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Optimization of transesterification Process in the production of Biodiesel from Pungam (Pongamia Glabra) Oil (December 2006)

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Abstract *- Biodiesel is found to be the ideal replacement for petroleum diesel among the alternative fuels. Bio-diesel is a clean burning fuel, produced from renewable resources (vegetable oils both edible and non-edible). It can be used in CI engines as a substitute for diesel oil with least modifications. It is completely miscible with diesel oil and it can be blended with diesel oil in any proportion. It is non-toxic and devoid of sulphur. It is obtained by the transesterification of vegetable oil. In the present investigation, Pungam (Pongamia Glabra) oil was taken up as the raw material. The most important process variables affecting the yield of the process are the percentage of excess alcohol required above the stochiometric requirement, the amount of catalyst used in the reaction and the temperature maintained during the reaction process. In this work, a parametric analysis was done to determine the optimum conditions, which would result in maximum yield of esters. These conditions in turn can be applied for mass production. From this analysis, it was concluded that the optimized conditions are 6:1 molar ratio of methanol to Pungam oil, 1.92 weight percent of volume of Pungam oil as catalyst (KOH) and 55^{0}C reaction temperature.*

Keywords **- Biodiesel, catalyst, methyl esters, molar ratio, Reaction temperature, Transesterification.**

1. INTRODUCTION

Biodiesel is a domestic renewable fuel derived from natural substances like vegetable oils. Vegetable oils have been tried as an alternative for conventional diesel in diesel engines. The neat vegetable oils have shown good performance for short-term operation [1]. The major drawbacks associated in using raw vegetable oil as diesel fuel for longer operations are (i). Fuel line and filter clogging due to fine particles, gums and waxes, (ii). Polymerization and partial oxidation during storage of the oil causing an increase in viscosity, (iii). Polymerization in the combustion chamber caused by heat and (iv). Improper atomization of fuel causing poor ignition and combustion characteristics. These problems occur due to the higher viscosity of vegetable oils [2].

Modification of vegetable oils is required to eliminate the above-mentioned drawbacks. Transesterification process is one of the popular methods, which is widely used [2, 3]. Generally transesterification process is used to convert the straight vegetable oil to the desired esters and to remove the free fatty acids. After this processing, unlike straight vegetable oil, methyl esters have physical and combustion properties close to diesel oil, and can replace it in most current applications. However, it is most often used as an additive to petroleum diesel, improving its lubricity. Methyl esters operated engines have less metal wear compared to the petroleum diesel operated engines [4]. It is one of the possible candidates to replace fossil fuel as the world's primary transport energy source, because of its renewability and also because it can be transported and sold using the current infrastructure.

Among the vegetable oils, the non-edible oils would be less expensive and also would not put pressure on cooking oil prices. Therefore, we selected Pungam oil, which is non-edible oil. This oil generally used in Soap, Candle, Fertilizers, Pesticides and medicines preparation.

For the past few years much work has been done on producing methyl esters from various types of vegetable oils (both edible and non-edible). The waste edible oils are also used for producing biodiesel by transesterification process [5 - 8]. But Pungam oil, which is indigenous to India, has not been given much attention and even less research has been involved in analyzing the parameters on which the reaction is dependent. This Parametric analysis of the transesterification process of Pungam oil is vital in order to determine the best conditions that result in the highest yield of ester (biodiesel), without sacrificing combustion quality.

Our objective is to optimize the process parameters, which can then be applied for mass production of biodiesel to reduce the cost.

Pungam-Background

The commonly found avenue tree, Pungam is a small to medium sized fast growing tree with a short trunk and a spreading umbrella like shady crown with slightly drooping branches. Common names for this plant are Karanja, Honge

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and Pongamia in India. The leaves are lopped for fodder and are also popular as green manure for rice sugarcane fields, areca gardens and coffee plantations. The seeds yield bitter, reddish brown, thick non-drying, non-edible oil. The seed oil is being tried as a substitute for diesel oil in electricity generation in rural Karnataka, India. This form of fuel is used in a project called SUTRA (sustainable transformation of rural areas) funded by the Indian Ministry of non-conventional energy and the local government. Fatty acid composition of pungam oil is palmitic: 3.7–7.9%, stearic: 2.4–8.9, arachidic: 2.2–4.7, behenic: 4.2–5.3, ignoceric: 1.1–3.5, oleic: 44.5–71.3, linoleic: 10.8–18.3, and eicosenoic: 9.5–12.4% [9].

Transesterification Process

Methyl esters are made through a chemical process called transesterification in which the vegetable oil containing triglyceride esters of long chain fatty acids is converted into mono-alkyl esters of alcohol (generally ethanol or methanol) along with glycerol as a bi-product. Diesel has a chain length of 11-13 carbons and vegetable oils have a chain length of 18 and waste vegetable oil has a chain length of up to 32. To burn in an engine the chain has to be broken to be similar in chain length to diesel molecules.

Transesterification works by cracking the vegetable oil molecules splitting the triglycerides from the hydrocarbons and shortening the carbon chain. The chain reaction equation given is below.

$$\text{Triglyceride} + \text{Methanol} \Leftrightarrow \text{Glycerol} + \text{Fatty acid esters} \quad (1)$$

It breaks the bond holding the fatty acid chains to the glycerin, the glycerin falls away and the fatty acid chains bond with the methanol. This happens in three stages. First the fatty acid chain breaks off the triglyceride molecule and bonds with methanol to form a methyl ester molecule, leaving a diglyceride molecule i.e. two chains of fatty acids bound by glycerin. Then a fatty acid chain breaks off the diglyceride molecule and bonds with methanol to form another methyl ester molecule leaving a monoglyceride. Finally the monoglycerides are converted to methyl esters thus completing the process. The first part of the process occurs rapidly. But the process proceeds more and more slowly as it nears completion and never reaches 100% completion [10].

The methyl esters molecule thus obtained is smaller and less complex since the triple chain triglyceride vegetable oil molecule is converted to three single chain methyl ester molecules. But the chain length of the fatty acids themselves remains the same. If the reaction is incomplete due to inadequate reagent or catalyst or agitation temperature or processing time then diglycerides may lead to coking problems and monoglycerides can lead to corrosion problems.

In the production of biodiesel, it is important to optimize the parameters to get better yield. Freedman. B et al. [10] studied the effect of reaction variables on the quality of fatty esters. Antolin G., et al. [11] optimized reaction temperature and proportions of reactants in production of sunflower methyl esters. Prasad.L et al. [12] carried out the optimization of transesterification process for biodiesel production from Jatropha oil. Freedman B., et al. [10] studied the effect of catalyst amount, alcohol molar ratio and reaction temperature on biodiesel production.

Important Parameters

The most important parameters that we have taken up for consideration in the current work, which affect the transesterification process are:

- Amount of catalyst
- Percentage of excess alcohol
- Reaction temperature

(i) Catalyst

Two types of catalyst are normally employed for the transesterification process namely acidic catalyst and basic catalyst [13]. Acidic catalyst has a slower reaction rate but can handle large amount of free fatty acids that might be present in the oil [14].

Basic Catalyst has faster reaction and also keeps the whole process slightly alkaline for neutralizing free fatty acids. It can be either NaOH or KOH. The KOH is easier to use as it dissolves easily in methanol and this is used in this work. This solution, obtained by dissolving the catalyst in methanol, is termed as methoxide solution and will be referred to so in the following text. It also provides a potash glycerate as a bi-product, which can be used as manure. Too much catalyst will make extra soap in the reaction and the product very alkaline that is difficult to wash resulting in the loss of yield or it can ruin the reaction.

After the catalyst attacks the ester bonds breaking them and leaving an open-ended fatty acid chain the affinity of the replacement methanol for the resulting open bond is strong enough to prevent the glycerin reattaching to the fatty acid. Excess catalyst will continue to attack ester bonds even those of product esters. Some of the broken bonds will mate with the catalyst and form excess soap. When the amount of catalyst is small, some of the oil is left unreacted. The stoichiometric requirement of catalyst was found to be 21.315 g/litre and was prepared by the procedure given by Tickell J [15].

***(ii)* Alcohol**

The alcohol that is used for transesterification process should be inexpensive, should be anhydrous and most importantly it should not absorb moisture so that experiments can be conducted in ambient conditions without much difficulty. The last property mentioned above is extremely important considering the fact that batch processing is to be carried out where preparations for the experiments are done in the open. Methanol was chosen for this work because it can be commercially obtained in anhydrous form.

The amount of methanol needed will also vary but the ideal is to use the least amount of methanol necessary in order to get the highest yield. Excess methanol is needed

to push the conversion process towards completion or else the process runs out i.e. reaches equilibrium before all the triglycerides are converted to esters. The excess methanol thus acts like a catalyst as it encourages the process and does not become a part of the final product and can be recovered afterwards.

(iii) Reaction temperature

Temperature values must be chosen in such a way that the higher end is less than the boiling point of methanol (≈70°C) and the lower end is around room temperature. The yield is expected to increase with increase in temperature and also the reaction is faster.

Determination of Parameter Values

In this work, the impact of various parameters on the yield of methyl esters was studied. As mentioned earlier, the parameters chosen were the amount of catalyst, molar ratio of methanol and oil and the reaction temperature. By keeping one parameter constant, the effects of other two parameters were studied. To optimize the parameter values a total of 27 experiments need to be conducted. The quantity of oil chosen was 200 ml for a batch. The three catalyst amounts considered for this work are 1.92%, 2.13% and 2.34% weight by volume of oil. For methanol the standard molar ratio of methanol and vegetable oil taken are 4.5:1, 6:1 and 9:1. The three temperatures chosen were 40°C, 55°C, and 65°C. It was observed that about 90% conversion of oil to ester was complete within 30 minutes and the reaction becomes slower afterwards. The duration of reaction time was taken as two hours to ensure complete reaction. Thus the time for the reactions was standardized as two hours for all the samples.

2. PROCEDURE FOR EXPERIMENTS

Experimental Setup

The experimental setup consists of a three-necked round-bottom flask. The flask is kept in an oil bath heated by an electrical heater. The motor driven stirrer is inserted into the flask through the center neck. The stirrer passes through an airtight gland, which prevents the methanol from escaping out of the flask. A thermocouple is inserted through the other neck for measuring the temperature of the oil inside the flask. The thermocouple in turn is connected to a temperature controller relay, which turns the heater on / off to maintain constant temperature of the oil. A variable voltage regulator was also used to regulate the voltage applied to the heating coil. The third neck is used for pouring the oil and methoxide (mixture of catalyst and methanol) into the flask.

Experimental Process

The oil is heated to the desired temperature. The stirrer enables uniform mixing of the oil to ensure both uniform temperature and also better contact with methanol molecules. The Potassium Hydroxide required is precisely weighed and dissolved in the methanol to form the methoxide solution. This methoxide solution prepared is poured into the flask. The Pungam Oil on reaction with methoxide solution undergoes a colour change from brown to bright red indicating the progress of the transesterification process. The reaction is allowed to continue for two hours. The reaction mixture is then taken out and is allowed to separate in a separating funnel. The cloudy looking part of the product is glycerin, which sinks to the bottom, and methyl ester, which is a translucent liquid, will remain on top. The mixture should be allowed to settle for at least 8 hours. The separation of methyl esters and glycerol occurs due to the density variation between methyl esters and glycerol.

Separation and Bubbling Process

The methyl esters obtained is separated and water is added to the methyl esters gently over the sides so that traces of glycerol present along with the methyl esters mixes with water to form soap and settles down. The process is repeated until all the impurities are removed completely. The biodiesel is then mixed with water and it is gently agitated through a bubbling process in which air is pumped into the methyl ester-water mixture. The bubbling process is done for about 30 minutes. Thus, the bio-diesel obtained after the bubbling process is completely devoid of glycerol. The yield is now measured using a graduated flask.

3. RESULTS AND DISCUSSION

The percentages of yield of methyl esters are presented as graphs for the different conditions of molar ratios of methanol to vegetable oil, reaction temperatures and catalyst amounts. The reaction temperature was indicated as Tr in the following figures and it is in degree Celsius. The percentage of yield of methyl esters is calculated by using equation (2).

$$\%\ \text{of yield} = \left(\frac{\text{methyl esters (in ml)}}{\text{vegetable oil (in ml) used in the reaction}} \right) \text{x } 100 \quad (2)$$

Effect of Temperature

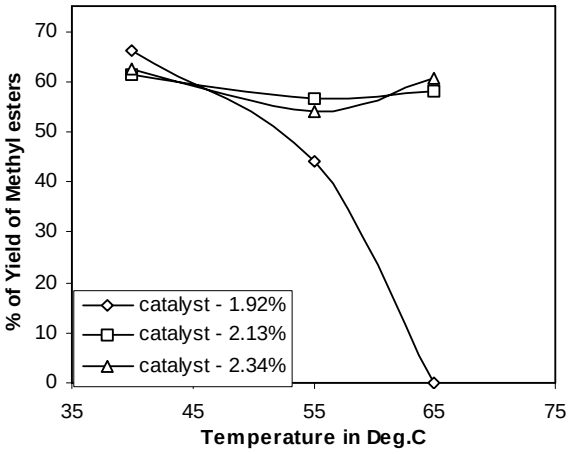

Fig. 1. The Variation of yield of methyl esters with temperature [methanol 4.5:1]

The variation in percentage of the yields of methyl esters with the reaction temperature for the different amount of catalyst for a methanol molar ratio of 4.5:1 is shown in Fig.1. It is observed that, the yield of methyl esters reduces with increases in temperature and falls to zero at 65^{0}C for low catalyst amount. This is may be due to reverse reaction occurring at higher temperatures and less molar ratio of methanol to vegetable oil in the reaction. It is also observed that the % of yield is slightly varied with temperature for 2.13 % and 2.34 % of catalyst amounts.

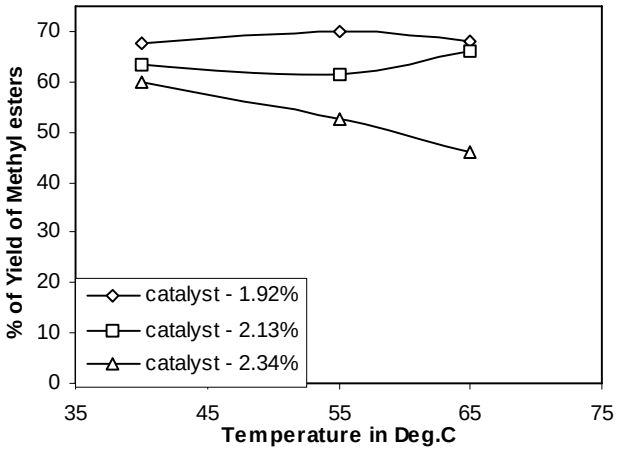

Fig. 2. The Variation of yield of methyl esters with temperature [methanol 6:1]

Figure 2 shows, the variation in the yields of methyl esters with reaction temperature at different amounts of catalyst at a molar ratio of 6:1. It is observed that the percentage of yield slightly varies with the reaction temperature. It is also observed that the yield is slightly higher for lower catalyst amounts irrespective of temperature.

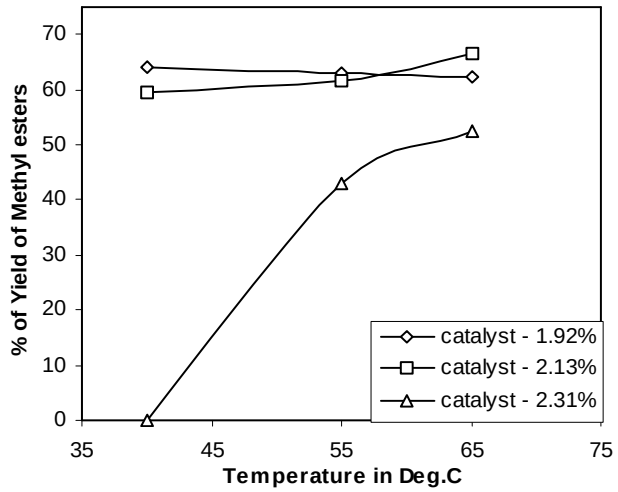

Fig. 3. The Variation of yield of methyl esters with temperature [methanol 9:1]

Figure 3 shows the variation of percentage of yield of methyl esters with temperature for different amounts of catalyst at a 9:1 molar ratio of methanol to vegetable oil. It is found that the yield of methyl esters increases with increase in temperature. This may be due to the influence of temperature on the reaction at higher catalyst amounts. Small variations in percentage yield of methyl esters are observed in the case of low amounts of catalyst. It is also observed that the yield of the esters reduces with increase in the amount of catalyst in the reaction.

It is observed that, more yields of methyl esters are higher at 55^{0}C for most of the experiments.

Effect of Molar Ratio of Methanol

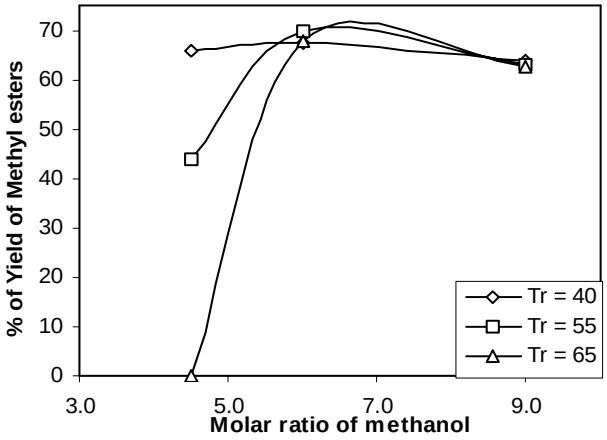

Fig. 4. The Variation of yield of methyl esters with methanol [1.92% of catalyst]

Figure 4 shows the yield of methyl esters variation with methanol and reaction temperature for 1.92% catalyst. It is observed that the percentage of yield is higher at a molar ratio of 6:1 compared to other molar ratios. Also, at 40^{0}C, the yield of methyl esters is high at a molar ratio 6:1 compared lower methanol molar ratios for all temperatures. It is also found that, there is no reaction at a temperature 65^{0}C below molar ratio of 4.5:1 methanol to vegetable oil.

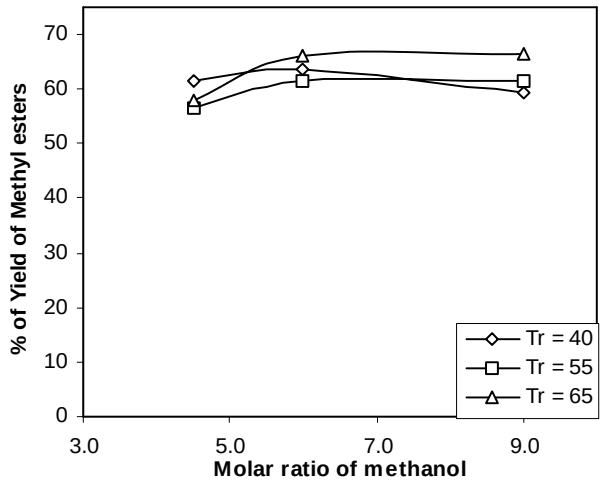

Fig. 5. The Variation of yield of methyl esters with methanol [2.13% of catalyst]

Figure 5 shows the yield of methyl esters for different amounts of methanol and different reaction temperatures at 2.13% of catalyst. The yields of methyl esters are slightly

lower at lower molar ratio of methanol for all reaction temperatures. This may be due to insufficient methanol which is unable complete the reaction. The yield of esters is observed to be almost constant at all molar ratios. The effect of reaction temperature also seems to be insignificant.

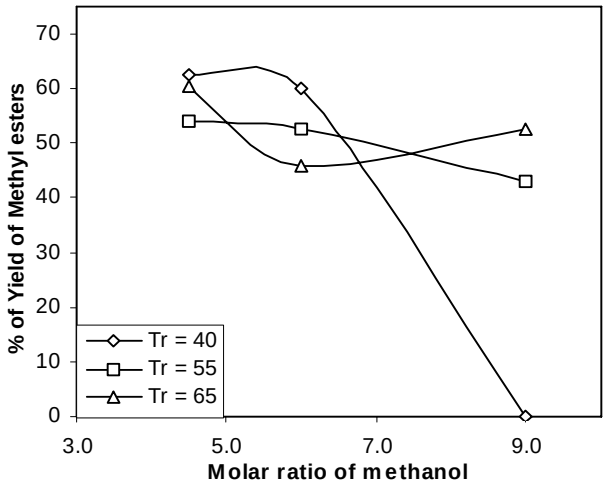

Fig. 6. The Variation of yield of methyl esters with methanol [2.34% of catalyst]

Yields of methyl esters for different molar ratio of methanol and different reaction temperatures at 2.34% of catalyst are shown in Fig. 6. The percentage yield of methyl esters decreases with increase in molar ratio of methanol at temperature 40^0C. It may be due to insufficient temperatures for the reaction to proceed. It is also observed that there is a

slight decrease in percentage yield with increase in molar ratio of methanol.

From this analysis, we conclude that the percentage yield of methyl esters is high at molar ratio of 6:1 compared to other molar ratios with a 1.92% catalyst amount.

Effect of Catalyst Amount

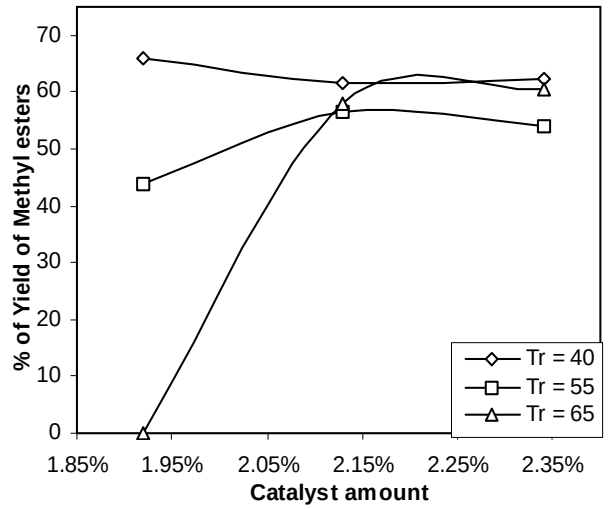

Fig. 7. The Variation of yield of methyl esters with catalyst [methanol molar ratio of 4.5:1]

Figure 7 shows the variation of yield with different amounts of catalyst and different reaction temperatures at methanol molar ratio of 4.5:1. It is observed that, there is no reaction for low catalyst amount and this increases with increase in catalyst amount at 65^0C temperature. This may be due to insufficient catalyst for reaction at that temperature. It is also observed that maximum yield of methyl esters found is at 40^0C with low amount of catalyst.

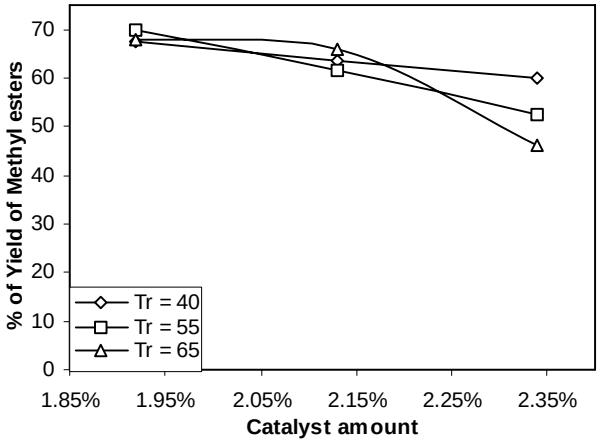

Fig. 8. The Variation of yield of methyl esters with Catalyst [methanol molar ratio of 6:1]

The variation in yields of methyl esters for different catalyst amounts and different reaction temperatures is shown in Fig. 8 for molar ratio of 6:1. It shows that, the percentage yield is high at low catalyst amount for all the temperatures. It is also observed that maximum yield of methyl esters occurs at 55^0C and low amount of catalyst.

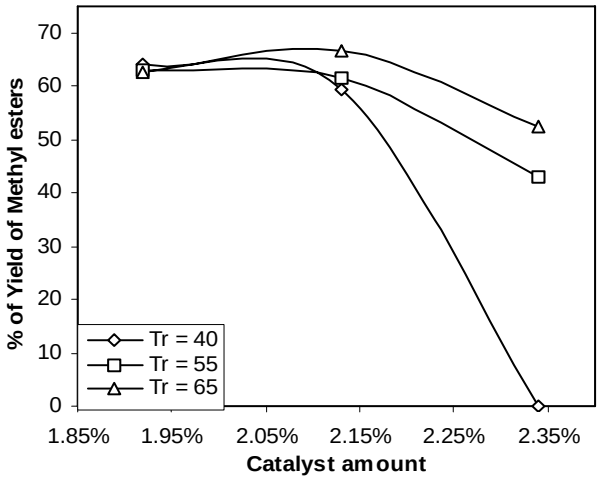

Fig. 9. The Variation of yield of methyl esters with Catalyst [methanol molar ratio of 9:1]

The variations of yields of methyl esters with catalyst amount and the reaction temperature are as shown in Fig 9. It observed that there is no reaction at a temperate of 40^0C at high amount of catalyst. This may be due to insufficient temperature for the reaction.

The percentage yield was found to reduce on further reduction of catalyst amount from 1.92%. The percentage

of methyl esters yield for 1.8% of catalyst amount is 62% and it is less than the corresponding value for 1.92% of catalyst.

The low yield of methyl esters is due to the crude vegetable oil taken for this work. Generally, yield of Methyl ester is 67% - 87% from crude vegetable oils when compared with the refined vegetable oils which gives yield of 92 - 98% [16, 17]. From the economical point of view, the crude oil cost is half of that of refined oils. The refining process increases the cost of vegetable oils.

The properties of Pungam oil and its methyl ester at maximum yield conditions are given in Table 1. From this table, it is observed that the viscosity of Pungam methyl esters was less compared to its original oil. The calorific value is higher for Pungam methyl esters compared to neat oil.

Table 1. Properties of Pungam, its methyl ester and diesel fuel

Property	Pungam oil	Pungam Methyl esters	Fossil diesel fuel
Density g/cc	0.934	0.892	0.821
Viscosity Cst	23.16	5.405	3.522
Flash point ^{0}C	270	250	48
Fire point in ^{0}C	220	184	59
Calorific value kJ/kg	35648	39149	44310

4. CONCLUSION

The yield variations for change in alcohol volume, catalyst concentration and temperature have been studied and the optimal conditions for the parameters are found to be

Molar ratio of methanol to vegetable oil – 6:1
Temperature – 55°C
Amount of Catalyst – 1.92% by weight of volume of oil.

The properties of methyl esters satisfied the standards of ASTM specified in literature [15].

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REFERENCES

[1] Aurore Bernardo et al. 2003. Camelia oil as a fuel for diesel transport engines. *Industrial Crops and Products* 17: 191-197

[2] Meher. L.C et al. 2004. Technical aspects of biodiesel production by transesterification- a review. *Renewable and Sustainable Energy reviews*. 10: 248-268

[3] Recep A et al. 2001. The potential of using vegetable oil fuels as fuel for diesel engines. *Energy conversion and Management*. 42 : 529-538

[4] Agrwal A.K. et al. 2003. Wear Assessment in a Biodiesel Fuelled Compression Ignition Engine. *ASME Journal of Engineering for Gas Turbines and Power*, 125: 820-826

[5] Guo.Y et al. 2002. A clean biodiesel fuel production from recycled oils and grease trap oils. *Proceedings of Better air quality in Asian and Pacific Rim Cities conference*, Hong Kong, 16-18 December 2002 retrieved June 21, 2005 from http: //www.cse.polyu.edu.hk/~activi/BAQ2002/BAQ2002 files/Proceedings/PosterSession/55.pdf

[6] Jan C et al. 2004. Used frying oils and their utilization in the production of methyl esters of higher fatty acids. *Biomass and Bioenergy*. 27: 173-181.

[7] Al-Widyan.M.I et al .2002. Experimental evaluation of transesterification of waste palm oil into biodiesel. *Bioresource technology*. 85: 253-256

[8] Felizardo. P et al. 2005. Production of biodiesel from waste frying oil. *Waste management*. 26: 487-494

[9] Mohibbe Azam M et al. 2005. Prospects and potential of fatty acid methyl esters of some non-traditional seed oils for use as biodiesel in India. *Biomass and Bioenergy*. 29: 293–302

[10] Freedman. B et al. 1984. Variables affecting the yield of fatty esters from Transesterified Vegetable Oils. *JAOCS*. 61: 1638-1643

[11] Antolin G et at. 2002. Optimization of biodiesel production by sunflower oil transesterification. *Bioresource Technology*, 83: 111-114

[12] Prasad. L et al. 2004. Optimization of transesterification process for biodiesel production and use of biodiesel in Compression injection engine. *Society of Automotive Engineers Inc*. 2004-28-029

[13] Schuchardt.U et al. 1998. Transesterification of vegetable oils: a review. *J. Braz. Chem*. Soc. 9: 199-210

[14] Canakci.M and Van Gerpen .J. 2001. Biodiesel production from oils and fats with high free fatty acids. *ASAE*. 44(6): 1429-1436.

[15] Tickell, J. 2003.*From the fryer to the fuel tank*. Neworleans, Lousiana: Joshua Tickell Publications.

[16] Barnwal B.K., Sharma M.P., 2005, Prospects of biodiesel production from vegetable oils in India, Renewable and Sustainable Energy Reviews, 9 (2005) 363–378

[17] Jon Van Gerpen. 2005. Biodiesel processing and production, Fuel Processing Technology, 86 (2005) 1097–1107