

# Optimization of Process Variables for the Production of Methyl Esters from Waste Cooking Oil

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**Abstract:** *The objective is to maximize the yield of the methyl ester from the waste cooking oil. Trials were made with reaction time, reaction temperature, catalyst concentration, and molar ratio as the process variables. After several iterations, for the particular waste cooking oil available, it is arrived that the reaction temperature is 55<sup>o</sup> C, reaction time 55 minutes, catalyst concentration of 7gm/liter of oil, and molar ratio of 6:1 for the yield to reach a maximum percentage of 95%.*

**Keywords:** Fatty acid compositions, Gas chromatography, Waste cooking oil methyl ester, yield.

## 1. Introduction

Numerous research and experiments were carried around the world to reduce the automotive tail pipe emissions especially diesel emissions such as HC, CO, CO<sub>2</sub>, NO<sub>x</sub>, smoke etc. To minimize these emissions methyl esters derived from vegetable oils known as biodiesel are the widely accepted alternative fuels [1]. In general biodiesel from plant oils possess improved properties like cetane number, latent heat, and 12% of oxygen in its molecular structure helps in improving combustion efficiency and these fuels are eco-friendly and helps in reducing the particulate matter (PM) emissions [2]. There are different feed stocks that are available for production of biodiesel. Some of there were palm, coconut, jatropha, cotton seed, Pongamia, linseed, coconut, sunflower and etc. However cultivation and processing costs of edible plants and vegetable oils are usually higher than petro-diesel. Therefore biodiesel from low cost feed stocks like animal fats and waste cooking oils can reduce the cost of biodiesel production [3]. Huge quantities of used cooking oils are disposed every day and some quantity of waste oil is used for manufacturing of soaps. In India 0.1 million tons per year of waste cooking is disposed where as in US 0.3, EU 0.7, UK 0.2 and Canada 0.13 million tons per year of waste oil was disposed [4-5]. This oil can be used in biodiesel production, which helps in reducing the cost as well as giving a solution to the environmental problems associated with their disposal. For conversion of raw oils to methyl esters transesterification is widely used method [6]. Raw vegetable oils can be used directly in the diesel engines as a fuel but due to high viscosity of the raw oils poor fuel injection and incomplete combustion occurs. To overcome the viscosity problem transesterification is used. In transesterification process alcohol reacts with vegetable oils in the presence of a catalyst and forms as methyl ester and glycerine as by-product. Literature [7-8] on biodiesel application reveals that biodiesel produced from renewable and often domestic

sources represents a more sustainable source of energy and will therefore play an increasing significant role in providing energy requirements for transportation. Particulate matter (PM) emissions of biodiesel are significantly reduced compared to neat diesel fuel operation, and the trend with PM emissions of biodiesel will be reduced due to lower aromatic and sulphur compounds and higher cetane number for biodiesel, but the more important factor is higher oxygen content.

In this paper an attempt was made in characterization of waste cooking oil into methyl esters, and presented various process parameters involved and their effect on methyl ester yield.

## 2. Materials used

Waste cooking oil (5 liters) was collected from local restaurant. Pure methanol (99.9% pure), Sodium hydroxide (NaOH) pellets were purchased from sigma aldrich chemicals limited. Royal scientific RSW 127 magnetic stirrer with hot plate of capacity 3 liters was used for stirring and maintaining the required temperatures.

## 3. Transesterification

Transesterification is a three step reversible reaction that converts the initial triglycerides into a mixture of fatty acid alkyl esters (FAAE) and glycerine, in the presence of a catalyst and alcohol. The fatty acid alkyl esters produced is known as biodiesel.

### 3.1 Process of transesterification for waste cooking oils

Waste cooking oil (WCO) of two litres was filtered with surgical cotton as shown in fig.1. to remove the food particles and other sediments that are present in the oil during their usage. For better yield of the methyl esters this pre filtration

has to be done with care otherwise any sediment in the WCO during the transesterification lead to soap formation. After filtering one litre of WCO was heated up to 110<sup>0</sup>C (fig.2) to remove any water content in the oil and it is analysed for basic properties like viscosity density and etc. In order to optimize the process for maximum yield the transesterification process was performed at variable catalyst concentration (gm/lit of oil), reaction time (min), temperature (<sup>0</sup>C) and methanol to oil molar ratio. From the iterative experimentations it is identified that the maximum yield occurs at the optimum conditions of 7 (gm/lit of oil) of catalyst concentration, reaction temperature of 55<sup>0</sup>C at a reaction time of 55 minutes and the molar ratio of 6:1. After the predetermined time of the reaction, the mixture was allowed to settle for over-night and there will be clear separation of methyl ester and glycerine will be appeared as shown in fig.3. The methyl ester was separated from the glycerine and water washing process with distil water was repeated until the clear separation of water and oil appears as shown in fig.5. The finally obtained methyl ester (Fig.6) was heated up to 110<sup>0</sup>C and it is preserved for properties test. The methyl esters were tested for fatty acid composition and elemental compounds by Chromatography and the results of the analysis are reported in table. 1 and 2. These properties are measured as per the ASTM standards are shown in the table 3. And table. 4 represent the comparison of obtained properties with standard diesel fuel.

**Table 1:** Fatty acid compositions of waste cooking oil methyl ester (WCOME)

S.No	Compound	Wt (%)
1	Linoleic acid	66
2	Oleic acid	0.5
3	Palmitic acid	26
4	Myristic acid	4
5	Caprylic acid	2.5
6	Remaining acids	1

**Table 2:** Elemental compounds of waste cooking oil methyl ester (WCOME)

S.No	Element	Wt (%)	Atomic (%)
1	Carbon	69.09	77.94
2	Nitrogen	6.13	5.93
3	Oxygen	13.04	10.93
4	Chromium	11.71	5.19
5	Cobalt	0.03	0.01

**Table 3:** Different properties and its International standards

S.No	Property	Standards
1	Calorific Value (kJ/kg)	ASTM-D2382
2	Viscosity (cSt)	ASTM-D445
3	Density (kg/m <sup>3</sup> )	ASTM-D1298
4	Flash Point ( <sup>0</sup> C)	ASTM-D93
5	Cloud Point ( <sup>0</sup> C)	ASTM-D3671
6	Pour Point ( <sup>0</sup> C)	ASTM-D97
7	Cetane Number	ASTM D 613

**Table 4:** Characterization of WCOME in comparison with standard diesel fuel

S.No	Property	Diesel Fuel	UCOME
1	Calorific Value (kJ/kg)	43000	38500
2	Viscosity (cSt)	2.8	3.9
3	Density (kg/m <sup>3</sup> )	830	875
4	Flash Point ( <sup>0</sup> C)	62	143
5	Cloud Point ( <sup>0</sup> C)	-15 to -5	-3 to 10
6	Pour Point ( <sup>0</sup> C)	-4	-5 to 7
7	Latent Heat (kJ/kg)	250	290
8	Cetane Number	47	55
9	Auto ignition temperature ( <sup>0</sup> C)	210	300



**Figure 1:** Filtering of raw WCOBD



**Figure 2:** Base Treatment



**Figure 3:** Glycerine separation



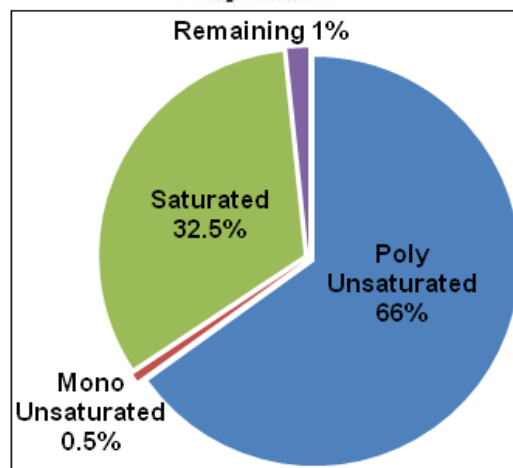
**Figure 4:** Water washing



**Figure 5:** Methyl ester and water separation



**Figure 6:** Final stage of WCOME



**Figure 7:** Pie chart representing the fatty acid composition of WCOBD

## 4. Results

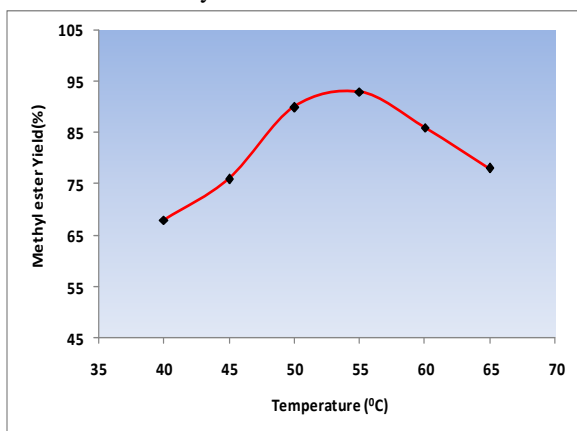
### 4.1 Effect of fatty acid compositions

Fatty acid compositions analysis is the important parameter to assess the biodiesel sustainability. For this purpose gas chromatography (Agilent 6890) was used. The obtained results are presented in Table.1. The results from the chromatography reveal that waste cooking biodiesel (WCOBD) possess poly unsaturated 66%, mono unsaturated 0.5% , saturated 32.5% and the others 1% as shown in the pie

diagram (Fig.7). The dominating fatty acids are Linoleic (66%), Palmitic (26%) followed by minor portions of Myristic (4%), Caprylic (2.5%), Oleic (0.5%) and 1% remaining acids. If the concentration of unsaturated fatty acid (Linoleic) is more in biodiesel it will not suitable as diesel engine fuel [9-10] due to high oxides of nitrogen emissions and low thermal efficiency. The indication of fatty acid compositions will play a dominating role in the indication of cetane number (CN) [11]. Despite the inherently relatively high CN of fatty compounds, NO<sub>x</sub> exhaust emissions usually increase slightly when operating a diesel engine on biodiesel [12]. The connection between structure of fatty esters and exhaust emissions was investigated by [13] studying the exhaust emissions caused by enriched fatty acid alkyl esters as fuel. NO<sub>x</sub> exhaust emissions reportedly increase with increasing unsaturation and decreasing chain length, which can also lead to a connection with the CN of these compounds [14].

#### 4.2 Effect of reaction temperature on yield.

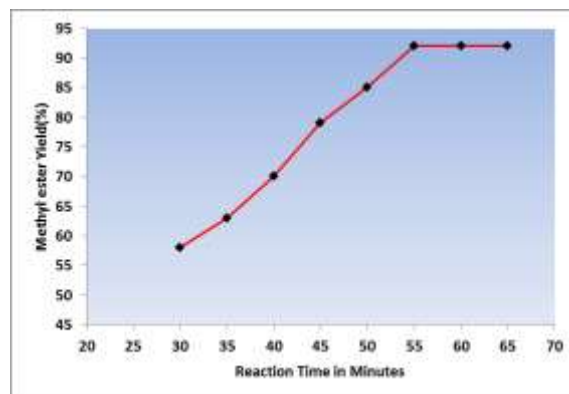
Fig. 8 represents the yield versus reaction temperature. From the figure it is clear that at 55°C there is a maximum waste cooking oil methyl ester yield. Other investigators [15-16] have achieved the maximum methyl ester yield between 50°C to 70°C. In general alcohols possess low boiling point, if the reaction temperatures exceed then the alcohol vaporize and form a large number of bubbles. In this experiment methanol is used as an alcohol and proper care was taken to minimize the loss of methanol by a reflux condenser.



**Figure 8:** WCOME Yield Verses Temperature

#### 4.3 Effect of Reaction Time on methyl ester yield

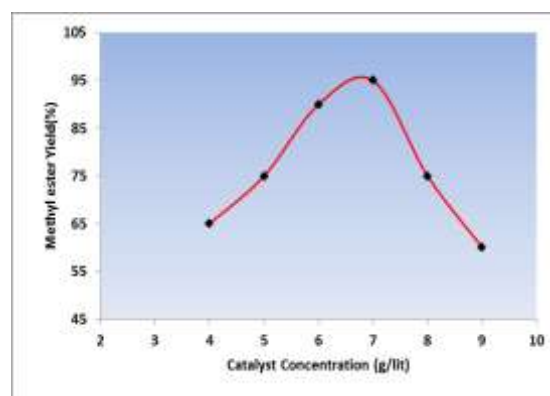
The effect of reaction time on the waste cooking oil methyl ester (WCOME) is shown in the Fig. 9. By the provision of uniform stirring there is a maximum yield of 92% when the reaction time is 55(min). And from the Fig. 9 it is clear that there is no observable change in the yield after the reaction time of 55(min). The reason for this is attainment of equilibrium reaction, and further increase of the time doesn't affect the methyl ester yield.



**Figure 9:** WCOME Yield Verses Reaction time

#### 4.4 Effect of catalyst concentration on methyl ester yield

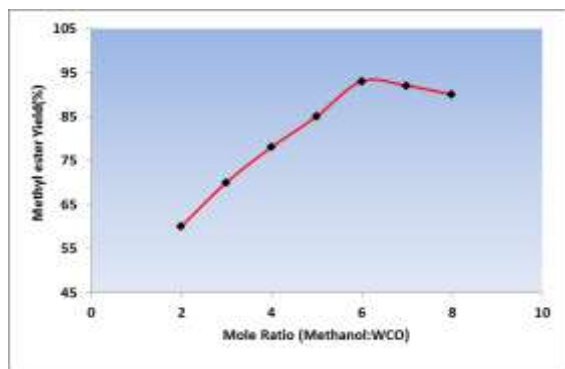
Sodium hydroxide (NaOH) was used as a catalyst. The effect of NaOH concentration was presented in the Fig. 10. Low concentration causes incomplete reaction where as high concentrations leads to soap formation and higher viscosity. Since for better yield this concentration was used in optimum. The maximum yield occurs at 7 gram/ litre of oil and yield gradually decrease when the catalyst concentration increases.



**Figure 10:** WCOME Yield Verses Catalyst concentration

#### 4.5 Effect of molar ratio on methyl ester yield

Molar ratio is an important factor that affects the biodiesel production cost, in this experimentation methanol was used as the alcohol. Theoretically, Stoichiometric molar ratio of alcohol to oil is 3:1, which can produce 3 moles of methyl esters and one mole of glycerine. Increase of molar ratio above stoichiometric ratio, has a positive effect on the methyl ester conversion up to 6:1, because the more concentration of alcohol accelerates the reaction and helps in the improvement of methyl ester yield. Fig. 11 represents the methyl ester yield to molar ratio and the maximum yield is at 6:1 molar ratio. If the molar ratio is above 6:1, causes a slight decrease of yield. Because the presence of excess alcohol may cause the reaction reversible and combines methyl esters formed to glycerine. The excess alcohol also creates a separation problem and requires more number of water washes.



**Figure 11: WCOME Yield Verses Mole ratio**

## 5. Conclusions

It has been concentrated on minimum of 92% of the methyl ester yield for which the iterations are made within the four parameters chosen. The optimum values of the parameters are listed below:

- 1) The optimum temperature is 55<sup>o</sup> C for the methyl ester yield of 93%.
- 2) The optimum time of reaction is 55 minutes for maximum yield of 92% of the biodiesel.
- 3) The catalyst concentration for the reasonable yield is 7gm/liter of oil. This resulted in a biodiesel of yield of 95%.
- 4) The molar ratio of alcohol to oil ratio is 6:1 for the best yield of 93% methyl ester.

For this process component design, the fatty acid component has been analyzed by chromatography and various fatty acid percentages are presented.

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