

FATTY METHYL ESTERS FROM VEGETABLE OILS FOR USE AS A DIESEL FUEL

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ABSTRACT

The world is confronted with the twin crisis of fossil fuel depletion and environmental degradation. The indiscriminate extraction and consumption of Fossil fuels have led to a reduction in petroleum. Due to the concern on the availability of recoverable fossil fuel reserves and environmental problems caused by the use of those fossil fuels, considerable attention has been given to biodiesel production. The methyl esters of vegetable oils, known as biodiesel becoming increasing popular, because of its potential as a green alternative fuel for diesel fuel. It has many advantages over conventional diesel fuels. These include biodegradable, non toxic, nil sulfur content, reduced aromatics. It can either be directly used in engine or can be blended with conventional diesel, and requires no engine modification. There are various methods available for the production of biodiesel such as micro emulsification, dilution, pyrolysis, transesterification and esterification, among which transesterification is the best process. Biodiesel is produced by transesterifying the parent oil or fat with an alcohol, usually methanol, in presence of a catalyst usually strong base such as NaOH or KOH or, preferably an increasingly more commonly alkoxide. The transesterification reaction variable that affect yield and purity of the product include molar ratio of alcohol to vegetable oil, type of catalyst, molar ratio of catalyst to oil, temperature and degree of refinement of vegetable oil. In this paper various vegetable oils transesterification was studied with the purpose of achieving the best conditions for biodiesel production.

Keywords: Vegetable Oils, Transesterification, Methyl Esters, Yield

1. INTRODUCTION

Majority of the worlds energy needs are supplied through petrochemical sources, coal and natural gases, with the exception of hydroelectricity and nuclear energy, of all, these sources are finite and at current usage rates will be consumed shortly (Srivatsava and Prasad 2000). Economic growth is always accompanied by commensurate increase in the transport. This has stimulated recent interest in alternative sources for petroleum-based fuels. One possible alternative to fossil fuel is the use of oils of plant origin like vegetable oils and tree borne oil seeds. This alternative diesel fuel can be termed as biodiesel. This fuel is biodegradable and non-toxic

and has low emission profiles as compared to petroleum diesel. Usage of biodiesel will allow a balance to be sought between agriculture, economic development and the environment. Chemically the oils/fats consist of triglyceride molecules of three long chain fatty acids that are ester bonded to a single glycerol molecule. These fatty acids differ by the length of carbon chains, the number, orientation and position of double bonds in these chains. Thus biodiesel refers to lower alkyl esters of long chain fatty acids, which are synthesized either by transesterification with lower alcohols or by esterification of fatty acids.

Recently, biodiesel has been receiving increasing attention due to its less polluting nature and since it is a renewable energy resource against the conventional diesel, which is a fossil fuel leading to a potential exhaustion. Mostly, biodiesel is prepared from oils like soybean, rapeseed, sunflower, safflower, etc. throughout the world (Dalai *et al*, 2001). These oils are essentially edible in nature. The use of edible vegetable oil and animal fat for Biodiesel production would not be an appropriate alternative as the demand for Vegetable oil for food has increased tremendously in the recent years. Hence use of non-edible oils would be the best alternative as it would reduce the cost of Biodiesel since the cost of raw materials contributes 70 % of the overall production cost. (Haas *et al*, 2004) Various non edible oils like Neem Azadirachta Indica), Simarouba Simarouba Indica), Mahua Madhuca indica), Jatropha Jatropha curcas), Karanja Pongamia pinnata) (Meher *et al*, 2006), soapnut sapindus mikorossi) (Meher *et al*, 2006) etc., are the various feed stocks available. We have chosen Neem Azadirachta indica), Karanja Pongamia pinnata), Sunflower oil. Azadirachta indica due to its oil content and its availability and it also can adapt itself in a wide range of Temperature 49 °C to 0 °C). This tree is present in various countries like Asia, Africa, and Central & South America. It grows almost in all types of soil including clay, saline, alkaline, dry, stony, shallow soils and even on solid having hard calcarious or clay pan. A mature tree can produce 30 – 50 kg of fruit every year and its life span is about 150 – 200 years. Hence there is a potential of about 5, 40,000 tonnes of seeds, which can yield about 1, 07,000 tonnes of oils and 4, 25,000 tonnes of cake. But this large untapped source is only 25 to 30 % utilized. This oil is light to dark brown in colour, bitter and has a rather strong odour and has a great potential to make biodiesel for supplementing other

conventional sources. Currently this oil is used for preparing cosmetics, ayurvedic medicines and biopesticides.

Oil of *Pongamia pinnata* Leguminosae; Pappilionaceae) is a nonedible oil of Indian origin (Lakshmikantan, 1978). It is found mainly in the native Western Ghats in India, northern Australia, and Fiji and in some regions of Eastern Asia. Presently *Pongamia* oil is being used by farmers in Karnataka a southern state in India) to run generators which irrigate their fields (Srinivasa 2001). The most commonly used edible oils for the production of biodiesel is sunflower oil (Antolin *et al.*, 2002). It is popular due to its low cost and ready availability. However, as for other oils there are limitations in the use of this nonedible oil as fuel. Its high viscosity and poor combustion characteristics can cause poor atomization, fuel injector blockage, and excessive engine deposit and engine oil contamination. Even though straight vegetable oil (SVO) is being used as a fuel instead of diesel, it is a well documented fact that esterified oil has better fuel properties (Ma and Hanna, 1999).

There are at least four ways in which oils and fats can be converted into biodiesel, namely, transesterification, blending, micro-emulsions and pyrolysis, of which Transesterification being the most commonly used method (Peterson *et al.*, 1991, Otera, 1993). Transesterification refers to a catalyzed KOH/NaOH) chemical reaction involving oil/fat triglyceride) and an alcohol (methanol/ethanol) to yield fatty acid alkyl esters (i.e., biodiesel) and glycerol. The main factors affecting transesterification are the amount of alcohol, catalyst, reaction temperature and Reaction time; the contents of free fatty acid (FFAs) and water in oils. Conversion is complicated if oil contains large amounts of FFA that will form soap with alkaline catalyst. The soap can prevent separation of the biodiesel from the glycerin fraction. Few researchers have worked with feedstock's having higher FFA levels using alternative processes, where they used a two-step pre-treatment to reduce the FFAs of yellow grease from 12% and brown grease from 33% to less than 1%, the transesterification reaction was completed with an alkaline catalyst to produce biodiesel (Canakci and Gerpen, 2001).

The investigation on the suitability of various non-edible oil seeds for the integral utilisation of their fractions for production of biodiesel and other products was carried out. The oil seeds considered were jatropha (*Jatropha curcas*), neem (*Azadirachta indica*), moringa (*Moringa oleifera*), trisperma (*Aleurites trisperma*), castor beans (*Ricinus communis*) and candlenut (*Aleurites moluccana*) (Martin *et al.*, 2010). The effect of process parameters such as molar ratio, preheating temperature, catalyst concentration and reaction time was studied to standardize the transesterification process for estimating the highest recovery of neem methyl ester with lowest possible viscosity has been studied. Based on the observations of the ester recovery and kinematic viscosity, it was found that filtered neem oil at 6:1 M ratio (methanol to oil) preheated at 55 °C temperature and maintaining 60 °C reaction temperature for 60 min in the presence of 2 percent KOH and then allowed to settle for 24 h in order to get lowest kinematic viscosity 2.7

cSt) with ester recovery 83.36%) (Ragit *et al.*, 2011). Among the various oilseeds widely available like Karanja, Sal, Mahua, Neem, etc. sustainable to the diverse socio-economic and environmental conditions of rural India, the evergreen neem with its wide availability and various useful uses may be a potential feedstock for biodiesel production (Karmakar *et al.*, 2012)

This paper discusses the findings of experiments carried out to optimize the pre-treatment process for reducing the FFA content of Neem, *Pongamia*, used cooking oil below 1% for maximum biodiesel production using an acid catalyst and to optimize the reaction parameters like Reaction temperature, Reaction time, Amount of Methanol, Amount of catalyst to complete the reaction and produce fuel grade biodiesel.

2. METHODOLOGY

2.1 Materials and Methods:

Crude Neem oil was obtained from Tanjore. Methanol AR grade), KOH were bought locally. The fatty acid profile of NO is given in Table 1. The Crude Neem oil (CNO) was degummed, dewaxed, filtered to remove precipitates in the oil. Minimal amounts of water present in the CNO had to be removed as every molecule of water will destroy a molecule of catalyst. Hence the filtered oil was subjected to heating at 70°C for 10 min. The properties of CNO are shown in Table 2. Its FFA content was determined by the standard titrimetry method. This oil had an initial acid value of 21.6 mg KOH/g, which is far above the 1% limit for satisfactory transesterification reaction using alkaline catalyst.

TABLE 1: Fatty acid profile of Neem oil

Fatty Acid	Systematic Name	Formula	Structure	Weight %
Palmitic Acid	Hexadecanoic	$C_{16}H_{32}O_2$	C 16:0	19
Stearic Acid	Octadecanoic	$C_{18}H_{36}O_2$	C 18:0	18
Oleic Acid	Cis-9-Octadecanoic	$C_{18}H_{34}O_2$	C 18:1	46
Linoleic Acid	Cis-9,Cis-12-Octadecadienoic	$C_{18}H_{32}O_2$	C 18:2	14

Pongamia pinnata was bought from local store with an acid value of 0.98 mg KOH/ g and Used Cooking oil were obtained from local restaurant with acid value of 0.3 mg KOH/ g. So these two feeds were directly subjected to base transesterification without pre-treatment.

2.2 Pre-treatment of crude Neem oil (CNO):

Therefore, FFA levels were first reduced in a multi-step pre-treatment process using acid catalyst H_2SO_4 1% v/v) to reduce the acid value of CNO below 1%. KOH/g is shown in Figure 1 and 2. Experiments were conducted in a

laboratory-scale setup which considered of 500cc glass flasks with air tight caps and a water cooled condenser that returned any vaporized methanol to the reacting mixture. The flasks were kept in an oil bath maintained at 60°C, just below the boiling point of methanol. The mixture was stirred using an agitator at the same rate for all runs. The same setup was also used for the alkaline catalysed transesterification reaction. At various time the progress of the reaction was monitored by measuring the acid value. The pre-treatment process comprised of two steps. In each step, different methanol to oil ratios (0.118, 0.15, 0.175, 0.2, 0.225, 0.25, 0.275 v/v) and reaction times (30, 45, 60, 75, 90 min.) were used to investigate their influence on the acid value of CNO. After the reaction, the mixture was allowed to settle for 1 h and the methanol- water fraction that separated at the top was removed in a separating funnel. The acid value of the product separated at the bottom was determined. The product having low acid value by using lowest quantity of methanol in minimum reaction time was used as the raw material for the second step. Again the effect of methanol to oil ratio and reaction time on reduction of acid value of this raw material was studied. The final product having acid value less than 1mg KOH/g using lowest methanol amount and reaction time in the second step was used for the main transesterification reaction

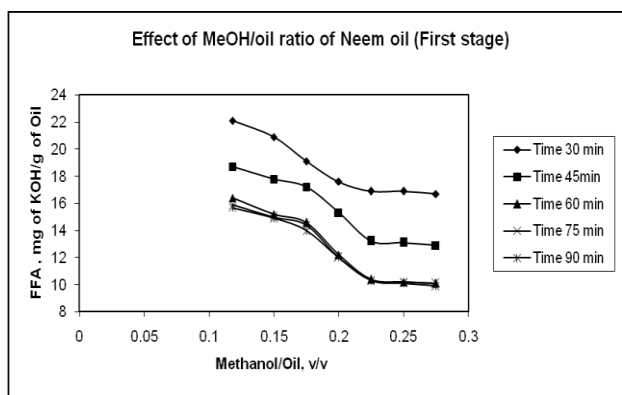


Figure 1 Effect of Methanol/ Oil ratio on the reduction of FFA First stage)

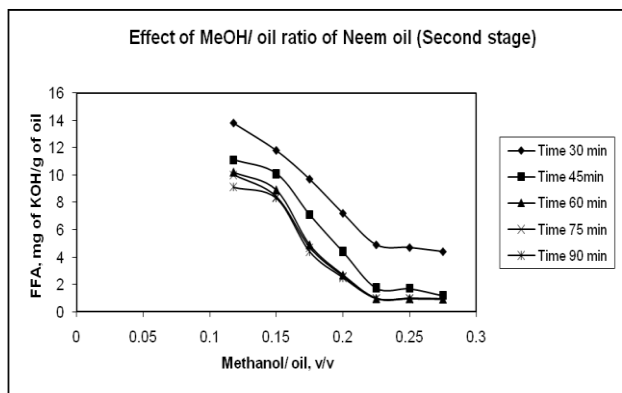


Figure 2 Effect of Methanol/ Oil ratio on the reduction of FFA Second stage)

2.3. Transesterification:

The transesterification reaction was carried out with 0.2 v/v methanol and 0.26% w/v KOH as an alkaline catalyst. The KOH amount was arrived at based on the stiochiometric amount and the amount need to neutralize the FFA after the second pre-esterification stage. The reaction was carried out at 60°C for one hour. The reaction mixture was taken out and is allowed to settle in a separating funnel for 12 hours. The bottom product (Glycerol) was removed and the top product (Esters) was distilled to remove the excess methanol added for the completion of the reaction. The ester layer was washed with hot water to remove impurities, and was dried over magnesium sulphate. The fuel properties namely, density at 15 °C, kinematic viscosity at 40 °C, flash point, fire point, pour point, calorific value, water content, carbon residue, acid value of crude oils, crude biodiesels and conventional diesels were determined as per the standards prescribed by ASTM for comparison with the latest American and European standards.

Table 2: Comparison of properties of CNO, CPO, UCO, NOME, POME, UCOME, Diesel and ASTM Standards.

Properties	CNO	CPO	UCO	NOME	POME	UCOME	Diesel	ASTM Standards
Density at 15 °C kg/m ³	930	934	920	880	892	885	840	860-890
Kinematic Viscosity at 40 deg C mm ² /s	38	43.16	42.91	3.2	5.4	4.73	2.6	2.5-6
Calorific value MJ/kg	36	35.6	36.7	39	39.14	38.65	43	not available
Flash point, °C	260	220	290	165	184	200	60	> 130
Specific heat capacity, J/kg deg C	2053	2088	2056	1940	1850	1789	1850	not available
Oxygen, % wt	10	8	9	10	10	10	0	11
Acid value mg of KOH/gm of oil	21.6	0.98	0.3	0.33	0.29	0.1	0.35	<0.8

3. RESULTS AND DISCUSSION

3.1 Effect of Catalyst Concentration:

The effect of Potassium hydroxide concentration on the transesterification of the edible and non-edible oils was investigated with its concentration varying from 1.9 to 2.5 wt. % based on the weight of raw oil) is shown in Figure 3. The operation conditions for the whole reaction process were fixed at the optimal level with reaction temperature of 60 deg C, reaction time of 60 min. and Methanol to oil ratio was 0.2 v/v. Experimental results showed changes in ester yield content with varied catalyst concentration. For lower catalytic concentration of 1.9% of KOH was insignificant catalyzed reaction to completion. As the KOH concentration increases, the conversion of triglyceride as well as the ester content also increased. However, 2.26% of KOH was optimal in the reaction with the higher yield for edible and non edible oils. Insufficient amount of KOH resulted in incomplete conversion

of triglycerides into the esters, as indicated from its lower ester content. It is evident from the graph, that neem gives the maximum yield. Increasing the amount of catalyst decrease the yield due to the fact that soap formation and also backward reaction were favoured. This is because of excess alkaline catalyst caused more triglycerides participation in the saponification reaction with KOH.

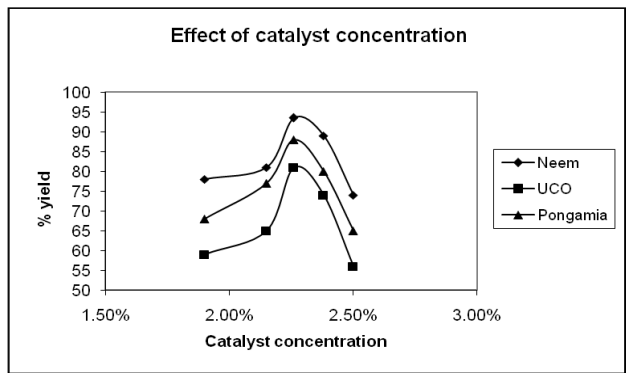


Figure 3 Effect of Catalyst Concentration in the yield of Methyl esters for various oils Reaction temperature 60°C, Reaction time 60min Methanol/Oil 0.2 v/v)

3.2 Effect of Reaction Time:

The reaction time of the transesterification reaction conducted at 60 deg C was optimized with highest achievable mixing degree with optimum catalyst concentration of 2.26%, methanol to oil ratio 0.2 v/v. It is clearly seen from the Figure 4 that the changes in the product composition with reaction time during the transesterification process. The conversion is maximum at 60 min. and there is only a slight acclivity in the graph. The efficient yield is obtained only at 60 min, as there are 95% of the triglycerides to the product. The extension of reaction time above 90 min. indicated that there is a decline in the yield. This is because of longer reaction time enhanced the hydrolysis of ester reverse transesterification), resulted in loss of esters as well as causing more fatty acids to form soap. From the graph it is clearly seen that the maximum ester content was obtained for neem.

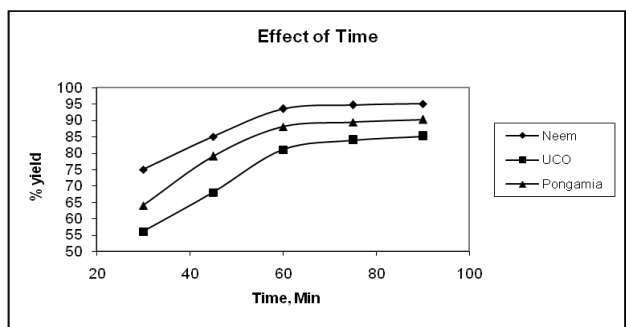


Figure 4 Effect of Reaction Time in the yield of Methyl esters for various oils Reaction temperature 60°C, Catalyst concentration 2.26%, and Methanol/Oil 0.2 v/v)

3.3 Effect of Reaction Temperature:

In order to study the effect of temperature on the formation of

Methyl esters, the following parameters were fixed via catalyst concentration 2.26%, reaction time 60 min., and methanol to oil ratio 0.2v/v for three different Oils respectively. The experiments were conducted at temperature ranging from 40 to 70 deg C at 10 deg C interval as shown in Figure 5. The results showed that the transesterification reaction increase with increase in temperature and after a certain range, it decreases greatly. The optimum temperature was found to be 60 deg C and thereafter the yield started decreasing the reason for this is that higher temperature accelerates the side saponification reaction of two triglycerides.

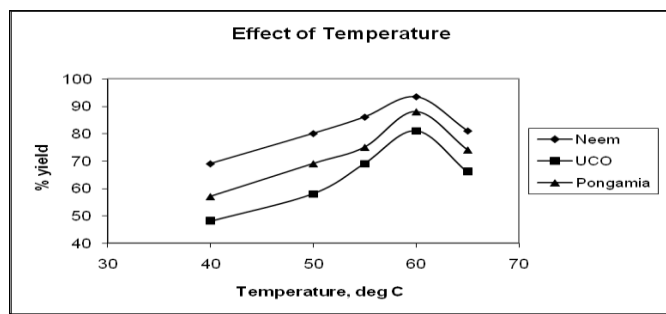


Figure 5 Effect of Reaction temperature in the yield of Methyl esters for various oils Methanol/Oil ratio 0.2v/v, Reaction time 60min, Catalyst Concentration 2.26%)

3.4 Effect of Methanol/Oil Ratio:

The effect of alcohol amount on the yield of transesterification experiments were conducted with different amounts of methanol oil ratio ranging from 0.1 to 0.3v/v. The optimized catalyzed concentration, reaction time, reaction temperature as obtained in the above sections was maintained. Maximum ester content was obtained at a ratio of 0.2 v/v. increasing the ratio above 0.2 had a very little effect on biodiesel yield. Further it was observed that for higher alcohol amount, the separation of ester layer from water layer becomes more difficult and required longer time. This is due to the fact that the hydroxyl group in the methanol can work as emulsifier which enhances emulsification.

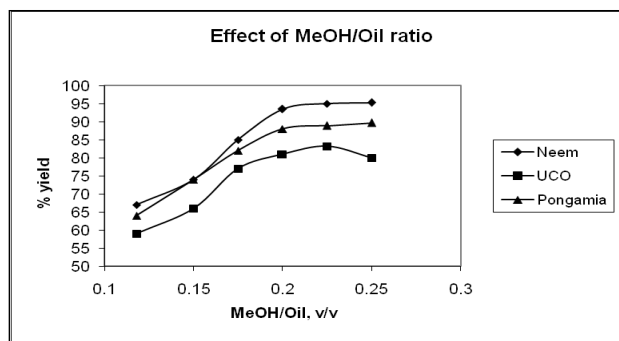


Figure 6 Effect of Methanol/Oil in the yield of Methyl esters for various oils Reaction temperature 60°C, Reaction time 60min, Catalyst Concentration 2.26%)

4. CONCLUSION

The study on the biodiesel production process optimization of edible and non-edible oils showed that the quantity of catalyst,

amount of methanol, reaction temperature and reaction time are the main factors affecting the production of methyl esters. The Optimal values of these parameters for achieving maximum conversion of oil to esters depended on the chemical and physical properties. The following conclusions are drawn from the study:

- Excess catalyst leads to the reduction of ester yield.
- There is an incomplete production process when the methanol/oil ratio is less than optimal value.
- Operating beyond the optimal value, the ester yield would not be increased but will result in additional cost for methanol recovery.
- Higher reaction temperature favours transesterification but beyond optimal level have negative impacts.
- Sufficient reaction time ensures complete conversion of triglycerides. But excess reaction time results in reverse transesterification.

The optimum conditions are established as follows: catalyst concentration 2.26%, Methanol to oil ratio 0.2 v/v, Reaction Temperature 60 deg C, Reaction time 60 min. With these optimum conditions, the yield was 93.5%, 88%, 81% for Neem, Pongamia, UCO respectively, and the fuel properties are within the limits prescribed by American standards of Biodiesel.

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