Two Step Process for Biodiesel Production from Ethiopian Energy Source of Coffee Spent Ground Waste

Ramachandran Kasirajan*, Wondwosen Sime

Abstract— Utilize the coffee spent ground (CSG) as a raw source for biodiesel production by the way of two steps: esterification and followed by transesterification reaction procedure. The achievability of lipids were extracted and characterized by Soxhlet solvent extraction and gas chromatography, respectively. Biodiesel production from CSG using H_2SO_4 pre-treatment (Esterification) were performed and alkali catalyst transesterification investigational condition such as reaction temperature, methanol-oil molar ratio, catalyst loading, reaction time and mixing intensity were studied. The premier conversion of CSG lipid to biodiesel was achieved as 98.6 wt% at the favorable circumstances of 65 $^{\circ}$C, 1 wt% of KOH and 1:9 molar ratio of oil and methanol, 400 rpm of mixing intensity with 50 min of reaction time. The conversion and methyl ester properties were confirmed by Nuclear magnetic resonance (^{1}H-NMR) and ASTM standards, respectively.

Index Terms— Biodiesel; Esterification; Transesterification; Coffee spent ground; Energy source.

————————————— ◆ —————————————

1 INTRODUCTION

Energy is an essential basis mainly for transport, industries and farming sectors. Right now, the petroleum energy utilization has been superior constantly, which speed up the reduction of limited petroleum deliver and unavoidably increase the petroleum prices [1, 2]. It is awfully important to find substitute energy, predominantly the fuel for transport diesel engines, in direct to enlarge the petroleum supply. Currently, renewable and sustainable fuel has acknowledged great concern as an alternate for current fossil fuels. Around 90% of the bio-fuel market is cramped by bio-ethanol and bio-diesel [3, 4].

A potential diesel oil substitute is fatty acid methyl ester (biodiesel). Biodiesel have been used in a straight line or blended with diesel oil at various scale in many countries [5]. It is resultant from a renewable and domestic resource, in this manner relieving dependence on petroleum imports. Weigh against to petroleum fossil diesel oil, biodiesel has a most favorable incineration emission outline such as less emission of unburned hydrocarbons, SO_2, CO, and particulate matters [6-8].

The energy scheme in Ethiopia is illustrated by the predominance of conservative fuels (firewood, crop residues, and animal waste or dung *etc.*) which report nearly 94% of the total public energy consumption. The requirement for modern energy supply such as petroleum fuels is increasing with augment in population and financial growth. Even though the share of petroleum fuels is about 7% of the total utilization, the increasing claim for it and the associated price augment have hit the national financial system very hard. As a grid importer of petroleum, Ethiopia is highly defenseless to price upset and supply harms of oil in the world market. This is the foundation for the government to incorporate large-scale commercial production of bio-fuels as part of the series of other improvement programs such as wind, biogas, associated liquids, solar energy, hydro-power and natural gas proposed to ensure supply of modern energy services [9].

Ethiopian Ministry of Mines and Energy (EMME) has prepared guiding principle for the accomplishment of projects to ensure the success of the objectives stated, while at the same time avoiding unintentional consequences. The policy has addressed bio-fuel enlargement and use that are imperative elements to ensure social and environmental sustainability. EMME is cheering investors who are engaged in bio-fuel production. Currently, over 68 developers engaged in the cultivation of energy crops of Castor bean, Palm oil and Jatropha for biodiesel production, in which 15 of them were developing Jatropha farm in the country. Even if such performance started, the production of biodiesel is not that much evident.

There are numerous sources presented for biodiesel production such as, used restaurant oil residues, industrial residues, waste greases, waste animal fats, and agricultural wastes [10, 11]. But, the coffee spent ground were having more than 20 wt % of lipids. Ethiopia is one of coffee bean producing fatherland in the world and exporting half of it. And the remains

———————————————————

- *Corresponding Author: Dr. Ramachandran Ksairajan is currently working as Assistant Professor in the school of Chemical engineering in Jimma University Institute of Technology, Ethiopia,.
  E-mail: ramactech@gmail.com*

- *Wondwosen sime is currently working as Lecturer in the school of Chemical engineering in Jimma University Institute of Technology, Ethiopia,.
  E-mail: wondeto@gmail.com*

used for coffee drink. After using, that the slurry of CSG will disposed to land fill. Therefore, rather than dispose or dump, it is better to use for biodiesel production as a feedstock.

In this study, we appraised the potential of the CSG source used for biodiesel production and optimized some of key variables distressing the alteration of acid- base catalyzed production of biodiesel such as the reaction time, temperature, molar ratio of oil and methanol, catalyst quantity and stirring rate. We also analyzed the most important fatty acid components of the CSG oil and assessed the fuel properties of the resultant biodiesel with the ASTM standard.

2 MATERIALS AND METHOD

2.1 Materials

The coffee spent ground has been collected in Jimma, Oromia regional state in Ethiopia. The sulphuric acid (98%) has been acquired from Merck. Methanol with 99.9 % of purity, Hexane with 99% of purity was purchased from SRL Chemical.

2.2 Lipid extraction process and characterization

The CSG was utilized as a raw source in this research. Primarily, CSG was dehydrated in a hot air oven at a stable temperature of 50 °C over night to achieve constancy of weight loss. Then the dehydrated CSG (25 gm of biomass) loaded in to the Soxhlet extraction equipment with n-hexane was utilize as a extraction solvent for 16 hours at solvent reflux temperature [12]. After the completion of extraction practice, n-hexane was separated using batch distillation and the traces amount of solvent has been removed by rotary vacuum evaporator. Finally, the obtained lipid content was measured as 21.3 wt%. The properties of CSG such as density, acid value, average molecular weight, iodine value, saponification value and free fatty acid content of extracted CSG lipid were analyzed by using standard procedures [13]. The fatty acid composition present in *CSG* lipid was analyzed by gas chromatography (GC) analysis. One gram of CSG lipid was taken and fatty acid composition analysis was carry out by gas chromatograph, which consisted of the column BPX-70 with CHEMIT GC 8610 flame ionization sensor. Nitrogen and Hydrogen gas were used as carrier gas and oxygen was used for detonation intention. The information was self-possessed with the use of Winchrom software [14].

2.3 Two Steps: Esterification & transesterification reaction procedure and Biodiesel characterization

The The primary step, only concentrated sulphuric catalyst (2 wt %) was used for pre-treatment (acid esterification) in the reactor to convert the free fatty acids present in the CSG oil into methyl ester. In this stage, required quantity of sulphuric acid (with respect to oil wt %) and 1:12 of oil to methanol molar ratio were used to study their influence on reduction of the free fatty acids of CSG oil. The three-neck round bottom flask reactor was connected with a water-cooled reflux condenser and filled with 25 gm of CSG oil and appropriate molar ratio of concentrated sulphuric acid and methanol. The reaction mixture was actively stimulated at 500 rpm and refluxed up to

the required reaction time. After the reaction completion, the excess reactant of methanol was separated from the liquid phase using rotary vacuum evaporation [15, 16].

At the second stage, potassium hydroxide catalyst was used for the reason that this base catalyst had a superior catalytic activity for the transesterification reactions. The pre-treated CSG by sulphuric acid esterification was considered as a feed stock material for transesterification process. The suitable process conditions such as molar ratio of oil to methanol, temperature, Catalyst loading, reaction time and mixing intensity for transesterification reaction were maintained. All reaction studies were performed in 250 mL of batch reactor with reflux condenser. After the completion of reaction, the mixture was allowed to settling overnight to separate the by-product of glycerol then the traces amount of methanol was removed by rotary vacuum evaporation [17].

The produced biodiesel from CSG oil was characterized by ^{1}H-NMR. ^{1}H-NMR spectra were obtained using a Bruker 500 MHz Avance III tool with the tetramethylsilane (TMS) as an internal standard and Chloroform-d (CDCl$_3$) as solvent. A ^{1}H spectrum was documented with pulse duration of 45 °C and 16 scan. The conversion of CSG oil to biodiesel was calculated using simple formula (Eq. 1).

$$PC = (2A_{ME})/(3A_{CH2}) \times 100 \qquad wt.\% \qquad (1)$$

Where PC - the percentage conversion of CSG oil to methyl ester, A_{ME} - an integration value of the methoxy protons of the methyl ester, A_{CH2} - an integration value of the methylene protons. Factors 2 and 3 were predicted from the fact, that the methylene carbon possesses 2 protons, while the methyl alcohol (alcohol derived) carbon has 3 attached protons. The properties such as density, flash point, fire point, viscosity, cetane number, moisture content, sulphur content and etc... of biodiesel were analyzed according to the ASTM standard [18, 19].

3 RESULT AND DISCUSTION

3.1 Characterization of CSG oil and Biodiesel

The Table 1 expresses the properties of CSG oil that were used in this study. Based on the GC results, the free fatty acid content of the CSG oil was determined as 6.7wt.% and the average molecular weight was predicted as 885.5. Fatty acids content of CSG oil are very important in identify the carbon chains and its properties. The results showed that the highest fatty acids were in the order of linoleic, palmitic, oleic and stearic. Additional minor acids present in the CSG extracts are lauric, myristic, alpha-linoleic and arachidic.

Figure 1 shows that the ^{1}H-NMR spectra of CSG biodiesel. The superiority signal formed from the protons of methylene group closest to the ester group of a molecule in TG (a-CH$_2$) was eluted at 2.3 ppm and the protons in the methoxy group of the methyl ester were identified at 3.66 ppm. The conversion of methyl ester was accomplished based on these attribute proton signals in the ^{1}H-NMR spectra. The conversion of the methyl ester from coffee spent ground oil was de-

termined as 98.6 wt%. The other properties of density, flash point, kinematic viscosity, cloud point, cetane number and etc were listed in Table 2.

Table 1. Properties of Coffee spent ground (CSG) oil.

Properties	Values	Units
Average molecular weight of CSG oil	885.5	g/mol
Density @15°C	0.90	g/cc
Acid value	13.4	mg KOH/g
Saponification value	185.6	mg KOH/g
Free fatty acids	6.7	wt%
Kinematic viscosity@40°C	46.95	mm²/sec.
Gross calorific value	39.6	MJ/kg
Iodine value	82	gI$_2$/100g
Fatty acids	**Carbon atoms**	**Relative %**
alpha-linolenic acid	C18:3	0.32
Arachidic acid	C20:0	0.28
Lauric acid	C12:0	3.23
Linoleic acid	C18:2	34.91
Myristic acid	C14:0	0.72
Oleic acid	C18:1	18.93
Palmitic acid	C16:0	30.31
Stearic acid	C18:0	11.26
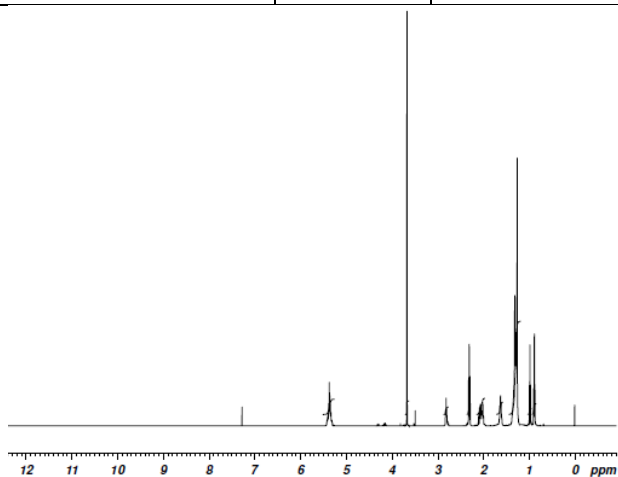
Fig. 1. CSG Biodiesel: ¹H-NMR spectra.

Table 2. Comparison of CSG biodiesel with ASTM standards.

Content	GST Biodiesel	ASTM D 6751
Acid value (mgKOH/g)	0.3	0.8
Carbon residue (wt.%)	0.015	0.05% max.
Cetane number	57	47 min
Cloud point (^{o}C)	2	N/A
Copper strip corrosion	1	No. 3 max.
Density @ 15 ^{o}C (g/cc)	0.83	0.82-0.9
Flash point (^{o}C)	156	>130 min.
Kinematic viscosity @40 ^{o}C (mm²/s)	3.8	1.9–6.0
Pour point (^{o}C)	-3	N/A
Sulphated ash (wt.%)	0.006	0.02% max.
Total glycerine content (wt.%)	<0.05	0.24% max.
Water content (vol.%)	0.003	0.05% max.

3.2 Reaction Studies

3.2.1 Effect of acid catalyst pre-treatment

CSG oil contains 6.7 percent of free fatty acids. It was originate that the pre-treatment step significantly reduced the acid value from 13.4 to below 1 mg KOH g^{-1}. The effect of acid value on reaction time is shown in Fig. 2(a). The investigational results recommended that the acid catalysis pre-treatment (esterification) take place in three phases i.e. fast, slow and stationary. In the fast phase, the reaction rate was fast for which the acid value reduced from 13.4 to 3 in 20 min and the dropdown of acid value was 77.6%. After 20 min the reaction rate slow down up to 30 min, the dropdown of acid value was 96.27%. In the stationary phase the esterification reached equilibrium after 30 min. The acid value was observed less than 1 mg KOH g^{-1} at 30 min, but it was attractive to keep a longer reaction time of 35 min to get a lower target of 0.5 mg KOH g^{-1}.

3.2.2 Effect of catalyst on alkali catalyst transesterification reaction

In Accordance with the results shown in Fig. 2(b), the CSG conversion to biodiesel was low for the catalyst quantity of 0.25–0.75%. This is due to the inadequate quantity of potassium hydroxide. It is examined that 1 wt. percentage of potassium hydroxide is optimal enough to get higher conversion of 79 wt.%. The excess quantities of catalyst addition were resultant in the soap generation, which decreases the yield by giving rise to emulsification of biodiesel and glycerol phase. Generally, from the journalism it was examined that alkali catalyst quantity of less than or equal to 1wt.% is necessary for a victorious conversion of oils and fats to methyl esters depending on the type of oil used as a feed for biodiesel production [20].
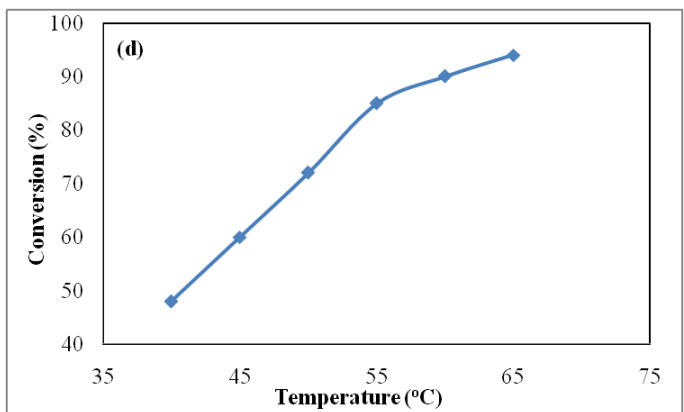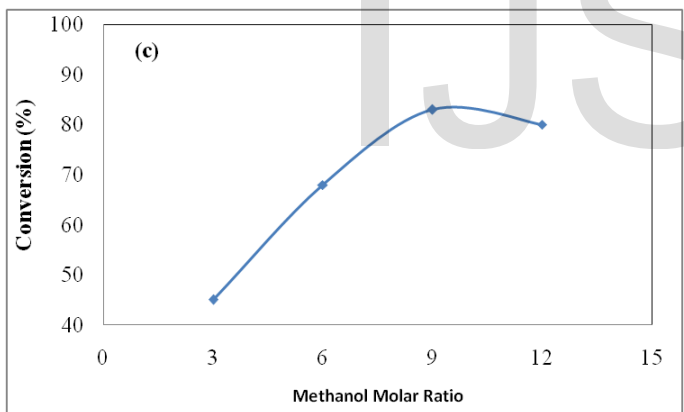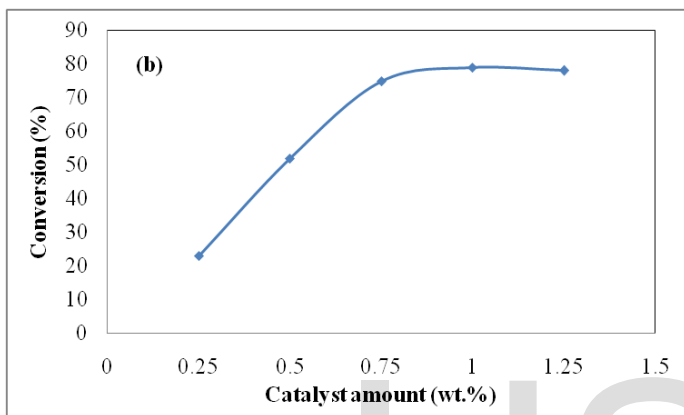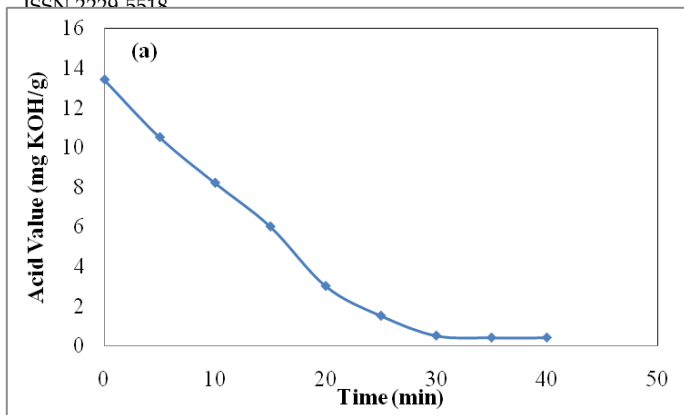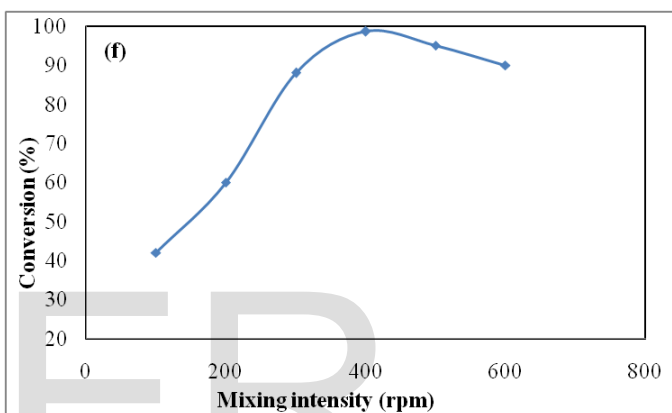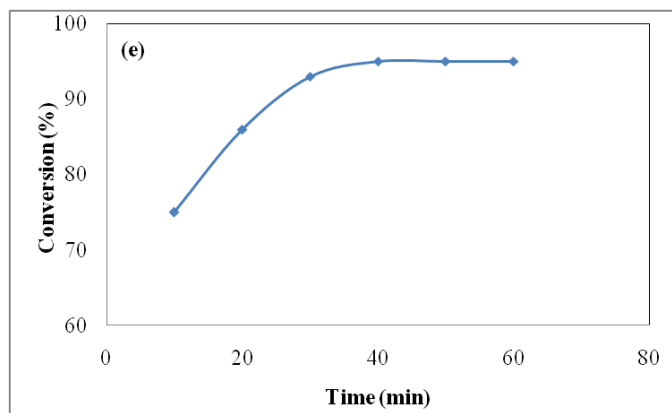
Fig. 2. Reaction studies: **(a)** effect of acid catalyst pre-treatment

@ 55ºC, 2 wt% of H_2SO_4, 500 rpm of mixing intensity and 1:12 molar ratio of oil-methanol; **(b)** Effect of catalyst on alkali catalyst transesterification reaction @ 55ºC, 30 min, 500 rpm of mixing intensity and 1:12 molar ratio of oil-methanol; **(c)** Effect of methanol to oil molar ratio on alkali catalyst transesterification reaction@ 55ºC, 30 min, 500 rpm of mixing intensity and 1wt%of catalyst; **(d)** Effect of reaction temperature on alkali catalyst transesterification reaction with 1wt% of catalyst, 30 min, 500 rpm of mixing intensity and 1:9 molar ratio of oil-methanol; **(e)** Effect of reaction time @ 65 ºC, 500 rpm, 1:9 molar ratio of oil-methanol with 1 wt% of catalyst and **(f)** mixing intensity on alkali catalyst transesterification reaction @ 65 ºC, 40 min, 1:9 molar ratio of oil-methanol with 1 wt% of catalyst.

3.2.3 Effect of methanol to oil molar ratio on alkali catalyst transesterification reaction

The molar ratio of oil to methanol is one of the most signify cant parameter influencing the conversion into methyl esters. Even though, the stoichiometric molar ratio of triglyceride to methanol for transesterification is 1:3, excess reactant of methanol is required to enhance biodiesel conversion [21]. The effect of oil to methanol ratio was studied in the range of 3, 6, 9 and 12. Fig. 2(c) represents the effect of oil to methanol molar ratio in the conversion of biodiesel was observed that the conversion increases with increase in molar ratio of methanol. The optimum conversion of 83% was obtained at 1:9 molar ration of oil-methanol with constant reaction temperature of 55ºC and reaction time of 30 min with catalyst of 1 wt.%. With further increase in molar ratio the rate of conversion was de-

creased due to the mass transfer limitation.

3.2.4 Effect of reaction temperature on alkali catalyst transesterification reaction

The reaction temperature also one of the key parameter which is extensively affect the yield of biodiesel. At least reaction duration of 30 min, during transesterification reaction was carried out at 40 °C, the conversion of biodiesel was achieved only 48 wt.%. Conversely, the highest conversion achieved as 94%, when the reaction temperature was augmented to 65 °C. Therefore, reaction temperature has a more considerable effect on the conversion at superior reaction temperature than inferior temperature. Fig. 2(d) represents the effect of reaction temperature on CSG to biodiesel conversion. At inferior reaction temperature, there was an inadequate energy to support extensive collisions between reactant particles. On the other hand, at superior reaction temperature, the possibility of collision between reactant particles became better and straightforwardly achieved the necessary activation energy [22].

3.2.5 Effect of reaction time and mixing intensity on alkali catalyst transesterification reaction

The Fig. 2(e) represents the effect of reaction time on CSG to biodiesel conversion. The enslavement of reaction time was studied at various time intermissions ranging from 10–60 min. The maximum conversion of 95 wt% was achieved at 40 min of reaction time. Further increase of reaction time it was observed that there is no significant changes on the conversion on CSG to biodiesel.

The mixing intensity is an essential factor for the transesterification reaction in order to enhance the diffusion mass transfer between the reactants with the catalyst. It enlarges the contact area among oil and catalyst in methanol solution to start the reaction. The inferior conversion is due to improper mixing, because the reaction takes place only at the boundary of the two layers. Agitation of oil and methanol-catalyst mixture enhances the reaction rate and leads to complete the reaction within short time period.

Mixing intensity was considered in the range from 100 to 600 rpm. Fig. 2(f) represents that an effect of mixing intensity on the dropdown of triglycerides to methyl ester. The outcome (98.6 wt %) exposed that the agitator rates of 400 rpm were sufficient for the completion of transesterification reaction. However, the conversion for 400 rpm was slightly higher than that for 500 rpm and above mixing rate. Inadequate mixing could lead to lower reaction rate, thus inferior the conversion rate. Therefore, 400 rpm agitation speed was selected as the optimum stirrer speed in the transesterification of CSG oil. On the other hand, higher mixing rate would harmfully impact to the reaction as well. The results shown that increasing the mixing intensity more than 400 rpm, not only consumes more energy but also results in a lower conversion than that of 400 rpm. The mixing rate of 500 rpm and above was not recommended because the interaction between the reactants was very less.

4 CONCLUSION

This study highly structured that the utilization of dumping waste of CSG oil as a renewable energy source to produce value added biodiesel. A two-stages: esterification and followed by for the biodiesel production including the effects of dissimilar variables were discussed. After the two step process end, the highest conversion of biodiesel was achieved as 98.6 wt% with optimum parameters conditions. The converted biodiesel was confirmed by ^{1}H-NMR spectrum. The properties of CSG biodiesel were in good conformity with ASTM standards. The potential use of CSG oil emerges to be hopeful promising applications in the biodiesel production. The production of CSG biodiesel could be an added value to an underutilized agricultural product. It has been recommended that Coffee spent ground could be used as a potential resource for biodiesel production.

REFERENCES

[1] Wondwosen Sime, Ramachandran Kasirajan, Samuel Latebo, MamushAbera, Ahmednur Mohammed, Eskedar Seraw, Wudnesh Awoke, "Coffee Husk Highly Available in Ethiopia as an Alternative Waste Source for Biofuel Production," *International Journal of Scientific & Engineering Research.* Vol. 8 (7), pp. 1874-1880, 2017.

[2] K. Ramachandran, P. Sivakumar, T. Suganya, S. Renganathan, "Production of biodiesel from mixed waste vegetable oil using an aluminium hydrogen sulphate as a heterogeneous acid catalyst," *Bioresource Technology.* Vol. 102, pp.7289-7293, 2011.

[3] Hamidreza Jaliliannosrati, Nor Aishah Saidina Amin, Amin Talebian-Kiakalaieh, Iman Noshadi, "Microwave assisted biodiesel production from Jatropha curcas L. seed by two-step insitu process: Optimization using response surface methodology," *Bioresource Technology.* Vol. 136, pp. 565-573, 2013.

[4] S. Jain, M.P. Sharma, "Prospects of biodiesel from Jatropha in India," *Renewable Sustainable Energy Rev.* vol. 14, pp. 763-771 (2010).

[5] J. Zeng, X. Wang, B. Zhao, J. Sun, Y. Wang, "Rapid in situ transesterification of sunflower oil," *Ind Eng Chem Res.* Vol. 48, pp. 850-856, 2009.

[6] K. Ramachandran, T. Suganya, N. Nagendra Gandhi, S. Renganathan, "Recent developments for biodiesel production by ultrasonic assist transesterification using different heterogeneous catalyst: A review," *Renew. Sust Energy Rev.* vol. 22, pp. 410-418, 2013.

[7] Sen Yang, Qing Li, Yang Gao, Longyu Zheng, Ziduo Liu, "Biodiesel production from swine manure via housefly larvae (Musca domestica L.)," *Renewable Energy.* Vol. 66, pp. 222-227, 2014.

[8] Y.C. Sharma, B. Singh, "An ideal feedstock, kusum (Schleichera triguga) for preparation of biodiesel," *Fuel.* Vol. 89, pp. 1470-1474, 2010.

[9] Melca Mahber. Forest of Sheka: Multidisciplinary case studies on Land use/Land cover changes, Southwest Ethiopia; Addis Ababa: 2007.

[10] E. Alptekin, M. Canakci, "Optimization of transesterification for methyl ester production from chicken fat," *Fuel.* Vol. 90, pp. 2630-2638, 2011.

[11] A.N. Phan, T.M. Phan, "Biodiesel production from waste cooking oils," *Fuel.* Vol. 87, pp. 3490-3496, 2008.

[12] T. Suganya, S. Renganathan, "Optimization and kinetic studies on algal oil extraction from marine macroalgae *Ulva lactuca*," *Bioresource*

Technology. Vol. 107, pp. 319-326, 2012.

[13] AOCS (American Oil Chemical Society). Official methods and recommended practices of AOCS, 5th Ed. American Oil Chemical Society, Champaign, IL; USA: 1998.

[14] Ramachandran Kasirajan, Sivakumar Pandian, Suganya Tamilarasan, Renganathan Sahadevan, "Lipid extraction from natural plant source of Adenanthera pavonina using mixed solvent by superheated extractor," *Korean J Chem Eng*. Vol. 31, pp. 509-513, 2014.

[15] Y.C. Sharma, B. Singh, S.N. Upadhya, "Advancements in development and characterization of biodiesel: a review," *Fuel*. Vol. 87, pp. 2355-2373, 2008.

[16] S. Chongkhong, C. Tongurai, P. Chetpattananondh, C. Bunyakan, "Biodiesel production by esterification of palm fatty acid distillate," *Biomass Bioenergy,* vol. 31, pp. 563-568, 2007.

[17] D.M. Pilar, B. Evaristo, J.L. Franscisco, M. Martin, "Optimization of alkali-catalyzed transesterification of brassica carinata oil for biodiesel production," *Energy Fuels*. Vol. 18, pp. 77-83, 2004.

[18] M. Leon-Camacho, I. Viera-Alcaide, I.M. Vicario, "A corn (Quercus spp.) fruit lipids: saponifiable and unsaponifiable fractions: a detailed study," *J Am Oil Chem Soc*. Vol. 81, pp. 447-453, 2004.

[19] C. Paquot, A. Hautfenne, Standard methods for the analysis of oils, fats and derivatives. Blackwell Scientific. 7th ed. London: 1987.

[20] H.D. Hanh, N.T. Dong, K. Okitsu, K.Y. Maeda, R. Nishimura, "Effects of molar ratio, catalyst concentration and temperature on transesterification of triolein with ethanol under ultrasonic irradiation," *J Jpn Petrol Inst*. Vol. 4, pp. 195-199, 2007.

[21] H. Noureddini, D. Harkey, V.A. Medikonduru. "Continuous process for the conversion of vegetable oils into methyl esters of fatty acids," *J Am Oil Chem Soc*. Vol. 75, pp. 1775-1783, 1998.

[22] M.I. Al-Widyan, A.O. Al-Shyoukh, "Experimental evaluation of the transesterification of waste palm oil into biodiesel," *Bioresource Technology*. Vol. 85, pp. 253-256 2002.