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Production of Bio-Diesel from Waste Cooking Oil

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Abstract
Waste cooking oils (WCO), which contain large amounts of free fatty acids produced in restaurants, are collected by the environmental protection agency in many parts of the world and should be disposed in a suitable way. Due to the high cost of the fresh vegetable oil, waste cooking oil attracted researcher to produce bio-diesel from waste cooking oil because it is available with relatively cheap price. In this research paper, the Transesterification of waste cooking oil with methanol as well as the main uses of the fatty acid methyl esters is reviewed. The cooking oil was transesterified with methanol using potassium hydroxide as catalyst to obtain bio-diesel by Mechanical Stirrer production technique was carried out. Results which obtained are significantly comparable to pure diesel and gives better performance than conventional diesel fuel.

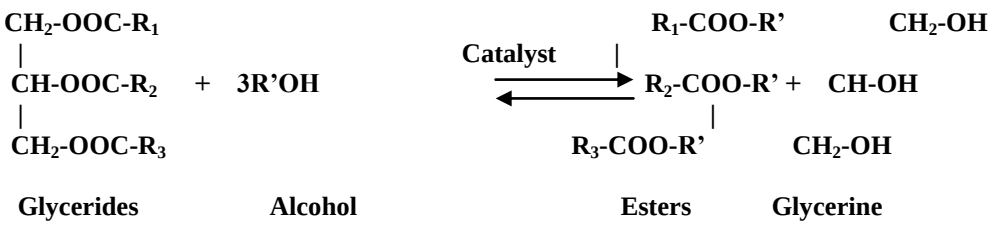
Keywords: Bio-diesel, Waste Cooking oil, Transesterification process, Mechanical stirrer technique.

I. Introduction

The major part of all energy consumed worldwide comes from fossil fuel sources, which are petroleum, coal and natural gas. They are important energy resources in heating, transportation, power generation, and agricultural and industrial sectors. Their utilization has been continuously increased, which accelerates the depletion of limited petroleum reserve and unavoidably increases petroleum prices. However, known fossil energy sources have been exhausted rapidly in recent years. The fossil fuel resources are shortening day by day. Thus, looking for alternative sources of new and renewable energy such as hydropower, biomass, wind, solar, geothermal, hydrogen and nuclear is of vital importance. Alternative new and renewable fuels have the potential to solve many of the current social problems and concerns, from air pollution and global warming to other environmental improvements and sustainability issues. It is urgent to find alternative fuels, especially the fuels for gasoline and diesel engines, in order to prolong the petroleum reserves. The alternative fuel to petroleum based fuel must be technically feasible, economically competitive, environmentally acceptable and readily available.

II. Production of Bio-diesel by Transesterification Process

Transesterification is the process of separating the fatty acids from glycerol to form fatty acid esters and free glycerol. Fatty acid esters commonly known as bio-diesel can be produced in batches or continuously by transesterifying triglycerides such as animal fat or vegetable oil with lower molecular weight alcohols in the presence of a base or an acid catalyst. This reaction occurs stepwise, with monoglycerides and diglycerides as intermediate products.The "R" groups are the fatty acids, which are usually 12 to 22 carbons in length. The large vegetable oil molecule is reduced to about 1/3 of its original size, lowering the viscosity making it similar to diesel fuel. The resulting fuel operates similar to diesel fuel in an engine.



Where, term R' represents different alkyl groups.

The process of transesterification brings about drastic change in viscosity of vegetable oil. The bio-diesel thus produced by this process is totally

miscible with mineral diesel in any proportion. Bio-diesel viscosity comes very close to that of mineral diesel hence no problems in the existing fuel handling system. Flash point of the bio-diesel gets lowered after esterification and the Cetane number gets improved. Even lower concentrations of bio-diesel act as Cetane number improver for bio-diesel blend. Calorific value of bio-diesel is also found to be very close to mineral diesel.

The overall process is normally a sequence of three consecutive steps, which are reversible reactions. In the first step from triglycerides, diglycerides are obtained. From diglyceride, monoglyceride is produced and in the last step from monoglycerides, glycerine is obtained. In all these reactions esters are produced. The stoichiometric relation between alcohol and the oil is 3:1. However, an excess of alcohol is usually more appropriate to improve the reaction towards the desired product**.**

$$\text{Triglycerides} + R'OH \rightleftharpoons \text{Diglycerides} + R'COOR_1$$

$$\text{Diglycerides} + R'OH \rightleftharpoons \text{Monoglycerides} + R'COOR_2$$

$$\text{Monoglycerides} + R'OH \rightleftharpoons \text{Glycerine} + R'COOR_3$$

III. Experimental Work for Bio-diesel Production Materials

WCO containing 2.14 wt% FFA was collected from local restaurant. Methanol (CH_3OH) and potassium hydroxide (KOH) were used as reacting agent and catalyst respectively during the transesterification process.

Bio-diesel Processes
Process Flow Chart

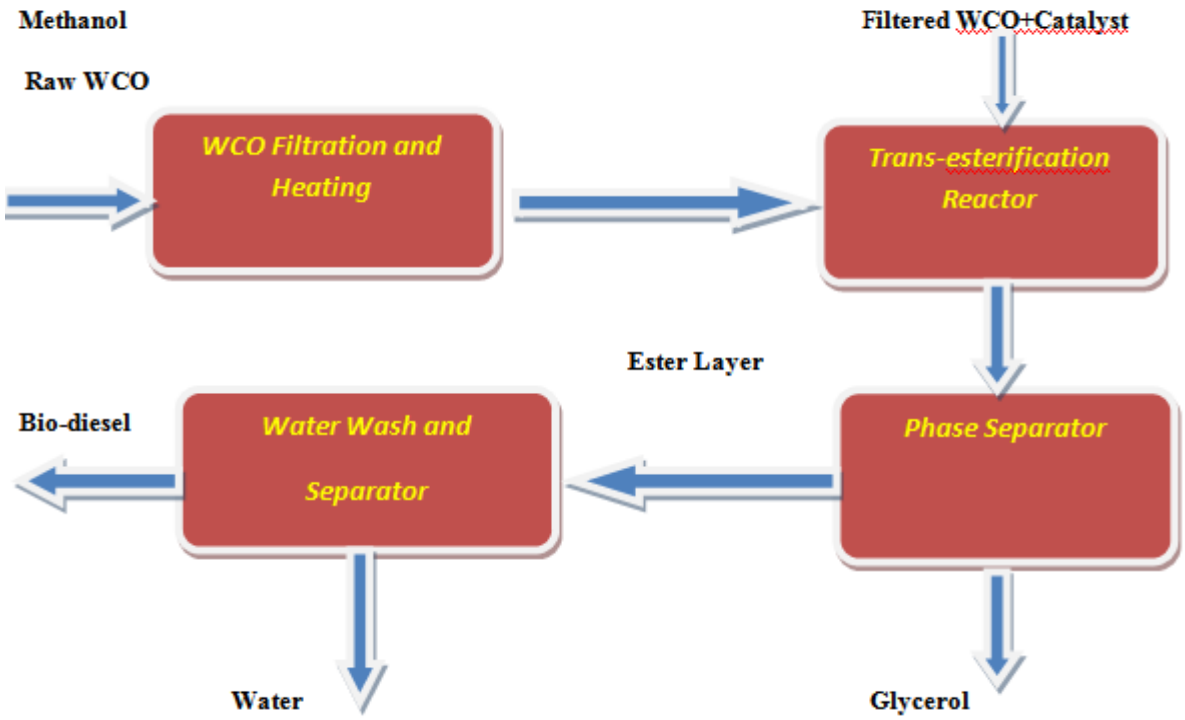


Figure 1. Bio-diesel Manufacturing Flow Sheet from Waste Cooking Oil (WCO).

Process Details
Filtration and Heating of Raw WCO

Non-oil components of the WCO were removed by separation using filter and moisture was removed by heating the oil at about 120^{o}C for 30 to 45 minutes. Heating with electric heater is usually the easiest way to bring the oil up to required temperature.

Determination of FFA

In order to determine the percent of FFA in the oil, a process called titration is used. The vegetable oil is first mixed with methanol. Next, a mixture of Sodium Hydroxide (NaOH) and water is added until all of the FFA has been reacted. This is confirmed by checking

the pH of the mixture. A pH of about 9 signifies all of the FFA has been reacted.

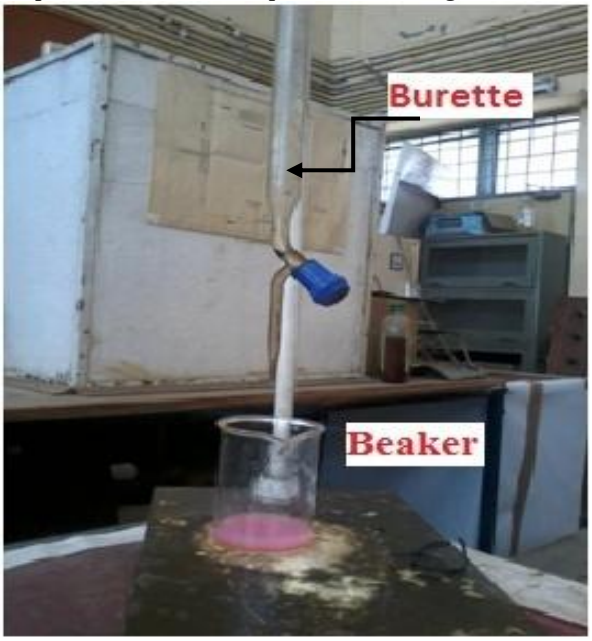


Figure 2.Determination of FFA

Figure 3.Alcohol and WCO mixture

One gram of NaOH was dissolved in 1 litre of distilled water (0.1%NaOH) solution. Phenolphthalein solution was used to get the end point. In a smaller beaker, 1ml of WCO oil is dissolved in 10ml of methanol. The mixture was stirred gently until all the oil dissolves in the alcohol and the mixture turns clear. Two to three drops of phenolphthalein solution was added. Using a burette, 0.1% NaOH solution was added drop by drop to the oil alcohol phenolphthalein solution, stirring all the time, until the solution stays pink. The number of ml of 0.1% NaOH solution gives the amount of NaOH to be used per litre of oil and FFA percentage.

Table 1.FFA information

ml titration	%FFA	NaOH (grams) per gallon
0	0	13.25
0.5	0.3578222	15.15
1	0.7156445	17.025
1.5	1.0734667	18.925
2	1.431289	20.825
2.5	1.7891112	22.7
3	2.1469334	24.6
3.5	2.5047557	26.5
4	2.8625779	28.3875
4.5	3.2204002	30.28
5	3.5782224	32.1725

Mixing of Methanol and Catalyst

The purpose of mixing methanol and the catalyst (NaOH) is to react the two substances to form Methoxide. The amount of Methanol used should be 20% of the volume of the oil. Methanol and KOH are dangerous chemicals by themselves, with Methoxide even more so. None of these substances should ever touch skin. Vapours should not be inhaled. Gloves and ventilation are required at all times when working with these substances.

Transesterification (bio-diesel reaction)

The methanol in excess is added to the oil in a beaker serving as a batch reactor. The mixture is then agitated for about 60 to 90 minutes and then left overnight for phase separation to take place due to gravity.

Draining of Glycerol

After the transesterification reaction, one must wait for the glycerol to settle to the bottom of the container. This happens because Glycerol is heavier then bio-diesel. The settling will begin immediately, but the mixture should be left for minimum of 8 hours to 12 hours.

Washing of Bio-diesel

The purpose of washing is to wash out the remnants of the catalyst and other impurities. Generally water washing is preferred in which lukewarm water (about one third of raw bio-diesel) is added to raw bio-diesel, stirred for a short duration and then impurities are allowed to settle down at bottom with water.

Bio-diesel Production Technology

This section contains the details of bio-diesel production methodology which is used in the present work like mechanical stirring.

Mechanical Stirring

In this method, mixing of WCO and methanol is done in a tank equipped with mechanical stirrer as shown in fig 5. An electric motor is used to rotate the shaft around which blades are provided to stir the mixture of immiscible liquids (oil and alcohol are not miscible with each other), as shaft starts rotating a turbulence is created which disrupt the phase boundary between two immiscible liquid and thus resulted in proper mixing. Temperature is measured with the help of a thermometer and kept in the range of the 60-65 °C.

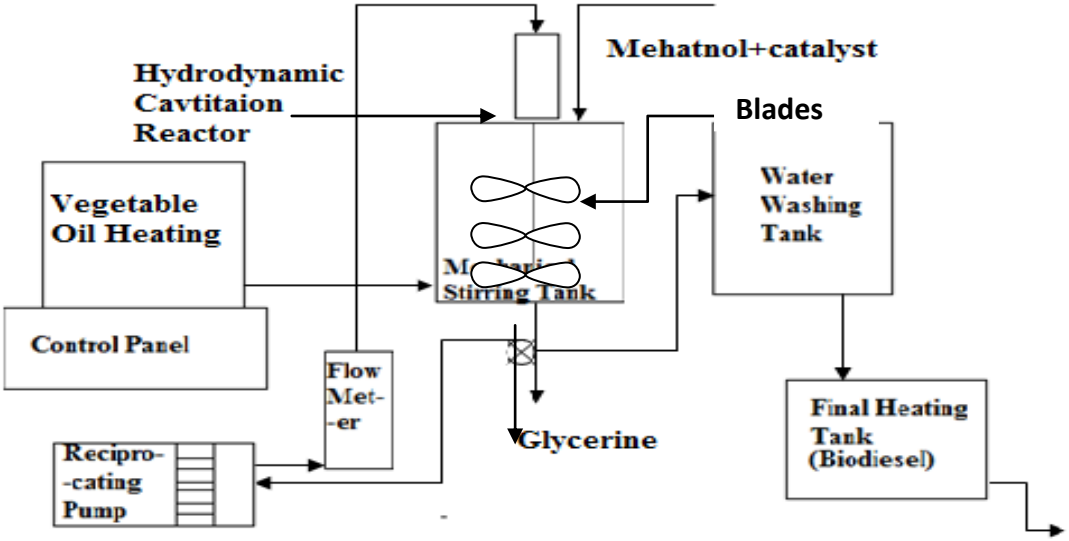


Figure 4.Schematic representation of bio-diesel reactor

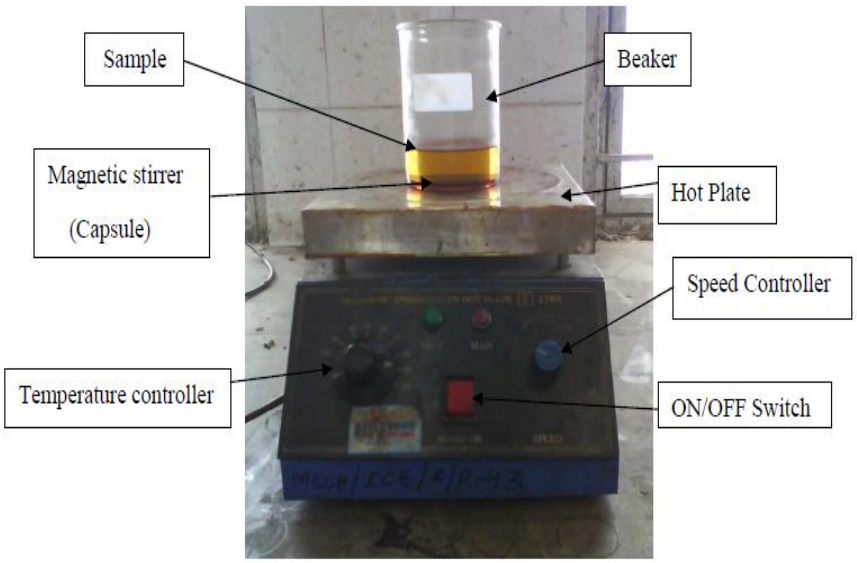


Figure 5.Experimental set-up of bio-diesel reactor with mechanical stirrer

IV. Reagents and materials used for experiment

1. Waste cooking oil for preparing bio-diesel.
2. Methyl alcohol (CH_3OH).
3. Base catalyst (KOH) for accelerating the reaction mixture.

Experiments Performed

This experiment has been performed to evaluate performance of mechanical stirring method of bio-diesel production in terms of yield (%).Experiment has been performed with the following steps:

1. Waste cooking oil (8 kg) is filtered and then heated to 65^{o}C and kept at this temp for about 05 min to remove impurities and moisture. This reduces the probability of soap formation during the tranesterification reaction because the reaction of transesterification and soap formation is same. The basic difference is that there are requirement

of preheating is very important in case of transesterification as compared to soap formation. The sample is then cooled to room temperature.

2. Methyl alcohol (CH3OH) is taken with a molar ratio of (1:4.5 & 1:6) and Catalyst (KOH) is taken as (0.75% and 1% by wt of oil).The mixture of methyl alcohol and KOH is stirred until KOH dissolve in methyl alcohol.
3. Now the WCO and mixture of methanol and catalyst are put together into the Beaker and mechanical stirring is applied. The methanol is immiscible with the oil.
4. A magnetic capsule is dipped in the mixture of oil, methanol and catalyst and rotated with the help of magnetic stirrer and mechanical stirring is applied for about10 minutes -30 minutes and more.
5. During the reaction the temperature of mixture is kept in between 60-65^{0}C.
6. While reaction taking place five samples are drawn each of 100 gm at a time interval of 35 min, 50 min, 65 min, 80 min and 95 min.
7. Samples are then allowed for phase separation of methyl ester and glycerol in separating flasks as shown in Figure 6.Fatty acid has higher specific weight therefore it will settle at bottom. Separation of methyl ester and glycerol will take 8 to 12 hr duration.
8. After complete separation bio-diesel (methyl Ester) is visible in the upper layer and glycerol at the bottom.
9. Bio-diesel is then separated from beaker for purification process and water washed. The catalyst present in the methyl ester is impurity.
10. Excess methanol present in bio-diesel has been removed by vaporization process.
11. To remove impurities and catalyst, water at around 40-50 ^{0}C is mixed with the methyl ester and left for settling down. Water due to its higher specific gravity collected at bottom. This is shown in Figure 7.
12. Excess water is removed by heating the bio-diesel up to 100^{0}C.

Figure 6: Glycerol separation process

Figure 7: Water washing process of bio-diesel

V. Experimental Results

The experiments are performed with alcohol to oil molar ratio as 6:1 and 4.5:1. The amount of oil, alcohol and catalyst taken is shown in Table 2.

Table 2.WCO, methanol and catalyst during the experiment

Molar ratio (methanol/oil)	Quantity of waste cooking oil (g)	Quantity of methanol (g)	Catalyst consumed (KOH)	
			0.75 % (Wt %)	1.0 % (Wt %)
6:1	8000	1765	60 g	80 g
4.5:1	8000	1324	60 g	80 g

➢ For calculation of molar ratio following data are used

Molecular weight of triglycerides from waste cooking oil = 870 g/mole

Molecular weight of methanol = 32

Hence, 1 gm mole of waste cooking oil = 870 g

And 1 gm mole of methanol = 32 g

Catalyst (KOH) = 0.75% and 1% by weight of oil

➢ Amount of methanol for 8000g of WCO

- For 1:6 molar ratio = (32 / 870) ×8000 × 6 = 1765.51 g
- 1:4.5 molar ratio = (32 / 870) ×8000 × 4.5 = 1324.13 g

➢ Sample Calculation for yield

- Quantity of WCO taken = 100 g
- Quantity of bio-diesel produced = 90 g (say)
- Yield % = (Quantity of bio-diesel produced/Quantity of oil taken)*100 = (90/100)*100= 90%

➢ Experimental Data for Mechanical Stirring Method

Time and yield of bio-diesel from waste cooking oil for corresponding molar ratio and catalyst (%) are shown in the table 3.

Table 3.Time and yield (%) of waste cooking oil for different molar ratio and catalyst percentage

Percentage of catalyst	Molar ratio 6:1		Molar ratio 4.5:1	
	Time (min)	Yield %	Time (min)	Yield %
0.75	35	76.85	35	72.45
	50	81.05	50	77.71
	65	88.46	65	86.05
	80	90.5	80	86.72
	95	91.40	95	87.49
1.0	35	81.95	35	74.95
	50	86.05	50	80.29
	65	91.71	65	87.95
	80	92.67	80	89.28
	95	93.11	95	89.57

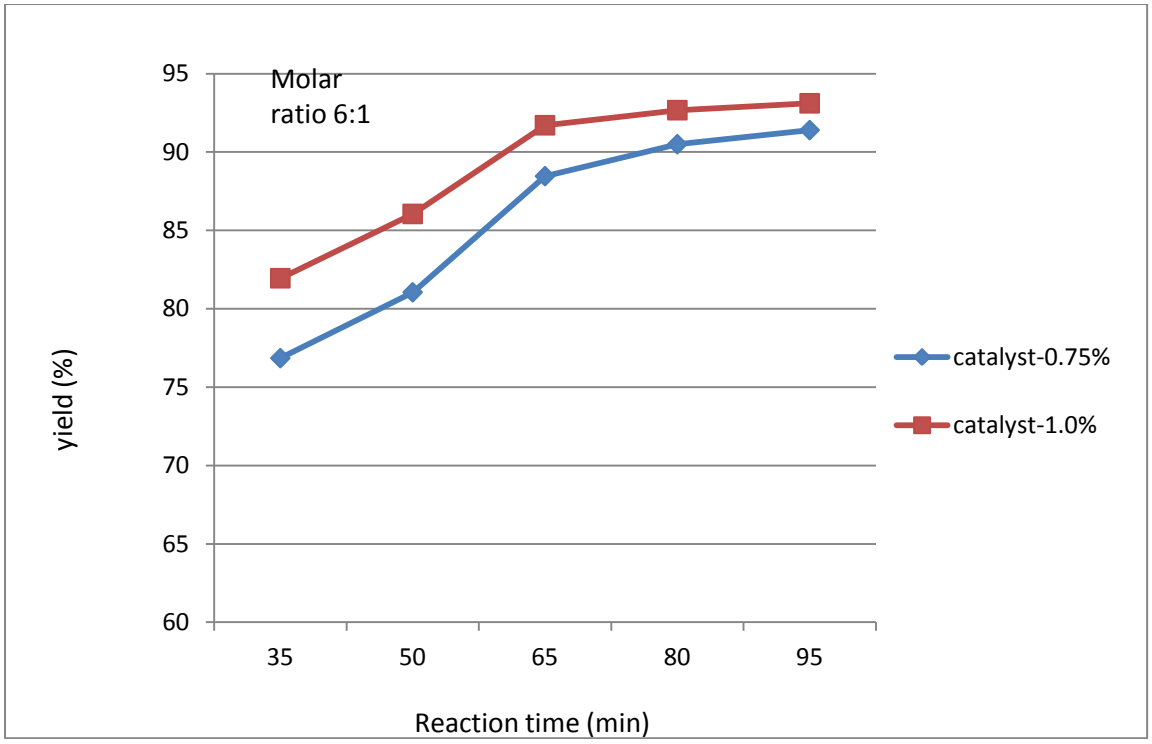


Figure 8.Time v/s Yield (%) for molar ratio 6:1 and different catalyst percentage

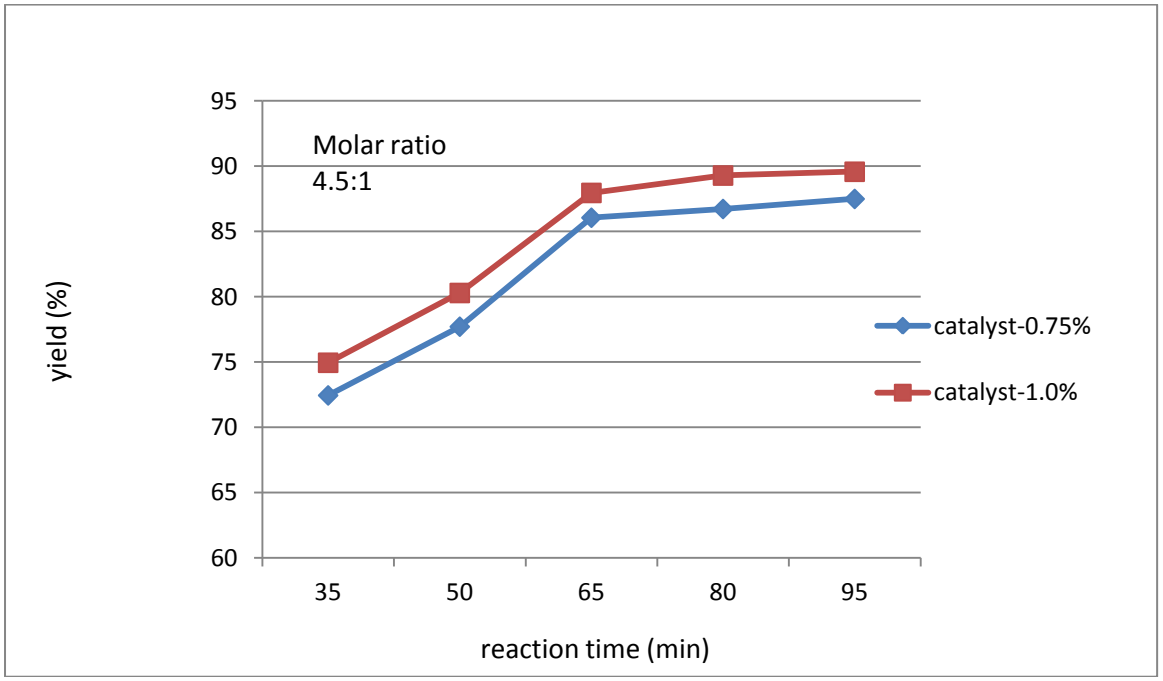


Figure 9.Time v/s Yield (%) for molar ratio 4.5:1 and different catalyst percentage

VI. Conclusion

The important conclusions are as follows: As shown in figures 8 and 9,

1) It is found that in mechanical stirring the yield obtained at 1% KOH is higher as compare to 0.75% KOH.

2) Bio-diesel yield increases as reaction time increases and eventually it becomes slight constant after 80 min of reaction time.

3) The yield is more for molar ratio 6:1 and 1 % catalyst (max value is 93.11%) as compared to molar ratio 4.5:1 and 0.75% catalyst (max value is 91.40%).

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