Project Report for Major

An experimental analysis of solar assisted bio diesel production from cotton seed oil

Submitted in the partial fulfilment of the requirement for the award of degree of

Master of Technology
In
Renewable Energy Technology

Submitted by:

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DECLARATION

I, hereby declare that the project entitled "**An experimental analysis of solar assisted production of bio diesel from cotton seed oil**" being submitted by me, is an authentic work carried out under the supervision of **Prof. R.S. Mishra**, head of the department and **Dr. Amit Pal** Associate Professor, Mechanical Engineering Department, Delhi Technological University, Delhi. This is also declared that this dissertation has not been submitted to any other Institute/University for the award of any degree or diploma.

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CERTIFICATE

This is to certify that the dissertation entitled "**An experimental analysis of solar assisted production of bio diesel from cotton seed oil**" submitted by **Ms. MANISHA (2K14/RET/10)** in partial fulfilment for the award of the Degree of Master of Engineering in Renewable Energy Technology of Delhi Technological University, Delhi, is an authentic record of student's own work carried out by her under our guidance and supervision.

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It is said that gratitude is a virtue. This part is dedicated to special thanks that I would like to deliver to the people who helped me in making the fulfilment of this project possible.

I take great pride in expressing my genuine appreciation and gratitude to my learned mentor **Prof. R.S. Mishra**, Head of the department and **Dr. Amit Pal,** Associate professor Department of Mechanical Engineering, for their invaluable inspiration, guidance and continuous encouragement throughout this project work. Their suggestions on my experiments have always guided me towards perfection. This work is simply the reflection of their thoughts, ideas, concepts and above all their efforts. Working under their guidance has been a privilege and an excellent learning experience that I will cherish for a long time.

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ABSTRACT

Due to the depletion of fossil fuel energy sources, new alternative energy sources are becoming dominant in our society. Biodiesel has been recognized as an alternative for depleting petro-fuels since it is produced mainly from edible and non-edible oils, is a clean, renewable resource, and is non-toxic. Transesterification is the most commonly used process for synthesis of biodiesel. The synthesis of biodiesel involves heating a triglyceride with methanol in presence of catalyst. In this project, Biodiesel was produced by using cotton seed oil and potassium hydroxide (KOH) as catalyst.

The conversion yield was maximized using Taguchi's method of optimization. This method was adequate for calculating the effect of control parameters and it also optimizes the experiment work with limited number of experiments. After performing conventional method of biodiesel production, solar assisted transesterification was used in which thermal energy of solar irradiation was utilized for chemical heating process in biodiesel synthesis. A small parabolic solar reflector was used for utilizing solar energy.

At last, Results were compared for both conventional and solar-assisted method of biodiesel production. It was concluded that the quality and conversion yield of biodiesel produced from solar-assisted method is better even when there is no requirement of mechanical stirring in this method.

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List of Abbreviations used

ANOVA -	Analysis of variance
ASTM -	American Society for Testing and Materials
CR -	Concentration ratio
CSO -	Cotton seed oil
CSOME -	Cotton seed oil methyl ester
DNI -	Direct normal irradiation
DPATs-	Diphenyl ammonium tosylate
DPABs-	Diphenyl ammonium benzenesulfonate
DPAMs-	Diphenyl ammonium mesylate
DPACs-	Diphenyl ammonium chloride
FAME -	Fatty acid methyl ester
FFA -	Free fatty acids
MSD -	Mean square deviation
SNR -	Signal to Noise ratio
SS -	Square of sum
WCO-	Waste cooking oil
CJCO-	Crude jatropha curcas seed oil
GWh-	Giga watt hour
DOE-	Design of experiments

List of Symbols

ϑ – Kinematic viscosity

t - Time

H_c - Heat of combustion of the fuel sample (kJ/kg)

W_c - Water equivalent of calorimeter assembly

M_S - Mass of sample burnt (kg/s)

ΔT - Rise in Temperature

Q_u - Heat energy falling on the absorber plate at focal point

Φ_{rim} - Rim angle of parabolic reflector

d - Aperture diameter of reflector

f - Focal length of reflector

h - Depth of parabolic reflector

S - Arc length

η - Efficiency of heating process from reflector

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Chapter 1

Introduction

Due to depletion of petroleum reserves and environmental pollution, there is need to develop alternative fuels for automotive engines. Biodiesel which is a clean renewable fuel, can be considered as the best substitution of petro-fuels. This chapter describes the need of biodiesel and discusses the motivation and objectives for the necessity of biodiesel production.

1.1 Energy Crisis

The role of energy and energy sources is quite significant for the development of a country. Industrial development over the years and population growth has led to a vast increase in the global demand of energy. Improper utilizations of energy resources over the past years have also created serious issue of energy crisis in the upcoming time. According to the Energy Statistics Report 2015 (released by Ministry of Statistics and Program Implementation), the consumption of crude oil and electricity is increased by a bigger margin. It can be seen from following table 1.1 that need of energy sources is increasing day by day and this has resulted in energy crisis i.e. the availability of conventional energy sources is not adequately meeting the global demand of the energy. The consumption of electricity and crude oil has increased So there is a need to develop unconventional and renewable sources of energy such as solar energy, wind energy, Bioenergy and Biofuels, Tidal power etc. [1]:

Table 1.1- Trends in Consumption of Conventional Energy Sources in India [1]

Year	Coal (Million Tons)	Lignite (Million Tons)	Crude Oil (MMT)	Natural Gas (Billion Cubic Meters)	Electricity (GWh)
2005-06	407.04	30.23	130.11	31.33	411,887
2006-07	430.83	31.29	146.55	30.79	455,748
2007-08	457.08	33.98	156.10	31.48	510,899
2008-09	492.76	32.42	160.77	31.75	562,888
2009-10	532.04	34.07	192.77	46.52	620,251
2010-11	532.69	37.73	196.99	51.25	684,324
2011-12	535.88	41.88	204.12	46.48	755,847
2012-13	567.60	46.31	219.21	39.78	912,057
2013-14	571.89	43.90	222.50	34.64	967,150
Compound annual growth rate (CAGR) 2005-06 to 2013-14(%)	**3.85**	**4.23**	**6.14**	**1.12**	**9.95**

1.2 Energy Scenario

Energy has undergone through a broad advancement from a general field of technologies. It is also an important issue in economic planning and international relations. Global demand for energy is continuously rising due to increased levels of activity as the world economy is growing. In India, Coal contributes to 55% of the primary energy production. India is counted as fourth largest producer of lignite and coal in the world. At least 84,396 million tonnes of proven recoverable coal reserves are found in India which is approximately 8.6% of the world reserve. In the current scenario, the share of oil is about 36% of India's total energy consumption. The annual crude oil production of India is about 32 million tonnes as against the present peak demand of about 110 million tonnes. There has also been a considerable increase in the share of natural gas in primary energy production. The current demand of natural gas is about 96 million cubic meters per day which is much higher than the availability (67 million cubic meters per day). Natural gas accounts for approximately 8.9% of India's energy consumption [2].

The difference between primary energy consumption and the losses that takes place in transportation, transmission, refinement and distribution is termed as final energy consumption which is the actual energy demand at the user end. The actual final energy consumption is shown in following table 1.2. The demand from oil products and electricity is increasing drastically if compare with demand of other commercial energy sources. In case of oil products, the demand is increased from 63.55 million tonnes since 1994-95 to 271.23 million tonnes at present. From these data it can be concluded that there is a need to develop alternative fuels which could replace oil products and petro-fuels in automotive engines.

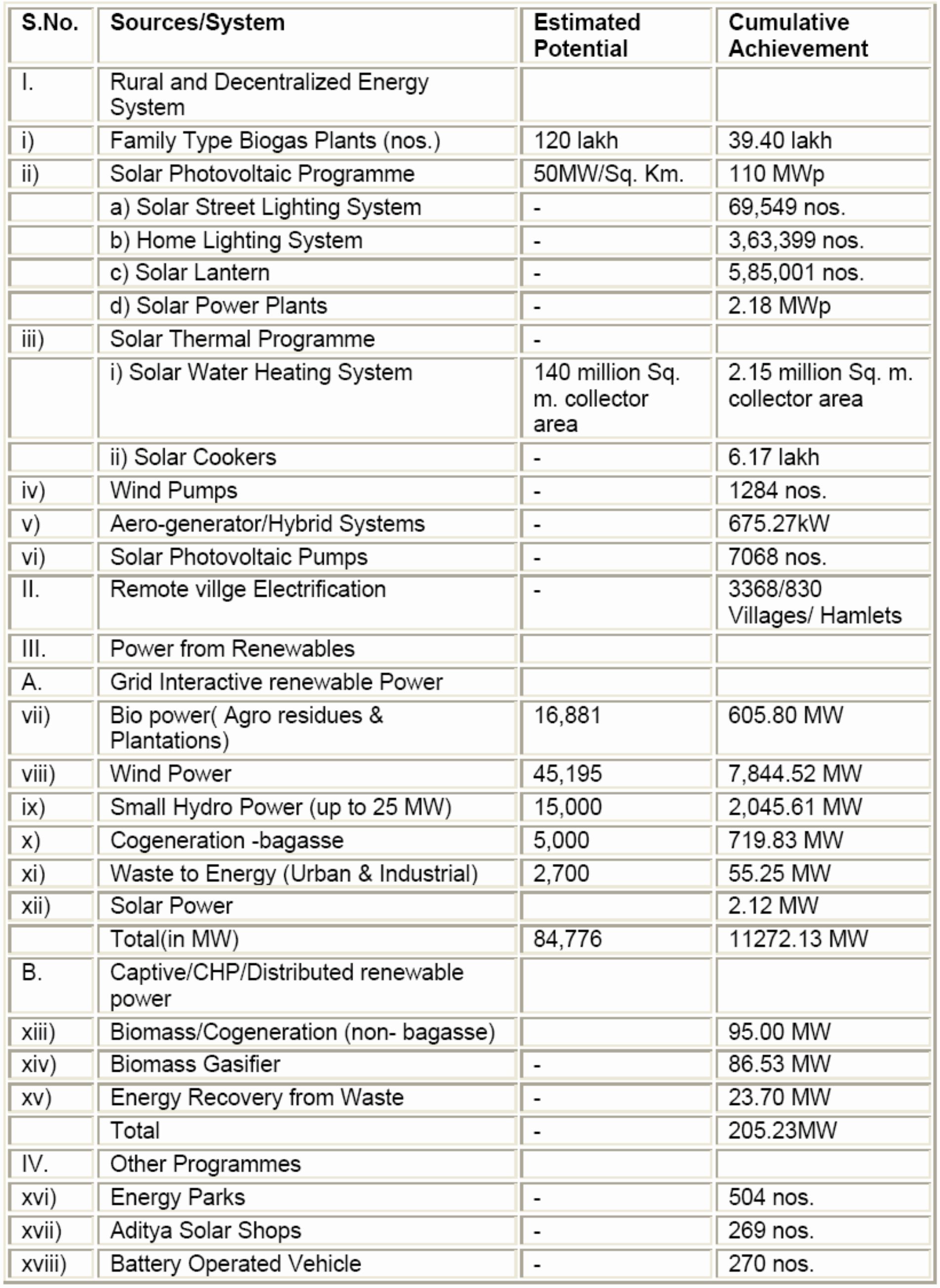
Table 1.2- Demand for commercial energy for final consumption [2]

Source	Units	1994-95	2001-02	2006-07	2011-12	2015-16
Electricity	Billion units	289.36	480.08	712.67	1067.88	1423.53
Coal	Million Tonnes	76.67	109.01	134.99	173.47	203.44
Lignite	Million Tonnes	4.85	11.69	16.02	19.70	22.25
Natural Gas	Million Cubic Meters	9880	15730	18291	20853	23726
Oil Products	Million Tonnes	63.55	99.89	139.95	196.47	271.23

1.3 Renewable Energy Sources

Present energy scenario and depletion of conventional energy sources have led to the development of renewable energy sources such as solar energy, wind energy, biofuels and bioenergy and geothermal energy etc. Renewable Energy Potential and Achievements in India are tabulated as follow:-

Table 1.3- Potential and achievement of renewable energy sources in India [3]



S.No.	Sources/System	Estimated Potential	Cumulative Achievement
I.	Rural and Decentralized Energy System		
i)	Family Type Biogas Plants (nos.)	120 lakh	39.40 lakh
ii)	Solar Photovoltaic Programme	50MW/Sq. Km.	110 MWp
	a) Solar Street Lighting System	-	69,549 nos.
	b) Home Lighting System	-	3,63,399 nos.
	c) Solar Lantern	-	5,85,001 nos.
	d) Solar Power Plants	-	2.18 MWp
iii)	Solar Thermal Programme	-	
	i) Solar Water Heating System	140 million Sq. m. collector area	2.15 million Sq. m. collector area
	ii) Solar Cookers	-	6.17 lakh
iv)	Wind Pumps	-	1284 nos.
v)	Aero-generator/Hybrid Systems	-	675.27kW
vi)	Solar Photovoltaic Pumps	-	7068 nos.
II.	Remote villge Electrification	-	3368/830 Villages/ Hamlets
III.	Power from Renewables		
A.	Grid Interactive renewable Power		
vii)	Bio power(Agro residues & Plantations)	16,881	605.80 MW
viii)	Wind Power	45,195	7,844.52 MW
ix)	Small Hydro Power (up to 25 MW)	15,000	2,045.61 MW
x)	Cogeneration -bagasse	5,000	719.83 MW
xi)	Waste to Energy (Urban & Industrial)	2,700	55.25 MW
xii)	Solar Power		2.12 MW
	Total(in MW)	84,776	11272.13 MW
B.	Captive/CHP/Distributed renewable power		
xiii)	Biomass/Cogeneration (non- bagasse)		95.00 MW
xiv)	Biomass Gasifier	-	86.53 MW
xv)	Energy Recovery from Waste	-	23.70 MW
	Total	-	205.23MW
IV.	Other Programmes		
xvi)	Energy Parks	-	504 nos.
xvii)	Aditya Solar Shops	-	269 nos.
xviii)	Battery Operated Vehicle	-	270 nos.

The table 1.3 shows that a considerable amount of energy can be produced from unconventional and renewable sources. Renewable energy sources can stand as alternative source of energy in the near future due to its greater scope and possibilities in India and worldwide. The renewable energy could be a better option when more than one technologies are incorporated such as hybrid solar-biomass technology, Cogeneration power plant, Combined solar thermal polygeneration system etc.

1.4 Need for Biofuels and Biodiesel

From Energy scenario it is clear that more dependency of modern society on fossil fuels may result in the depletion of fossil fuels in the next sixty years. It is well known fact that fossil fuel constitute a finite resource, so biofuel can be an alternative source for energy in place of petroleum fossil fuels. Biofuels are generally organic combustibles derived from biomass. These are mainly used for combustion to produce heat for industrial processes, electricity generation and heat engine carburation in IC engines. Edible and Non-edible different kinds of crops used as feedstock material for biofuel. Bioethanol and butanol are produced by fermentation of starch or sugars while biodiesel is produced by transesterification of oil seed crops. In the present scenario, although petroleum-based fuels can’t be entirely replaced by biodiesel, there are various advantages of biodiesel over diesel fuel. It is biodegradable and more than 90% biodiesel can be biodegraded within 21 days. Cetane number and combustions efficiency are higher for biodiesel than in case of diesel fuel. The Sulfur and aromatic content is lower in case of biodiesel i.e. use of biodiesel for combustion process in engines does not produce toxic emission gases. Additionally, it reduces most exhaust emissions such as monoxide, unburned hydrocarbons, and particulate matter except oxides of nitrogen (NO_x) [4]. So biodiesel can provide an alternative solution to avoid the problems of petro-fuel crisis and environmental degradation.

1.5 Various Feedstocks for biodiesel production

At present, more than 300 biodiesel-feedstock have been identified. Biodiesel can be produced from both edible and non-edible oil-seeds. Edible oils such as soybean, rapeseed, Sunflower, palm, peanut, corn, cotton seed, camelina, pumpkin, canola etc. can be used as feedstock for biodiesel production and in case of non-edible oil crops jatropha curcas, pongamina pinnata, sea mango, palanga, karang, tallow, nile tilapia, poultry etc. are mainly used. Recently non-conventional feedstock (algae, fungi, microalgae etc.) for biodiesel are becoming area of interest. Various conventional and non-conventional feedstock, used for the production of biodiesel, are shown in Table 4. These include edible oils, non-edible oils, wild oils, waste cooking oils, animal fats and non-conventional feedstocks [5]. The most commonly used biodiesel feedstock in India are jatropha and waste cooking oil.

Table 1.4 – Conventional and Non-conventional feedstock for biodiesel [6]

Edible Oils	Non-edible oils	Animal Fats	Other resources
Soybeans	Almond	Lard	Bacteria
Rapeseed	Babassu	Fish Oil	Algae
Canola	Brassica carinata	Tallow	Fungi
Safflower	Camelina	Poultry Fat	Micro algae
Barely	Cynara		Tarpenes
Coconut	Jatropha Curcus		Latexes
Copra	Jatropha nana		Cooking oil (yellow grease)
Cotton Seed	Jojoba oil		Microalgae (Chlorella vulgaris)
Ground nut	Pongamia glabra		
Oat	Laurel		
Rice	Lesquerella		
Sorghum	Mahua		
Wheat	Palm		
Winter rapeseed oil	Karang		
	Tobacco seed		
	Rice bran		
	Sesame		

In India, main source of biodiesel is non-edible oil. Non-edible oils obtained from plants which can be grown on waste lands are more suitable. Minor oils like Karang (Pongamia), Neem and Jatropha should be promoted as raw materials for the availability of Triglyceride. Most of the non-edible oils available in India contains high FFA (2-12%). Each State should have a comprehensive plan towards the area coverage and seed production so as to achieve the target in biodiesel production.

For different countries, feedstock oil for biodiesel production are different [6]:-

- USA- Soybean

- Malaysia and Indonesia- Palm oil
- Europe- Rapeseed and sunflower oils
- India and Africa – Jatropha
- Spain- Linseed
- Greece- Cotton seed
- China- Waste cooking oil
- Western Canada- Canola
- Philippines-Coconut

1.6 Objectives

At present, there are many research and developments are taking place in every aspects of human life, but still millions of people are facing the problem of deficient-electricity in India and all around the world. It's true that biodiesel can be an alternative to petroleum-fuels (Gasoline and Diesel), but the production process of biodiesel is still not so cost effective that it can be used commercially in automobiles.

In conventional transesterification process, a triglyceride with methanol (or ethanol) is heated under strongly basic condition. This heat is given by means of an electrical heater. Our objective is to skip the use of electrical heater in transesterification process. In place of electrical heater, a point focusing solar reflector is properly designed and intensity of solar irradiation is greater than 400 W/m^2. By doing so, synthetic production of biodiesel can be made more sustainable and cost-effective.

1.7 Problem Statement

Use of solar energy for heating purpose in transesterification process is a good concept but on experimental level we need to analyze the type of solar reflector used because excess temperature may cause evaporation and less temperature may cause improper production of biodiesel. Sometimes in case of less heat and temperature, the chemical heating process remains incomplete and biodiesel does not produce.

There is also a need to optimize the design of the solar reflector set up. Many parameters such as area of reflector, angle of inclination of reflector and design of focal point area should be analyzed according to the type and quantity of oil used for esterification process. For small scale production the area of reflector needed is small and for medium and large scale production reflector design is modified. The oil used should have low FFA content otherwise production process of biodiesel using solar energy will be very tedious.

1.8 Organization of the Report

In this thesis, an experimental analysis of solar assisted biodiesel production was presented and compared with the conventional method. First chapter briefly describe the need of biofuels as alternative of fossil fuels. Second chapter presents a detailed literature review of various technologies of biodiesel production. Third chapter relates with basic theory related to the biodiesel production such as transesterification, refinement of biodiesel etc. and this chapter also presents theory of taghuchi approach of optimizing process parameters. The method of harnessing solar energy in transesterification reaction is also discussed along with the mathematical analysis of parabolic solar reflector used. The fourth chapter discusses the experiment of biodiesel production using conventional method along with the optimization technique using taguchi approach. Similarly chapter five discussed experimental analysis of solar assisted biodiesel production and its optimization. In the chapter six, results based on the both conventional and solar assisted biodiesel production are studied and compared. Chapter seven presents the concluding remark from the experimental analysis of solar assisted biodiesel production.

Chapter 2

Literature Review

2.1 Conventional method of biodiesel production:-

Transesterification is the most commonly used process of biodiesel production. Leung et al. (2010) presented a review of biodiesel production using transesterification process with the use of catalyst. In this work the stress is given on different methods of reducing free fatty acids in the raw oil and refinement of biodiesel was also the objective. When the oil contain a high percentage of FFA content, soap-formation occurs due to reaction of alkali catalyst with the free fatty acids. Higher water content in oil also enables hydroxylation of triglycerides into diglycerides and due to this more free fatty acid forms. These undesirable reactions should be avoided because these cause the reduction in the yield of the biodiesel product. Mainly three methods were discussed to reduce the FFA content in feedstock-oil [8]:

i. Esterification of Free fatty acids with methanol (CH_3OH) in presence of acidic catalyst.
ii. Adding glycerol into the acidic feedstock with a catalyst like zinc chloride and heated to a high temperature.
iii. Using iodine as a catalyst.

The reaction rate of first method is slower but it can eliminate the separation, toxicity, corrosion, and environmental problems. In second method, no alcohol is needed and the water, formed from the reaction, can be immediately vaporized and vented from the mixture. Generally four factors i.e. alcohol quantity, reaction temperature, reaction time and catalyst concentration affect the yield of biodiesel. The optimal temperature range in transesterification lies between 50˚C and 60˚C, depending on the feedstock-oil used. The most commonly used catalyst are KOH and NaOH, optimal condition of catalyst concentration is approximately 1.5 % by weight for NaOH [8].

Shahid et al. (2011) studied the performance of alkaline, acidic and enzymatic catalyst in the transesterification process. Some modern techniques of biodiesel production were also discussed such as use of microwave and super critical alcohol. According to this study it is possible to run engine directly with vegetable oils but for short term only. For long term, the properties and chemical structure of vegetable oils are required to be altered before using them in CI engine [9].

The commonly used method for altering the properties and chemical structure of vegetable oils is transesterification. Many factors such as type of feedstock, type and amount of alcohol and catalysts, reaction temperature and reaction time are responsible for the conversion efficiency of transesterification. Generally sodium hydroxide or potassium hydroxide are used as catalyst in biodiesel production process. But when feedstock contains moisture and having higher value of FFA content, Acid catalysts are preferred over base catalysts. For example in biodiesel production from Jatropha oil, acid catalyst (H_2SO_4) is used. Bio-catalysts (enzymes) are also used for transesterification but these are expensive and the reaction time is longer with use of enzymes. Transesterification can be enhanced using microwaves irradiations. Use of microwave irradiation technique makes transesterification process very fast and efficient. The conversion and settling time is drastically decreased. Just 4 minutes required for conversion in comparison of 2 hours of conventional method. Microwave assisted biodiesel production does not require any catalyst and produced biodiesel is of excellent quality [9].

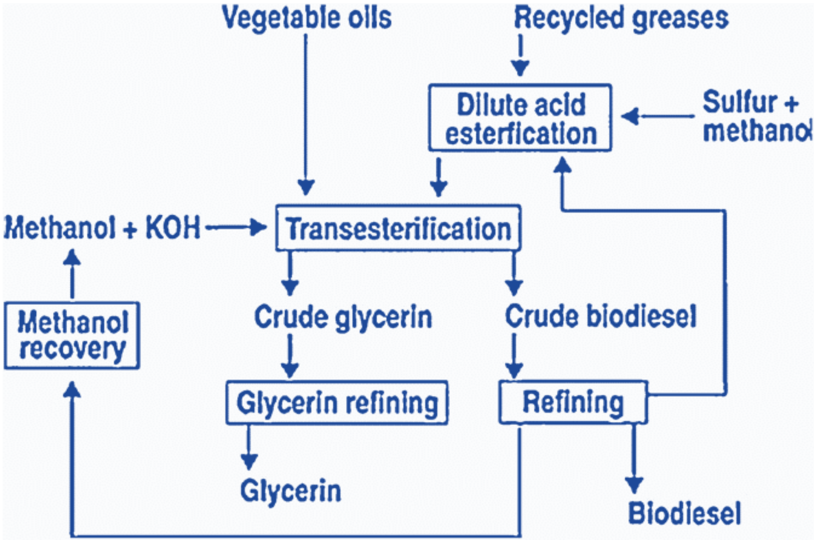


Figure 2.1- Schematic of Transesterification process [9]

Uddin et al. (2013) presented the study related to synthesis of biodiesel from waste cooking oil. A three-step method was used in which first step was the saponification of the oil, second was acidification to produce FFA and the third step was transesterification to produce biodiesel. For saponification process, the reaction time was noted as 2 hours when heated at 100˚C and the optimum molar ratio was 1:2 oil to NaOH. The molar ratio of soap to hydrochloric acid in acidification process was 1:2 and in the third step of esterification, the molar ratio of CH_3OH to FFA was 6:1. The concentration of HCl was 5 wt% of FFA, the chemical reaction temperature was 60°C and the reaction time was 2 hour, with silica gel reaction time was reduced to 80 min and FFA content was reduced to 0.94%. A factorial design was applied which enabled the esterification reaction to occur in optimum conditions. The result showed that 79% wt/wt yield was found at optimum condition. Various properties of produced biodiesel from waste cooking oil (such as viscosity, specific gravity, cloud point, pour point, flash point etc.) are nearer to the properties of diesel-fuel. The experimental results supported the production of biodiesel effectively from waste cooking oil [10].

Berchmans et al. (2008) discussed a technique of biodiesel production from high FFA containing oil. For example, crude jatropha curcas seed oil (CJCO) contains high free fatty acids and use of alkali base catalyst in transesterification could reduce the yield of methyl esters of fatty acids by a considerable amount. So in such cases of high FFA oil, Acid pretreatment is done as first step. The FFA content of crude jatropha curcas seed oil is reduced to less than 1% after acid pretreatment. In second step, transesterification process with alkali base catalyst gives 90% yield of jatropha oil methyl esters [11].

Huang et al. (2010) presented the process of biodiesel production using microalgae in place of conventional biodiesel feedstock. Microalgal oil have fatty acids content similar to common vegetable oils and it has short term growth cycle. Composition of microalgae is relatively single. Heterotrophic cultivation of microalgae is preferred for lipids production. The result showed that biodiesel was produced by acidic transesterification with molar ratio of methanol to microalgal oil equals to 56:1. The reaction temperature was maintained at 30˚C and 100% catalyst quantity was achieved. But on large scale production of biodiesel from microalgal oil is not successful due to many drawbacks such as high cost of production process, low lipid content and low biomass [12].

Martin et al. (2011) discussed the optimal production of biodiesel using cooking oil and algae oil. In this work, five different technologies were considered for transesterification of oil.

These technologies are homogeneous acid catalyzed, homogenous alkali catalyzed, heterogeneous basic catalyzed, enzymatic and supercritical non-catalyzed transesterification [13]. Based on the result, the production costs, thermal energy required and water consumption for algae and cooking oil are expressed for all five technologies in following table:-

Table 2.1 - Production Cost, energy required and water consumption for algae and cooking oil in different methods of esterification [13].

	Alkali Catalyzed	**Acid catalyzed**	**Supercritical**	**Heterogeneous base catalyst**	**Enzymatic**
Production Cost ($/gal)					
Algae	**0.42**	0.50	0.49	0.45	0.48
Cooking oil	0.83	0.72	0.92	**0.66**	0.71
Thermal Energy (MJ/gal)					
Algae	**1.94**	1.94	3.91	1.94	2.08
Cooking Oil	2.20	2.19	4.32	**1.94**	3.36
Water (gal/gal)					
Algae	**0.60**	0.87	0.78	0.59	0.72
Cooking oil	0.32	0.67	0.61	**0.33**	0.59

The optimization result showed that for algae feedstock, the optimal process is homogeneous alkali catalyzed transformation and for cooking oil, the heterogeneous base catalyzed esterification is the optimal process.

Pal et al. (2013) discussed two different technologies of biodiesel production from thumba oil and waste cooking oil (WCO). These two technologies are low frequency ultrasonic energy (28-33 kHz) and conventional mechanical stirrer method. The experiments were performed for alcohol to oil molar ratios of 4.5:1 and 6:1 respectively with different concentrations of KOH (0.5%, 0.75% and 1%). The results showed that the viscosity and density values of thumba and WCO biodiesel are with in permissible limits but these value in comparison to petroleum diesel were slightly higher. This research finally concluded that the ultrasonic technology is efficient, time saving, eco- friendly and industrial viable [14].

2.2 New Trends in Biodiesel Production

To enhance the process of biodiesel production, some new technologies are developed such as microwave irradiation techniques, Supercritical transesterification, ultrasonic baths, ultrasonic reactors techniques and use of solar energy in chemical heating process of esterification. The use of these technologies reduce reaction time and enhance the quality of biodiesel as a product.

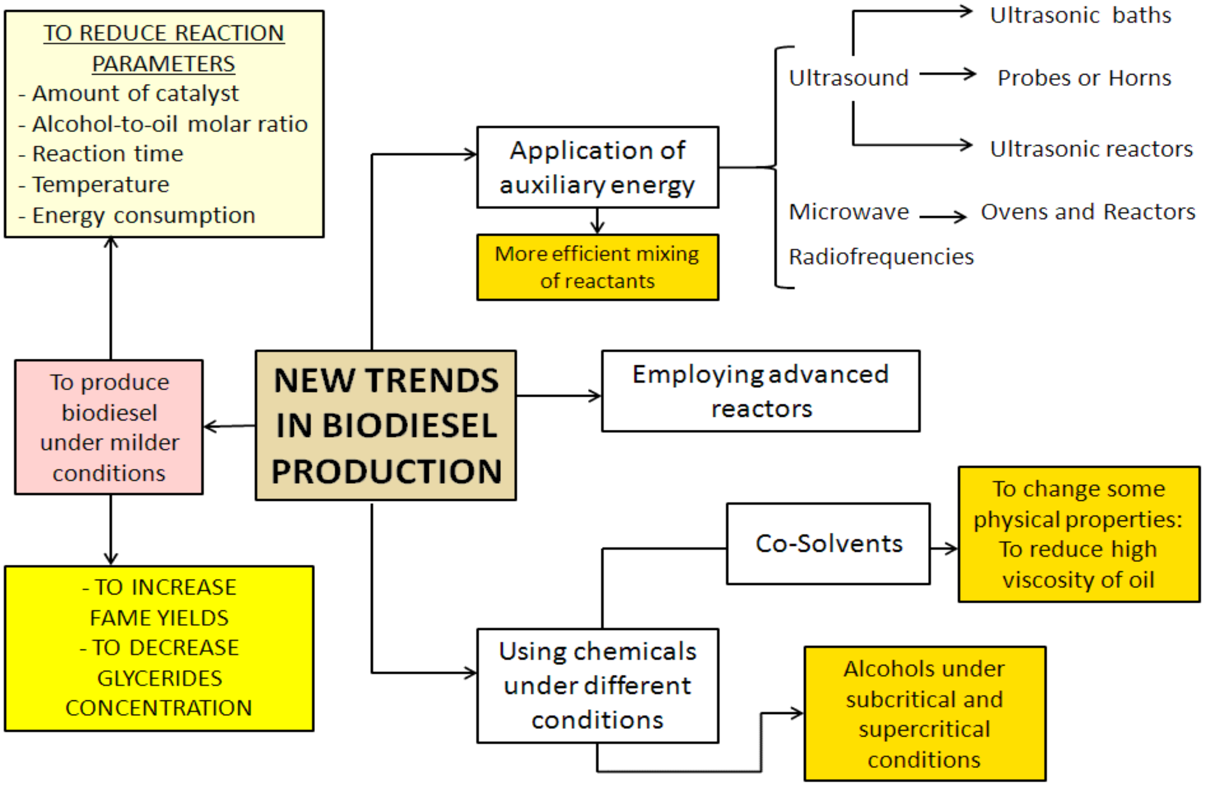


Figure 2.2- New trends in production process of biodiesel [14]

2.2.1 Microwave assisted production of biodiesel

Chen et al. (2012) discussed the methods of improving biodiesel yield from waste cooking oil. In this work, sodium methoxide and sodium hydroxide were used as catalyst. The best performance were under both 0.75 wt% NaOH and 0.75 wt% CH_3ONa for waste cooking oil. The yield of biodiesel produced is greater with CH_3ONa than with NaOH catalyst. Besides it, a microwave heating system was also used to enhance the quality of biodiesel production process. The maximum yield of biodiesel produced from waste cooking oil under conventional heating was 96.6%. In microwave assisted system, the reaction time reduced to 1-6 minutes. The yield of biodiesel produced increased with reaction time from 1 to 3 min, but then decreased from 3 to 5 min. For the microwave assisted production, the maximum yield of biodiesel produced was 97.9%. The result showed that optimal condition in this work were use of 0.75 wt% CH_3ONa catalyst, a methanol to oil molar ratio of 6:1, microwave power of 750 W and reaction time 3 min [15].

Production of biodiesel from used cooking oil using microwave irradiation technique was discussed by Lertsathapornsuk et al. (2003). They reported a reduction in reaction time with the assistance of microwave technique. In this study, experiment was done for different molar ratios of ethanol to oil, i.e. variation in the molar ratio was from 3:1 to 18:1. The reaction time of production process also varied from 10 seconds to 100 seconds. The optimum condition in this experiment were the use of 1.0 wt% NaOH catalyst with ethanol to oil ratio equals to 9:1. The optimum reaction time was 10 seconds using microwave irradiation technique in biodiesel production [16].

Azcan and Danisman (2007) used microwave technology for transesterification of cotton seed oil in the presence of methanol (CH_3OH) and potassium hydroxide (KOH). For this purpose, a Start S model microwave unit was used which is shown in figure 3. Both conventional and microwave irradiation assisted method of biodiesel production were compared by the estimation of critical reaction parameters such as the amount of catalyst, reaction temperature and reaction time. High conversion yield of biodiesel, produced from cotton seed oil, were obtained in the range of 89.3-92.8% at the reaction temperature of 333K for both types of methods. Also the optimal catalyst to oil ratio for both methods was same as 1.5% except the reaction time. Microwave irradiation technique consume only 7 min in comparison of 30 min used for reaction in conventional biodiesel production process [17].

Figure 2.3- Start S microwave unit [17]

Yaakob et al. (2008) presented the method of Fatty acid methyl ester preparation form jatropha curcas oil with the assistance of microwave oven for heating required in chemical process. In this experiment the maximum yield of biodiesel produced was obtained as 86.3% with excess methanol to oil molar ratio of 30:1. The catalyst used in this experiment was 4% NaOH at a reaction temperature of 55˚C. The quality of FAME prepared from jatropha curcas oil using microwave assisted method was better and reaction time also magically reduced. So this method could provide a better biodiesel production method which could enhance the performance of process and maintain better quality than in case of conventional method [18].

Biodiesel production from corn and soybean oil using microwave assisted transesterification was investigated by Majewski et al (2009). In this experiment to get higher yield, four different types of Diphenyl ammonium salt catalyst were applied. These diphenyl ammonium catalyst were tosylate (DPATs), benzenesulfonate (DPABS), mesylate (DPAMs) and chloride (DPAC). In this process conversion yield from corn oil was remarkable (approx. 100%) within 20 min, while in case of microwave heating for 17.5 min more than 80% conversion yield of biodiesel is found. As the reaction time is further reduced to 15 and 10 min, the conversion yield also decreases. DPATs, DPABS, and DPAMs demonstrated a significant ability for transesterification of soybean and corn oil using microwave-assisted systems [19].

Kamath et al. (2010) studied the method of biodiesel production from Pongamia pinnata non-edible oil under batch microwave irradiation technique. The free fatty acid content in Pongamia pinnata oil is higher, so a two-step method was adapted. The conversion yields were different for both one-step and two-step approaches. In one-step approach the yiels was 80% while in two-step approach, the yield was 90% with a molar ratio of alcohol to oil equals to 10:1 and amount of catalyst KOH as 1 wt%. Assistance of microwave irradiation technique not only accelerated the reaction but also reduced the reaction time to 4–5 min. Besides it, the separation time of glycerin from biodiesel produced was also decreased by at least 90% in comparison with the conventional method. Thus microwave irradiation possess an efficient, cost effective and faster technology which reduce the cost of feedstock and processing in synthesis of biodiesel from Pongamia pinnata oil [20].

Sherbiny et al. (2010) discussed the production of biodiesel from jatropha oil using microwave irradiation method and then compared the various properties of prepared biodiesel using microwave irradiation technique with the properties of biodiesel produced from conventional method. In this experiment, same optimum reaction conditions to the microwave irradiation technique as in the case of conventional method. In conventional process the best conversion yield was 99.8% using optimum methanl to oil molar ratio as 7.5:1 and 1.5% potassium hydroxide as the catalyst. The optimum reaction temperature in this was 60˚C and reaction time was 60 min. On the other hand, under the same reaction conditions for 2 min, conversion yield was found as 97.4% using the microwave irradiation technique. Thus, in case of microwave assisted production of biodiesel, the reaction time decreased to only 2 min. While in conventional method approximately 150 min needed (90 min for the pretreatment process and 60 min for transesterification). Finally it was concluded that microwave irradiation technique can also be beneficial for efficient and qualitative production of biodiesel for high free fatty acid content feedstock like jatropha oil [21].

Kanitkar et al. (2011) discussed transesterification process for rice bran oil and soybean oil with the use of both type of alcohols methanol and ethanol. A batch microwave system was used to obtain methyl and ethyl esters of rice bran and soybean oils. The main objective was to compare the use of both alcohols (methanol and ethanol) in terms of yields, quality, and reaction kinetics. Reaction time and reaction temperature were also varied to prepare various samples of biodiesel and then properties of these samples were compared. Reaction time was varied from 5 to 20 min with a step of 5 min and temperature was varied from 60˚C to 80˚C with a step of 10˚C. The results showed that microwave technology reduce reaction time with both types of alcohols used and also reduce the catalyst demand in comparison with conventional production. But alcohol to oil molar ratio was higher for ethanol than methanol. It was observed that ethanol is better in terms of environmental issue and methanol is better in terms of cost effectiveness and performance [22].

Kumar et al. (2011) carried out a microwave-assisted transesterification of Pongamia pinnata using methanol as the alcohol and two types of alkaline catalyst, NaOH and KOH. In this process, applied reaction temperature was 60˚C and alcohol to oil molar ratio was 6:1. The experiment was performed at different reaction times (3, 5, 7, and 10 min) and catalyst concentration was also varied from 0.5% to 1.5% (wt/wt) with a step of 0.5%. The results indicated that optimum concentration for NaOH was 0.5% (wt/wt) and for KOH was 1% (wt/wt). An appropriate amount of methyl esters were optained as 97.5% using 1.0% (w/w) KOH for 10 min and 96.0% yield using 0.5% (w/w) NaOH for 5 min. In both condition, the optimum reaction temperature remained at 60˚C. Finally. the fuel properties were investigated for all the reaction conditions and it was concluded that biodiesels produced from pongamia pinnata oil met the ASTM standards for biodiesel. Microwave irradiation technique also reduced reaction time significantly from 3 hours in convention process to 5-10 min which makes the production process cost effectiveon a small scale [23].

Hsiao et al. (2011) discussed the microwave-assisted biodiesel production from soybean oil using Nano powder calcium oxide as catalyst. In this study, critical parameters such as alcohol to oil molar ratio, reaction temperature, catalyst amount and reaction time were varied to detect the optimum condition for biodiesel production using microwave technique. The different alcohol to oil molar ratio were 6:1, 7:1, 8:1, 9:1, and 10:1, different reaction temperature were 323K, 328K, 333K, 338K, and 343 K, reaction time was varied from 15 min to 75 min with a step of 15 min and catalyst amount was varied from 1.0% (w/w) to 5.0%(w/w) with a step of 1.0%. The condition for maximum possible conversion yield were found as: alcohol to oil molar ratio of 7:1, a reaction temperature of 338 K, a reaction time of 60 min and 3.0 wt% of catalyst. The maximum conversion yield under optimum condition was 96.6%. The results indicated that combined use of microwave irradiation technique with nano powder calcium oxide (nano CaO) catalyst make the biodiesel production from soybean oil very efficient and qualitative. In this study biodiesel produced from soybean oil met the EN-14214 standards [24].

Motasemi et al. (2011) discussed the production of biodiesel from waste cooking oil using microwave-assisted transesterification process. In this work, a domestic microwave oven was modified to perform the experiments effectively. The methanol to oil molar ratio used was 1:4 (v/v) and percentage of catalyst KOH used was 2 wt%. Different samples of methyl ester were prepared from waste cooking oil using different reaction times (5, 7, and 9 min) and different microwave exit powers (100, 180, and 300 W). The optimum condition was at 128˚C using microwave power of 300 W for 9 min. Finally, a comparison between conventional heating and microwave-assisted methods was analyzed and the results indicated a significant decrease in reaction time from 60 to 180 min in case of conventional heating to 5 to 9 min in case of microwave-assisted transesterification [25].

Priambodo et al. (2015) conducted the experiments using novel technology to create bio-diesel product from cooking oil and waste cooking oil using microwave irradiation technique. They used the SrO catalyst which is a heterogeneous base catalyst and insoluble into any liquid solution. Therefore, it can be recycling and reused. They studied the optimum condition and reaction time for the given work. The optimum condition using commercial SrO were, 40 to 180 seconds reaction time, around 80˚C reaction temperature, methanol to oil molar ratio equals to 6:1 and 1000 W microwave power output. They determined the conversion yield as 99% for the cooking oil and 93% for waste cooking oil. Finally they concluded that derived fuel will become the alternative for diesel and could be used in engine without a major modification [26].

Gude et al. (2013) presented potential of microwave energy for biodiesel production. Firstly they described the characteristics of microwave irradiation and energy associated with microwave. The influence of microwave energy is not strong enough to break chemical bonds, so microwaves cannot induce chemical reaction. Microwave heat transfer mechanism was also discussed which was more complex than conventional heating. There is rapid increase of solvent temperature and quick cooling too in case of microwave heating method. In microwave enhanced transesterification process, catalyst may or may not be required, heat losses are low. Reaction temperature is kept at 40-100˚C for a very short period (0.05-0.1 hr). Heating is done by electrical energy applied through microwaves. Process efficiency is high, in the end, catalyst and soaps are extracted from biodiesel produced [27]. In this study the following advantages of microwave assistance in biodiesel production were discussed:

- Low energy consumption
- Substantial reduction in reaction time of esterification
- Reduction in amount of solvent requirement
- Enhanced selectivity for production process
- The conversion yield increases with less by-product formation
- Many reaction that did not occur in conventional heating, could be completed with high conversion yield under microwave irradiation technique.

So, it can be concluded that microwave irradiation assisted technique of biodiesel production can be better option for biodiesel production on a commercial level. Combining the microwave technique with other innovative heating methods such as ultrasonic technology can also be beneficial. The schematic of microwave assisted biodiesel production process is as follows:-

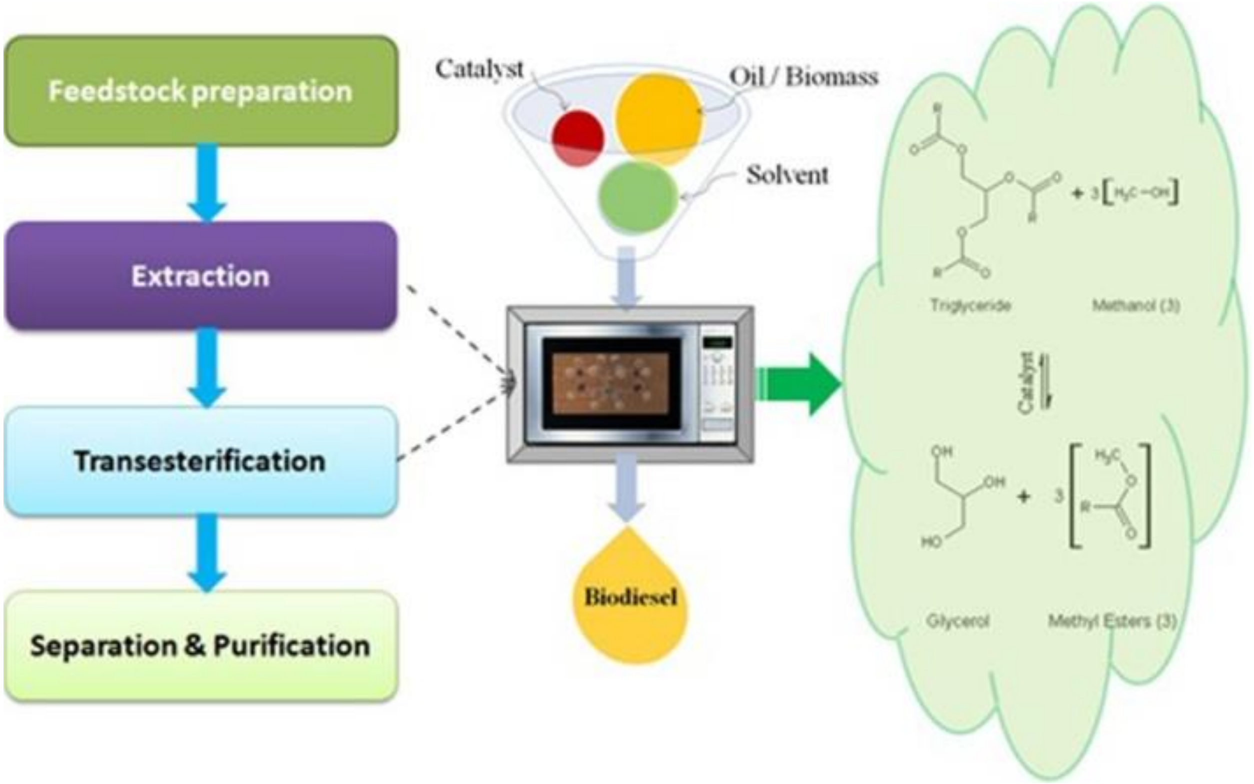


Figure 2.4 – microwave assisted production of biodiesel [27]

2.2.2 Ultrasonic assisted production of biodiesel

Pal et al. (2013) discussed the production of biodiesel from waste cooking oil as feedstock using power ultrasound and hydrodynamic cavitation technology. In this work the stress was given to the development of laboratory test rigs for ultrasound cavitation technique which enhanced the biodiesel production from waste cooking oil. The best conversion yield was above 90% with optimum conditions of methanol to oil molar ratio equals to 4.5:1 and amount of catalyst concentration equals to 0.5% (w/w). The transesterification process using ultrasound cavitation techniques appeared to be effective and rapid in comparison of conventional transesterification. The reaction time was also sufficiently reduced. High yield obtained for methyl ester make this process viable for industries [28].

Koberg et al. (2011) reported the direct method of biodiesel production from microalgae biomass of Nannochloropsis using two promising techniques. In the first technique, Microalgae was cultivated by the application of a biotechnological environmental system, so the cost of algae production was reduced significantly. In the second method, microwave and ultrasonic irradiation technique were compared with the assistance of SrO catalyst. For the second case, the result showed that direct transesterification using microwave oven technique is more simple and efficient than the ultrasonic assisted technique. The yield of biodiesel was also observed higher (37.1%) for microwave oven technique in reaction time of 5 min, while ultrasonic technique could provide only 20.9% yield in same reaction time [29].

Lin et al. (2012) presented production of biodiesel from waste frying oil with the assistance of ultrasonic energy. In this work, waste frying oil was preferred over refined vegetable oil for biodiesel production. So it was an effective way to reduce the cost of biodiesel-feedstock oil. Ultrasonic energy was used as heat source and in this process, a two-step catalyzing process was used. In the first step, the acid value of the waste frying oil was reduced by acidification process. The FFA content of waste frying oil was found higher, so transesterification process took place with H_2SO_4 catalyst. Observations were taken under various oil to alcohol molar ratio from 6:1 to 11:1 with a step of 1. The amount of catalyst was also varied from 1.0 to 3.0 wt%. In the second step, triglycerides in waste frying oil (acid value $<$ 2.0) were transesterified with oil to alcohol molar ratio of 6:1. The alkali-base catalyst NaOH was used (1.0 wt%) in this second step. After this two-step reaction, FAMEs were found as the top layer in the separating funnel which were removed in a beaker after settling minimum 30 minutes, then water washing process of FAMEs took place at least three times with acetate 30% and distilled water. At last the separated FAME was dried in an oven at 378 ± 3 K. The ultrasonic mixing in second step increase yield of FAME in this process. 97.1% of conversion rate of waste frying oil into FAME was achieved, therefore assistance of ultrasonic energy has a better potential in effective and qualitative production of biodiesel [30].

Mootabadi et al. (2010) used alkaline earth metal oxide as the heterogeneous catalyst in ultrasonic-assisted biodiesel production from palm oil. The catalyst used in this experiment were CaO, SrO and BaO, ultrasonic energy assisted as a heat source for transesterification. In this study, batch process was carried out to study the effect of reaction time (10-60 min), 20 KHz ultrasonic cavitation, palm oil to alcohol ratio of 3:1 to 15:1 with a step of 3. Catalyst concentration used were from 0.5 to 3 % (w/w) and there were variation in the amplitudes of ultrasonic irradiation from 25% to 100%. They studied the activities of catalyst related to their basic strength. They also concluded that the 60 min was the most appropriate reaction time to achieve 95% yield. This reaction time is considerably less than the 2 to 4 hours reaction time in conventional method of biodiesel production. The yield for CaO increased from 5.5% to 77.3%, for SrO increased from 48.2% to 95.2% and for BaO from 67.3% to 95.2% in the same reaction time of 60 minutes. It was also concluded that 50% amplitude of ultrasonic radiation was the most suitable range for successful results and catalyst dissolution was the main factor responsible for activity drop of the reversed catalysts, especially with BaO catalyst [31].

2.3 Use of Solar Energy in biodiesel production

Agee et al. (2014) discussed the production of biodiesel using solar energy for processing heat in transesterification. In this work, a parabolic solar reflector made of satellite dishes was developed to concentrate solar irradiation on its focal point. Feedstock oil with alcohol and catalyst was placed on the focal point of the reflector and then transesterification process takes place in approximately in 1 hour. Generally oil with low FFA content should be used to produce biodiesel with assistance of solar energy. In this work soybean oil was used. For successful processing of transesterification, Solar irradiation should be greater than 400-450 W/m^2. In this experiment, synthetic process of biodiesel took place without generating any chemical and electrical waste. As waste glycerol was recovered and purified to utilize in other processes. All thermal energy was supplied through solar without any electricity use, so no electrical waste was there [32].

The result indicates that solar assisted biodiesel production is successful at milli-molar and small molar scale. So further improvisation is needed to enhance the quality of biodiesel production. Design modification such as making large size of solar reflector should be developed. Besides it transesterification process should be performed at optimum conditions [32].

Hou et al. (2009) proposed a new concept of utilizing solar energy application to supply steam and electricity for biodiesel production. As in the biodiesel production process, the combustion of fossil fuels takes place to supply steam and electricity needed for the refinement of crude FAME. In this process, some pollutant gases such as CO_2, NO_x and SO_x are also released into the environment. To reduce these disapproving condition, solar energy appliances can be utilized. For example, thermoelectric or PV cells can directly converted the energy of solar irradiation into electricity. Also the solar collectors can directly convert solar radiation into steam [33].

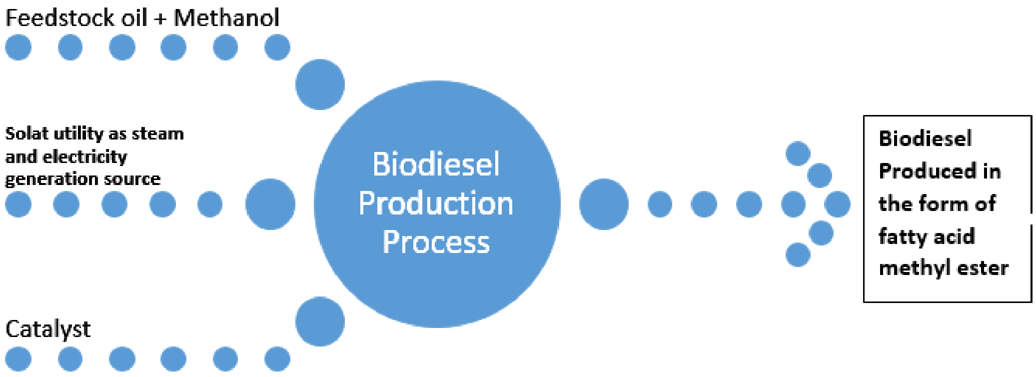


Figure 2.5 - Schematic of Solar energy utilization in steam and electricity generation during biodiesel production.

In this work a new parameter ‘renewability index’ was also introduced. It is the ratio of exergy of renewable to the total exergy.

$$\mathrm{Renewability\quad Index}\quad \psi_R = \frac{\varepsilon_R}{\varepsilon_T} = 1 - \frac{\varepsilon_{NR}}{\varepsilon_T} \qquad [33]$$

In this experiment, the proposal started with the reported process of biodiesel production using fossil fuels utility; then a alkali- catalyzed transesterification process was developed with the use of solar energy utility on a 8000 t per annum scale. The simulation was done using the Aspen Plus software. The results indicated that renewability index of the biodiesel production process with solar utility is 99.9% which is 10.5% higher than the renewability index in conventional method. Also the 4676 t of CO_2 gas release were eliminated in a year. 1275 t of coal consumption was saved per year. Hence using solar utility, hazardous environmental impacts can be eliminated during biodiesel production process [33].

Rasmussen et al. (2014) presented a review regarding development of photobioelectrochemical cells over the past few decades. In this work, they used photosynthetic catalysts (e.g. Thylakoid membrane) for biodiesel production and also for solar energy conversion. Several types of photobioelectro-catalyst were discussed such as whole cells, organelles and enzymes [34].

The analytical review of solar energy potential in biofuel production was discussed by Agrawal et al. (2014). It was stated that available biomass can’t supply the liquid biofuel in sufficient amount which is needed for the transport sector on a large scale. But alternative should be found for sustainable future. In this work, the biomass was converted into liquid biofuels with utilizing the solar energy as supplementary energy option for the production process. At last, they presented an enabled data for such kind of future transport infrastructure in which liquid biofuel would be used as a source of energy and solar energy would be used to supplement the conversion process of biomass into liquid biofuels [35].

2.4 Concluding Remark from the Literature Review

We can conclude from the detailed literature review that selection of biodiesel production method is mainly depends on various parameters such as type of feedstock used, reaction time, reaction temperature, alcohol to oil molar ratio and amount of catalyst used. The yield of biodiesel produce is also determined by these factors. For maximum yield of biodiesel, we should do our experiment on optimum conditions. In this review, some other technologies such as microwave irradiation, ultrasonic cavitation and solar irradiation are also presented which enhance the quality and effectiveness of biodiesel production process.

2.5 Present work

The work done in this project is the solar-assisted production of biodiesel. In this project we will use the solar energy for chemical heating in transesterification process. This concept of assistance of solar irradiation in biodiesel production is new but it is similar to microwave irradiation technique of biodiesel production. Whereas in microwave irradiation, we utilize heat from microwave as discussed in literature in detail, similarly we will utilize solar energy for heating process. The main difference between these two techniques is of reaction time. In microwave technique, no catalyst is used and reaction time is only 2-6 minutes. While in solar assisted biodiesel production reaction time is around one hour and catalyst is also used in this process.

Chapter 3

Basic Theory Related to Solar assisted Biodiesel production

There are various phenomenon which should be studied in the solar assisted production of biodiesel. In this project, thermal energy of solar radiation was used for the chemical heating required in transesterification process. But before discussing about the experimental set up, there is need to discuss about the conventional process of biodiesel and basic terminology of solar energy utilization separately. Biodiesel has been recognized as an alternative for depleting petro-fuels since it is produced mainly from edible and non-edible oils, is a clean, renewable resource, and is non-toxic. Transesterification is the most commonly used process for synthesis of biodiesel. The synthesis of biodiesel involves heating a triglyceride with methanol in presence of catalyst. In this project, Biodiesel was produced using cotton seed oil and potassium hydroxide is used as catalyst. The conversion yield was maximized using Taguchi's method of optimization. This method was adequate for calculating the effect of control parameters and it also optimizes the experiment work with limited number of experiments. After performing conventional method of biodiesel production, solar assisted transesterification was used in which thermal energy of solar irradiation was utilized for chemical heating process in biodiesel synthesis.

3.1 Basic phenomenon of Biodiesel production

The biodiesel production method in described in the following subheadings-

3.1.1 Process flow chart

The amount of FFA content in feedstock oil decide which type of catalyzed process should be used for biodiesel production. When the FFA content is below 2.5 wt%, the alkali-catalyzed transesterification process is used. But when FFA content is above 2.5 wt%, acid pretreatment is necessary before transesterification [36]. The process flow chart for this phenomenon is shown in figure 3.1 which depicts that synthesis of biodiesel from edible or non-edible oil is a step by step method and transesterification is the main step after which crude biodiesel is produced along with glycerol.

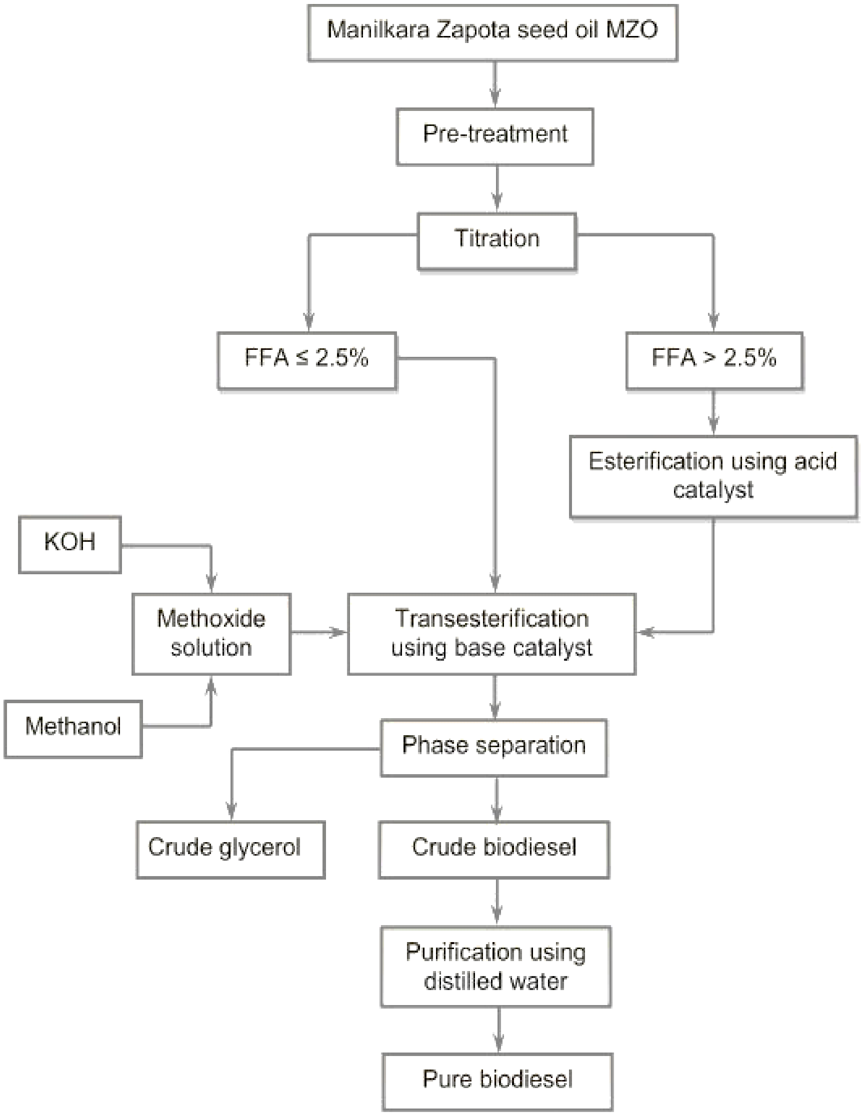


Figure 3.1– Process flow chart of biodiesel production using Alkali base catalyst and acid catalyst

1.1.1 Treatment of biodiesel feedstock

The edible or non-edible feedstock oils, used in biodiesel production process, may contain free fatty acids, water, triglycerides and other contaminants in different quantity. So there is need of various pretreatment before transesterification. For example, some undesirable contaminants in feedstock oil can be removed by different kinds of degumming methods. The name of degumming methods are:-

i. Membrane Filtration
ii. Acid micelles degumming
iii. Hydration

iv. Supercritical extraction

Selection of degumming method is done on the basis of characteristics of feedstock oil. The phospholipids solubility can be significantly reduced in case of hydration degumming method, but this method is only applicable to hydratable phospholipids. Non-hydratable phospholipids are extracted by acid micelles degumming method in which phosphoric acid is added into the feedstock oil. The supercritical extraction method can effectively extract the free fatty acids from the crude oil by the refinement with supercritical CO_2 extraction. But the requirement of high pressure in this process restraints its application.

3.1.2 Selection of catalyst for Transesterification process

For Transesterification process, the catalyst should be selected properly. Three types of catalyst are generally used**-** Alkali, Acid and enzymes. Alkali and Acid catalyst are subdivided into homogeneous and heterogeneous catalyst. The table 3.1 clearly shows that selection of catalyst is based on FFA content of feedstock oil and the scale of biodiesel production i.e. how much quantity of biodiesel to be produced.

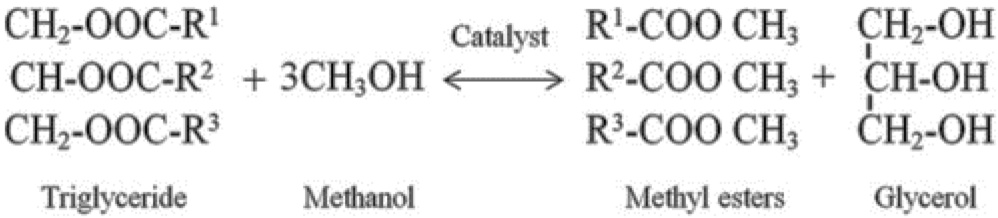
Table 3.1- Different types of catalysts used in transesterification [37]

Type	Example	Advantages	Disadvantages
Alkali Homogeneous	NaOH, KOH	High catalytic activity, low cost, favorable kinetics, modest operation conditions	Low FFA requirement, anhydrous conditions, saponification, emulsion formation, more waste water from purification, disposable
Alkali Heterogeneous	CaO, $CaTiO_3$, $CaZrO_3$, CaO–CeO_2, $CaMnO_3$, $Ca_2Fe_2O_5$, KOH/Al_2O_3, KOH/NaY, Al_2O_3/KI, ETS-10 zeolite, alumina/silica supported K_2CO_3	Noncorrosive, environmentally benign, recyclable, fewer disposal problems, easily separation, higher selectivity, longer catalyst lifetimes	Low FFA requirement, anhydrous conditions, more wastewater from purification, high molar ratio of alcohol to oil requirement, high reaction temperature and pressure, diffusion limitations, high cost
Acid Homogeneous	Concentrated sulphuric acid	Catalyze esterification and transesterification simultaneously, avoid soap formation	Equipment corrosion, more waste from neutralization, difficult to recycle, higher reaction temperature, long reaction times, weak catalytic activity
Acid Heterogeneous	carbon-based solid acid catalyst, carbohydrate-	Catalyze esterification and transesterification simultaneously, recyclable, eco-	Low acid site concentrations, low Micro-porosity, diffusion

	derived catalyst, Vanadyl phosphate, niobic acid, sulphated zirconia, Amberlyst-15, Nafion-NR50	friendly	limitations, high cost
Enzymes	Candida antarctica fraction B lipase, Rhizomucor mieher lipase	Avoid soap formation, nonpolluting, easier purification	Expensive, denaturation

3.1.3 Basic Chemical Reactions

Both Edible and Non-edible oils can be converted into fuels by several procedures such as pyrolysis, micro-emulsification, cracking, blending and Transesterification. These fuels have properties comparable to petro-fuels. Mostly, Transesterification method is used for biodiesel production due to its merits over other biodiesel production processes. For example, Transesterification is carried out under normal conditions and the yield of biodiesel produced is comparatively good. Transesterification is a chemical method in which the triglyceride is converted into diglyceride and diglyceride is converted into monoglyceride which is methyl or ethyl ester named as biodiesel. The reactions consist of consecutive reversible processes are shown below. In transesterification process, triglyceride is ultimately converted into methyl or ethyl ester of oil, which is named as biodiesel. Triglycerides are esters of saturated and unsaturated monocarboxylic acids which found in common feedstock oils along with trihydric alcohol glyceride. Triglyceride reacts with alcohol in presence of the catalyst and converts into diglyceride and then into monoglyceride into consecutive processes. The chemical reaction is shown below:-



$$\begin{matrix} CH_2\text{-}OOC\text{-}R^1 \\ CH\text{-}OOC\text{-}R^2 \\ CH_2\text{-}OOC\text{-}R^3 \end{matrix} + 3CH_3OH \xleftrightarrow{\text{Catalyst}} \begin{matrix} R^1\text{-}COO\,CH_3 \\ R^2\text{-}COO\,CH_3 \\ R^3\text{-}COO\,CH_3 \end{matrix} + \begin{matrix} CH_2\text{-}OH \\ CH\text{-}OH \\ CH_2\text{-}OH \end{matrix}$$

Figure 3.2- Simplified form of chemical reaction in transesterification [38]

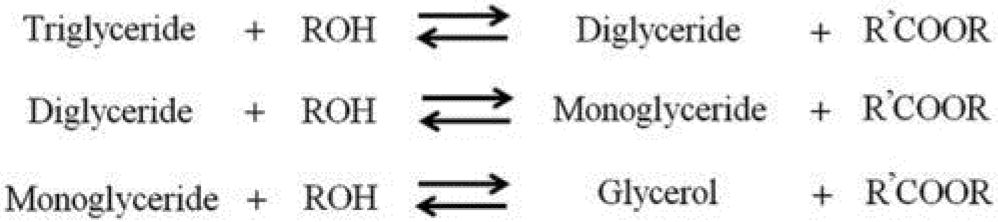
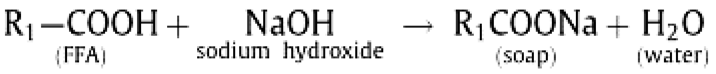


Figure 3.3- Three reversible reactions in Transesterification of triglycerides [38]

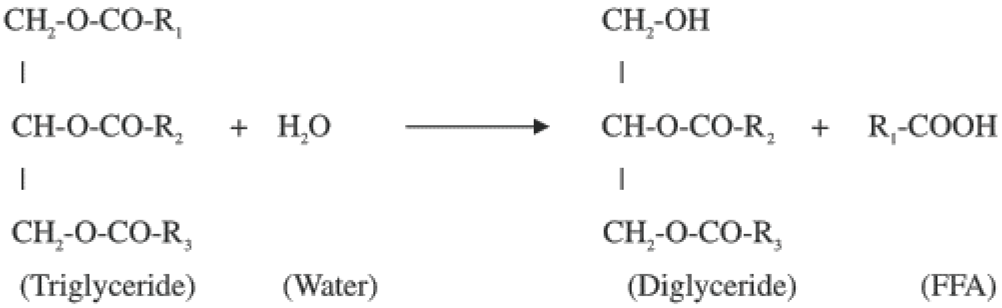
Here R^1, R^2 and R^3 are long-chain hydrocarbons, sometimes these are also called fatty acid chains. Generally, there are five main types of chains in vegetable oils and animal oils: palmitic, stearic, oleic, linoleic, and linolenic. In case of transesterification, when the triglyceride is converted stepwise to diglyceride, monoglyceride and finally to glycerol, 1 mole of fatty ester is liberated at each step [39]. Usually, the alcohol preferred for transesterification is methanol because of its less cost.

Biodiesel feedstock oils may contain small amounts of water and free fatty acids (FFA). In case of an alkali-catalyzed transesterification, the free fatty acid react with the alkali base catalyst which is used in the transesterification reaction. This reaction results in the formation of soap, so it is named as Saponification reaction. Eq. shows the saponification reaction of the FFA with sodium hydroxide (NaOH). Here, NaOH is used as alkali base catalyst and products are soap and water.



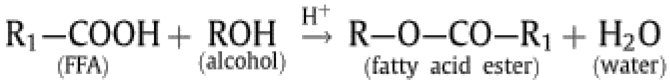
$$\underset{\text{(FFA)}}{R_1-COOH} + \underset{\text{sodium hydroxide}}{NaOH} \rightarrow \underset{\text{(soap)}}{R_1COONa} + \underset{\text{(water)}}{H_2O}$$

The above reaction is unfavorable because the yield of the biodiesel reduces due to formation of soap and it also prevents the separation of the esters from the glycerol. Moreover, the soap formed in the reaction binds with the catalyst which means that more catalyst will be required. Hence the transesterification process will implicate a higher cost [40]. The other product of saponification reaction is water which also retard the transesterification reaction due to hydrolysis reaction, Triglycerides can be hydrolyzed into diglycerides due to water which induce formation of more FFA. The hydrolysis reaction can be shown as below-



$$\underset{\text{(Triglyceride)}}{\begin{array}{l}CH_2\text{-}O\text{-}CO\text{-}R_1\\ |\\ CH\text{-}O\text{-}CO\text{-}R_2\\ |\\ CH_2\text{-}O\text{-}CO\text{-}R_3\end{array}} + \underset{\text{(Water)}}{H_2O} \longrightarrow \underset{\text{(Diglyceride)}}{\begin{array}{l}CH_2\text{-}OH\\ |\\ CH\text{-}O\text{-}CO\text{-}R_2\\ |\\ CH_2\text{-}O\text{-}CO\text{-}R_3\end{array}} + \underset{\text{(FFA)}}{R_1\text{-}COOH}$$

In case of feedstock oil with higher FFA (more than 2.5%), an acid-catalyzed esterification reaction is used for synthesis of biodiesel in the form of ester. The chemical reaction of oil with alcohol in presence of acid catalyst is shown below-



$$\underset{\text{(FFA)}}{R_1-COOH} + \underset{\text{(alcohol)}}{ROH} \overset{H^+}{\rightarrow} \underset{\text{(fatty acid ester)}}{R-O-CO-R_1} + \underset{\text{(water)}}{H_2O}$$

Generally, Sulphuric acid (H_2SO_4) is used as acid catalyst in the acid-catalyzed esterification reaction. But the reaction rate is slow in this case and also the oil to methanol molar ratio is high in this case in comparison of alkali base catalyzed transesterification. So, Acid-catalyzed esterification has not grown as much attention as the alkali-catalyzed transesterification [41].

Though conventional alkali catalyst are very popular for transesterification, some problems are still associated with these conventional catalytic processes. For example, removal of the catalyst and glycerol, requirements of high energy and the need to pretreat feedstocks containing FFAs or to post-treat large amounts of waste water. These drawbacks of conventional catalytic process can be weakened by using enzymes. So it can be said that enzymatic catalysts such as lipases are more significant when there is need to effectively catalyze the transesterification process of triglycerides with high selectivity either in aqueous or in non-aqueous systems. To get a better yield of FAMEs is also an objective when enzymatic catalysts are used [42].

3.1.4 Separation

There are two major products found after the transesterification reaction. One is biodiesel in the form of ester and other is the glycerol. The separation process is necessary for the extraction of biodiesel. The density of glycerol is higher than ester, so glycerol comes at the bottom of the reaction vessel after around 4 hours. Then, we can separate the glycerol from the biodiesel. Extracted Crude glycerol can be refined by fermentation because it also has numerous application in soaps and cosmetic industries [43].

3.1.5 Refinement of Crude Biodiesel

After separation process of glycerol layer, there is a need to purify the crude biodiesel which generally contains some contaminants such as residual catalyst, free glycerol, unreacted alcohol, water and soaps that were generated during the chemical process of biodiesel synthesis. The methods used for purification of biodiesel are as follows:

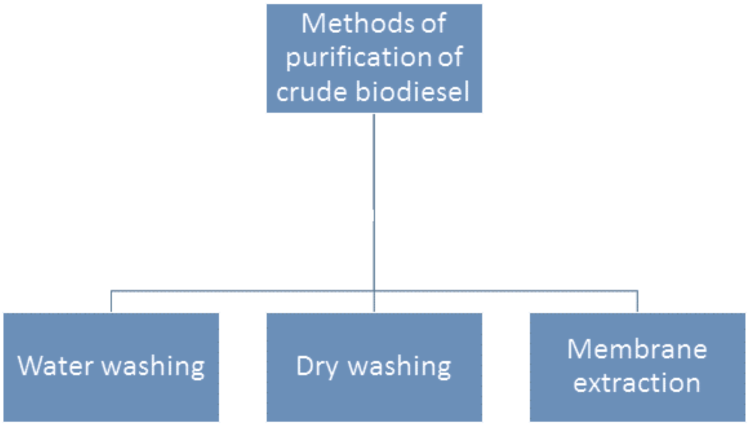


Figure 3.4- Types of purification methods for crude biodiesel

Water washing - Water washing is very effective for removing the contaminants of glycerol and alcohol because both contaminants have high solubility in water. The residual contaminants of catalysts, such as sodium salts and soaps, can also be removed by water washing process. Distilled warm water in primarily used in water washing process. Warm water avoids the precipitation of saturated fatty acid esters and hinders the formation of emulsions due to a moderate washing process. Softened water (slightly acidic) is also used for water washing. The advantage of slightly acidic softened water is that it eliminates calcium and magnesium contamination and neutralizes any residual alkali base catalyst in the biodiesel.

Dry washing- In dry washing process, an ion exchange resin or a magnesium silicate powder is used in place of distilled warm water. This method is also effective for the removal of soaps from the crude biodiesel.

Membrane Extraction- Gabelman and Hwang [44] verified that use of a hollow fiber membrane extraction can remove the impure-contaminants from the crude biodiesel in an effective manner. In this method, a hollow fiber membrane of diameter 1 mm and length 1 meter is used. This membrane is immersed into the reactor (20˚C) after filling it with distilled water. The crude biodiesel (flow rate: 0.5 ml/min) is pumped into the hollow fiber membrane at an operating pressure of 0.1 MPa. After this step, biodiesel is passed over heated sodium sulphate (Na_2SO_4). At last, a few quantity of water is removed by filtration process. This approach is very promising and conforms to ASTM standards.

3.2 Factors affecting Yield of biodiesel produced-

In transesterification process, the yield of biodiesel is mainly affected by some concerned parameters. To achieve the maximum yield of biodiesel, the following parameters should be optimized-

i. FFA content of oil
ii. Reaction temperature
iii. Reaction time
iv. Catalyst type and concentration
v. Mixing intensity(stirring)
vi. Use of organic co-solvents
vii. Moisture and water content in oil.
viii. Molar ratio of alcohol to oil type/chemical structure of alcohol.

Taguchi method is used for the optimization of transesterification process. We will discuss Taguchi method further in this chapter.

3.3 Physio-chemical properties of biodiesel

The physio-chemical properties are those which influence the process taking place in the engine such as burning of the fuel–air mixture, exhaust formation, quality and heating value, ignitions qualities, ease of starting, cold weather properties (cloud point, pour point and cold filter plugging point). Other fuel properties related to transport and depositing are oxidative and hydrolytic stability, flash point, induction period, microbial contamination, filterability limit temperature etc. The properties related to wear of engine parts are lubricity, cleaning effect, viscosity, compatibility with materials used to manufacture the fuel system etc. We can discuss these properties of biodiesel in following subheadings-

Density-

Density is the mass per unit volume. The measurement was made at room temperature. The density was measured with the help of a U-Tube Oscillating True Density meter. The density of biodiesel was measured and then compared with that of diesel fuel.

Figure 3.5- U-Tube Oscillating True Density Meter

Viscosity

When a fluid is subjected to external forces, it resists flow due to internal friction. Viscosity is a measure of internal friction. The viscosity of the fuel affects atomization and fuel delivery rates. It is an important property because atomization and mixing of air and fuel in combustion chamber gets affected. Viscosity studies were conducted for different test fuels. Absolute viscosity sometimes called dynamic or simple viscosity is the product of Kinematic viscosity and fluid density. Kinematic viscosity of liquid fuel samples were measured using Kinematic viscometer shown in plate 3.4 at 40^0 C as per the specification given in ASTM D445. A suitable capillary tube was selected, and then a measured quantity of sample was allowed to flow through the capillary. Efflux time was measured for calculating Kinematic viscosity using the formula given below:

$$\nu = C \cdot t$$

Where, $\nu = Kinamatic \quad viscosity$

C = Constant (in mm^2/sec^2)

t = Time (sec)

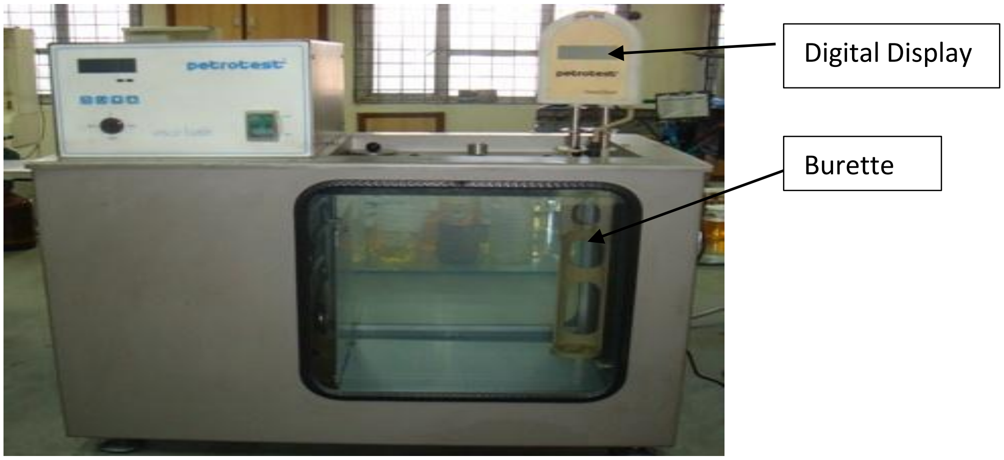


Figure 3.6- Kinematic Viscometer

Flash and Fire point

Flash point is the minimum temperature at which the oil vapour forms an ignitable mixture when mixed with air and gives a momentary flash on application of a small pilot flame. The flash and fire point of the test fuels were measured as per the standard of ASTM D 93. The sample was heated in a test cup at a slow and constant rate of stirring for proper and uniform heating. A small pilot flame was directed into the cup through the opening provided at the top cover at the regular intervals. The temperature at which these vapour catches flash is observed and called as the flash point of that liquid. Fire point is an extension of flash point in a way that it reflects the condition at which vapour burns continuously for at least for 5 seconds. Fire point is generally higher than the flash point by 5-8° C. A Pen sky Martens apparatus used in the study for determination of flash point is shown in figure 3.7.

Figure 3.7- Pen sky Marten Flash Point Apparatus

Cloud and Pour Point

Cloud and Pour points are important for determining the feasibility of using the fuel in engine at lower ambient temperatures. Fuels with high pour points give flow problems at lower temperature, therefore it cannot be recommended for use in engine at low temperatures. Pour point for fuel oils, lubricating oils and diesel fuels is used as criteria in cold surroundings. The cloud and pour point of the fuel were measured as per the specification given of ASTM D2500 and ASTM D97 respectively. The cloud and pour point apparatus used for determination of these properties is shown in the figure 3.8.

Figure 3.8- Cloud and Pour Point Apparatus

The cloud point is the temperature at which a solid material, usually paraffin waxes and similar compounds in the case of petroleum liquid begins to separate when the sample is cooled under carefully controlled conditions. Likewise, the pour point is the lowest temperature at which the liquid will flow in a specific way when cooled under controlled conditions. The cessation of flow results from an increase in viscosity or from the crystallization of wax from the oil. Fuel oils of wax bearing crude oils have much higher pour point then those derived from crude oils of low wax content. A low pour point is a desired property of oil in respect of handling in cold atmosphere. The pour point is determined by cooling a sample of the oil in a test jar, to a temperature when the jar is displaced from the vertical to the horizontal position, no perceptible movement of the oil will occur within the first 5 second.

Calorific Value

The calorific value is defined in terms of the number of heat units liberated when unit mass of fuel is completely burnt in a calorimeter under specified conditions. Higher calorific value of fuel is the total heat liberated in kJ per kg or m^3. All fuels containing hydrogen in the available form will combine with oxygen and form steam during the process of combustion. If the products of combustion are cooled to its initial temperature, the steam formed as a result will condense. Thus maximum heat is abstracted. This heat value is called the higher calorific value. The calorific value of the fuel was determined with the Isothermal Bomb Calorimeter as per the specification given in ASTM D240. The combustion of fuel takes place at constant Volume in a totally enclosed vessel in the presence of oxygen. The sample of fuel was ignited electrically. The water equivalent of bomb calorimeter was determined by burning a known quantity of benzoic acid and heat liberated is absorbed by a known mass of water. Then the fuel samples were burnt in bomb calorimeter and the calorific value of all samples were calculated. The Bomb Calorimeter used for determination of Calorific value is shown in figure 3.9. The heat of combustion of the fuel samples was calculated with the help of equation given below

$$H_c = (W_c * \Delta T)/M_s$$

Where, H_c = Heat of combustion of the fuel sample (kJ/kg)

W_c = Water equivalent of calorimeter assembly (kJ/˚C)

ΔT = Rise in Temperature (˚C)

M_s = Mass of sample burnt (kg)

Figure 3.9- Bomb Calorimeter

3.4 Optimization approach of reaction parameters in Transesterification

Taguchi method is used for the optimization of reaction parameters in transesterification. The main purpose of using this method is to maximize the yield of biodiesel produced. We can describe this method is following paragraphs-

3.4.1 Introduction of Taguchi Method

The Taguchi method allows us to improve the consistency of biodiesel production. Taguchi method recognize that not all factors that cause variability can be controlled. These uncontrollable factors are called noise factors. This method also try to identify controllable factors that minimize the effect of the noise factors. During experimentation, control factors are manipulated to evaluate variability that occurs and then determine optimal control factor settings that minimize the variability of process. If biodiesel synthesis is handled with this Taguchi approach, the conversion yield will be more and efficiency of biodiesel production process will also more.

3.4.2 Design of experiment for transesterification process using Taguchi method-

To optimize the process parameters in transesterification, 'Minitab 17' software was used to apply Taguchi approach. After opening Minitab 17 software, select the 'Stat' option. Then there is a need to create Taguchi design by selecting type of design and number of factors. Software display an orthogonal array based on the number of factors and type of design. The number of runs in orthogonal array are also decided according to the type of design. Some standard orthogonal array are shown in following table 3.2-

Table 3.2- Standard Orthogonal arrays [45]

Orthogonal Array	**Number of rows**	**Max no. of Factors**	**Maximum number of columns at these levels**			
			2	3	4	5
L4	4	3	3	-	-	-
L8	8	7	7	-	-	-
L9	9	4	-	4	-	-
L12	12	11	11	-	-	-
L16	16	15	15	-	-	-
L16'	16	5	-	-	5	-
L18	18	8	1	7	-	-
L25	25	6	-	-	-	6
L27	27	13	-	13	-	-
L32	32	31	31	-	-	-
L32'	32	10	1	-	9	-
L36	36	23	11	12	-	-
L36'	36	16	3	13	-	-
L50	50	12	1	-	-	11
L54	54	26	1	25	-	-
L64	64	63	63	-	-	-
L64'	64	21	-	-	21	-
L81	81	40	-	40	-	-

The signal to noise ratios (S/N) for different number of runs help in the optimization for process. S/N ratios are generally the log functions of desired output and these ratios are used as the objective functions for optimizing process. S/N ratios also help in data analysis and the estimation of the optimum results. The optimization problems are treated by two method in Taguchi approach. One is static problem and other is dynamic problem optimization. In the static problem, process parameters directly decide the desired value of output. After this the best levels of the control factor are determined by this optimization technique so that the output remains as the target function. P-diagram (Process diagram or product diagram) is used to properly explain the Taguchi approach based on the static problem. P-diagram clearly shows that the output is not affected due to the presence of noise. Thus, the variation in the output values are minimized which is primary objective of the Taguchi experiments. So the process becomes robust.

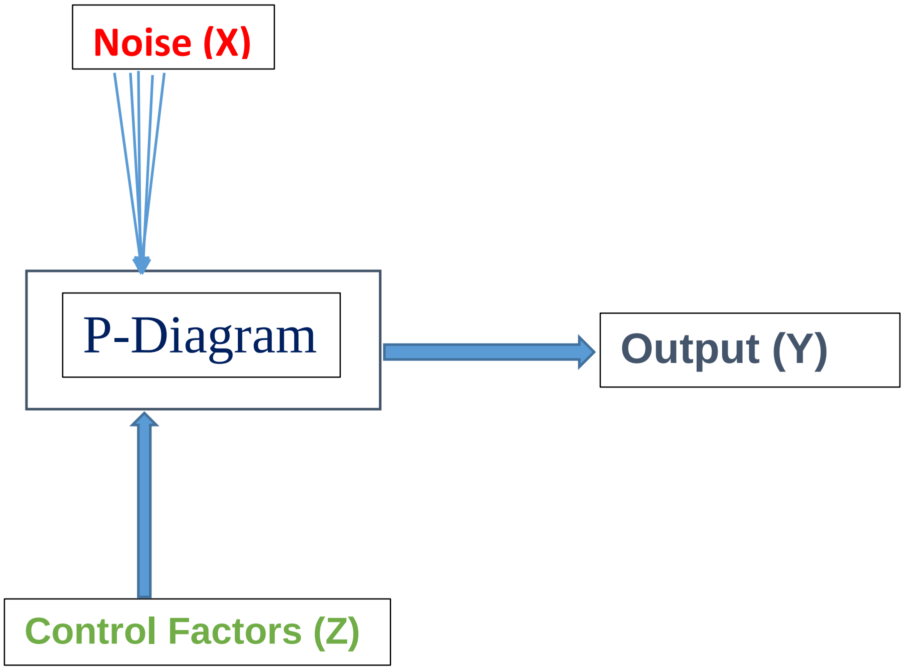


Figure 3.10- P-diagram in Taguchi optimization approach using static problem [45]

In case of transesterification process, process parameters are alcohol to oil molar ratio, catalyst concentration, reaction time and temperature. Orthogonal array is decided on the basis of the number of these parameters and types of level of design (for example, 2-level design, 3-level design, 4-level design, 5-level design and mixed level design). Level of design generally decided by the number of values taken for process parameter.

For example, the following table 3.3 shows the different iterations of four process parameters at 5-level design-

Table 3.3- Design of experiments with four parameters at five levels

Parameters	**Levels**				
	1	**2**	**3**	**4**	**5**
Molar ratio	4.5:1	5:1	5.5:1	6:1	6.5:1
Time (min)	50	60	70	80	90
Temp (˚c)	50	55	60	65	70
Catalyst Conc.	0.5	0.75	1.0	1.25	1.50

On the basis of above table, the following orthogonal array is developed by the Taguchi software. The columns of an orthogonal array represent factors to be studied and the rows represent individual experiments-

Table 3.4- Orthogonal array used to design of experiments (DOE) with four parameters at five levels

S.No.	Molar Ratio	Time	Temperature	Catalyst Concentration
1.	1	1	1	1
2.	1	2	2	2
3.	1	3	3	3
4.	1	4	4	4
5.	1	5	5	5
6.	2	1	2	3
7.	2	2	3	4
8.	2	3	4	5
9.	2	4	5	1
10.	2	5	1	2
11.	3	1	3	5
12.	3	2	4	1
13.	3	3	5	2

14.	3	4	1	3
15.	3	5	2	4
16.	4	1	4	2
17.	4	2	5	3
18.	4	3	1	4
19.	4	4	2	5
21.	5	1	5	4
22.	5	2	1	5
23.	5	3	2	1
24.	5	4	3	2
25.	5	5	4	3

If 5-level, 4-parameter design is used without Taguchi method, there will be a need to do $5^4= 625$ experiments. But Taguchi method reduces the total number of experiments to only 25. So this method greatly helps in optimizing process parameter.

3.4.3 Determination of optimal experimental condition by the design of experiment-

The yield of biodiesel produced under twenty five sets of experimental conditions are estimating by performing experiments under the same experimental conditions. This study is associated with four parameters with each at five levels for which L25 orthogonal array is used as design matrix. After conducting all the twenty five experiments and measuring the percentage yields so that there are twenty five observations in total for each experiment. According to the analysis for the case of larger the better the mean squared deviations (MSD) of each experiment were evaluated using the following equation [45]-

$$\text{MSD} = \frac{1}{n} \sum_{i=1}^{n} \left(\frac{1}{y_i}\right)^2$$

Where n is the number of repetitions of each experiment and y_i is the yield of biodiesel.

Signal to Noise (S/N) Ratio-

In Taguchi optimization Signal to Noise Ratio is a significant parameter which is used to estimate the extent of deviation of quality function from the expected value.

Taguchi approach uses three types of S/N Ratios on the basis of objective of the problem.

i. Nominal-the-Best
ii. Smaller-the-Better
iii. Larger-the-Better

In normal-to-best S/N ratio, normalization problems are solved. Smaller-the-better S/N ratio is used for minimization problem and larger-the-better is used for maximization of problem. In the transesterification process, there is a need to maximize conversion yield of biodiesel, so larger-the-better ratio is used.

The mathematical equation for these three types of S/N ratios are as follow-

$$SNR_i = 10\ log\left(\frac{\bar{y}_i^2}{s_i^2}\right)\ (Nominal\ the\ best)$$

$$SNR_i = -10\ log\left(\sum_{j=1}^{n}\frac{y_j^2}{n}\right)\ (smaller\ the\ better)$$

$$SNR_i = -10\ log\ \frac{1}{n}\left(\sum_{j=1}^{n}\frac{1}{y_j^2}\right)\ (larger\ the\ better)$$

Where

$$\bar{y}_i = \frac{1}{n}\left(\sum_{j=1}^{n} y_{i,j}\right)\ (mean\ value\ of\ response)$$

$$s_i^2 = \frac{1}{n-1}\left(\sum_{j=1}^{n} y_{i,j} - \bar{y}_i\right)\ (variance)$$

Where, i – Experiment number

j – Trial number

n – Number of trials

So the optimum level of design factor will be the level with maximum signal to noise ratio.

3.4.4 ANOVA Table

The optimal value of different process parameters can be simply determined by signal to noise ratio analysis. But this S/N ratio analysis can’t distinguish the reason for different fluctuation of each factor level. Improper experimental conditions or experimental errors might be the reason for this. Therefore, the experimental error can’t be estimated by S/N ratio analysis. Additionally, S/N ratios cannot systematically calculate the differences among the mean values and specify the magnitudes of the factor effects using the same standard.

Due to these drawbacks of S/N ratio analysis, ANOVA analysis is necessary for calculating the magnitudes of the factor affecting the index. The analysis of variance (ANOVA) is conducted for identification of the optimum set of process parameters. Response data is used for ANOVA analysis. The most significant process parameter can be identified by calculating the percentage contribution of each parameter on the conversion yield of biodiesel. The percentage of contribution can be calculated using the following equations-

$$\%\, contribution = \frac{SS_i}{SS_T} \times 100$$

Here SS_i is the sum of the square for ith parameter and SS_T is the total sum of the square of all parameters.

$$SS_i = \sum_{j=1}^{3}[(SNR_L)_{ij} - SNR_T]^2$$

$$SS_T = \sum_{i=1}^{4} SS_i$$

3.4.5 Maximum yield prediction

The theoretical maximum yield of biodiesel can be predicted by using the following equation. The process parameters are taken in optimum condition.

$$Y_o = 10^{\left(\frac{SNR_o}{5}\right)}$$

Where, SNR_o – S/N ratio under optimum conditions

Y_o - Theoretical optimum yield

3.5 Harnessing solar energy in biodiesel production

The concept of use of solar energy in biodiesel production is new, but it is similar to the concept of solar thermal applications. There are various types of solar collectors available for utilizing the thermal energy of solar irradiation. Selection of solar collector is done on the basis of heat flux and temperature needed.

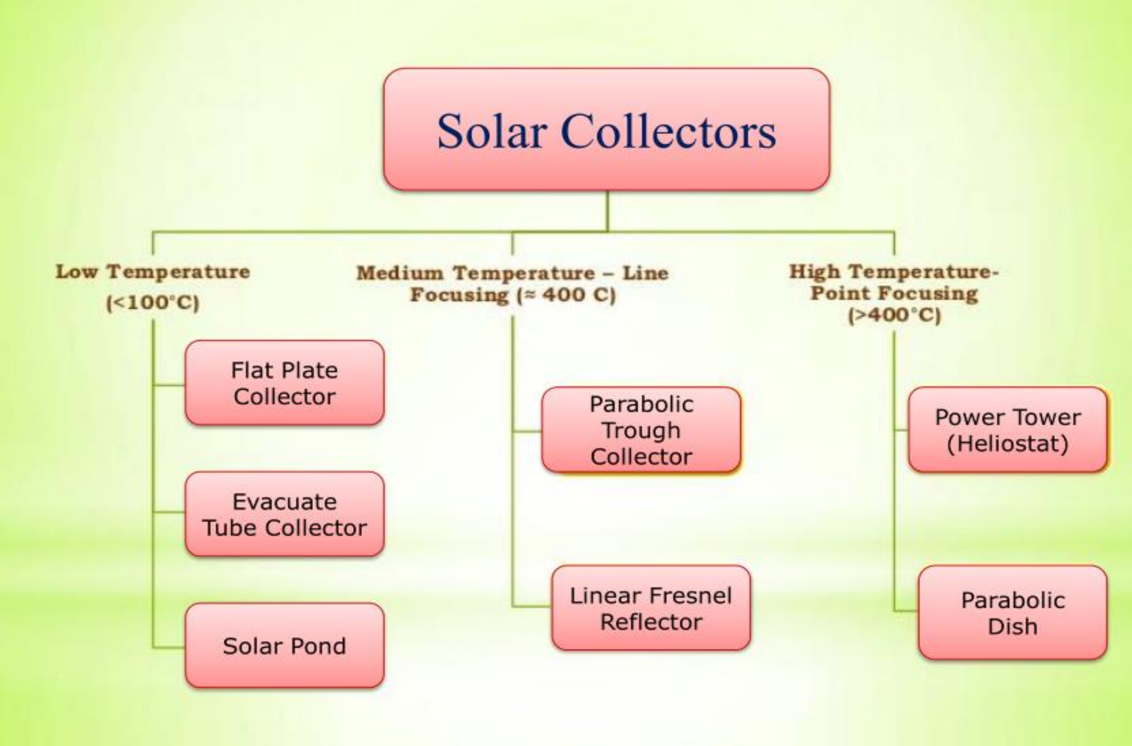


Figure 3.11- Types of Solar collectors

In this project work, a small reflective parabolic mirror was used which served as the only heat source in the chemical heating during transesterification process.

3.5.1 Mathematical analysis of Concentrating Solar paraboloid reflector

Stine et al. (1985) discussed about various design parameters for paraboloid collector. The knowledge of actual amount of heat required and flux temperature range is necessary to design point focusing solar reflector of paraboloidal shape. We can mathematically analyze these type of solar collector as follow:-

The following formula is used for calculating the focal length of paraboloid [47]-

$$f = \frac{h^2}{4 * R}$$

Heat energy falling on the absorber plate at the focal point in reaction time can be determined as [47]-

$$Q_u = H \cdot \rho(\tau \cdot \alpha)_e \alpha \cdot \gamma$$

Where, H = Mean insolation per unit area

ρ = Specular reflectance of the reflector

$(\tau\alpha)_e$ = Effective Transmittance absorptance ratio

α = Absorptance

γ = intercept factor

The equation for three dimensional revolution of the paraboloid is determined as:

$$X^2 + Y^2 = 4fZ$$

The rim angle ϕ_{rim} of solar paraboloidal reflector can be calculated as [47]:

$$\tan \varphi_{rim} = \frac{1}{\left(\frac{d}{8h}\right) - \left(\frac{2h}{d}\right)}.$$

The surface area of the solar paraboloid reflector can be calculated for following formula-

$$AS = \frac{8\pi f^2}{3}\left[\left(\left(\frac{d}{4f}\right)^2 + 1\right)^{3/2} - 1\right]$$

Where, ‘d’ is the aperture diameter, ‘f’ is the focal length and h is the depth of paraboloid. The arc length ‘S’ can be given by [47]-

$$S = \frac{d}{2}\sqrt{\left(\frac{(4h)}{d}\right)^2 + 1} + 2f\ln\left(\left(\frac{4h}{d}\right) + \sqrt{\left(\frac{4h}{d}\right)^2 + 1}\right).$$

The circumference length of circular aperture for the paraboloid reflector equals to 2ΠR and we can determine the concentration ratio for the reflector as follows-

$$\boldsymbol{CR = \frac{A_a}{A_r}}$$

Where A_a is the projected area of the reflector on a plane normal to its axis and A_r is the receiver area. The receiver size is determined after fabrication of paraboloidal solar reflector. Firstly, the plane and sectional elevation of the reflector are drawn on the drawing sheet for the purpose of fabrication. A G.I sheet can be used as the base of the reflecting material. A circle of circumference 2πR was drawn on the plane sheet, where R is the distance between the origin and the end point. When the paraboloid is flattened, it occupies a smaller circumference equal to 2πX in the paraboloid after fabrication, where X is the aperture radius of the paraboloid. For a symmetric paraboloid, R can be calculated in terms of X as follows-

$$R = X + \frac{X^3}{24f^2}\text{cm}.$$

For general conditions, the non-symmetric 'R' would be-

$$R = \frac{1}{4f}X(X + 4f)^{1/2} + 4f^2\log\frac{X + (X^2 + 4f^2)^{1/2}}{2f}.$$

The efficiency of using paraboloid solar reflector for chemical heating in transesterification process can be given as the ratio of heat utilized in transesterification to the total heat received due to solar irradiation. Efficiency can be estimated as:

$$\eta = \frac{m \cdot C \cdot \Delta T}{A_s \cdot \int_o^t I \cdot dt}$$

Here, m is the mass of the oil and chemicals used in transesterification and C is the specific heat, ΔT is the temperature change in the oil and chemicals mixture during transesterification. Denominator shows the total heat supplied by solar irradiation during reaction time ‘t’. A_s is the surface area of paraboloid and I is the intensity of solar irradiation in watt/m^2 [48].

3.5.2 Heat Transfer Mechanism in solar assisted transesterification

Heat energy of solar irradiation is transferred to the mixture of oil and chemicals by four mechanisms. First, by direct solar rays i.e. sunlight directly strike the vessel containing oil and alcohol mixture. Second mechanism of heat transfer in transesterification process is by convection in which the hot air surrounding the oil-alcohol mixture inside the vessel. Third mechanism is by conduction in which heat is transferred from the platform on which the vessel rests. The fourth mechanism of heat transfer to oil-alcohol mixture by reflected solar rays from the surface of paraboloid solar reflector [48].

3.6 Concluding Remark from the theory of solar assisted transesterification

Transesterification is the most commonly used process among the process for production of biofuels. Process parameters in transesterification are alcohol to oil molar ratio, catalyst concentration, reaction time and reaction temperature. These parameters can be optimized using Taguchi method in Minitab 17 software and conversion yield of biodiesel can be increased by this method. Although the conventional method of biodiesel synthesis is not typical, we can use solar energy as the source of chemical heating in transesterification process. Paraboloid solar reflector can provide better arrangement for this kind of setup in which thermal energy of solar energy is entrapped in chemical heating for biodiesel synthesis.

Chapter 4

Conventional Method of biodiesel production from cottonseed oil

In this chapter, the experimental work related to conventional method of biodiesel production is discussed. Cottonseed oil is used as the feedstock oil in this work and methanol and potassium hydroxide (KOH) are used as alcohol and catalyst in the transesterification process. Cottonseed oil is a non-edible oil, so there is no conflicts of food vs fuel, when cottonseed oil is used for biodiesel production. Taguchi approach for optimization of process parameters is also used to make the production process efficient and effective.

4.1 Determination of FFA content in the cottonseed oil

Determination of FFA content is necessary because it decides which type of transesterification process to be used. If the FFA content is less than 2.5 wt%, alkali base catalyzed transesterification is used and in case FFA higher than 2.5 wt%, acid catalyzed transesterification is used. So, method of titration is used to determine the FFA content in feedstock oil. In this method, a solution of phenolphthalein indicator was prepared in which 0.05 g phenolphthalein is mixed with 50 ml ethanol and 50 ml of distilled water and then this solution is stirred for a few seconds and phenolphthalein indicator is prepared. Then another solution is made in which 1 gram of NaOH is mixed in 100 ml of distilled water and then we make it dilute by adding 900 ml of distilled water. This solution is poured in burette.

Figure 4.1- (a) Titration process taking place in beaker; **(b)** Mixture of cottonseed oil and methanol

Then another solution was prepared in beaker by mixing 1 ml of cottonseed oil in 10 ml of methanol. Then we mix two or three drops of phenolphthalein indicator in this solution. After this 0.1% NaOH solution is added in oil alcohol phenolphthalein solution using burette until the solution in the beaker appears pink. When pink color appears in beaker, titration is assumed to be completed. The FFA content is decided according to the amount of 0.1% NaOH solution used in titration [49]. The following table give FFA content information according to milliliters of 0.1% NaOH solution used in titration.

Table 4.1- FFA content details according to ml of 0.1% NaOH used in titration [49]

ml of 0.1% NaOH used	FFA content in wt%	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

According to the above described method for determination of FFA content, the percentage of FFA in cottonseed oil in three samples was estimated as follows-

Table 4.2- Data of FFA content for three samples of cottonseed oil

S. No.	ml used in titration	%FFA
1.	1.1	0.79
2.	1.0	0.72
3.	1.0	0.72

Taking an average value from above table, we can say that the FFA content in cottonseed oil is around 0.74 wt%. This value of FFA content is less than 2.5 wt%, so we use alkali base catalyzed transesterification for production of biodiesel from cottonseed oil.

4.2 Design of experiments for biodiesel production from cottonseed oil (CSO) using Taguchi method

For optimization of process parameters, Taguchi's approach was used in which four process parameter: molar ratio, reaction time (minutes), reaction temperature (˚C) and Catalyst concentration (wt%) were taken into consideration. A 3-level design was used in this experiment. The following table 4.3 clearly show the factors and their levels-

Table 4.3- Process parameters and their levels

	Factors			
Level	Molar Ratio	Time (min)	Temperature (˚C)	Catalyst Conc. (wt%)
1	4:1	30	50	0.50
2	5:1	40	60	0.75
3	6:1	50	70	1.00

On the basis of this 3-level 4-factor design, we adapt L9 orthogonal array by creating Taguchi design in Minitab 17 software. The following table shows the possible nine iterations of experiment as described by L9 orthogonal array along with the corresponding conversion yields of biodiesel found after performing nine experiments-

Table 4.4- L9 orthogonal array

	Levels of design for different Factors				
S. No.	Molar Ratio	Time	Temperature	Catalyst Concentration	**Yield (%)**
1.	1	1	1	1	**90.33**
2.	1	2	2	2	**92.36**
3.	1	3	3	3	**94.60**
4.	2	1	2	3	**94.26**
5.	2	2	3	1	**93.36**
6.	2	3	1	2	**93.21**
7.	3	1	3	2	**96.20**
8.	3	2	1	3	**95.64**
9.	3	3	2	1	**94.12**

Taguchi software shows the response table for signal to noise ratio and mean using 'larger is better' condition.

<u>Table 4.5- Response table for Signal to Noise ratios (larger is better)</u>

Level	Molar Ratio	Time	Temperature	Catalyst Concentration
1	39.31	39.42	39.37	39.33
2	39.43	39.44	39.42	39.45
3	39.58	39.46	39.53	39.54
Delta	0.27	0.04	0.16	0.21
Rank	1	4	3	2

<u>Table 4.6- Response table for Means</u>

Level	Molar Ratio	Time	Temperature	Catalyst Conc.
1	92.43	93.60	93.06	92.60
2	93.61	93.79	93.58	93.92
3	95.32	93.98	94.72	94.83
Delta	2.89	0.38	1.66	2.23
Rank	1	4	3	2

From the response table of signal to noise ratios and means, we can determine that conversion yield of biodiesel mostly affected by molar ratio and then by catalyst concentration, reaction temperature, time respectively. Main effect plots for signal to noise ratio and mean data are found using taguchi approach as shown in following figures-

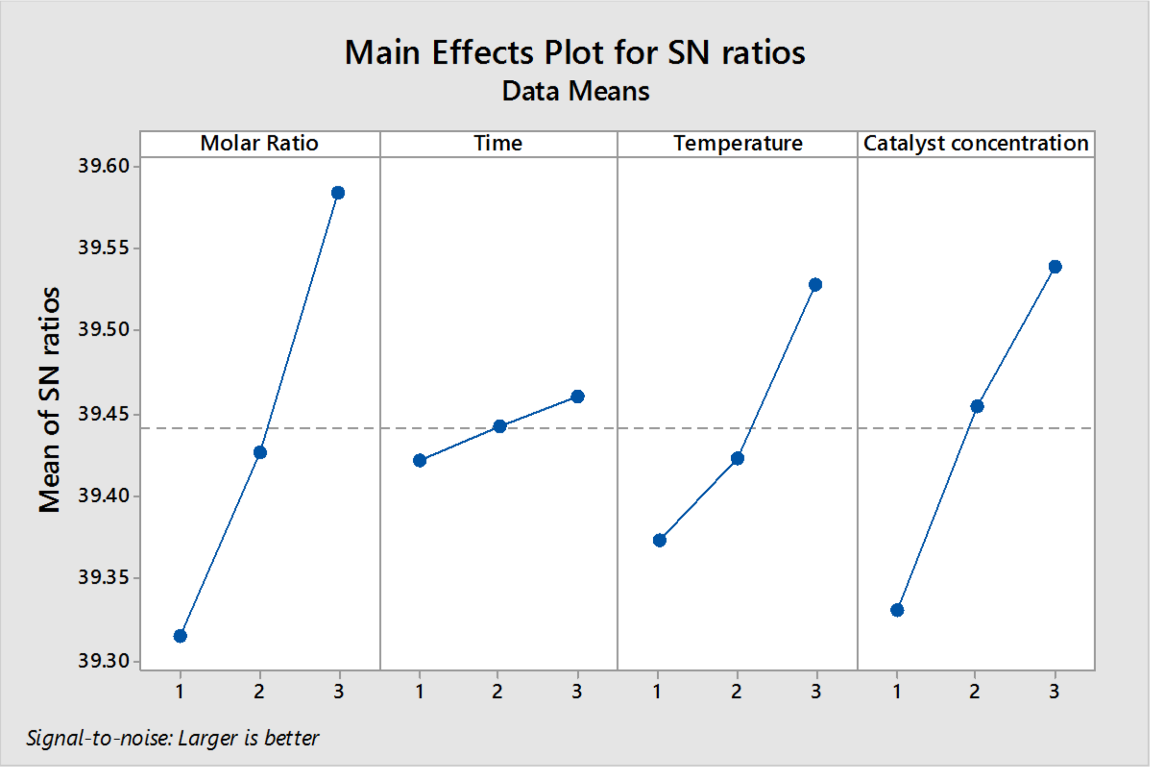


Figure 4.2- Main effects Plot of signal to noise ratios with respect to factors

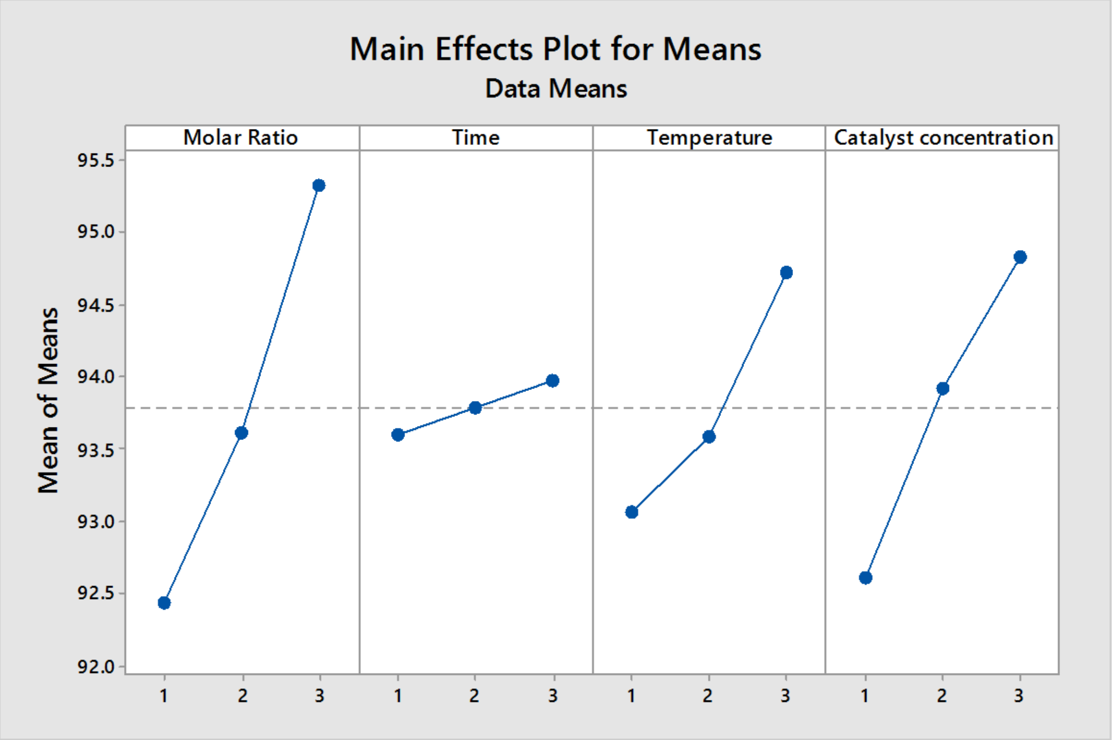


Figure 4.3- Main effect plot for means

4.2.1 Effect of Molar ratio on conversion yield of biodiesel

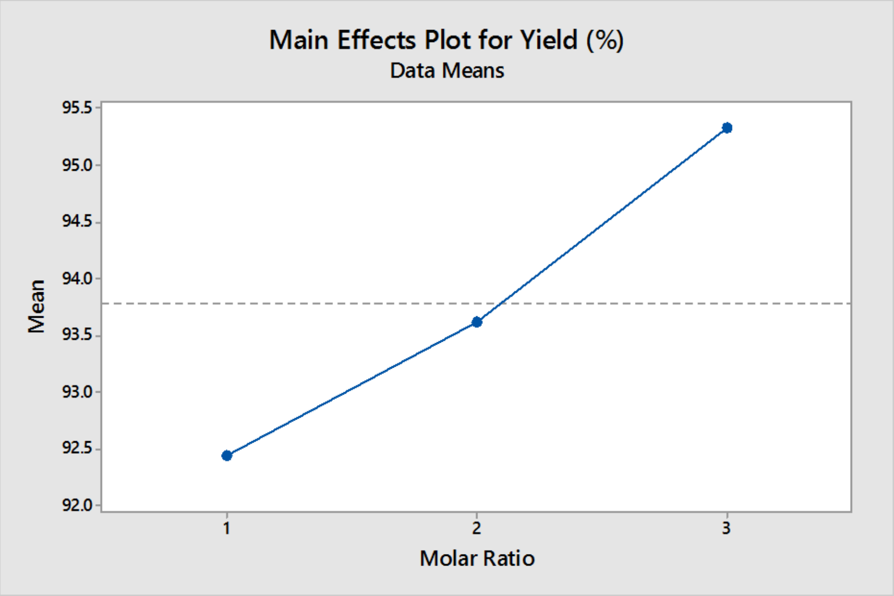


Figure 4.4– Main effect plot for Yield vs Molar ratio

The most important factor, which affects the yield of biodiesel, is molar ratio. The main effect plot generated after application of taguchi approach clearly shows that conversion yield increases with increase in oil to alcohol molar ratio from 4:1 to 6:1.

4.2.2 Effect of reaction time on yield

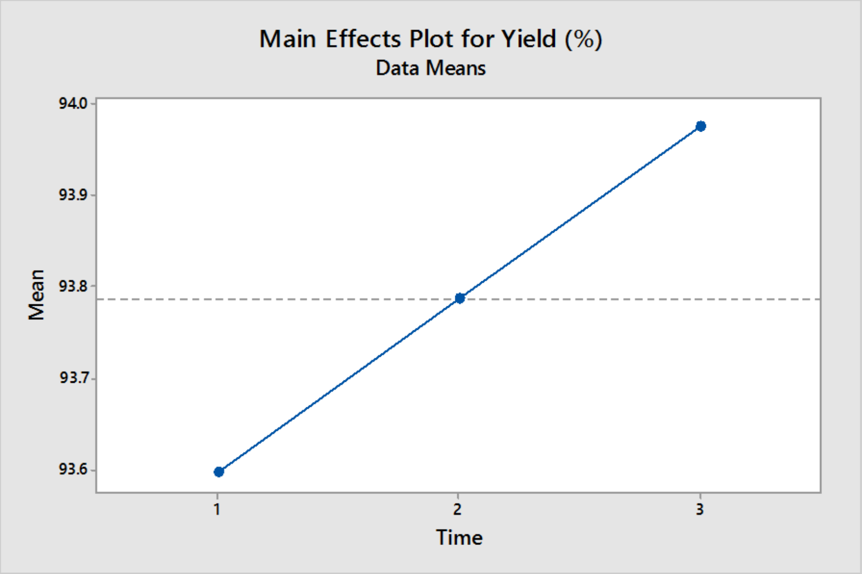


Figure 4.5- Main effect plot for yield vs time

The conversion yield increase when reaction time increases from 30 minutes to 50 minutes.

4.2.3 Effect of reaction temperature on yield

In this experiment, reaction temperature was kept in the range of 50˚C to 70˚C. The main effect plot for yield with respect to temperature show that the conversion yield increases when reaction temperature is increased from 50˚C to 70˚C.

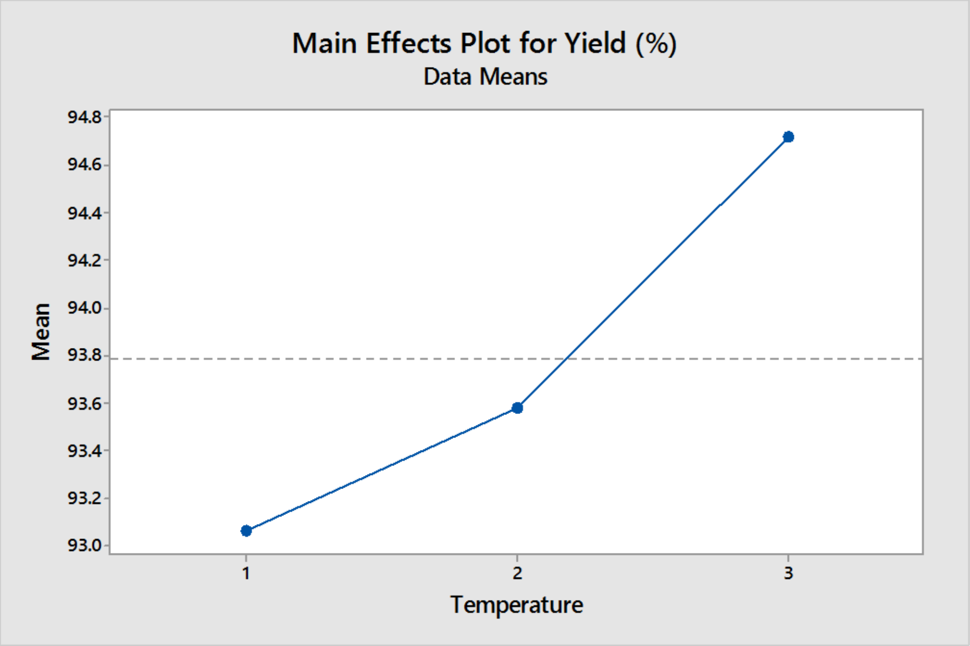


Figure 4.6- Main effect plot of yield vs temperature

4.2.4 Effect of catalyst concentration on yield

In this experiment, KOH was used as catalyst in transesterification reaction. The experiments are performed on various wt% of catalyst concentration such as 0.5 wt%, 0.75 wt% and 1.0 wt%. The conversion yield increases as the catalyst concentration increased from 0.5 wt% to 1.0 wt%. The reason for less yield in case of 0.5% KOH is that it is not enough to enhance the chemical reaction. It is observed that transesterification reaction does not take place due to insufficient amount of catalyst concentration. The maximum yield occurs at the level 3.

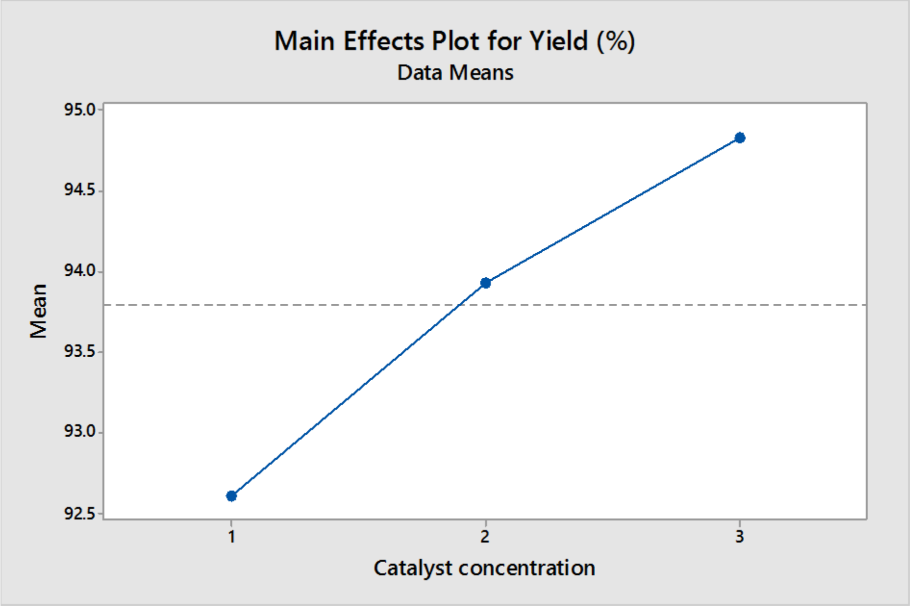


Figure 4.7- Main effect plot for yield vs catalyst concentration

4.2.5 ANOVA table

Different parameters affect the conversion yield of biodiesel to a different extent. The relative magnitude of the parameter effects are listed in table. A better feel for the relative effect of the different factors is obtained by the decomposition of variance, which is commonly known as analysis of variance (ANOVA).The ANOVA table made by taguchi software is as follow:-

Table 4.7- Analysis of Variance

Source	**Degree of Freedom**	**Sum of Squares**	**Mean of Squares**	**F-value**	**P-value**
Molar ratio	2	12.6686	6.3343	3.14	0.116
Reaction time	2	0.2166	0.1083	0.03	0.974
Reaction temp	2	4.3256	2.1628	0.64	0.562
Catalyst conc.	2	7.5434	3.7717	1.31	0.336
Error	0	*	*		
Total	8	24.7542			

In the present study, the degrees of freedom for the error are zero. Hence an approximate estimate of the error sum of squares is obtained by pooling the sum of squares corresponding to the factors. The larger the contribution of a particular parameter to the total sum of squares, the larger will be the ability is of that factor to influence S/N ratio. Moreover, the lower P-value, the larger will be the factor effect in comparison to the error mean square. For the molar ratio P-value is very small, hence it has more contribution in the yielding of biodiesel.

4.2.6 Optimum conditions

The optimum conditions for all factors in this experiment are at level 3. Hence, the conversion yield will be maximum when oil to alcohol molar ratio is 6:1, reaction time is 50 min, reaction temperature 70˚C and catalyst concentration is 1.0 wt%. At these condition, the experiment was performed and the conversion yield was found as 96.58% which is quite higher than the yields found at other conditions.

4.2.7 Physio-chemical Properties of Cottonseed oil methyl ester (CSOME)

Table 4.8: properties of CSOME

Name of Properties	Diesel	CSOME
High Calorific Value (MJ/kg)	42.232	39.5
Density (kg/m^3)	0.831	0.9148
Kinematic Viscosity@ 40°C(mm^2/s)	3.21	18.2
Cloud Point, °C	-12	1.7
Pour Point, °C	-17	-15

The table depicts that the properties of CSOME (biodiesel) is comparable to the properties of diesel. Hence it can be used in vehicle with and without making its blends.

Chapter 5

Experimental analysis of Solar-assisted biodiesel production from cottonseed oil

In the previous chapter, we have discussed about the conventional method of biodiesel production. To make this process economical, we use solar energy for heating required in transesterification process. In this chapter we will focus on the experimental work done in biodiesel production using thermal energy of solar irradiation. As the concept of utilizing solar energy for chemical heating in transesterification is similar to the concept of solar cooking where the vessel is heated by utilizing thermal energy of solar irradiation.

5.1 Experimental Setup

In this experiment, a small paraboloid solar reflector was used which concentrate heat at the platform placed on its focal point. The specifications of the solar reflector are shown in following table-

Table 5.1- Specifications of the parabolic dish collector

Diameter of outer ring	1.4 m
Focal length of dish	0.2 m
Dish rim angle	120.5^{o}
Aperture area of dish	1.539 m^2
Concentration ratio of dish	33

The high concentration ratio of parabolic dish collector helps in rapidly increasing the temperature of the oil, alcohol and catalyst mixture. The condition for feasibility of this method is that the intensity of solar irradiation should be greater than 400 W/m^2. The objective of this type of setup is to produce biodiesel without the use of any fossil fuels for electricity. The vessel containing oil, methanol and catalyst mixture should be placed at the platform provided at the focal point of the reflector. The parabolic solar collector should be installed in such a way that it concentrate reflected solar rays to the base of the vessel used for transesterification process. The figure of solar reflector is shown in figure 5.1.

Figure 5.1- Concentrating solar reflector used in the experiment

The need of magnetic stirrer is omitted in solar-assisted transesterification and black-painted or thermally conductive vessel is preferred in this experiment.

5.2 Design of Experiments in solar assisted biodiesel production using taguchi method

As taguchi optimization technique was used in conventional method of biodiesel production, similarly a mixed-level 5-factor design for experiments is used in solar assisted biodiesel production. In this experiment, 4-levels for average intensity of solar radiation were used while only 2-levels are used for other factors. The catalyst used in this experiment is alkali base catalyst KOH, so transesterification completes in one step and alcohol used is methanol (CH_3OH).

Table 5.2: factors and levels for design of experiments

	Factors				
Level	Average Intensity of Solar Radiation (W/m^2)	Molar Ratio	Time (min)	Temperature (˚C)	Catalyst Conc. (wt%)
1	562	4.5:1	50	60	0.75
2	678	6:1	60	70	1.0
3.	750	-	-	-	-
4.	813	-	-	-	-

On the basis of this mixed-level 5-factor design, we adapt L8 orthogonal array by creating Taguchi design in Minitab 17 software. The following table shows the possible iterations of experiment as described by L8 orthogonal array along with the corresponding conversion yields of biodiesel found after performing eight experiments-

Table 5.3- L8 orthogonal array

	Levels of design for different Factors					
S. No.	Intensity of solar radiation	Molar Ratio	Time	Temperature	Catalyst Concentration	**Yield (%)**
1.	1	1	1	1	1	**89.28**
2.	1	2	2	2	2	**93.46**
3.	2	1	1	2	2	**93.24**
4.	2	2	2	1	1	**93.48**
5.	3	1	2	1	2	**95.20**
6.	3	2	1	2	1	**95.68**
7.	4	1	2	2	1	**96.48**
8.	4	2	1	1	2	**97.28**

Based on the design of experiments according to the above L8 orthogonal array, the mean effective plots for means and signal to noise ratios are found as follow-

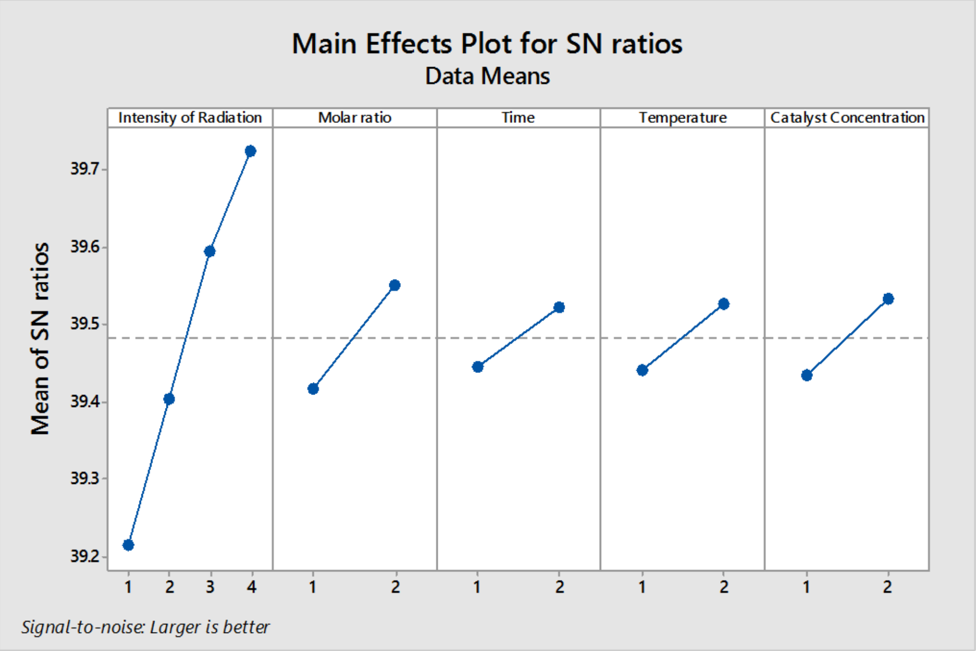


Figure 5.2 – Main effect plot for SN ratio

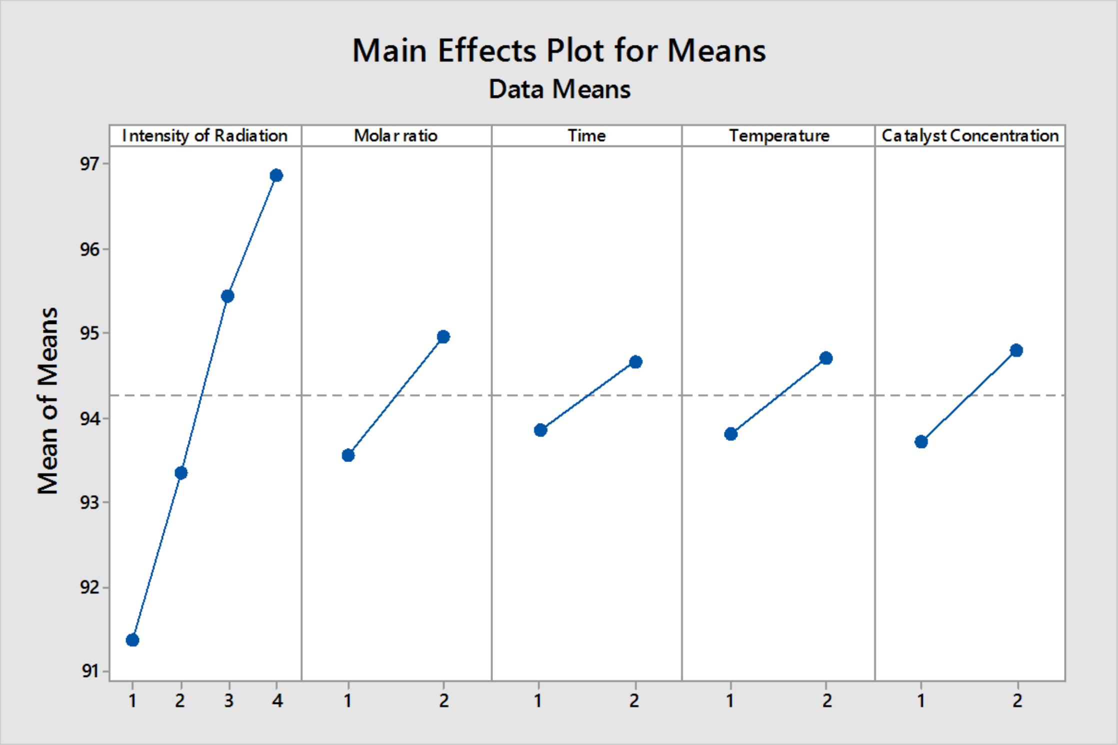


Figure 5.3- Main effect plot for means

The main effect plots for signal to noise ratios and means of yield depict that optimum condition for solar assisted transesterification process is A4B2C2D2E2. It means that yield will be maximum if average intensity of solar radiation is 813 W/m^2, oil to alcohol molar ratio equals to 6:1, reaction time is 60 min, temperature is 70˚C and catalyst concentration equals to 1.0 wt%. On performing the experiment under these condition, the conversion yield of biodiesel is found as 97.46%.

5.3 ANOVA Table

The analysis of variance (ANOVA) is done on Minitab 17 software by selecting option ANOVA and then general linear model is fitted in which ANOVA table is found as the result displayed by the software. The table for analysis of variance (ANOVA) in case of solar irradiation assisted biodiesel production is as follow-

Table 5.4: ANOVA table made by taguchi software

Source	Degree of Freedom	Sum of Squares	Mean of Squares	F-value	P-value
Intensity of Radiation	3	34.838	11.613	5.05	0.076
Molar ratio	1	4.061	4.061	0.61	0.465
Reaction time	1	1.232	1.232	0.17	0.692
Reaction temp	1	1.638	1.638	0.23	0.647
Catalyst conc.	1	2.268	2.268	0.33	0.589
Error	0	*	*		
Total	7	44.038			

In the present study, the degrees of freedom for the error are zero. Hence an approximate estimate of the error sum of squares is obtained by combining the sum of squares corresponding to the factors. The larger the contribution of a particular parameter to the total sum of squares, the larger will be the ability is of that factor to influence S/N ratio. Additionally, for the lower P-value of a factor, the factor effect will be larger in comparison to the error mean square. For the intensity of solar radiation P-value is smallest, hence it has the most contribution in the yielding of biodiesel among the five factors.

5.4 Experiment Procedure

In this experiment, there is a requirement to maintain the flux temperature around 70˚C for one hour. At first, experiments were performed at small level. The cotton seed oil quantity used was just 50 gram and other process parameters were oil to methanol molar ratio, reaction time, reaction temperature and catalyst (KOH) concentration. Taguchi software makes L8 orthogonal array for a mixed level 5-factor design. Steps in this process of solar-assisted transesterification are with the help of diagram in following paragraphs-

i. Take 50 gram of cotton seed oil and heat up the oil using solar energy to remove the water content present in it.
ii. Then cool the heated oil up to 60 ˚C in ambient air.

iii. Then prepare a mixture of methanol and KOH in separate beaker and after mixing, this solution is poured into cotton seed oil.

iv. Transesterification reaction starts after this, maintain flux temperature around 70˚C for one hour to accomplish the transesterification reaction properly.

v. After completion of transesterification, two layers appears in the beaker. The lower layer is of glycerol which is higher in density and appears as dark brown color. The upper layer is of cottonseed oil methyl ester (CSOME) which is our required product.

vi. CSOME is separated from glycerol using a burette and then purified using the water washing process. In this process, warm water (30% of oil quantity at 60˚C) is poured into the crude CSOME and the contaminants of remaining alkali catalyst are neutralized due to water washing process.

vii. The final product is gained by heating the CSOME after water washing to remove remaining water content. Thus, quality of biodiesel production is maintained.

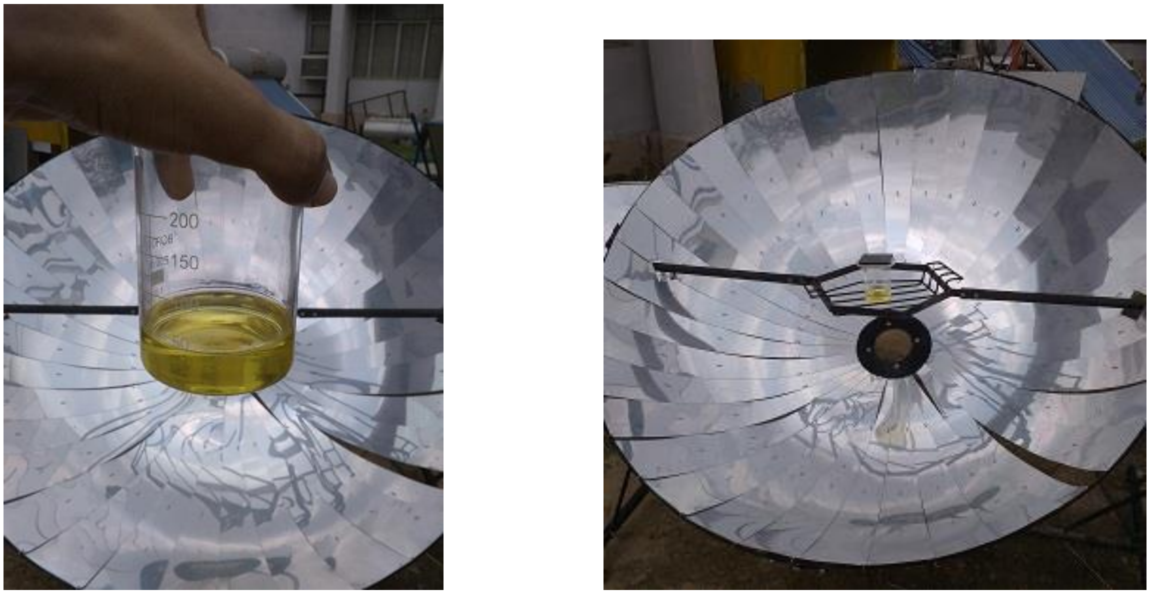


Figure 5.4- (a) Cotton seed oil used**; (b)** heating of oil before transesterification

Figure 5.4: (c) Measuring temperature of mixture **(d)** two beakers system to maintain temp. **(e)** Prepared crude biodiesel after transesterification **(f)** preparation of different sample at same solar intensity

5.5 Biodiesel preparation at medium scale using solar energy

To perform solar assisted transesterification at medium scale, a scheffler reflector was used in place of small solar paraboloid reflector as it can rapidly heat up the oil-methanol-KOH mixture to flux temperature and then the solution is maintained at flux temperature approximately for 40 to 50 minutes. The specifications of scheffler reflector are as follow-

Table 5.5- Specifications of the scheffler reflector

Major axis	2.2 m
Minor axis	1.6 m
Focal length of reflector	2.45 m
Aperture area of reflector	2.7 m^2
Concentration ratio of reflector	135

Figure 5.5- Transesterification process using Scheffler reflector

The advantage of using scheffler reflector over small parabolic collector is that the reaction time is reduced without affecting the yield too much. In our experiment, we use 500 grams of cottonseed oil to produce CSOME (biodiesel). The rest parameters are used same as the optimum parameters in case of small scale production except the reaction time i.e. oil to methanol molar ratio 6:1, reaction temperature 70˚C and catalyst (KOH) concentration equals to 1.0 wt%. But the reaction time is reduced to around 40 min or less depending upon the intensity of radiation.

Figure 5.6- Crude biodiesel produced after transesterification at medium scale

Conversion yield calculation in medium scale

Cotton seed oil used = 500 grams

Methanol quantity = 500/6 = 83.33 grams

Catalyst (KOH) amount = 1.0 wt% = 5 grams

Amount of Cottonseed oil methyl ester (CSOME) produced after transesterification and separation from glycerol = 468 grams

Hence the percentage yield of CSOME (biodiesel) produced = 468 * 100/500 = 93.60 %

Chapter 6

Results and Discussions

In this chapter, the comparative analysis of biodiesel production between conventional method and solar assisted method is discussed. The effect of various process parameters will also be studied in this chapter.

6.1 Results based on the experiments done using conventional method of biodiesel production

Nine experiments were performed using convention method of biodiesel production from cottonseed oil. The conversion yield found from these experiments show that yield was greater for oil to molar ratio 6:1 than in case of molar ratio of 4:1 or 5:1. The figures 5.1-5.3 show the variation of yield with respect to reaction time at different catalyst concentrations-

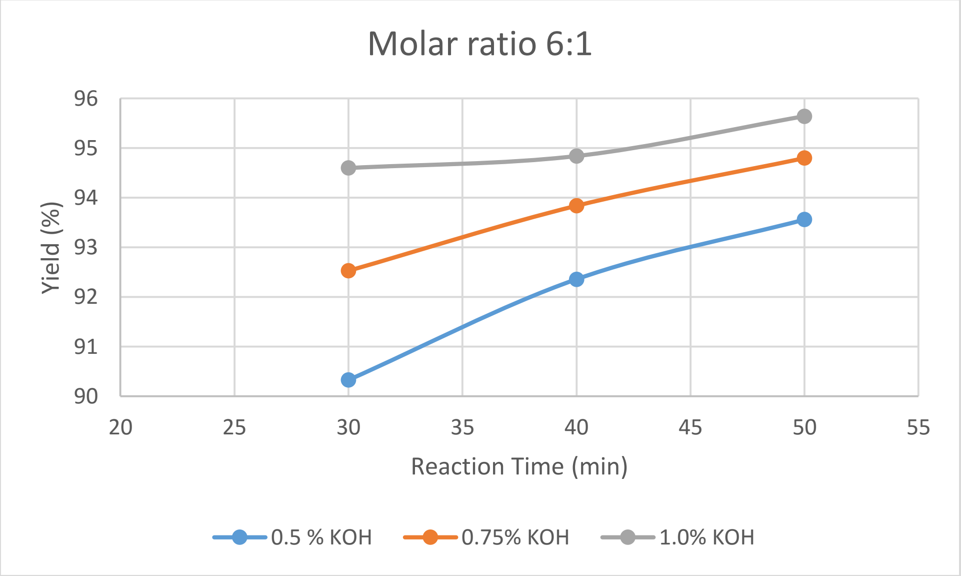


Figure 6.1- Yield vs time curve for molar ratio 6:1 and different catalyst percentage

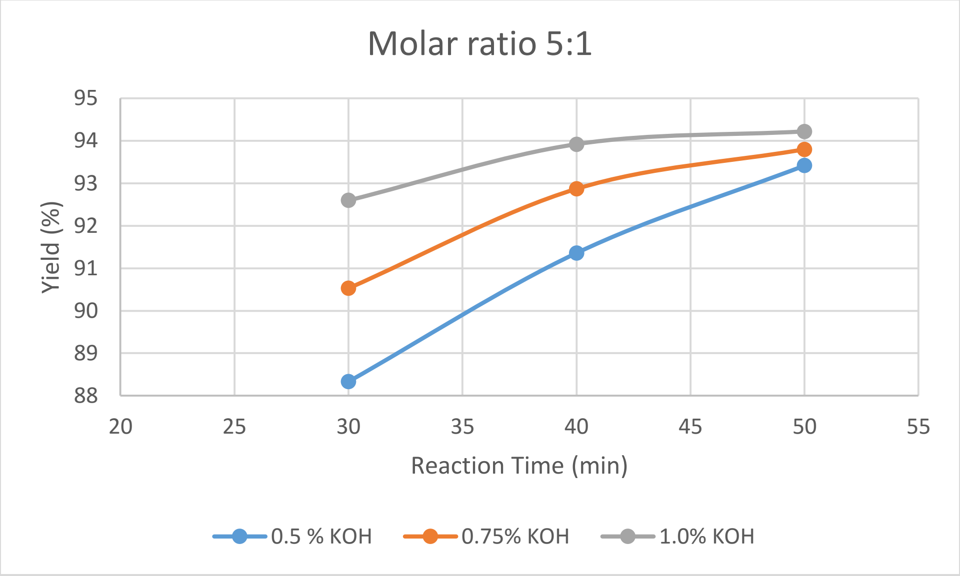


Figure 6.2- Yield vs time curve for molar ratio 5:1

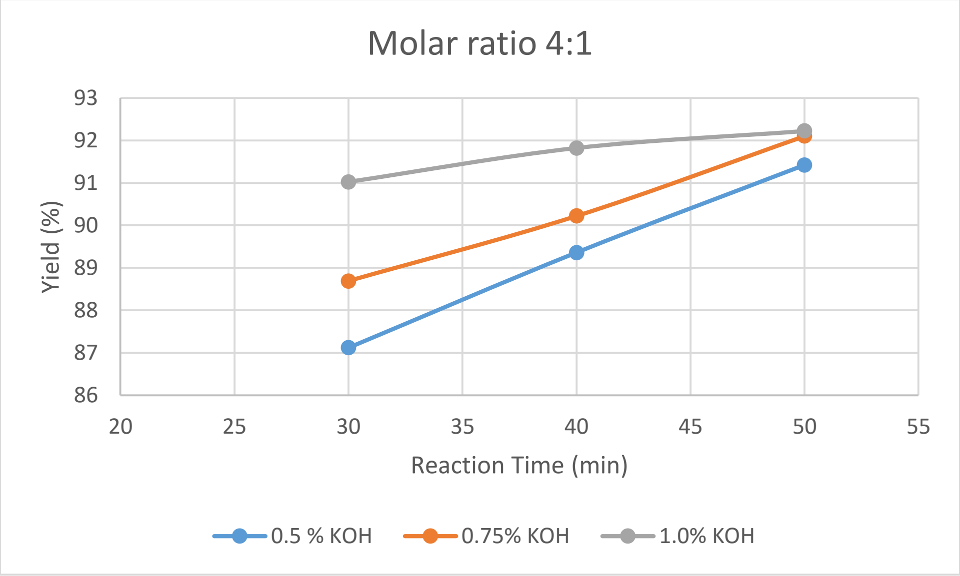


Figure 6.3- Yield vs time graph for molar ratio 4:1

Figure 5.1-5.3 clearly shows that yield of biodiesel is higher for molar ratio 6:1 and 1.0% KOH concentration. Yield also shows an increasing trend when reaction time is increased from 30 minutes to 50 minutes.

6.2 Effect of various factors on yield in case of solar assisted biodiesel production

In solar assisted biodiesel production we used five factor in taguchi optimization, such as average intensity of solar irradiation, oil to alcohol molar ratio, reaction time, reaction temperature and catalyst concentration. So, the dependency of yield on these factors can be seen as follow-

6.2.1 Effect of average intensity of solar irradiation

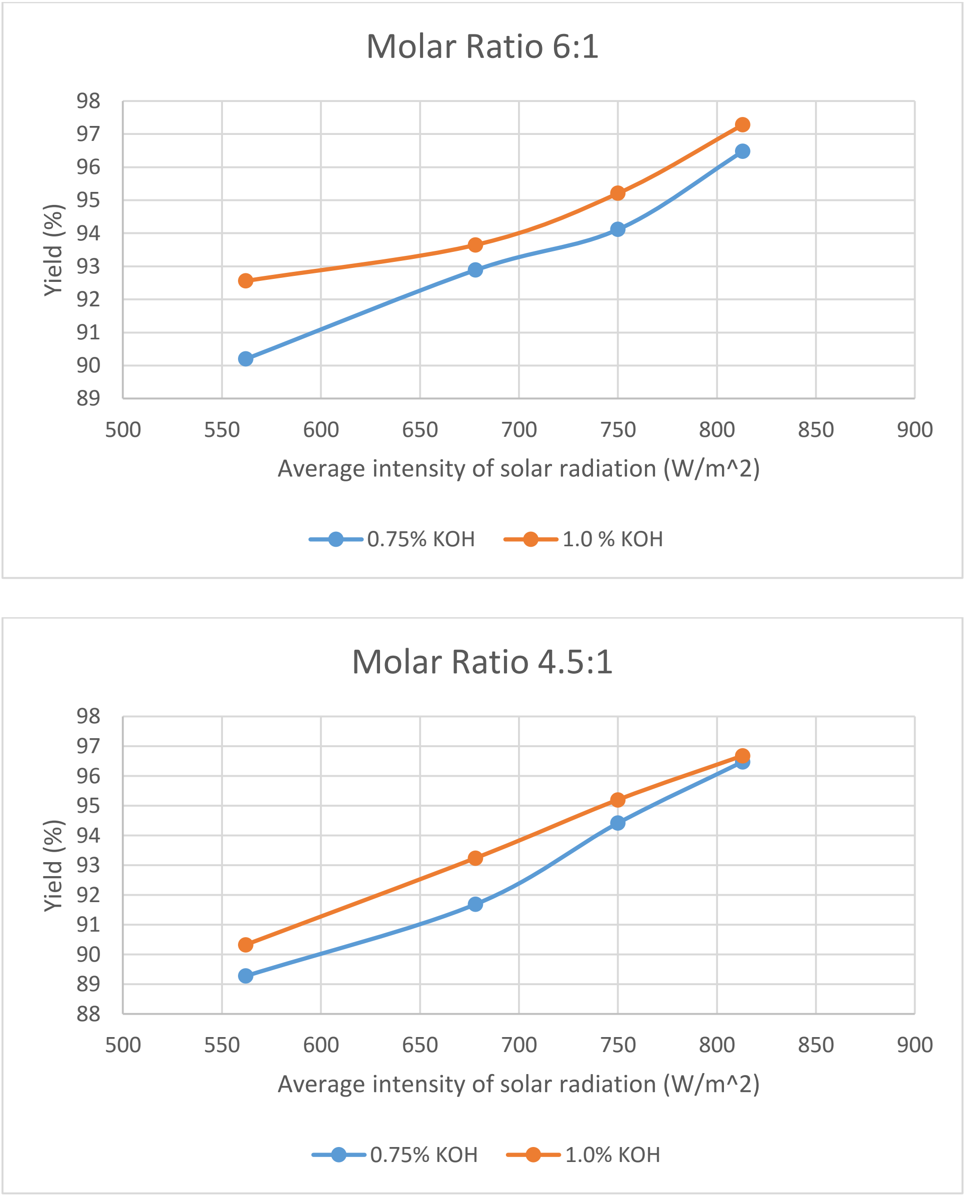


Figure 6.4- Yield vs average intensity of solar irradiation, (a) at molar ratio 6:1 (b) at molar ratio 4.5:1

The figure 5.4 (a) and 5.4 (b) show the variation of yield with respect to solar intensity for different concentration of KOH at oil to alcohol molar ratio of 6:1 and 4.5:1 respectively. Reaction time and temperature is kept constant in determining this correlation. Yield increases with increase in solar radiation intensity. Hence it can be said that yield of biodiesel will be more in case of solar assisted biodiesel production if experiment is performed when higher intensity of solar radiation is available. But it should be keep in mind whenever there is a solar intensity is much higher around 1000 W/m^2 or higher, we need to use two beaker system in which inner beaker contains oil-methanol-KOH solution and outer beaker contains water. We maintain temperature in the inner beaker around 70˚C by adding cold water in outer beaker. In this way, the reaction time needed for transesterification does not vary or vary a few minutes.

6.2.2 Effects of reaction time

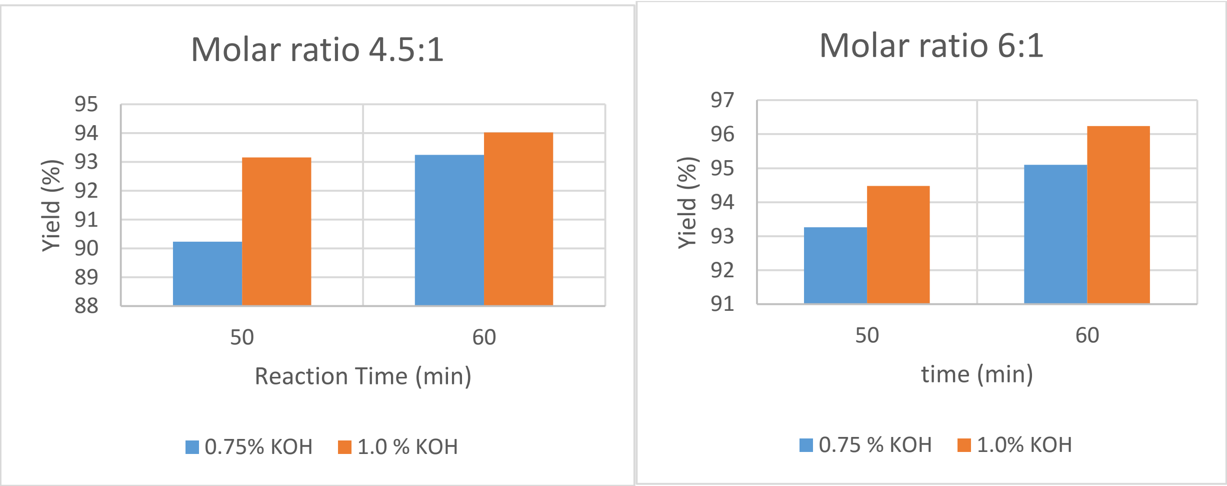


Figure 6.5- Bar chart of yield vs time at different catalyst conc. (a) for molar ratio 4.5:1 (b) for molar ratio 6:1

In our experiment of solar assisted biodiesel production, we take readings at reaction times of 50 minutes and 60 minutes. The better yield is found at 60 minutes. In this case, reaction temperature is kept constant at 70˚C and average intensity of solar radiation is assumed 700 W/m^2. Though yield shows an increasing trend when reaction time is increased from 50 min to 60 min, there is possibility that yield may reduce at certain temperature after 60 min reaction time. So we need to take more reading using higher size orthogonal array using taguchi approach for optimization of transesterification.

6.2.3 Effect of reaction temperature

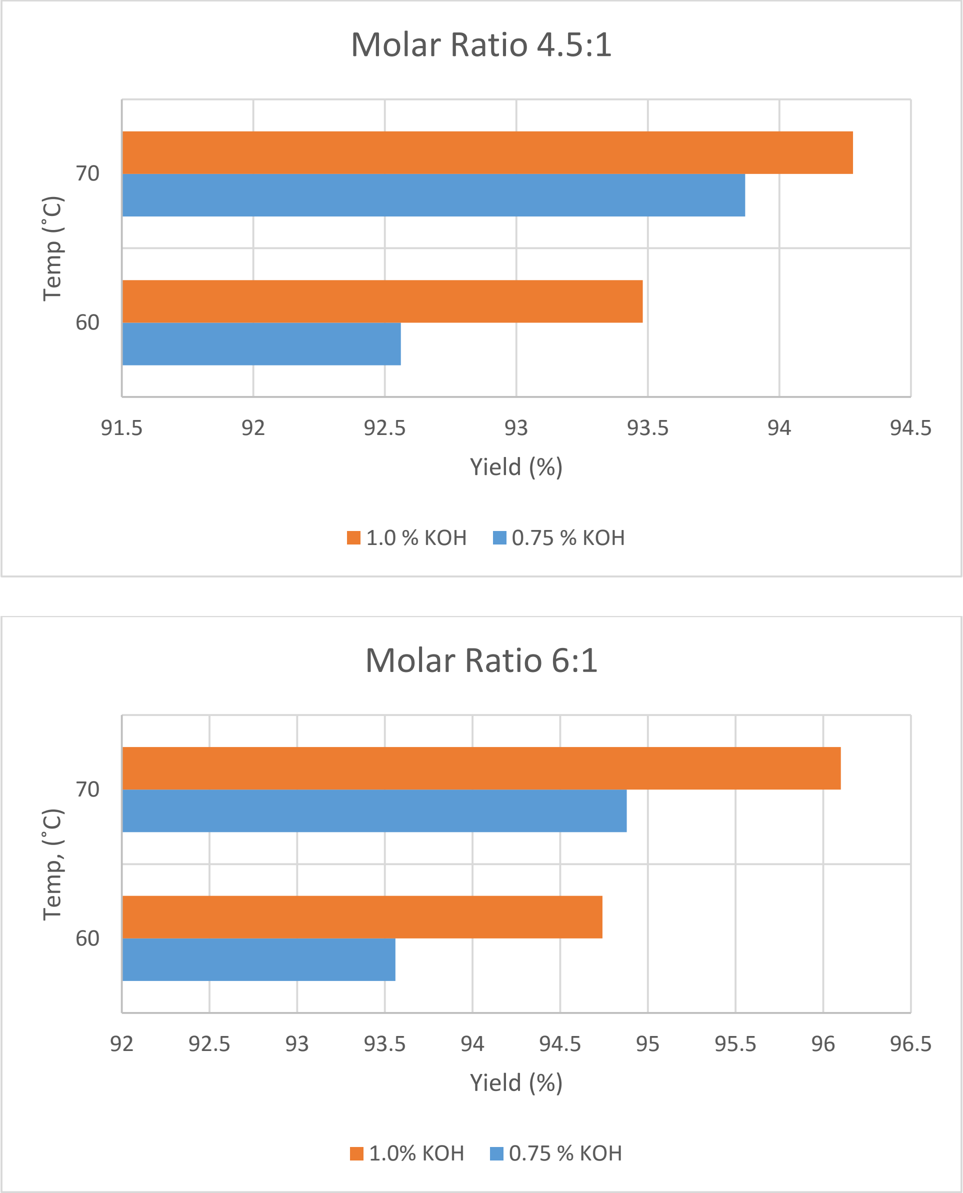


Figure 6.6-Effect of temperature on yield on different catalyst conc. (a) at molar ratio 4.5:1 (b) at molar ratio 6:1

Reaction temperature is a significant factor which affects yield of biodiesel produced. In this experiment, the flux temperatures of mixture were maintained at 60˚C and 70˚C respectively. Results show that better yield is found in case of 70˚C reaction temperature than in case of 60˚C.

6.3 Comparison of yields in different methods of biodiesel production

The following table 6.1 shows the conversion yield of biodiesel at different scale and also for different method of biodiesel production.

Table 6.1 Comparison of yield for different method at small and medium scale

Method of biodiesel production	**Yield at small scale (50 gm oil)**	**Yield at medium scale (500 gm oil)**
Conventional	96.58	93.2
Solar assisted	97.46	93.60

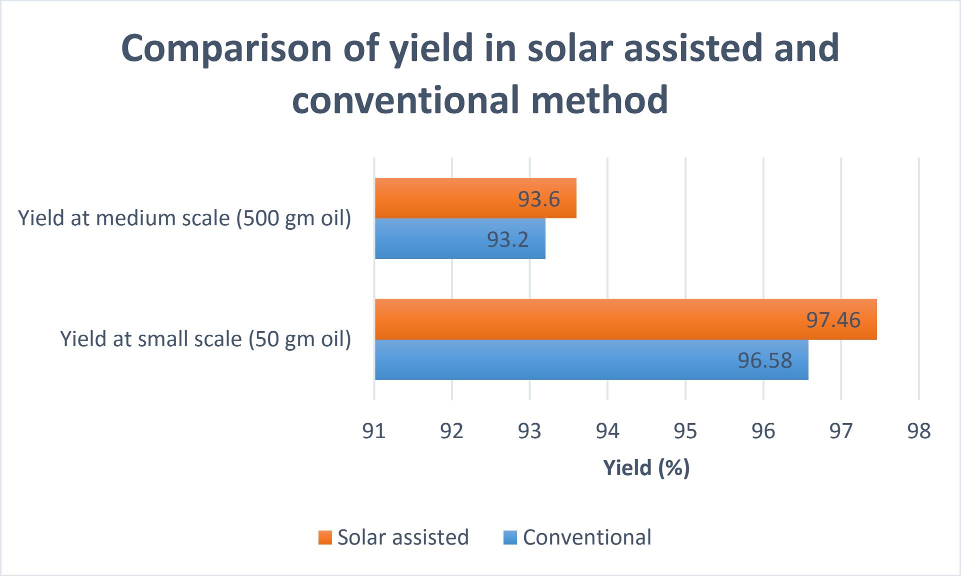


Figure 6.7 – Comparison of yield at different scale

We can also compare the yield of convention, microwave assisted and solar assisted method of biodiesel production in case when optimum conditions are used in all these processes-

Table 6.2- Maximum yield of CSOME in different method of biodiesel production

Technique of biodiesel production	Maximum yield of CSOME at optimum condition (%)
Conventional	96.58
Microwave Irradiation assisted [50]	98.12
Solar Irradiation assisted	97.46

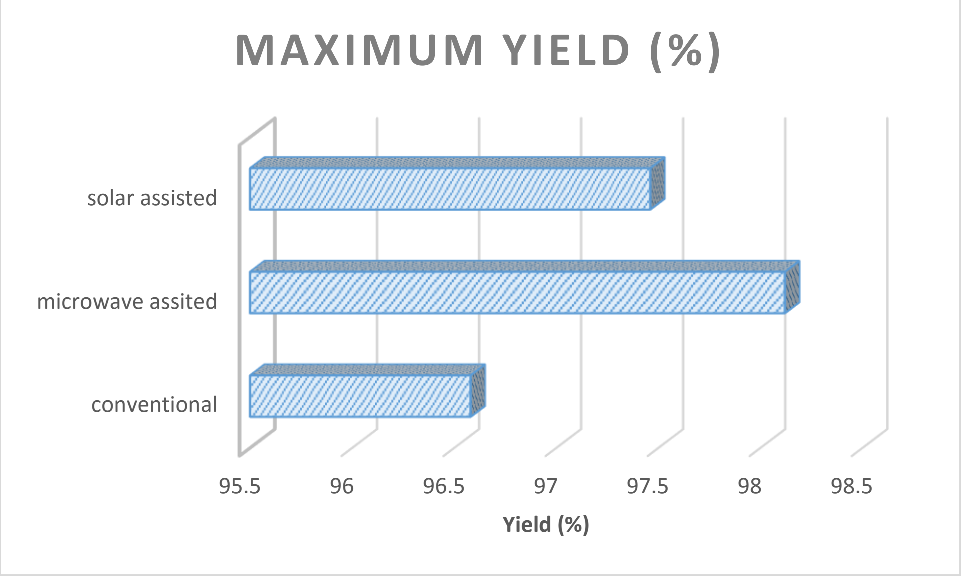


Figure 6.8- Maximum yield of CSOME in different method of biodiesel production

6.3 Properties of biodiesel prepared from conventional and solar assisted method

Properties	**Conventional**	**Solar assisted**
Density (kg/m^3)	852	846
Kinematic Viscosity (mm^2/s) at 40˚C	6.1	5.9
Higher calorific value (MJ/kg)	41.68	42.05

Table 6.3 depicts that the properties of biodiesel produced from solar assisted transesterification process are better than the properties of biodiesel produced from conventional method. Hence, solar assisted biodiesel production is an effective and qualitative way of producing biodiesel if the values of process parameters are selected properly.

Chapter 7

Conclusion and future recommendations

In this thesis, we have discussed about an experimental analysis of solar assisted biodiesel production. It can be concluded that using solar energy for heating in transesterification could be a better option as conventional method of biodiesel production requires heating from electrical sources. Conventional method of biodiesel production is also not so cost effective that it can be commercialized easily. So to make it cost effective, we used solar parabolic reflector setup in which the necessary flux temperature is maintained by utilizing the thermal energy of solar irradiations. The main advantage of solar assisted biodiesel production is that the need of magnetic stirrer is skipped. We don't need to stir mixture during transesterification. Also the conversion yield of biodiesel produced is better than the in case of conventional method. So efficiency and quality of biodiesel production becomes greater.

In the future, researches should be focused on optimizing the transesterification process using the solar energy and efforts should be made to use this method commercially. Selection of site for solar assisted production of biodiesel is also a field in which there is a need to do further research. If such kind of setups are installed in a location where the availability of biodiesel feedstock is easily available, the transportation cost of supplying feedstock to biodiesel production plant can be reduced. The sunshine should be better at installation location as average intensity of solar radiation needed more than 400 W/m^2 for transesterification. In India, we can think to develop such kind of setup in Rajasthan, Gujrat, Haryana and all those place where the availability of sun shine remains sufficient throughout the year.

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