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Chapter 1

INTRODUCTION

Today Diesel engines has become a major source for transportation, creation of power and applications in marines, etc. Therefore, diesel has been used largely in every place as a source of power. But due of the gradual decrease in fossil fuel deposits and their large harmful impact on environment because of pollution; there is a critical need for different fuels which are suitable for C.I. engines. Because of this condition, Oils produced from crops have become more favorite now a days as a result of their less impact on environment because of less pollution, as well as the undeniable fact that these are made from inexhaustible sources of energy. Oils used for cooking are inexhaustible source, probably renewable energy source with energy contented practically near to diesel. Before 100 years now, Rudolf Diesel uses vegetable oil for the combustion in a CI engine. With the arrival of low cost diesel and petrol, vegetable oils are not in use. But during the period of 1930s and 1940s vegetable oils were also used in emergency conditions to run the CI engine in place of diesel. Now, the focus has been transferred on the use of vegetable oil and biodiesel fuel.

There are varieties of vegetable oil and bio-diesel which have been tested in diesel engines time to time. Its characteristics for reduction in greenhouse gases, and it also helps on reducing a country's dependence on fossil fuel imports, and it can generate a new marketplace for domestic crops in agriculture, additionally it has lubrication property that eliminates the requirement of any lubricating agent and its wide acceptance to locomotives makers may be listed as the most important benefits of the bio-diesel fuel. There are over 350 crops which can produce oil are identified, out of which only sunflower, soya bean, cottonseed, rapeseed, waste cooking oil and peanut oils are only being thought of potential different fuels for diesel engines.

Need of different fuels
The motivation for development and generation of the different fuel are following:

 a. *Depleting oil reservoirs***:**

      The gasoline and diesel are obtained from petroleum. These are explored from the crust of the earth. But the amount of petroleum in the crust of the earth is limited and approximately non-inexhaustible, hence these oil reserves are depleting with a very high rate. When these reservoirs would completely finished, at that time we would have neither gasoline nor diesel to run automobiles, so a different fuel should be there to decrease dependence on gasoline and diesel. In a country like ours, the 80% of fuel used by country is imported, which is one of the main reasons of such a high trade deficit. In these present situations of increased terrorism and arm rebellion, it is very difficult to have assurance about the regular supply of oil. Also, the price of oil may fluctuate. So it becomes much important for us to switch to non-conventional fuel and solve these problems permanently. There is a depletion of oil in well and oil field. There are geographic areas which are responsible for the generation of oil.

      There is small number of areas of oil fields, where large amount of oil is produced. According to Hubbert peak theory, generation starts off slowly, rises faster and faster, next slows down and flattens until it reaches a peak, after which generation declines. In the late stage, generation often enters a period of exponential decline in which the decline become less and less steep. Oil generation may never reach zero, but eventually becomes very low.

 b. *High emissions***:**

      A very large amount of CO_2 is emitted by automobiles which use gasoline and diesel as fuel. Other gases are also emitted like NOx, Carbon mono-oxide and unburned hydrocarbons, which have harmful effect on health. To reduce the emission of these harmful gases a much cleaner fuel is needed which has good combustion properties as well as low emission characteristics. Atmospheric air pollution contains particulates, biological molecules, or other harmful gases. These harmful gases cause diseases, which leads to death to humans, damage the crops as well as living organisms.

      The atmosphere consists of complicated natural gaseous which are essential to support life on Earth. There is depletion in stratosphere due to pollution. Because of atmospheric air pollution there has been a threat to human life and to the ecosystems of earth. Indoor atmospheric air pollution and urban atmospheric air quality are listed as two of the world's

worst problem related to pollution. This was confirmed by 2008 Institute World's Worst Polluted Places report. According to the 2014 WHO report, around 7 million of people died due to atmospheric air pollution in 2012 worldwide.

The air pollutants are the harmful substances. These are present in the atmospheric air that can cause adverse effect on humans beings and on the ecosystem. These pollutants can be liquid droplets, solid particles, or gases. A pollutant can be produced by natural processes or by man-made. Therefore pollutants can be classified as primary or secondary. Pollutants which are produced by a natural process, such as ash from a volcanic eruption are called primary pollutants. Other examples are monoxide gases released due to combustion in motor vehicle, and the SO_2 releases from industries. Secondary pollutants are those pollutants which are not directly emitted. But, they react with primary pollutants in the atmospheric air and form new compound. Ozone in Ground level is a best example of a secondary pollutant. There are some other pollutants which can be both primary pollutants and secondary pollutants. Because they are emitted directly in air and sometimes also formed by reaction with primary pollutants.

Different fuel
The major fuels for an internal combustion engine are Biodiesels, Alcohols and Hydrogen. Inexhaustible type of fuel can be used in an internal combustion engine. These are as:

 a. *Bio diesel*:

Now, the present time Biodiesel is attraction for all, as a substitute fuel, which is non-toxic and bio-degradable. Biodiesel is generally produced by the process of trans-esterification of animal fat or vegetable oil or waste cooking oil and many inexhaustible resources, with short chain alcohol such as ethanol or methanol. In the Biodiesel, the found percent of oxygen content is more as compared to the petroleum or diesel. Due to its use in internal combustion engines, diesel engines have to show great reductions in the emission of particulate matter, carbon monoxide, sulphur, poly-aromatics, hydrocarbons, smoke, nitrogen oxide, and noise. Because vegetable oil based fuels are made from agricultural used or raw materials which are produced by the process of photosynthetic carbon fixation, therefore these do not contribute to net atmospheric carbon-dioxide levels on burning.

The Biodiesel can be differentiated into two categories on the basis of their source.

- Biodiesel from plants: Plants like jatropha have an ability to produce bio-diesel. After some synthesis, the fuel can be used as diesel in internal combustion engine. But our country has a very large population and we have very limited agricultural land. If we utilize the land to grow these plants, the food supply will be affected so this is not suitable in a country like India.

- Biodiesel from eatable oils: after some chemical and physical reactions, the eatable oils can be converted into the biodiesel. But our country imports a large amount of eatable oil annually to fulfil its demand so we can't even think of the conversion.

b. Hydrogen:

Hydrogen has the highest calorific value and it is more clean fuel, produces pure water as the exhaust. But the process of combustion of hydrogen requires very high-quality equipment so the cost becomes so high which is not suitable from automobile point of view. It uses electrochemical cells to provide hydrogen in internal combustion engines. Electrochemical cells are used to power electric devices and vehicles. Hydrogen combustion is also used in spacecraft for propulsion. Hydrogen has potential to be mass-produced. This can be commercially used for atmospheric aircraft and passenger vehicles. It is the first element of the periodic table. Hydrogen gas is very light. Therefore it rises up in the atmosphere. That is why it is very difficult to obtain hydrogen in pure form. When hydrogen gas is burned in atmospheric air, the H_2 reacts with O_2 to form H_2O with release of energy. The energy released during the combustion process, makes the hydrogen to be used as a fuel. If hydrogen is used in electrochemical cell, the energy can be utilized with high efficiency.

Due to less free hydrogen gas, in practice it can be only used as energy carrier like in electricity. Therefore cannot be used as an energy resource. The production of hydrogen gas requires more energy than the energy received from the gas, when used as a fuel. There is a limitation of the physical law of the conservation of energy. Production of hydrogen produces harmful environmental impacts.

c. Alcohols:

Throughout history, an alcohol has also been used as a fuel. The first four alcohols i.e. methanol, ethanol, butanol and propanol are the important alcohols and can be used as fuels. The main advantage of alcohol is that, they could be easily synthesized chemically or

biologically. The properties of alcohol are such that they can be allowed to be used in IC engines. The chemical formula for alcohol is $C_nH_{2n+1}OH$.

Most of the methanol is produced from natural gas. It can also be synthesised from biomass by chemical processes. Fermentation is a process in which the ethanol is produced from a biological material. Ethanols which are obtained from petroleum are harmful because the mixture contains about 5% methanol. It may cause blindness or death to humans. The main advantage of bio-butanol is that it has energy density which is closer to gasoline. The production of butanol is very difficult to produce in comparison to ethanol or methanol. The main advantage of the four major alcohol fuels is that, they have high octane number.

Basically alcohols are extracted from waste biomass like an agricultural waste. Alcohols have good fuel properties and can easily blend with gasoline. As these are extracted from waste so they help in waste management. The combustion of alcohols doesn't need any extra arrangement so these fuels are cost-effective. Also, the storage and transportation are also very easy.

d. **Butanol**:

Butanol is a four-carbon alcohol. The chemical formula of Butanol is C_4H_9OH. The butanol is present in four type of isomeric structure. The butanol produced by the biological process is known as bio-butanol.

The most of the butanol is produced commercially from fossil fuels. The mostly used reaction is the hydroformylation reaction, to form butyraldehyde. The reaction starts with propane (propylene), but dehydrators produced are next reacted with hydrogen and form 1-butanol and or 2-butano1.The reaction with isobutene produces the propylene oxide along with tert-butanol.

Another way of butanol generation is by fermentation reactions. In fermentation, bacteria reduce the biomass into butanol. The method is mostly used before 1950 and at the present time Clostridium acetobutylicum was used for fermentation processes to produce Butanol at the industrial level. There are some other microorganisms that can produce butane.

The butanol can be used as a fuel in an IC engine without any modification because its properties are much similar to diesel. The butanol has a four link hydrocarbon chain and possesses the good fuel properties.

The butanol is toxic in nature but not much toxic like other alcohols so it is safe to work with butanol as compared to other alcohols. The exposure to butanol can cause only minor skin irritation and minor eye irritation. So butanol can be used without much security concern.

Biodiesel synthesizing process

There are many different ways by which biodiesel can be synthesize, which are given below:

a. ***Direct Use and Blending***: The use of vegetable oils directly in IC engine is not favourable. There are certain problems related to working conditions. Due to its many inherent failing properties. The vegetable oils has similar properties that as of biodiesel fuel. But it requires some chemical modification. Before it can be used as a fuel in the engine. There has been a rigours research for the last couple of decades.

b. ***Emulsion Process***: The high viscosity of vegetable oils is a problem which can be solved by micro emulsions. It uses solvents such as ethanol, methanol, and 1-butanol. This process is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1-150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles. Micro-emulsion results in an increase in cetane number and reduction in viscosity. It provides good spray character to the biodiesel. However, continuous use of micro-emulsified diesel in engines causes problems like injector needle sticking, carbon deposit formation and incomplete combustion.

c. ***Pyrolysis***: It is a process in which one substance is converted into another with the help of heat in the absence of atmospheric air (or oxygen). It is also defined as the process of conversion by heat in the presence of a catalyst. This will results in cleavage of bonds and formation of variety of small molecules. The pyrolysis of vegetable oil to produce biodiesel has been analysed. It is used to produce alkenes, aromatics, alkanes, alkadienes, and carboxylic acids in various proportions. The equipment used for the process of thermal cracking and pyrolysis is costly. For the production of biodiesel, it is a costly process. The main disadvantage of pyrolysis is that separate distillation equipments are required for separation.

d. **Trans-esterification:** The trans-esterification method is the most general process to produce biodiesel. It is similar to the chemical reactions which uses catalyst. Edible oils and alcohol react to produce fatty acid alkyl esters, which is biodiesel and glycerol. A catalyst is required in this reaction, which would be a strong base, such as NaOH and KOH or sodium methylate. The rate of reaction and the yield is improved by the use of catalyst. Due to the reversible reaction, excess amount of alcohol is used. This excess alcohol is used to shift the equilibrium to the right side. Due to low cost of methanol, it is used as alcohol in chemical reaction. The advantage of methanol can rapidly react with vegetable oil. The NaOH can easily diffuse in it. For the completion of trans-esterification reaction, molar ratio of 3:1 is required i.e. 3 moles of alcohol and 1 mole of triglycerides required for the reaction. In general, the molar ratio should be bigger so that the equilibrium shifts forward to maximum ester yield. The reaction of triglycerides with a suitable alcohol in the presence of a catalyst, by controlled temperature for a given period of time. The ultimate products are Alkyl esters and Glycerine.

Biodiesel

Biodiesel is an alternative fuel, which burns clean. It is produced from the inexhaustible sources like used or pure vegetable oils. Eatable and non-eatable both types of oils can produce biodiesel. By making little modifications or no modification in CI engine biodiesel can be used. The use of biodiesel is very simple. It is nontoxic, biodegradable, and free of aromatics and sulphur. Storage of biodiesel is very simple and can be stored just like petroleum diesel. Therefore a separate infrastructure is not required for storage. There is an extraordinary reduction of unburnt carbon monoxide, hydrocarbons and particulate matters, if used in conventional diesel engines. Ignition quality increases because of high cetane number, when blended with diesel.

Due to big gap between demand and supply of edible oils in India, the use of edible oils for the production of biodiesel is not profitable. Indian plants like Neem (Mellia azadirachta) , Mahua (Madhuca Indica), Jatropha (Jatropha curcas), Karanja (Pongamia pinnata), and cotton seed oil contain 30% or more oil in their seed. Due to short supply of edible oils in India, non-eatable tree borne oilseeds (TBOs) of Jatropha, Karajan, Neem, Mahua, and cotton seed are being examined as the source of vegetable oil (SVO) and hence the potential source

of biodiesel. The species of plants, which produces 30% or more oil in their kernel or seeds, have been analysed. Traditionally the collection of seeds and selling of tree-based oilseeds was generally practiced by poor people of India. These oils are used as fuel for lighting. Now days, these oils are used in making lubricants, soaps, candles, varnishes, cosmetics, etc. After all, the present utilization of non-eatable oilseeds is minimum.

Use of biodiesel can increase the better environmental performance. The greening of wastelands can be done. It will create new employment opportunities. These are the main advantages of use of bio fuels.

There are many methods and techniques to convert eatable oils into a Diesel. The process of trans-esterification is one of the most important methods. Trans-esterification is the method of using an alcohol (e.g. propanol, methanol, ethanol or), in the existence of catalyst, such as NaOH or KOH, which is used to break the molecules of the raw oil chemically into methyl or ethyl esters of the inexhaustible oil. The glycerol formed is a by-product. Trans-esterified oils have proved that these can be used with different diesel engine. The combustion characteristics of biodiesel are similar to that of Diesel. The chemical and physical properties which are required for the working of diesel engine are very much similar to diesel fuel.

Trans-esterification is a chemical reaction that aims at substituting the glycerol of the glycerides with three molecules of mono alcohols such as methanol thus leading to three molecules of methyl ester of vegetable oil. The cost of methanol is very low i.e. why it is used in trans-esterification process. The alkali hydrolysis of the oil is done when acid number is less than 1. The moisture content of oil should be less than 0.5%. Acid catalyst such as sulphuric acid (H_2SO_4) is used for esterification process. More than 350 crops which can produce oil have been identified. From which only soybean, sunflower, mango seed, cottonseed, rapeseed and peanut oils are marked as likely different fuels for diesel engines.

Biodiesel generation in India

There is a short supply of eatable oils in India. Therefore to fulfil the requirement of country's need, India has to import up to 40% of oil required. Therefore the prices of eatable oils are higher than the Diesel. Mostly used edible oils do not get rancid, and are stable. The oils which are used to produce biodiesel do not decompose on storage. Therefore these edible

oils are approved for Trans-esterification Process. But the non-Eatable oils are not very much stable. Therefore the cost of producing biodiesel increases because a lot of pre treatment is required. Government policy is also very important in generation of biodiesel in India. Government of India started biodiesel objective in 2003. But the announcement of biodiesel Policy did on 11th September 2008. According to government policy a suggestive target of 20% is set by the end of 2017. This will use as blend of biodiesel in diesel fuel. It is also proposed that biodiesel generation will be taken up from non-eatable oil seeds. These will be grown in degraded, waste, and marginal lands. Biodiesel plantations on community, Government, forest waste lands would be encouraged while plantation in fertile irrigated lands would not be encouraged.

Factors Affecting Biodiesel Generation by Trans-esterification

a. *Temperature*: The temperature of the reaction is very essential parameters which effects the production of biodiesel. By increasing the temperature, rate of reaction increases. By the increase in rate of reaction the time of reaction decreases. Due to which the viscosity also decreases rapidly. But if the temperature increases beyond the limit, it causes the vaporisation of alcohol, due to which yield decreases. Saponification of triglycerides also occurs at high temperature. Due to this reason the temperature of reaction should be kept below the boiling point of alcohol, so that the alcohol cannot evaporate. Therefore the range of optimal temperature of trans-esterification can vary from 50°C- 60°C which will depend on the fats or oils. That is why; the temperature of reaction should be kept around the boiling point of the methanol, which is approved by various works of literature. At room temperature, there is up to 78% conversion after 60 minutes.

b. *Reaction Time*: With the increase in reaction time in process of trans-esterification, the conversion of fatty acid esters increases. The rate of reaction is very slow at the start of reaction. Because mixing and diffusion of alcohol and oil takes longer time. After the process of mixing, the rate of reaction increases rapidly. However, the maximum yield occurs in a time less than 90 minutes. If the reaction time further increases there is no increase in the yield product i.e. biodiesel. But, if the reaction time further increases, this can leads to the shrinkage of the biodiesel production due to the reverse reaction of trans-esterification, which results in soap formation.

c. *Methanol to oil molar ratio*: Methanol is used to react with triglyceride to form glycerine. The production of biodiesel is affected by the amount of alcohol used. The significant parameter which affects the production of biodiesel is the molar ratio of methanol to triglyceride. Stoichiometrically 3 moles of methanol and 1 mole of triglyceride are required for trans-esterification. This will produce 3 moles of fatty acid methyl esters and 1 mole of glycerol is formed. It is varied from 3:1to 7.5:1. By increasing the amount of methanol, the equilibrium of reaction shift towards right and the production of biodiesel increase.

d. *Type of Catalyst*: The production of biodiesel can be altered by the amount of catalyst. There are large numbers of catalyst which are used in production of biodiesel. But the most important catalysts which are used for biodiesel production are Potassium hydroxide (KOH) and sodium hydroxide (NaOH). The selection of catalyst and its quantity are depends on the quality of the feedstock. By increasing the amount of catalyst, the yield of fatty acid alkyl esters increases.

e. *Free Fatty Acid*: If the free fatty acid value is less than 2 it directly trans-esterification in single stage and when the value of free fatty acid is more than 2 the trans-esterification occurs in two stages. The processes of finding the free fatty acid value of trans-esterification we make the solution of sodium hydroxide and distilled water. After the process methanol is added into the mixture and two three drop of phenolphthalein in the mixture. The chemical reaction occurs by the help of catalyst concentration to the mixture till it turns into pink colour and checks the free fatty acid contents into the table. Next step after this process is to filter these impurities. The solution of methyl alcohol and potassium hydroxide is now mixed into the vegetable oil. And next step is the separation by different methods and at last wash with water to obtain purest form of biodiesel.

Cotton seed oil as biodiesel fuel

Cotton (Gossypium hirsutumL.) belongs to the Malvaceae family. Cotton is a critical crop, which harvest the natural fibre. This fibre is used by the textile industry to produce clothes. Cotton seed oil comes in ninth place, for producing oil. It is also one of the second best sources of plant proteins. The best source of plant proteins is soybeans. Seeds of cotton plants

are used to extract oil. Cotton lint is removed from plants before oil extraction. The chemical and physical properties of cotton seed oil are similar, to the leading vegetable oils. Cotton seed oil also contains heterogeneous triglycerides.

Cotton comes amongst most important commercial crops of India. It is the biggest source of natural fibre. It is the backbone of textile industry of India. The textile industry consumed about 70% of total country's fibre production. 38% of export of India is related to cotton. It produces around Rs. 42,000 crores annually to the stock. Therefore, the production of cotton plays an important role in economy of India. It provides employment around one million farmers and employees in the domestic textile industry. But, textile is one of the great stories of cotton.

The cotton plants also produce food for man and animals other than fibre. The elements of cotton seed are considered as "Golden Goose". Kernels, linters, and hulls can be used in various products, such as delightful food and nourishing feeds for animals. The hull which is present in cotton plant produces linters and fibre. The kernel of seed also contains protein, oil, carbohydrate. It also contains other essentials such as minerals, vitamins, sterols, lecithin etc. Cotton seed kernel is used to extract oil. Cotton seed oil is also termed as "Heart Oil". Therefore it is placed amongst the top most unsaturated eatable oils. Cotton seed oil is advised as one of the purest cooking medium available in the market, when it is refined and deodorised. It contains high level of anti-oxidants such as tocopherols, which is also a benefit of cotton seed oil.

a. Cottonseed Oil Quality

Cotton seed oil is the most unsaturated oils among the other oils. The other oils are corn, saffron, soybean, sunflower seed and rapeseed oil. The ratio of polyunsaturated to saturated fatty acids is 2:1 in cotton seed oil. The composition of cotton seed oil is 65 to 70% unsaturated fatty acids and 18 to 24% monounsaturated (oleic). It also includes 42 to 52% polyunsaturated (linoleic) and 26 to 35% saturated (palmitic and stearic).

Table1: free fatty acids present in cotton seed oil.

FATTY ACID	COTTONSEED COOKING OIL
Myristic (14:0)	0.8
Palmitic (16:0)	24.4
Palmitoleic (16:1)	0.4
Stearic (18:0)	2.2
Oleic (18: 1)	17.2
**Linoleic (18:2)	55.0
**Linolenic (18:3)	0.3
SUMMARY	
% Saturates	27
% Monounsaturates	18
% Polyunsaturates	55

Objective of Study

The main aim of this thesis is to produce the biodiesel by using cottonseed oil with the help of microwave energy. Next step is the optimization of biodiesel production by using parameters molar ratio, time and catalyst. Comparison of yield of biodiesel produced by using microwave energy with conventional method of generation i.e. magnetic stirrer method is done to analyse the merits of microwave energy over magnetic stirrer method.

The overall cost estimation of biodiesel generation from cotton seed oil using microwave heating is done, to find out net cost of producing biodiesel in mass generation.

Chapter 2

LETERATURE REVIEW

S. Awad et al.[2] has studied the trans-esterification of three types of waste cooking oil (WCO) with methanol and ethanol was studied using alkali catalyzed process. The catalyst used in this study was sodium hydroxide. The effects of temperature, catalyst amount, alcohol to oil ratio, and the time of reaction on the yield were studied. The temperature and the catalyst amount were the most important factors affecting the yield of biodiesel. Also the process exhibited some sensitivity to the level of free fatty acids (FFA) in the WCO and to the type of alcohol. The yields of methyl esters varied from 97% with the lowest acidity (0.4% FFA WCO) to 76% with the highest acidity (3.25% FFA WCO). The ethyl esters yields were inferior and the difference increased with the level of FFA in the oil, the maximum yield was 95% and 73% with the lowest and the medium acidities respectively and no reaction was registered with the highest one. The chromatographic analysis of the produced biodiesel showed high contents of fatty acid methyl esters varying from 96.5% to 98%.

T Sathya et al.[4] has been investigated that vegetable (mainly non edible oil) having high free fatty acids (FFA), more than 2% could not be transesterified with alkaline catalyst because the alkaline catalyst react with FFA to form soap. So in this study, two-step process was developed to convert FFA to its methyl ester (Biodiesel). The first step is acid treatment it reduces the FFA content of oil to less than 2% using acid catalyzed (0.5 % v/v H_2SO_4) reaction with methanol (0.45 v/v) at 50˚C temperature and 45 min reaction time. First step is known as esterification. After acid treatment alkaline trans-esterification reaction was carried out at 1% KOH, 30% methanol, 55˚C and 60 min. The second step is known as trans-esterification. The maximum yield is 90±2%. The effect of molar ratio, catalyst, reaction temperature and reaction time are analyzed in each step process. Excess addition of sulphuric acid darkens the product which leads to more generation cost.

Amit Pal et al.[5] has studied that cotton seed has huge capability for biodiesel generation. The most important feature of the cotton seed is that it grows in the form of climbing plant in sandy soil with in a six month crop cycle. As we know that availability of the raw material controls the economics of the product. So, there should be a proper management for the plantation of neglecting trees and their usage to investigate the benefits from the cotton seed Oil Plant. Bio-diesel is found better substitute for petroleum diesel and also most advantageous over petro-diesel for its environmental friendliness. The quality of biodiesel fuel was found to be considerable for its doing well use on compression ignition engines and ensuing replacement of non-inexhaustible fossil fuels. Biodiesel produce from cotton seed oil also yield comparable results with petroleum diesel. It is found that in mechanical stirring the yield obtained at 1% KOH is higher. Maximum yield up to 97.90% is obtained from cotton seed oil by mechanical stirrer technique. From results of experimental investigation of cotton seed Biodiesel, it is found that it is having the properties similar to diesel. So blends are having the potential to reduce the over burden of the imports of diesel fuel.

Umer Rashid et al.[6] produces biodiesel from cottonseed oil by trans-esterification with methanol, using sodium hydroxide, potassium hydroxide, sodium methoxide and potassium methoxide as catalysts. A series of experiments were conducted in order to evaluate the effects of reaction variables such as methanol/oil molar ratio (3:1–15:1), catalyst concentration (0.25–1.50%), temperature (25–65 °C), and stirring intensity (180– 600 rpm) to achieve the maximum yield and quality. The optimized variables of 6:1 methanol/oil molar ratio (mol/mol), 0.75% sodium methoxide concentration (wt.%), 65 °C reaction temperature, 600 rpm agitation speed and 90 min reaction time offered this maximum methyl ester yield (96.9%).

Dennis Y.C. Leung et al.[7] has investigated that there are four primary factors affecting the yield of biodiesel, i.e. alcohol quantity, reaction time, reaction temperature, and catalyst concentration. To ensure a complete trans-esterification reaction, the molar ratio of alcohol to triglycerides should be increased to 6:1 with the use of an alkali catalyst. For used cooking oils or for oils with a high percentage of free fatty acids, a higher molar ratio is needed for acid-catalyzed trans-esterification. Because the conversion rate of fatty acid esters increases with reaction time but the yield of the biodiesel product reaches a maximum at an optimal reaction time. Higher reaction temperature can decrease this viscosity of oils, enhancing the reaction rate. The optimal temperature ranged between 50 ^{0}C and 60 ^{0}C, depending on the oil

used. The optimal condition of catalyst concentration is about 1.5 wt. % for NaOH which is the most commonly used catalyst.

Vimal Katiyar et al.[9] has studied that Microwave assisted trans-esterification reaction of soybean oil leads to the maximum biodiesel conversion (99%) within 5 min. Due to reversible nature of the reaction, the conversion decreased with the reaction time higher than 5 min. Similar observation can be made for cloud point and pour point also, where the increase in conversion had positive effect on cloud point but minor increase in pour point is observed.

S. Murugavelh et al.[10] has studied waste cooking cotton seed oil. A maximum yield of 92% biodiesel was reported when the reaction temperature, time, methanol/oil ratio and catalyst loading rate were 60◦C, 50min, 12:1 and 3% (wt.%), respectively. The flash point and the fire point of the biodiesel were found to be 128°C and 136°C, respectively. This Brake thermal efficiency of WCCO B10 biodiesel was 26.04% for maximum load, specific fuel consumption for diesel was 0.32 kg/kW hat maximum load. The use of biodiesel blends showed a reduction of carbon monoxide and hydrocarbon emissions and a marginal increase in nitrogen oxides (NO_x) emissions improved emission characteristics.

Veera Gnaneswar Gude et al.[11] has investigated that Microwave-enhanced organic/inorganic synthesis is considered as green chemistry and a preferred method due to several advantages such as inferior energy consumption, substantial reduction in reaction times and solvent requirements, enhanced selectivity, and improved conversions with less by-product formation. Many reactions that do not occur under classical methods of heating can be carried out with high yields under microwave irradiation. Microwaves have the potential for large scale applications specifically in biodiesel generation due to their ability to interact with a variety of reagents.

V.K. Rathod et al. [12] has studied that Enzymatic processes are more efficient at inferior temperatures as compared to chemical catalysis processes. The effective temperature range of 323 K–353 K was reported for maximum activity of the lipase enzyme. As temperature increases it starts dam-aging the enzyme's structural conformation that leads to loss of enzyme activity. Although maximum conversion of 85.1% was duly observed at343 K, which is barely higher than 83.3% conversion obtained at333 K. The close resemblance in results

has taken up enzyme activity and energy consumption as criteria for selection of optimum temperature. It is obvious that increase in temperature ultimately increases the energy demand. The power imparted by microwave to maintain the required temperature was observed to increase from 48W to 51W with temperature rise from 333 K to 343 K.

The Very low catalyst loading may execute slow reaction rate while high catalyst loading increases this operating cost of the reaction. Hence; enzyme loading in this range 5–15% (w/w) with respect to oil was considered for the biodiesel generation. At higher molar ratios, excessive DMC dilutes the concentration of oil and reduces the collision frequency of reactants and catalyst. Therefore 4.5:1 was considered as optimum ratio for given process so as to give maximum yield of 84.1%. Reaction studied without application of microwave was reported 6:1 as the optimized ratio which is more than the optimised value for microwave assisted reaction. It can be observed that conventional reaction requires about 1380 min to reach to equilibrium while microwave assisted process takes 240 min only. Therefore, reaction with microwave irradiation was completed in short duration with uniform heating converse to prolonged reaction by conventional method with high energy losses.

Chee Loong Teo et al.[13] has studied that simultaneously cooling and heating by microwave (SCMH) trans-esterification was proven to consume 40.26% of conventional method's total energy consumption with 83.33% (Nannochloropsis sp.) and 77.14% (Tetraselmis sp.) biodiesel productivity. The biodiesel productivity efficiency achieved in SCMH trans-esterification was highest compared to conventional trans-esterification and microwave assisted trans-esterification method. In addition, the optimization of parametric study on SCMH was successfully performed to increase the efficiency of conversion biodiesel. Finally it was revealed that the quality of biodiesel obtained using SCMH trans-esterification was more superior producing FAMEs of low carbon content <19, exhibited reasonably CN and IV and thus has both good ignition and lubricating properties.

Dominic Okechukwu Onukwuli et al.[14] has studied the generation of Biodiesel by trans-esterification of refined cotton seed oil with methanol and potassium hydroxide (KOH) as a catalyst using batch mode. The physicochemical properties of cotton seed oil and biodiesel as a different fuel for diesel engine was characterized by ASTM standards for fuel tests. The functional groups of the biodiesel were investigated using Fourier transform infrared spectroscopy. Impact of key parameters like reaction temperature, reaction time, catalyst

concentration and methanol/oil molar ratio were determined using batch mode. These process parameters were optimized using response surface methodology (RSM) and analysis of variance (ANOVA). The significance of these different process parameters and their combined effects on the trans-esterification efficiency were established by a full factorial central composite design. The results obtained are in good agreement with published data for other vegetable oil biodiesel as well as various international standards for biodiesel fuel. An optimum yield of 96% was achieved with optimal conditions of methanol/oil molar ratio, 6:1; temperature, 55^0C; time, 60 min; and catalyst concentration, 0.6%. This investigation has shown that cotton seed oil from Nigeria can be used to produce biodiesel.

Dae Hee Lee et al.[20] has studied a highly efficient low-emission co-generation system using a 2000-cc common-rail direct-injection (CRDI) diesel engine with an after-treatment device (re-combustor) is developed. This co-generation concept is utilized to produce electric power by a generator as well as to recover waste heat from the exhaust gases. A re-combustor is installed at the exhaust gas outlet to perform secondary burning of the exhaust gases, resulting in an improvement of this system's thermal efficiency as well as a reduction of exhaust gas emissions. These main components of the re-combustor are coiled Pyromax wires installed in a ceramic housing, diesel oxidation catalyst (DOC), and diesel particulate filter (DPF).

The tests are conducted at four water flow rates (10, 15, 20, and 25 LPM) and four electric power outputs (5, 15, 25, and 35 kW). In general, a great deal of time and expense are required to determine these optimum experimental conditions for this maximum efficiency of a co-generation system. However, in this present study, the optimum experimental conditions for the present system are found using the Taguchi method and analysis of variance (ANOVA), resulting in significant savings of time and expense. The results show that the present co-generation system achieves a maximum total efficiency of 85.7%, and a significant reduction of CO, NOx, and PM by 73.3%, 34.3%, and 94%, respectively.

Achanai Buasri et al. [21] has studied the optimization of experimental parameters, such as reaction time, reaction temperature, methanol/oil molar ratio and catalyst loading, on the trans-esterification for the generation of biodiesel has been studied. A Taguchi L9 (3^4) orthogonal array was used to evaluate this factors affecting the conversion of palm oil to fatty acid methyl ester (FAME). This scallop waste shell was calcined at $1,000^0$C for 4 h and

catalyst characterizations were carried out by XRD, XRF, SEM, and BET surface area measurements. Under these optimal reaction conditions of 10 wt. % of catalyst, 9:1 methanol/oil molar ratio and at a temperature of 65^0C, the FAME conversion was 95.44% and it was achieved in 3 h. It was found that the scallop waste shell catalyst shows high catalytic activity and ecologically friendly properties, having the potential opportunity to be used in biodiesel generation process as heterogeneous base catalyst.

The conversion of TG was 95.44%, at the reaction time of 3 h, reaction temperature of 65 °C, CaO catalyst amount of 10 wt. % and methanol/oil molar ratio 9. A range of conditions were established that would produce a high-quality product of considered to be a more economic solution. This catalyst performed equally well as this laboratory-grade CaO. Scallop waste shell is therefore a useful raw material for this generation of a cheap catalyst for trans-esterification. Calcination of the catalyst derived from the waste shell resulted in an increase in surface area, leading to better catalytic activity. The final product is a light brown material, meeting these requirements of the Thai biodiesel standard.

Horng-Wen Wu et al. [22] has studied a Taguchi method which is used to determine these optimal combinations of concentrations for a diesel engine with diesel/biodiesel blend using H_2 and cooled exhaust gas recirculation (EGR) at the inlet port. These authors determined the optimal operating factors for achieving good combustion performance, low NO_X and smoke, at various engine loads and at 1500 rpm. Furthermore, the combustion performance and emissions are compared between the optimum combination factors and original baseline diesel engine. Experimental results show that predictions by Taguchi's parameter design technique are in adequate agreement with the confirmation results, with a confidence interval of 95%, and the technique saves 67% of this time taken to perform the experiment in the research. The best brake thermal efficiency (BTE) and brake specific fuel consumption (BSFC), NO_X and smoke at each load is achieved for a combination of B20 (A_2), 30% hydrogen (B_3) and 40% EGR ratio (C_3).

Furthermore, the heat release rate with a variable specific heat ratio is calculated from the experimental cylinder pressure. The combination is more suitable for obtaining various parameters that affect the combustion performance such as the BTE, cylinder pressure, and heat release rate, than those of the baseline diesel engine for various loads. In addition, the best combination reduces the BSFC and inhibits both NOX and smoke emissions. At a load

of 60%, the reduction rate is 25.4% for BSFC, 74.1% for NO_X and 29.6% for smoke. The Taguchi method was a good method to find out these optimum combinations. The predictions using Taguchi's parameter design technique are in adequate agreement with the confirmation results, with a confidence interval of 95%, and the technique saves 67% of the time taken to perform this experiment in this research. From ANOVA method, the factor of biodiesel/diesel mixture (A) affects BTE for a 34.1% contribution at 30% load; affects NO_X for a 22.9% contribution at 30% load and affects smoke for 66.9% contribution at 60% load. The factor of hydrogen-energy-share ratio (B) impacts BSFC higher than 87% contribution at various loads, and smoke emission around 20% contributions at 45% load. The EGR ratio (C) has higher effect on NOX than on other objectives.

Cheng-Han Hung et al. [23] has investigates combustion characteristics and decides the optimal operating factors by a Taguchi method on a diesel engine using diesel/biodiesel mixture with liquefied petroleum gas (LPG) and cooled exhaust gas recirculation (EGR) inducted in the intake port. These optimal operating factors for acquiring the largest fuel consumption time, the lowest smoke and NO_X are decided for 1500 rpm and different loads.

In addition, this study compares the combustion characteristics (heat release rate and ignition delay) and emissions (NO_X and smoke) between the optimum combination of factors and baseline diesel engine. The results display that predictions by Taguchi method are in favour of atmospheric air consistence with the confirmation results, and this method decreases the number of experimental runs in the study. The best fuel consumption time, smoke, and NO_X at each load is acquired at a combination of B10 (A1), 40% LPG (B3) and 20% EGR ratio (C1). Moreover, the heat release rate for engine conditions is computed using a variable specific heat ratio by the experimental in-cylinder pressure. Furthermore, the best combination decreases both smoke and NO_X emissions. This decrease rate is 52% for smoke and 31% for NO_X at 60% engine load.

Zhan-Yi Wu et al. [24] has studied the L9 orthogonal array of the Taguchi method to find out the best hydrogen injection timing, hydrogen-energy-share ratio, and the percentage of exhaust gas circulation (EGR) in a single DI diesel engine. The injection timing is controlled by an electronic control unit (ECU) and the quantity of hydrogen is controlled by hydrogen flow controller. For various engine loads, the authors determine the optimal operating factors for low BSFC (brake specific fuel consumption), NO_X, and smoke. Moreover, net heat-

release rate involving variable specific heat ratio is computed from the experimental in-cylinder pressure. In-cylinder pressure, net heat-release rate, A/F ratios, COV (coefficient of variations) of IMEP (indicated mean effective pressure), NOX, and smoke using the optimum condition factors are compared with those by original baseline diesel engine. These predictions made using Taguchi's parameter design technique agreed with the confirmation results on 95% confidence interval. At 45% and 60% loads the optimum factor combination compared with the original baseline diesel engine reduces 14.52% for BSFC 60.5% for NOX and for 42.28% smoke and improves combustion performance such as peak in-cylinder pressure and net heat-release rate. Adding hydrogen and EGR would not generate unstable combustion due to inferior COV of IMEP.

T. Ganapathy et al. [25] proposes a methodology for thermodynamic model analysis of Jatropha biodiesel engine in combination with Taguchi's optimization approach to determine the optimum engine design and operating parameters. A thermodynamic model based on two-zone Weibe's heat release function has been employed to simulate the Jatropha biodiesel engine performance. Among the important engine design and operating parameters 10 critical parameters were selected assuming that there are no interactions between the parameters. Using linear graph theory and Taguchi method an L16 orthogonal array has been utilized to determine the engine test trials layout. In order to maximize the performance of Jatropha biodiesel engine the signal to noise ratio (SNR) related to higher-the-better (HTB) quality characteristics has been used. This present methodology correctly predicted the compression ratio, Weibe's heat release constants and combustion zone duration as the critical parameters that affect the performance of the engine compared to other parameters.

Hülya Karabas [26] has studied that acorn kernel oil with high free fatty acid content is used as feedstock to produce biodiesel. Two stages are used to produce biodiesel after obtaining the acorn kernel oil. This 3.38% free fatty acid content is decreased to 0.14% in the first stage, whereas the acid ester biodiesel is produced using alkaline trans-esterification reaction in the second stage. The biodiesel generation process parameters are the alcohol:oil molar ratio, catalyst concentration, reaction temperature and reaction time. Taguchi experimental design is used for acorn kernel oil methyl ester generation via process parameter optimisation. The optimal process parameters are determined to be a catalyst concentration of 0.7 wt%, an 8:1 alcohol: oil molar ratio, a 50 ^{0}C reaction temperature and 40 min of reaction time using a KOH catalyst in experimental studies. According to the Taguchi method, the

most efficient process parameter in acorn kernel oil methyl ester generation. Finally, the acorn kernel oil methyl ester yield is 90% under the optimal process parameters obtained by the Taguchi method. Based on the S/N ratio, the optimal parameters are reaction time at level 1 (40 min), alcohol:oil molar ratio at level 2 (8:1), reaction temperature at level 1 (50^0C) and catalyst concentration at level 2 (0.7 wt%). Under these conditions, the AKOME yield in this confirmation experiment is 90%.

Je-Lueng Shie et al.[27] has studied the economic costs of three biodiesel plants with capacities of 8000, 30 000, and 100 000 tons year^{-1}. The plants employ continuous processes using an alkali catalyst and the raw material of soybean oil. Six major economic cost factors were computed and examined. These include the fixed capital cost (FCC), total capital investment cost (TCC), total production cost (TMC), net annual profit after taxes (NNP), after-tax rate of return (ARR), and biodiesel break-even price (BBP). The NNP and ARR of plants with capacities of 8000, 30 000, and 100 000 tons year^{-1} are -24 × 103, 1975×103, and 8879×103 U.S. dollars (USD), and -10.44, 40.23, and 67.38%, respectively. The values of BBP of the three plants are 862, 724, and 678 USD ton^{-1} (price in July 2007). The plant with a capacity of 100 000 tons year^{-1} is economically feasible, providing a higher NNP and more attractive ARR with a inferior BBP. Among the system variables of the plants examined, plant capacity, price of feedstock oil and diesel, and yields of glycerine and biodiesel were found to be the most significant variables affecting this economic viability of biodiesel manufacture.

Kondaveeti srinivasa rao [28] present the work which is focused on biodiesel generation from waste chicken fat and its cost estimation. It includes the process of chicken fat biodiesel preparation and various costs involved for raw materials, energy and labour. Chicken fat biodiesel was produced by trans-esterification process and generation cost was estimated using some existing data and suitable assumptions. It was estimated that the chicken fat biodiesel generation cost come around 24.7 per litre. Hence the waste chicken fat proves to be suitable for biodiesel generation, safe passage of dispose of waste and economically viable.

Chapter 3

THEORY

Biodiesel is a fuel which can be used in place of diesel fuel in compression ignition engines. Biodiesel is produced from the oils which are extracted from the plants. These oils include cotton seed oil, canola oil, soybean oil etc. Biodiesel can also be produced by waste cooking oils and greases for e.g., yellow grease. The animal fats can also be used in production of biodiesel for e.g., pork lard and beef tallow. Because oil is produced in the plants with the help of air and sunlight, by the process called photosynthesis. Because of this oil can be produced, crop after crop and the oil is produced every year. Due to this oil can be called as inexhaustible source of energy. Animal fats are formed when the animal takes their food from plants or animals. Animal fat is also a renewable source of energy.

Waste cooking oils are generally derived from plants, but it may also contain animal fats. Waste cooking oils can be recycled. Biodiesel and long-chain mono alkyl esters are the products of chemical reaction. This chemical reaction converts oils and fats with methanol in presence of catalyst into biodiesel. This process is called as trans-esterification. And the chemicals are revered as fatty acid methyl esters. The analysis shows that, if oils from plants or greases are used in compression ignition engines at combinations as low as 10% to 20%, it will produce long-term deposits, lubricating oil gelling, and other problems related to maintenance. These problems can reduce the life of engine. The main problem is caused due to higher viscosity of the raw oils, which is around 40 mm^2/s. This is much higher as compared to the diesel fuel. With the process of trans-esterification, the viscosity of biodiesel fuels is reduced.
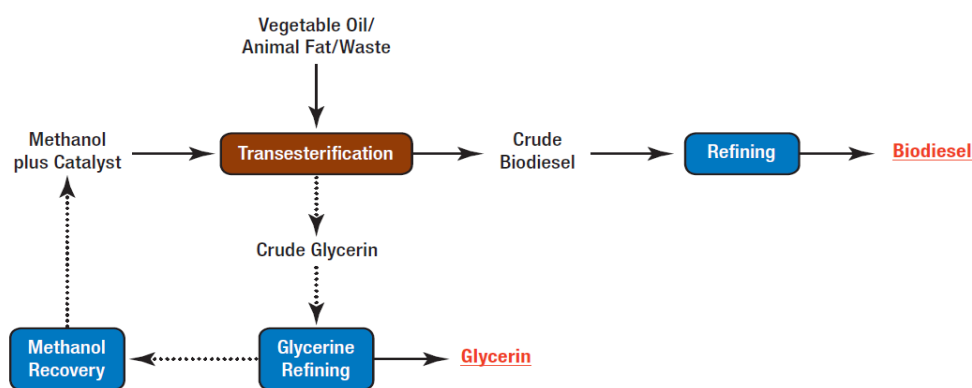

Fig1: Trans-esterification process.

Benefits of Biodiesel Use

a. ***Biodiesel Provides a High Energy Return and Displaces Imported Petroleum***: By analysing the life-cycle, it is confirmed that, the energy content of biodiesel is 2.5-3.5 units. This is more as compared to the energy of each unit of fossil fuel. Because of the high energy content, biodiesel can replace petroleum at nearly a ratio of 1:1 on a life-cycle basis. This energy value is analysed on the diesel equipments worked on farm and vehicles used for transportation e.g. trucks and tractors. Biodiesel is an energy-efficient fuel, it will substitute petroleum products.

b. ***Biodiesel Reduces Life-Cycle Greenhouse Gas Emissions:*** If biodiesel is used in place of petroleum, there is extreme reduction in greenhouse gases (GHG). These green house gases emission estimates, include CO_2, NOx and methane are decreased by 41%. Because biodiesel is generated from the crops therefore emission is low. During the growth of soybean plants, CO_2 is absorbed by soybean plants from the atmospheric air. This CO_2 is used to produce the leaves, stems, roots, and seeds (soybeans). When the oil is extracted from the seeds called as soybeans, and then biodiesel is produced from oil. When this biodiesel is used in diesel engines, CO_2 and other pollutants are discharged into the environment. This CO_2 is then absorbed by plants again. Therefore there is no net addition of CO_2 in the atmosphere. If fossil fuels for example diesel or coal are used in combustion chamber, all of the carbon dioxide produced released in the atmosphere.

c. ***Biodiesel and Human Health:*** The emission from diesel contains pollutants. These pollutants consist of some PM and hydro carbons (HC_s) emissions from diesel fuel combustion are harmful or carcinogenic. With the use of 100% biodiesel i.e. B100 can wipe out as much as 90% of the atmospheric air pollutants. With the use of 20% biodiesel i.e. B20 can eliminate atmospheric air pollutants by 20%- 40%. The positive effect of biodiesel use on atmospheric air pollutants has been demonstrated by many studies.

d. ***Biodiesel Improves Engine Operation:*** Even when biodiesel is used in very small concentrations value, biodiesel boost lubrication property of fuel and also increases the cetane number of the fuel. Lubrication property is necessary for the diesel engines because there are moving parts, such as fuel pumps. The inadvertent side effect of these federal regulations, there is constantly reduction in allowable fuel sulphur to only 15 ppm. It can also reduce the aromatics components. It has also reduced the lubrication property of petroleum diesel.

e. ***Biodiesel Is Easy To Use:*** Finally the considerable merits of use of biodiesel are that it can be produced easily. Biodiesel in ratio of 20% is used called as B20 or less percentage is used in a diesel engine. There is on modifications in equipments and no new equipments are necessary. B20 can be easily stored in tanks which are used to store diesel fuels and can be pumped with diesel equipment.

Comparison of biodiesel fuel with diesel

Table 1. Select Properties of Typical No. 2 Diesel and Biodiesel Fuels		
Fuel Property	Diesel	Biodiesel
Fuel Standard	ASTM D975	ASTM D6751
Higher Heating Value, Btu/gal	~137,640	~127,042
Lower Heating Value, Btu/gal	~129,050	~118,170
Kinematic Viscosity, @ 40°C (104°F)	1.3–4.1	4.0–6.0
Specific Gravity kg/l @ 15.5°C (60°F)	0.85	0.88
Density, lb/gal @ 15.5°C (60°F)	7.1	7.3
Carbon, wt %	87	77
Hydrogen, wt %	13	12
Oxygen, by dif. wt %	0	11
Sulfur, wt %	0.0015 max	0.0–0.0024
Boiling Point, °C (°F)	180–340 (356–644)	315–350 (599–662)
Flash Point, °C (°F)	60–80 (140–176)	100–170 (212–338)
Cloud Point, °C (°F)	-35 to 5 (-31 to 41)	-3 to 15 (26 to 59)
Pour Point, °C (°F)	-35 to -15 (-31 to 5)	-5 to 10 (23 to 50)
Cetane Number	40–55	48–65

Fig2: comparison of diesel and biodiesel properties.

Microwave energy for biodiesel generation

a. Microwave energy

Energy associated with microwaves is inferior than the energy associated with Brownian motion therefore the energy associated with microwaves is less than the energy required to break chemical bonds of compounds. Therefore microwaves cannot activate chemical reactions. There is both thermal and non thermal effect on chemical reactions due to microwave energy. The quantum energy of microwave is presented by the equation, $W = hv$. The energy associated with the microwaves frequency range from 300 MHz to 300 GHz, the energy related to 300MHz is 1.24×10^{-6} and to 300GHz is 1.24×10^{-3} eV. The ionisation energy of chemical compound is 13.6 eV, which is much larger than energy associated with microwaves. Microwaves, transfer heat at molecular level without altering the molecular structure. Microwave heating have many benefits over conventional heating.

The main advantage is that, microwave heating is non-contact heating (less material heating surfaces), therefore it is called as energy transfer instead of heat transfer, which helps in reduction in temperature gradient, there is less variety of materials, and it produces rapid heating. The time taken to initiate the reaction is very low and it stops easily. Microwave heating is also called as reverse thermal effect, i.e. heating starts from the inner parts of material body. In terms of biodiesel generation, it produces: more effective heating, fast effect of catalysts, the size of equipment is reduced, fastest way to control heating, faster start-up, increased generation, and process steps can be reduced[11].

b. Microwave heat transfer mechanism

Heating by microwave energy is a complex phenomenon. The main difference between conventional heating method and microwave heating is that, there is the difference in heating method, which further realizes the merits of microwave heating. In the methods of conventional heating and supercritical heating. Transfer of heat is used to increase the temperature of the surface of the container. Then the heat is transferred to internal material and temperature starts increasing. This transfer of heat is called "wall heating". That is why; the most part of energy supplied by conventional energy source is lost into the surrounding by the conduction method and convection. The effect of heating in conventional method is heterogeneous and it depend on specific heat, thermal conductivity, and density of the materials, therefore there is high surface temperature which causes heat transfer from the

outer surface to the internal sample size as seen in Figure 3. As a result, there is a non-uniform temperature of sample and there is higher thermal gradients.[11].
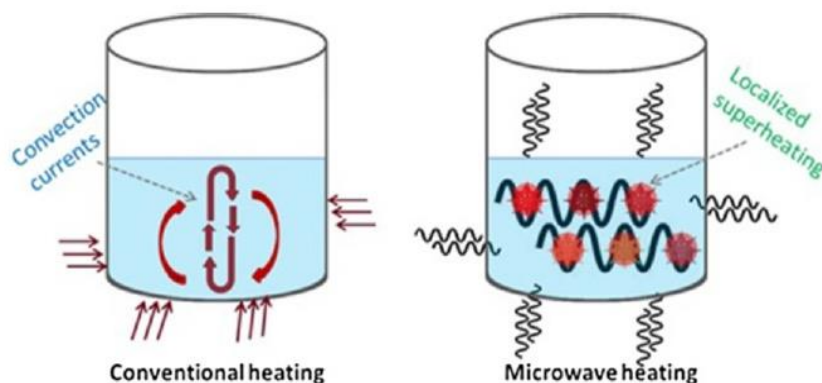

Fig3: difference between conventional and microwave heating

If there is a dipole moment in a molecule, and now the compound is disclosed to microwave irradiation. The dipole of molecule tries to adjust its orientation with the electric field applied to it. Due to this continuous oscillation of electric field, the dipoles regularly try to adjust with changing electric field. Therefore dipole follows the motion of electric field. At the frequency of 2.45 GHz, the molecules have the time to adjust with the oscillating electric field but the exact motion of oscillation is not followed by the molecule. Therefore there is friction due to continuous relocation of the molecules of compound. Due to friction heat is produced.

If the molecule has charge, next to the component of electric field, which is correlated with microwave irradiation, it produces the motion of the ions back and forth. Due to this there is a collision between the molecules. Due to this to and fro motion heat is generated additionally. The interaction of energy occurs at a very fast rate, due to interaction of molecules. Therefore there is no time to relax for the molecules and thus the heat generation increases. Therefore for the short duration, there is a greater temperature of the overall recorded bulk reaction mixture. In core, there is a rapid localized superheating. Therefore, the bulk temperature cannot be assumed as accurate value of the temperature, at which the actual reaction is taking place. The interfacial polarization method can be considered as a combination of the conduction and dipolar polarization mechanisms [11].
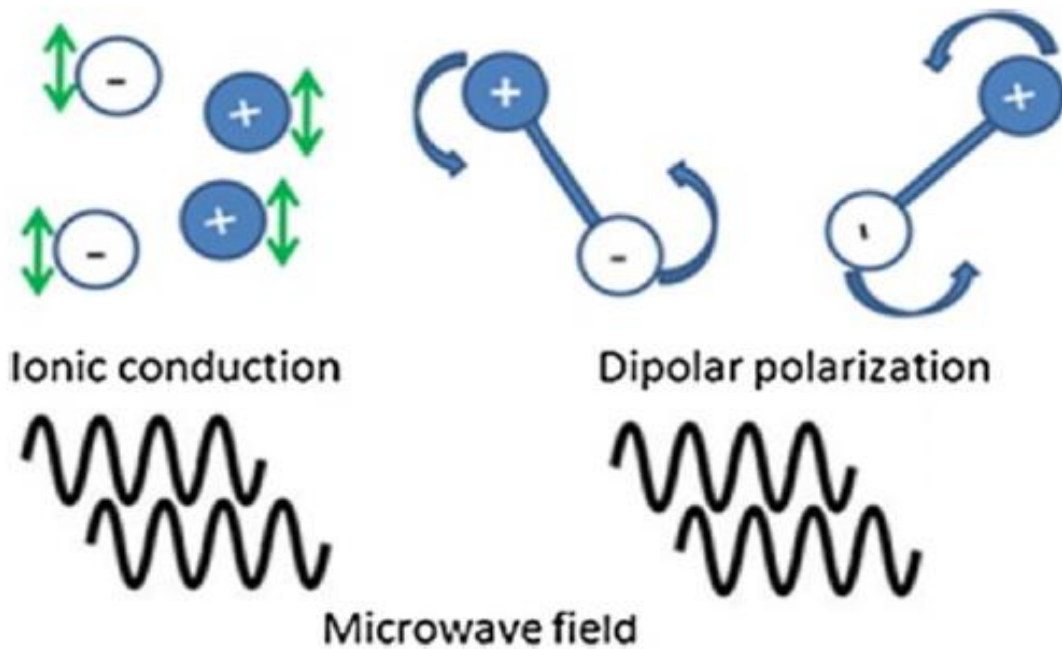
Fig4: microwave heating mechanism

c. *Classification of material based on interaction with microwave*

In general, the materials can be categorised into three different parts which is based on their microwave interaction:

(1) Bulk metals and alloys are those materials which can reflect microwaves, e.g. copper.

(2) Fused quartz, Teflon, glasses made of borosilicate, ceramics etc are those materials which can pass the microwaves through it.

(3) Polar solvent, aqueous solutions etc. Are those materials which can absorb the microwaves, this is the most important classification of materials in terms of microwave synthesis, e.g. aqueous solutions, etc

Chapter 4

INTRODUCTION TO TAGUCHI METHOD

Background

The procedure of laying out the circumstances of experiment which involve multiple factors was first projected by the Englishman, Sir R. A. Fisher. The technique is commonly known as the factorial design of experiments. The classification of all probable combination for a given position of factors is done in full factorial design. Since most experiments frequently occupy an important numeral of factors, a large numeral of experiments is mandatory in full factorial design. To decrease the numeral of experiments to a sensible level, only a little set from all the possibilities is selected. The process of choice of limited numeral of experiments which are used to create the most information is known as a partial fraction experiment. Although the process is well known, there is no universal guiding principle for its claim or the examination of the outcomes obtained by conducting the experiments. Taguchi build an extraordinary set of universal design guidelines for factorial experiments that cover a lot of applications.

Definition

Taguchi has measured a new method of designing experiments that are based on well-defined guidelines. The method uses a set of particular matrices called orthogonal. The standard matrix stipulates how to perform the minimum number of experiments that can provide complete information on all factors affecting the performance parameter. The core of the orthogonal matrices method lies in choosing the combinations of levels of the input design parameters for each experiment.

A typical orthogonal array

Currently, there are so a lot of benchmark orthogonal arrays which are accessible, every one of the orthogonal arrays are intended for a precise numeral of autonomous design variables and levels.

a. Properties of an orthogonal array

The orthogonal arrays contain the subsequent particular properties that decrease the numeral of experiments to be performed.

1. There is a particular grouping of level settings of autonomous variables beneath each column. All the level settings become visible an equal numeral of times. This is known as the balancing property of orthogonal arrays.

2. All the level values of autonomous variables are used for performing the experiments.

3. The series of level values for performing the experiments shall not be distorted.

b. Minimum numeral of experiments to be conducted

The experiment design orthogonal matrix is most effective when compared to many other statistical projects, in most cases. The minimum number of experiments required to use the Taguchi method to estimate the approach is the degree of freedom.

Assumptions of the Taguchi method

Another assumption means that the individual or the main effects of the independent variables are individually the performance parameters. Due to the effect of certain factors, assumptions can be linear, quadratic or higher. In the model, the main assumption is that there is no effect between products (interactions) between individual factors. This means that the first effect of the independent variable output parameter does not depend on any other level settings other than independent variables, and vice versa. If at any time you violate the premise, the main effects are not additives to maintain and interact with variables.

Designing an experiment

The design of an experiment contains the subsequent steps

1. Independent variables selection

2. Selection of numeral of level settings for each independent variable

3. Orthogonal array selection

4. Assigning the independent variables to each column

5. Performing the experiments

6. Analysis of data

7. Inference.

a. Selection of the independent variables

Prior to the product / process knowledge experiment you are currently investigating, identify priority factors that can affect the point of view of the results. To compile a comprehensive list of factors is usually derived from the test entry of all humans involved in the project.

b. Deciding the numeral of levels

After selecting the independent variables, determine the number of individual variable levels. Select the number of levels depends on the performance parameters due to the impact of different levels of settings. If the performance parameter is a linear function of the independent variable, the level adjustment number should be 2. However, if the independent variable is not a linear relationship then 3, 4, or higher levels can be achieved, which depends on whether the connection is quadratic, cubic or higher. If the relationship between the variable parameter and independent performance is incorrect, you can select a two-level configuration. After studying the experimental data, deciding to adjust the assumption level is correct or not, which is based on the percentage of contributions and the calculation error.

c. Selection of an orthogonal array

Select the minimum number of experiments to perform on the basis of degrees of freedom in the general digits study, and then select the Orthogonal Arrays option.

The minimum number of attempts required to examine the factors must be greater than all available freedoms. To calculate the extent of freedom to test a degree of freedom from the mean of the responses analyzed. The number of degrees of freedom that are related to the factors studied a number equal to less than the available data for this factor. Therefore, the degrees of freedom in total, without the effect of the interaction of one, as was the equation. For example, for 11 independent variables, each of which has two stages, with a total of degrees of freedom 12. Therefore, the selected orthogonal arrangement must contain at least 12 experiments. An orthogonal L12 meet the requirement. If you select a minimum number of experiments, one more selection is based on orthogonal arrays for independent and independent variables for each independent variable factor levels.

d. Assigning the independent variables to columns

The order is very important independent variables associated with the vertical column. In case of interaction at the mixed level between variables and variables, variables must be given to the orthogonal matrix in the right column. Finally, it is necessary to determine the actual value of each level of project variables before performing the experiment. Note that the meaning of independent variables and the percentage varies depending on the assigned value.

e. Conducting the experiment

After the selection is an orthogonal matrix, experimentally, we perform the combinations of levels. It is a necessary condition that the experiments should be carried out. Columns for Interaction and False Variables columns need not be taken into account to complete the experiment, but analysis of data is needed to understand this interaction. Based on the performance parameter, an examination of the sensitivity analysis for each experiment should be noted.

f. Analysis of the data

Since all attempts at different levels of combined factors, sharing the specific impact of independent variables is essential. The operation can be done at the right level of power by summing configurations. For example, attempts to summarize the first, fourth, and seventh values of performance parameters to determine the impact of the second major definition of independent first-level variable. Similarly, compare the results 2, 5 and 7. If a pilot is calculated the mean value of each level of an independent variable given second level, the calculation of the mean value of each a large deviation from the mean value. A variable amount of deviation indicates that the performance of the parameters sensitive to changes in the level of adjustment. If the sum of the squared deviations closes to zero or insignificant, one can conclude that the design variables do not affect the performance of the process. In other words, the analysis of sensitivity and analysis of variance (ANOVA) implementation of determine whether more dominant factor, which is independent and that the percentage contribution of independent variables.

g. Inference

The above experimental analysis that the larger the square sum of independent variables, the greater the impact on performance parameters. The ratio between the amounts of an

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individual is an independent variable in the square where he can calculate the sum total of the squares of all variables. The ratio gives the percentage contribution of independent variable performance parameters. We can find almost ideal solution to the problem, in addition to the above. The ideal near value is not necessarily the ideal global solution. However, the solution can be used as the starting / initial value for conventional optimization techniques.

h. Robust Design

The production process is a major cause of the weak production yield differential. These manufacturing variations include variations in temperature or humidity, changes in raw materials and drift process parameters. These sources of noise / variations are variables that are impossible or expensive.
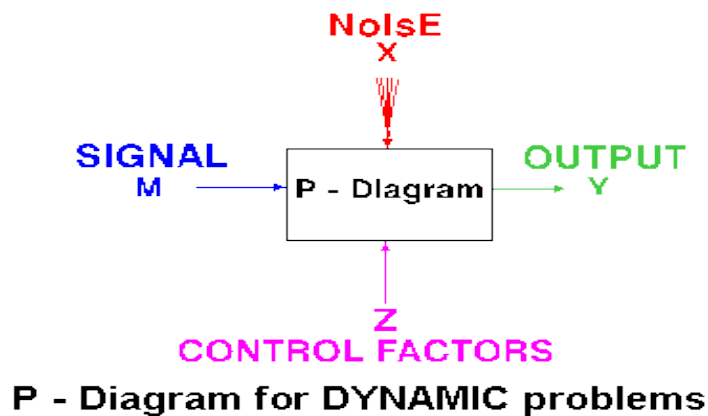

P - Diagram for DYNAMIC problems

Fig5: signal to noise diagram of taguchi method

The chief purpose of the robust design is to discover the procedure limitation which can be controlled. The procedure restriction situation for which noise or variation has a least effect on the products or process's practical description. The major plan of this design is to discover the parameter settings for the convenient design variables, but not for the unmanageable noise variables. To obtain this purpose, the systematize parameters which are also known as inner array variables, are analytically varied as predetermined by the inner orthogonal array. For every experiment of the inner array, sequences of new experiments are performed by altering the level settings of the unmanageable noise variables.

The level combinations of noise variables are completed by means of the outer orthogonal array. The impact of noise on the performance characteristics can be establish by means of the ratio where S is the standard deviation of the performance parameters for every inner

array experiment and N is the sum numeral of experiment in the outer orthogonal array. The ratio shows the practical variation due to noise. Using the result, it is promising to forecast which control limitation settings will create the method insensible to noise. Though, when the purposeful characteristics are not exaggerated by the outside noises, there is no need to conduct the experiments by means of the outer orthogonal arrays. This is right in case of experiments which are conducted by means of the computer simulation as the repeatability of a computer simulated experiments is very high.

Chapter 5

METHODOLOGY

There are several methods to produce biodiesel from crude oil like, Pyrolysis, Micro-emulsions, Trans-esterification and microwave assisted trans-esterification but microwave heating is the most easy and suitable method to produce biodiesel. Trans-esterification is a simplest reaction of cotton seed oil with methanol in the existence of KOH but Micro-emulsions and pyrolysis are very difficult process. Time taken in trans-esterification process by magnetic stirrer method is very much. But trans-esterification using microwave heat is very fast process, it completes in within minutes.

Generation of Biodiesel

To produce biodiesel from cotton seed oil four process such as oil filtration, FFA (free fatty acid) number, alkaline trans-esterification and washing process, are used.

a. *Oil filtration*: Cotton seed oil has higher content of moisture and some other impurities. So refining of cotton seed oil is done to remove the moisture and other impurities. The purification is done by boiling oil with 20 % water. The boiling is continued until no bubble of water vapour is present. After one hour the oil appears clear. The cotton seed oil which is free from impurities and moisture is taken as raw material to find out FFA number.

b. *Determination of FFA*: To find out the percentage amount of FFA in the cotton seed oil. The chemical process which is called as titration is used. The cotton seed oil is first mixed with alcohol (methanol). Then, a mixture of Sodium Hydroxide (NaOH) and water is added to mixture of alcohol and oil. This process continues until all of the FFA has been reacted. This can be proved by finding the pH of the mixture.

When the pH of about 9 reaches it confirms that all of the FFA has been reacted. One gram of NaOH was mixed in 1 litre of distilled water (0.1%NaOH) solution. Phenolphthalein solution which is an indicator was used to get the end point i.e. completion of reaction. In a smaller beaker, 1ml of Cotton seed oil is mixed in 10ml of methanol. The mixture was stirred gently till all of the oil was dissolves in the alcohol

and the solution turns clear. Two or three drops of phenolphthalein solution is added to the solution by using a burette, 0.1% NaOH solution was added drop by drop to the mixture of oil, alcohol, and phenolphthalein solution, stirring the solution all the time, till the solution becomes pink. The number of ml of 0.1% NaOH solution gives the amount of NaOH to be used per litre of oil and FFA percentage.

Table2: FFA cottonseed oil data

S. NO.	MI titration	%FFA
1	1	0.72
2	0.9	0.64
3	1	0.72

From the above table we find out the percentage of free fatty acid in cottonseed oil is up to 0.66 which is below 2.5 therefore it is one step process .Acid esterification is not required in process of generation of biodiesel from cotton seed oil.

c. *Mixing of Methanol and Catalyst*:

By mixing alcohol (methanol) and the catalyst (KOH) we found a new compound on the completion of reaction which is called as Methoxide. The quantity of alcohol used should be 20% of the quantity of the cotton seed oil. Alcohol and KOH are the chemicals compounds which are harmful, but Methoxide is more harmful. These substances should not come in contact with skin. Inhalation of vapour should not be done. Gloves are used while working. There should be proper ventilation at the place all times when working with these substances.

d. *Microwave irradiated trans-esterification of cotton seed oil*:

The equipment used for the microwave irradiation is Samsung 28 domestic microwave with power output of maximum 900 W and frequency 2450 Hz.

Methanol was mixed with potassium hydroxide (KOH). The mixture of catalyst and methanol was next poured into the conical flask containing the cotton seed oil. The conical flask containing the cotton seed oil was placed in the cavity of the microwave for

microwave irradiation. During the trans-esterification process, the reaction solution was agitated time to time.

e. *Removal of Glycerol*

After the trans-esterification process, the time should be given for the glycerol to settle to the bottom of the container. This happens because Glycerol is heavier than biodiesel. The settling will begin immediately, but the mixture should be left for minimum of eight hours to 12 hours. After that glycerol settles down and biodiesel floats above glycerol. Next glycerol is removed from the biodiesel.

f. *Washing process:*

Purification of biodiesel was done by adding 3/4th of distilled hot water with impure biodiesel and shaking gently. The upper layer was of biodiesel and impurities collected into inferior layer.

Experimental work of bio-diesel generation by microwave heating

The experiments are performed in Samsung domestic microwave oven with variation of methanol to cotton seed oil, molar ratio as 6:1, 4.5:1 & 7.5:1. The variation of KOH is as 1%, 0.75%, 0.5%. Time variation is from 20 min, 22 min and 25 min.

Data calculations:

Molecular weight of triglycerides of non-edible oil   = 870 (approximately)

Molecular weight of methanol   = 32

Therefore,   1 gram mole of non-edible oil   = 870 g

And,   1 gram mole of methanol   = 32 g

For 4.5:1 molar rario= 32/870*400*4.5   = 66.24 g

For 1:6 molar ratio= 32/870*400*6   = 88g

For 7.5:1 molar ratio=(32/870)*400*7.5   =110.34g

Oil used for the generation of biodiesel is cotton seed oil. KOH pellets as a catalyst and methanol. Sample of 400 gm oil is taken in a conical flask. Solution of alcohol and catalyst is prepared. Reaction is carried in a microwave oven. Sample is agitated time to time. Table shown below calculate the variation of yield and viscosity with molar ratio, catalyst and time.

Table 3: experimental data

S.NO.	Molar ratio	Catalyst(%)	Time(min)	Yield(%)	viscosity
1	4.5:1	1	20	90.14	6.37
2	4.5:1	0.75	22	89.23	6.43
3	4.5:1	0.5	25	86.39	6.52
4	6:1	1	20	95.61	4.53
5	6:1	0.75	22	94.58	4.73
6	6:1	0.5	25	93.69	5.23
7	7.5:1	1	20	89.66	5.34
8	7.5:1	0.75	22	89.21	5.56
9	7.5:1	0.5	25	89.39	5.78

Chapter 6

RESULT AND DISCUSSION

Taguchi analysis

Taghuchi method is an efficient procedure for planning experiments so that the data obtained can be analysed to achieve the optimum yield and viscosity with minimum number of experiments. Using MINITAB 18, statical analysis was carried out as per the taguchi method.
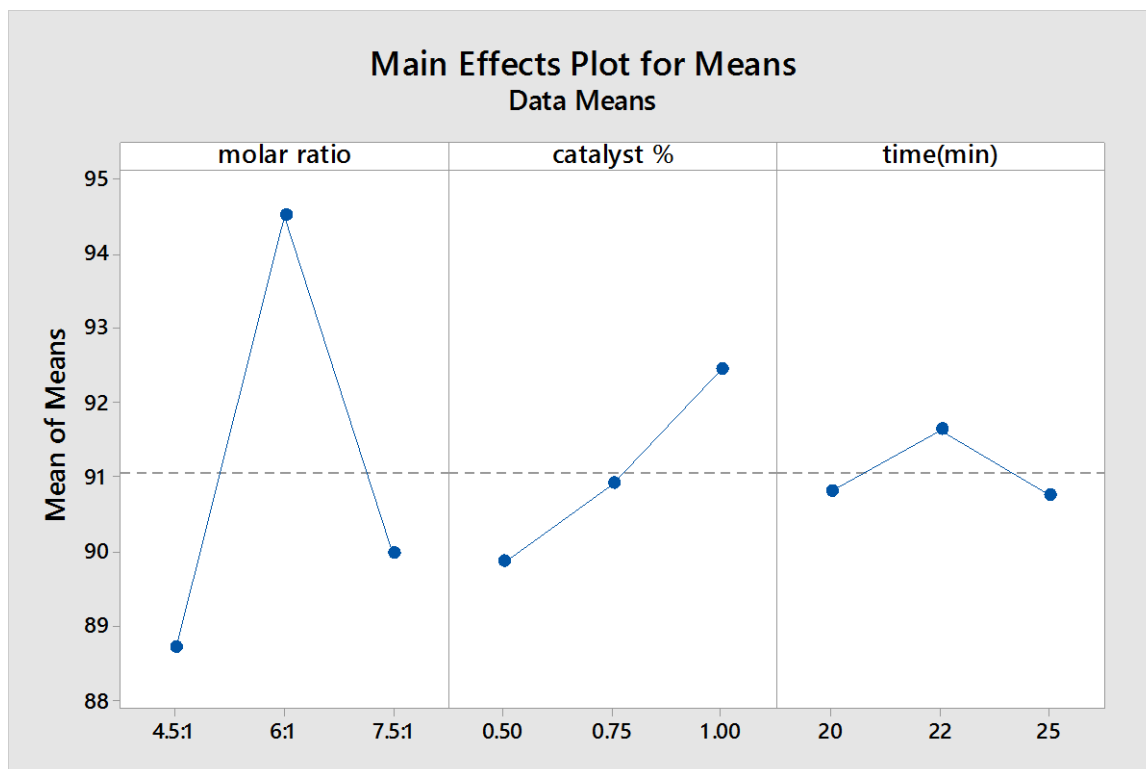

Fig6: mean graph between %yield and molar ratio, %yield and %catalyst, %yield and time.

Table4: Response Table for Means

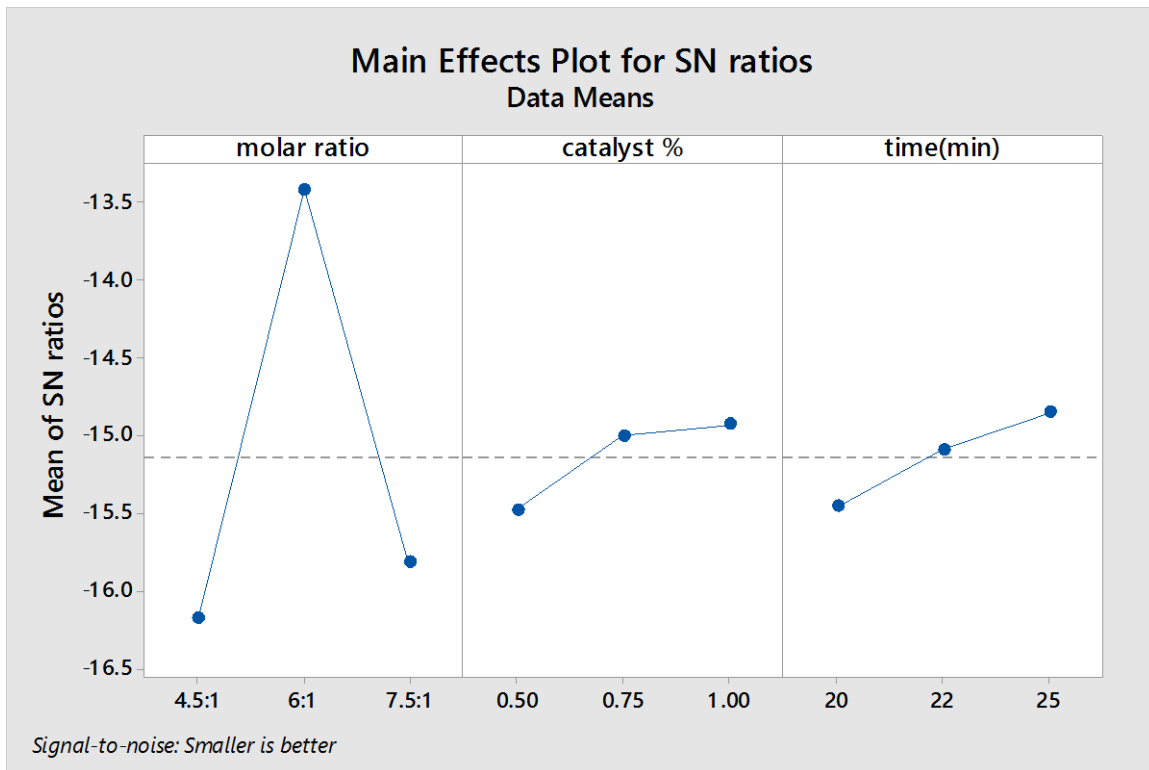| Level	Molar ratio	Catalyst %	Time(min)
1	88.72	89.87	90.81
2	94.50	90.91	91.63
3	89.98	92.44	90.76
Delta	5.78	2.57	0.87
Rank	1	2	3
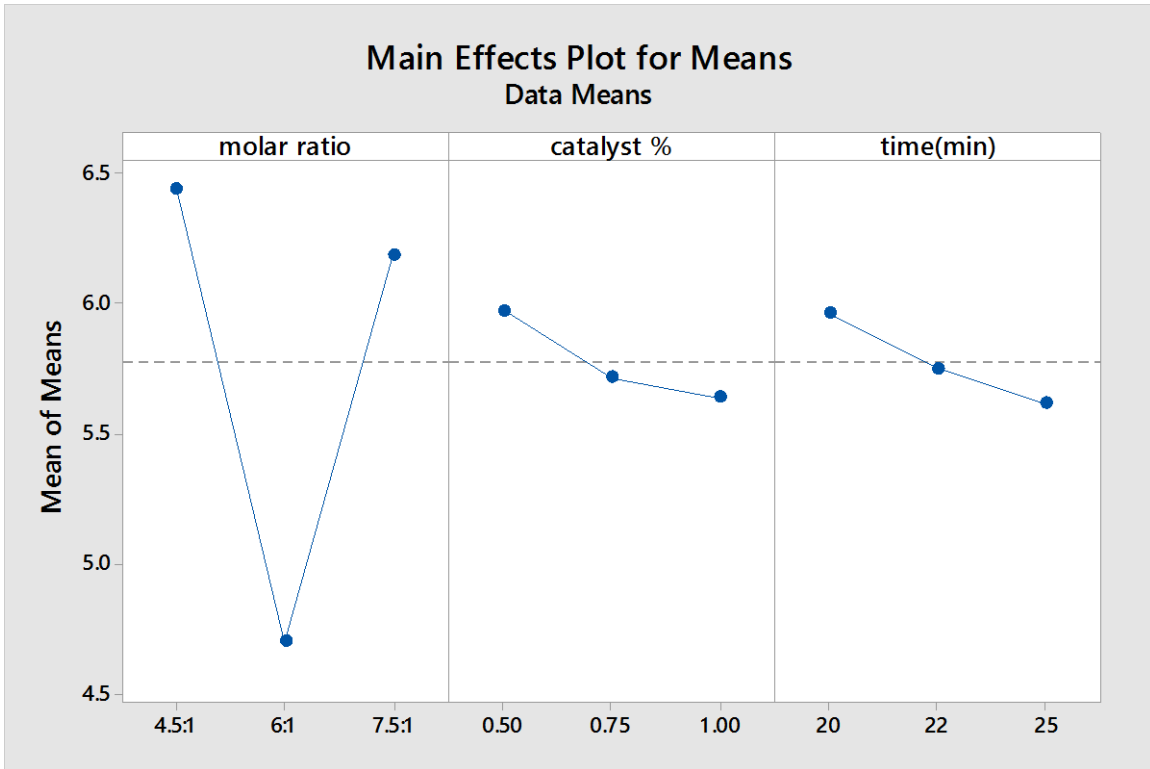
Fig7: mean graph between viscosity and molar ratio, viscosity and catalyst %, viscosity and time.

Table5: Response Table for Means

Level	Molar ratio	Catalyst %	Time (min)
1	6.440	5.960	5.960
2	4.700	5.713	5.750
3	6.183	5.637	5.613
Delta	1.740	0.337	0.347
Rank	1	3	2
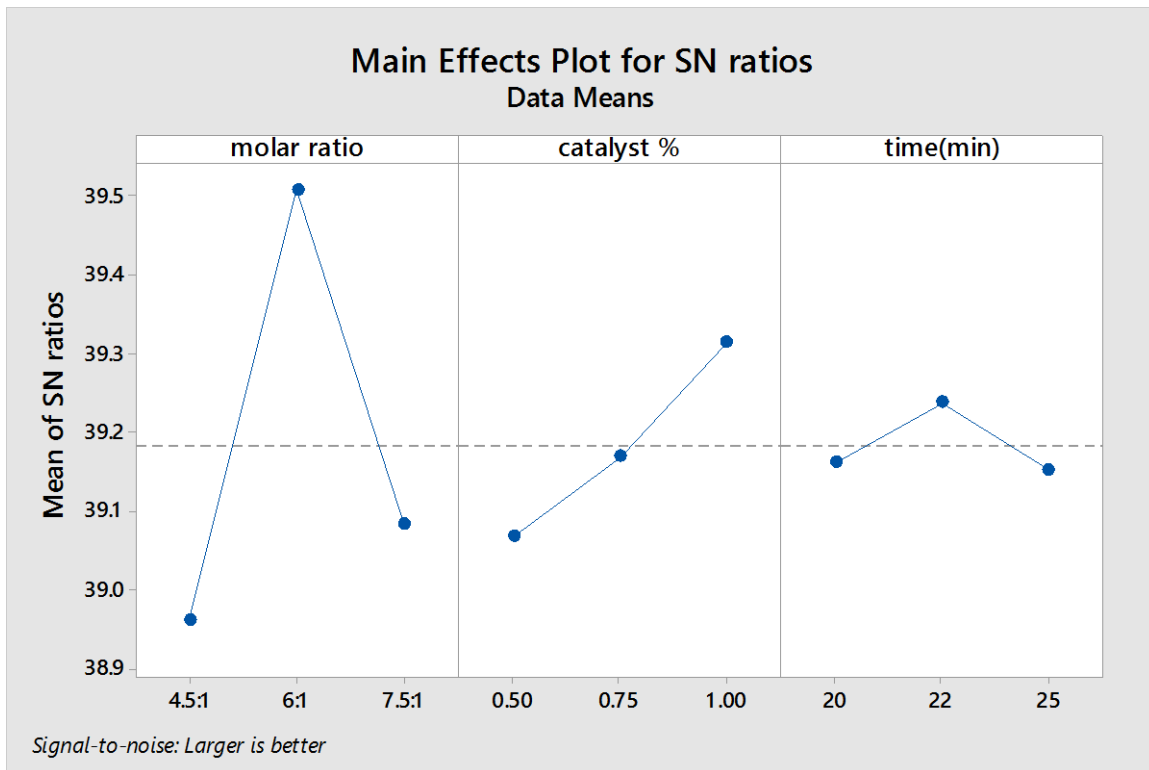
Fig8: SN ratio graph between %yield and molar ratio, %yield and catalyst%, %yield and time.

Table6: Response Table for Signal to Noise Ratios Larger is better

Level	Molar ratio	Catalyst %	Time(min)
1	38.96	39.07	39.16
2	39.51	39.17	39.24
3	39.08	39.31	39.15
Delta	0.55	0.25	0.08
Rank	1	2	3

Fig9: SN ratio graph between viscosity and molar ratio, viscosity and catalyst%, viscosity and time.

Table7: Response Table for Signal to Noise Ratios Smaller is better

Level	Molar ratio	Catalyst %	Time
1	-16.18	-15.48	-15.46
2	-13.42	-15	-15.10
3	-15.82	-14.94	-14.86
Delta	2.76	0.55	0.60
Rank	1	3	2

Factors affecting the biodiesel generation

a. *Effect of reaction time*:

It can be concluded from above results that as we increase the time from 20 minute to 25 minute at molar ratio of 6:1 and catalyst at 1%. The yield first increase and next decrease. The optimum result i.e. maximum yield of 91.67 occurs when time is 22minute.

The viscosity also changes as we change the time. Viscosity keeps on increasing as we increase the time. The minimum value of viscosity is 4.7 which occurs when the time of generation is 25 minutes.

b. *Effect of molar ratio*:

As we increase the molar ratio from 4.5:1 to 7.5:1, the yield increases and next decrease as we increase the molar ratio. The optimum yield of 94.5% occur at molar ratio is 6:1. Viscosity of biodiesel first decreases, and next reaches a minimum value of 4.7 at the molar ratio of 6:1.

c. *Effect of change in catalyst percentage*:

By increasing the catalyst in biodiesel generation from 0.5% to 1%, the yield increases. The maximum yield of 92.44% occurs at 1% catalyst. A similar trend is also seen for viscosity. As there is change in % catalyst, viscosity decreases and reach a minimum value of 5.637. The minimum value achieve at 1% catalyst.

Comparison of methods of generation of biodiesel i.e. mechanical stirrer method and microwave heating method.

Two methods are used for the generation of biodiesel from cottonseed oil. Mechanical stirring method is a conventional method which is used to produce biodiesel. But it takes longer time to produce biodiesel. Another method is microwave heating method which is advance method for producing biodiesel. It takes less time to produce biodiesel; hence it is fast process to produce biodiesel from cottonseed oil. The detailed comparisons of both methods are as follows.

- **The comparison of mechanical stirrer and microwave heating at time 20 minutes.**

  Following table contains the details of experiment at constant time, which is 20 minute. The catalyst and molar ratio are varied from 0.5% to 1% and 4.5:1to 7.5:1 respectively.

Table8: The comparison of mechanical stirrer and microwave heating at time 20minutes.

| s. no.	catalyst %	molar ratio 4.5:1		molar ratio 6:1		molar ratio 7.5:1	
		MS(%yield)	MW(%yield)	MS(%yield)	MW(%yield)	MS(%yield)	MW(%yield)
1	0.5	48.34	86.39	53.34	95.61	58.34	87.66
2	0.75	52.56	89.64	60.65	94.58	62.76	88.21
3	1	56.98	90.14	63.54	95.61	68.9	92.66
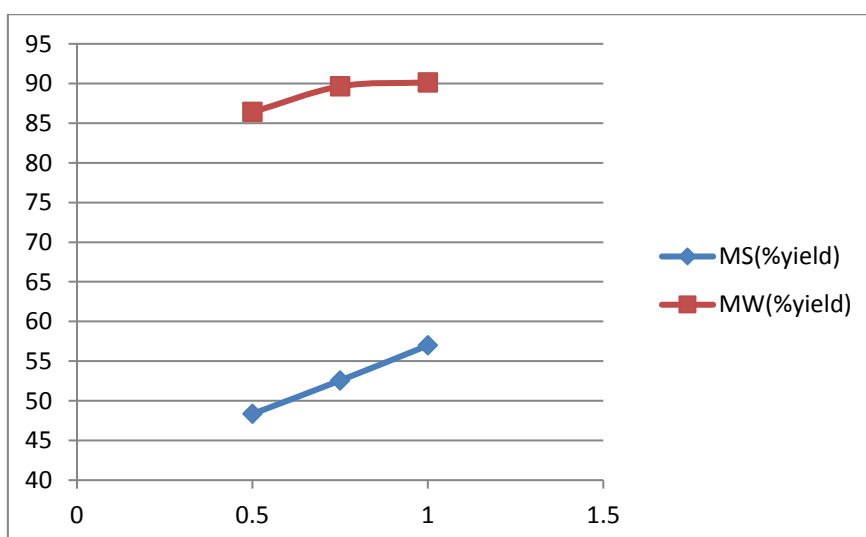
Fig10: comparison of yield and %catalyst by two methods MS and MW at 20 minutes and molar ratio of 4.5:1
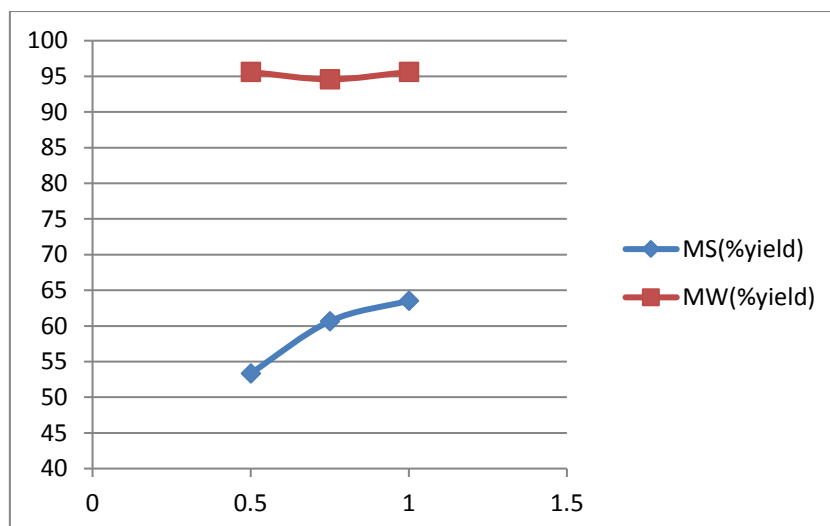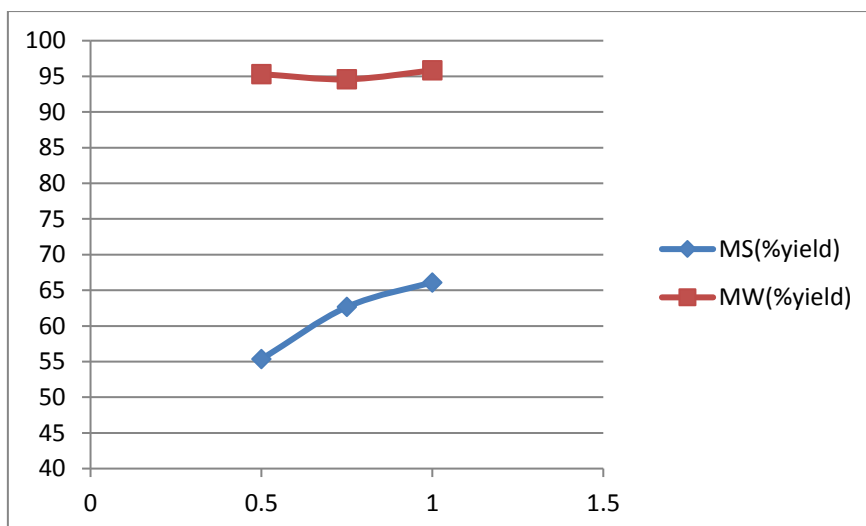
Fig11: comparison of yield and %catalyst by two methods MS and MW at 20 minutes and molar ratio of 6:1
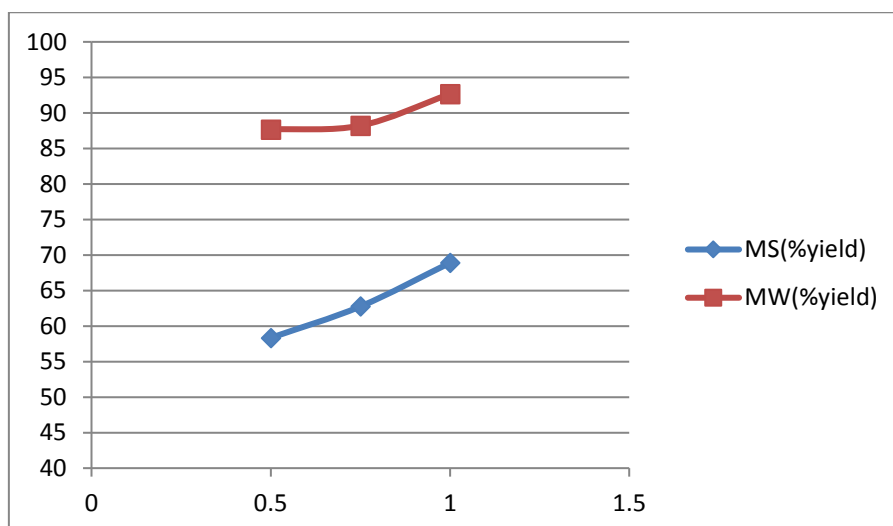
Fig14: comparison of yield and %catalyst by two methods MS and MW at 20 minutes and molar ratio of 7.5:1

It is clear that yield obtained is higher for microwave heating as compared to conventional stirring method for different molar ratios of 4.5:1, 6:1 and 7.5:1. The time for experiment is 20 minute. The change is percentage is from 0.5, 0.75 and 1. For molar ratio 4.5 the yield obtained in mechanical stirring method are 48.34, 52.56 and 56.98 as the catalyst changes from 0.5% to 1%. Whereas for molar ratio 4.5:1 the yield obtained in microwave heating method are 86.39, 89.64 and 90.14 as the catalyst changes from 0.5% to 1%. Similarly the data for molar ratio of 6:1 and 7.5:1 are given in above table.

- **The comparison of mechanical stirrer and microwave heating at constant time 22 minutes.** Following table contains the details of experiment at constant time, which is 22 minute. The catalyst and molar ratio are varied from 0.5% to 1% and 4.5:1to 7.5:1 respectively.

Table9: The comparison of mechanical stirrer and microwave heating at time 22 minutes.

s. no.	catalyst %	molar ratio 4.5:1		molar ratio 6:1		molar ratio 7.5:1	
		MS(%yield)	MW(%yield)	MS(%yield)	MW(%yield)	MS(%yield)	MW(%yield)
1	0.5	50.65	87.12	55.34	95.31	60.65	90.01
2	0.75	55.53	89.23	62.66	94.58	63.66	91.21
3	1	58.23	90.1	66.1	95.85	70.1	92.1
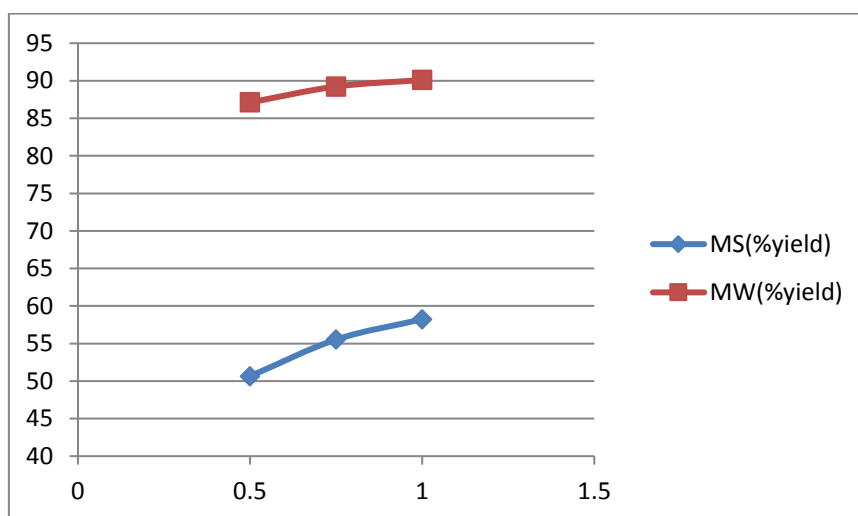
Fig13: Comparison of yield and %catalyst by two methods MS and MW at 22 minutes and molar ratio of 4.5:1

Fig14: Comparison of yield and %catalyst by two methods MS and MW at 22 minutes and molar ratio of 6:1
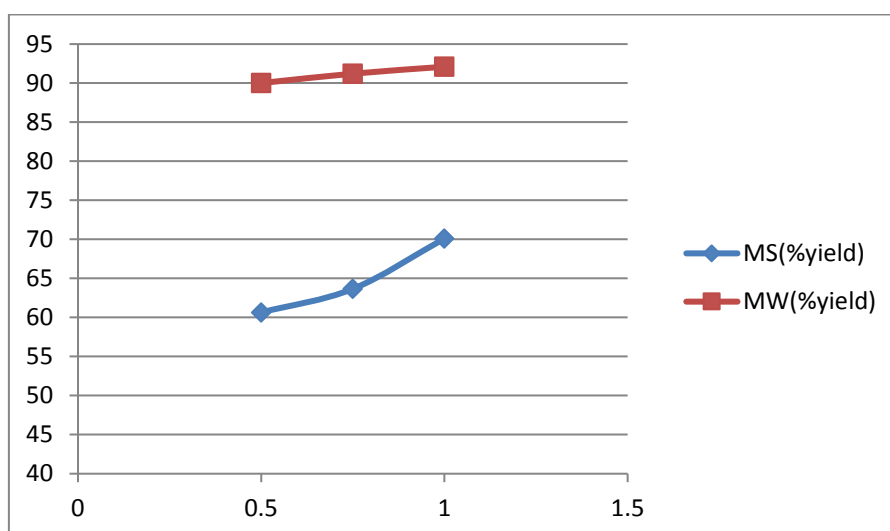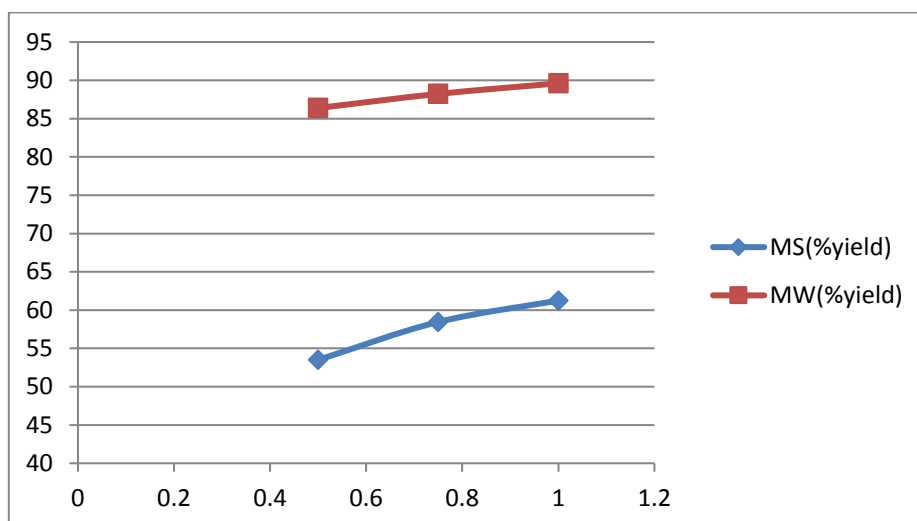

Fig15: Comparison of yield and %catalyst by two methods MS and MW at 22 minutes and molar ratio of 7.5:1

It is clear that yield obtained is higher for microwave heating as compared to conventional stirring method for different molar ratios of 4.5:1, 6:1 and 7.5:1. The time of experiment is 22 minutes. The change is percentage is from 0.5, 0.75 and 1. For molar ratio 4.5:1 the yield obtained in mechanical stirring method are 50.65, 55.53 and 58.23 as the catalyst changes from 0.5% to 1%. Whereas for molar ratio 4.5:1 the yield obtained in microwave heating method are 87.12, 89.64 and 90.1 as the catalyst changes from 0.5% to 1%. Similarly the data for molar ratio of 6:1 and 7.5:1 are given in above table.

- **The comparison of mechanical stirrer and microwave heating at constant time 25 minutes.** Following table contains the details of experiment at constant time, which is 25 minute. The catalyst and molar ratio are varied from 0.5% to 1% and 4.5:1to 7.5:1 respectively.

Table10: The comparison of mechanical stirrer and microwave heating at time 25 minutes.

s. no.	catalyst %	molar ratio 4.5:1		molar ratio 6:1		molar ratio 7.5:1	
		MS(%yield)	MW(%yield)	MS(%yield)	MW(%yield)	MS(%yield)	MW(%yield)
1	0.5	53.5	86.39	57.77	93.69	67.44	89.39
2	0.75	58.45	88.23	64.89	95.01	69.79	91.45
3	1	61.23	89.61	67.99	95.98	72.45	92.67

Fig16: Comparison of yield and %catalyst by two methods MS and MW at 25 minutes and molar ratio of 4.5:1
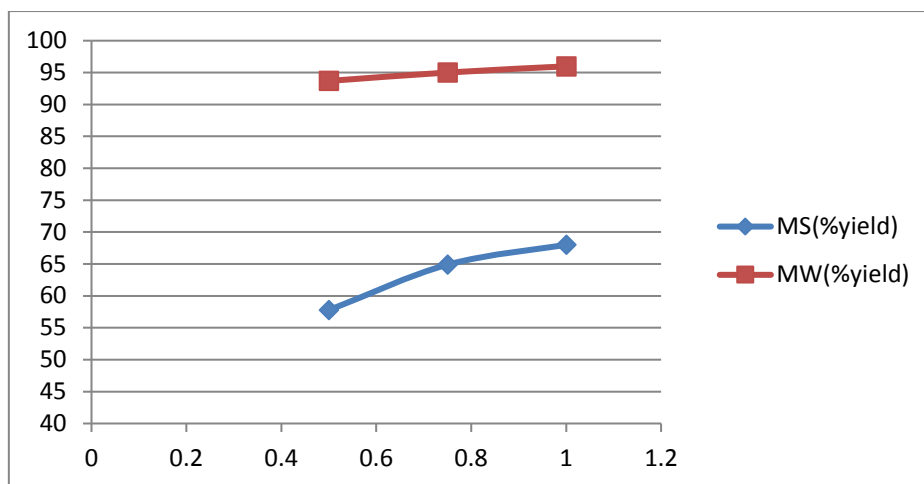
Fig17: Comparison of yield and %catalyst by two methods MS and MW at 25 minutes and molar ratio of 6:1
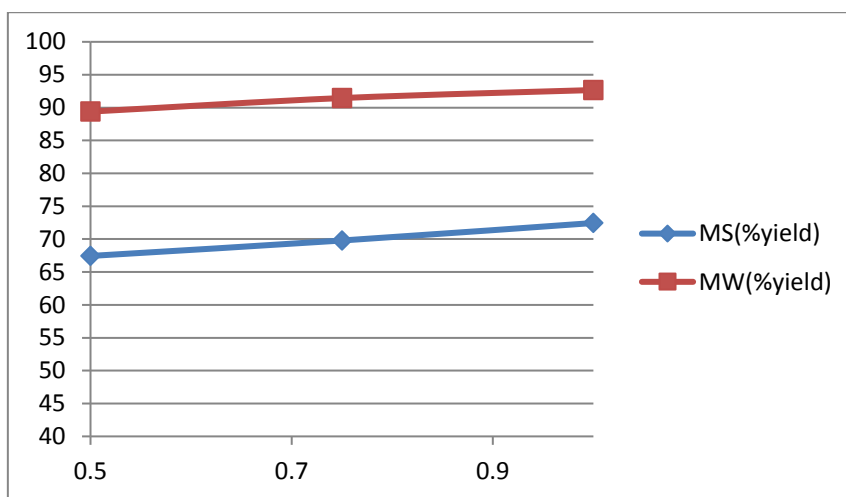

Fig18: Comparison of yield and %catalyst by two methods MS and MW at 25 minutes and molar ratio of 7.5:1

It is clear that yield obtained is higher for microwave heating as compared to conventional stirring method for different molar ratios of 4.5:1, 6:1 and 7.5:1. The time of experiment is 25 minutes. The change is percentage is from 0.5, 0.75 and 1. For molar ratio 4.5:1 the yield obtained in mechanical stirring method are 53.5, 58.45 and 61.23 as the catalyst changes from 0.5% to 1%. Whereas for molar ratio 4.5:1 the yield obtained in microwave heating method are 86.39, 88.23 and 89.61 as the catalyst changes from 0.5% to 1%. Similarly the data for molar ratio of 6:1 and 7.5:1 are given in above table.

- **The comparison of mechanical stirrer and microwave heating at constant molar ratio of 4.5:1.** Following table contains the details of experiment at constant molar ratio, which is 4.5:1. The catalyst and time are varied from 0.5% to 1% and 22 minutes to 25 minutes respectively.

Table11: The comparison of mechanical stirrer and microwave heating at molar ratio of 4.5:1

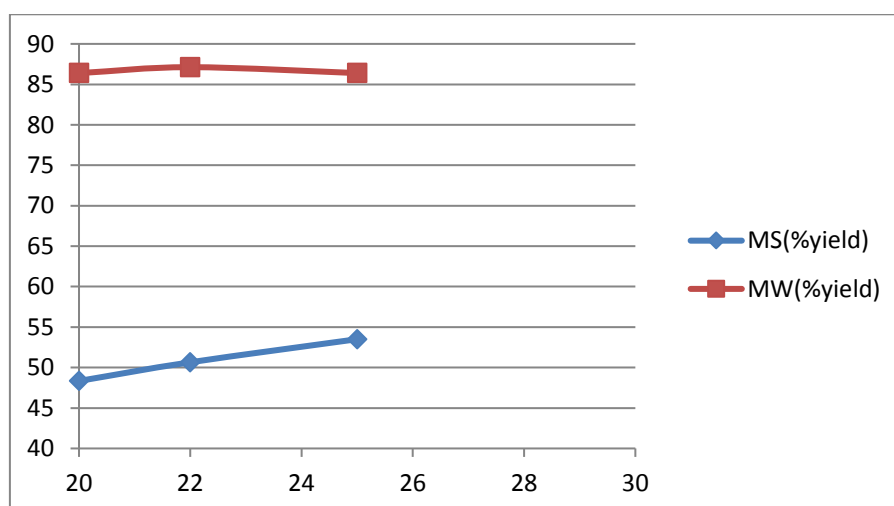| s.no.	time(min)	catalyst(KOH) =0.5%		catalyst(KOH)=0.75%		catalyst(KOH) =1%	
		MS(%yield)	MW(%yield)	MS(%yield)	MW(%yield)	MS(%yield)	MW(%yield)
1	20	48.34	86.39	52.56	89.64	56.98	90.14
2	22	50.65	87.12	55.53	89.23	58.23	90.1
3	25	53.5	86.39	58.45	88.23	61.23	89.61

Fig19: Comparison of yield and time of two methods MS and MW at 0.5% catalyst and molar ratio of 4.5:1
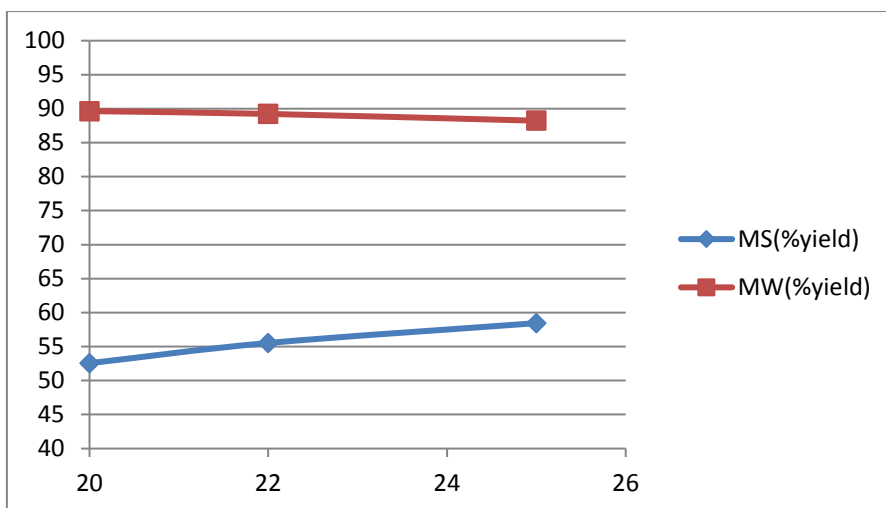
Fig20: Comparison of yield and time of two methods MS and MW at 0.75% catalyst and molar ratio of 4.5:1
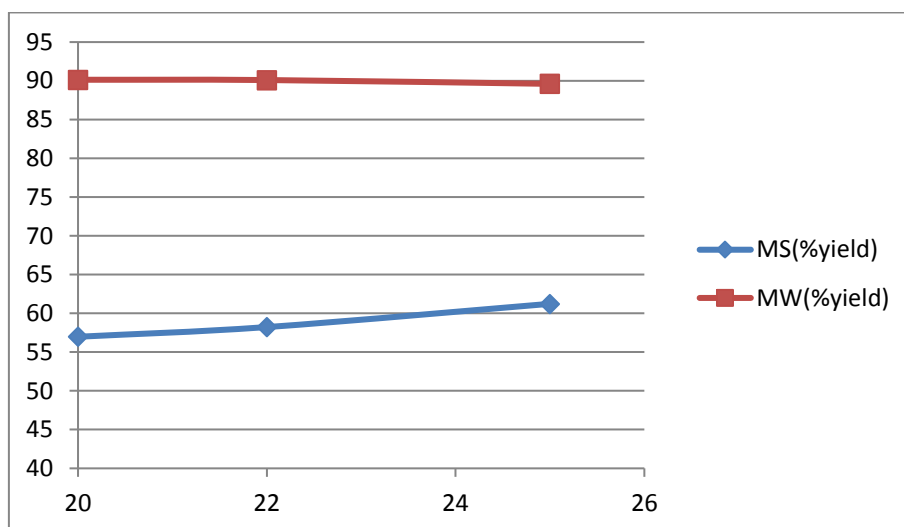

Fig21: Comparison of yield and time of two methods MS and MW at 1% catalyst and molar ratio of 4.5:1

It is clear that yield obtained is higher for microwave heating as compared to conventional stirring method for different time of 20, 22 and 25. The molar ratio of experiment is 4.5:1. The change is percentage of catalyst is from 0.5, 0.75 and 1%. For 0.5% amount of catalyst, the yield obtained in mechanical stirring method is 48.34, 50.65 and 53.5 as the time changes from 20 to 25. Whereas for 0.5% amount of catalyst, the yield obtained in microwave heating method are 86.39, 87.12 and 86.39 as the time changes from 20 minutes to 25 minutes. Similarly the data for 0.75% and 1% catalyst are given in above table.

- **The comparison of mechanical stirrer and microwave heating at molar ratio of 6:1.**

  Following table contains the details of experiment at molar ratio, which is 6:1. The catalyst and time are varied from 0.5% to 1% and 22 minutes to 25 minutes respectively.

Table12: The comparison of mechanical stirrer and microwave heating at molar ratio of 6:1.

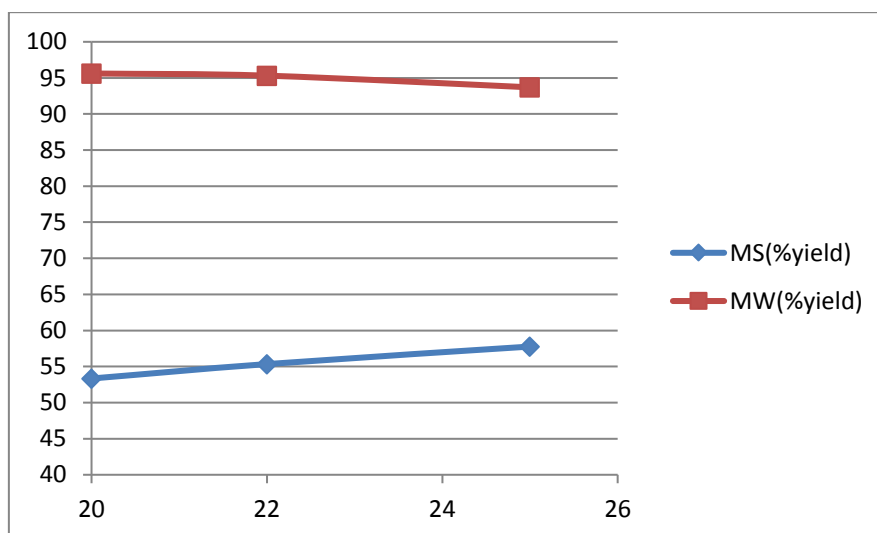| s.no.	time(min)	catalyst(KOH) =0.5%		catalyst(KOH)=0.75%		catalyst(KOH) =1%	
		MS(%yield)	MW(%yield)	MS(%yield)	MW(%yield)	MS(%yield)	MW(%yield)
1	20	53.34	95.61	60.65	94.58	63.54	95.61
2	22	55.34	95.31	62.66	94.58	66.1	95.85
3	25	57.77	93.69	64.89	95.01	67.99	95.98

Fig22: Comparison of yield and time of two methods MS and MW at 0.5% catalyst and molar ratio of 6:1
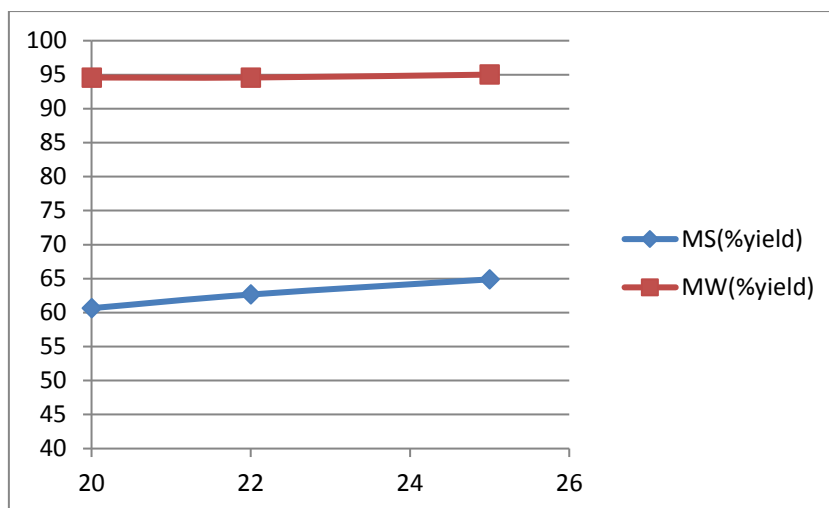
Fig23: Comparison of yield and time of two methods MS and MW at 0.75% catalyst and molar ratio of 6:1
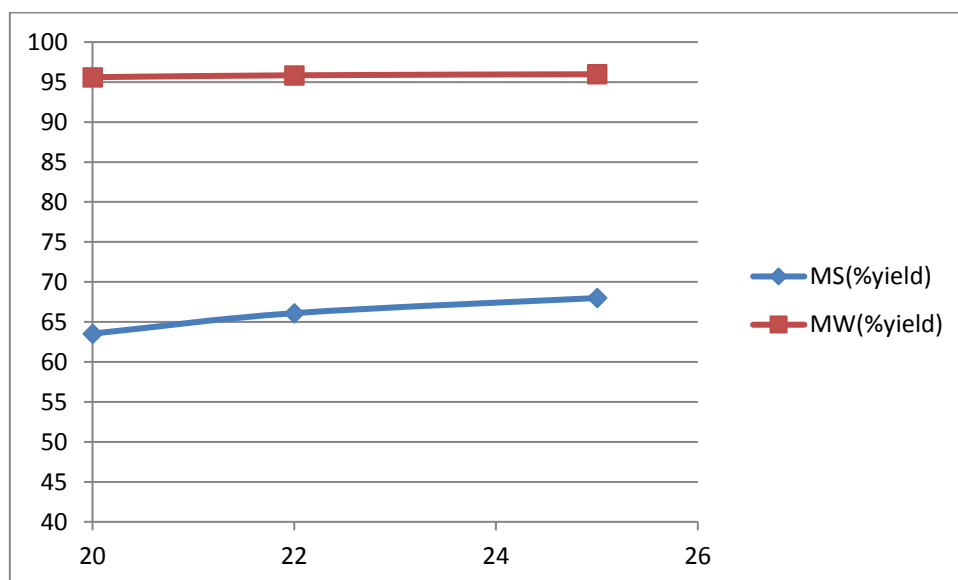

Fig24: Comparison of yield and time of two methods MS and MW at 1% catalyst and molar ratio of 6:1.

It is clear that yield obtained is higher for microwave heating as compared to conventional stirring method for different time of 20, 22 and 25. The molar ratio of experiment is 6:1. The change is percentage of catalyst is from 0.5, 0.75 and 1%. For 0.5% amount of catalyst, the yield obtained in mechanical stirring method is 53.34, 55.34 and 57.77 as the time changes from 20 to 25. Whereas for 0.5% amount of catalyst, the yield obtained in microwave heating method are 95.61, 95.31 and 93.69 as the time changes from 20 minutes to 25 minutes. Similarly the data for 0.75% and 1% catalyst are given in above table.

- **The comparison of mechanical stirrer and microwave heating at molar ratio of 7.5:1 which is constant.** Following table contains the details of experiment at molar ratio, which is 7.5:1. The catalyst and time are varied from 0.5% to 1% and 22 minutes to 25 minutes respectively.

Table13: The comparison of mechanical stirrer and microwave heating at molar ratio of 7.5:1.

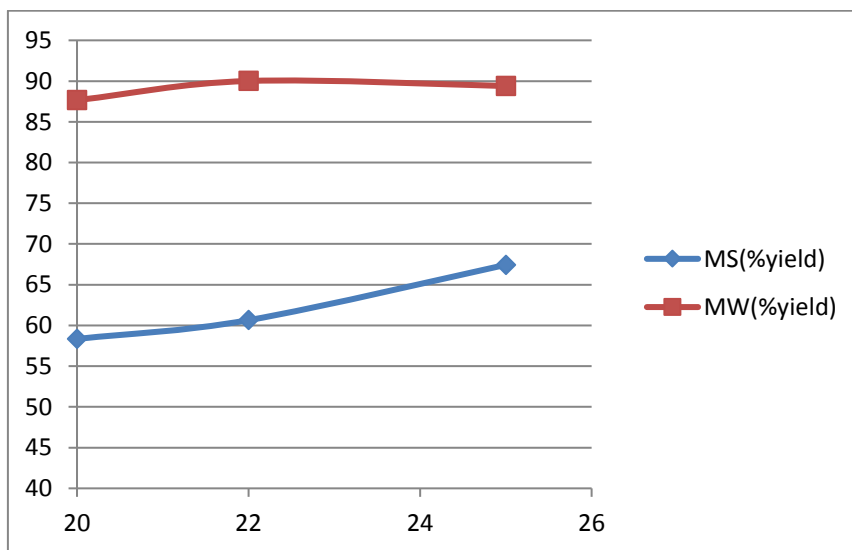| s.no.	time(min)	catalyst(KOH) =0.5%		catalyst(KOH)=0.75%		catalyst(KOH) =1%	
		MS(%yield)	MW(%yield)	MS(%yield)	MW(%yield)	MS(%yield)	MW(%yield)
1	20	58.34	87.66	62.76	88.21	68.9	92.66
2	22	60.65	90.01	63.66	91.21	70.1	92.1
3	25	67.44	89.39	69.79	91.45	72.45	92.67

Fig25: Comparison of yield and time of two methods MS and MW at 0.5% catalyst and molar ratio of 7.5:1.
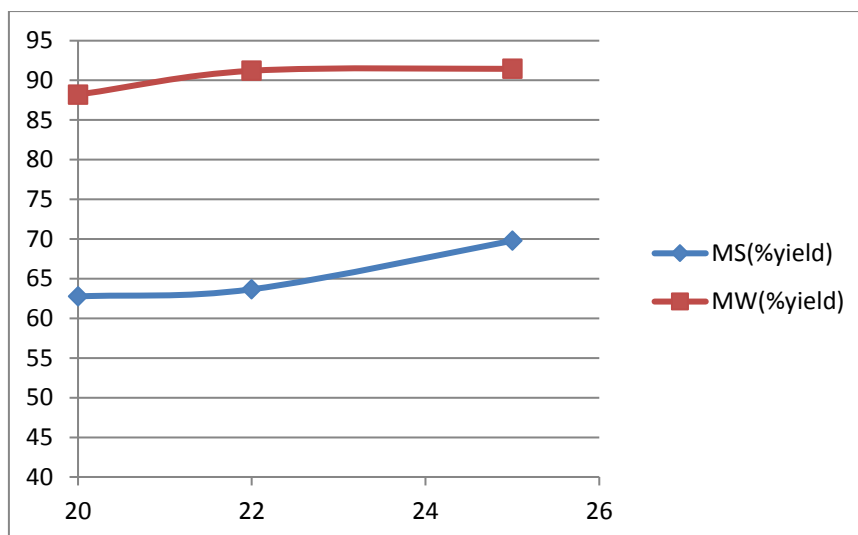
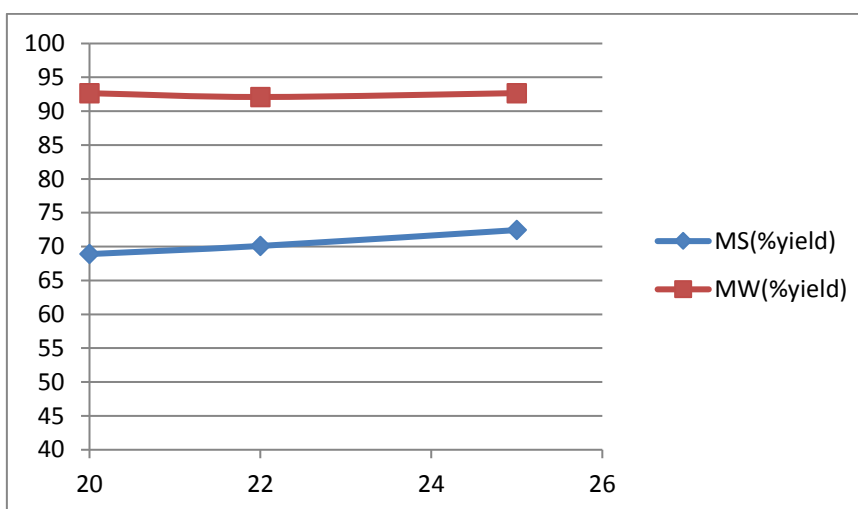Fig26: Comparison of yield and time of two methods MS and MW at 0.75% catalyst and molar ratio of 7.5:1.

Fig27: Comparison of yield and time of two methods MS and MW at 1% catalyst and molar ratio of 7.5:1.

It is clear that yield obtained is higher for microwave heating as compared to conventional stirring method for different time of 20, 22 and 25. The molar ratio of experiment is 7.5:1. The change is percentage of catalyst is from 0.5, 0.75 and 1%. For 0.5% amount of catalyst, the yield obtained in mechanical stirring method is 58.34, 60.65 and 67.44 as the time changes from 20 to 25. Whereas for 0.5% amount of catalyst, the yield obtained in microwave heating method are 87.66, 87.01 and 87.39 as the time changes from 20 minutes to 25 minutes. Similarly the data for 0.75% and 1% catalyst are given in above table.

- **The comparison of mechanical stirrer and microwave heating at constant amount of catalyst i.e. 0.5%.** Following table contains the details of experiment at constant amount of catalyst, which is 0.5%. The molar ratio and time are varied from 4.5 to 7.5 and 22 minutes to 25 minutes respectively.

Table14: The comparison of mechanical stirrer and microwave heating at 0.5% catalyst.

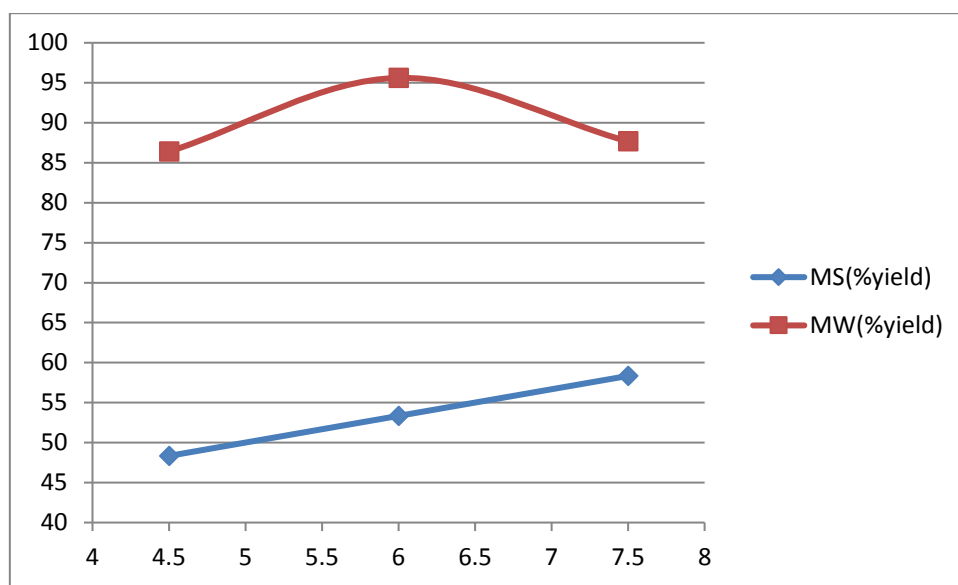| s.no.	molar ratio	time 20 minutes		time 22 minutes		time 25 minutes	
		MS(%yield)	MW(%yield)	MS(%yield)	MW(%yield)	MS(%yield)	MW(%yield)
1	4.5	48.34	86.39	50.65	87.12	53.5	86.39
2	6	53.34	95.61	55.34	95.32	57.77	93.69
3	7.5	58.34	87.66	60.65	90.01	67.44	89.39

Fig28: Comparison of yield and molar ratio of two methods MS and MW at 0.5% catalyst and constant time of 20 minutes.
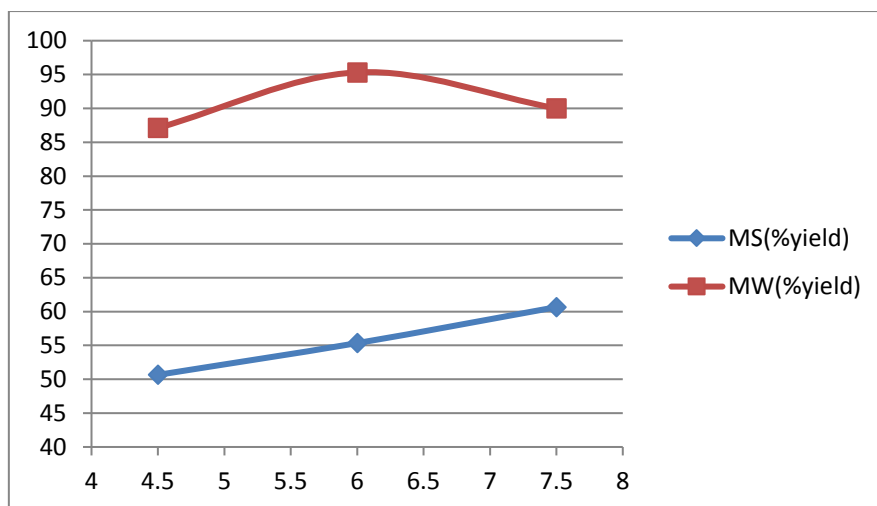
Fig29: Comparison of yield and molar ratio of two methods MS and MW at 0.5% catalyst and constant time of 22 minutes.
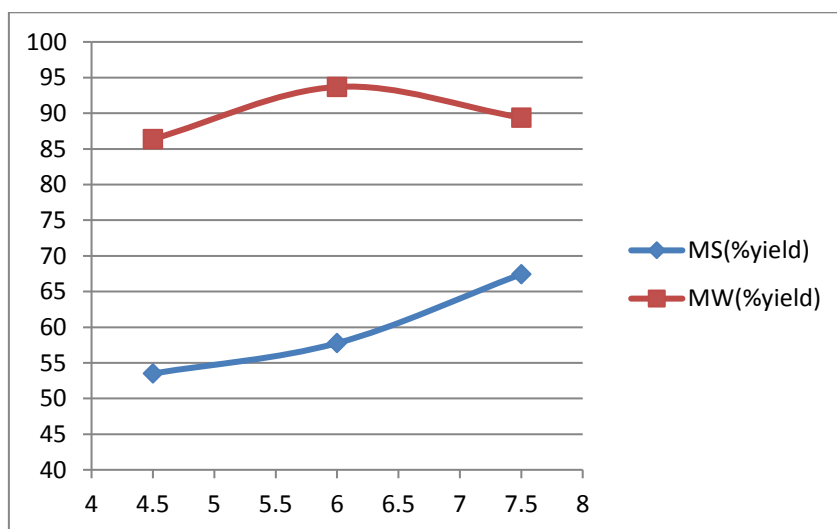

Fig30: Comparison of yield and molar ratio of two methods MS and MW at 0.5% catalyst and constant time of 25 minutes.

It is clear that yield obtained is higher for microwave heating as compared to conventional stirring method for different molar rati0 of 4.5, 6 and 7.5. The % amount of catalyst of experiment is 0.5%. The change in time is from 20, 22 and 25 minutes. For constant time of 20 minutes, the yield obtained in mechanical stirring method is 48.34, 53.34 and 58.34 as the molar ratio changes from 4.5 to 7.5. Whereas for constant time of 20 minutes, the yield obtained in microwave heating method are 86.39, 95.61 and 87.66 as the molar ratio changes from 4.5   to 7.5. Similarly the data for 22 minutes and 25 minutes of time are given in above table.

- **The comparison of mechanical stirrer and microwave heating at constant amount of catalyst i.e.0.75%.** Following table contains the details of experiment at constant amount of catalyst, which is 0.75%. The molar ratio and time are varied from 4.5 to 7.5 and 22 minutes to 25 minutes respectively.

Table15: The comparison of mechanical stirrer and microwave heating at 0.75% catalyst.

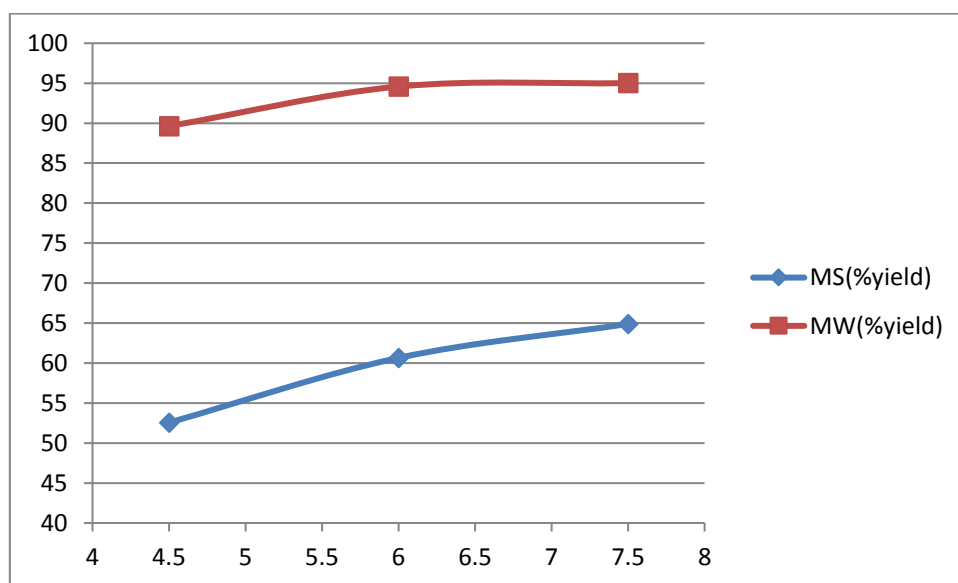| s.no.	molar ratio	time 20 minutes		time 22 minutes		time 25 minutes	
		MS(%yield)	MW(%yield)	MS(%yield)	MW(%yield)	MS(%yield)	MW(%yield)
1	4.5	52.56	89.64	55.53	89.23	58.45	88.23
2	6	60.65	94.58	62.66	94.58	64.89	95.01
3	7.5	64.89	95.01	63.66	91.21	69.79	91.45

Fig31: Comparison of yield and molar ratio of two methods MS and MW at 0.75% catalyst and constant time of 20 minutes.
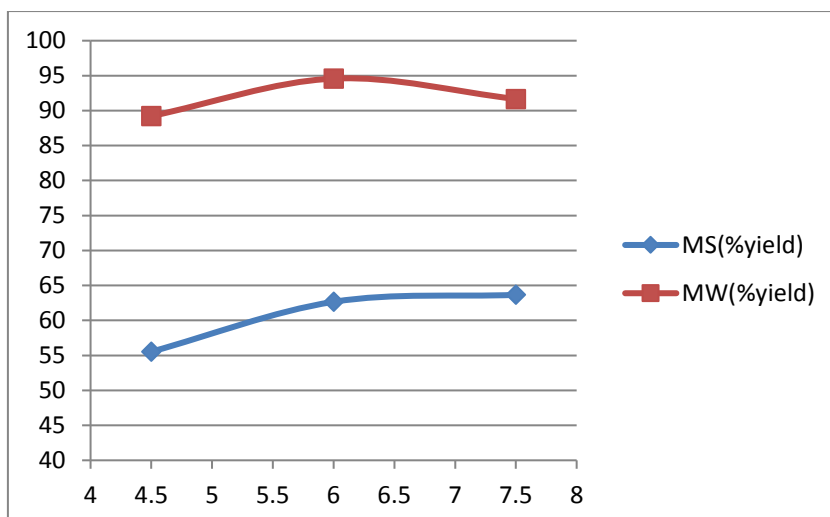
Fig32: Comparison of yield and molar ratio of two methods MS and MW at 0.75% catalyst and constant time of 22 minutes.
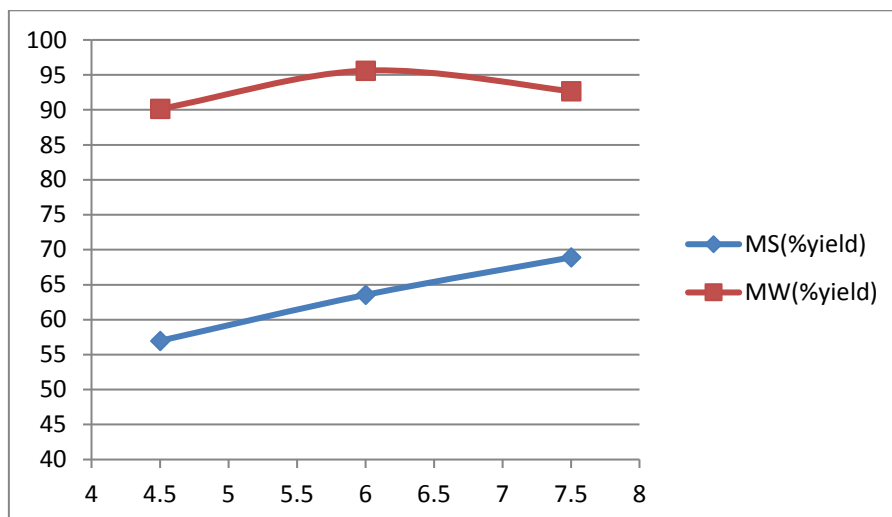

Fig33: Comparison of yield and molar ratio of two methods MS and MW at 0.75% catalyst and constant time of 25 minutes.

It is clear that yield obtained is higher for microwave heating as compared to conventional stirring method for different molar rati0 of 4.5, 6 and 7.5. The % amount of catalyst of experiment is 0.75%. The change in time is from 20, 22 and 25 minutes. For constant time of 20 minutes, the yield obtained in mechanical stirring method is 52.56, 60.65 and 64.89 as the molar ratio changes from 4.5 to 7.5. Whereas for constant time of 20 minutes, the yield obtained in microwave heating method are 89.64, 94.58 and 95.01 as the molar ratio changes from 4.5 to 7.5. Similarly the data for 22 minutes and 25 minutes of time are given in above table.

- **The comparison of mechanical stirrer and microwave heating at constant amount of catalyst i.e. 1%.** Following table contains the details of experiment at constant amount of catalyst, which is 1%. The molar ratio and time are varied from 4.5 to 7.5 and 22 minutes to 25 minutes respectively.

Table16: The comparison of mechanical stirrer and microwave heating at 0.1% catalyst.

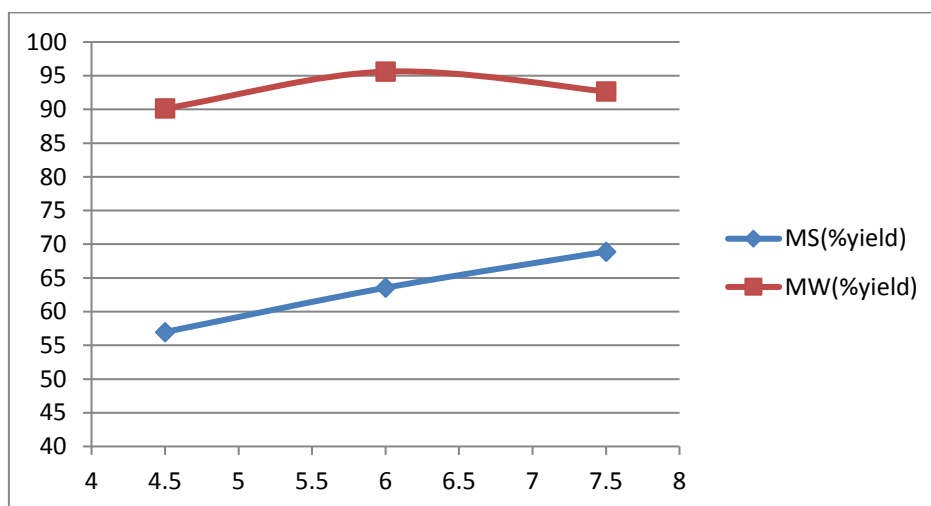| s.no.	molar ratio	time 20 minutes		time 22 minutes		time 25 minutes	
		MS(%yield)	MW(%yield)	MS(%yield)	MW(%yield)	MS(%yield)	MW(%yield)
1	4.5	56.98	90.14	58.23	90.1	61.23	89.61
2	6	63.54	95.61	66.1	95.85	67.99	95.98
3	7.5	68.9	92.66	70.1	92.1	72.45	92.67

Fig34: Comparison of yield and molar ratio of two methods MS and MW at 1% catalyst and constant time of 20 minutes.
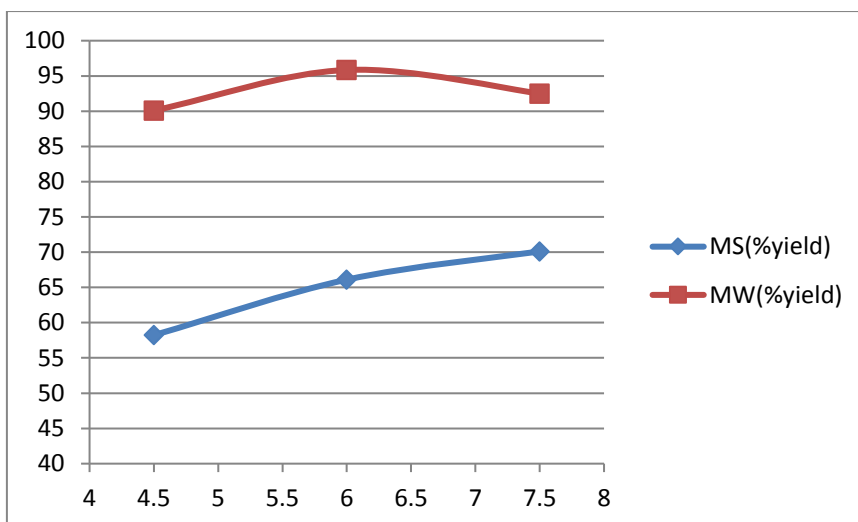
Fig35: Comparison of yield and molar ratio of two methods MS and MW at 1% catalyst and constant time of 22 minutes.
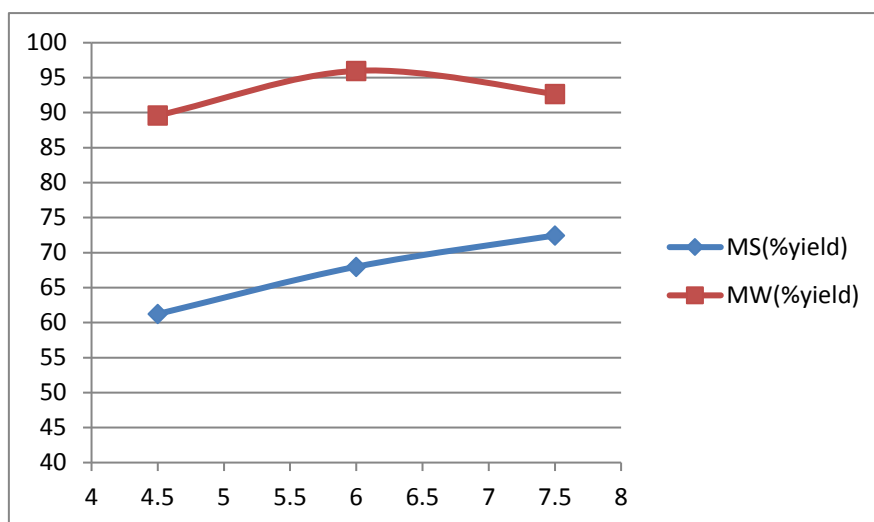

Fig36: Comparison of yield and molar ratio of two methods MS and MW at 1% catalyst and constant time of 25 minutes.

It is clear that yield obtained is higher for microwave heating as compared to conventional stirring method for different molar rati0 of 4.5, 6 and 7.5. The % amount of catalyst of experiment is 1%. The change in time is from 20, 22 and 25 minutes. For constant time of 20 minutes, the yield obtained in mechanical stirring method is 56.98, 63.54 and 68.9 as the molar ratio changes from 4.5 to 7.5. Whereas for constant time of 20 minutes, the yield obtained in microwave heating method are 90.14, 95.61 and 89.66 as the molar ratio changes from 4.5 to 7.5. Similarly the data for 22 minutes and 25 minutes of time are given in above table.

Generation of biodiesel by conventional stirring method

In mechanical stirring method, the time taken to produce the biodiesel is varies from 40 minutes to 60 minutes. It is the time taking process. The following graph shows percentage of yield with time with varying molar ratio from 3:1 to 6:1. The amount of catalyst is 1%.
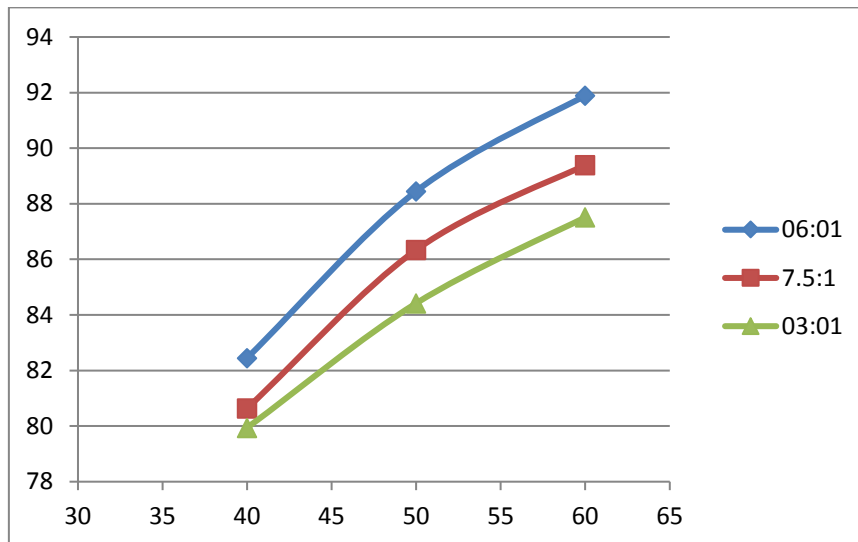
Fig37: graph between %yield and time at constant amount of catalyst 1%.

It clear from above fig that maximum percentage yield of 93.9 is obtained at molar ratio of 6:1 at 1%. The time taken for the process is 45 minutes.

But the time taken to produce biodiesel from cotton seed oil, by microwave heating method is 22 minutes at 100W power. The time is less than 45 minutes. Therefore microwave heating method is used for the biodiesel generation from cotton seed oil.

Chapter 7

ECONOMIC COST ANALYSIS

The estimation of cost production of biodiesel was based on the following assumptions:

(1) The capacity of the plant, which produces biodiesel is estimated to be 500 kg per day.

(2) Hours of operation were assumed to be 8hours/day.

(3) Virgin Cotton seed oil, is used for biodiesel production, was free of impurities and any water.

(4) The cost of all chemicals, which includes cotton seed oil, catalyst, and solvent, are given in Table.

(5) The transportation fee, insurance, and tax, being assumed as 15% of the costs purchased.

Table17: cost of raw materials used in biodiesel generation

Product	Quantity	Price(INR)
Cotton seed oil	1 kg	70
Methanol	1 kg	40
KOH	1 kg	300

Cost of biodiesel generation from cottonseed oil is estimated for a day for a plant which uses 500 litres feedstock per day in Indian Rupees.

1. Cost of raw material

The raw materials required are feedstock, methanol and KOH.

a) Cost of feedstock

Cost of cotton seed oil   = 70Rs/kg

Cost of collection of cotton seed oil & transportation

$$= (5/ kg)*(500 kg/day)$$
$$= 2500/day$$

Total cost of feedstock per day = cost of cotton seed oil +collection

& transportation cost

$$= 70*500 +2500$$

$$= 37500Rs/day$$

b) Cost of methanol

Price of 1 litre of methanol $\quad$ = Rs40

Requirement of methanol per day $\quad$ = 110.5kg

Cost of methanol per day $\quad$ = 110.5*40

$$= 4420Rs/day$$

c) Cost of KOH

Price of 1 Kg of KOH $\quad$ = Rs300

Daily requirement of KOH $\quad$ = 5 kg

Cost of KOH per day $\quad$ =5*300

$$=1500Rs/day$$

The total cost of raw materials per day $\quad$ = oil cost+ cost of alcohol+ cost of KOH

$$= 37500+ 4420 + 1500$$

$$= 43420Rs/day$$

2. Electricity cost

Assumptions:

1 kWh of electricity price $\quad$ = 10 (for industrial use)

Specific heat of water $\quad$ = 4.18 kJ/kgK

Heat loss in radiation by microwave $\quad$ =1%

a) Electricity cost for stirring methanol and KOH

Assume power of motor $\quad$ =10 kW

Duration of stirring for thorough mixing $\quad$ = 10 min

Electricity cost for the stirring per day $\quad$ = 10*(10/60)*10 = 16.66Rs/day

b) Electricity cost for trans-esterification process in microwave processor

Working power of microwave processor = 100W

Duration of trans-esterification in microwave processor = 22 minutes (for 400gm sample)

Energy required for trans-esterification of 500kg in microwave = P*time

= 100*165000J

= 45.833 kWhr

Electricity cost for the process per day = 45.833*10

= 458.33Rs/day

c) Electricity cost for heating of water from 20°C to 50°C for water washing in microwave

Requirement of water for washing of 500kg of oil = 200 kg (around 40% of oil)

Heat energy required for the heating Q = mcpdT/ efficiency

= 200*4.18*(50-20)/0.99

= 25333.33 kJ

= 7.037kWhr

Electricity cost for the process per day = 7.037*10

= 70.37Rs/day

d) Electricity cost for final heating of oil to 110°C for removing water if present in microwave processor

Power of microwave processor is maintained at 180W

Energy required for heating of oil from 20°C to 110°C = P*time

= 180*37500J

= 18.75 kWhr

Electricity cost for the process per day = 18.75 *10

= 187.5Rs/day

Total electricity cost = 16.66 + 458.33 + 70.37 + 187.5

= 732.86Rs/day

3. Apparatus and equipment cost

Total cost of microwave processor and equipment is about 500000, assuming these apparatus works for 10 years and taking 15% interest rate.

Apparatus and equipment cost for 15 years = 500000(1+15*10/100)

$$= 1250000Rs$$

Apparatus and equipment cost per day = 1250000/(10*12*30)

$$= 347.22Rs/day$$

4. Miscellaneous cost

Labour cost per month = 25000Rs

Rent per month = 10000Rs

Maintenance = 1000Rs

Total miscellaneous cost per month = 36000Rs

Total miscellaneous cost per day =1200Rs/day

Grand total cost per day = 43420 + 732.86 +347.22 + 1200

$$= 45700.08Rs/day$$

5. Income from by product (glycerine)

Quantity of glycerine produced per day = 30 kg

Income from glycerine per day (@ 300 per kg) = 300*30

$$= 9000Rs/day$$

Net cost per day = 45700.08 - 9000

$$= 36700.08Rs/day$$

Quantity of biodiesel produced per day = 500*0.94 (yielding efficiency is 0.94)

$$=470 \ kg$$

Cost of cotton seed biodiesel per kg = 36700.08/470

$$=78.08Rs/kg \ of \ oil$$

Conversion cost of biodiesel from cotton seed oil   =78.08-70

                                                      =8.08Rs/kg of oil

On the basis of above calculations it can be concluded that the bio diesel conversion cost comes about 8.08 rupees per kg, hence with cotton seed oil net biodiesel cost comes at 78.08 rupees per kg where as diesel cost without subsidies. Hence cotton seed oil biodiesel found to be a better different to petro diesel.

Chapter 8

CONCLUSION AND FUTURE SCOPE

Conclusion

a. Biodiesel Generation Technique:

Following has been made from the experiment;

1. The yield obtained is maximum for the microwave heating method for the fixed value of reaction time, molar ratio and catalyst percentage.

2. The time taken for the generation of biodiesel by using microwave heating is very less as compared to mechanical stirring method.

3. The production rate is very high in microwave heating method.

4. The experimental results shows that time taken to complete the process of biodiesel production from cottonseed oil is 22 minutes for 400gm of sample at 100W power in microwave heating method.

5. Higher biodiesel productivity is obtained using molar ratio of 6:1 in biodiesel production method as compared to molar ratio of 4.5:1 and 7.5:1.

6. The percentage amount of catalyst which gives higher percentage yield is 1% as compared to 0.5% and 0.75%.

7. The minimum value of viscosity is obtained at 6:1 molar ratio as compared to molar ratio of 4.5:1 and 7.5:1.

8. The amount of catalyst which gives minimum amount of viscosity is 1%.

9. Optimum time of 25 minutes is required to obtain minimum viscosity.

10. Microwave heating method can also be used for mass generation. It gives good quality of biodiesel in shorter time, in comparison to conventional stirring method.

b. Economic Cost Estimation:

On the basis of present work it can be concluded that the bio-diesel conversion cost comes about 8.08 rupees per kg, hence with cotton seed oil net biodiesel cost comes at 78.08 rupees per kg. Hence cotton seed oil biodiesel found to be a better replacement to petro diesel and in future help to acquire the energy security for coming generations and provide a safe passage for eco friendly fuel for future generation.

Future Scope

1. Work is to be done in continuous generation of biodiesel using microwave energy method. It will provide an energy efficient method for mass generation.

2. Generation of biodiesel by varying power of microwave processor can also be studied to obtain the minimum time of production of biodiesel. The will increase the generation rate.

3. Different parameters such as rotational velocity in microwave processor can be studied to increase the percentage yield of biodiesel.

4. The cost of generation of biodiesel can also be decreased, if proper parameters of microwave heating can be analysed.

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