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Full Length Research Paper

Utilization of Cotton seed Oil for Eco-friendly Fuel

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Energy is the chief mover of economic growth, and plays a vital role in sustaining the modern economy and society. Utilization of waste is also way to help the nation by environmentally as well as economically. In this study cotton seed oil was used to produce biodiesel. Biodiesel is the name for a variety of ester based fuels (fatty ester) generally defined as monoalkyl ester made from renewable biological resources such as vegetable oils, recycled waste vegetable oil and animal fats. This renewable source is as efficient as petroleum diesel in powering unmodified diesel engine. Today's diesel engines require a clean burning, stable fuel operating under a variety of conditions. Using biodiesel not only helps maintaining our environment, it also helps in keeping the people around us healthy.

Keywords: Biodiesel; high-acid oil; saturated fatty acids; transesterification

INTRODUCTION

Biofuels are considered in part, a solution to such issues as sustainable development, energy security and a reduction of greenhouse gas emissions. Biodiesel, an environmental friendly diesel fuel similar to petro-diesel in combustion properties, has received considerable attention in the recent past worldwide. Our future economic growth considerably depends on the long-term accessibility of energy from the sources that are easily available, safe and affordable (Liaquat et al., 2010). The global economic growth has seen a dramatic increase in the energy demand of the world. Energy consumption is expected to increase by 84 percent by 2035 in most of the developing countries. Ethiopia faces a dreadful challenge in meeting its energy needs and in providing sufficient energy of preferred quality in various forms in a sustainable manner and at competitive prices (Lin and Huang,2012; Boey et al., 2012). If Ethiopia has to eradicate poverty and meet its human development goals, then it has to sustain an 8% to 10% economic growth rate, over the next 25years. For delivering a sustained growth rate of 8%, Ethiopia needs to increase its primary energy supply by 3 to 4 times. New sources of energy like biofuels may play a significant role in meeting the energy demands (Anitescu and Bruno, 2001). Biomass sources have turned out to be more effective in the recent days because of the insufficiency of conventional fossil fuels, their price hike and increased emissions of pollutants generated during combustion (Haas et al., 2001). The petroleum-based fuel reserves are concentrated in only some parts of the world and these resources are depleting day by day (Park et al., 2010 and Boer and Bahri,2011). The likelihood of producing biofuels from locally grown sources and using them as an alternative for various petrol products is one of the best attractive method to overcome the energy crisis. Any investments in biofuels will lead to a considerable boost in economic development (Haas, 2005). It is expected that with suitable production process, biofuels will produce significantly lesser greenhouse gas emissions than are produced by fossil fuels.

The diesel engine came into its existence in the year 1893 when the paper titled "The theory and construction of a rational heat engine" was published by a great German inventor Dr. Rudolph Diesel (Azocar et al., 2010). The use of vegetable oil was first started by Rudolph Diesel. He developed the first diesel engine working on peanut oil at the World's Exhibition in Paris, 1900 (Anitescu et al., 2008). The main focal points for biodiesel production to expand were the oil seed crops. Until 1920s vegetable oils were utilized as the source of energy in the diesel engine. The factors like profitability, availability, low sulfur content, low aromatic content, biodegradability and renewability makes vegetable oils

Table 1. Fatty acid composition of sunflower oil

S.No	Fatty Acid	Content (%)
1	Palmitic (16:0)	6.08
2	Stearic (18:0)	3.26
3	Oleic (18:1)	16.93
4	Linoleic (18:2)	71.73
5	Linolenic (18:3)	0.56

more advantageous over diesel fuel (Bunyakiat et al., 2006). At present higher market values for challenging uses restricted the utilization of crops for biodiesel production. Biodiesel refers to a processed fuel resulting from the biological sources and it is equivalent to petro-diese (Operational Manual for the Supercritical-Methanol Reacting System, 2006). Biodiesel acts as a safe alternative fuel for substituting traditional petroleum diesel. It is a clean burning fuel with high lubricity. Biodiesel produced from renewable sources acts like petroleum diesel but produces significantly less air pollution. It is bio-degradable and very safe for the environment. Biodiesel production can be achieved in different methods. Biodiesel is a mono alkyl ester of fatty acids produced from both edible and non edible vegetable oils or animal fat and various other bio fuels such as methanol, ethanol etc. (Operational Instruction Manual for the 1266 Isoperibol Bomb Calorimeter, 1988 and Pulkrabek, 2004).

In recent times biodiesel has been produced from sources like vegetable oils, animal fats, soap stock and also recycled frying oils. In order to know which vegetable oil is best suited for the production of biodiesel, certain factors like geography, climate, and economics must be considered (Lin and Chiu, 2010). Vegetable oils are considered as the renewable forms of fuel and they are more attractive in environmental benefits as they are made from renewable resources. Vegetable oil potentially forms the unlimited source of energy; with an energy content equivalent to that of diesel fuel (Hoekman et al., 2012). Direct use of vegetable oil in diesel engines gives rise to many problems such as jamming and gumming of filters, lines and injectors; engine knocking; starting problem during cold weather; coking of injectors on piston and head of engine; extreme engine Wear; carbon deposition on piston and head of engine (Demirbas, 2008). Vegetable oils are of high viscosity and in order to reduce their viscosity and to overcome their problems to enable their use in many diesel engines, a process called transesterification must be carried out. The product so formed after transesterification is called as biodiesel. Biodiesel has relatively higher heating values. Biodiesel is 100% pure and hence it is referred as “neat fuel” or “B100”. The high heating values (HHV’s) of biodiesel ranges from 39 to 41MJ/kg. Biodiesel can be utilized by blending with petrol diesel and those blends are referred as BXX where XX represents the amount of biodiesel in the blend. Pure biodiesel can be denoted as B100 (Focke et al., 2012).

Biodiesel production can be achieved using waste vegetable oils due to their low cost. They are collected from large food processing units and service facilities. They include several chemical reactions such as hydrolysis, polymerization and oxidation during food frying process, which leads to increased efficiency of fatty acids. In this regard’s an effort has been made to produce the low-cost ecofriendly and high efficiency biodiesel by Cotton seed oil. The effect of temperature, catalysis loading reaction time and methanol oil ratio was also studied

MATERIALS AND METHODS

Material

Cotton seed oils were collected from local area and were used as feedstocks. Prior to transesterification, the waste food oil samples were dried over calcium chloride ($CaCl_2$) and filtered through a cellulose filter to remove any suspended matter and $CaCl_2$ crystals. Chromatographic grade methanol (99.5 %), phosphoric acid, potassium hydroxide, sodium hydroxide, anhydrous sodium sulfate and calcium chloride were supplied by Lachema. (China), silica gel from Fluka (Buchs, Netherland), while the reference standard for the gas chromatographic determination of fatty acid methyl esters was obtained from Supelco (Bellefonte, USA). The fatty acid compositions of sunflower oil are shown in Table.1.

Transesterification procedure

Biodiesel produced through the process known as transesterification. The reaction involved for the production is shown in Figure 1.

Methyl esters (biodiesel) were synthesized in a batch type reactor using alkali catalysts. The ester preparation involved a two-step transesterification followed by purification and drying. The amount of Cotton seedoil used in the reaction was 200 g, which was placed in a dry two necked flask equipped with a thermometer and a reflux condenser. Dryness was absolutely necessary as water in the reactor would consume some of the

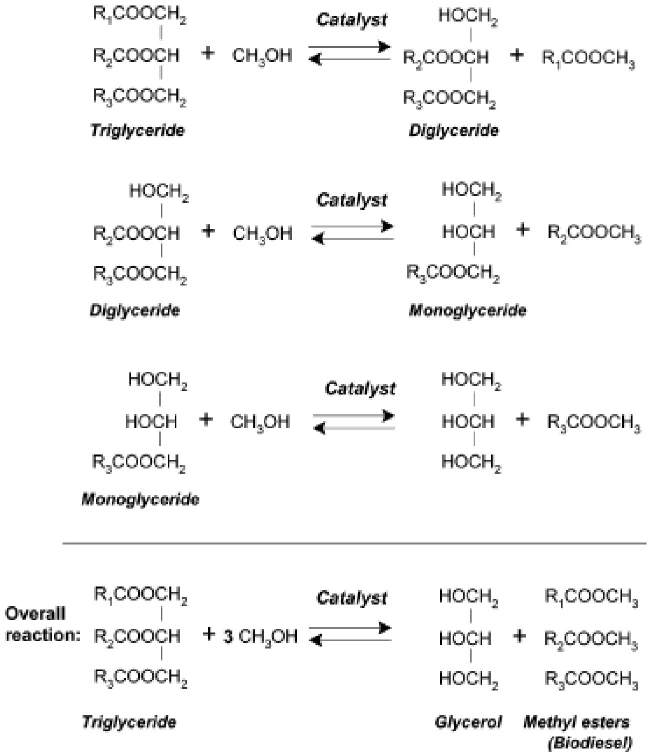

Figure 1. Reaction occur in Transesterification

catalyst, thereby slowing the reaction. The methanol and catalyst were added into the flask in the quantities to obtain the desired ratios relative to the oil. Namely, the study was realized using a mole ratio of methanol to Cotton seedoil of 6:1 and of 9:1, whereas the catalyst (either NaOH or KOH) was added in quantities equivalent to 1 and 1.5 mass % of Cotton seedoil. In the first step, the mixture was stirred for 30 min at 30 °C and 400 rpm, and then it was poured into a separation funnel. After one hour separation, glycerol was removed from the bottom of the flask, while the top esters layer was transferred into second two-necked flask, heated to 60 °C and mixed with a second methanol/ catalyst solution. After stirring the mixture for 30 min at 400 rpm, it was poured into a separation funnel and allowed to separate for 12 h. The glycerol was removed by gravity settling and the methanol was removed from the thus-obtained crude esters layer by rotary evaporation at 65 °C and 20 kPa. The obtained crude methyl esters were weighed and further purified by passing them through a bed of silica gel with a top layer of anhydrous sodium sulfate in order to remove the remaining salts and glycerol, as it was shown previously that high yields could be obtained in this manner from acidic feedstocks. The obtained dried methyl esters were then bottled and kept for characterization studies. The systematic flow diagram for the biodiesel production is shown in Figure 2.

Characterization of feed stocks and methyl esters

The feedstock WFO was characterized after drying and filtering (i.e., prior to transesterification) in a series of tests. Furthermore, the physical and chemical properties of the methyl esters (ME) obtained by two-step alkali transesterification after purification on silica gel were determined by the methods listed in the JUS EN 14214:2004 standard.8 This standard is equivalent to EN 14214: 2004 and defines the requirements and test methods for fatty acid methyl esters (FAME) to be used in diesel engines. Even though it is not required by JUS EN 14214:2004, the saponification value (Sv) was also determined using the titration method described in ISO 3657:2002. The iodine value (Iv) and Sv were also calculated based on the fatty acid (methyl ester) composition determined by gas chromatography (Arisoy, 2008). In this way, an attempt was made to see if the calculated values could predict satisfactorily these two properties and be alternatively employed instead of the corresponding experimental procedures for their determination. A method for an estimation of the cetane

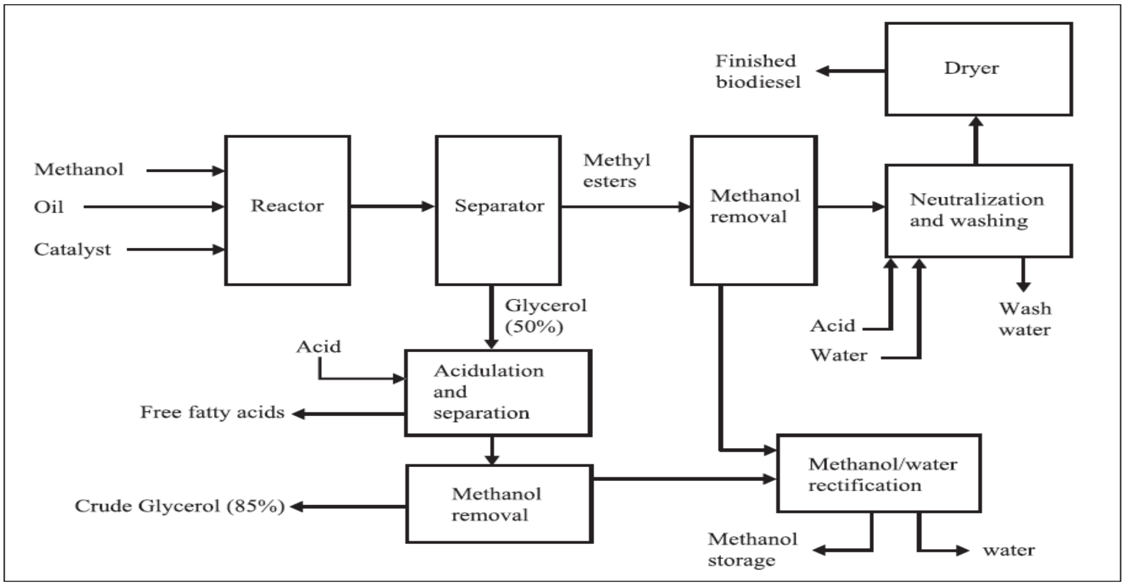

Figure 2. Flow diagram for the production of biodiesel

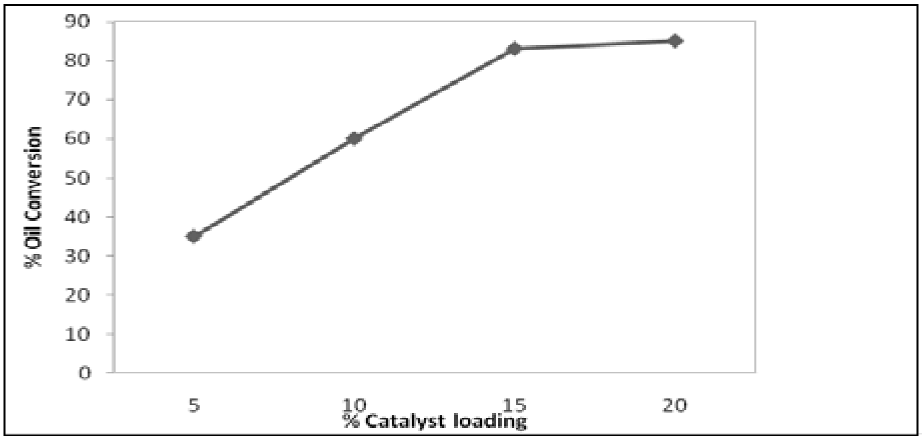

Figure 3. Effect of catalysis loading on oil conversion under condition

index (CI) based on Sv and Iv was previously described, (Aktas et al., 2010) as a simpler and more convenient method than the experimental procedure, for the determination of the cetane number utilizing a cetane engine (EN ISO 5165:1998). In this work, the experimentally obtained values of *Sv* and *Iv* were used for calculating *CI*. However, the proposed equation for *CI* is not recommended for feedstock characterization as it has been previously documented that the cetane indexes of oils are generally much lower than those of methyl ester derivates, despite the fact that they have similar *Sv* and *Iv* values (Lapuerta et al., 2009).

RESULTS AND DISCUSSION

Effect of catalysis loading

The effect of the amount of catalyst used in the conversion of the triglyceride to methyl esters was studied as the % loading of catalyst with respect to oil was varied from 5 to 20% wt /wt keeping all other reaction parameters identical. As shown in Fig. 3, it was observed that the oil conversion increased with an increase in catalyst loading. The highest conversion of 87.45% was obtained at a catalyst loading of 20% wt/wt which was comparative with the conversion value of 86.56% at 15%wt/wt. From the view-point of the reaction kinetics, a larger amount of catalyst leads to a higher yield of methyl esters in a shorter reaction time, however here we can say that this is sufficient from the viewpoint of economics. As a consequence, the optimal amount of catalyst used in this pilot was 15wt % loading as it was sufficient in catalyzing the reaction despite the challenge posed by the three phase reaction system where initial mass transfer control is inhibited due to heterogeneous kinetics. This is because of the fact that the solid catalyzed process is an immiscible liquid/liquid/solid 3-phase system (corresponding to oil, methanol and catalyst) that is highly mass transfer limited (Lin and Li, 2009) in figure 3.

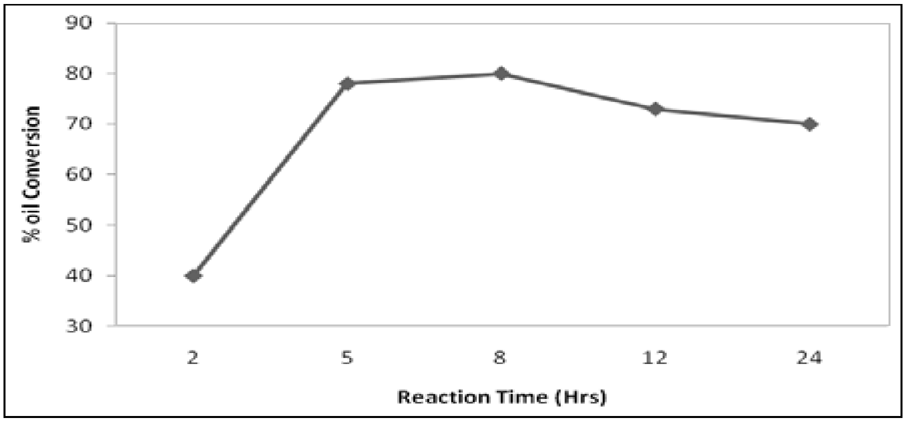

Figure 4. Effect of reaction time on oil conversion under condition

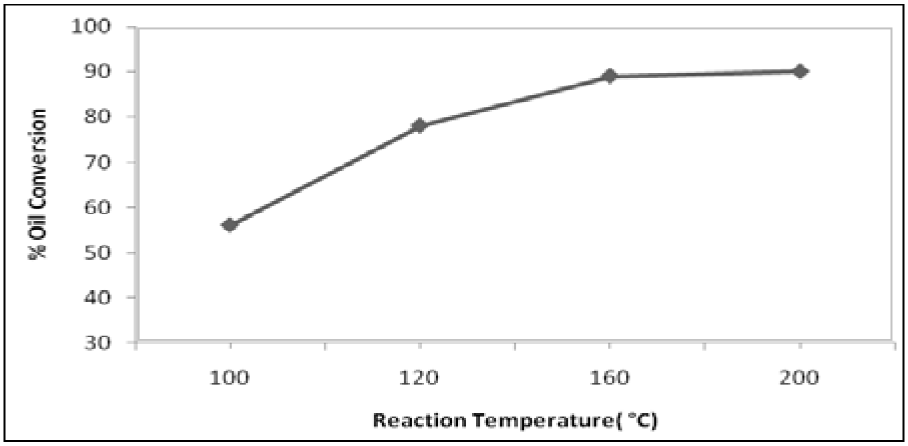

Figure 5. Effect of reaction temperature on oil conversion under condition

Effect of reaction time

In order to study the influence of the reaction time on the oil conversion using the KNO3/flyash catalyst, a set of experiments were carried out at 2, 5, 8, 12 and 24 hours. The results are shown in Figure 4. It can be observed that the oil conversion was not greatly affected by an increase in the reaction time. This implied that, the reaction equilibrium had been reached after 5hrs when the reaction temperature was 160ºC. A study by Kotwal et al. (2009) showed that reaction times higher than 8 hrs had a negative impact on the oil conversion.

Effect of reaction temperature

Transesterification can occur at different temperatures depending on the oil used and temperature is a crucial parameter as it influences the reaction rate and yield of the methyl esters and in order to determine the effect of reaction temperature on the oil conversion, experiments were conducted at 100, 120, 160, and 200°C. The results are shown in Figure 5 and from the activity profile, it was observed that as reaction temperature increased, there was a corresponding increase in the conversion of the triglycerides to methyl esters, showing peaks at temperatures ≥ 160°C. The highest conversion was 89.34% at a reaction temperature of 200°C which compares to the conversion value of 87.12% at the reaction temperature of 160°C. Artkla et al. (2008) carried out the transesterification of palm oil with methanol at 60, 120 and 150ºC in the presence of K2O loaded on MCM-41 synthesized from rice husk. The performance depended on the K2O loading and temperature with the highest conversion observed on 8% K2O/RH-MCM-41 at 100 °C. However reports by Ramos et al. (2008) showed that a methyl ester content of 95.1 wt% was obtained at 60ºC by transesterification of sunflower oil over zeolites as catalyst using different metal loading.

Effect of methanol and oil ratio

One of the most important factors that affect the yield of ester is the molar ratio of alcohol to triglyceride. It is of important for screening catalyst performance. Although the stoichiometric molar ratio of methanol to triglyceride for transesterification is (Figure 1), higher molar ratios are used to enhance the solubility and to increase the

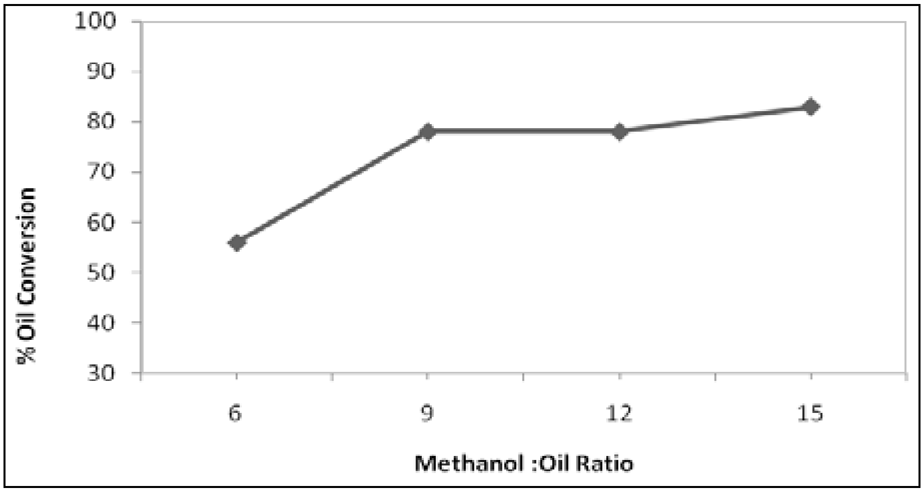

Figure 6. Effect of methanol and oil ration on oil conversion under condition

Table 2: Comparatively result biodiesel with ASTM

S.No	Biodiesel properties	Measured values	ASTM Standard
1	Density at 20^{o}C (kg/m^{3})	839-843	875-900
2	Kinematic viscosity 40^{o}C (mm^{2}/s)	2.90 -4.50	1.9-6.0
3	Flash point (^{o}C)	132 – 150	≥130
4	Acid value (mgKOH/g)	0.68 -0.89	≤0.8
5	Saponification value (mgKOH/g)	115.5-124.5	-
6	Moisture content % (w/w)	0.011 -0.019	< 0.03
7	Ash content% (w/w)	0.019 -0.029	< 0.02
8	Iodine value (I_2g/100g)	-	<120
9	Cetane number	-	>47

contact between the triglyceride and alcohol molecules. Specifically, it has also been proven that that the use of excess alcohol is a good option in improving the rate of the transesterification reaction where heterogeneous catalysts are considered (Knothe, 2005). The effect of the molar ratio was of methanol to oil on the conversion of the methyl ester was examined by varying the amount of methanol with a fixed amount of sunflower oil (20g) in the reactions at 160°C. The initial amounts of methanol were set and amounts corresponding to the methanol: oil molar ratios of 6:1, 9:1, 12:1, 15:1 were used. The result is illustrated in Figure 6.

From the Figure, it can be seen that the highest methyl ester conversion of 86.1% was observed at a methanol: oil molar ratio of 15:1. It can be also be observed from the activity profile that as the molar ratio increased from 6:1 to 15:1, the conversion was found to increase from 56.23 to 86.1%. Further addition of methanol into the reaction phase did not show any significant increase in the conversion. Moreover, a limitation to the use of a greater amount of methanol needed to propel the forward reaction is that an occurrence of flooding of the active sites by the methanol molecules rather than triglyceride molecules which might hinder the completion of the triglyceride conversion to methyl esters as conversion at methanol oil ratios higher than 15 appeared to decline (Ramadhas et al., 2006). Also, feeding too much alcohol adversely affects the transesterification process by rendering the product separation difficult as glycerol; co-product specie of methyl ester is highly soluble in methanol, which reverses the transesterification progress according to Le Chatelier’s principle. Another important variable affecting the yield of methyl ester is the type of alcohol to triglyceride. In general, short chain alcohols such as methanol, ethanol, propanol, and butanol can be used in the transesterification reaction to obtain high methyl ester yields.

Physicochemical parameter of biodiesel

The calculated quality parameters are summarized in Table 2, and compared with the ASTM standards value. Acid value of the biodiesel varied from 0.68mgKOH/g to 0.89mgKOH/g. The acid value is used to determine the amount of free fatty acid content in biodiesel. The lower acid value indicates that the quantity of free fatty acid in the biodiesel is also lower. Saponification value of the biodiesel was from 100.1mgKOH/g to 111.5 mgKOH/g. Saponification value shows the amount of biodiesel that changes to soap by KOH in the at high temperature in presence of water. Lower saponification value of the result is higher in quality of the product. Thus, the residual soap is about 1.6%, and the waste water was taken at the first to get the maximum amount of waste in terms of soap during glycerol separation when biodiesel was being washed. Density of the biodiesel was from 839kg/m3 to 843kg/m3. Kinematic viscosity of biodiesel was from 2.90mm2/s to 4.5mm2/s. Thus, transesterification reaction reduced density and kinematic viscosity. Flash point of the biodiesel was between 132oC to 150oC. Flash point shows the first temperature where biodiesel is going up in to flames. From Table 2, high flash point values of the biodiesel were observed. Therefore, the flash point of the biodiesel is good for handling, storage or transportation. Moisture content was determined to be from 0.011% (w/w) to 0.019% (w/w) in the biodiesel. If there is high moisture content in the biodiesel, it causes further oxidation due to microbial growth during storage which reduces the shelf life and the product quality. The source of moisture in the biodiesel is highly related to wash water although there are other sources, such as poor drying (Georgogianni et al., 2009). Thus, the moisture content was obtained in the biodiesel was very small in amount as the biodiesel was dried in an oven for longer period of time at 105oC. The ash content of biodiesel was from 0.019% (w/w) to 0.029% (w/w). If high ash content is present, it shows that the biodiesel has solid materials that are resulted from catalysts during transesterification reaction or seed cake during oil extraction process. But the feed oil was refined and the biodiesel was washed with warm water and distilled water, with better mixing, low ash content was gained. Properties of biodiesel were under standard specification of ASTM. Iodine value and cetane number were not done due to lack of reagent chemicals and equipment. The lower density fuel burns quickly and consumed immediately while higher density fuel burns for longer time. The lower flash point fuel is more favor for spontaneous ignition while it is transported or stored for longer time. However higher flash point fuel resists such problems.

CONCLUSION

Fossils fuels are non renewable forms of energy resources and they are depleting day by day so the production of biofuels such as biodiesel is increasing rapidly. Biofuels like biodiesel are renewable, eco-friendly and non-toxic energy resources. Biodiesel is similar to petroleum diesel in its properties but biodiesel emits very less amount of CO_2, sulfur and particulates compared to petroleum diesel. It can be produced by a simple transesterification process using acid or base catalyst or enzymes as catalyst. From the experiment it was found that oil conversion increases with increased catalyst loading. The highest conversion of oil was obtained at a catalyst loading of 20%wt/wt. Influence of process parameters such as reaction time, reaction temperature and molar ratio of methanol to oil were also carried out. The oil conversion was not greatly affected by an increase in the reaction time. However, reaction time between 5 to 8 hours will lead to better oil conversion. The highest conversion was observed at a temperature of 200^{o}C. The activity profile shows that increase in the methanol to oil ratio from 6:1 to 15:1 resulted in increased conversion from 52.23% to 86.1%. A decline in the oil conversion was observed when the recovered catalyst was recycled for use. It is concluded that the biodiesel is one of the cheap and ecofriendly source for energy.

REFERENCE

Liaquat AM, Kalam MA, Masjuki HH, Jayed MH (2010). Potential emission reduction in road transport sector using biofuel in developing countries. Atmos. Environ. 44, 3869–3877.

Lin CY, Huang TH (2012). Cost–benefit evaluation of using biodiesel as an alternative fuel for fishing boats in Taiwan. Mar. Policy 2012, 36, 103–107.

Boey PL, Ganesan S, Maniam GP, Khairuddean M, Lim SL (2012). A new catalyst system in transesterification of palm olein: Tolerance of water and free fatty acids. Energy Convers. Manag. 56, 46–52.

Anitescu G, Bruno TJ (2001).Fluid properties needed in supercritical transesterification of triglyceride feedstocks to biodiesel fuels for efficient and clean combustion—A review. J. Supercrit. Fluids , 63, 133–149.

Haas MJ, Scott KM, Alleman TL, McCormick RL (2001). Engine performance of biodiesel fuel prepared from soybean soapstock: A high quality renewable fuel produced from a waste feedstock. Energy Fuels , 15, 1207–1212.

Park JY, Wang ZM, Kim DK, Lee JS (2010). Effects of water on the esterification of free fatty acids by acid catalysts. Renew. Energy , 35, 614–618.

Boer K, Bahri PA (2011). Supercritical methanol for fatty acid methyl ester production: A review. Biomass Bioenergy , 35, 983–991.

Haas M (2005). Improving the economics of biodiesel production through the use of low value lipids as feedstocks: Vegetable oil soapstock. Fuel Process. Technol., 86, 1087–1096.

Azocar L, Ciudad G, Heipieper HJ, Navia R (2010). Biotechnological processes for biodiesel production using alternative oils. Appl. Microbiol. Biotechnol. 88, 621–636.

Anitescu G, Deshpande A, Tavlarides LL (2008). Integrated technology for supercritical biodiesel production and power cogeneration. Energy Fuels 22, 1391–1399.

Bunyakiat K, Makmee S, Sawangkeaw R, Ngamprasertsith S (2006). Continuous production of biodiesel via transesterification from vegetable oils in supercritical methanol. Energy Fuels, 20, 812–817.

Operational Manual for the Supercritical-Methanol Reacting System; Jeoou Rong Industrial Corp.: Taipei, Taiwan, 2006.

Operational Instruction Manual for the 1266 Isoperibol Bomb Calorimeter; Parr Instrument Company: Moline, IL, USA, 1988.

Pulkrabek WW (2004). Thermochemistry and Fuels. In Engineering Fundamentals of the Internal Combustion Engine, 2nd ed, Pearson Prentice-Hall Inc.: Singapore, ; pp. 168–169.

Lin CY, Chiu CC (2010). Characteristics of palm-oil biodiesel under long-term storage conditions. Energy Convers Manag. 51, 1464–1467.

Hoekman SK, Broch A, Robbins C, Ceniceros E, Natarajan M (2012). Review of biodiesel composition, properties, and specifications. Renew. Sust. Energy Rev. 16, 143–169.

Demirbas A (2008). Studies on cottonseed oil biodiesel prepared in non-catalytic SCF conditions. Bioresour. Technol. 99, 1125–1130.

Focke WW, Westhuizen I, Grobler, ABL, Nshoane KT, Reddy JK, Luyt AS (2012). The effect of synthetic antioxidants on the oxidative stability of biodiesel. Fuel, 94, 227–233.

Arisoy K (2008). Oxidative and thermal instability of biodiesel. Energy Source, 30 1516–1522.

Aktas DF, Lee JS, Little BJ, Ray RI, Davidova IA, Lyles CN, Suflita JM (2010). Anaerobic metabolism of biodiesel and its impact on metal corrosion. Energy Fuels, 24, 2924–2928.

Lapuerta M, Rodrıguez-Fernandez J, Fermın Oliva F, Canoira L (2009). Biodiesel from low-grade animal fats: diesel engine performance and Emissions. Energy Fuels, 23, 121–129.

Lin CY, Li RJ (2009). Fuel properties of biodiesel produced from the crude fish oil from the soapstock of marine fish. Fuel Process. Technol. 90, 130–136.

Kotwal MS, Niphadkar PS, Deshpande SS, Bokade VV, Joshi PN (2009). Transesterification of sunflower oil catalyzed by fly ash-based solid catalysts. Fuel:88:1773–78.

Artkla S, Grisdanurak N, Neramittagapong S, Wittayakun J (2008). Characterization and catalytic performance on transesterification of palm olein of potassium oxide supported on RH-MCM-41 from rice husk silica. Suranaree J. Sci. Technol; 15(2):133-38.

Ramos MJ, Casas A, Rodriguez L, Romero R, Perez A (2008). Transesterification of sunflower oil over zeolites using different metal loading: A case of leaching and agglomeration studies. Applied Catalysis A: General; 346 (1-2):79-85.

Knothe G (2005). Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. Fuel Process. Technol. 86, 1056–1070.

Ramadhas AS, Jayaraj S, Muraleedharan C, Padmakumari K (2006). Artificial neural networks used for the prediction of the cetane number of biodiesel. Renew. Energy, 31, 2524–2533.

Georgogianni KG, Katsoulidis AP, Pomonis PJ, Kontominas MG (2009). Transesterification of soybean frying oil to biodiesel using heterogeneous catalysts. Fuel Processing Technology; 90:671–76.