimental solution with distilled water at constant standard temperature. The specific gravity of palm oil is 0.9072 and of ghee is 0.9390, where as the specific gravity of biodiesel is 0.866 and 0.876 respectively, thus there is decrease in specific gravity of biodiesel. This indicates that the product obtained is lighter than the feed. The specific gravity of Diesel fuel is 0.858, which is just matching the specific gravity of biodiesel. Hence the biodiesel can be used in diesel engine as an alternative as per the gravity is concern.

As API gravity is inversely proportional to the specific gravity hence palm oil biodiesel have high API gravity than that of ghee biodiesel and less than standard diesel fuel.

3.2.2. Viscosity

Viscosity is the most important property of biodiesels since it affects the operation of fuel injection equipment, particularly at low temperatures when an increase in viscosity affects the fluidity of the fuel. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors. The lower the viscosity of the biodiesel, the easier it is to pump and atomize and achieve finer droplets The conversion of triglycerides into methyl or ethyl esters through the transesterification process reduces the molecular weight to one third that of the triglyceride and reduces the viscosity by a factor of about Biodiesels have a viscosity close to that of diesel fuels. As the oil temperature increases its viscosity decreases [32]. Vegetable oils can be used as fuel for combustion engines, but their viscosity is much higher than that of common diesel fuel and requires modifications to the engines. The major problem associated with the use of pure vegetable oils as fuels for diesel engines is high fuel viscosity in the compression ignition. Therefore, vegetable oils are converted into their methyl esters (biodiesel) by transesterification. The viscosity values of vegetable oils are between 27.2 and 53.6 mm2/s, whereas those of vegetable oil methyl esters are between 3.6 and 4.6 mm2/s. The viscosity values of vegetable oil methyl esters decrease sharply following the transesterification process.

Here kinematic viscosity of Palm methyl ester and Ghee (Clarified butter) methyl ester were found to be 4.1 and 5.2 mm^2/s (cSt) respectively.

3.2.3. Flash point

Flash point of palm and Ghee methyl ester are much lower than pure vegetable oil and higher than diesel. The flash point of Palm and Ghee Biodiesel are 140^0C and 164^0C respectively, i.e; higher than conventional diesel fuel (55 ^0C). Liquid fuel with a higher flash point can prevent auto ignition and fire hazard at high temperature during transportation and storage periods. Hence, once the higher the flash point, for instance, the higher is the safety during handling, transportation, and storage.

3.2.4. Pour point and cloud point

Two important parameters for low-temperature applications of a fuel are cloud point (CP) and pour point (PP). The CP is the temperature at which wax first becomes visible when the fuel is cooled. The PP is the temperature at which the amount of wax from a solution is sufficient to gel the fuel; thus it is the lowest temperature at which the fuel can flow. Biodiesel has a higher CP and PP compared to conventional diesel.

3.2.5. Heat of Combustion

It measures the energy content in a fuel. It is an important property of Biodiesel that determines the suitability of these materials as alternative to diesel fuel. The heat of combustion (heating value) of biodiesel from Palm oil and Ghee are 40.01MJ/Kg and 37.6MJ/Kg respectively.Since, the esters were denser, the energy content of a full tank biodiesel fuel would be only 4-9% less than diesel fuel.

The esters were found to be considerably less volatile than diesel fuel. However, compression ignition (diesel) engine generate a nonfiring temperature of about 800^0C as air is compressed inside the combustion chamber [33]. Therefore compression ignition of the esters as an alternative fuel should not be a problem.

3.2.6. Acid value

The acid value is defined as the milligrams of potassium hydroxide necessary to neutralize the free acids in 1 g of sample. The ASTM standard for pure biodiesel sets the maximum acid value (acid number) at 0.8 mg KOH/g.The evaluated acid value of palm oil biodiesel and ghee biodiesel is 0.27 and 0.32,thus within the recommended range.Convntional diesel fuel possessed a very low acid value of less than o.12

3.2.6. Refractive Index

Refractive Index is the method of quick evaluation of petroleum liquid samples. The petroleum has the refractive index in between 1.38 to 1.49. The refractive index for mineral diesel is found to be 1.425. From observations, biodiesel has refractive index 1.430 and 1.431. These values indicate that heavier molecules get converted into lighter one during transesterification process.

4. Conclusion

Biodiesel is a notable alternative to the widely used petroleum-derived diesel fuel since it can be generated by domestic natural sources such as Palm oil, Ghee (Clarified Butter) and thus reduces dependence on diminishing petroleum fuel from foreign sources. A variety of biolipids can be used to produce biodiesel. With recent increases in petroleum prices and uncertainties concerning petroleum availability, there is renewed interest in vegetable oil fuels and other biolipids as source for diesel engines. Vegetable oils and fats have the potential to substitute a fraction of petroleum distillates and diesel fuel in the near future.

Transesterification is a chemical reaction between triglyceride and alcohol in the presence of catalyst. The purpose of the transesterification process is to lower the viscosity of the oil. Methanol being cheaper is the commonly used alcohol during transesterification reaction. The alkaline transesterification of vegetable oils and clarified butter by methanol has proved to be the most promising process. Also this process proved to be useful and technically feasible.

Alkaline catalysts have the advantages, e.g. short reaction time and relatively low temperature can be used with only a small amount of catalyst and with little or no darkening of color of the oil. The main advantages of biodiesel derived from the article include its domestic origin, its potential for reducing a given economy's dependency on imported petroleum. The biodiesel policy will help reducing of petroleum imports and saving of foreign exchange. The biodiesel high flash point makes it possible for its easy storage and transportation. A Biodiesel fuel as alternative to petrodiesel is technically feasible, economically competitive, environmentally acceptable, and easily available; since it is renewable, biodegradable, non-toxic, and essentially free of sulfur and aromatics; thus, Biodiesel seems to be a realistic fuel for future.

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