BIO-DIESEL PRODUCTION FROM NON-EDIBLE OIL

A DISSERTATION

Submitted in the partial fulfillment of the

requirement for the award of the degree

Of

MASTER OF TECHNOLOGY

In

CHEMICAL ENGINEERING

(With Specialization in Industrial Pollution Abatement)

By

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CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented by me in this dissertation report entitled "Biodiesel production from non-edible oil " submitted in partial fulfillment of the requirement for the award of the degree of, "**Master of Technology in Chemical Engineering**" with specialization in "**Industrial Pollution Abatement**", and submitted to the Department of Chemical Engineering, Indian Institute of Technology, Roorkee, is an authentic record of the work carried out by me during the period June 2012 to June 2013, under the guidance of Dr. Vimal Kumar**,** Assistant professor of Chemical Engineering, Indian institute of Technology, Roorkee.

Date:

Place: IIT, Roorkee **Rahul Goyal**

CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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Date:

Place: IIT Roorkee **(Rahul Goyal)**

ABSTRACT

Biodiesel is the Fatty acid methyl esters (FAME) and derived from renewable feedstocks which fall in the carbon range C_{12}-C_{22}, and have similar properties as diesel. Typically the biodiesel is produced with transeterification reaction, where vegetable oil is reacted with methanol in the presence of catalysts. The biodiesel yield is affected by various factors: type of alcohol, molar ratio of alcohol to vegetable oil, type of catalyst (acid or basic), amount of catalyst, reaction temperature, reaction time and feedstock quality (e.g. free fatty acid content, water content etc.). In the present work the fatty acid methyl esters are synthesized from non-edible feedstock (jatropha oil) of Indian origin. The synthesis of FAME from jatropha oil is carried out in two-step process**.** Transesterification of jatropha oil is carried out using various co-solvents: diethylether (DEE), tert-butyl methyl ether (tBME), and tetrahydrofuran (THF). The catalyst used was sodium methoxide (CH_3ONa). The study is carried out to find the optimal operating parameters for jatropha oils in batch reactor. The transesterification reaction is carried out for the following conditions for different solvents: 1.0 wt% of CH_3ONa, by taking a temperature of 30 ºC with the agitation rate of 700 rpm, methanol:oil molar ratio is 9:1 and co-solvent/methanol is 1:1. The result of the experimental study shows that the yield of triglyceride into ester increases with increase in time. It has been observed that the approximately 85% reaction completes in 30 sec. The qualitative analysis of vegetable oils is carried out using thin layer chromatography (TLC). DEE and THF are found as the best solvent as compared to the other solvents used in the present work. A similar yield is obtained with both DEE and THF; however separation process is difficult and takes longer time as compared to DEE. The studies were conducted to characterize the fuel properties (e.g., density, viscosity, flash point, fire point, cloud and pour point and carbon content) of biodiesel.

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CHAPTER 1

INTRODUCTION

1.1 General

The main requirement for the economic development based on the energy and every sector for requires the energy for their development. Since independence, to fulfill the energy demand many economic development plans have been implemented. However the consumption of energy in India is steadily rising due to the increase of population. In India, the demand for automobiles and mobility is growing day by day along with economic development. To meet this energy demand, India imports about 72% of its crude oil. The petroleum import bill constitutes about 30% of national import bill which burden on indian foreign currency. Over the last twenty years automobiles pollution have increased eight times in India. Among the total percentage of air pollution, only automobiles are contributing about 70%. India is rank fifth after China, U.S, Russia and Japan. In releasing the carbon by utilize the fossil fuels with a very of 243.3 million and in the upcoming year it is expected to increase more , due to the rapid pace of urbanization, shift from non-commercial to commercial fuels.

An increase in the energy consumption has also been forcing the country to depend more on fossil fuels like as oil, coal and natural gas. Coal, being cheaper and abundantly available, is the major energy resource of the country and accounts 52% of total energy production. Oil largely imported from Arab countries which accounts for 22% of the total energy consumption. For the security of energy supply, it is needed to insure about large pool of energy resource to enhance our economic growth. Due to which the country needs to create some sustainable way for the development of energy. Energy conservation and increased use of renewable energy sources are the two paths which can meet the supply demand imbalance of energy.

1.2 Renewable Energy

India is full of different renewable energy sources, such as biomass, biogas, solar energy, wind energy, and small hydropower plants. India is the one among the world who has implemented largest programms in renewable energy. In the world, India's rank second in biogas utilization and fifth in photovoltaic cell and wind power production. In India renewable sources contribution is around 5% of the total potential of power. The estimated potential and cumulative installed capacity of renewable energy sources are given in Table 1.

Table1.1 Renewable energy in India (Source: www.mnes.nic.in)

Sl. no.	Source /system	Estimated potential (MW)	Cumulative installed capacity (as on March 2009) MW
1	Wind power	45195	10242.5
2	Biomass power	16881	703.00
3	Bagasse cogeneration	5000	1048.73
4	SHP (<25 MW)	15000	2429.98
5	Waste to energy(MWe)	2700	92.97
6	Solar photovoltaic	20MW/km^2	2.80 MW/km^2
7	Biogas plant (No.)	12 Million	3.428 Millions
8	Improved chulha (No.)	120 Millions	34 Millions

1.3 Fuels for Transport

Transportation sector consume largest portion of total power resources in India. The International Energy Agency (IEA) published statistics on consumption share of oil in different sector between 1990and 2010 shows that the transport sector consumes maximum oil.

Fig 1.1 shows that the oil consumption in 1990 was only 42% which increased to 57 % in the year 2010 in transport sector. This drastic change in oil demand is due to increasing population, increasing rate of industrialization, its frequency of mobilization as well as obsoleting the animal power in transport sector. In term of percentage oil accounts 98 %for transport, 29%for industry, 4%for electricity generation and 10%for other sector. The other serious options are electric vehicles, railway's electrification, hydrogen based vehicles and urban mass transportation.

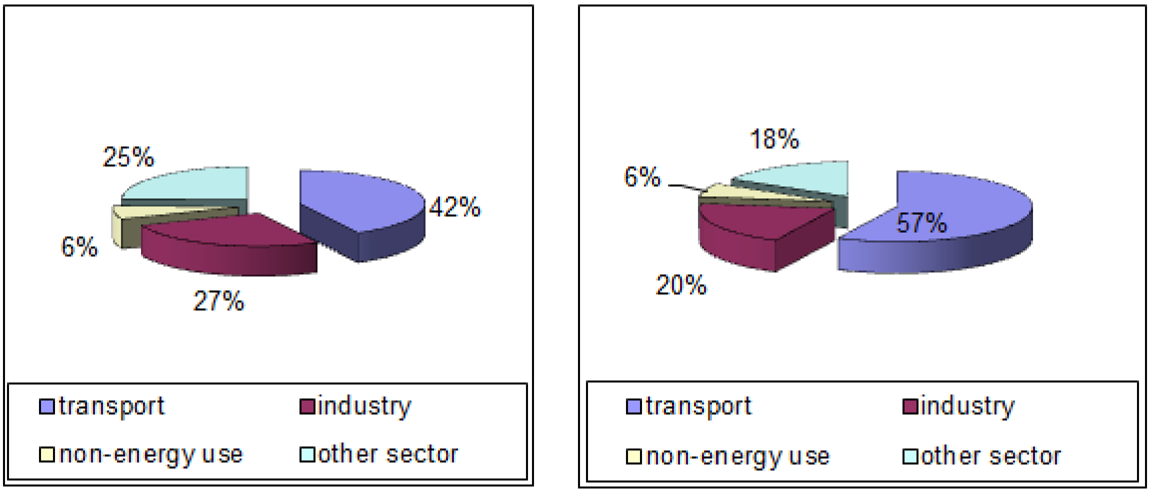


Figure1.1 World oil consumption share in 1990 and 2010 (Source: World Energy Outlook, 2012)

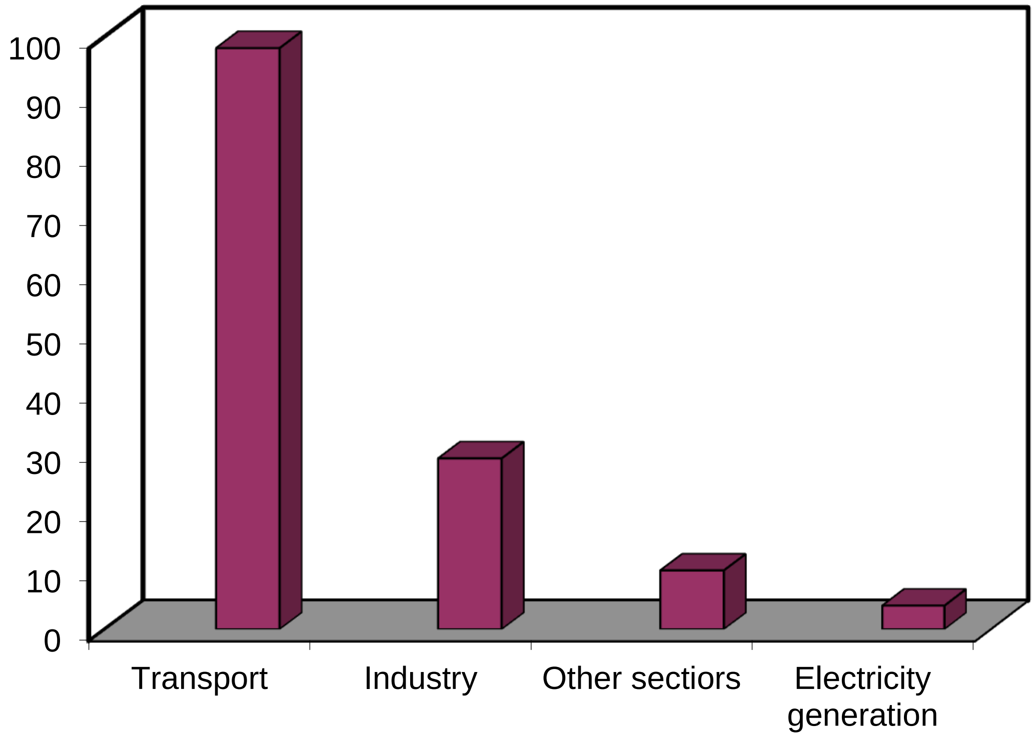


Figure 1.2 Percentage share of oil consumption in different sector (Source: World Energy Outlook, 2012)

1.3.1 Alternative diesel fuel

The main requirements of alternative fuels are:

- Easily available
- Environment friendly
- Techno-economically competitive.

Triglycerides and their derivatives are commonly used as vegetable oils. Vegetable oil causes less environment problem then diesel as it contains low sulphur content and also widely available for a various source. These are manufactured in huge quantity in the country for food and other applications.

1.3.2. Triglyceride as diesel fuels

From the past ninety years, vegetable oils like soya bean, sunflower, peanut, palm and olive oil are using alternative fuels for diesel engine but now it is highly encouraged in the develping countries as renewable liquid fuel due to depletion of crude oil resources. Now countries are seeking various types of vegetable oils as an alternative of fossil fuels as per their soil and weather conditions. For example, sunflower and rapeseed oils in Europe, soya bean oil in the US, coconut oil in the Philippines and palm oil in South-east Asia (mainly Malaysia and Indonesia) are being considered. Non-edible oils, e.g. curcus ie also known as jatropha, Pongamia ie. karanja, Rubber seed, Salvadora and Mahua are used as energy resources. These two plants may be grown in large number on degraded or agricultural or waste lands, so that the significant resource may be available easily to produce biodiesel on ‘farm scale.

Table 1.2 gives the countries of the world engaged in the growing of different vegetable oil resources and biodiesel production. Table 1.2 represents that most of the country’s uses palm oil, soybean oil, rapeseed oil for production of biodiesel but in India these oils are generally used for edible purposes thus India is showing their huge interest in non-edible oil sources for biodiesel production especially in Jatropha curcas oil, mahua oil, pongamia oil, Neem oil etc. World status of biodiesel production during 1990-2010 is shown in Figure1.3.

Table 1.2 Country wise BD production practices in the world (Source: www.presidentofindia.nic.in)

Sl.no	Country	Source of biodiesel
1	USA	Soybean, mustard (under study)
2	Brazil	Soybean
3	Nicaragua	Jatrophacurcas
4	Europe	Rapeseed oil and sunflower oil
5	Spain	Linseed and olive oil
6	France	Sunflower oil
7	Italy	Sunflower oil
8	Ireland	Animal fats and beef tallow
9	Indonesia	Palm oil
10	Malaysia	Palm oil
11	Australia	Animal fats, beef tallow and rapeseed oil
12	Canada	Vegetable oil/animal fats
13	India	Jatrophacurcas oil, pongamia oil, mahua oil, Neem oil, Sal oil etc (Nonedible oil).
14	China	Guang pi
15	Germany	Rapeseed oil

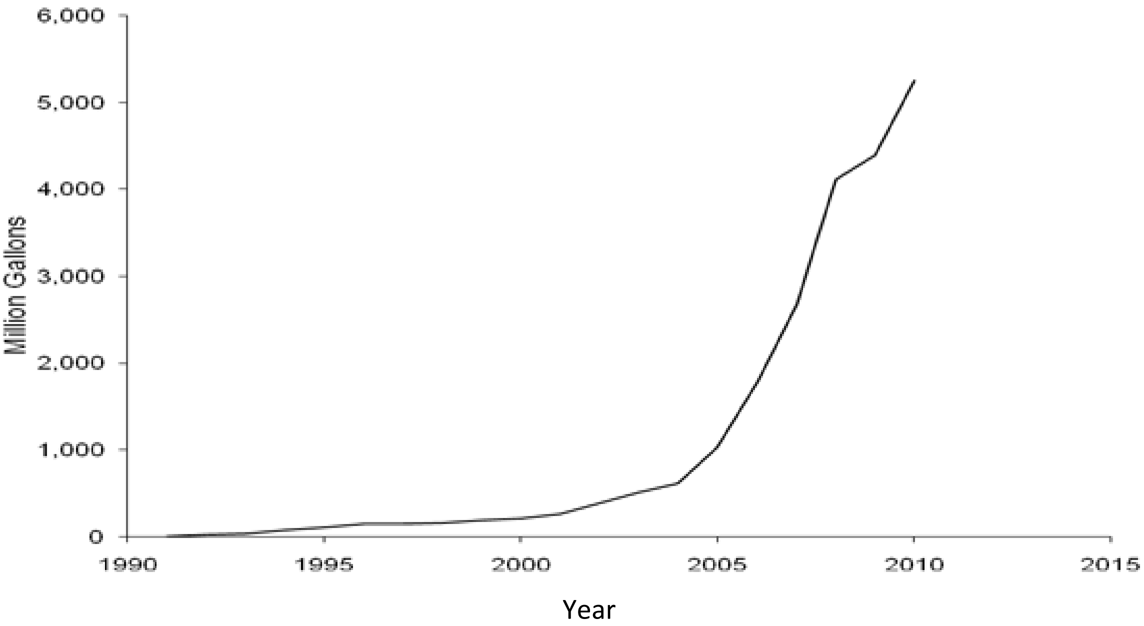


Figure 1.3 World biodiesel productions during 1990-2010 (Source: Panchayat.nic.in)

Figure 1.3 shows that worldwide production of biodiesel started in 1990and reached a production of 150 million gallon in 1996 and after that during 1996-2002 production were almost constant and after 2002 production increased at faster rate and till 2010 production reached 5000 million gallon. Biodiesel production in India is at infant stage so there is no published data on the production status of biodiesel in India although India is producing biodiesel at pilot or lab scale.

1.3.3 Chemical compositions

Chemical structure (that contain the arrangement of molecules) of triglycerides is shown in Fig 1.4 in which there are 98% triglycerides and 2% of mono- and di glycerides. Triglycerides are made up of 1 molecule of glycerol and 3 molecules of fatty acid with appropriate amount of oxygen in it. Only length of the carbon chain and number of double bonds varies in the fatty acids of fats and oil.

Different types of oils and fats have different types of fatty acids. Fatty acids contain hydrogen, carbon and oxygen organized as a carbon chain structure and at the end of fatty acid carboxyl group is attached. Structures (chemical nature) of different types of fatty acid are given in Table 1.3.

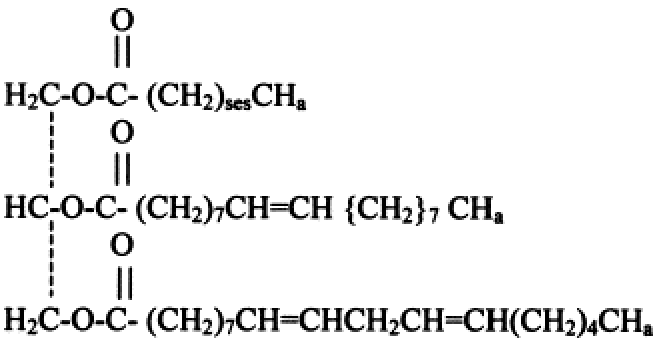


Figure 1.4 Structure of a typical triglyceride molecule.

Table1.3 shows that carbon atoms' number in triglyceride and fats varies from 4 to 24 and number of double bond present in structure could be one to three. But carbon 18 is the major component of vegetable oil.

1.3.4 Fatty acid analysis of vegetable oil

Plant oils consist generally the glycerides of fatty acids. Fatty acids are composed of saturated and unsaturated aliphatic mono-carbon acids, whose structure consist of 4 to24 carbon atoms. Tri-glycerides are the most common amongst plant oils. In these 3 hydroxyl groups (OH^-) of glycerin are replaced by fatty acids. The different oils have different composition of fatty acids. These composition influences chemical and physical properties of the plant oil. The fatty acid composition of different oils is shown in Table1.4 and Table 1.5.

Jatropha oil consist 20% of saturated acid and remaining unsaturated fatty acid. Oleic acid ($C_{18}H_{34}O_2$) is the most abundant followed by palmitic acid ($C_{16}H_{32}O_2$), linoleic acid ($C_{18}H_{32}O_2$), and stearic acid ($C_{18}H_{36}O_2$) while composition of the oil is similar to other oil, which are generally used for edible purpose. According to the variety found in nature, 0.06% to 6.7 % of the oil can be free fatty acids. Trace amount of sulfur and nitrogen may present up to 0.13 % and 0.11 %, respectively.

1.3.5 Fuel properties of vegetable oil

The fuels properties of vegetable oils are given in Table 1.6, which shows the range of kinematics viscosity of vegetable is from 30–55 cSt at 40 °C. These vegetable oils have high viscosity from 600–900 because of their large molecule mass, which is more than 20 times as comparison to diesel fuels. The range of flash point for vegetable oils is 200 °C and the range of value of volumetric heating of vegetable oils is from 39–40 MJ/kg, though for diesel fuels its value is approximately about 45 MJ/kg. Heating value of vegetable oils is low by 10% of diesel fuel due to the presence of oxygen in vegetable oils. The range of Cetane number is 52–66. The calorific value of vegetable oil lies between 37-38 MJ/kg, which is lower than the diesel fuel.

Table 1.3 Common fatty acids structures (Chemical) (Source: www.scientificpsychic.com and Foidl et al, 1996)

Formula	Name of fatty acid	Chemical name of fatty acids	Structure (*xx*: *y*)
$C_4H_8O_2$	Butyric	Butanoic acid	4:0
$C_6H_{16}O_2$	Caproic	Hexanoic acid	6:0
$C_8H_{16}O_2$	Caprilic	Octanoic acid	8:0
$C_{10}H_{20}O_2$	Capric	Decanoic acid	10:0
$C_{12}H_{24}O_2$	Lauric	Dodecanoic	12:0
$C_{14}H_{28}O_2$	Myristic	Tetradecanoic	14:0
$C_{16}H_{32}O_2$	Palmitic	Hexadecanoic	16:0
$C_{18}H_{30}O_2$	Linolenic	*cis*-9,*cis*-l2,*cis*-15-Octadecatrienoic	18:3
$C_{18}H_{32}O_2$	Linoleic	*cis*-9,*cis*-12-Octadecadienoic	18:2
$C_{18}H_{34}O_2$	Oleic	*cis*-9-Octadecenoic	18:1
$C_{18}H_{36}O_2$	Stearic	Octadecanoic	18:0
$C_{20}H_{32}O_2$	Arachidonic	*cis*-5,*cis*-8,*cis*-11,cis-14-eicosatetraenoic acid	20:4
$C_{20}H_{38}O_2$	Gadoleic acid	*cis*-9-eicosenoic	20:1
$C_{20}H_{40}O_2$	Arachidic	Eicosanoic	20:0
$C_{22}H_{42}O_2$	Erucic	13-docosenoic acid	22:1
$C_{22}H_{44}O_2$	Behenic	Docosenoic	22:0
$C_{24}H_{48}O_2$	Lignoceric	Tetracosanoic	24:0

Table 1.4 Fatty acid compositions vegetable oils that are non-edible (Source: Gui et al., 2008)

Oil	Lauric Acid C12	Myristic acid C14	Palmitic Acid C16	Stearic Acid C18:0	Oleic Acid C18:1	Linoleic Acid C18:2	Linolenic Acid C18:3	Arachidic Acid C20	Any special fatty acid
Castor	……..	…….	2.0	1.0	7.0	5.0	…….	……..	Ricinoeic - 86-90
Karanja	…….	…….	3.7-7.9	2.4-8.9	44.5-71.3	10.8-18.3	…….	2.2-4.7	Behenic-4.2-5.3
Jatropha	……..	…….	11.3	17.0	12.8	47.2	…….	4.7	Behenic-0.6
Mango seed	…….	…….	6.38	37.51	46.67	7.21	2.2	……	…….
Neem	…….	0.2-2.6	13.6-16.2	14.4-24.0	49-62	2.3-15.8	…….	0.8-3.4	…….
Mahua	……..	…….	20-25	20-25	41-51	10-14	…….	0.0-3.0	…….
Kokum	…….	0-1.2	2.5-5.3	53.6	40.7	1.7	……	…….	……

Table 1.5 fatty acid compositions of edible oils (Source: Gui et al., 2008)

Oil	Lauric acid C12	Myristic acid C14	Palmitic acid C16	Stearic acid C18:0	Oleic acid C18:1	Linolic acid C18:2	Linolenic acid C18:3	Arachidic acid C20	Any special fatty acid
Coconut	44.0-52.0	13-19	8-11	1-3	5-8	0-1	…..	0-0.5	Palmitoleic – 2.5
Corn	0.042	…	12.427	11.442	36.992	47.189	1.312	.298	Behenic-0.151
Palm	0.230	.849	36.768	….	49.482	11.745	0.539	0.161	…………
Olive	………..	.65	………	……………	65-80	4-10	……….	0.1-0.3	………….
Soyabean	……….	0.5	11	4.1	22	54.07	7.5	………	………….
Sunflower	………	………	3-6	1-3	14-35	44-75	………	0.6-4.0	Behenic – 0.8
Rapeseed	………	………..	1.5	0.4	22	14.2	6.8	………	Erucic- 47.0 Behenic – 2.0
Cotton seed	…….	0.4	20	2.0	35	42	…….	…….	……..
Peanut	……	……	6-9	3-6	52-60	13-27	…….	2-4	Lignoceric-1-3 behenic-2

Table 1.6 Fuel properties of non-edible vegetable oils (Source: Demirbas et al., 2003)

Vegetable oil	Specific gravity	Kinematic viscosity at 40^0C(cSt)	Calorific value (MJ/kg)	Flash point (^{0}C)	Pour point (^{0}C)	Cetane no.	Iodine value
Jatropha	0.917	40.95	37.612	240	6	52.31	93
Mahua	0.904	37.18	38.863	238	15	56.61	74.2
Neem	0.9245	53.05	37.548	N.A	6.5	57.83	69.3
Pongamia	0.909	33.54	37.304	232	5	55.84	80.9
Sal	N.A	N.A	N.A	N.A	N.A	66.13	7.6
Diesel	0.8285	2.44	44.031	47	<-5	42.0	-

1.3.6 Use of vegetable oils in place of diesel fuel

In conventional diesel engines, vegetable oils can replace the diesel fuels but it results into few problems such as oil grading and reasonable weather condition. Also few properties of vegetable oil such as injection, atomization and combustion are different as found in diesel fuel. High viscosity of vegetable oil creates a problem in atomization of fuel by distracting the injection process. Mixing of vegetable oil and air is also a big problem which causes incomplete combustion and generates heavy smoke. If flash point of vegetable oil becomes high it volatility characteristic goes down. Coupling of vegetable oil reactivity and incomplete combustion, stop the engine in a very short period of time. Through chemical modification of biodiesel, these problems can be solved. By producing vegetable oil derivatives which have similar fuel properties and performance to diesel fuels that can match with the hydrocarbon-based diesel engine. The vegetable oils can be modified to suitable liquid fuels by the following methods.

- Pyrolysis: a chemical process obtained in absence of nitrogen an air with addition of heat is known as pyrolysis. Through this process vegetable oil is decomposed into some liquid form like diesel fuel. The final product of pyrolysis had lower viscosity, pour point, cetane number and flash point as compared to the diesel fuel, but calorific values are equal in both cases. The product of pyrolyzed process consists of desired amount of water, sulphur, sediment and copper corrosion values.

- Micro-emulsification: the problem of vegetable oil viscosity can be solved by the formation of micro-emulsion. Micro-emulsions are transparent colloidal dispersions that are thermodynamically stable. In micro- emulsion processes, the droplet diameters lie in between 100 to 1000 Å. In micro-emulsion, water is present so that it can use lower ethanol therefor tolerance of water is increased in the solution.
- Dilution: Materials such as diesel fuels, solvent or ethanol are helpful to achieve dilution of vegetable oil.
- Transesterification: viscosity of triglycerides can be reduced by Trans-esterification process through replacing ester alcohol by another alcohol as found in hydrolysis.

1.3.7. Fuel properties of biodiesel

Biodiesel is simply an alkyl ester of fatty acid produced from used vegetable oils (either edible or non-edible), oil obtained from algae and animal fats. The main sources of origin for biodiesel production in our country are the non-edible oils derived from plant species such as JatrophaCurcas , PongamiaPinnata (Karanja) etc.

Biodiesel and diesel fuels properties have many similarities, and therefore, biodiesel is best rated as good replacement to diesel fuels. This is because the conversions of triglycerides into alkyl esters by the trans-esterification process decreases the viscosity by about one-eighth, decrease the molecular weight to one-third, and also enhance the volatility a bit. Biodiesel contains about one-tenth oxygen (weight %), thereby enhancing process of combustion in an engine. Ignition quality of the biodiesel can be improved by tertiary fatty amines and amides and there is no negative effect on properties of cold flow. However, problems while starting persist in cold environment. Biodiesel contains the high flash point, low heating range and high cetane number. Biodiesel has high cloud points and flash points about 15–25 °C higher than currently used diesel fuels.

From the Table1.7 it can be seen that methyl ester produced from vegetable oil meets almost all desired properties of diesel, as viscosity of diesel is 3.06 mm^2/s while that of biodiesel from 3.39 for pongamia oil and jatropha oil 4.54 mm^2/s. Heating value and specific gravity of vegetable oil methyl ester is also nearly same as dies

Table 1.7 Properties of biodiesel from different oils (Sorce: Berchmans et al., 2008)

Sl.no.	Vegetable oil methyl esters (biodiesel)	Kinematic viscosity (mm^2/s)	Cetane no.	Heating value (MJ/kg)	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Specific gravity
1	Jatropha	4.54	51	37.2	2	6	191	0.879
2	Pongamia	3.39	N.A	38.28	N.A	7	187	0.876
3	Mahua	3.98	N.A	37	N.A	6	208	0.880
4	Soya bean	4.5	45	33.5	1	−7	178	0.885
5	Sunflower	4.6	49	33.5	1	–	183	0.860
6	Palm	5.7	62	33.5	13	–	164	0.880
7	Diesel	3.06	50	43.8	–	−16	76	0.855

Biodiesel can be used as in its pure form or blend with diesel in different proportion to enhance fuel characteristics. Bio diesel can be used in compression ignition engine instead of diesel fuel because its properties well matched with diesel fuels. Biodiesel can be stored like the petroleum diesel fuel and hence there is no requirement of modification in structure. On using of biodiesel in common diesel engines results into reduction in un-burnt hydrocarbons, carbon monoxide and hazardous particulate matters. Due to 0% sulphur content, 0% aromatics content and around 10% oxygen , it is said to be a clean fuel, so it can burn completely. When it combined with the diesel its higher cetane number improves the ignition characteristic. Indian government proposed basic requirements for new vehicles, there should be low sulphur content and high cetane number in the production of diesel by Indian refineries. Biodiesel already meets these important characteristics and would help in improving the lubricity of low sulphur diesel. Regarding safety Biodiesel will help in improving the flash point. The flash point for petroleum diesel is 35°C in India, which is less than all the countries in the world that have greater than 55°C.

B20 (a combination of 20 % biodiesel with 80 % petroleum diesel) has reported important environmental advantages in US with a minimum improvement of cost for other consumers. The Environmental Protection Agency (EPA) of US has been registered it as a fuel and fuel additive and matches clean diesel standards given by the California Air Resources Board. The US Department of Energy and the Department of Transportation considered biodiesel as an alternative fuel. By many times study has been carried with biodiesel on engines and shown substantial decrease in particulate matter. However, usage of De-NOx catalyst optimizes the increase in NOx (1-6%). Emissions are not regulated like Poly Aromatic Hydrocarbon (PAH) was found to be lower.

Biodiesel has been proved as alternative fuel. Now a day’s production capacity of biodiesel is about 10 million Gallons. Rapeseed, Sunflower and Soya bean oils are the raw materials for different countries. Some also uses frying oils; palm oil and animal fats. Biodiesel has very apt properties and used to decrease the overall sulphur content from diesel. Due to high kinematic viscosity, pure biodiesel has a disadvantage of gum formation but 20% blend doesn’t. A modification is required for the use of pure biodiesel rather 20% is sufficient to run on the existing engine. US is using B20 and B100 biodiesel while France is using B5 as necessary in all diesel fuel. Indian government setup a target for achieving the low blending ratios i.e. 5%, 10% and 20% for next 5 years (Table1.8).

Table1.8 Biodiesel requirement for blending (Source: planningcommission.nic.in)

Year	Diesel demand (Million tons)	Biodiesel requirement for blending (Million tons)		
		@ 5%	@10%	@20%
2005-06	49.56	2.48	4.96	9.9
2006-07	52.33	2.62	5.24	10.48
2011-12	66.90	3.35	6.69	13.38

India used half of its wasteland for the plantation like "Jatropha" whereas life span of "Jatropha" is about 50 years. The production cost of biodiesel is very low of Rs. 20/lt. Biodiesel is neutral of carbon and many expensive by-products flow from these agro-industries. For attaining of energy scrutiny India needs a deep research and efficient development programme.

1.4 Status of Research and Development on Biodiesel in India

In India, the investigation on the production of biodiesel is basically in its early phase, there is an urgent requirement to approve various intensive methods in the advancement of technology for its generation, consumption of secondary products and analysis in engine w.r.t releases, limitations etc. For effective manufacture of biodiesel, Research and development work is required to yield good quality raw material and to create an enhanced, economic and competent biodiesel making technology. Biodiesel from various feedstocks may vary in the case of lubrication, composition and stability against oxygen. It is needed to carry out runs on biodiesel from all possible edible or non-edible oils available and prepare comparative values on fuel emissions, configuration etc. Toxic investigation is main requirement for introducing any new fuel.

R&D needs to be focus on the following three areas:

1. production technology,
2. raw material specifications, and
3. consumption of biodiesel as fuel

In India, alcohol and vegetable oil are the main feedstock use for biodiesel production. In India vegetable oils are expensive and are in limited stock so Jatrophacurcas, pongamia piñata etc. that are available at economic prices are usually preferred feedstock for bio-diesel production by trans-esterification reaction. In India, the strength of non-edible oils is reported to be 0.1 MMT/ annum. The different Research and Development matters which require devotion are collection of seed, valuation of resource, setting for seeds, accessibility of seed, usage of high yielding crops, quality of oil, bio-diesel production methodology using new catalyst like elastomers, , toxicity and mixing with cheaper products etc.

1.5 Motivation and Objectives

It is found that biodiesel production and utilization is in infancy stage in India. Feedstocks for biodiesel production in India is nonedible vegetable oils viz. Jatropha curcas oil, Pongamia oil, Neem oil, Mahua oil, Sal oil etc. Most of nonedible oil in India contains high FFA ranging from 2 to 12%. Since the production and processing of biodiesel requires detail reaction information and optimization of reaction parameter to maintain the product quality economically and get product in minimum time. The objectives of this study were to study the behavior of transesterification reaction for Jatropha oil under changing reaction parameter.

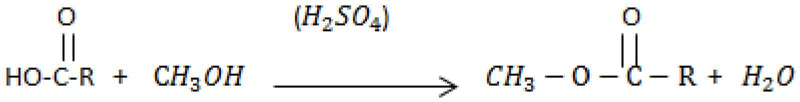
- Potential of non-edible oil over edible oils.
- Optimize the reaction time.
- Optimize the reaction condition for maximum yield.
- Reduction of energy requirement.

CHAPTER 2

LITERATURE REVIEW

2.1 Esterification

Acid catalyzed transesterification is mainly used when oil contain large amount of free fatty acid. Main purpose to choose an acid catalyst is to lower the content of free fatty acid in oil to less than 1%. Generally, when esterification is carried out, in the presence of acid catalyst a high alcohol to oil molar ratio is necessary as comparision to trans-esterification reaction. Reaction time would be shortened if high molar ratio of alcohol is used but it will have no effect on the yield of ester. The reaction scheme of esterification reaction is shown in Figure 2.1. When electrophilic species which are present in acid catalyst are matched with stronger nucleophile species present in base of catalyst, a more direct route is followed by base catalyst to activate the reaction between species that are active catalytically and due to this base catalyst tends to have an edge over acid catalyst in terms of speed of catalytic activity (Helwani et al., 2009). Acid catalyst slow reaction rate is slow and due to this they have been ignored even if they can be used in transesterification of vegetable oils with high FFA content. However, if FFA content is high alkaline catalyzed transesterification is followed by use of acid catalyst so as to reduce FFA content. To completely esterify free fatty acid in vegetable oil reaction temperature of 60^0C could be used.

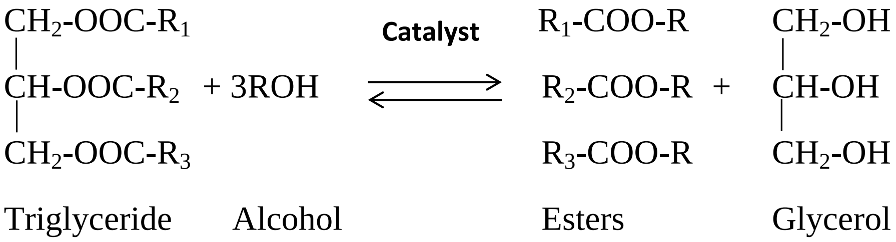


$$HO-\overset{\overset{O}{||}}{C}-R + CH_3OH \xrightarrow{(H_2SO_4)} CH_3-O-\overset{\overset{O}{||}}{C}-R + H_2O$$

Figure 2.1 Esterification reaction scheme (Source: Hingi et al., 2010)

2.2 Transesterification

In transesterification reaction alcohol and oil are combined in the presence of catalyst to form esters and glycerol. The reaction scheme is shown in Figure 2.2. Excess alcohol is used to shift the equilibrium to the products side because the reaction is reversible. Alcohols are usually primary and secondary monohydric aliphatic alcohols containing 1 to 4 carbon atoms such as methanol, butanol and amyl alcohol can be used in transestrification reaction (Sprules and Price, 1950). Mainly methanol and ethanol are used, and methanol is preferred due to its physical and chemical properties and low cost. The reaction of methanol with triglyceride is quick and dissolution of catalyst is easy. Stoichiometrically three moles of alcohol and one mole of triglycerides is required to carry out a transesterifcation. The molar ratio should be higher to have a maximum yield of ester as it is an equilibrium reaction.



$$\begin{array}{llcll} CH_2\text{-}OOC\text{-}R_1 & & & R_1\text{-}COO\text{-}R & CH_2\text{-}OH \\ | & & & & | \\ CH\text{-}OOC\text{-}R_2 & +\ 3ROH & \xrightleftharpoons{\text{Catalyst}} & R_2\text{-}COO\text{-}R\ + & CH\text{-}OH \\ | & & & & | \\ CH_2\text{-}OOC\text{-}R_3 & & & R_3\text{-}COO\text{-}R & CH_2\text{-}OH \\ \text{Triglyceride} & \text{Alcohol} & & \text{Esters} & \text{Glycerol} \end{array}$$

Figure 2.2 Transesterificationof triglycerides with alcohol (Source: Ma et al., 1999)

Acid, base or enzymes catalyst can be used in the reaction. Some examples of base catalyst are NaoH and KOH. Among acid catalyst sulfuric acid, SO_3 and HCl acid are mainly used. Enzyme catalyst includes lipases. Transesterification using base catalyst is used commercially compared to acid-catalyzed transesterification as the reaction with base catalyst is faster.

The glycerides and alcohols used in alkali catalyzed transesterification should be anhydrous (Wright et al., 1944) or otherwise saponification may happen due to water and this may cause low ester yield. Saponification may also result in difficulties for separation of ester and glycerol, water washing. For alkali catalyzed transesterification FFA content should be low otherwise acid catalyzed transesterification needs to be done initially to reduce FFA content. (Keim, 1945). Saponification can be used to purify triglycerides and then alkali catalyst is used for transesterification.

The physical properties of chemical products used in transestrifiaction are shown in Table 2.1. The properties such as boiling and melting points of oil enhances with increase in count of carbon atom in the chain and vice-versa in case of double bond. The polarity and hydrogen bonding increases from tri to mono glycerides and due to this melting point also increases in the same sequence. The products produced followed by transesterification of triglycerides are a mixture of esters, glycerol, alcohol, catalyst and tri-, di- and monoglycerides (Ma, 1998).

The ester turbidity generally caused by monoglycerides present in the esters. It was found mainly for trans-esterification of animal fats. The impurities enhanced the pour and cloud points while, there is a huge portion of fatty acid esters in tallow (beef) esters. This quantity makes the pour and cloud points beyond the vegetable oil. The saturated elements have other applications in foods, cosmetic and detergents. The glycerol has to be recovered because of its application as a speciality chemical like USP glycerol, CP glycerol and dynamite glycerol. Glycerol may be separate by centrifuging or gravitating settling.

Wang et al. (2011) studied the biodiesel preparation possibility from a promising non-edible feedstock, known as Daturastramonium L. oil or DSO oil. They determined the physical as well as chemical properties, such as acid value, oil content and fatty acid of oil. The transesterification reaction was carried out under the optimum operating conditions. The fatty acid methyl ester (FAME) yield was 87% and FAME content was more than 98 wt%. They compared the Jatrpha curcas L. (JC) and beef tallow (BT) biodiesel. The biodiesel possessed the best possible kinematic viscosity (4.33mm^2/s) and also cold filter plug point (-5 ^{0}C).

Table 2.1 Physical properties of chemicals connected to transesterification (Source: Zhang, 1994

Name	**Specific gravity, g/ml (°C)**	**Melting point (°C)**	**Boiling point (°C)**	**Solubility (>10%)**
Methyl Myristate	0.875 (75)	18.8	_	_
Methyl Palmitate	0.825 (75)	30.6	196.0	Acids, benzene, EtOH, Et2O
Methyl Stearate	0.850	38.0	215.0	Et2O, chloroform
Methyl Oleate	0.875	-19.8	190.0	EtOH, Et2O
Methanol	0.792	-97.0	64.7	H_2O, ether, EtOH
Ethanol	0.789	-112.0	78.4	H_2O(1), ether (1)
Glycerol	1.280	17.9	290.0	H_2O, EtOH

Also the effect of different parameters was studied on acid-catalyzed based esterification reaction:

1. Impact of the methanol to oil molar ratio on acid-catalyzed esterification reaction
2. Impact of the methanol/oil molar ratio
3. Impact of reaction time
4. Impact of base-catalyzedtransesterification conditions

Based on their results, D. stramonium L. was known to be a favorable feedstock for biodiesel production.

According to **Juan et al. (2010)** biodiesel (fatty acids alkyl esters) is replacing petroleum-based diesel as biodiesel is produced from animal fat, vegetable oil, and waste cooking oil and they are renewable in nature. As comparison to waste cooking oil and animal fat, Vegetable oils are appropriate way to produce biodiesel as it is renewable in nature. But production of biodiesel from vegetable oil is changing the food market. Production of biodiesel from jatropha oilis also found suitable as it is non-edible in nature and may be grown in an extreme environment. Transesterification or alcoholysis of jatropha oil using different types of catalyst is shown in Figure 2.4. In many countries, biodiesel produce from alkyl esters of jatropha oil is meeting the standards. They also compared the exhaust gas emission from biodiesel and petrodiesel. Figure 2.3 shows Effect of type of pollutants on percentage of emission for petrtrodiesel and biodiesel.

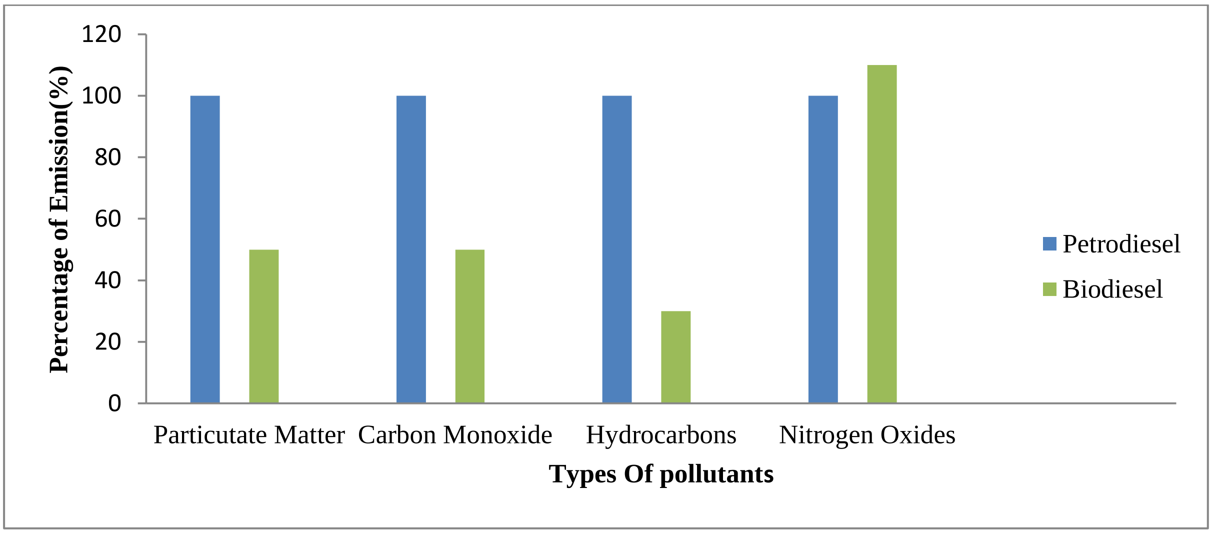


Figure 2.3 Effect of type of pollutants on percentage of emission for petrtrodiesel and biodiesel (Source: National Biodiesel Board, 2010)

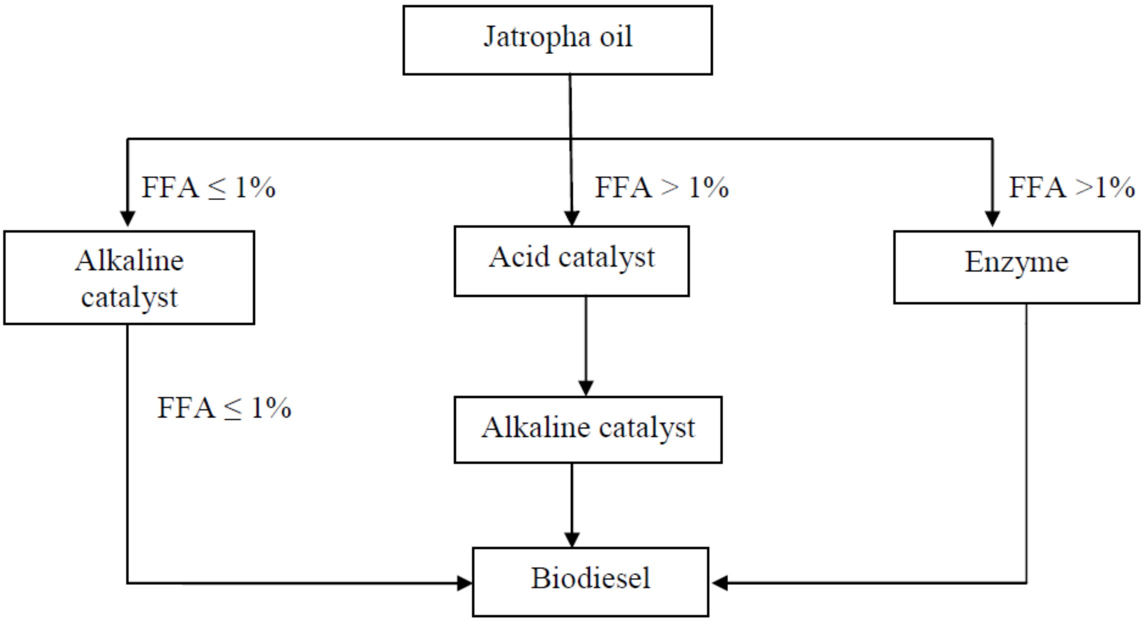


Figure 2.4 Biodiesel from high free fatty acid (FFA) content jatropha oil (Source: Helwani et al., 2009)

Ivana et al. (2012) prepared biodiesel from non-edible plant through transesterification of triacylglycerols. They also reviewed the production of biodiesel through various methods from available non-edible oils using alcoholysis reactions. They presented the maximum possibilities of biodiesel production from non-edible oils and considered the different methods for handling of non-edible oils. Also the effect of the reaction and operating conditions on the ester yield was reported. Different tranesterification methods were also reviewed, such as homogeneously catalysed transesterification processes, heterogeneously catalysed transesterification processes, enzyme-catalysed transesterification processes, Supercritical transesterification processes. Homogeneous ones in place of solid catalyst were found more suitable because it reduced environmental pollution and higher qualities of biodiesel and glycerol.

Kafuku et al. (2010) used croton megalocarpus oil to produce sulfated tin oxide and biodiesel as catalyst improved with SiO_2. Without any kind of improvement, 95% of yield was achieved although oil have more free fatty acid and the reaction conditions found as 180^0C, 2h and 15:1 methanol/oil molar ratio, while keeping same catalyst concentration (3wt.%), stirring velocity, and 350–360 rpm. The biodiesel derived from croton megalocarpus oil meet the ASTM D6751 standard and favourable as an altercroton megalocarpus oil to methyl esters (biodiesel).

Gui et al. (2008) studied usability of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock. They expressed that biodiesel has high potential as a renewable and new energy supply with in the future, and might be employed as a substitution fuel for petroleum-derived diesel and also may be used in existing diesel engine without modification. However, mass production of biodiesel from edible oil without any proper planning lead to harm like as scarcity in the supply of food which is imbalancing the economy leading to economic imbalance. A potential resolution to beat this drawback was to use non-edible oil or waste edible oil (WEO). All these problems were self-addressed discoursing the benefits and drawbacks of WEO vs non-edible vs edible oil as feedstock for the production of biodiesel.

Berchmans et al. (2008) developed a method for biodiesel production from crude Jatropha curcas seed oil containing more content 15% of FFA. By two-step pre-treatment method, content of FFA in JCJO was decrease to 1%. The primary step was conceded with 0.60 w/w methanol-to-oil ratio in the existence of an acid catalyst that was 1% w/w H_2SO_4 as in one hour reaction at 50 ^{0}C. The mixture was then made to settle down for 2 hours and the layer was removed from above. The next step was trans-esterification using 0.24 w/w methanol to oil and 1.4% w/w NaOH to oil as alkaline catalyst to manufacture biodiesel at a temperature of 65 ^{0}C. The ultimate yield for methyl esters of fatty acids was achieved as 90% in 2 h.

Koh et al. (2011) reviewed the various methods accustomed to produce biodiesel from Jatropha oil. The main causes that affect the yielding of biodiesel like catalyst concentration, the molar ratio of alcohol/oil, and reaction time and temperature were mentioned. They also addressed the environmental issues and economic aspects of biodiesel.

They listed four main approaches for biodiesel production i.e. blending, transesterification microemulsion and pyrolysis. Among all the four method, transesterification of triglycerides is mostly used method in existence of a catalyst. Use of jatropha oil is increasing day by day for the production of biodiesel as it is non-edible, renewable in nature and also not affects the food market. Due to the toxicity of non-edible oils, they are not appropriate for the consumption of human. They also introduced the economics aspects of biodiesel. The cost of feedstock comprises 75% of the total cost use in the production of biodiesel. The cost brakedown for biodiesel production is given in Figure 2.5.

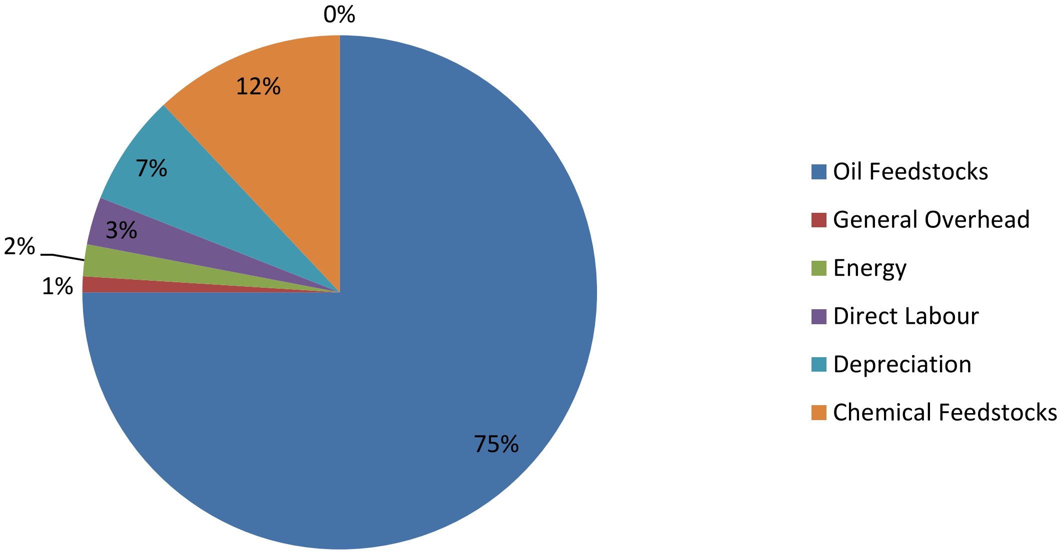


Figure 2.5 General cost production breakdown of biodiesel (Source: Lim et al., 2010)

Lu et al. (2009) developed a process for biodiesel production from crude jatropha curcus oil. The process consisted of two step in which first was pre-esterification followed by trans-esterification. In pre esterification, catalyst used was H_2SO_4 or solid acid prepared by calciningmetatitanic acid to convert free fatty acids (FFAs) to methyl esters. They used the acid value of oil and reduced from the initial 14 mg-KOH/g-oil to below1.0 mg-KOH/g-oil in 2 h under the conditions of 12 wt% methanol, 1 wt% H_2SO_4 in oil at 70 ^{0}C and obtained the FFAs conversion at 90 ^{0}C in two hours was higher than 97% when 4 wt% solid acids and 20:1 molar ratio of methanol to FFA was used. Prior to pre-esterification process separate degumming operation was not required as elimination of Phospholipid compounds was done during pre-esterification. The biodiesel yield was greater than 98% in 20 min when 1.3% KOH was used as catalyst and a molar ratio of methanol to oil 6:1 at 64 ^{0}C.

Kansedo et al. (2009) extracted oil from the seeds of C. odollam fruits was extracted and then transesterification was carried out to convert oil into FAME. Three catalyst were used for transesterification reactions in which one was used as a homogeneous catalyst and other two were heterogeneous catalyst. Among the homogeneous catalyast was sodium hydroxide and heterogeneous catalyst were sulfated zirconia alumina and montmorillonite KSF. The seeds contained upto 54% of oil and yield of FAME was up to 83.8% when sulfated zirconia was used as a catalyst.

According to **Patil et al. (2009)** for non-edible vegetable oils such as jatropha curcas and pongamiaglabra (karanja) and edible oils such as corn, canola were found to be good sources for biodiesel production. Different edible and non-edible vegetable oils were used for production of biodiesel to optimize the production process and different oil and fuel properties were analyzed. Biodiesel was produced from high free fatty acid (FFA) non-edible oils and edible vegetable oils using single and two-step transesterification processes. These processes give yields of about 90–95%, 80-85%, 80-95% and 85-96% for jatropha curcas, pongamiaglabra, canola and corn oils, respectively, when KOH was used as a catalyst.

Karmee et al. (2005) prepared biodiesel from the non-edible oil of pongamia pinnata with methanol using KOH as catalyst. A maximum of 92% conversion was achieved using 1 mole of oil with 10 moles of methanol at a temperature of 60 ^{0}C. Conversion was increased to 95% when tetrahydrofuran (THF) was used as co-solvent. For transesterification solid acid catalysts such as Hb-zeolite, montmorillonite K-10 and ZnO were used. Methyl esters of pongamia oil (biodiesel) have fuel properties such as (viscosity = 4.8 Cst @ 40 ^{0}C and flash point = 150 ^{0}C) which are comparable to ASTM standards.

Encinar et al. (2010) studied the production of biodiesel from rapeseed oil using different solvents such as (diethyl ether (DEE),tert-butyl methyl ether (tBME), dibutyl ether (diBE), diisopropyl ether (diIPE) and tetrahydrofuran (THF). They investigated the variables affecting the yield of ester during the trans-esterification reaction, such as catalyst content, methanol:oil molar ratio, catalysts type, methanol:co-solvent molar ratio, reaction temperature, co-solvent type, catalysts type, and agitation rate. Among co-solvents investigated, the tBME and DEE were in good agreement with the results, however results using diIPE and diBE were not improved satisfactorily. The results were in good agreement using 0.7wt.% of KOH, a molar ratio co-solvent/methanol 1:1, a molar ratio methanol/oil of 9:1, at 700 rpm agitation rate, and 30 ºC temperature.

2.3 Factors affecting biodiesel production

2.3.1 Free fatty acid and moisture

To determine capability of development of transesterification process the main factors are moisture content and free fatty acid (FFA). In order to complete the base catalyzed reaction; value of FFA should be less than 1%, which is suitable for oil. Conversion efficiency is reducing when value of free fatty acid (FFA) is greater than 1%. Excess amount of FFA and moisture content can result in soap formation after combining with catalyst.

2.3.2 Catalyst, type and concentration

For the transesterification of triglycerides, catalyst are used and are classified as acid, alkali or heterogeneous catalysts, among which alkali catalysts like potassium hydroxide, sodium hydroxide, sodium methoxide, and potassium methoxide are more efficient. Generally, Acid catalyst is suitable when high content of free fatty acid (FFA) and moisture in the oil. Base catalyst is slower than alkali catalyst. The acids could be sulfuric acid, phosphoric acid, hydrochloric acid or organic sulfonic acid. Comparing the two catalysts, CH_3ONa is significantly better than NaOH. in alkaline methanolysis, mostly NaOH or CH_3ONare used as a catalyst having concentration from 0.5 to 2% w/w of oil.

2.3.3 Molar ratio of alcohol to oil and type of alcohol

The molar ratio of alcohol to triglycerides is the important variable which is affected the ester yield. Transesterification reaction requires 3:1 molar ratio of alcohol and triglycerides to yield 3:1 molar ratio of FAME and glycerol. For high yield of fatty acid alkyl ester, a molar ratio of 6 moles of alcohol and 1 mole of triglycerides should be used. Iodine, acid and saponification value of methyl ester are not affected by the molar ratio but separation of glycerin is affected due to increasing solubility. When glycerine remains in solution it affects the yield of esters.

2.3.4 Reaction temperature and time

The conversion rate increases with reaction time. Transesterification can occur at different temperatures and different molar ratio of alcohol to oil, depending on the kind of oil used. Transesterification reaction of refined oil with methanol (6:1) and 1% NaOH was studied under various temperatures. Yields of ester were 64, 87 and 94%, for temperature of 32, 45 and 60°C, respectively after 0.1 h. Formation of ester was approximately same for 60 and 45 °C runs and for the 32 °C run it was slightly low after 1 h. Reaction rate and ester yield was clearly influenced by temperature.

2.3.5 Mixing Intensity

In transesterification reaction oils and fats are not miscible with methanol -sodium hydroxide solution hence mixing is required. After mixing of two phase's reaction starts taking place and stirring is not required any longer. Mixing effect on transesterification of beef tallow was initially studied by **Ma et al (1999)**, No reaction could be detected if mixing was not done and when MeOH–NaOH was added to the melted beef tallow while stirring no significant effect was found of stirring speed. Controlling factor is the reaction time to determine the methyl esters' yield. This showed that the stirring speeds tested in reaction exceeded the mixing requirements.

2.3.6 Effect of use of organic solvent

The methoxide base catalyzedmethanolysis of soybean oil at 40 °C (methanol–oil molar ratio 6:1) shows that formation of methyl esters proceeds relatively at a slow rate than butanolysis at 30 °C. This is due to reaction in two phases in which methanolysis happens to be only in the methanol phase. Low concentration of oil in methanol leads to slow reaction rate; an initiation period is there due to slow rate of dissolution of oil in methanol. Deviation from second order kinetics can be explained due to intermediate mono- and di-glycerides that remain in methanol whose further reaction takes place. Hydroxide ion catalyzedmethanolysis can be explained same as the above.

For a single phase reaction to be conducted, co-solvents like THF, tert-butyl methyl ether and diethyl ether were used. Initially reaction was conducted using THF. At the 9:1 methanol–oil molar ratio the addition of 1.0 mole of THF per mole of methanol produces a one phase system in which oil is dominant due to this one phase system rate of methanolysis increases and becomes comparable to that of butanolysis. The reason to choose THF is its boiling point of 67 ^{0}C which is very close to the methanol' boiling point of 65 ^{0}C. Due to comparable boiling point of the methanol and THF, the unreacted reactants can be recycled and co-distilled after completion of reaction.

Biodiesel can be produced using multiple options. According to different conditions and feed-stocks various technologies for production of biodiesel can be combined in many ways. The choice of technology depends upon desired catalyst recovery, capacity, and type of feedstock, quality and alcohol recovery. The dominating factor in production of biodiesel is the cost of feedstock, with capital cost that contributes approximately about 7 % of the cost of final product. However, a variety of feed-stocks and qualities can be handled by reaction system, while others cannot be handled. Also, different reaction system requirements such as operation, water use and mode of operation are required depending on approaches to the process of esterification. Generally, batch systems are suggested for smaller capacity plants and variable feedstock quality. Continuous systems are operated on a 24/7 basis, and are required for large capacity plant as large staff and uniform feed-stock quality is required.

Based on the literature carried out, in the present work, two-step process i.e. acid catalyzed esterification followed by base catalyzed transesterification was considered due to the higher free fatty acid content of jatropha oil and also this process was faster than acid catalyzed transesterification reaction and less energy consuming. Thus this process could be used for biodiesel production at large/commercial scale.

CHAPTER 3

FEEDSTOCK AND BIODIESEL CHARACTERIZATION

3.1 Determination of acid value and free fatty acid (FFA)

Acid value is a key parameter which indicates the quality of vegetable oil. Acid value is the amount of KOH (in milligrams) which is neutralizes free fatty acids contained in 1 g of oil. Acid value was determined using the titration method. In this method,an ethanolic solution of oil with ethanolic KOH is used to visually determine phenolphthalein endpoint. Solvent was developed by adding diethyl ether with ethanol (2:1(v/v)) and phenolphthalein indicator solution was prepared using 1% phenolphthalein in 95% ethanol. The oil was dissolved in the prepared solvent and standard (0.1N) KOH solution. After that 50 ml of the solution was taken and neutralized by 0.1N standard KOH solutions till the pink color persisted for at least 30 second by 1%of phenolphthalein. The weight of the oil taken for estimate and the strength of the alkali used for titration shall be such that is equal to the volume of alkali required for complete titration.

$$Acid\ value = \frac{56.1VN}{W} \tag{3.1}$$

V = Volume in ml of standard potassium hydroxide (KOH).

N = Normality of the KOH

W = Weight in gm of the sample

$$Free\ fatty\ acid\ (FFA) = \frac{Acid\ value}{1.99} \tag{3.2}$$

3.2 Determination of moisture content –

Karl Fischer is an analytical technique used to measure the moisture (water) content in solids, liquids or gases.

In general, K-F titration can be summarized into a series of steps:

- Add reagent (“titrant”) to a burette (The reagents include alcohol, SO_2, a base and I_2),
- Add sample solvent to the titration vessel,
- Begin stirring the vessel,
- Zero the instrument by titrating unwanted moisture in the system,
- Add the weighed sample to the titration vessel,
- Begin adding reagent from the burette while stirring,
- When the endpoint is reached, the electrode will detect no change in current upon addition of more reagent,
- By knowing how much titrant was added, the water content can be calculated,
- Normally, the K-F instrument does the calculations and reports the results as “%water” or “ppm water.”

- Normally, the K-F instrument does the calculations and reports the results as “%water” or “ppm water.”

Figure 3.1 Karl-Fischer Titrator

3.3 Determination of specific gravity and density

The specific gravity and density of the samples were determined at 15 °C by using pycnometer in which mass of empty bottle(w_1) was taken and then mass of bottle(w_2) filled with water and then with oil(w_3) was taken.

$$sp \text{ gravity} = \frac{w_3 - w_1}{w_2 - w_1} \quad (3.3)$$

Density = sp gravity*1000kg/m^3

Figure 3.2 Pycnometer

3.4 Determination of flash point and fire point

The flash point of a fuel is essentially lowest temperature at which vapors from a test fraction combines with air to give a flammable and a flash when ignition source is supplied. Fire point is the lowest temperature at which test flame causes oil surface to ignite and burn continuously for more than 5 seconds.

These are determined using apparatus as per specification IP36 IS: 1448(1169) 1969. It consists of a cup, heating plate, thermometer and test flame attachment. Sample is taken in the cup and thermometer is placed and then heating is started. Reading of thermometer is taken at which vapor ignites which is flash point. Temperature at which sample catches fire is taken using thermometer and it is the fire point of the sample.

Figure 3.3 Pensky Marten Flash Point Tester (ASTM D93)

3.5 Determination of cloud and pour point

The temperature at which the solubility of dissolved solids is less and precipitates as another phase which gives the fluid a cloudy look is called fluid's Cloud point. This point is very significant to some applications with various results. In reference to the industry, it is the temperature less than which diesel of wax or biodiesels of biowax form a cloudy look. The pour point for a liquid is actually the lowest temperature at which it turns semi solid and loses its characteristics of flow. In crude oil a high pour point is generally attributed to high paraffin content.

Cloud and pour point is determined using cloud point and pour point tester which consists of a compartment made of stainless steel insulated by PUF to minimize heat exchange. Compartment have fully automated solid state electronic temperature controller and digital indicator with PT-100 sensor and cooling kit. Glass thermometer conforming to ASTM 5C and 6C with calibration certificate are also provided. Sample is put in the compartment and then cooling is started. Temperature is taken at which sample just starts to solidify to form wax and is called cloud point. Sample is further cooled down and temperature is noted at which sample becomes semi solid and totally lose its flow characteristics and this temperature is called pour point.

Figure 3.4 Cloud and Pour point Tester (ASTM D93)

3.6 Determination of viscosity

The viscosity of a fluid is defined as a measure of its resistance to its deliberate deformation by shear stress or tensile stress. Viscosity is determined using Redwood viscometer which is comprised of a vertical cylinder with an orifice at the centre of the base of the inner cylinder. The cylinder has a water bath around it which can level the temperature of the liquid to be evaluated at the required temperature. The water bath is heated till it reaches the required temperature. Then the orifice is opened and the amount of time that it needed to pass 50 ml of oil is noted down with the help of stopwatch.

The relation between Kinematic viscosity of the liquid and time required to pass 50 ml of liquid is given by the following expression:

$$X = At - \frac{B}{t} \tag{3.4}$$

Where X is kinematic viscosity of the liquid, t is time required in seconds to pass 50 ml of liquid, A is constant with value 0.264 for t in the range of 40 to 85 or 0.247 for t in the range of 85 to 2000, and B is constant with value 190 for t in the range of 40 to 85 or 65 for t in the range of 85 to 2000

Figure 3.5 Redwood Viscometer

3.7 Thin layer chromatographic (TLC) analysis of vegetable oil and biodiesel

TLC was carried out on a silica-gel TLC-plates of dimensions (20cm×20 cm, 10 cm×20cm or 10cm×10cm (height×width)) on plastic support instead of aluminum support since in the last stages, resistant soaking in the water is provided by aluminum support. The development of loaded samples of undiluted lipid (0.1-4L / lane) at a length of 1.8-2.5cm from one another and 1-2 cm from the bottom was proceeded by 10% of ethyl acetate in hexane (20cm×20cm plates, 1.5 h) or it can also be carried out with 15% ethyl acetate in hexane (10cm×20 cm, 10 cm×10cm plates, 15 min) till then the solvent visible reached at the plate top. After getting a bit dried, plates can either be moved to another development in water (1–2 h) or can be slightly dipped by tilting the plate (1–2 min) in to a water bath. The water development is somewhat slow but renders a more similar saturation of the gel. In a solution of 100 ml of 1% of $KMnO_4$ in 4% NaOH, wet plate was stained with constant agitation for roughly 20 s. This procedure should not be continued over sixty seconds because after a lengthy staining formation of a slight background may start. After applying the staining liquid to about 10 plates (20cm×20 cm), it can be restored after being recovered, before the quality of results starts weakening. The stained plate should be washed with water (3–4 changes for 3–4 min) and then is dried on a surface which is even and smooth to stop gel cracking. Experimental continuation of 10 samples placed on one plate takes some four h (20cm×20cm plate, two developments), 2 h (20cm×20cm plate, one development and immersion) or thirty min (10cm×20cm plate, one development plus immersion).

3.8 Gas Chromatography (GC) Analysis

GC analysis is used to measure the quality of finished biodiesel. The content of methyl ester of the biodiesel produced from the oil at optimum conditions will be determined by the Gas chromatography (GC) technique. The GC of Agilent 6890A is equipped with a flame ionization detector and HP-1methyl siloxane capillary column (30 m × 320 µm × .25µ m) was used. The GC oven is kept at 280°C. The carrier gas is nitrogen at a flow rate of 0.8ml/min. Then 1 µl of sample solution is injected into the GC. The sample solution was prepared with a solvent (n-heptane). Comparison of the produced methyl esters retention time with standard methyl esters retention time was carried out, which identified the conversion of vegetable oil into FAME. Quantitative analysis of the methyl ester produced is determined by the decane internal standard method using methyl heptadecanoate as the internal standard.

3.9 CHNS Analysis

CHNS analyzer is used to determine the weight percent of carbon, nitrogen and sulfur. Firstly dried samples are freeze and then crushed and then for 5-10 mg of weight, they are mixed with vanadium pentoxide (V_2O_5) in a capsule which is of tin. And then its combustion at 1000°C in a reactor is done. The container and sample melt, and in a temporarily enriched oxygen atmosphere the tin promote a violent reaction (flash combustion). A constant flow of carrier gas (helium) carries the combustion products CO_2, SO_2, and NO_2 and it is passed through an oxidation catalyst of tungsten trioxide and a copper reducer packed in a glass column and is kept at 1000°C. the nitrogen oxide is reduced to N_2 At this temperature. A 2-m-long packed column (Poropak Q/S 50/80 mesh) is used to separate The N_2, SO_2, and CO_2 are conveyed by helium and are quantified with a TCD (set at 290°C). Pre analyzed standards are used to calibrate the chromatographic responses and weight percent of the CHNS elemental contents are reported

CHAPTER – 4

EXPERIMENTAL SETUP AND METHADOLOGY

The biodiesel was produced using both edible and non-edible oils, where soybean oil was used as edible oil and jatropha oil was used as non-edible oil. In case of soybean oil it was refined oil therefore the reaction was carried out in single step. However jatropha oil was crude oil, comprising of impurities, therefore the biodiesel was produced in two-steps: esterification and then trans-esterification. The procedure followed for esterification and trans-esterification reactions are discussed in the present chapter. Section 4.1 discusses the transesterification reaction.

4.1 Transesterification for Biodiesel Production

4.1.1 Steps for biodiesel production

The synthesis of biodiesel is carried out in following steps:

A. Pretreatment of vegetable oil

1. Determination of moisture content,
2. Determination of free fatty acid,
3. Esterification/removal of free fatty acid

B. Transesterification of soyabean and jatropha oil

1. Preparation of alcohol and catalyst mixture,
2. Heating of oil as well as alcohol and catalyst mixture at desired temperature,
3. When desired temperature is reached then catalyst and alcohol mixture is poured into oil slowly and agitator/stirrer was switched on, kept on throughout the reaction period.

C. Refining of product/byproduct

1. Separation of ester and glycerol: separation of ester and glycerol form reaction product is carried out using gravity settler. In the gravity settler (separating funnel) reaction mixture is separated in two phases as per their specific gravity.

Glycerol settles at the bottom and biodiesel at the top due to their density differences.

2. Washing of ester/biodiesel: Washing of biodiesel is done to remove /separate the FAME from glycerol, methanol and catalyst.
3. Removal of water from biodiesel.

4.2 Experimental procedure

4.2.1 Materials

Jatropha curcas oil and soyabean oil were collected from local market. Free fatty acid analysis of jatropha oil and soyabean oil is determined according to American Oil Chemists' Society (AOCS) method i.e. titration method. The acid value of jatropha oil was 14.79 mgKOH/g of oil and corresponding free fatty acid was 7.43 % which was higher than the permissible value for base catalysed transesterification (i.e.<2 %(w/w). Methyl alcohol, sulphuric acid and sodium methoxide of analytical reagent grade were used for the biodiesel production using esterification and trans-esterification reactions.

4.2.2 Reaction condition

Reaction rate constant determines with the help of designed experiments. A molar ratio of alcohol to jatropha oil and soyabean oil were varied from 6:1 to 9:1 and the dependence of temperature of the reaction rate constants at different temperature (30^0C and 60^0C) was studied. Reactions were carried out at atmospheric pressure.

4.2.3 Apparatus

Transesterfication reactions were carried out in a 500 ml three-necked flask made of glass equipped with a thermometer, reflux condenser and a sampling port. The three-necked flask was dipped in a constant temperature silicon oil bath which is controlled a temperature controller. Agitation was provided by a stirrer with the help of magnetic beads, which could be set at any speed throughout the experiment. The experiment setup is shown in Figure 4.1.

4.2.4 Esterification and trans-esterification procedure

(A) Esterification:

In the esterification process, 200 gm of jatropha oil was taken in the reactor and heated at 60^0C, 40gm of methanol and 10 gm H_2SO_4 solution was added and mixed with constant stirring. The reaction mixture was stirred and maintained at 60^0C for 2 hour and the product is esterified oil which contains low FFA (<0.5%)

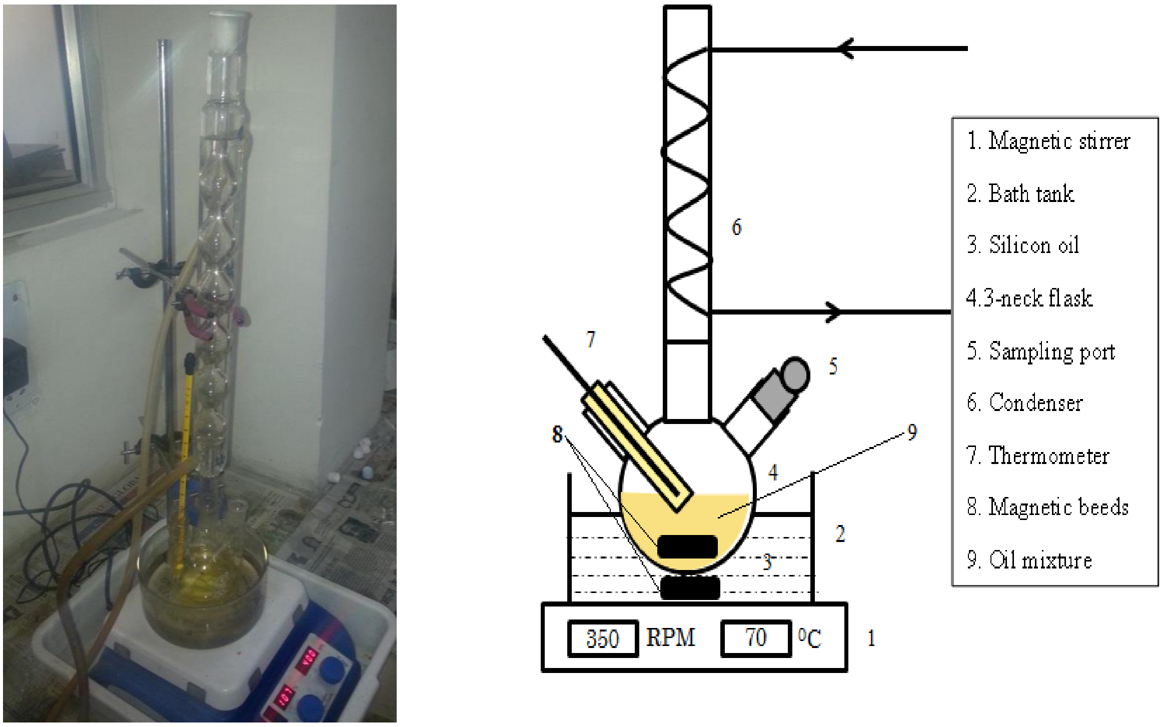


Figure 4.1(A) Experimental set up **(B) schematic diagram of experimental set up**

(B) Transesterification:

The reactor was initially filled with esterified jatropha/soyabean oil heated to known temperature. A required amount of CH_3ONa catalyst was mixed in the known methanol' quantity and heated to the required temperature. After that the sodium methoxide was then mixed deliberately in the flask to avoid the loss of methanol due to evaporation. As the reactions proceed, 2 ml samples were withdrawn at pre-specified time interval. The frequency of sample withdrawn varied was dictated by reaction condition. Beginning of reaction, molar ratio and mixing intensity required more rapid sampling at higher temperature. Samples were withdrawn at 1-minute interval at the beginning of reaction and at 5 to 10 minute interval thereafter. Samples were taken in 10 ml bottles and mixed in the ice bath at about 0^0C, properly capped and kept for further analysis and the remaining reaction mixture in the flask was poured into separating funnel, where separation in two layer appears. The upper layer was jatropha oil methyl ester /soyabean oil methyl ester and lower was glycerol. At first, lower layer was separated from separating funnel. Then upper layer was poured into another vessel.

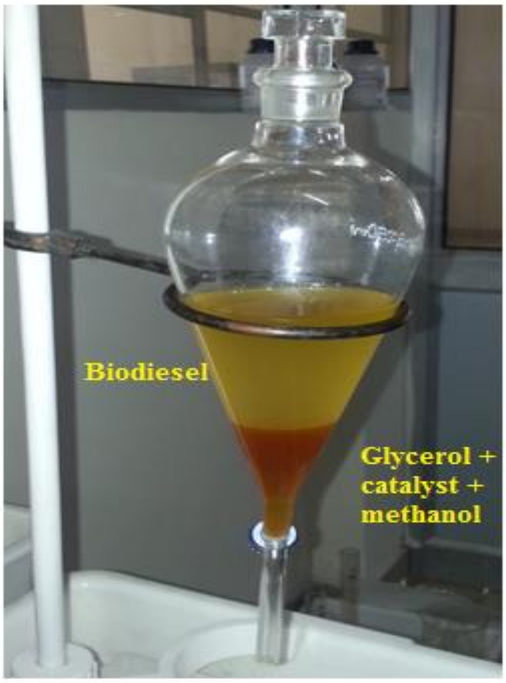


Figure 4.2 Phase separation of reaction product

(C) Washing and drying of biodiesel

The aim of washing is to remove/separate the glycerol, methanol and catalyst from FAME. Although separation using a separating funnel was done but complete separation was not achieved, consequently an agitation washing was performed twice with warm distilled water (temperature about 50^0C). During first washing emulsion of FAME with water of milky white color was formed and after 30 minutes layer separation appear slower one was water and upper layer was ester as per their density. The upper layer was separated out and this process was repeated twice or even four times with agitation till the lower layer does not appear clean water. The washing of biodiesel (jatropha oil methyl ester/soyabean oil methyl ester) is shown and after washing esters was looking hazy due to the presence of water. In order to remove water, the biodiesel was dried in vacuum evaporator till the ester become clear, and light yellow.

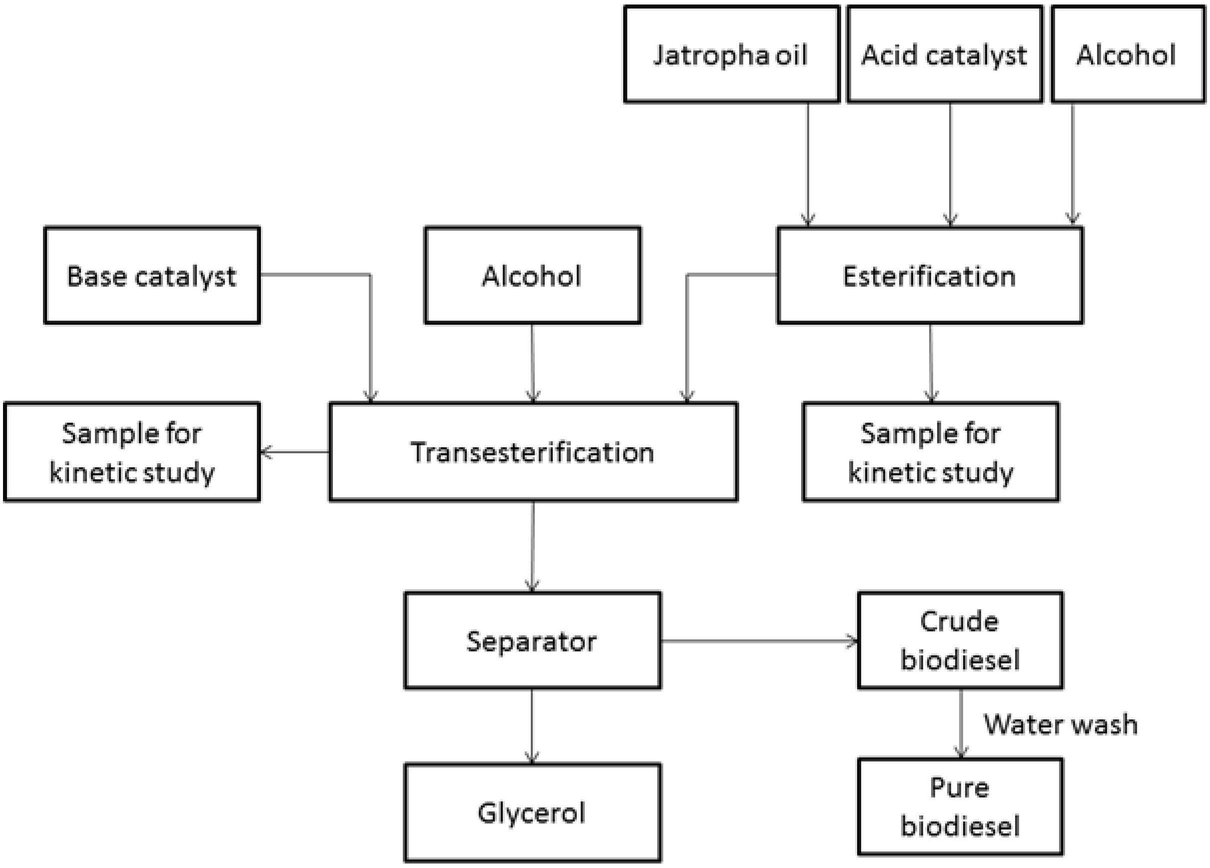


Figure 4.3 Schematic diagram of acid catalyzed esterification followed by transesterification of jatropha oil

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 Physical and Chemical Properties of Feedstock and Biodiesel

Phyical properties like acid value, free fatty acid and % moisture content for both soybean and jatropha oils are shown in Table 5.1. From Table 5.1 it can see that the acid value, FFA and moisture content in case of jatropha oil are higher than the soybean oil. The free fatty acid content in jatropha oil is 7.43 (acid value 14.79), which is very high. However the desired value of FFA content for transestrifiction reaction is 1 wt%, therefore it is required to carry out the esterification reaction prior to transesterification reaction, else it can lead to saponification if direct transesterification is carried out.

Major properties of biodiesel (e.g. kinematic viscosity, specific gravity, density, flash and fire points, etc.) obtained from jatroha and soybean oil are compared with that of standard biodiesel and are given in Table 5.3**.**

Table 5.1 Properties in the feed stocks

Property	Soya bean oil	Jatropha oil
Acid value	2.03	14.79
% FFA	1.02	7.43
% Moisture content	0.0487	0.1202

5.2 GC analysis

After conversion of jatropha and Soya bean oil to biodiesel, GC analysis was carried out in order to find % content of different fatty acids in biodiesel. Gas chromatograms results are shown in Table 5.2

Table 5.2 % content of different fatty acids in biodiesel

Fatty acid	Biodiesel from Jatropha oil	Biodiesel from Soya bean oil
C16	16.24	10.92
C18:1+C18:2	78	83.38
C18:0	4.5	3.54

Table 5.3 Comparison of Physical and chemical properties of biodiesel

Fuel property	Standard Biodiesel*	Present work	
		Biodiesel from Soybean oil	Biodiesel from jatropha oil
Kinematic viscosity @40^{0}C, mm^2/s	4.0-6.0	5.1	4.8
Specific rravity, @15.5^{0}C	0.88	0.88	0.86
Density @15.5^{0}C, kg/m^3	880	880	860
Carbon, wt%	77	79	76
Flash Point ^{0}C	100-170	160	165
Fire Point ^{0}C	110-200	180	180
Cloud Point ^{0}C	-3 to15	-1	0
Pour point ^{0}C	-5 to10	-4	-2

*Biodiesel Handling and Use Guide

5.3 Qualitative analysis of conversion of vegetable oil to FAME using TLC

Fig. 5.1 shows the conversion of soya bean oil to biodiesel using thin layer chromatography from the beginning of the reaction upto 2 hours considering suitable time intervals. It can be seen from Fig. 5.1 it can be seen that upto 15 min there are small and light spots on the TLC plate, which shows that reaction has not been completed. After 20 min one dark and clear spot can be seen which leads to interference that reaction has been completed.

In Fig.5.2, TLC Plate 1 shows that transesterification reaction of soya bean oil with methanol in the presence of catalyst has been completed. The left spot is of soya been oil and the right one is of biodiesel. If biodiesel would not have converged then there would have been a spot parallel with the soybean oil spot. The position of biodiesel spot with respect to soya bean shows that conversion is greater than 95%.

Similarly TLC Plate 2 shows the formation of biodiesel from jatropha oil. The left spot is of jatropha and right one is of biodiesel from jatropha oil. The small spots below the main spots shows impurities present in reactant.

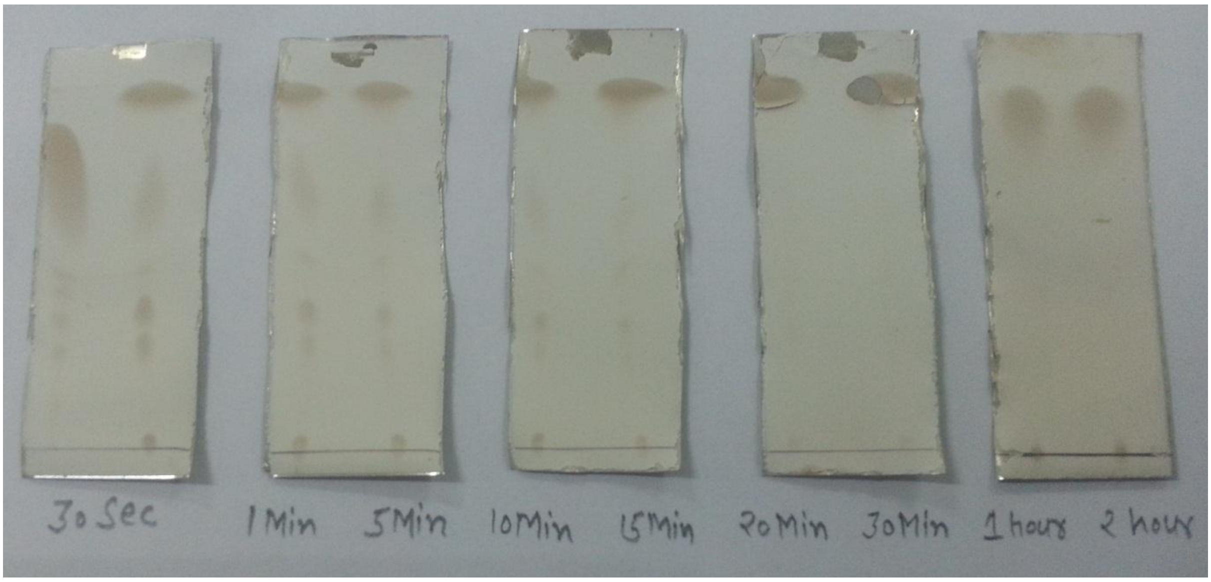
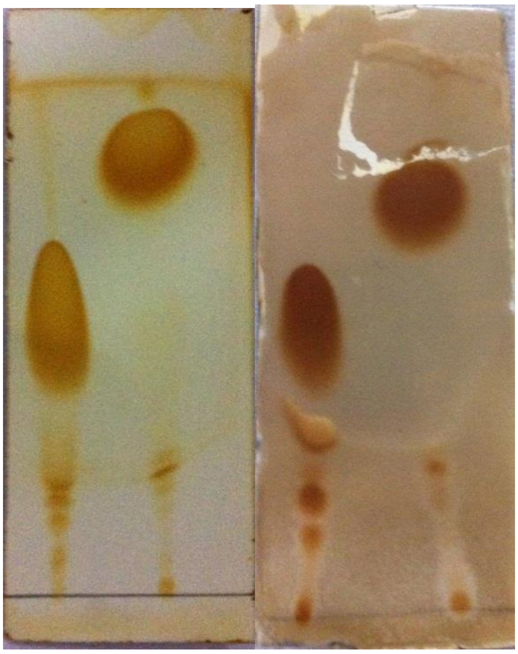


Figure 5.1 Analysis of conversion of triglyceride to FAME at different time



(a) TLC Plate 1 (b) TLC plate 2

Figure 5.2 Thin layer chromatography analysis of vegetable oil and biodiesel.

5.4 Physical and chemical properties of biodiesel with different solvents

Further study was extended to carry out the transesterification reaction in the presence of co-solvent: diethyl ether, tetrahydrofuran (THF), and tert butyl methyl ether. In Table 5.4, the properties of biodiesel obtained from transerterification process by two methods (with and without solvent) are compared. It can be concluded from Table 5.3 that the values of kinematic viscosity, flash and fire point of the biodiesel obtained from without solvent are more while compared to with solvent method, which indicates that the biodiesel obtained from with solvent method has high suitability for diesel engine. Biodiesel which has lower kinematic viscosity are better fuel for diesel engine. In the present work, it was observed that the diethyl ether, tetrahydrofuran and tert butyl methyl ether solvent used to produce biodiesel shows similar properties for density, carbon, flash point, fire point, cloud and pour point.

Table 5.4 Comparison of Physical and chemical properties of biodiesel with or without solvents

Fuel property	Biodiesel from jatropha oil without solvent	Biodiesel from jartopha oil with solvents		
		diethyl ether	tetrahydrofuran	tBME
Kinematic viscosity @40^0C, mm^2/s	4.8	3.2	2.9	3.1
Specific Gravity, @15.5^0C	0.86	0.8621	0.8655	0.8691
Density @15.5^0C, kg/m^3	860	862.1	865.5	869.1
Carbon, wt%	76	68	67	70
Flash Point ^{0}C	165	105	100	110
Fire Point ^{0}C	180	110	105	118
Cloud Point ^{0}C	0	0	-1	-1
Pour point ^{0}C	-2	-1	-3	-2

5.5 Effect of time on the yield of biodiesel production with different solvents

To understand the effect of time on transestirification reaction experiment were conducted at different time intervals (30, 60 and 120 sec) for different solvents (tetrahydrofuran, diethyl ether and tert butyl methyl ether). The biodiesel products were analysed in terms of %yield of methyl ester with solvents, and it was found nearly 80 to 90 %. Percentage yield of methyl ester (with tetrahydrofuran) increases with time while yield (of biodiesel production) remain constant with diethyl ether and tert-butyl methyl ether solvent.

5.6 Qualitative analysis of conversion of vegetable oil to FAME (with different solvent) using TLC

TLC images are shown in Figure 5.5 which indicates the quick and qualitative conversion of methyl ester with different solvents. TLC image for diethyl ether, tetrahydrofuran and tert-butyl methyl ether showed that the conversion was achieved in 30 s, 30 s and 60 s, respectively. TLC image of biodiesel (with diethyl ether) is clear and bright which indicates the high quality of biodiesel production. Conversion of methyl ester was found above 90% with all three solvents.

To understand the effect of time on transestirification reaction experiment were conducted at different time intervals (30, 60 and 120 sec) for different solvents (tetrahydrofuran, diethyl ether and tert butyl methyl ether). For the % yield of methyl ester with solvents was found nearly 80 to 90 %. Percentage yield of methyl ester (with tetrahydrofuran) increases with time while yield (of biodiesel production) remain constant with diethyl ether and tert butyl methyl ether solvent.

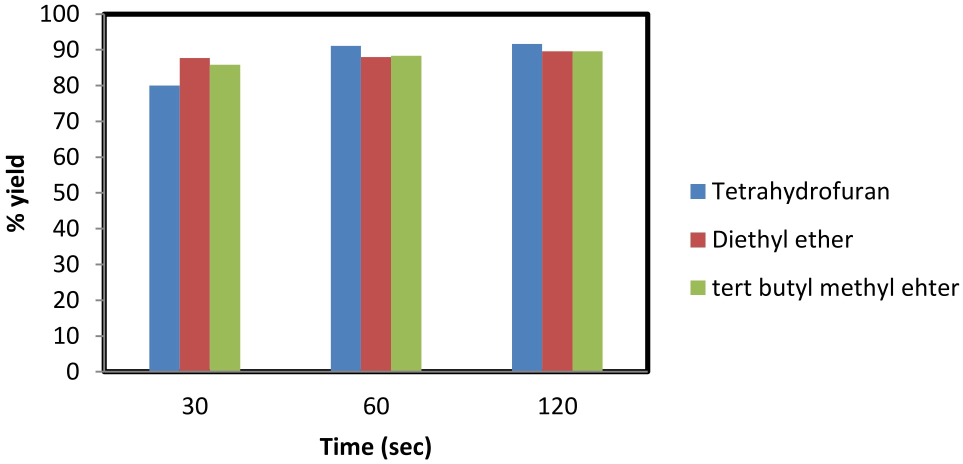
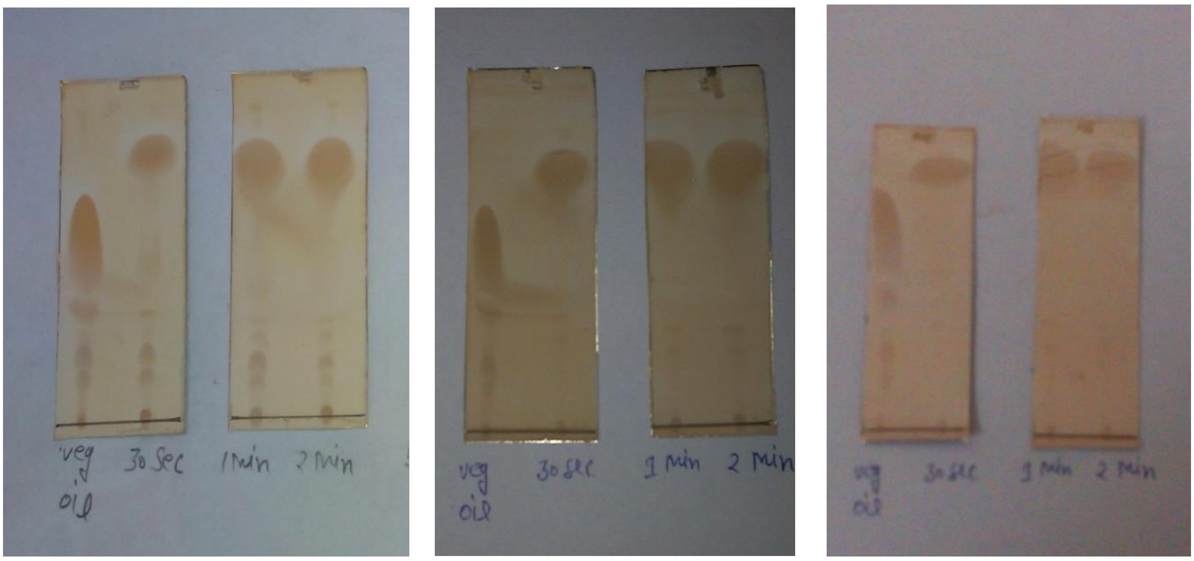


Figure 5.3 Effect of time on methyl ester yield



Tert butl methyl ether tetrahydofuran Diethy ether

Figure 5.4 TLC images of conversion of triglyceride to FAME with different solvent at different time

5.7 Comparison of biodiesel production by methyl ester with different solvents

The boiling point of diethylether is 34 ^{0}C, which makes it better to use in biodiesel production as solvent because during separation it remove automatically at room temperature.

Separation of biodiesel and glycerol was found faster while prepared with diethyl ether as compared to other solvents. Separation of biodiesel and glycerol was found difficult while prepared with tert-butyl methyl ether because it makes a dense phase which is difficult to separate. Separation as well as yield of bisodiesel produced by tetrahydrofuran was found better in present study. Quality of biodiesel produced with all three solvents was found to be better than the biodiesel produced without solvent.

CHAPTER 6

CONCLUSIONS

Alternate transport fuels have become increasingly important due to depleting petroleum reserves, increasing cost of crude oil and increased environmental concern. India has also shown its keen interest for production of biodiesel from nonedible oil. In the present work it has been reported that the equilibrium conversion of triglycerides (TG) is affected by various factors, namely, type of alcohol used, molar ratio of alcohol to triglyceride, type of catalyst, and amount of catalyst, reaction temperature and time, and feedstock quality.

In the present work the fatty acid methyl esters has been synthesized from both edible (soybean oil) and non-edible feedstock (jatropha oil) of indian origin. The study also reported the optimal operating parameters for jatropha oils in batch reactor. The synthesis of FAME from jatropha oil has been carried out in two-step process i.e. acid catalysed esterification followed by base catalysed transesterification for the production of biodiesel. From the result of the experimental study it has been concluded that the conversion of triglyceride into ester increases with increase in time. It has also been observed that the reaction completes in 20 minutes and the thin layer chromatography (TLC) used for the qualitative analysis of vegetable oils.

The study was conducted to optimize the reactions conditions for both esterification and transesterification reactions using different solvents (diethyl ether, tetrahydrofuran and tert butyl methyl ether). For diethyl ether, tetrahydrofuran and tert butyl methyl ether, the conversion was achieved in 30 s, 30 s, and 60 s, respectively. TLC image of biodiesel (with diethyl ether) is clear and bright which indicates the better quality of biodiesel production. Conversion of methyl ester was found above 90% with all three solvents. Based on present experimental work, it can be concluded that biodiesel production can be achieve in continuous flow reactor.

REFERENCES

1. Committee report on biofuel, Planning commission, Government of India,.2003
2. www.cpcb.com
3. www.mnes.nic.in
4. World Energy Outlook, 2012
5. www.presidentofindia.nic.in/ scripts/**independence**detail.jsp ,/
6. Panchayat.nic.in/round/DrAKGupta, IIP.ppt
7. www.scientificpsychic.com/fitness/fatty acids.html
8. Foidl, N., and S. Hackel; *"Jatropha curcas* L. as a source for the production of biofuel in Nicaragua", Bioresource *Technology, 58(1), 77-82, 1996*
9. M. Mohibbe Azam, Amtul Waris and N.M. Nahar "Prospects and potential of fatty acid methyl esters of some non-traditional seed oils for use as biodiesel in India", Biomass *and Bioenergy,* 2005
10. Demirbas, Ayhan "Biodiesel fuels from vegetable oils via catalytic and noncatalytic supercritical alcohol transesterification and other methods: a survey Energy conversion and management (44) 2093-2109, 2003.
11. Hanny Johanes Berchmans ,Shizuko Hirata; Biodiesel production from crude Jatropha curcas L. seed oil with a high content of free fatty acids, Bioresource Technology 99 (2008) 1716–1721.
12. Fangrui Ma, Milford A. Hanna, Biodiesel production: a review, Bioresource Technology 70 (1999) 1-15.
13. Rui Wang, Wan-Wei Zhou , Milford A. preparation, optimization, and fuel properties from non-edible feedstock, Datura stramonium L, Fuel 91 (2012) 182–186Hanna , Yu-Ping Zhang , Pinaki S. Bhadury, Yan Wang, Bao-An Song , Song Yang , Biodiesel.
14. Joon Ching Juan , Damayani Agung Kartika , Ta Yeong Wub, Taufiq-Yap Yun Hin, Biodiesel production from jatropha oil by catalytic and non-catalytic approaches:An overview, Bioresource Technology 102 (2011) 452–460.
15. Ivana B. Bankovi-Ili , Olivera S. Stamenkovi, Vlada B. Veljkovi, Biodiesel production from non-edible plant oils, Renewable and Sustainable Energy Reviews 16 (2012) 3621– 3647.

16. Jibrail Kansedo, Keat Teong Lee , Subhash Bhatia, Cerbera odollam (sea mango) oil as a promising non-edible feedstock for biodiesel production, Fuel 88 (2009) 1148–1150.
17. M.M. Gui, K.T. Lee, S. Bhatia, Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock, Energy 33 (2008) 1646– 1653.
18. Gerald Kafuku , Man Kee Lam , Jibrail Kansedo , Keat Teong Lee, Makame Mbarawa , Croton megalocarpus oil: A feasible non-edible oil source for biodiesel production, Bioresource Technology 101 (2010) 7000–7004.
19. Emil Akbar, Zahira Yaakob, Siti Kartom Kamarudin, Manal Ismail, Jumat Salimon, Characteristic and Composition of *Jatropha Curcas* Oil Seedfrom Malaysia and its Potential as Biodiesel Feedstock, European Journal of Scientific Research ISSN 1450-216X Vol.29 No.3 (2009), pp.396-403.
20. Prafulla D. Patil, Shuguang Deng, Optimization of biodiesel production from edible and non-edible vegetable oils, Fuel 88 (2009) 1302–1306.
21. Mustafa Balat, Potential alternatives to edible oils for biodiesel production – A review of current work, Energy Conversion and Management 52 (2011) 1479–1492.
22. Ashwani Kumar, Satyawati Sharma, Potential non-edible oil resources as biodiesel, Renewable and Sustainable Energy Reviews 15 (2011) 1791–1800.
23. Sanjib Kumar Karmee, Anju Chadha, Preparation of biodiesel from crude oil of Pongamia pinnata, Bioresource Technology 96 (2005) 1425–1429.
24. Vivek, A K Gupta, Biodiesel production from Karanja oil, journal of Scintific & Industrial Research vol.63, January (2004)pp 39-47.
25. May Ying Koh, Tinia Idaty Mohd. Ghazi, A review of biodiesel production from Jatropha curcas L. oil, Renewable and Sustainable Energy Reviews 15 (2011) 2240–2251.
26. Sivashunmugam Sankaranarayanan, Churchil A. Antonyraj, S. Kannan, Transesterification of edible, non-edible and used cooking oils for biodiesel production using calcined layered double hydroxides as reusable base catalysts, Bioresource Technology 109 (2012) 57–62.
27. Zhang, D., Crystallization characteristics and fuel properties of tallow methyl esters. Master thesis, Food Science and Technology, University of Nebraska-Lincoln (1994).
28. Ayhan Demirbas. Biodiesel. a realistic fuel alternative for diesel engines. Science and energy (2008) Turkey.
29. Sprules, F.J., Price, D., Production of fatty esters. US Patent 2(1950)366-494.

30. Wright, H.J., Segur, J.B., Clark, H.V., Coburn, S.K., Langdon, E.E., DuPuis, R.N., A report on ester interchange. Oil and Soap 21(1944) 145-148.
31. Lim S, Teong LK. Recent trends, opportunities and challenges of biodiesel in Malaysia: an overview. Renewable and Sustainable Energy Reviews(2010) 14:938–54.
32. Singh SP, Singh D. Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of biodiesel:a review. Renewable and Sustainable Energy Reviews (2010)12:200–16.
33. H. Fuduka, A. Kondo and H. Noda, "Biodiesel fuel production by transesterification of oils", *J Biosci Bioeng* **92**(5) 405–416, (2005).
34. Shashikant, Vilas Ghadge and Hifjur Raheman; "Biodiesel production from mahua oil having high free fatty acids"; Biomass *and Bioenergy, **28(6),** 601-605, (2005)*
35. J.M. Encinar, J.F. Gonzalez, A. Pardal and G. Martinez; "Transesterification of rapeseed oil with methanol in the presence of co-solvent", Italy (2010).
36. Malaya Naik, L.C. Meher, S.N. Naik and L.M. Das; "Production of biodiesel from high free fatty acid Karanja (Pongamia pinnata) oil", Biomass and bioenergy (2008) 354 – 357.
37. P.K. Sahoo, L.M. Das; "Process optimization for biodiesel production from Jatropha, Karanja and Polanga oils", Fuel 88 (2009) 1588–1594.