KINETICS OF TRANSESTERIFICATION OF JATROPHA OIL FOR BIODIESEL PRODUCTION

A DISSERTATION

Submitted in partial fulfillment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
ALTERNATE HYDRO ENERGY SYSTEMS

By

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CANDIDATE'S DECLARATION

I hereby certify that the work being presented in the dissertation, entitled **"KINETICS OF TRANSESTERIFICATION OF JATROPHA OIL FOR BIODIESEL PRODUCTION "**, in partial fulfillment of the requirement for the award of the degree of Master of Technology in "Alternate Hydro Energy Systems", submitted in Alternate Hydro-Energy Centre, Indian Institute of Technology, Roorkee is an authentic record of my own work carried out during the period from July 2005 to June 2006 under the supervision of **Dr. M.P.Sharma**, Senior Scientific Officer, Alternate Hydro Energy Centre, Indian Institute of Technology, Roorkee.

I have not submitted the matter embodied in this dissertation for award of any other degree.

Ashish Ranjan

Date: 30 June, 2006 (ASHISH RANJAN)

Place: Roorkee

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

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ABSTRACT

Biodiesel derived from renewable plant sources is monoalkyl esters of long chain fatty acids which fall in the carbon range C12-C22 and has similar properties as mineral diesel. There are various processes to convert vegetable oils (mainly triglycerides) into biodiesel. Transesterification is one of the most promising and successful of these processes. 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, amount of catalyst, reaction temperature, reaction time and feedstock quality (like free fatty acid content, water content etc.).

The present work reports the production of biodiesel from non-edible feedstock oils of Indian origin, separation, and characterization of biodiesel. This study also reports the optimal operating parameters for Jatropha oils in batch reactor. The main thrust of the present work was to study the kinetics, modeling and simulation of alkali-catalyzed transesterification of Jatropha curcas oils. This involved experimental work carried out in a 1.5 four-necked batch reactor to generate kinetic data, fitting reversible kinetic model, and simulating the batch reactor. The effects of temperature, catalyst concentrations, and molar ratios of methanol to triglycerides and stirring rates were investigated.

A reversible kinetic model was developed and model parameters were obtained from the literature, Arrhenius equation was used for the temperature dependency of rate constant and model was simulated using *Simulink.* This model could be used for the study of changing reaction condition and to optimize the reaction condition. In the present study two-step process i.e. acid catalyzed esterification followed by base catalyzed treanesterification for the production of biodiesel as well as kinetic study.

The result of the experimental study shows that the conversion of triglyceride into ester increases with increase in molar ratio and temperature. The optimum condition for Jatropha oil transesterification was 65 ^{0}C, 1 % catalyst concentration (w/w) and 6:1 molar ratio.

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Dated: 30 June 2006

Place: Roorkee

Ashish Ranjan

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NOMENCLATURE

TG	Triglyceride
DG	Diglyceride
MG	Monoglyceride
GL	Glycerol
ME (E)	Methyl ester (Ester)
A	Soap
ROH	Alcohol
OH	Alkali catalyst
k	Rate constant
FFA	Free Fatty Acid

INTRODUCTION

1.1 GENERAL

Energy is a basic requirement for economic development. Every sector of Indian economy –agriculture, industry, transport, commercial and domestic needs input of energy. The economic development plans implemented since independence have necessarily required increasing amount of energy. As a result, consumption of energy in all forms has been steadily rising all over the country.

India is home to a billion people, about a sixth of the world's population. The demand for mobility and automobiles in India has also been growing along with the economic progress. Passenger vehicle sales in India crossed the million mark last year and this has been spread over different classes of vehicles. The country faces problems with regard to the fuel for increasing transportation demand and now imports about 70 % of its petroleum requirement. Widely fluctuating world prices of oil have long been a destabilizing element for the country's balance of payments. The petroleum import bill is now about $13 billion forming about 30 % of the national import bill, which is expected to reach $15.7 billion by 2006-07. The current yearly consumption of diesel is about 40 million tonnes forming 40 % of the total petroleum product consumption. This is expected to reach 52.32 million tonnes by 2006-07 growing at about 5.6 % annually [1]. India's vehicular pollution is estimated to have increased eight times over the last two decades. This source alone is estimated to contribute about 70 % of the total air pollution. With 243.3 million tonnes of carbon released from the consumption and combustion of fossil fuels in 1999, India ranked fifth in the world behind the U.S., China, Russia and Japan [2]. India's contribution to world carbon emissions is expected to increase in the coming years due to the rapid pace of urbanization, shift from noncommercial to commercial fuels, increased vehicular usages and continued use of conventional and more inefficient coal-fired power plants.

Although India ranks fifth in the world in total energy consumption, its per capita electricity consumption is one of the lowest in the world i.e. 355 kWh against 800 kWh in China and a World average of 2200 kWh. India account around 17 % of the world population but accounts only for 3.5% of world commercial energy demand. Thus, the demand is expected to grow at the rate of around 5.6% per annum [1].

This growing consumption of energy has also been forcing the country becoming increasingly dependent on fossil fuels such as coal, oil and natural gas. Coal, being cheaper and abundantly available, is the major resource of the country and accounts 52% of total energy production. Oil accounts for 22% of the total energy production, which are largely imported .the country's dependence on imported oil has grown steadily due to steeper rise in demand. Rising prices of oil and gas, potential shortage in future and increasing environmental concern leads to concern about the security of energy supply needed to sustain our economic growth. Against this background, the country urgently needs to develop a sustainable path of energy development. Promotion of energy conservation and increased use of renewable energy sources are the twin planks of a sustainable energy supply.

1.2 RENEWABLE ENERGY

Fortunately, India is blessed with a variety of renewable energy sources, the main one being biomass, biogas, the solar, wind and small hydropower. Municipal and industrial wastes can also be useful source of energy, but are basically different forms of biomass. India is implementing one of the world's largest programmes in renewable energy the country ranks second in the world in biogas utilization and fifth in wind power and photovoltaic production. Renewable sources already contribute to around 5%

of the total power generating capacity in the country. The major renewable energy sources are given in Table 1 along with their potential and present status in terms of the number of installations or total capacity.

Table1. 1 Renewable energy in India [3]

Sl. no.	**Source /system**	**Estimated potential (MW)**	**Cumulative installed capacity (as on 31 Dec. 2005) MW**
1	Wind power	45,000	4434.00
2	Biomass power	16,000	376.00
3	Bagasse cogeneration	3,500	491.00
4	SHP (<25 MW)	15,000	1747.98
5	Waste to energy(MWe)	2,700	45,76
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 is the fastest growing sector for energy consumption. World energy statistics from the International Energy Agency (IEA) on consumption share of oil in different sector between 1973 and 2002 shows that the transportation sector is the fastest growing oil consumer.

Fig 1.1 shows that the oil consumption in 1973 was only 42% and increased to 57%in the year 2002 in transport sector. This drastic change in oil demand is due to

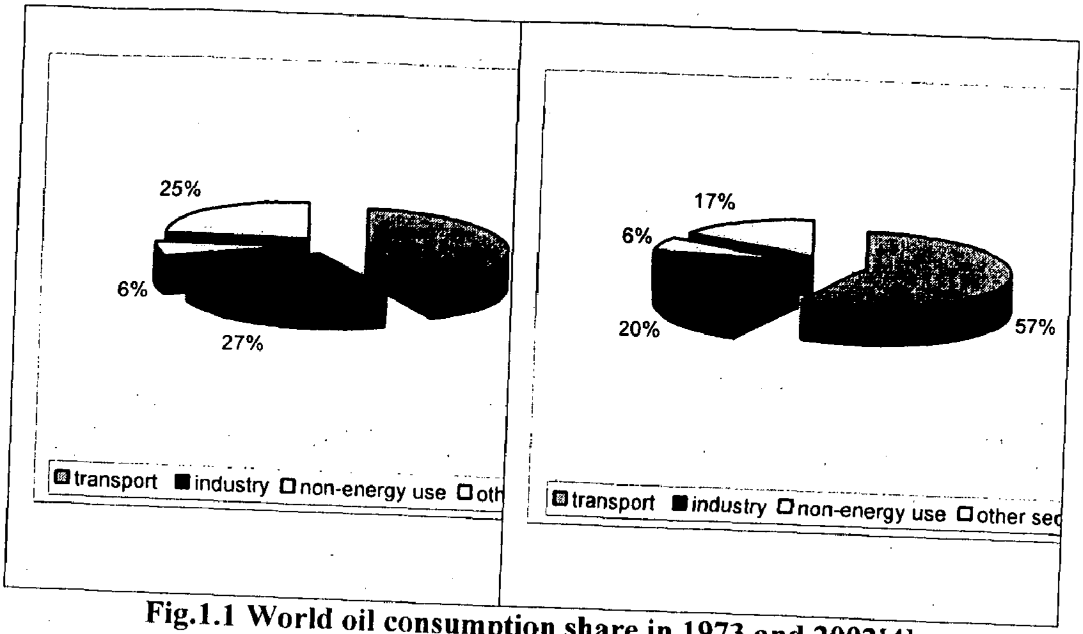


Fig.1.1 World oil consumption share in 1973 and 2002[4]

increasing population, its frequency of mobilization as well as obsoleting the animal power in transport sector. India account oil consumption 33 MTOE for transport, 30 MTOE for industry, 23 MTOE for other sector (i.e. agriculture, commercial and public service, residential and non-specified) and 27MTOE for electricity generation. In term of percentage oil accounts 98 %for transport, 29%for industry, 4%for electricity generation and 10%for other sector. .

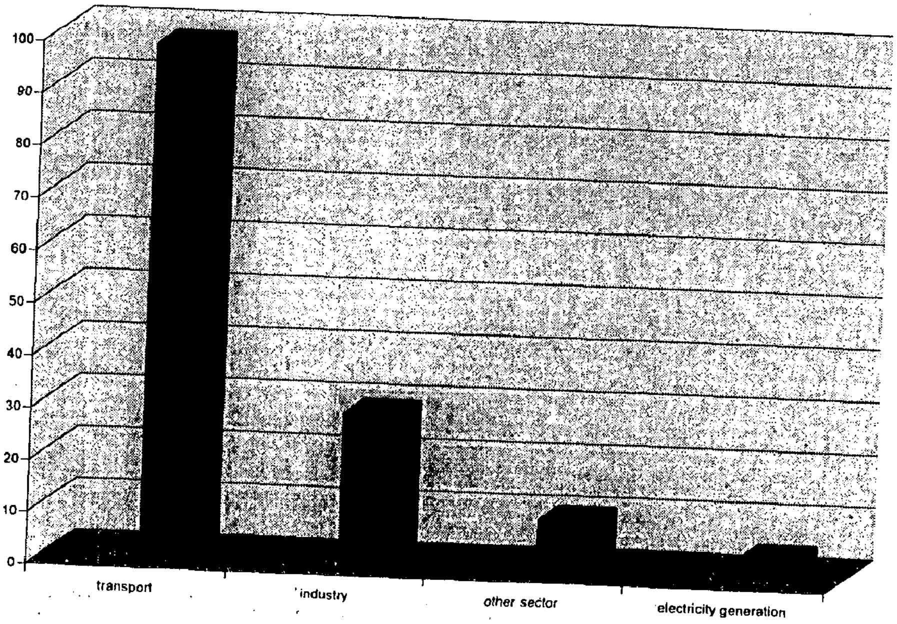


Fig.1.2 Percentage share of oil consumption in different sector [4]

India has 17% of the world's population, and just 0.8% of the world's known oil and natural gas resources. Our annual requirement of oil is 114 million tonnes. Significant part (around 98%) of this is consumed in the Transportation Sector only. We produce only about 25 % of our total requirement. The existing resources and future exploration of oil and gas may give mixed results. Today import cost of oil and natural gas is over Rs. 120,000 crores. Oil and gas prices are escalating; the barrel cost of oil has doubled within a year [5].

The other critical options are development of electric vehicles; hydrogen based vehicles, electrification of Railways and urban mass transportation, apart from the development of biofuel in the country.

1.3.1 ALTERNATE DIESEL FUEL

Alternative fuels should be easily available, environment friendly and techno-economically competitive. One of such fuels is triglycerides (vegetable oils/animal fats) and their derivatives. Vegetable oils, being renewable, are widely available from a variety of sources and have low sulphur contents close to zero, and hence cause less environmental damage (lower greenhouse effect) than diesel. Besides, vegetable oils and their derivatives are produced widely in the country for food and other purposes.

1.3.2. Triglyceride as diesel fuels

The use of vegetable oils, such as palm, soya bean, sunflower, peanut, and olive oil, as alternative fuels for diesel engines dates back almost nine decades, but due to the rapid decline in crude oil reserves, it is again being promoted in many countries as alternative liquid fuel. Depending upon the climate and soil conditions, different countries are looking for different types of vegetable oils as substitutes for diesel fuels. For example, soya bean oil in the US, rapeseed and sunflower oils in Europe, palm oil in South-east Asia (mainly Malaysia and Indonesia) and coconut oil in the Philippines are being considered. Besides, some species of plants yielding non-edible oils, e.g. Jatropha (ratanjyot), Pongamia (karanja), Salvadora (sal), Rubber seed and Mahua may play a significant role in providing resources. Both these plants may be grown on a massive scale on agricultural/degraded/waste lands, so that the chief resource may be available to produce biodiesel on 'farm scale. Table 1.2 gives the countries of the world engaged in the growing of various vegetable oil resources and production of biodiesel.

Table 1.2 Country wise BD production practices in the world [5]

Sl.no	**Country**	**Source of biodiesel**
1	USA	Soybean, mustard (under study)
2	Brazil	Soybean
3	Nicaragua	Jatropha curcas
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**	Jatropha curcas oil, pongamia oil, mahua oil, Neem oil, Sal oil etc (Nonedible oil).
14	China	Guang pi
15	Germany	Rapeseed oil

Table 1.2 states that most of the countries uses soybean oil, palm oil, rapeseed oil for biodiesel production but in India these oils are used for edible purposes thus India is showing their interest in non-edible oil as source of biodiesel especially in Jatropha curcas oil, pongamia oil, mahua oil, Neem oil, Sal oil etc. World status of biodiesel production during 1991-2003 is shown in figure1.3

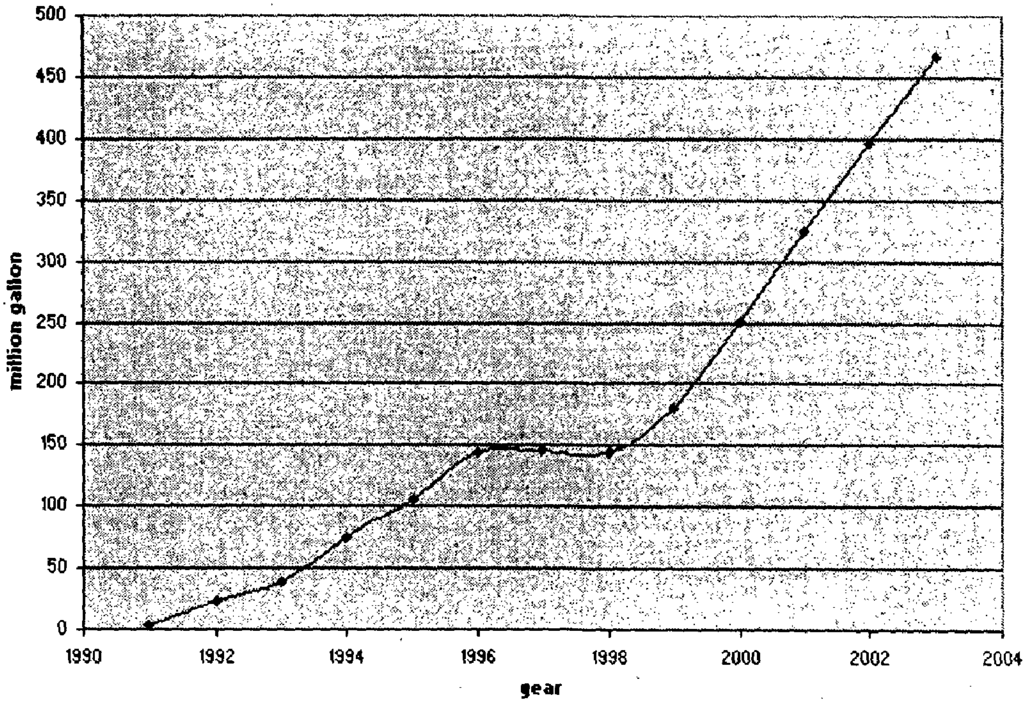


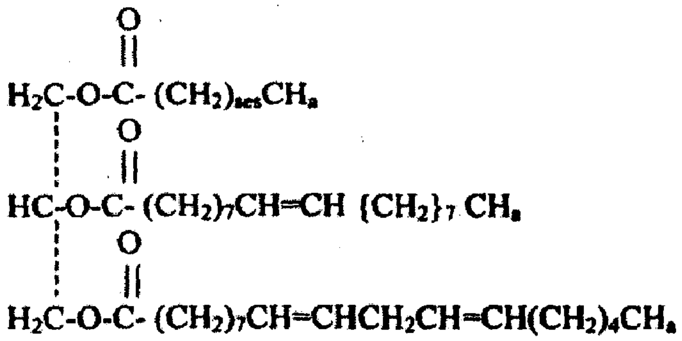
Fig 1.3 World biodiesel production during 1991-2003[6]

Figure 1.3 shows that worldwide production of biodiesel started in 1991and reached a production of 150 million gallon in 1996 and after that during 1996-98 production was almost constant and after 1998 production increased at faster rate and till 2003 production reached 460 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

Vegetable oils, also known as triglycerides, have the chemical structure given in Fig 1.4 comprise of 98% triglycerides and small amounts of mono- and diglycerides.

Triglycerides are esters of three molecules of fatty acids and one of glycerol and contain substantial amounts of oxygen in their structure. The fatty acids vary in their carbon chain length and in the number of double bonds.



$$\begin{array}{l} H_2C\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_{\text{[illegible]}}CH_3 \\ \;\vdots \\ HC\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_7CH{=}CH\ \{CH_2\}_7\,CH_3 \\ \;\vdots \\ H_2C\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_7CH{=}CHCH_2CH{=}CH(CH_2)_4CH_3 \end{array}$$

Fig. 1.4 Structure of a typical triglyceride molecule.

Different types of oils have different types of fatty acids. Fatty acids consist of the elements carbon, hydrogen and oxygen arranged as a carbon chain skeleton with carboxyl group (-COOH) at one end. The empirical formula and structure of various fatty acids present in vegetable oils are given in Table 1.3.

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

1.3.4 Fatty acid analysis of vegetable oil

Plant oils consist mainly of glycerides of fatty acids. Fatty acids are saturated and unsaturated aliphatic monocarbon acids, whose chain length is between 4 and 24 carbon atoms. Amongst plant oils tri-clycerides are the most common. In these all 3 hydroxyl groups of glycerines are replaced by fatty acids. The different species have different composition of fatty acids. The composition influences physical and chemical properties of the plant oil as well as its burning characteristics.

Table 1.3. Chemical structure of common fatty acids [7, 8]

Sl no.	**Name of fatty acid**	**Chemical name of fatty acids**	**Structure (*xx*: *y*)**	**Formula**
1	Butyric	Butanoic acid	4:0	$C_4H_8O_2$
2	Caproic	Hexanoic acid	6:0	$C_6H_{16}O_2$
3	Caprilic	Octanoic acid	8:0	$C_8H_{16}O_2$
4	Capric	Decanoic acid	10:0	$C_{10}H_{20}O_2$
5	Lauric	Dodecanoic	12:0	$C_{12}H_{24}O_2$
6	Myristic	Tetradecanoic	14:0	$C_{14}H_{28}O_2$
7	Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}O_2$
8	Stearic	Octadecanoic	18:0	$C_{18}H_{36}O_2$
9	Arachidic	Eicosanoic	20:0	$C_{20}H_{40}O_2$
10	Behenic	Docosenoic	22:0	$C_{22}H_{44}O_2$
11	Lignoceric	Tetracosanoic	24:0	$C_{24}H_{48}O_2$
12	Oleic	*cis*-9-Octadecenoic	18:1	$C_{18}H_{34}O_2$
13	Linoleic	*cis*-9,*cis*-12-Octadecadienoic	18:2	$C_{18}H_{32}O_2$
14	Linolenic	*cis*-9,*cis*-12,*cis*-15-Octadecatrienoic	18:3	$C_{18}H_{30}O_2$
15	Gadoleic acid	*cis*-9-eicosenoic	20:1	$C_{20}H_{38}O_2$
16	Arachidonic	*cis*-5,*cis*-8,*cis*-11,cis-14-eicosatetraenoic acid	20:4	$C_{20}H_{32}O_2$
17	Erucic	13-docosenoic acid	22:1	$C_{22}H_{42}O_2$

xx: y indicates number of carbons, and *y* number of double bonds in the fatty acid chain.

Table 1.4: Fatty acid compositions of non-edible vegetable oils [9]

Vegetable oil	**Fatty acid composition (%)**
Jatropha oil	Myristic acid (1.4), Palmitic acid (15.6), Stearic acid (9.7), Oleic acid (40.8), Linoleic acid (32.1), Arachidic acid (0.4)
Mahua oil	Myristic acid (1.0), Palmitic acid (17.8), Stearic acid (14.0), Oleic acid (46.3), Linoleic acid (17.9), Arachidic acid (3.0)
Neem oil	Palmitic acid (14.9), Stearic acid (14.4), Oleic acid (61.9), Linoleic acid (7.5), Arachidic acid (1.3)
Pongamia oil	Palmitic acid (10.6), Stearic acid (6.8), Oleic acid (49.4), Linoleic acid (19.0), Arachidic acid (4.1), Gadoleic acid (2.4), Behenic acid (5.3), Lignoceric acid (2.4)
Sal oil	Capric acid (0.8), Lauric acid (35.6), Myristic acid (50.7), Palmitic acid (4.5), Oleic acid (8.3), Linoleic acid (0.1)

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

1.3.5 Fuel properties of vegetable oil

The fuel properties of vegetable oils as listed in table 1.5 indicate that the kinematics viscosity of vegetable oils varies in the range of 30–55 cSt at 40 °C. The high viscosity of these oils is due to their large molecular mass in the range of 600–900, which is about 20 times higher than that of diesel fuel. The flash point of vegetable oils is very high (above 200 °C). The volumetric heating values are in the range of 39–40 MJ/kg, as compared to diesel fuels (about 45 MJ/kg). The presence of chemically bound oxygen in vegetable oils lowers their heating values by about 10%. The cetane numbers are in the range of 52–66.

Table 1.5: Fuel properties of non-edible vegetable oils [10]

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	-

Table 1.5 states that viscosity of nonedible vegetable oil 13 to 22 times of diesel fuel at 40 ^{0}C and flashpoint is also high (above200^{0}C). The only one property that is calorific value of vegetable oil in the range of 37-38 MJ/kg lower than the diesel.

1.3.6 Use of vegetable oils as diesel fuel

It has been found that these neat vegetable oils can be used as diesel fuels in conventional diesel engines, but this leads to a number of problems related to the type and grade of oil and local climatic conditions. The injection, atomization and combustion characteristics of vegetable oils in diesel engines are significantly different from those of diesel. The high viscosity of vegetable oils interferes with the injection process and leads to poor fuel atomization. The inefficient mixing of oil with air contributes to incomplete combustion, leading to heavy smoke emission, and the high flash point attributes to lower volatility characteristics. These disadvantages, coupled with the reactivity of unsaturated vegetable oils, do not allow the engine to operate trouble free for longer period of time. These problems can be solved, if the vegetable oils are chemically modified to biodiesel, which is similar in characteristics to diesel.

Developing vegetable oil derivatives that have similar fuel properties and performance and make them compatible with the hydrocarbon-based diesel fuels .the vegetable oil derivatives can be prepared or vegetable oil can be modified to liquid fuels having properties similar to diesel but different from raw vegetable oils. The vegetable oils can be modified to suitable liquid fuels by the following methods.

- Micro-emulsion
- Pyrolysis
- Dilution
- Transesterification

1.3.6.1 Pyrolysis: Pyrolysis refers to a chemical change caused by the application of thermal energy in the absence of air or nitrogen. The liquid fractions of the thermally decomposed vegetable oil are likely to approach diesel fuels. The pyrolyzate had lower viscosity, flash point, and pour point than diesel fuel and equivalent calorific values. The cetane number of the pyrolyzate was lower. The pyrolyzed vegetable oils contain acceptable amounts of sulphur, water and sediment and give acceptable copper corrosion values but unacceptable ash, carbon residue and pour point.

1.3.6.2 Micro-emulsification: The formation of micro emulsions (co-solvency) is one of the potential solutions for solving the problem of vegetable oil viscosity. Micro-emulsions are defined as transparent, thermodynamically stable colloidal dispersions. The droplet diameters in micro-emulsions range from 100 to 1000 Å. A micro-emulsion can be made of vegetable oils with an ester and dispersant (co-solvent), or of vegetable oils, an alcohol and a surfactant and a cetane improver, with or without diesel fuels. Water (from aqueous ethanol) may also be present in order to use lower-proof ethanol, thus increasing water tolerance of the micro-emulsions.

1.3.6.3 Dilution: Dilution of vegetable oils can be accomplished with such materials as diesel fuels, solvent or ethanol..

1.3.6.4Transesterification: Trans-esterification also called alcoholysis is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis. This process has been widely used to reduce the viscosity of triglycerides.

1.3.7. Fuel properties of biodiesel

The properties of biodiesel and diesel fuels, as given in table 1.5, show many similarities, and therefore, biodiesel is rated as a strong candidate as an alternative to diesel. This is due to the fact that the conversion of triglycerides into methyl or ethyl esters through the transesterification process reduces the molecular weight to one-third, reduces the viscosity by about one-eighth, and increases the volatility marginally. Biodiesel contains 10–11% oxygen (w/w), thereby enhancing the combustion process in an engine. It has also been reported that the use of tertiary fatty amines and amides can be effective in enhancing the ignition quality of the biodiesel without having any negative effect on its cold flow properties. However, starting problems persist in cold conditions. Further, biodiesel has low volumetric heating values (about 12%), a high cetane number and a high flash point. The cloud points and flash points of biodiesel are 15–25 °C higher than those of diesel.

From the table1.6 it is clear that vegetable oil methyl ester meets almost all desired properties of diesel, as viscosity of diesel is 3.06 mm^2/s while that of biodiesel from jatropha oil 4.54 mm^2/s and 3.39 for pongamia oil. Heating value and specific gravity of vegetable oil methyl ester is also nearly same.

Biodiesel is methyl or ethyl ester of fatty acid made from virgin or used vegetable oils (both edible & non-edible) and animal fats. The main commodity sources for biodiesel in India can be non-edible oils obtained from plant species such as Jatropha Curcas

(Ratanjyot), <u>Pongamia Pinnata</u> (Karanja), <u>Calophyllum inophyllum</u> (Nagchampa), <u>Hevca brasiliensis</u> (Rubber) etc

Table 1.6. Properties of biodiesel from different oils [11]

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 contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend or can be used in its pure form. Just like petroleum diesel, biodiesel operates in compression ignition (diesel) engine, which essentially require very little or no engine modifications because biodiesel has properties similar to petroleum diesel fuels. It can be stored just like the petroleum diesel fuel and hence does not require separate infrastructure. The use of biodiesel in conventional diesel engines results in substantial reduction of unburned hydrocarbons, carbon monoxide and particulate matters. Biodiesel is considered clean fuel since it has no sulphur, no aromatics and has about 10 % built-in oxygen, which helps it to burn fully. Its higher cetane number improves the ignition quality even when Blended in the diesel

For new vehicles (except 2 and 3 wheelers) compliance of Bharat Stage II emission norms are to be enforced in the entire country from 1.4.2005 and Euro III equivalent norms by 1.4.2010. In addition to 4 metros where Bharat Stage II norms are already in place, Bangalore, Hyderabad, Ahmedabad, Pune, Surat, Kanpur and Agra should also meet this norm from 1.4.2003. The four metros and the other seven cities should comply with Euro III and Euro IV equivalent emission norms from 1.4.2005 and 1.4.2010 respectively. The 2 and 3 wheelers should conform to Bharat Stage II norms from 1.4.2005 all over the country and Bharat Stage III norms preferably from 1.4.2008 but not later than 2010. For new vehicles, a drastic reduction in sulphur content (< 350 ppm) and higher cetane number (>51) will be required in the petroleum diesel produced by Indian Refineries. Biodiesel meets these two important specifications and would help in improving the lubricity of low sulphur diesel. The present specification of flash point for petroleum diesel is 35°C, which is lower than all the countries in the world (>55°C). Biodiesel will help in raising the flash point, a requirement of safety.

B20 (a blend of 20 percent by volume biodiesel with 80 percent by volume petroleum diesel) has demonstrated significant environmental benefits in US with a minimum increase in cost for fleet operations and other consumers. Biodiesel is registered as a fuel and fuel additive with the US Environmental Protection Agency and meets clean diesel standards established by the California Air Resources Board. Neat (100 %) biodiesel has been designated as an alternative fuel by the Department of Energy and the Department of Transportation of US. Studies conducted with biodiesel on engines have shown substantial reduction in Particulate matter (25–50%). However, a marginal increase in NOx (1-6%) is also reported; but it can be taken care of either by optimization of engine parts or by using De-NOx catalyst (De-NOx catalyst will be necessary for Bharat-III / IV compliant engines). HC and CO emissions were also reported to be lower. Non-regulated emissions like Poly Aromatic Hydrocarbons etc were also found to be lower.

Biodiesel has been accepted as clean alternative fuel by US and its production presently is about 100 million Gallons. Each State has passed specific bills to promote the use of biodiesel by reduction of taxes. Sunflower, rapeseed oils etc. are used as raw material in Europe whereas Soya bean oil is used in USA. Thailand uses palm oil, Ireland uses frying oil and animal fats. Due to its favorable properties, biodiesel can be used as fuel for diesel engines (as either B5-a blend of 5% biodiesel in petroleum diesel fuel or B20/B100).

USA uses B20 and B100 biodiesel. France uses B5 as mandatory in all diesel fuel. It can also be used as an additive to reduce the overall sulfur content of blend and to compensate for lubricity loss due to sulfur removal from diesel fuel. The viscosity of biodiesel is higher (1.9 to 6.0 cSt) and is reported to result into gum formation on injector, cylinder liner etc if used in neat form. However, blends of up to 20% should not give any problem. While an engine can be designed for 100% biodiesel use, the existing engines can use 20% biodiesel blend without any modification and reduction in torque output. In USA, 20% biodiesel blend is being used, while in European countries 5-15% blends have been adopted.

Targets set up for biodiesel production in India to achieve blending ratios of 5, 10 and 20 percent in phased manner with petroleum diesel over the period of next 5 years are given in Table1.6:

Table1.8 Biodiesel requirement for blending [1]

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 has around 60 million hectares of wasteland, of which 30 million hectares are available for energy plantations like "Jatropha". Once grown, the crop has a life of 50 years. Each acre will produce about 2 tonnes of bio-diesel at about Rs. 20 per liter. Biodiesel is carbon neutral and many valuable by-products flow from this agro-industry. Intensive research is needed to burn bio-fuel in internal combustion engines with high efficiency, and this needs to be an urgent R&D programme. India has a potential to produce nearly 60 million tones of bio-fuel annually, thus making a significant and important contribution to the goal of Energy Independence.

1.4 STATUS OF R&D ON BIODIESEL IN INDIA

In India, the research on bio-diesel is in infant stage, there is a dire need to adopt vigorous programs on the technological development for its production, utilization of by products and evaluation in engine with respect to shortcomings, emissions, additive response etc. For efficient production of bio-diesel concerted R&D effort is needed to produce high quality feedstock material and to develop an improved, cost effective and efficient biodiesel production system. Biodiesel from different feedstocks may vary in composition, lubricity, oxidation stability, etc. It is desirable to carry out tests on biodiesel from all possible feedstocks available in India and generate comparative data on fuel composition emissions and materials compatibility, etc. Toxicological study is a pre-requisite for introduction of any fuel. It is recommended that such studies in India should be initiated through concerned R&D centers. Procedure for detecting percentage of biodiesel in the blended fuel and to check adulteration of the fuel should also be developed. Emission norms for biodiesel vehicles may be similar to that of the conventional diesel vehicles.

Research and Development needs in broadly three areas viz. Raw Material, Production Technology and Utilization of bio-diesel as fuel have been considered. The major raw materials used for the production of bio-diesel are vegetable oil and alcohol. In India vegetable oils are costly and are in short supply therefore, non-edible oils such as **Jatropha curcas, pongamia piñata, Salvodra (sal), Mahua and Neem oil etc.** are preferred feedstock for bio-diesel production. The potential of total non-edible oils in India is around 0.1 MMT/ annum. There is a need to increase the production of nonedible oil even to achieve a humble target of 5.0% replacement of diesel with bio-diesel. The other R&D issues which need attention are seed resource assessment, collection and their cryo-preservation, increasing availability of seed, seed setting, inter-cropping with TBOS, selection of high yielding crops, developing agro-technologies for different agro climatic regions, oil quality, bio-diesel production technology using new catalyst systems like heterogeneous catalysts, lipase catalyst and supported catalysts on smart polymers, utilization of by-products apart from issues related to utilization of bio-diesel as fuel including compatibility with additives and elastomers, engine performance, toxicity adulteration etc.

In India a number of organization have been working on various aspect of biodiesel production, processing and utilization viz. NOVOD, NBRI Lucknow, Central Salt &Marine Research Institute (CSMCRI) Bhavnagar, IIP Dehradun, IOC Faridabad (R&D), IISc Banglore, IICT Hydrabad, Punjab Agricultural University (PAU), Delhi College of Engineering (DEC), various IITs and other leading universities and institutions.

Alternate Hydro Energy Center (A.H.E.C) of Indian institute of technology, Roorkee is also involved in generating kinetic data for transesterification of different vegetable oil.

1.5 LITERATURE REVIEW

Ballesteros et al. [12] has developed the automatic method for online preparation of fatty acid methyl ester from olive oil and other type of oil prior to their gas chromatographic determination. Kang and Wang [13] has developed a simplified method for analysis of fatty acid in which extraction procedure was omitted in comparison to conventional one in which extraction was followed by methylation.Khan A.K. [14] has developed the quantitative analysis of the product mixture during transesterification reaction. Plank & Lorbeer [15] has developed a new method for simultaneous determination of glycerol, and mono-, di- and triglycerides in vegetable oil. Several analytical procedures have been developed for determination of glycerol, and mono-, di- and triglycerides in vegetable oil methyl ester. Based on the extraction of glycerol from VOMEs into an aqueous phase and its subsequent gas chromatographic analysis were described by Bondioli et al. [16]. Bailer and De Hueber [17] have described an enzymatic determination of glycerol in an aqueous extract of fatty acid methyl ester]. Mittelbach [18] carried out analysis of glycerol after dramatization with N, O-bis (trimethylsilyl) trifluoro acetamide (BSTFA) directly in the VOME sample. Capillary gas chromatograph is normally used for the analysis of mono-, di- and triglycerides in vegetable oil methyl ester. Freedman et al. [19] applied Capillary gas chromatograph, for studying transesterification of soybean oil to methyl ester. The fatty acid methyl esters together with mono-, di- and triglycerides in vegetable oil derivatives were estimated by Mariani et al [20]. It was also reported that mono-, di-, and triglyceride in VOME could be quantitatively determined using Capillary gas chromatography.

Freedman et al. [21] presented the results of a parametric study of the transesterification reaction variables that included temperature, molar ratio of alcohol to oil, type of catalyst, and the degree of refinement of the oil. They observed that the reaction proceeded to completion in 1 h at 60 °C but took 4 h at 32 °C.fig1, from that work, shows how the degree of reaction depends on the alcohol-to-oil ratio. Significant amounts of partially reacted mono- and diglycerides will be present when the alcohol-to-oil ratio is too low. The figure shows that an alcohol-to-oil ratio of 6:1 is necessary for a complete single-step reaction. Mono- and diglycerides of saturated fatty acids crystallize easily from the biodiesel fuel and can cause fuel filter plugging and other performance problems. Freedman compared both crude and refined vegetable oils as feedstocks and found that the yield of methyl esters was reduced from 93% to 98% for the refined oil to 67% to 86% for the crude oil. This was attributed mostly to the presence of up to 6.66% free fatty acids in the crude oil, although phospholipids were also suggested as a source of catalyst destruction

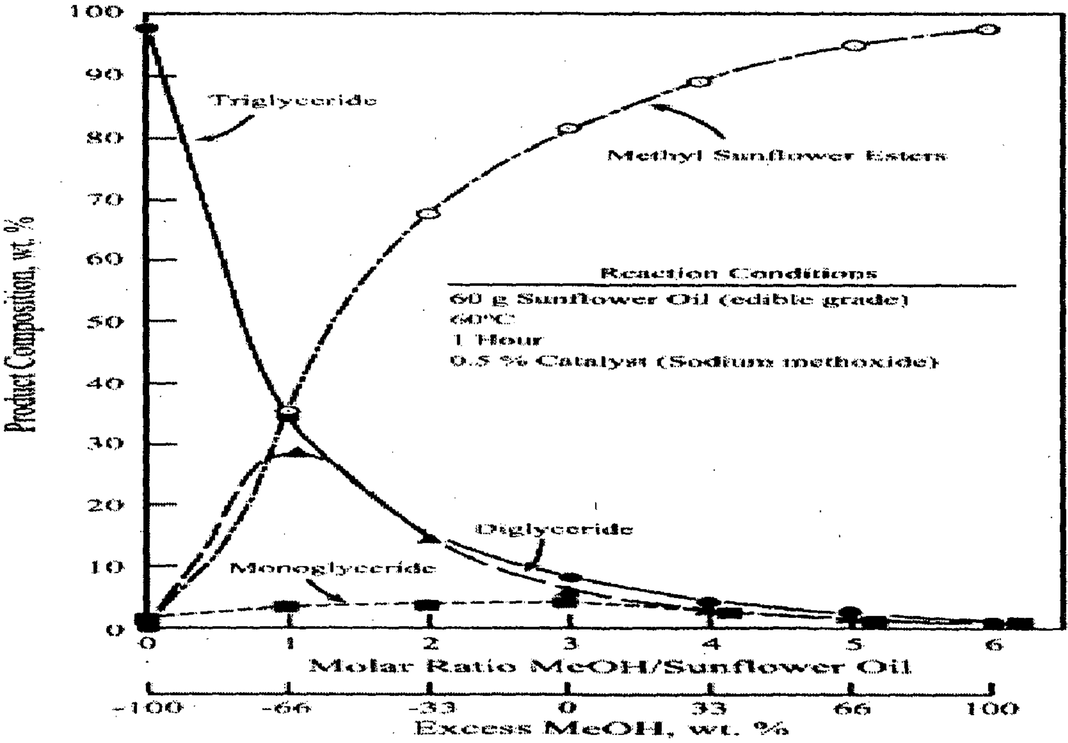


Fig. 1.5 Effect of molar ratio on product composition for transesterification [21]

Freedman et al. [22] analyzed reaction mixture of transesterified soybean oil by thin layer chromatography with flame ionization detection (TLC-FID) for the kinetic studies.

All the methods, reported above are for the determination of free glycerol or mono-, di-, and triglyceride in VOME. Noureddini & Zhu [23] studied the kinetics of transesterification of soybean oil, who used HPLC to determine the composition of various reaction products at 50^0 C and then used MATLAB to solve the rate equation. A method for predicting the viscosity of biodiesel fuels from their fatty acid ester composition was developed and general formula for viscosity determination of various saturated and unsaturated methyl ester derived by Allen et al. [24]. Srivastva and Prasad [25] studied the Indian aspect of triglycerides-based diesel fuel and its economic and environmental feasibility. Darnoko and Cheryan [26] studied the kinetics of palm oil transesterification in a batch reactor assuming transesterification reaction a pseudo second order model for the initial stages of the reaction, followed by first order or zero order kinetics. To test this hypothesis, they developed a model based on the kinetics of TG. They postulated that for the hydrolysis of TG, a plot of reaction time (t) vs1/[TG] would be straight line if the model were valid. The value of k and its corresponding correlation coefficient there is an increase in rate constant at higher temperature and the order of magnitude of k is kMG >kDG>kTG.

In a study of the effects of phospholipids on biodiesel production, Van Gerpen and Dvorak found [27] that phosphorus compounds in the oil did not carry over into the methyl esters, and while yield was reduced by 3–5% for phosphorus levels above 50 ppm, this was due mostly to added difficulty separating the glycerol from the esters.

Saka and Kusiana [28, 29] claim that the reaction of oil and methanol can be possible without a catalyst, which eliminates the need for the water-washing step. However, temperatures of 300 °C–350 °C and methanol to oil molar ratios of 42:1 are required. While the reaction only requires 120-240 s, the purity of the final product needs to be fully characterized, and formation of nonmethyl ester compounds in significant amounts is possible.

Dasari et al. [30] measured reaction rates without catalysts at temperatures of 120 °C to 180 °C. They noted the difficulty of reproducing reaction kinetics results of other researchers and attributed it to catalytic effects at the surfaces of the reaction vessels and noted these effects would be exacerbated at higher temperatures. Not including the effect of surface reactions could cause difficulties when scaling up reactors due to the decrease in the ratio of reactor surface area to volume.

Kreutzer [31] has described how higher pressures and temperatures (90 bar, 240 °C) can transesterify the fats without prior removal or conversion of the free fatty acids. However, most biodiesel plants use lower temperatures, near atmospheric pressure, and longer reaction times to reduce equipment costs.

Boocock et al. [32] have developed a novel technique for accelerating the transesterification reaction rate. During its early stages, the transesterification reaction is limited by the low solubility of the alcohol, especially methanol, in the oil. Boocock proposed the addition of a cosolvent to create a single phase, and this greatly accelerates the reaction so that it reaches substantial completion in a few minutes. The technique is applicable for use with other alcohols and for acid-catalyzed pretreatment of high free fatty acid feed stocks. The primary concerns with this method are the additional complexity of recovering and recycling the cosolvent although this can be simplified by choosing a cosolvent with a boiling point near that of the alcohol being used. Additional concerns have been raised about the hazard level associated with the cosolvents most commonly proposed, tetrahydrofuran and methyl tertiary butyl ether.

Mittelbach [33] describes a process for esterifying these free fatty acids and then returning them to the transesterification reaction. Keim [34] describes using this approach to convert palm oil containing 50.8% free fatty acids to methyl esters. Methanol (77% of the weight of oil) and sulfuric acid (0.75% of the weight of oil) were added to the oil while stirring at 69 °C for 1 h. After neutralization, 1.25% sodium methoxide was added, and the mixture was stirred for an additional hour at 50 °C. Analysis showed a yield of 97% but a residual acid value equivalent to about 5% palmitic acid. The incomplete reaction was probably due to water in the reactant mixture. As shown in the reaction, water is formed, and if it accumulates, it can stop the reaction well before completion. Kawahara and Ono [35] propose allowing the alcohol to separate from the pretreated oil or fat following the reaction. Removal of this alcohol also removes the water formed by the esterification reaction and allows for a second step of esterification or proceeding directly to alkali-catalyzed transesterification. Jeromin et al. [36] has described using acidic ion exchange resins in a packed bed for the pretreatment. Haas et al. [37, 38] have shown that acid-catalyzed esterification can be used to produce biodiesel from low-grade by-products of the oil refining industry, such as soapstock. Soapstock, a mixture of water, soaps, and oil, is dried, saponified, and then esterified with methanol or some other simple alcohol using an inorganic acid as a catalyst. The procedure relies on a large excess of alcohol, and the cost of recovering this alcohol determines the feasibility of the process.

Zhang et al. [39, 40] have reviewed the commonly used procedures for producing biodiesel; including a process simulation using the commercial software package HYSYS. Their economic assessment indicated that use of waste cooking oil feed stocks provided a higher rate of return than refined vegetable oils even after including the additional capital and operating costs of acid-catalyzed pretreatment.

Gupta et al [41] worked on transesterification reaction of Jatropha oil in a solvent-free system to produce biodiesel and three different lipases (Chromobacterium viscosum, Candida rugosa, and Porcine pancreas) were screened but only lipase from Chromobacterium viscosum was found to give appreciable yield. Immobilization of lipase (Chromobacterium viscosum) on Celite-545 enhanced the biodiesel yield to 71% from 62% yield obtained by using free tuned enzyme preparation with a process time of 8 h at 40 degreesC. Further addition of water to the free (1%, w/ v) and immobilized (0.5%, w/ v) enzyme preparations enhanced the yields to 73 and 92%, respectively. Immobilized Chromobacterium viscosum lipase can be used for ethanolysis of oil. It was seen that immobilization of lipases and optimization of transesterification conditions resulted in adequate yield of biodiesel in the case of the enzyme-based process.

Enciner et al. [42] studied the variable affecting the yields and characteristics of the biodiesel produced from used fried oil. Ju et al. [43] studied the effect of temperature, moisture and storage time on the accumulation of FFA in rice bran oil and employed a two-step process for the production of biodiesel from rice bran oil. Dube et al. [44] has studied the kinetics of acid catalyzed transesterification of waste frying oil from in excess methanol to form biodiesel. May et al. [45] has studied the effect of reaction parameters on transesterification of palm oil.

1.6 BRIEF OUTLINE OF PROPOSED WORK.

Based on literature survey, 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 like kinetics and mechanism for design of reactor and optimization of reaction parameter to maintain the product quality economically and get product in minimum time. As per literature survey it was found that the there are only few literature on the kinetics of transesterification of vegetable oil and almost nil literature on kinetics related to nonedible oil. In India, nonedible oil is the suitable source for biodiesel due to increased population load on agricultural land. Among the nonedible oil jatropha is the suitable candidate for biodiesel and there is no work on kinetics study for transesterification of jatropha oil. Thus this topic was selected for the study. The present work deals with carrying out kinetic studies of transesterification of jatropha oil using methanol and NaOH as catalyst. The result of the study provided the kinetic behavior of the transesterification reaction that could be helpful to choose the optimum condition for design of biodiesel reactor. In the present study a model of transesetrification reaction for biodiesel reaction has been developed and model has been simulated in *matlab/simulik.*

The objectives of this study were to study the behavior of transesterification reaction for Jatropha oil under changing reaction parameter and optimize the reaction condition for maximum yield.

1.7 OVERVIEW OF THE THESIS

The first chapter gives the overview of the energy scenario in India and world, renewable energy potential and status, literature review on biodiesel, R&D status of biodiesel in India is presented. Second chapter gives idea of biodiesel production technologies proposed as well as used in commercial production of biodiesel among these technologies biodiesel productions by base catalyzed transesterification is used commercially but it requires the low free fatty acid content as well as moisture free oils. But all nonedible oil contains high free fatty acid thus a two-step process acid catalyzed esterification followed by base catalyzed transesterification for this study. Third chapter gives the idea on experimental procedure starting from oil expelling to washing and drying of jatropha oil methyl ester and for kinetics study, sampling methodology and analysis methodology. This chapter also deals with the physical and chemical properties of oil and its ester and a kinetic model for transesterification of vegetable oil and simulation is also been done with the help of MATLAB. Result and discussion is being presented in chapter 4. Conclusion and recommendation is presented in fifth chapter.

1.7 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. Nonedible oils in India contain more FFA (2-12%) than edible oil and also FFA content of nonedible vegetable oil increases from 1-20% during three year of storage [6]. Looking at the importance of Biodiesel as alternate transport fuel in near future there is an urgent need to carryout considerable R&D on various aspects of production of resource, and biodiesel production in economically and technically viable manner.

TECHNOLOGY FOR BIODIESEL PRODUCTION

2.1 GENERAL

Fats and oils are composed of molecules called triglycerides. Each triglyceride is composed of three long-chain fatty acids of 8 to 22 carbons attached to a glycerol backbone. Biodiesel is composed of fatty acid chains that are chemically bonded to one methanol molecule. The glycerol molecules are almost completely removed from the final biodiesel product. Biodiesel is sometimes called fatty acid methyl esters or FAME. The glycerin byproduct has thousands of industrial chemical uses in common household products and foods. When the fatty acid chains break off the triglyceride, they are known as free fatty acids. Free fatty acids are desirable biodiesel feed stocks, but require different conversion processes compared to triglycerides.

2.2 FEED STOCKS FOR BIODIESL PRODUCTION

- Vegetable oil
- Animal fats and grease

2.2.1 CLASSIFICATION OF FEEDSTOCK

Biodiesel feedstocks are classified on the basis if their free fatty acid content as follows [47]:

(i) Refined oils, such as soybean or refined canola oil (FFA <1.5%)

(ii) Low free fatty acid yellow greases and animal fats (FFA<4%)

(iii) High free fatty acid greases and animal fats (FFA > 20%)

There are also other potential feedstocks available, namely trap and sewage grease etc.very high free fatty acid greases, who's FFA exceed 50%. The suitable technology needs to be developed before these feedstocks can be used for biodiesel production.

2.3 TECHNOLOGY FOR BIODIESEL PRODUCTION

Commercial biodiesel technologies can be grouped as follows:

(i) Base catalyzed transesterification with refined oils

(ii) Base catalyzed transesterification with low free fatty acid greases and fats

(iii) Acid esterification followed by transesterification of low or high free fatty acid greases and fats

There are basically two approaches for transesterification of vegetable oil for the production of biodiesel. The first is a catalytic one in which alcoholysis of vegetable oil by methyl or ethyl alcohol in presence of catalyst is carried out to produces biodiesel and glycerol. The second approach is the catalyst free process in which transesterification takes place at supercritical temperature and pressure using alcohol (supercritical methanol transesterification).

2.3.1. Catalytic transesterification:

2.3.1.1 Acid-Catalyzed Processes

Bronsted acids catalyze the transesterification process, preferably by sulfonic and sulfuric acids. These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring, typically, temperatures above 100 °C and more than 3 h to reach complete conversion. This process is more suitable for glycerides that have relatively high free fatty acid contents and more water. This process is generally best suited for low-grade material i.e. waste vegetable oil, olive oil etc. Pryde *et al.* showed that the methanolysis of soybean oil, in the presence of 1 mol% of H_2SO_4, with an alcohol/oil molar ratio of 30:1 at 65 °C, takes 50 h to reach complete conversion of the vegetable oil (> 99%), while the butanolysis (at 117 °C) and ethanolysis (at 78 °C), using the same quantities of catalyst and alcohol, take 3 and 18 h, respectively.

The alcohol/vegetable oil molar ratio is one of the main factors that influence the transesterification. An excess of the alcohol favors the formation of the products. On the other hand, an excessive amount of alcohol makes the recovery of the glycerol difficult, so that the ideal alcohol/oil ratio has to be established empirically, considering each individual process.

The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in fig.2.1, for a monoglyceride. However, it can be extended to di- and triglycerides[31]. The protonation of the carbonyl group of the ester leads to the carbocation II which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate III, which eliminates glycerol to form the new ester IV, and to regenerate the catalyst H^+.

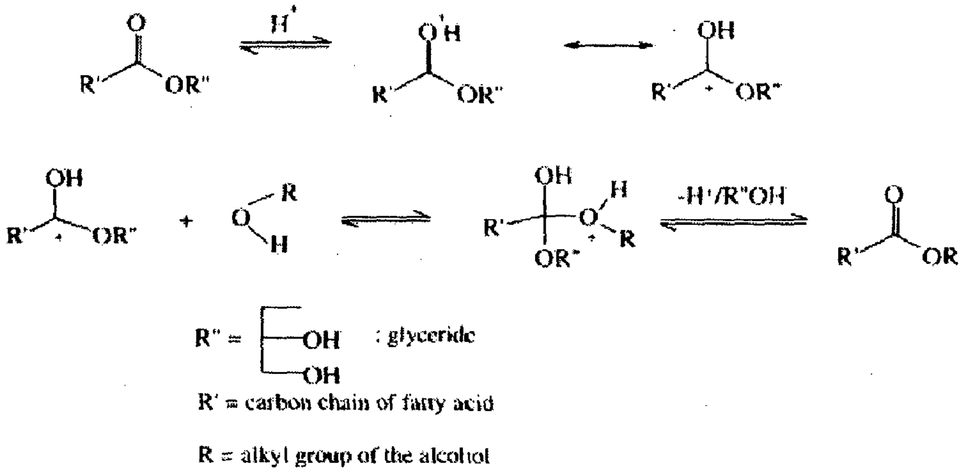


Fig. 2.1Mechanism of acid catalyzed transesterification [48].

According to this mechanism, carboxylic acids can be formed by reaction of the carbocation II with water present in the reaction mixture. This suggests that an acid-catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids, which reduce the yields of alkyl esters.

2.3.1.2 Base-Catalyzed Processes

Alkalis used for transesterification includes NaOH, KOH, carbonates, alkoxides such as sodium methoxide, sodium ethoxide etc. The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. Due to this reason, together with the fact that the alkaline catalysts are less corrosive than acidic compounds, industrial processes usually favor base catalysts, such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates. Thus most often used commercially. For base catalyzed transesterification purity (i.e. free fatty acid and moisture) of oil and water content of alcohol plays an important role. In this process if water is present in oil and alcohol then water causes a partial reaction change to saponification, which produces soap. The soap consumes catalyst and reduces the catalytic efficiency, as well as causing an increase in viscosity, the formation of gels, and difficulty in achieving separation of glycerol.

The mechanism of the base-catalyzed transesterification of vegetable oils is shown in fig 2.2. The first step (equation1) is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (equation2), from which the alkyl ester and the corresponding anion of the diglyceride are formed (equation3). The latter deprotonates the catalyst, thus regenerating the active species (equation4), Which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol.

Alkaline metal alkoxides (as CH_3ONa for the methanolysis) are the most active catalysts, since they give very high yields (> 98%) in short reaction times (30 min) even if they are applied at low molar concentrations (0.5 mol%). However, they require the absence of water, which makes them inappropriate for typical industrial processes[30]. Alkaline metal hydroxides (KOH and NaOH) are cheaper than metal alkoxides, but less active. Nevertheless, they are a good alternative since they can give the same high

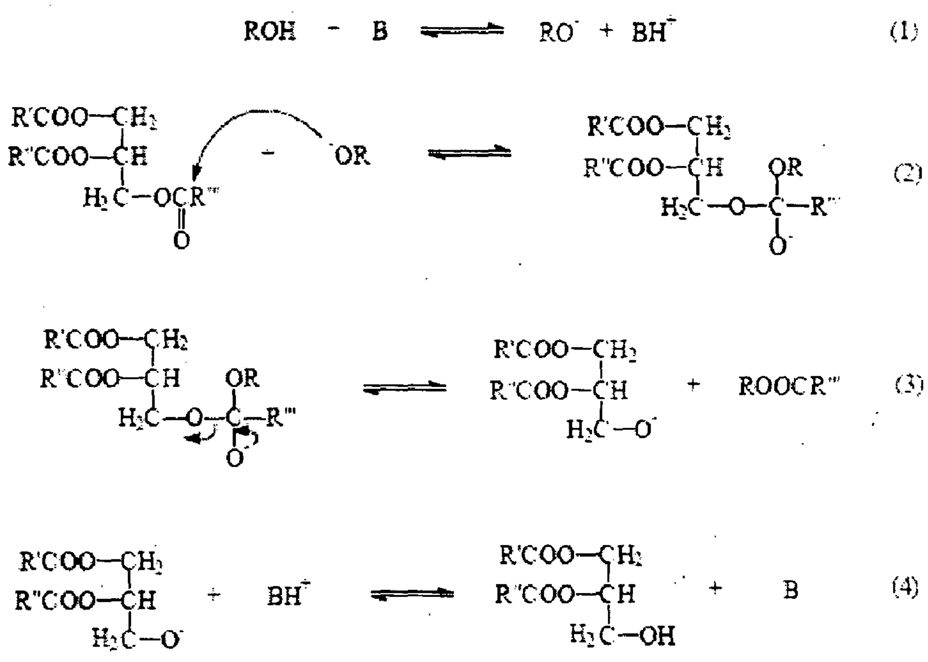
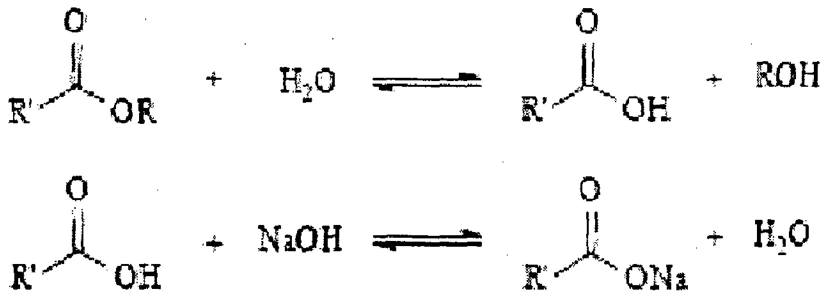


Fig.2.2 Mechanism of base catalyzed transesterification [49]

conversions of vegetable oils just by increasing the catalyst concentration to 1 or 2-mol%. However, even if a water-free alcohol/oil mixture is used, some water is produced in the system by the reaction of the hydroxide with the alcohol. The presence of water gives rise to hydrolysis of some of the produced ester, with consequent soap formation fig.2.3. This undesirable saponification reaction reduces the ester yields and considerably difficults the recovery of the glycerol due to the formation of emulsions.



R'=carbon chain of fatty acid

R=alkyl group of alcohol

Fig 2.3 Saponification reaction of the produced fatty acid alkyl ester [49]

Potassium carbonate used in a concentration of 2 or 3 mol% gives high yields of fatty acid alkyl esters and reduces the soap formation. This can be explained by the formation of bicarbonate instead of water fig.2.4, which does not hydrolyse the esters.

$$K_2CO_3 + ROH \rightleftharpoons ROK + KHCO_3$$

R=alkyl group of alcohol

Fig .2.4 reaction of potassium carbonate with the alcohol [49]

2.3.1.3 Lipase-Catalyzed Processes

Although chemical transesterification using an alkali catalysis process gives high conversion levels of triglyceride to their corresponding esters in short retention time, the reaction has several drawbacks: it is energy intensive, recovery of glycerol is difficult, catalyst has to be removed from the product, alkaline waste water treatment, and free fatty acid and water interfere with the reaction.

Due to their ready availability and the ease with which they can be handled, hydrolytic enzymes have been widely applied in organic synthesis. They do not require any coenzymes, are reasonably stable, and often tolerate organic solvents. Their potential for regioselective and especially for enantioselective synthesis makes them valuable tools. Although the enzyme-catalyzed transesterification processes are not yet commercially developed. Gupta et al [41] worked on transesterification reaction of Jatropha oil in a solvent-free system to produce biodiesel and three different lipases (Chromobacterium viscosum, Candida rugosa, and Porcine pancreas) were screened but only lipase from Chromobacterium viscosum was found to give appreciable yield. Immobilization of lipase (Chromobacterium viscosum) on Celite-545 enhanced the biodiesel yield to 71% from 62% yield obtained by using free tuned enzyme preparation with a process time of 8 h at 40 ^{0}C. Further addition of water to the free (1%, w/ v) and immobilized (0.5%, w/ v) enzyme preparations enhanced the yields to 73 and 92%, respectively. Immobilized Chromobacterium viscosum lipase can be used for ethanolysis of oil. It was seen that immobilization of lipases and optimization of transesterification conditions resulted in adequate yield of biodiesel in the case of the enzyme-based process. The common aspects of these studies consist in optimizing the reaction conditions (solvent, temperature, pH, type of microorganism which generates the enzyme, etc) in order to establish suitable characteristics for an industrial application. However, the reaction yields as well as the reaction times are still unfavorable compared to the base-catalyzed reaction systems.

2.3.2 Noncatalytic or Supercritical Methanol Method

The transesterfication of triglycerides by supercritical methanol (SCM), ethanol, propanol and butanol has proved to be the most promising process. A non-catalytic biodiesel production route with supercritical methanol has been developed that allows a simple process and high yield because of simultaneous transesterification of triglycerides and methyl esterification of fatty acids. The basic idea of supercritical treatment is based on the effect of the relationship between pressure and temperature upon the thermophysical properties of the solvent, such as dielectric constant, viscosity, specific weight and polarity. The transesterification of sunflower oil was investigated in SCM and supercritical ethanol at various temperatures (475–675 K). The most important variables affecting the methyl ester yield during the transesterification reaction are the molar ratio of alcohol to vegetable oil and the reaction temperature. The variables affecting the ester yield during the transesterification reaction are the molar ratio of alcohol to vegetable oil, reaction temperature, reaction time, water content and catalyst. It was observed that increasing the reaction temperature, especially to supercritical temperatures, had a favorable influence on ester conversion. The stoichiometric ratio for the transesterification reaction requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid ester and one mole of glycerol. Higher molar ratios result in greater ester production in a shorter time. The vegetable oils were transesterified with 1:6–1:40 vegetable oil–alcohol molar ratios in catalytic and supercritical alcohol conditions.

When a fluid or gas is subjected to temperatures and pressures in excess of its critical point, there are a number of unusual properties exhibited. There no longer is a distinct liquid and vapor phase, but a single, fluid phase present. Solvents containing a hydroxyl (OH) group, such as water or primary alcohols, take on the properties of super-acids.A non-catalytic approach is the use of a high (42:1) alcohol to oil ratio. Under supercritical conditions (350 to 400 °C and > 80 atm or 1200 psi) the reaction is complete in about 4 minutes. Capital and operating costs can be more expensive, and energy consumption higher. An intriguing example of this process has been demonstrated in Japan, where oils in a very large excess of methanol have been subjected to very high temperatures and pressures for a short period of time. The result is a very fast (3 to 5 minute) reaction to form esters and glycerol. The reaction must be quenched very rapidly so that the products do not decompose. The reactor used in the work to date is a 5 ml cylinder that is dropped into a bath of molten metal, and then quenched in water.Clearly, while the results are very interesting, the scale-up to a useful process may be quite difficult. Figure 3 depicts one conception of a configuration for a supercritical esterification process.

The stoichiometric ratio for the transesterification reaction requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid ester and one mole of glycerol. Higher molar ratios result in greater ester production in a shorter time. The

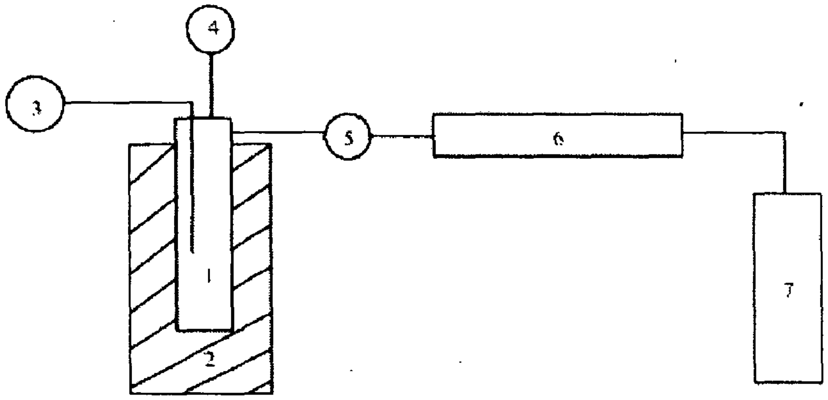


Fig. 3.2 Supercritical methanol transesterification system. (1) Autoclave, (2) Electrical furnace, (3) Temperature control monitor, (4) Pressure control monitor, (5) Product exit valve, (6) Condenser, (7) Product collecting vessel [28].

vegetable oils were transesterified at 1:6–1:40 vegetable oil-alcohol molar ratios in catalytic and supercritical alcohol conditions [28]. A summary of the advantages and disadvantages of each technological possibility to produce biodiesel could be found in Table2.1.

Table 2.1. Comparison of the different process for the production of Biodiesel [50]

Sl.no	**Variable**	**Alkali catalyzed reaction**	**Lipase catalyzed reaction**	**Supercritical alcohol method**	**Acid catalyzed method**
1	Reaction temperature (°C)	60–70	30–40	239–385	55–80
2	Free fatty acid in raw materials	Saponified products	Methyl esters	Esters	Esters
3	Water in raw materials	Interference with reaction	No influence	No influence	Interference with reaction
4	Yield of methyl esters	Normal	Higher	Good	Normal
5	Recovery of glycerol	Difficult	Easy		Difficult
6	Purification of methyl esters	Repeated washing	None		Repeated washing
7	Reaction time	1-2 h	48 h	0.067 h	8-48 h
8	Production cost of catalyst	Cheap	Relatively expensive	Medium	Cheap

Table 2.1 states the comparison of process, in alkali-catalyzed reaction free fatty acid present in vegetable oil /animal fats is converted into soap or saponified product and also

water interferes with the reaction. In lipase catalyzed reaction though doesn't interfere with reaction but suitable lipase is difficult to find because of changing pH of reaction medium thus replacement of lipase is costly. Though supercritical methanol method has no influence of water and yield of methyl ester if higher but this method requires high temperature and pressure. Thus maintaining high temperature adds extra cost on cost of production of biodiesel by this method. Though acid catalyzed method require 55-80°C but this method is quite slow and takes more time to complete the reaction.

2.4 FACTORS AFFECTING BIODIESEL PRODUCTION

2.4.1 Free Fatty acid and moisture:

The free fatty acid and moisture content are key parameters for determining the viability of the vegetable oil transesterification process. To carry the base catalyzed reaction to completion; a free fatty acid (FFA) value lower than 2% for oil is needed. The higher the acidity of the oil, smaller is the conversion efficiency. Both, excess as well as insufficient amount of catalyst may cause soap formation

2.4.2 Catalyst, type and concentration:

Catalysts used for the transesterification of triglycerides are classified as alkali, acid, enzyme or heterogeneous catalysts, among which alkali catalysts like sodium hydroxide, sodium methoxide, potassium hydroxide, potassium methoxide are more effective. If the oil has high free fatty acid content and more water, acid catalyzed transesterification is suitable. The acids could be sulfuric acid, phosphoric acid, hydrochloric acid or organic sulfonic acid. Methanolysis of beef tallow was studied with catalysts NaOH and NaOMe. Comparing the two catalysts, NaOH was significantly better than NaOMe. As a catalyst in the process of alkaline methanolysis, mostly sodium hydroxide or potassium hydroxide have been used, both in concentration from 0.4 to 2% w/w of oil.

2.4.3 Molar ratio of alcohol to oil and type of alcohol:

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid alkyl esters and one mole of glycerol. However, transesterification is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction to the right. For maximum conversion to the ester, a molar ratio of 6:1 should be used. The molar ratio has no effect on acid, peroxide, saponification and iodine value of methyl esters. However, the high molar ratio of alcohol to vegetable oil interferes with the separation of glycerin because there is an increase in solubility. When glycerin remains in solution, it helps drive the equilibrium to back to the left, lowering the yield of esters.

2.4.4 Reaction temperature and time:

The conversion rate increases with reaction time. Transesterification can occur at different temperatures, depending on the oil used. For the transesterification of refined oil with methanol (6:1) and 1% NaOH, the reaction was studied with three different temperatures [20]. After 0.1 h, ester yields were 94, 87 and 64% for 60, 45 and 32 °C, respectively. After 1 h, ester formation was identical for 60 and 45 °C runs and only slightly lower for the 32 °C run. Temperature clearly influenced the reaction rate and yield of esters [38].

2.4.5 Mixing Intensity:

Mixing is very important in the transesterification reaction, as oils or fats are immiscible with sodium hydroxide–methanol solution. Once the two phases are mixed and the reaction is started, stirring is no longer needed. Initially the effect of mixing on transesterification of beef tallow was study by Ma et al. [52]. No reaction was observed without mixing and when NaOH–MeOH was added to the melted beef tallow in the reactor while stirring, stirring speed was insignificant. Reaction time was the controlling factor in determining the yield of methyl esters. This suggested that the stirring speeds investigated exceeded the threshold requirement of mixing.

2.4.6 Effect of using organic solvent (if any):

The methoxide base catalyzed methanolysis of soybean oil at 40 °C (methanol–oil molar ratio 6:1) shows that to form methyl esters proceeds approximately more slowly than butanolysis at 30 °C. This is interpreted to be the result of a two phase reaction in which methanolysis occurs only in the methanol phase. Low oil concentration in methanol causes the slow reaction rate; a slow dissolving rate of the oil in methanol causes an initiation period. Intermediate mono- and di-glycerides preferentially remain in the methanol, and react further, thus explaining the deviation from second order kinetics. The same explanations apply for hydroxide ion catalyzed methanolysis.

In order to conduct the reaction in a single phase, cosolvents like tetrahydrofuran, 1,4-dioxane and diethyl ether were tested. Although, there are other cosolvents, initial study was conducted with tetrahydrofuran. At the 6:1 methanol–oil molar ratio the addition of 1.25 volume of tetrahydrofuran per volume of methanol produces an oil dominant one phase system in which methanolysis speeds up dramatically and occurs as fast as butanolysis. In particular, THF is chosen because its boiling point of 67 °C is only two degrees higher than that of methanol. Therefore at the end of the reaction the unreacted methanol and THF can be co-distilled and recycled [32]

There are multiple operating options available for making biodiesel. Many of these technologies can be combined under various conditions and feedstocks in an infinite number of ways. The technology choice is a function of desired capacity, feedstock type and quality, alcohol recovery, and catalyst recovery. The dominant factor in biodiesel production is the feedstock cost, with capital cost contributing only about 7

% of the final product cost. However, some reaction systems are capable of handling a variety of feedstocks and qualities, while the others are not. Also, the different approaches to the esterification process result in quite different operating requirements, different water use requirements, and different operating modes. In general, smaller capacity plants and variable feedstock quality suggest use of batch systems. Continuous systems generally lead the operation on a 24/7 basis, requiring larger capacities to justify larger staffing requirements and require a more uniform feedstock quality.

For present work, two-step process i.e. acid catalyzed esterification followed by base catalyzed transesterification was selected 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.

There are basically two approaches for the study the kinetics of transesterification reaction. The first is experimental which requires a lot of data on changing concentration with time under different reaction condition and attempt to establish the order of reaction. The second is theoretical, propose a set of mechanisms and then derive the rate equations using the law of mass action and use Arrhenius reaction to correlate the rate constant with time. In fact both approaches required establishing a predictive model. In the present study first approach was tried but due to unavailability of standard chemicals and reagents for analysis of sample and second approach was adopted. Though no work on kinetics of jatropha oil was done therefore a model was developed, which can predict the behavior of transesterification reaction for any vegetable oil under varying reaction condition and to validate this model required data was extracted from the prior work on reaction kinetics for vegetable oil for production of esters.

KINETICS OF TRANSESTERIFICATION FOR BIODIESEL PRODUCTION

3.1 GENERAL

Transesterification reactions are reversible and take place in three stages. The kinetics study of transesterification reaction has been carried out in this study to investigate the behavior of reaction with respect to varying condition of reaction parameter and to optimize the reaction conditions. Up till now only batch process is being used for the production of biodiesel on commercial scale, which directly affect the cost of the resulting fuel. Darnoko and cheryan [26] studied the kinetics of transesterification of palm oil and reported that reaction was initially first order but after sometime, it attained first order and then zero order. Noureddini & Zhu [23] studied the kinetics of transesterification of soybean oil and reported that it is pseudosecond order reaction. Saka and Kusiana [28] found that reaction of non-catalytic transesterification of rapeseed was found to be of first order. The literature reveals that very little work is reported on the transesterification of vegetable oil and this ahs been reason of selection of the present work which aims to study the kinetics

3.1.1 STEPS FOR BIODIESEL PRODUCTION

There is following Steps for biodiesel production:

A. **EXTRACTION OF VEGETABLE OIL**

1. Dehulling of seed
2. Expelling of oil from kernel
3. Filteration of oil

B. PRETREATMENT OF VEGETABLE OIL

1. Removal of excess moisture

2. Determination of free fatty acid

3. Esterification/removal of Free Fatty Acid

C. TRANSESTERIFICATION OF JATROPHA OIL

1. Preperation of alcohol and catalyst mixture

2. Heating of oil as well as alcohol& catalyst mixture at desired temperature.

3. When desired temperature is reached then catalyst &alcohol mixture is poured into oil slowly and agitator/stirrer was switched on, kept on throughout the reaction period.

D. REFINING OF PRODUCT/BYPRODUCT

1. Seperation of ester and glycerol: separation of ester and glycerol form reaction product id being done 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.

3.2 EXPERIMENTAL PROCEDURE

3.2.1 COLLECTION OF SEED

The Jatropha seed were collected from the Uttaranchal Biofuel board, Dehradun, its godown was located at Sahaspur that was30km away from Dehradun. The board had

opha in various part and acting as a nodal agency for
about cultivation of jatropha plant, production and use of bodies in the
of single seed was weighed, 750 mg and 60% of seed was kernel. The c
seed was white patch in light dark. Jatropha seed is shown in fig 3.1.

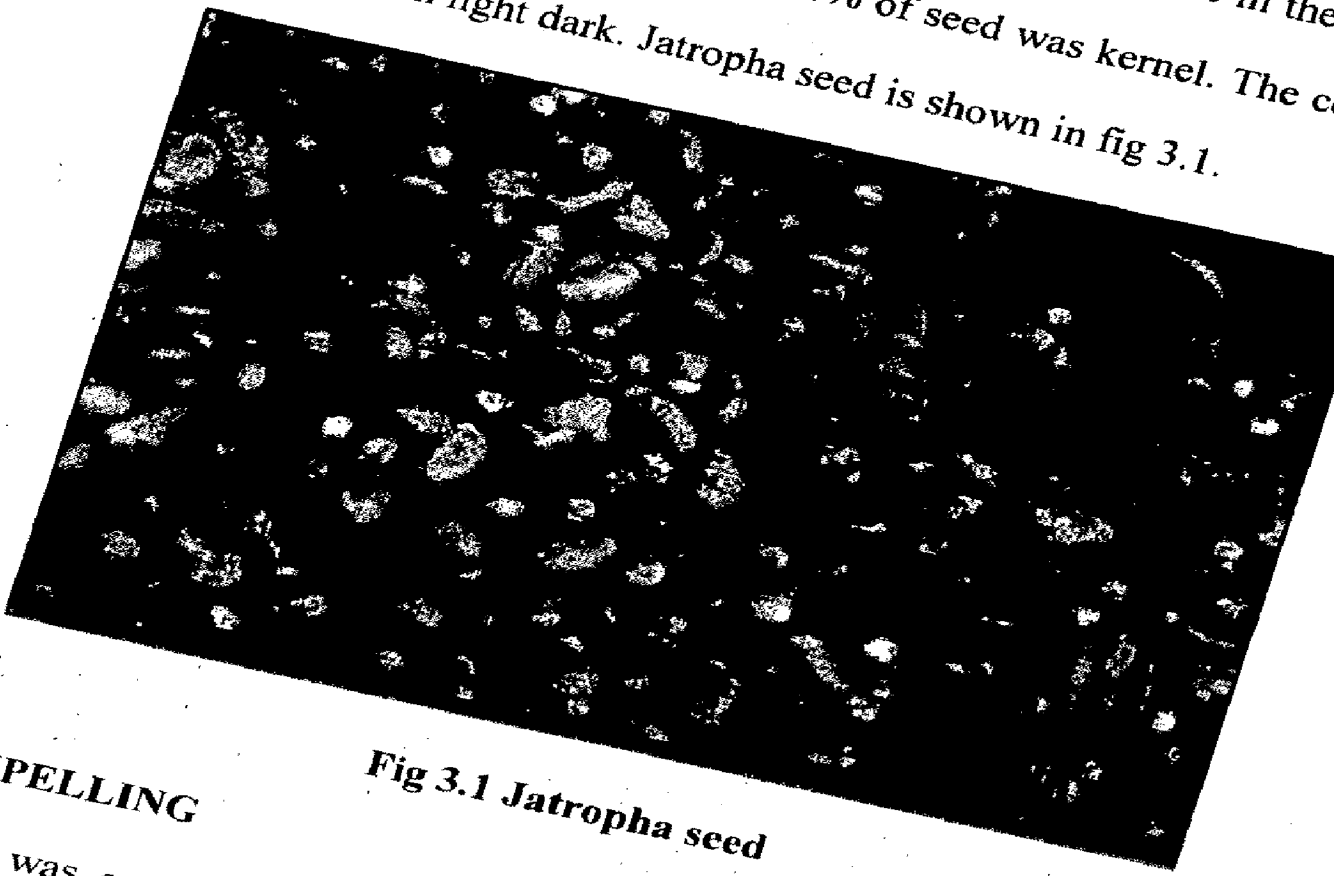


Fig 3.1 Jatropha seed

3.2.2 OIL EXPELLING

The oil was expelled from the seed at locally available oil expeller, which is
nerally used for expelling mustard oil, in the market. The oil was expelled three times
e expeller, during expelling; small quantity of water (about250 ml for 15 kg) was
. Major portion of additional water was evaporated in the form of steam. The
d oil was left to settle for 24 hours so that present solid particles could be settled
fter that the upper layer was taken out slowly so that settled particle could not
the oil and complete oil was filtered to remove even smaller solid particle (if
tered oil was dried in vacuum evaporator to remove moisture. The oil yield
esser than the yield of jatropha oil in literature (30-40%). The colour of oil
n. Then the oil was kept in airtight container made of tin to avoid the

rancidity of oil and this oil was used for the study of transesterification reaction. The deoiled cake cannot be used directly for animal feed due to its toxicity.

3.2.3 MATERIALS

As mentioned earlier jatropha curcas seed was collected from Uttaranchal Biofuel Board and expelling of oil was done at local market. Free Fatty Acid of jatropha oil is determined according to American Oil Chemists' Society (AOCS) method i.e. titration method. The acid value of jatropha oil was 6.1mgKOH/g of oil and corresponding free fatty acid was 3.5 % which was higher than the permissible value for base catalysed transesterification (i.e.<2 %(w/w)[57]. Methyl alcohol and sodium methoxide of analytical reagent grade were used to the study. The gas chromatograph (Model no. MICHRO 9100) was used for the analysis of reaction products. The standard chemicals of Sigma Aldrich Germany were used for the analysis of reaction products i.e. yield of various constituents.

3.2.4 REACTION CONDITIONS

Experiments were designed to determine the reaction rate constant. A molar ratio of alcohol to jatropha oil were varied from 3:1to 9:1and the temperature dependency of the reaction rate constants at different temperature; at different temperature 30^0 C, 40^0 C, 50^0 C, 60^0 C and 70^0 C was studied. All reactions were carried out at atmospheric pressure

3.2.5 APPARATUS

Transesterfication reactions were carried out in a 1.5L four-necked flask made of stainless steel equipped with a reflux condenser, a thermometer a sampling port and motored stirrer. The reactor was immersed in a constant temperature water bath equipped with a temperature controller, capable of maintaining the temperature within ± 0.20C.

Agitation was provided by a stirrer, which could be set at any speed throughout the experiment. The experiment setup is shown in figure 3.2.

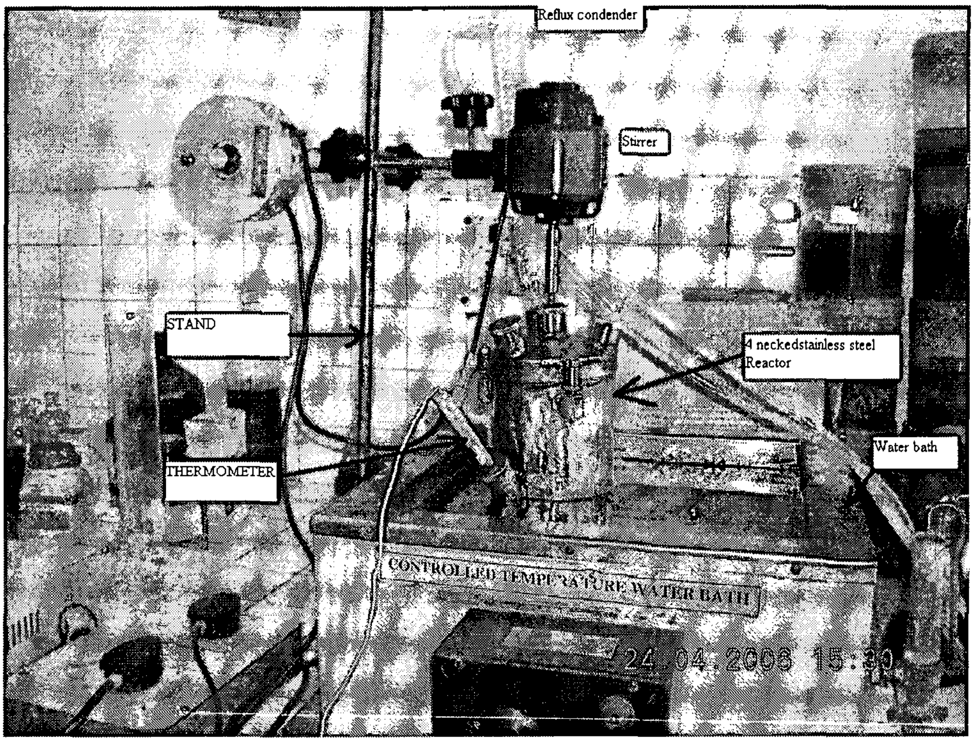


Fig 3.2 Experimental set up

3.2.6 PROCEDURE

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

Acid value (AV) is an important indicator of vegetable oil quality. AV is expressed as the amount of KOH (in milligrams) necessary to neutralize 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 to a visually determined phenolphthalein endpoint. Solvent was prepared by mixing diethyl ether with ethanol (2:1(v/v)) and phenolphthalein indicator solution was prepared using 1% phenolphthalein in 95% ethanol. Then oil was dissolved in the solvent and standard (0.1M) KOH solution. After that 50 ml 0f the solution was extracted and neutralized by 0.1M standard KOH solutions till the pink color persisted for at least 30 second by 1%of phenolphthalein. Free Fatty Acid (FFA content) of jatropha oil was determined as 3.5%while the acid value of jatropha oil as 6.1mgKOH/g of oil since FFA content is more than 0.5% so acid catalyzed esterification followed by transesterification was used for production of biodiesel.

(B) Esterification:

In the esterification process, 1000 gm of Jatropha oil was taken in the reactor and heated at 45^0C, 70g of methanol (2.25g per gram of FFA) and 1 ml H_2SO_4 (0.05 g per gram of FFA) solution was added and mixed with constant stirring and reaction mixture was stirred and maintained at 40^0C for 1 hour and the product is esterified oil which contains low FFA (<0.5%)

(C) Transesterification:

The reactor was initially filled with 300ml of esterified jatropha oil and heated to desired temperature. A known amount of NaOH catalyst was dissolved in the known amount of methanol and heated separately to the desired temperature. The heated sodium methoxide was then added slowly in the reactor to avoid the loss of methanol due to evaporation. The weight of one mole of jatropha oil was determind from the calculated average molecular weight of different fatty acid of jatropha oil. As the reactions proceed, 1 ml Samples were withdrawn at prespecified time interval. The frequency of sample withdrawn varied was dictated by reaction condition. Reactions at higher temperature, molar ratio and mixing intensity required more frequent sampling at the beginning of reaction. As the reaction temperature and mixing intensity were decreased, an initial delay in the reaction was experienced and sample collection was delayed accordingly. Samples were withdrawn at 5-minute interval at the beginning of reaction and at 10 to 15

minute interval thereafter. Samples were collected in 30 ml bottles and quenche
ice bath at about 0^0C,properly capped and kept for further analysis and the rem
reaction mixture in the reactor was poured into separating funnel, where separation i
layer appears, the upper layer was jatropha oil methyl ester and lower was glycero
first, lower layer was separated from separating funnel.then upper layer was poured i
another vessel.

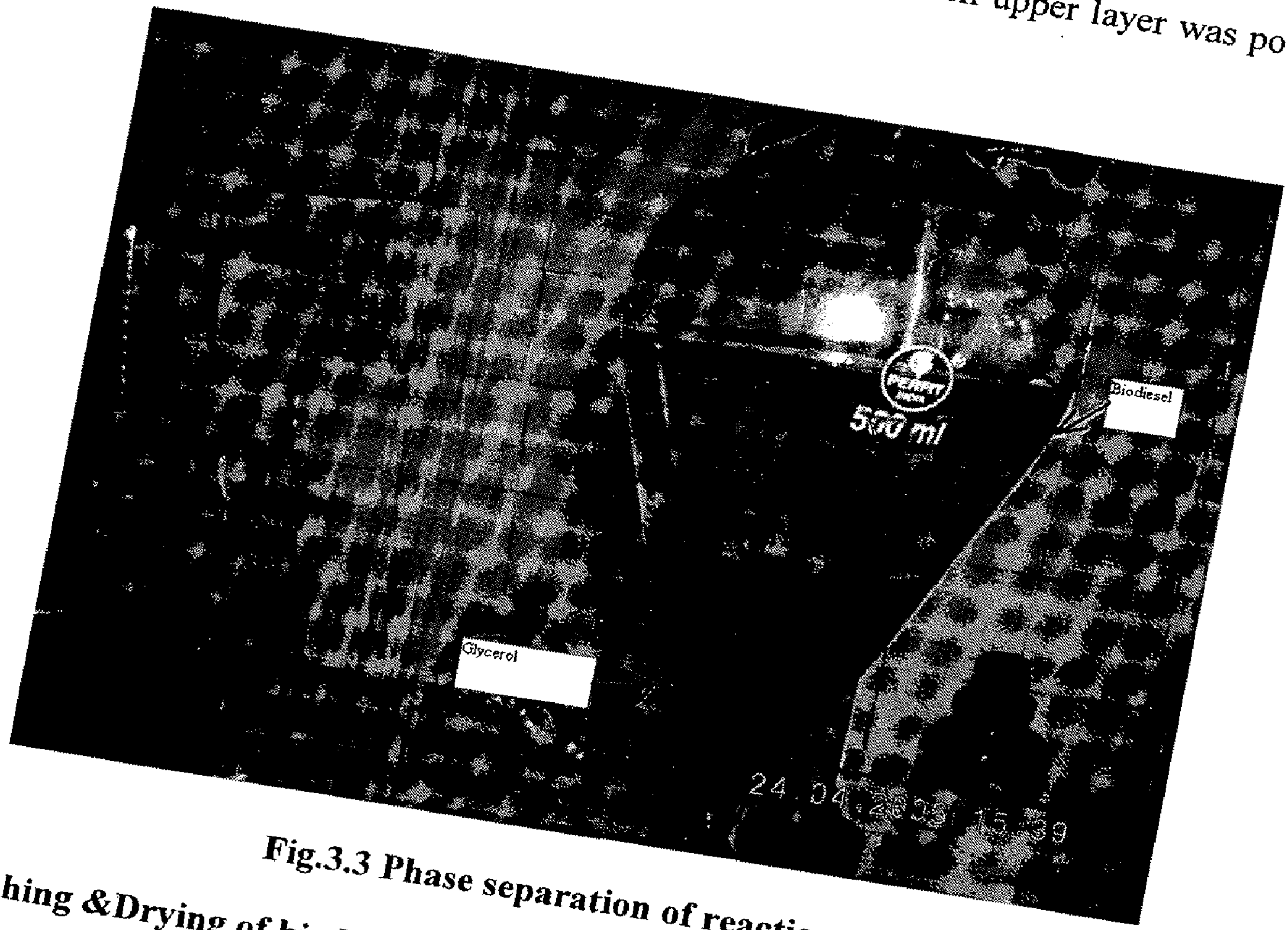


Fig.3.3 Phase separation of reaction product

(D) Washing &Drying of biodiesel

The aim of washing of ester is to remove /separate the FAME from glycerol,
methanol and catalyst. Although separation using a gravity settler was done but complete
eparation was not achieved, consequently an agitation washing was performed thrice
ith warm distilled water (temperature about 45 ^{0}C). During first washing emulsion of
ME with water of milky white colour was formed and after 20-minute layer separation
ears upper layer was ester and lower one was water as per their density. The upper

layer was separated out and this process was repeated thrice or even four times with agitation till the lower layer does not appear clean water. The washing of biodiesl (jatropha oil methyl ester) is shown in Figure and after washing esters was looking hazy due to presence of water .in order to remove water, the biodiesel was dried in vacuum evaporator till the ester become clear, light yellow.

3.2.5 Safety

Care should be taken to protect the eye from the vapors to avoid inhalation of vapors (if any) and to make use of proper gloves and apron etc. Methanol can cause blindness and death. Sodium hydroxide can cause severe burns and death. Reactor should be closed to the atmosphere, with no fumes escaping. All methanol containers should be kept tightly closed to prevent water absorption from the air.

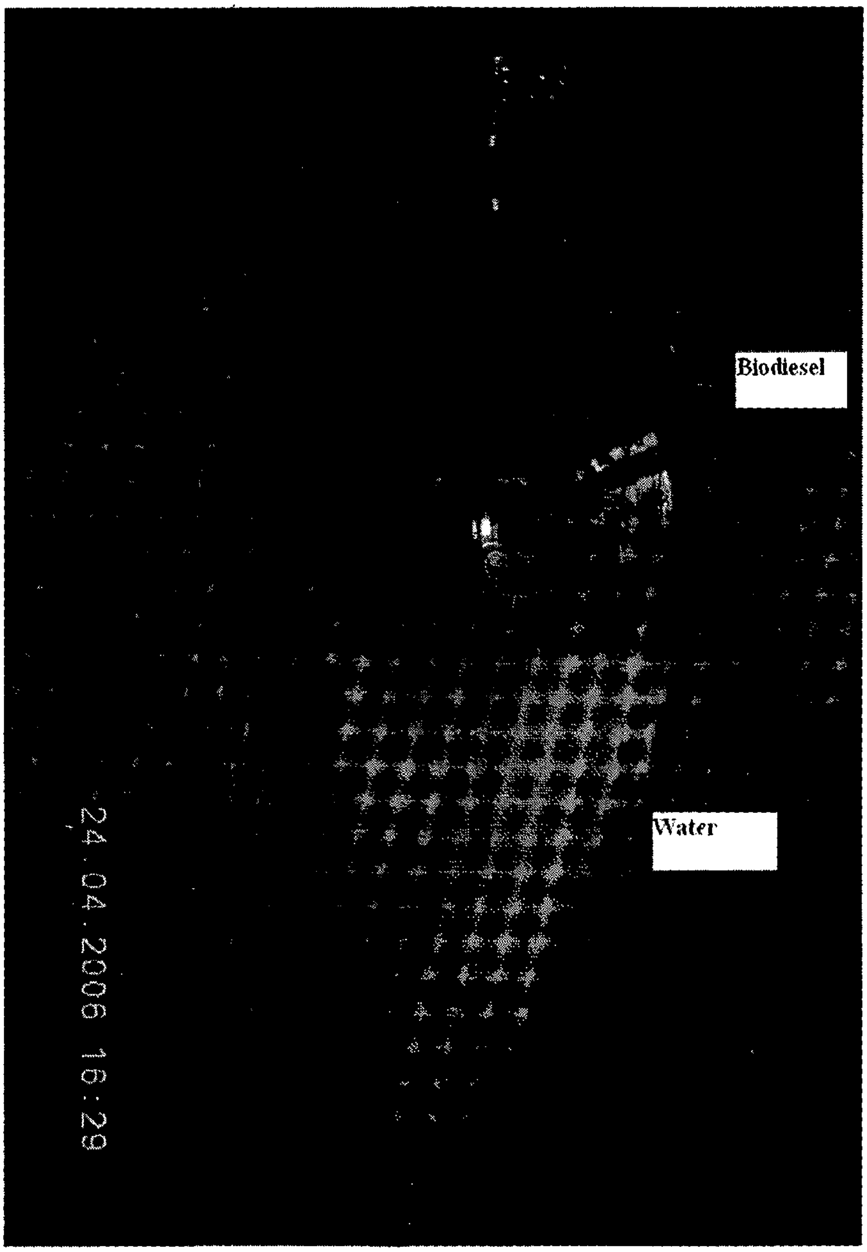


Fig.3.3 Washing of biodiesel

3.2.6 Physical and chemical properties of Jatropha oil

Some fuel properties of jatropha oil as well as its methyl ester were determined in laboratory and presented in table3.1.

Table 3.1 Physical and chemical properties of Jatropha oil

Sl.no.	Properties	Literature[10,48]		Present work	
		Jatropha oil	Biodiesel	Jatropha oil	Biodiesel
1	Density (kg/m^3) at 15^0C	917-923	889	912	887
2	Kinamatic viscosity (mm^2/s)	52.6	4.84	55	5.5
3	Gross calorific value (MJ/kg)			39.2	39.83
4	Flash point (^0C)	240	192	239	184
5	Acid value (mgKOH/g of sample)	1.0-38	0.24	7.5	0.31
6	Free Fatty acid (%)	3.095	0.249	3.8	N.A
7	Saponification Number	188-198	-	197.7	
8	Iodine value	90.8-112.5	-	98.24	
9	Cetane number	52.31	51	51.7	51.7

The saponification number (SN), Iodine value (IV) were calculated from fatty acid methyl ester composition of jatropha oil using following equation.

$$SN=\sum\frac{(560\times A_i)}{MW_i} \quad (1)$$

$$IV=\sum\frac{(254\times D\times A_i)}{MW_i} \quad (2)$$

Where A_i is the percentage is the number of double bonds and MW_i is the molecular mass of each component.

CN of fatty acid methyl ester was calculated from equation (3)

$$CN=46.3+5458/SN-0.225\times IV \quad (3)$$

3.2.7 Fatty acid analysis of Jatropha oil

2 ml of filtered oil was taken and 2 ml of solution containing BF_3, CH_3OH and toluene (1:1:1) was mixed and heated at 70^{0}C for 45minutes on heating plate after that 1 ml distilled water and 2ml of hexane was added and shaked well till two layer was formed then upper layer was separated out and heated on plate to concentrate the sample till it became 2 drop. The samples were injected into Gas Chromatography (MICHRO 9100) of GC laboratory of AHEC, IIT Roorkee, using Chrompack TAP capillary column 25m x 0.25mm (J and W Scientific, Köln, Germany) and auto injector. The carrier gas was nitrogen maintained at 4kg/cm^2 Air and hydrogen was maintained at 3kg/cm^2 and 2 kg/cm^2 respectively. The temperature was programmed as follows: for oven 1 initial temperature was 130°C for 5 min and then temperature increased to 230°C at 4°C per min; injector port temperature was 130 °C and flame ionization detector (FID) temperature was kept at 250°Cand a run time was 30 minutes. A chromatogram showing the retention time of different fatty acids present in jatropha oil is shown in

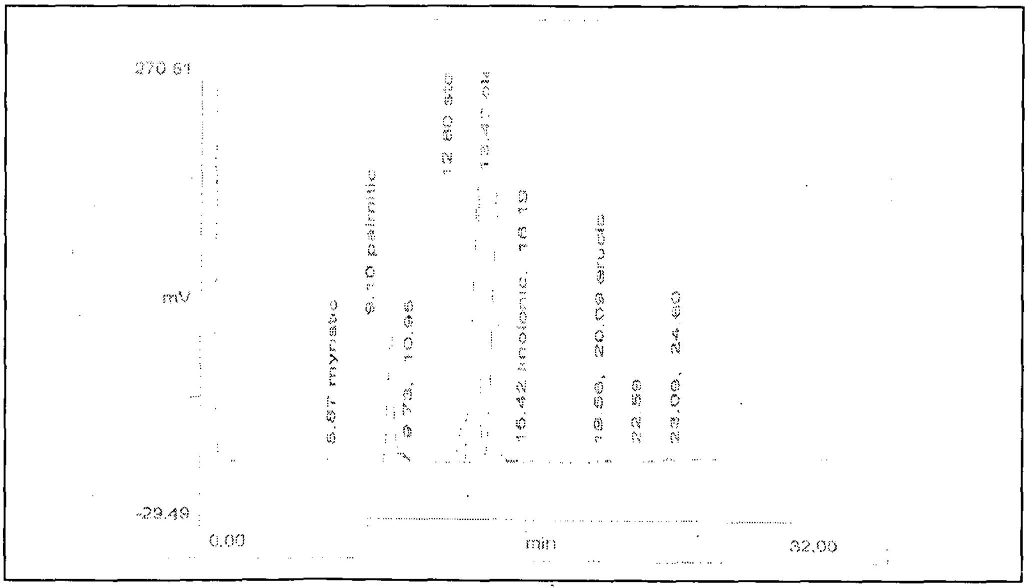


Fig.3.4 Retention time of different fatty esters of Jatropha oil

Table 3.2 Fatty acid composition of jatropha oil

Sl. No.	**Fatty acid**	**Composition (in %)**	
		Literature [10]	**Present work**
1	Myristic acid	0.38	0.0085
2	Palmitic acid	16.0	16.9952
3	Stearic acid	6.7	5.15
4	Oleic acid	42-43.5	42.2182
5	Linoleic acid	33-34.4	34.5575
6	Linolenic acid	>0.80	-
7	Arachidic acid	0.20	0.02

Table 3.2 states that the major constituent oleic acid, followed by linolenic acid followed by palmitic acid and stearic acid these fatty acid analysis also gives the idea about the saponification number ,iodine value and cetane number, which was calculated using equation (1),(2) and (3) and presented in table 3.1

Table 3.3 Kinetic data and activation energy at 50 ^{0}C from literature [23, 26]

Sl.no.	**Literature [23]**		**Literature [26]**		**Reactions**	**Rate constant**
	k	**Ea**	**k**	**Ea**		
1	0.050	13145	0.018	14.7	TG→DG	k2p
2	0.110	9932	-	-	DG→TG	k2rp
3	0.215	19860	0.036	14.2	DG→MG	k4p
4	1.228	14639	-	-	MG→DG	k4rp
5	0.242	6421	0.112	6.4	MG→E	k6p
6	0.007	9588	-	-	E→MG	k6rp
7	0.0002216	0	0.0002216	0	E→A	k8
8	0.005726	33032	0.005726	33032	TG→A	k9
9	0.012456	33032	0.012456	33032	DG→A	k10
10	0.007757	33032	0.007757	33032	MG→A	k11

3.6 Kinetic modeling of transesterification reaction

There are two complementary approaches to establishing a kinetic model for a given set of reactions. The first is empirical (experimental) take a lot of data and attempt to establish the order of reaction. The second is theoretical, propose a set of mechanisms and then derive the rate equations using the law of mass action. In fact both approaches required establishing a predictive model. The best theory requires data to validate it and a model based purely on fitting of empirical data cannot be used to predict outcomes outside of the range of experiment.

Assumptions for development of kinetic model are:

1. The concentration of free fatty acid is negligible.
2. Of all the possible reactions only two proceed to form products:

   The alcoholysis of triglycerides (TG, DG, MG) and the saponification of TG, DG, MG
3. All of the isomers of TG, DG, MG and E proceed at the same rate, with the same mechanism.
4. Alcoholysis is catalyzed by OH^- or RO^- ions. Concentrations of OH^- or RO^- ions are much smaller than those of TG and ROH.

The reactions involved in biodiesel production are

Formation of alkoxide:

$$ROH + OH^- \xrightarrow{k1} RO^- + H_2O \qquad (1)$$

Alcoholysis:

$$TG + RO^- \leftrightarrow DG^- + E \qquad (2)$$

$$DG^- + ROH \leftrightarrow DG + RO^- \qquad (3)$$

$$DG + RO^- \leftrightarrow MG^- + E \quad (4)$$

$$MG^- + ROH \leftrightarrow MG + RO^- \quad (5)$$

$$MG + RO^- \leftrightarrow GL^- + E \quad (6)$$

$$GL^- + ROH \leftrightarrow GL + RO^- \quad (7)$$

Saponification:

$$E + OH^- \xrightarrow{k8} ROH + A \quad (8)$$

$$TG + OH^- \xrightarrow{k9} DG + A \quad (10)$$

$$DG + OH^- \xrightarrow{k10} MG + A \quad (11)$$

$$MG + OH^- \xrightarrow{K11} GL + A \quad (12)$$

Where A is the soap of the corresponding fatty acid chain.

The above reactions are assumed to be elementary, thus obeying the law of mass action (LMA). Straightforward application of LMA produces thirteen differential equations describing the thirteen species present in the reactions. The number of differential equation and their complexity can be reduced through simplifying assumptions. There are two common approaches. The rate limiting step assumption holds that the slowest reaction controls the rate of conversion, and that faster reactions can be assumed to have reached equilibrium. The steady state assumption holds that certain species react so much faster than others that their rate of change is essentially zero. The steady state assumption is the weaker of the two. Its application results in an algebraic equation, which contains the rate constants for every reactions in which the species in question participates. The rate limiting step assumption, on the other hand, leads to a set of equilibrium conditions that typically contains fewer terms for a given species.

Reaction (!), (3), (5) and (7) in equation (), which are simple exchanges of hydrogen atoms, proceed much faster than the others, that is

K2, k2r<< k3, k3r

K4, k4r<< k5, k5r (13)

K6, k6r<< k7, k7r

K3, k3r, k5, k5r, k7, k7r<< k8, k9, k10, k11

It is therefore follows that

$$\frac{d[H2O]}{dt} = \frac{d[RO^{-}]}{dt} = \frac{d[DG^{-}]}{dt} = \frac{d[MG^{-}]}{dt} = \frac{d[GL^{-}]}{dt} = 0 \qquad (14)$$

Eliminating small terms and substituting the equilibrium relations into the rate equations for the corresponding species, we obtain Komers normalizes the remaining species by the initial concentrations of triglyceride and alcohol, as follows:

TG= [TG]/a, where a= $[TG]_0$

DG= [DG]/a,

MG= [MG]/a,

A= [A]/a, (15)

OH= $[OH^{-}]$/a,

W= $[H_2O]$/a,

ROH= [ROH]/b, where b= $[ROH]_0$,

E= [E]/b,

The resulting differential equations are:

$$\frac{dTG}{dt} = -b.OH.\left(k_{2p}.TG.ROH - k_{2rp}.DG.E\right) + a.OH..k_9.TG \qquad (16a)$$

$$\frac{dDG}{dt} = -b.OH\left(-k_{2p}.TG.ROH + k_{2rp}.DG.E + k_{4p}.DG.ROH - k_{4rp}.MG.E\right) + a.OH.(-k_9.TG + k_{10}.DG) \tag{16b}$$

$$\frac{dMG}{dt} = -b.OH\left(-k_{4p}.DG.ROH + k_{4Rp}.MG.E + k_{6p}.MG.ROH - k_{6rp}.GL.E\right) + a.OH.(-k_{10}.DG + k_{11}.MG) \tag{16c}$$

$$\frac{dGL}{dt} = -b.OH\left(k_{6p}.MG.ROH - k_{6rp}.GL.E\right) + a.OH.k_{11}.MG \tag{16d}$$

$$\frac{dROH}{dt} = \frac{dE}{dt} = -b.OH\begin{pmatrix} -k_{2p}.TG.ROH + k_{2rp}.DG.Ek_{4p}.DG.ROH + k_{4Rp}.MG.E + \\ k_{6p}.MG.ROH - k_{6rp}.GL.E - k_8.E \end{pmatrix} \tag{16e}$$

$$\frac{dOH}{dt} = \frac{dA}{dt} = -b.OH.k_8.E + a.OH.\left(k_9.TG + k_{10}.DG + k_{11}.MG\right) \tag{16f}$$

Where

$$\begin{aligned} k'_2 &= \frac{k_2 K1}{W} \\ k'_{2r} &= \frac{k_{2r} K1}{K3W} \\ k'_4 &= \frac{k_4 K1}{W} \\ k'_{4r} &= \frac{k_{4r} K1}{K_5 W} \\ k'_6 &= \frac{k_6 K1}{W} \\ k'_{6r} &= \frac{k_{6r} K1}{K_7 W} \end{aligned} \tag{17}$$

And

$$K_1 = \frac{k_1}{k_{1R}} = \frac{[RO^-][H_2O]}{[ROH][OH^-]}$$

$$K_3 = \frac{k_{13}}{k_{3R}} = \frac{[RO^-][DG]}{[ROH][DG^-]} \qquad (18)$$

$$K_5 = \frac{k_{15}}{k_{5R}} = \frac{[RO^-][MG]}{[ROH][MG^-]}$$

$$K_7 = \frac{k_7}{k_{7r}} = \frac{[RO^-][GL]}{[ROH][GL^-]}$$

Mass balance equations involved in transesterification are as followes:

(1) Glycerol backbone common to all the glyceride i.e. TG, DG, MG and GL. Since this backbone never destroyed, the sum of these chains must equal the initial amount, which in Komers' model is found solely in the triglyceride molecules.

$$TG+DG+ME+GL=1 \qquad (19)$$

(2) In the overall reaction, the alcohol molecules are only consumed to make alkyl esters. Thus, the second balance equation states that the sum of the alcohol molecules and the ester molecules must equal the original quantity of alcohol molecules.

$$ROH+E=1 \qquad (20)$$

(3) The hydroxide ions are only consumed in the production of soap. Therefore, the number of hydroxide ions plus the number of soap molecules must equal the original amount of hydroxide ions.

$$OH+A=p \qquad (21)$$

(4) Since fatty acid chains are not destroyed either, their total number is also constant, equal to three times the initial amount of triglyceride. The ester variable, E, is multiplied by the initial molar ratio of alcohol to triglycerides in order place each non-dimensional variable on the same scale.

$$nE+3TG+2DG+MG+A=3; \qquad (22)$$

The initial conditions are

$$\begin{aligned} &TG_0=1 \\ &ROH_0=1 \\ &OH_0=p \end{aligned} \tag{23}$$

And $DG_0=MG_0=GL_0=E_0=A_0=0$

Using equilibrium relations, Komers was able to develop an algebraic solution for the end product concentrations. Assuming that all reactions have reached equilibrium, we have the additional equilibrium equation.

$$\begin{aligned} K_2' &= \frac{k_2}{k_{2r}} = \frac{[DG^-][E]}{[TG][RO^-]} \\ K_4' &= \frac{k_4}{k_{4r}} = \frac{[MG^-][E]}{[MG][RO^-]} \\ K_6' &= \frac{k_6}{k_{6r}} = \frac{[GL^-][E]}{[MG][RO^-]} \end{aligned} \tag{24}$$

On combining, the new constants are:

$$\begin{aligned} K_2' &= K_2K_3 = \frac{[DG][E]}{[TG][ROH]} = \frac{DG \cdot E}{TG \cdot ROH} = \frac{k_2'}{k_{2r}'} \\ K_4' &= K_4K_5 = \frac{[MG][E]}{[DG][ROH]} = \frac{MG \cdot E}{DG \cdot ROH} = \frac{k_4'}{k_{4r}'} \\ K_6' &= K_6K_7 = \frac{[GL][E]}{[MG][ROH]} = \frac{GL \cdot E}{MG \cdot ROH} = \frac{k_6'}{k_{6r}'} \end{aligned} \tag{25}$$

This directly leads to

$$DG = K_2' \frac{1-E}{E} TG \tag{26}$$

$$MG = K_4' \frac{1-E}{E} DG = K_2' K_4' \left(\frac{1-E}{E} \right)^2 TG \tag{27}$$

$$GL = K_4' \frac{1-E}{E} MG = K_2' K_4' K_6' \left(\frac{1-E}{E} \right)^3 TG \tag{28}$$

Substituting (25), (26), (27) into the molecule balance for glycerol backbone (24) provides

$$TG = \frac{1}{1 + K_2''\left(\frac{1-E}{E} \right) + K_2' K_4' \left(\frac{1-E}{E} \right)^2 + K_2' K_4' K_5' \left(1 + K_6' \frac{1-E}{E} \right)^3} \tag{29}$$

3.7 SIMULATION OF KINETIC MODEL

MATLAB provides a powerful computing environment for solving mathematical equations, modeling, and analysis and algorithm development. Its accurate numeric computation and built-in-visualition make it easy to work with complex systems and data arrays. MATLAB Toolboxes offer specialized functions and easy-to-use graphical user interface tools that speed up the solution of application to specific problems.

3.7.1 MODEL SIMULATION

SIMULINK adds an intuitive block-diagram tool to the MATLAB environment for interactive block-diagram tool to the MATLAB environment for interactive simulation of non-linear dynamic systems.

3.7.2 KINETIC MODEL IN SIMULINK

Arrhenius equation for temperature dependency was written in SIMULINK as shown in figure. In this model 10 Arrhenius equation was written taking one for each rate constant so that only one temperature input can take care for all rate constant and all the differential equation derived for study of rate of reaction was written using simulink as

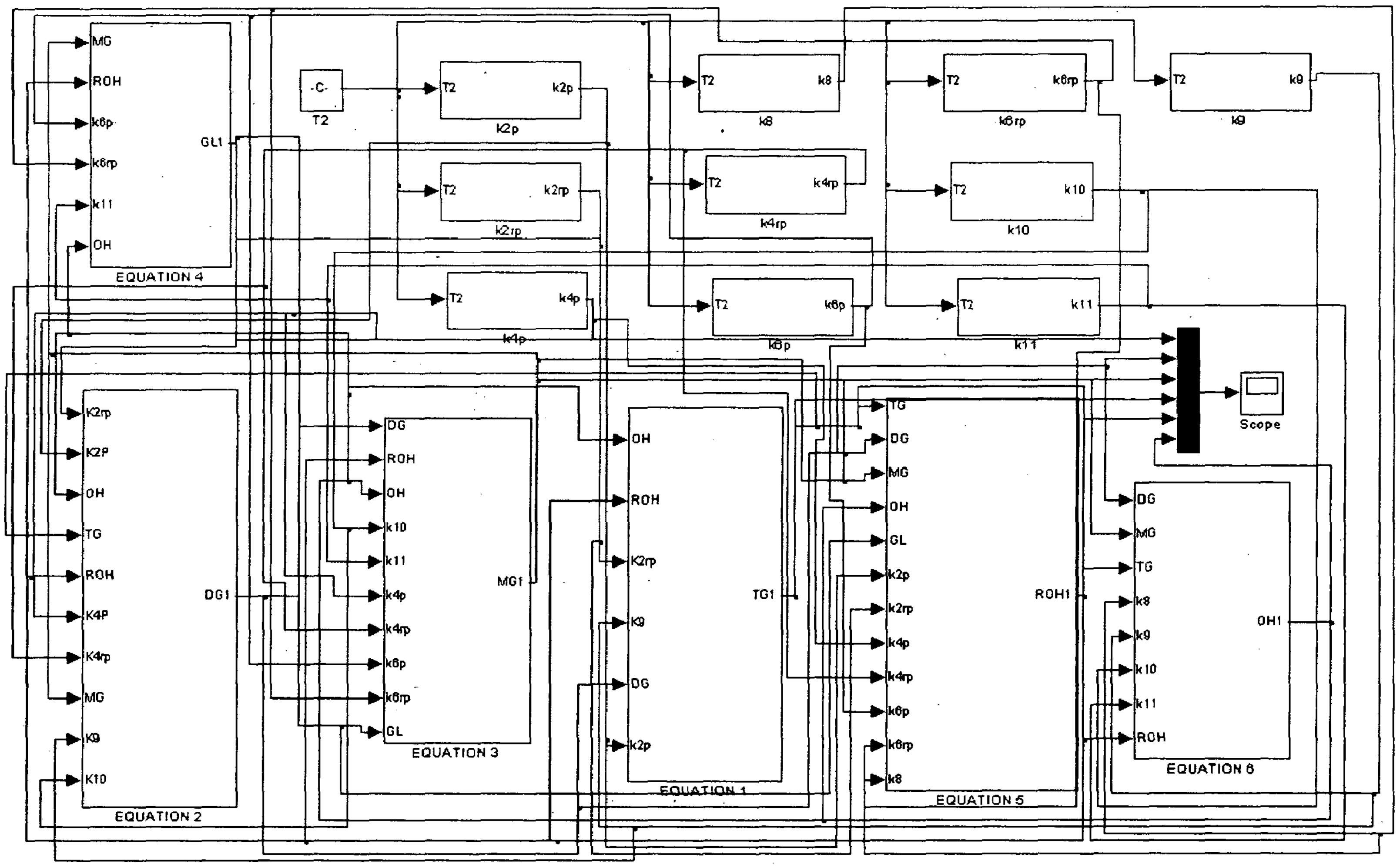


Fig 3.6 Kinetic model in simulink

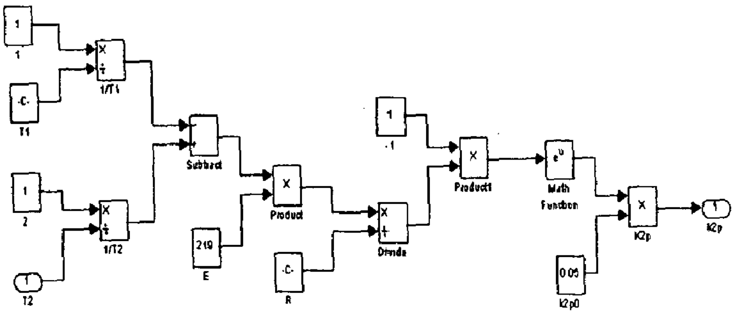


Fig. 3.7 Arrhenius equation in simulink for rate constant k2p

$$k_{new} = k_i e^{-\frac{E}{R}\left(\frac{1}{T2} - \frac{1}{T_1}\right)}$$

Where Ki – rate constant at initial/reference temperature (T1), K

Knew – rate constant at desired temperature (T2), K

E- Activation energy in cal/mol.

R- Gas constant, 1.987cal/mol.K

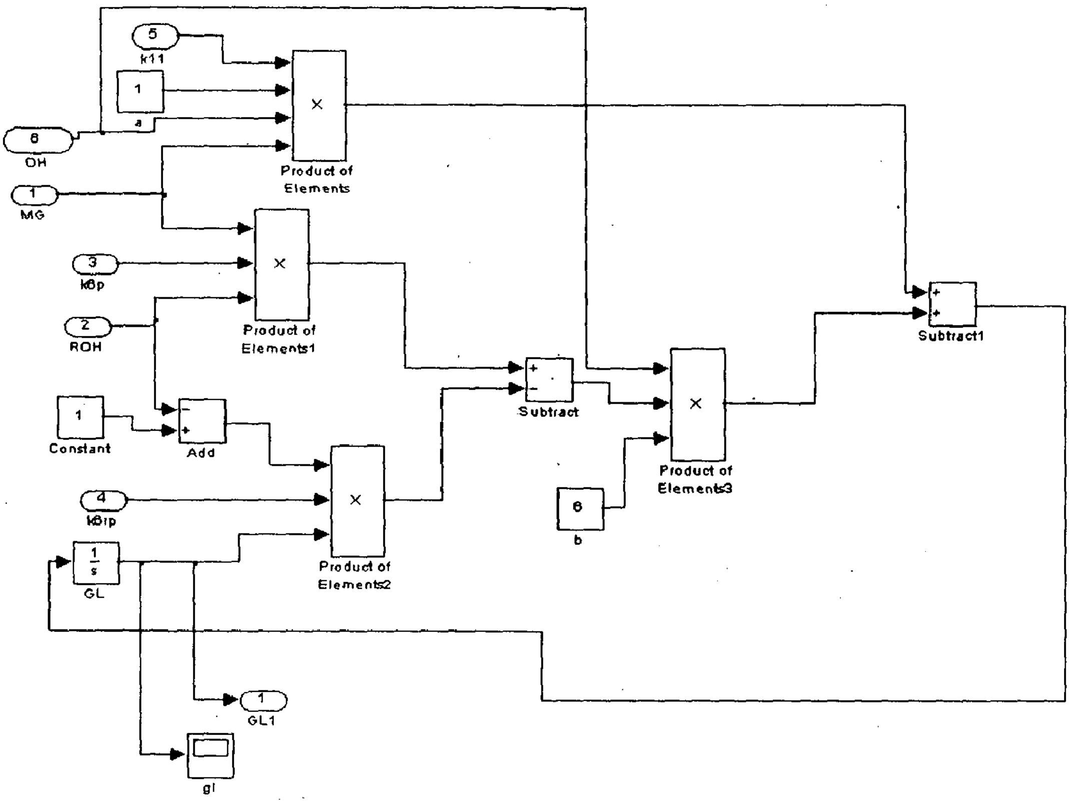


Fig 3.8 Glycerol

Figure 3.7 shows the differential equation for glycerol

$$\frac{dGL}{dt} = -b.OH\left(k_{6p}.MG.ROH - k_{6rp}.GL.E\right) + a.OH.k_{11}.MG$$

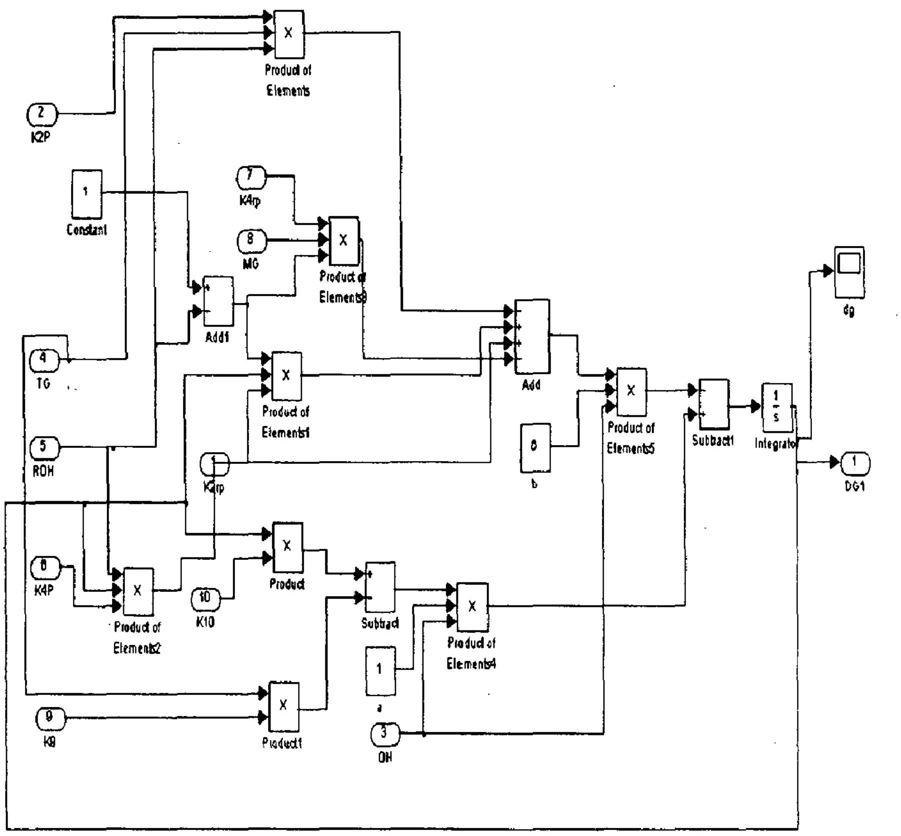


Figure 3.9 Diglycerides

Figure 3.8shows the differential equation for diglycerides

$$\frac{dDG}{dt} = -b.OH\left(-k_{2p}.TG.ROH + k_{2rp}.DG.E + k_{4p}.DG.ROH - k_{4rp}.MG.E\right) + a.OH.(-k_9.TG + k_{10}.DG)$$

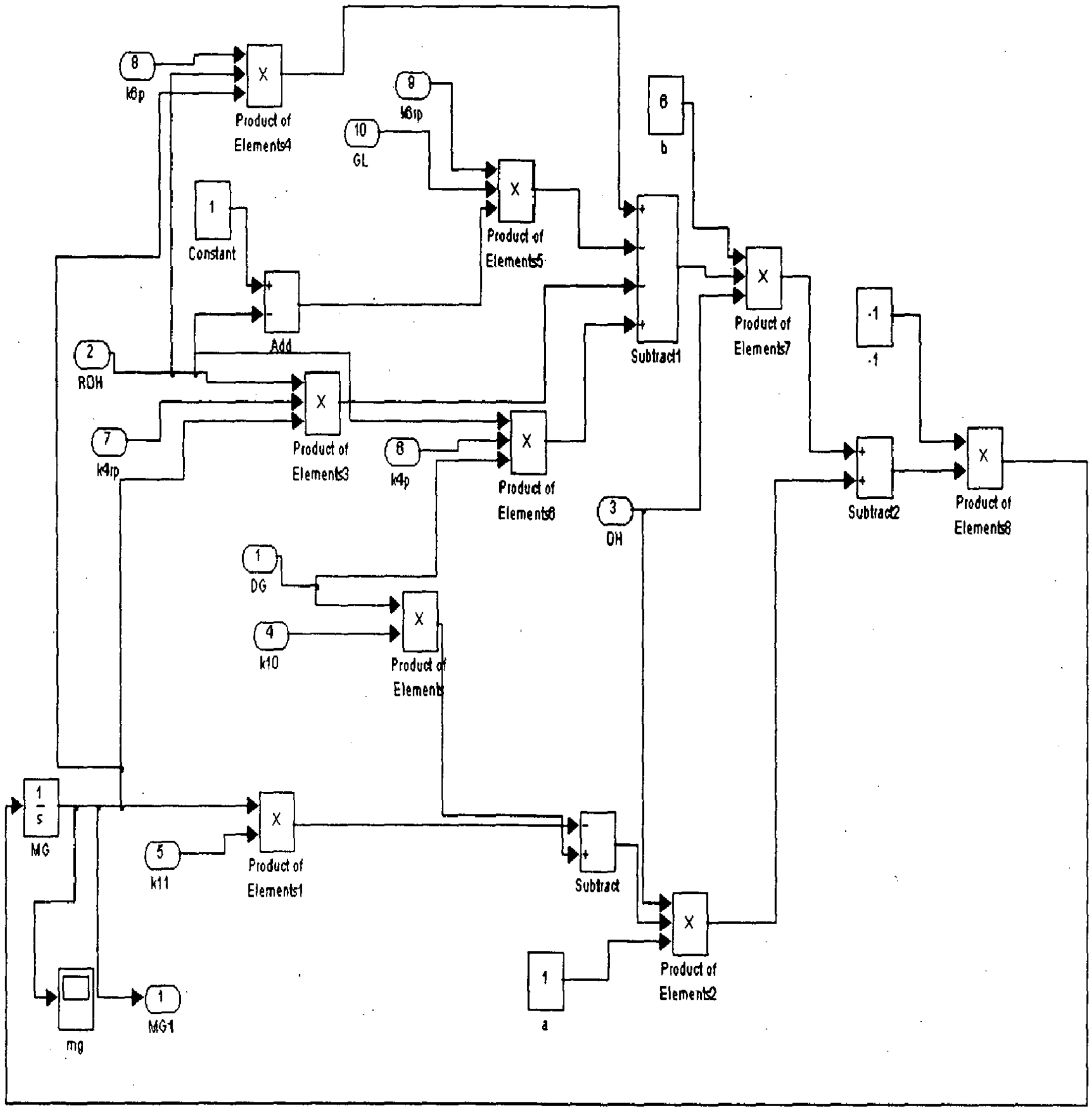


Figure 3.10 Tri glycerides

Figure 3.9 shows the differential equation for triglycerides

$$\frac{dTG}{dt} = -b.OH.(k_{2p}.TG.ROH - k_{2rp}.DG.E) + a.OH..k_9.TG$$

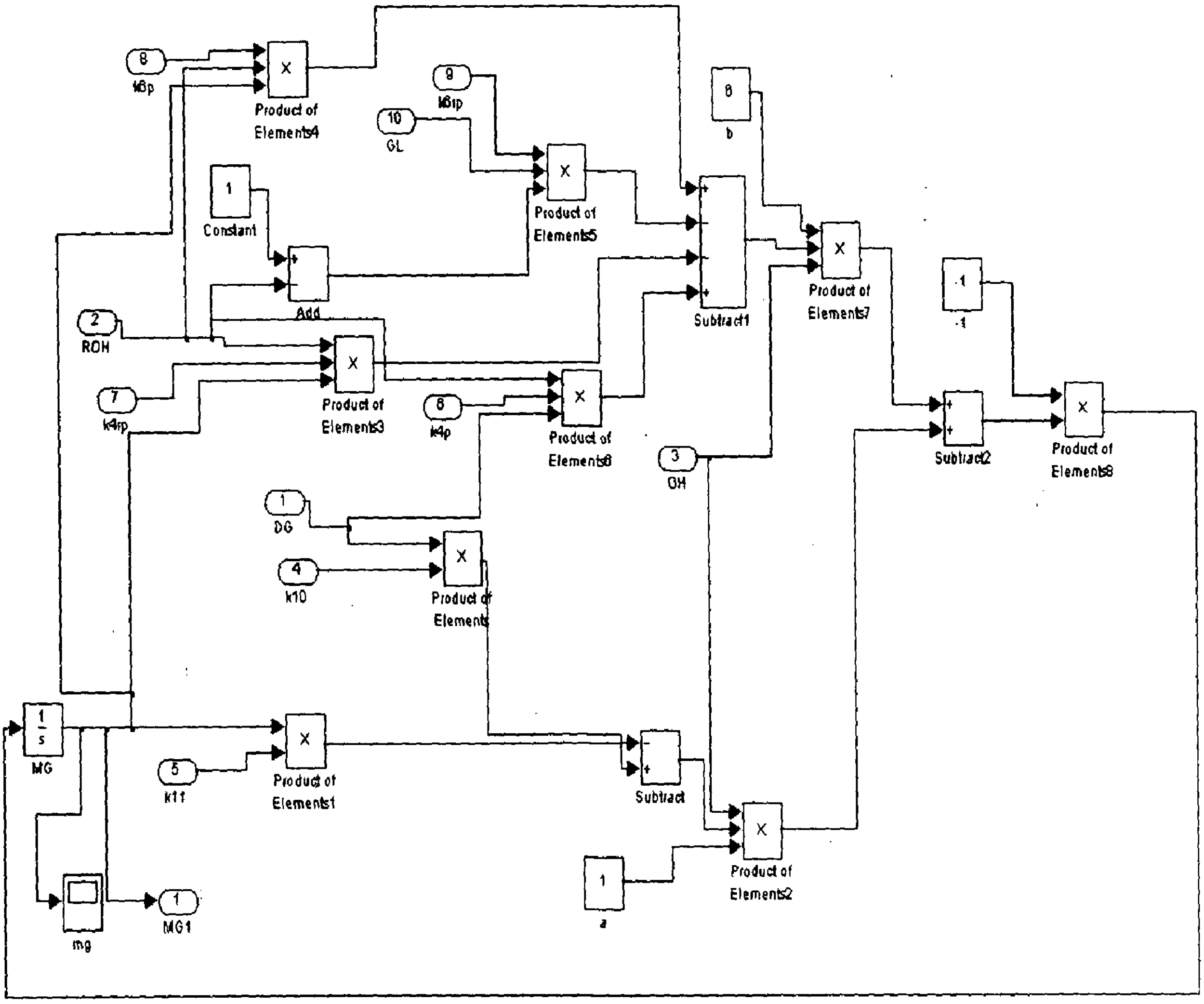


Figure 3.11 Monoglycerides

Figure 3.10 shows the differential equation for monoglycerides

$$\frac{dMG}{dt} = -b.OH\left(-k_{4p}.DG.ROH + k_{4Rp}.MG.E + k_{6p}.MG.ROH - k_{6rp}.GL.E\right) + a.OH.(-k_{10}.DG + k_{11}.MG)$$

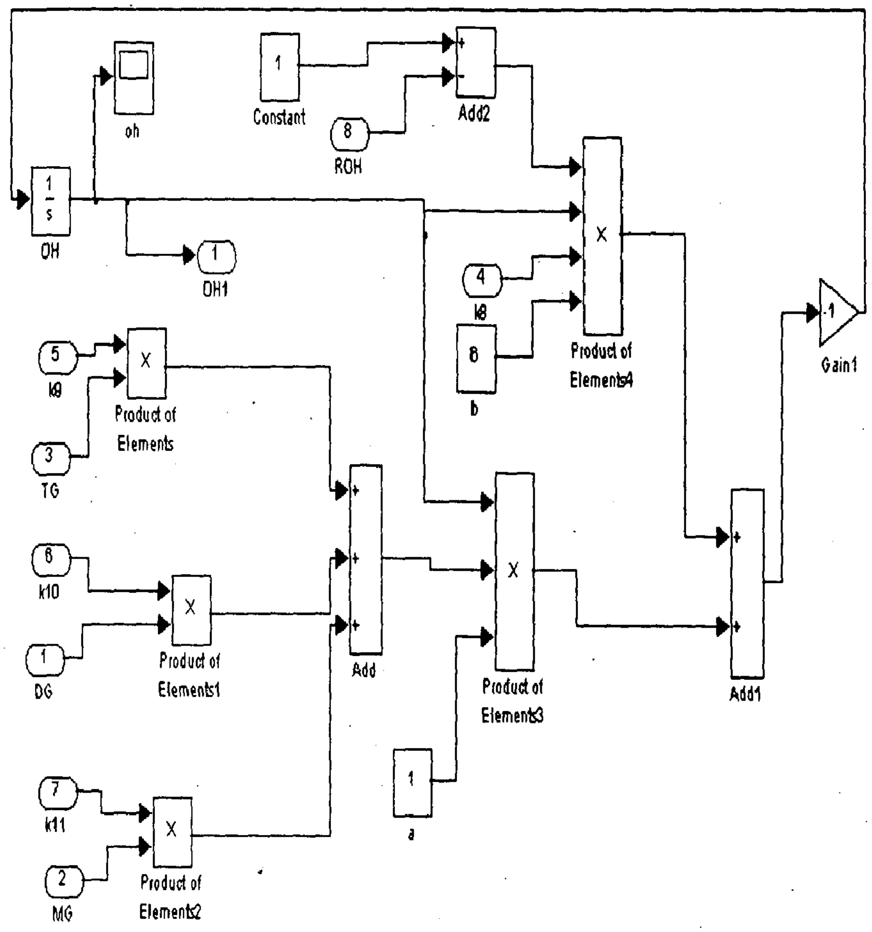


Figure 3.12 Catalyst

Figure 3.11 shows the differential equation for catalyst

$$\frac{dOH}{dt} = \frac{dA}{dt} = -b.OH.k_8.E + a.OH.(k_9.TG + k_{10}.DG + k_{11}.MG)$$

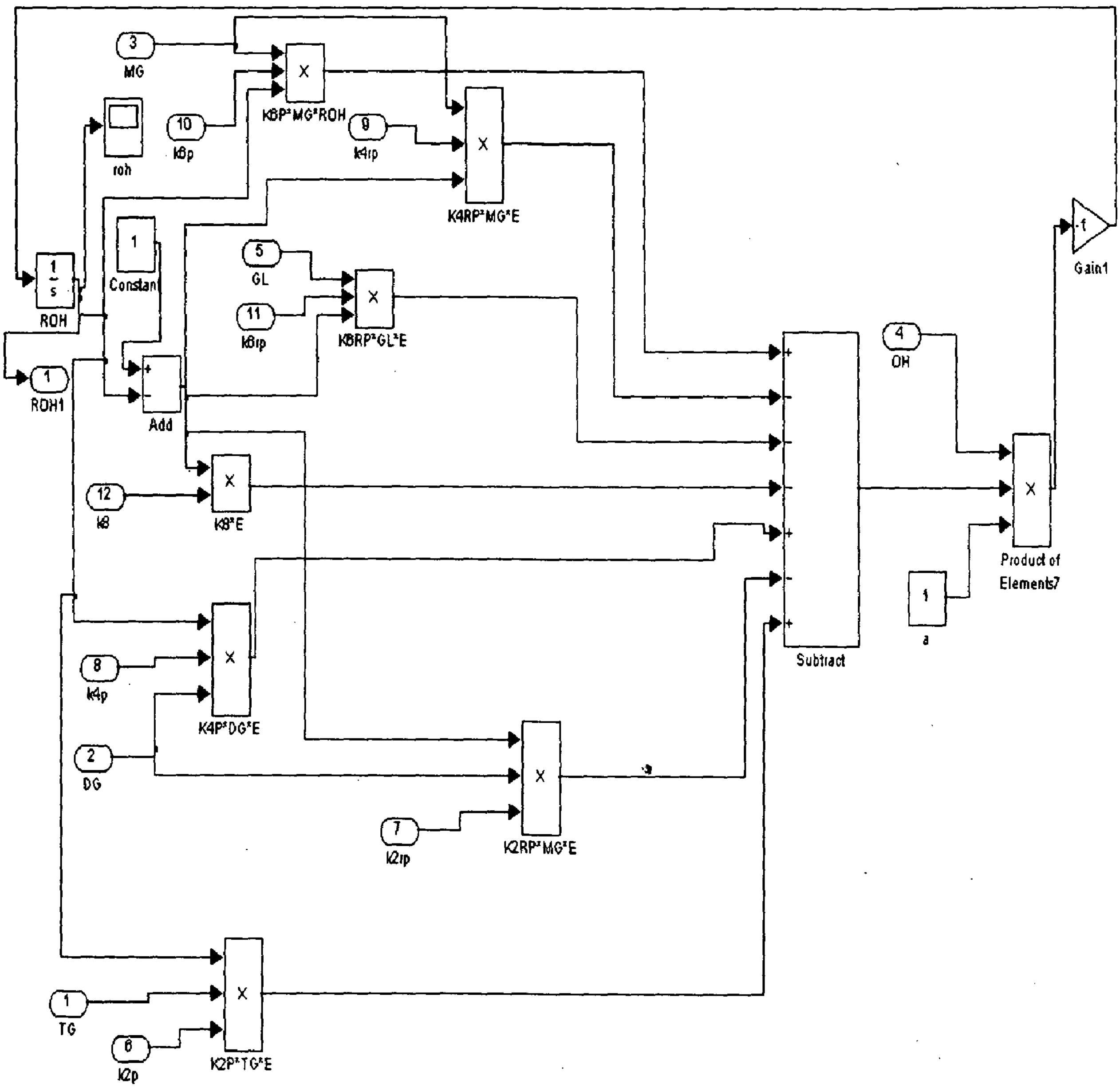


Figure 3.13 Alcohol

Figure 3.12 shows the differential equation for alcohol

$$\frac{dROH}{dt} = \frac{dE}{dt} = -b.OH\begin{pmatrix} -k_{2p}.TG.ROH + k_{2rp}.DG.Ek_{4p}.DG.ROH + k_{4Rp}.MG.E + \\ k_{6p}.MG.ROH - k_{6rp}.GL.E - k_{8}.E \end{pmatrix}$$

3.7.3 HOW TO USE THIS MODEL

To use this model requires **MATLAB 7.0.1** software to be installed in personal computer .and then following steps to be followed.

1 Open MATLAB and go to simulink

2 In the simulink open this file and click on the parameter which you want to change and then click OK and save it. After that click on simulation and change the configuration parameter if desired, click on apply then OK. And again click on start and thus simulation will start and when simulation completes the screen will show flickering action. Then click on scope, it will show you a graph.

RESULTS AND DISSCUSSION

4.0 GENERAL

The change in reaction parameter affects the transesterification reaction, was estimated with the help of experimentation. The experiment for optimization of reaction parameter and to study the behavior of transesterification reaction both experimental as well as theoretical like modeling of transesterification reaction was done and all the obtained results have been discussed in this chapter.

4.1 EXPERIMENTAL

4.1.1 Effect of Temperature: In the present study temperature variation was from 40 ^{0}C,50^{0}C, 60^{0}C,65^{0}C and 70^{0}C for 90 minutes at 3:1 molar ratio.

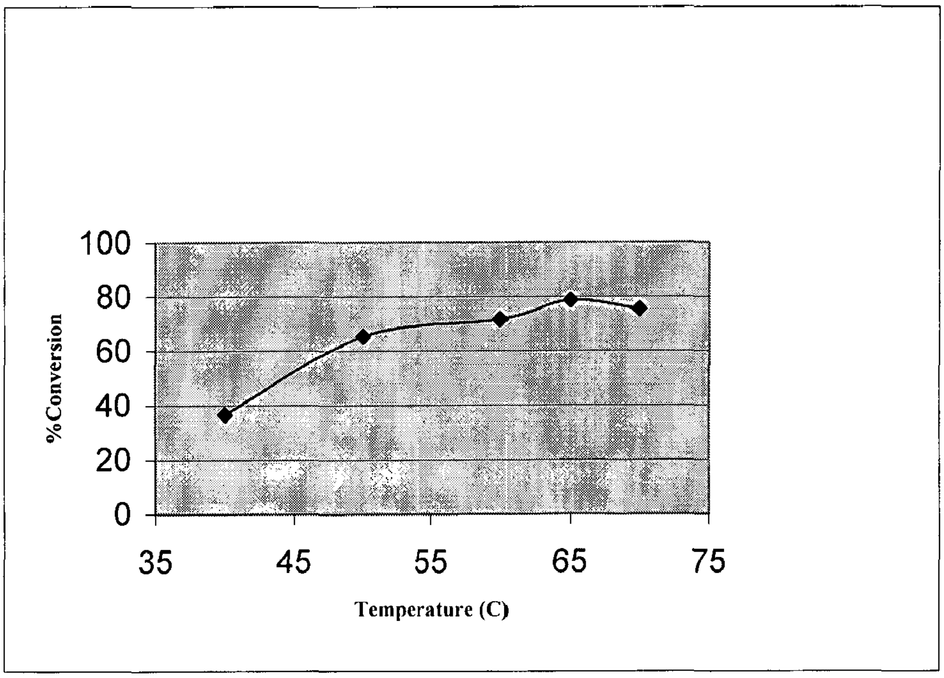


Fig 4.1 Effect of temperature on transesterification reaction at 3:1 molar ratio

Figure 3.1 shows that the maximum conversion was achieved at65^{0}Ctemperature. It clearly shows that the Conversion was proportionally increased with the increase in reaction temperature except at 70⁰C.At 70⁰C reaction temperature there was loss of methanol due to evaporation. Thus reaction temperature was kept below the boiling point of methanol

4.1.2 Effect of methanol: The molar requirement for methanol to alcohol was found to be 3:1. In present study molar ratio was varied from 3:1 to 12:1 the concentration of catalyst, reaction temperature and reaction time was kept constant throughout the study of effect of methanol on reaction

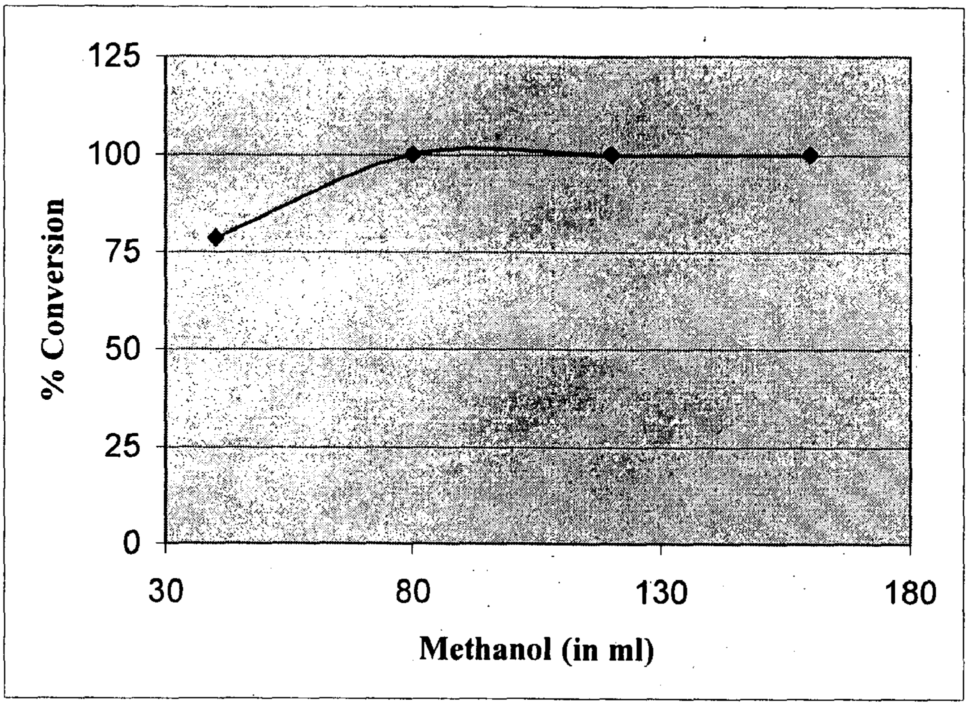


Fig 4.2 Effect of methanol on transesterification reaction at 65⁰C

Fig 3.2 shows that the effect of molar ratio on transesterification reaction from 3:1(40ml) molar ratio to 12: 1(160ml). The result clearly indicates that the optimum concentration of methanol required for effective transesterification of jatropha oil was 6:1. However, it was found that when the molar ratio was increased above or decreased below the 6:1, there was not significant increase in biodiesel but excess or short fall in molar ratio only contributed to the increased formation of glycerol and emulsion. Thus phase separation becomes difficult.

4.1.3 Effect of catalyst concentration: The catalyst (NaOH) concentration variations adopted in this study were 0.5%, 1.0% and 1.5%.

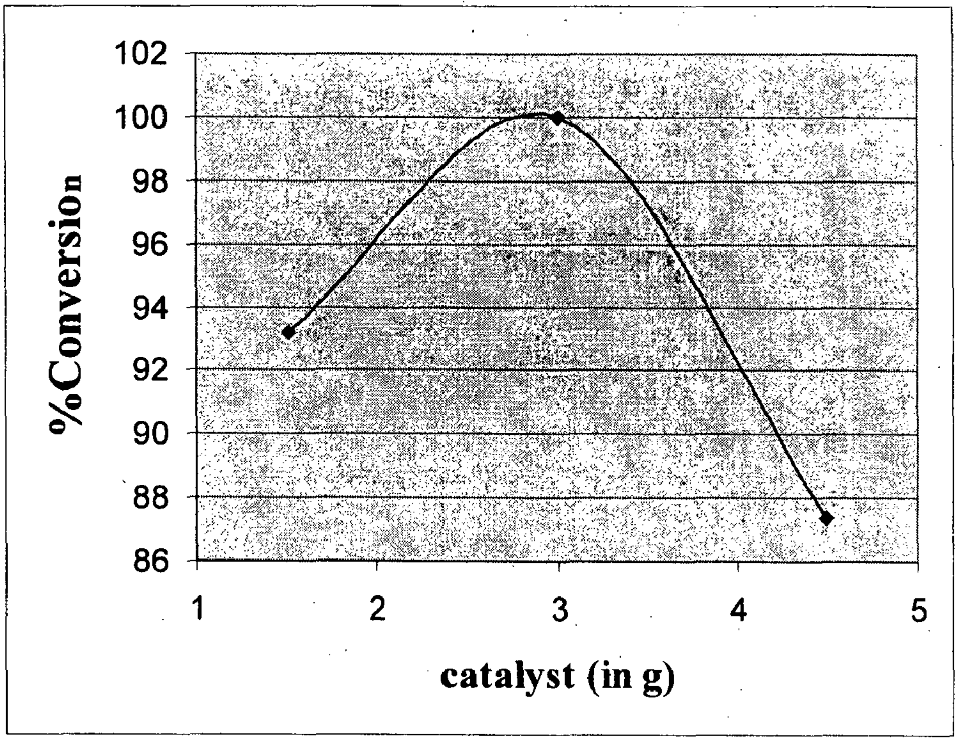


Fig 4.3 Effect of catalyst concentration on transesterfication reaction

Fig 4.3 shows that the effect of catalyst concentration on transesterification reaction at 6:1 molar ratio and 65^0C. The result clearly indicates that the optimum concentration of catalyst required for effective transesterification was 1.0%. It was observed that, if the NaOH concentration was decreased below and increased above the optimum, there was no significant increase in conversion but there was increased formation of side product like glycerol and emulsion.

4.1.4 Effect of molar ratio on triglycerides conversion into methyl ester

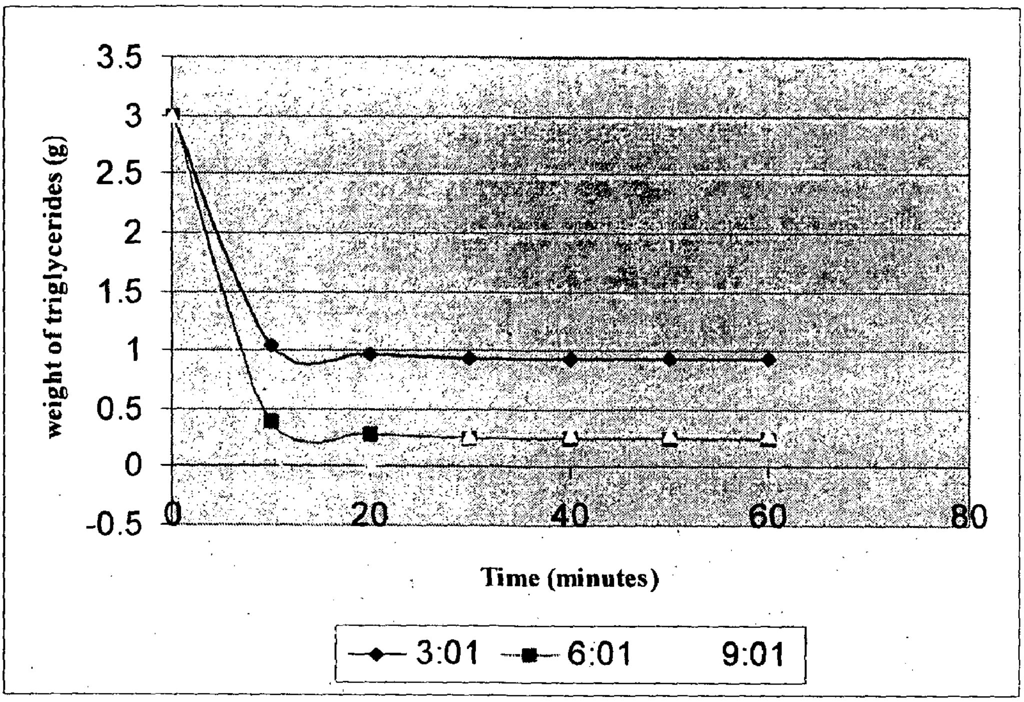


Fig. 4.4 Triglycerides conversion at different molar ratio and at 65^{0}C

Fig 4.4 shows that the effect of molar ratio on transesterification reaction from 3:1(40ml) molar ratio to 12: 1(160ml). The result clearly indicates that the optimum concentration of methanol required for effective transesterification of jatropha oil was 6:1. However, it was found that when the molar ratio was increased above or decreased below the 6:1, there was not significant increase in biodiesel but excess or short fall in molar ratio only contributed to the increased formation of glycerol and emulsion. Thus phase separation becomes difficult.

Figure 4.[illegible]shows that the maximum conversion was achieved at 65^{0}C temperature. It clearly shows that the Conversion was proportionally increased with the increase in reaction temperature except at 70^{0}C.At 70^{0}C reaction temperature there was loss of methanol due to evaporation. Thus reaction temperature was kept below the boiling point of methanol

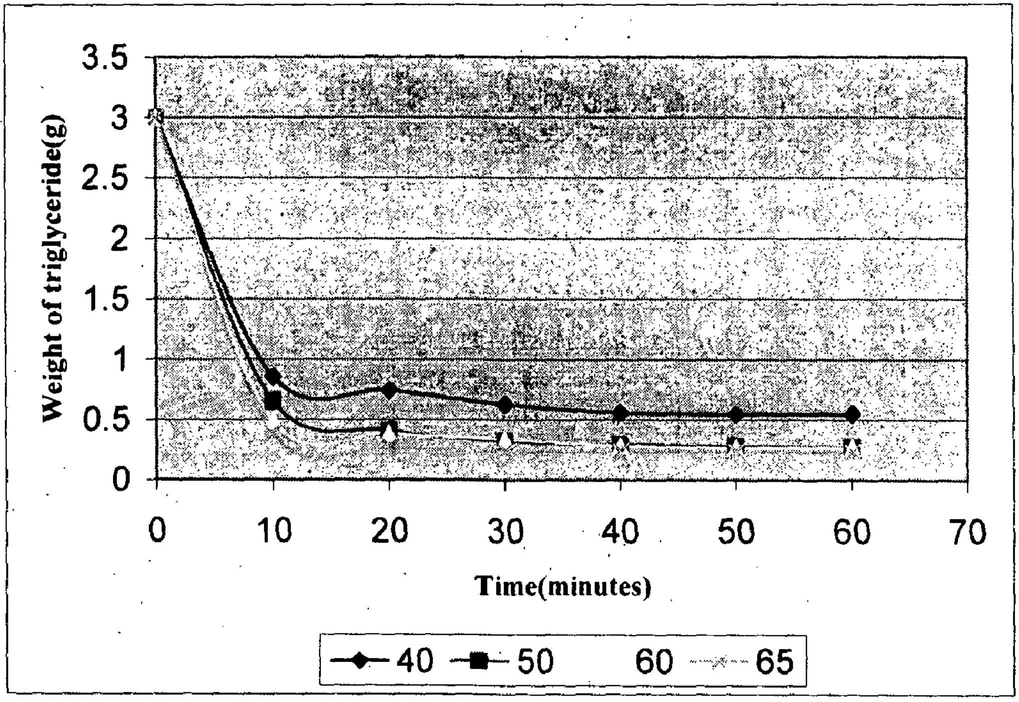


Fig. 4.5 Triglycerides conversion at different temperature and 6:1 molar ratio.

4.2 MODELLING

Kinetic modeling for transesterification of vegetable oil was done in previous chapter using Arrhenius equation for the temperature dependency of rate constant, initial condition as well as molecular balance and simulation of model was performed using simulink. In this study, temperature, molar ratio and catalyst concentration was varied. Here, normalized concentration was used assuming 1 for triglyceride and accordingly the concentration of alcohol and catalyst was determined e.g. 300g oil requires 32 g alcohol and 3 g catalyst, and then on normalized scale concentration for triglyceride is 1, 0.1 for alcohol and 0.01 for catalyst.

Figure 4.6 shows the conversion of triglyceride at 50^0C and 6:1 molar ratio was 0.76 and remaining 0.24 was unconverted after 1000 s. Above figure shows that as the time passes the concentration of triglyceride decreases fast till 200 s after that the triglycerides reaction reaches at equilibrium. OH is continuously decreases and becomes zero at 700 second. Formation of glycerol stars from zero, initially it goes negative and then at around 80 second it becomes positive, reaches around 0.0045 and after that continuously decreases and becomes 0.003 at 1000 s.Initial value of diglyceride and monoglyceride was zero , increase in diglyceride concentration was observed after150 second and at 1000 second it was 0.028.and for monoglyceride it starts increasing after 85 second and becomes high between 200 to 300 s and after that starts decreasing ,at 1000s concentration was 0.003.ROH concentration decreased continuously up to 0.044 at 100 s after that it starts increasing and reaches equilibrium at 0.06.

Figure 4.7 shows that the conversion of triglyceride at 333K and 6:1 molar ratio was 0.76 and remaining 0.24 was unconverted after 1000 s. There was no considerable change in conversion at 1000s.

Figure 4.8 shows that as the temperature were increased from 323K to 343K the decrease in conversion from 0.76 to 0.37.Thus in this case only 37% conversion was achieved even though the temperature was increased.

Figure 4.9 shows the effect of increased temperature to 363 K the conversion was decreased to 0.28.this may be due to the vaporization of alcohol at 363 K temperatures which is much higher than the boiling point of methanol (338K).

Figure 4.10 shows the effect of decrease in molar ratio at 333K, the conversion was decreased to 0.29 compared to 0.76 at same temperature and catalyst concentration.

Figure 4.11 shows the effect of increased catalyst, the conversion was decreased to 0.56 compared to 0.76 at same temperature and molar ratio.

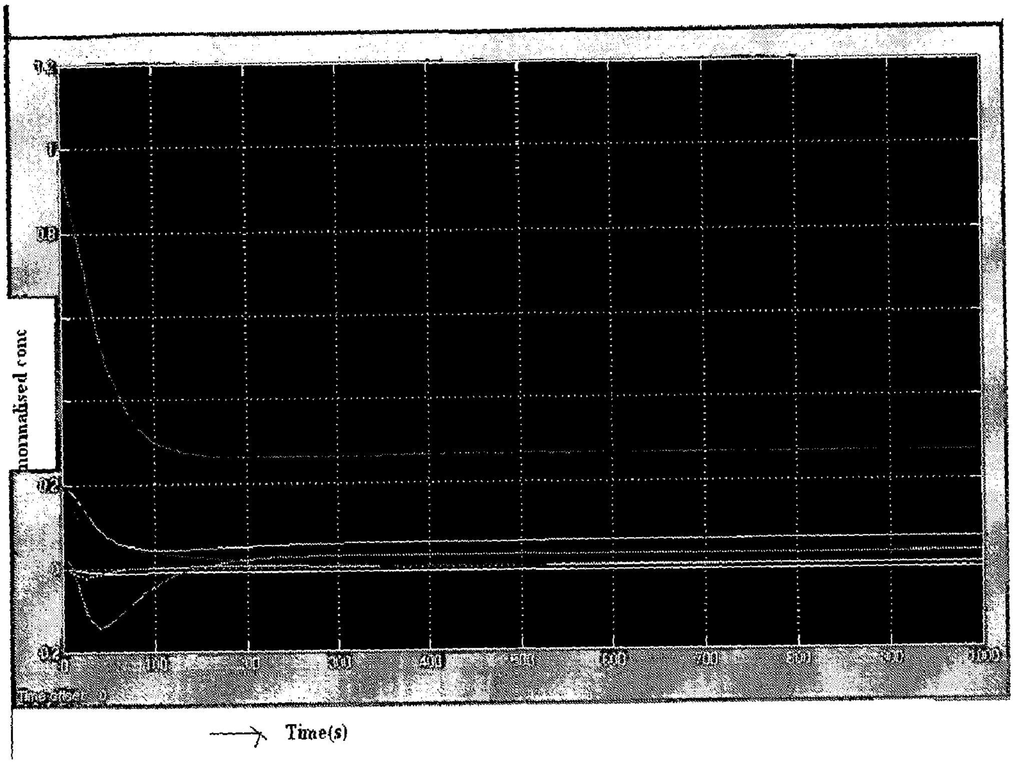


Figure 4.6 Transesterification of oil at 323 K (50^{0}C) and 6:1 molar ratio

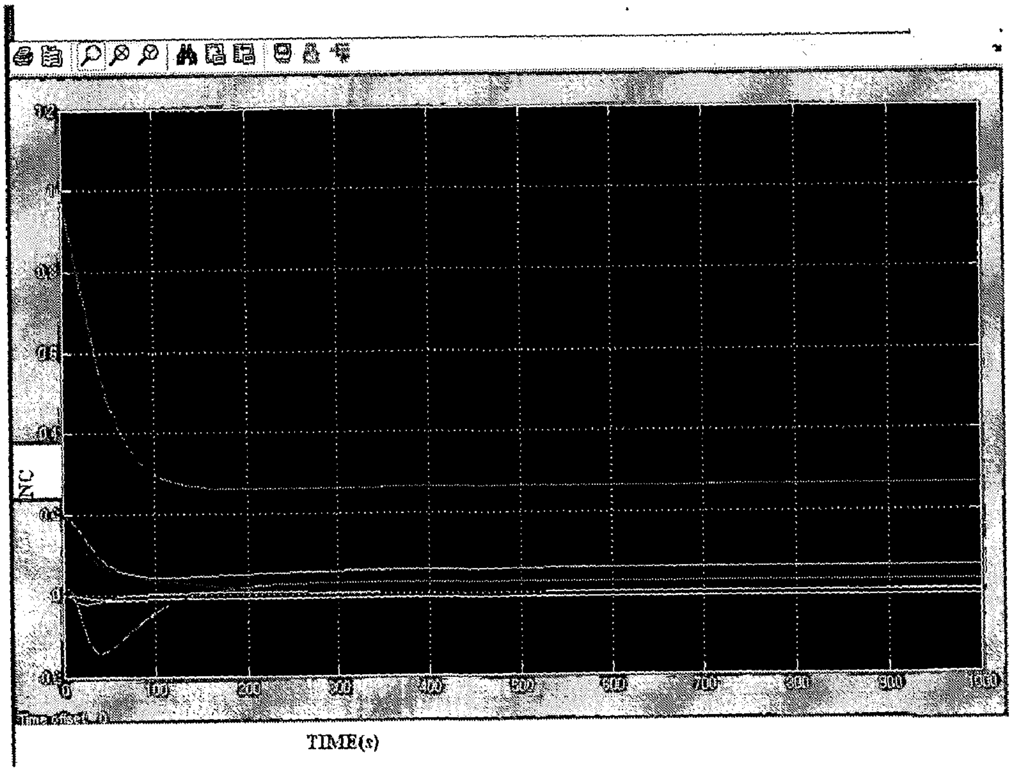


Figure 4.7 Transesterification of oil at 333 K and 6:1 molar ratio

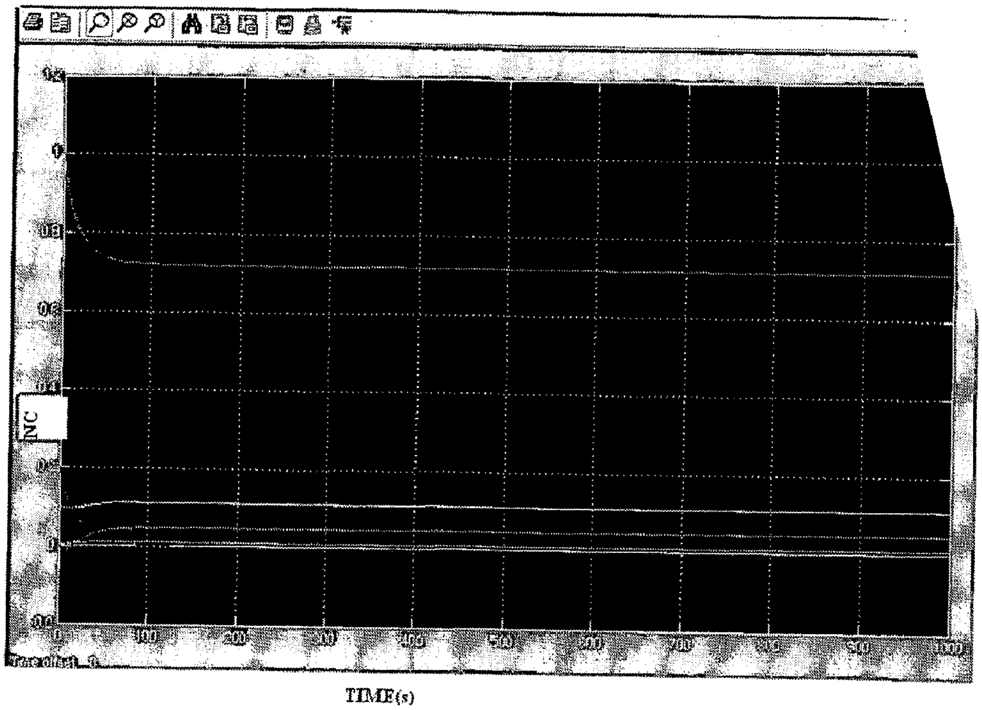
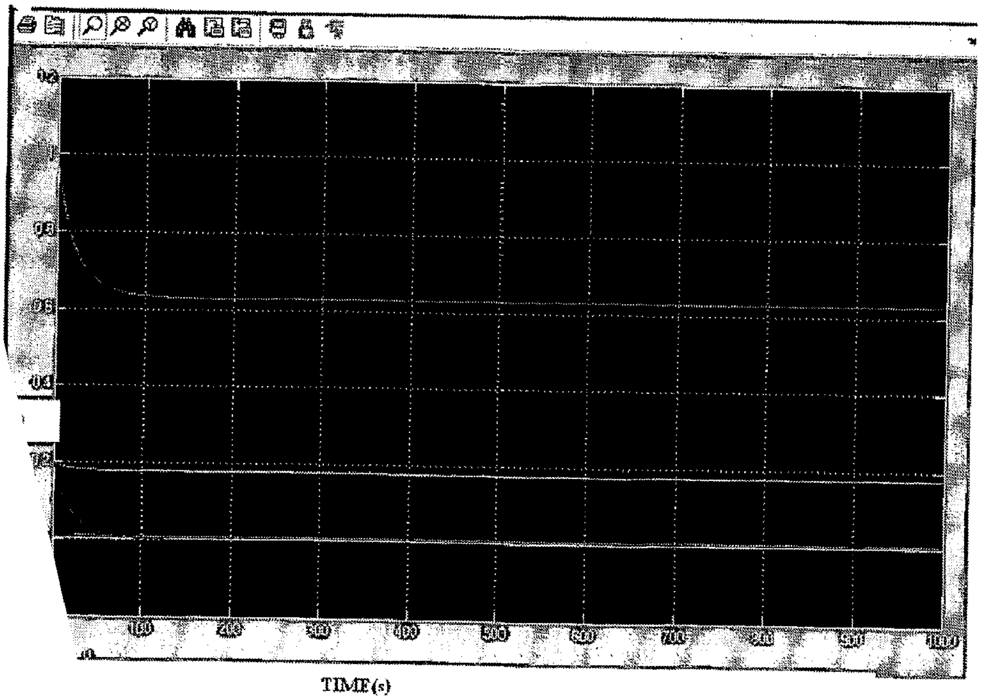


Figure 4.8 Transesterification of oil at 343 K and 6:1 molar ratio



re 4.9 Transesterification of oil at 363 K and 6:1 molar ratio

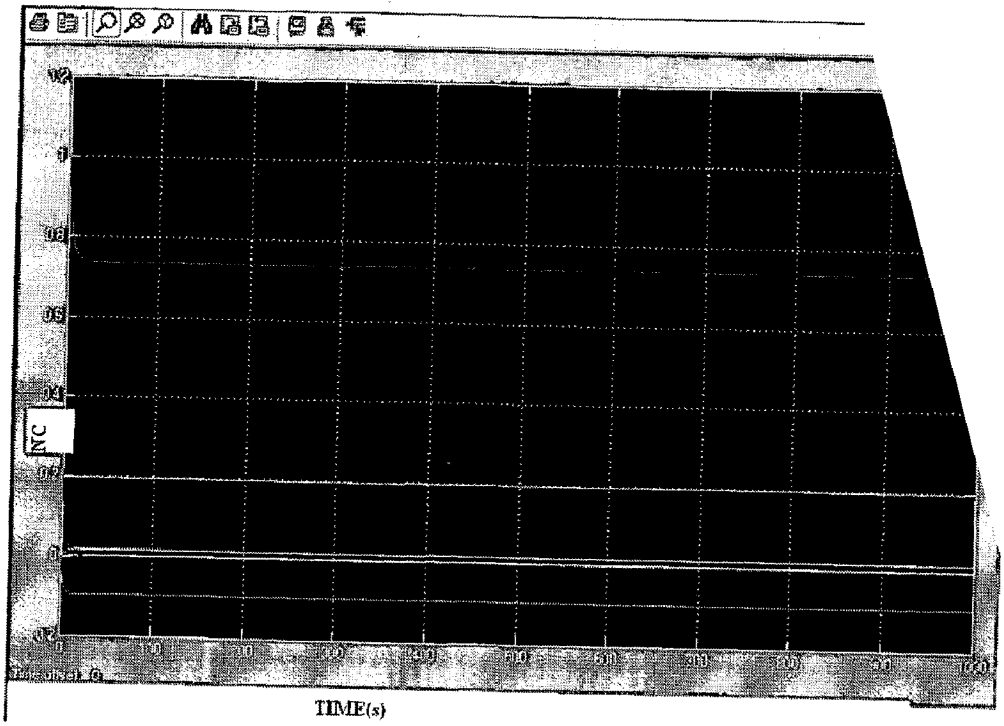
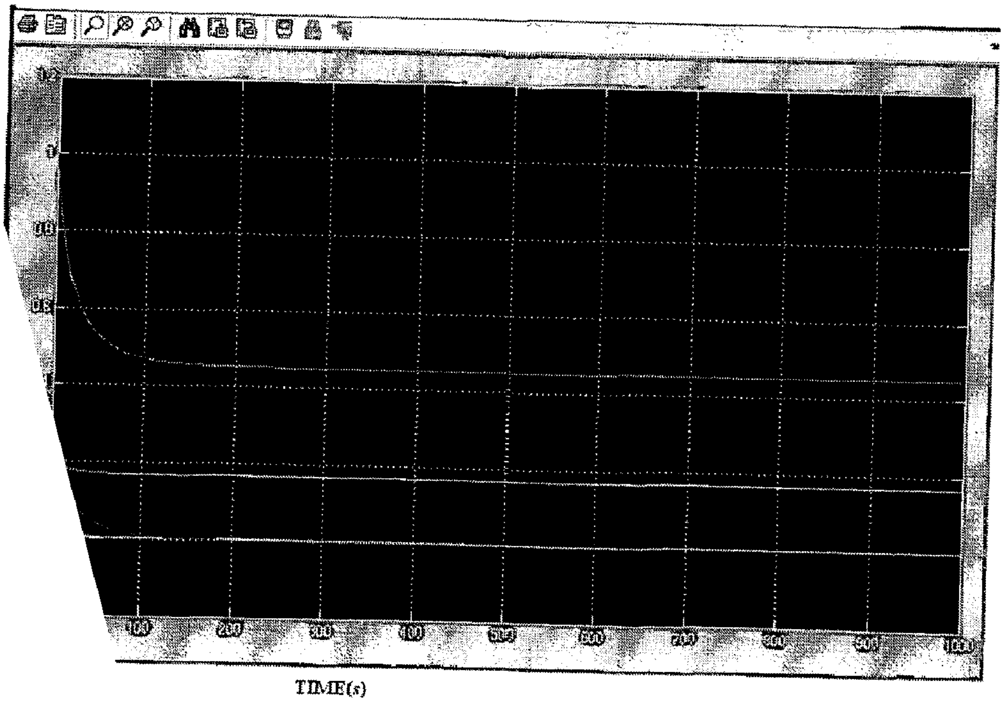


Figure 4.10 Transesterification of oil at 333 K and 3:1 molar ratio



ansesterification of oil at 333 K and 6:1 molar ratio, catalyst 0.3

Summarily the effect of various parameters was observed as follows and given in table below

Table 4.1 Effect of various parmeter on triglyceride conversion

Sl.no.	Temperature (K)	Molar ratio	Final concentration at1000 s	% Conversion
1	323	6:1	0.24	76
2	333	3:1	0.71	29
3	343	6:1	0.74	26
4	363	6:1	0.64	36
5	333	6:1	0.24	76

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSIONS

Based upon the experimental work and modeling of transesterification process following conclusions is drawn

Jatropha oil in India contains more FFA (2-12%) than edible oil and also FFA content of nonedible vegetable oil increases from 1-19% during three year of storage. FFA content of Jatropha oil leads to problem of saponification. Thus to avoid soap formation either removal of FFA or its conversion is required before transesterification. Fatty acid composition varies from oil to oil and for particular oil (in this case Jatropha oil) varies from place to place and species to species.

The reaction depending upon the FFA content normally takes 1 hrs for base catalyzed and 8 h for acid catalyzed transesterification for formation of monoalkylester and glycerol. The laboratory experiment have rebuild that the % conversion of Jatropha oil to monoalkyl ester and glycerol has been about 99.57.and 0.043 respectively.

Transesterification reaction is reversible and takes place in 6 different stages. For the study of kinetics the datas were extracted from literature, model was developed and solved in simulink. The model indicates that the %conversion of triglyceride at constant catalyst concentration and molar ratio indicates that as temperature increases from 313K to 323 K the yield increases from 37 to 76.

5.2 RECOMMENDATION

The following points may be recommended for production of biodiesel from vegetable oil:

- Any nonedible oil resource should be checked for its FFA content before selecting the process. Two-step process developed above can be used for vegetable oils or fats having high FFA content (>0.5%) for the biodiesel production.
- This developed model can be used to know theoretically the yield of different constituents at different temperature under the standard condition. This will help in knowing the behavior of reaction after taking in account the kinetic constant and activation energy of reaction for process development. The model can be used for any vegetable oil resources for prediction of biodiesel yield for any duration of time (>1000s).

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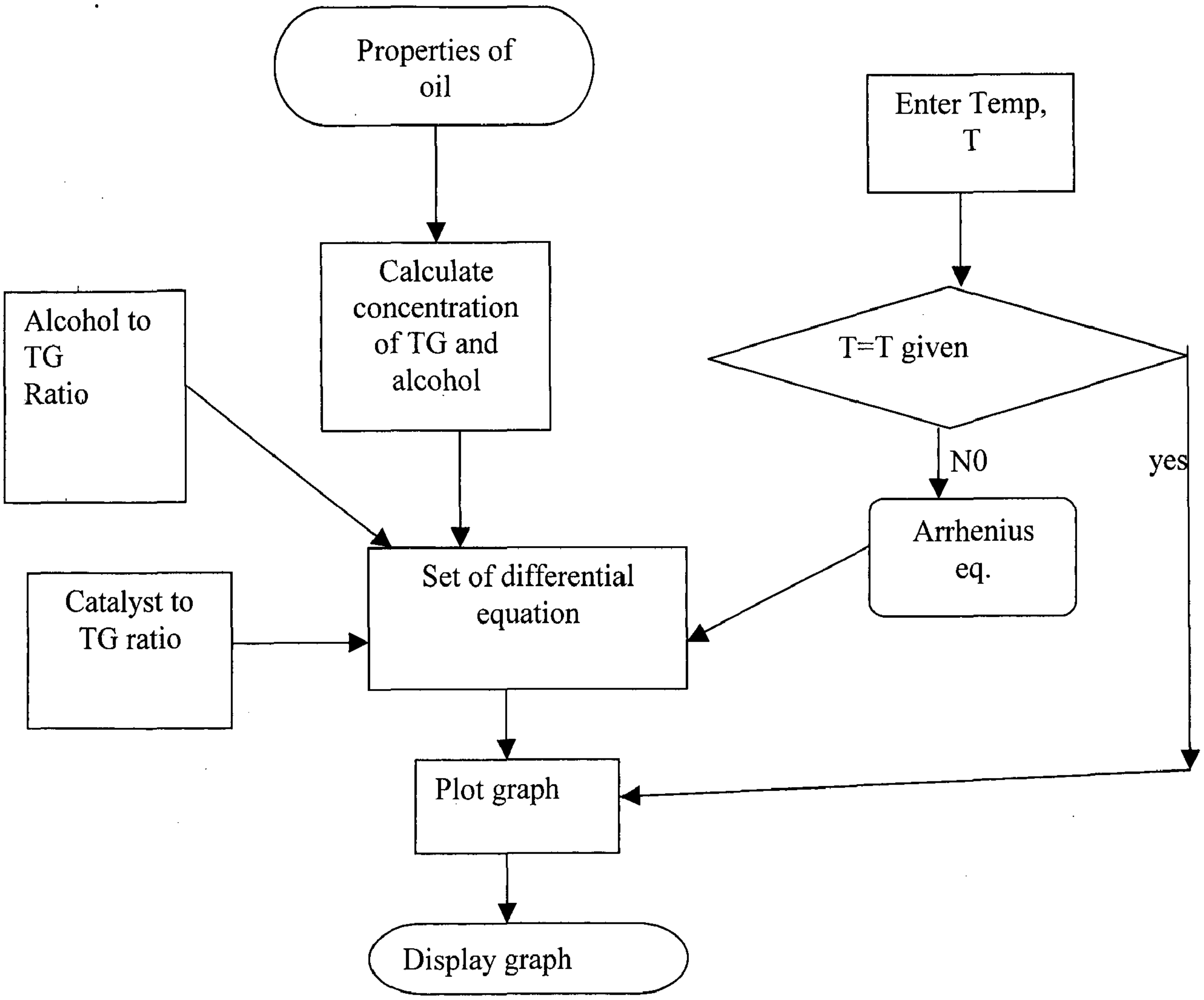
Flow chart for the simulation of model



PROCESS FLOW DIAGRAM FOR TRANSESTERIFICATION OF JATROPHA OIL

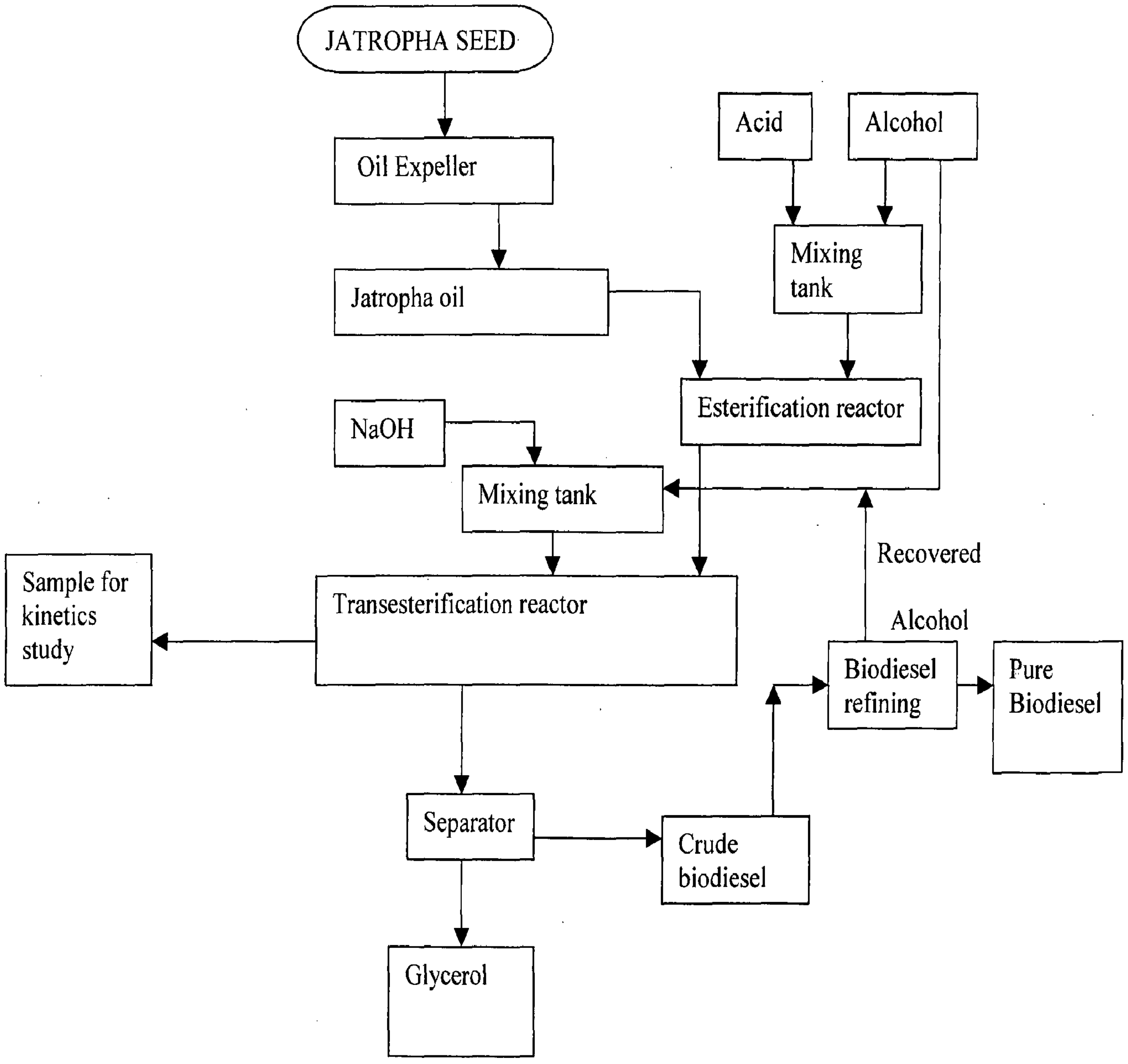


Fig.A-1 Schematic diagram of acid catalyzed esterification followed by transesterification of jatropha oil

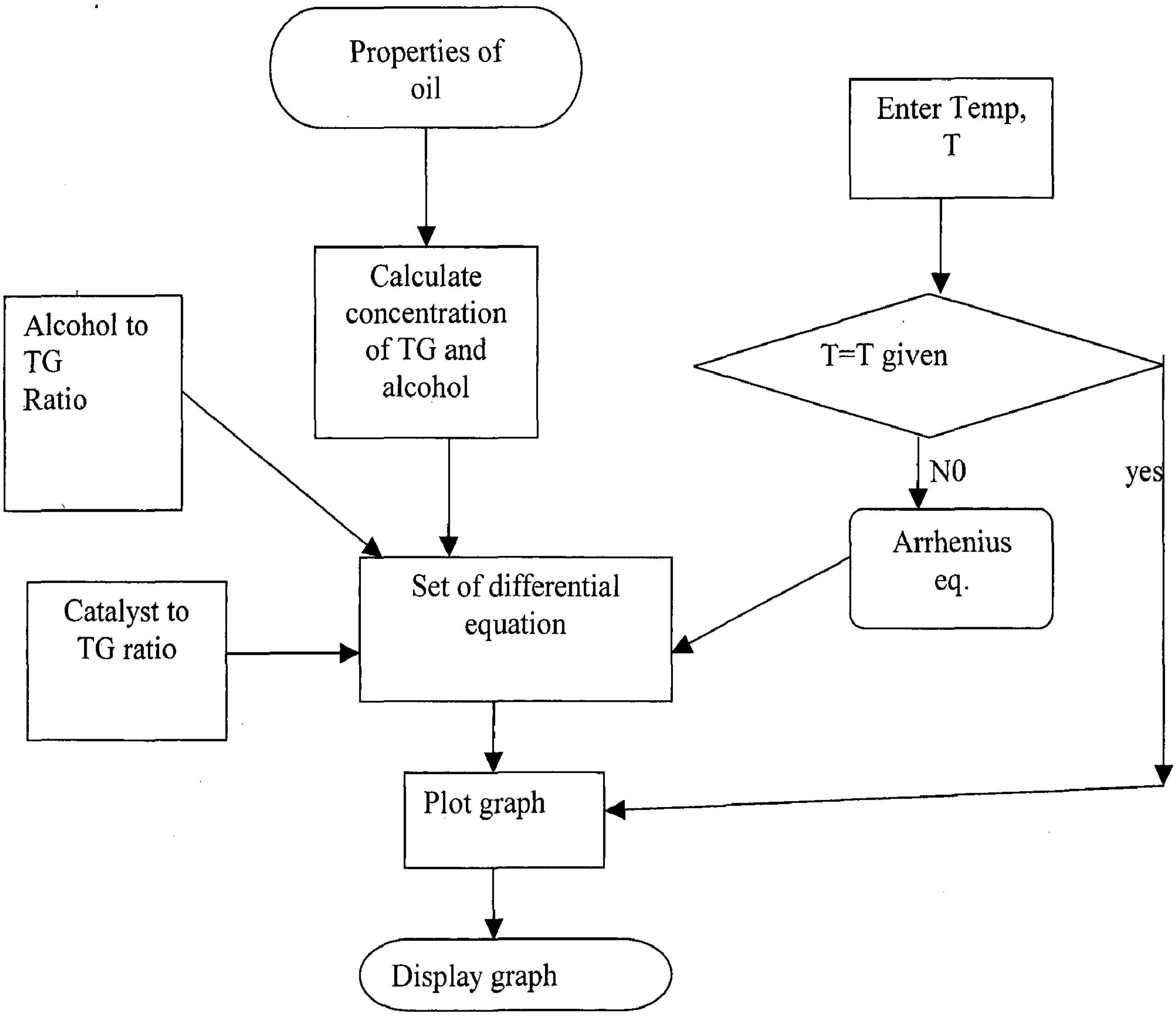
TABLE A-1Conversion of triglycerides into methyl ester (biodiesel).

Batch no.	Reactant			Product yield		Reaction condition		% Conversion
	Jatropha oil (g)	Methanol (ml)	Catalyst (g)	Crude Biodiesel	Crude Glycerol	Temperature (^{0}C)	Time	
1	300	40	3	-	-	30	90	Not analyzed
2	300	40	3	110.00	243.00	40	90	36.48
3	300	40	3	196.00	157.00	50	90	65.26
4	300	40	3	215.00	138.00	60	90	71.50
5	300	40	3	235.89	117.11	65	90	78.63
6	300	40	3	226.00	127.00	70	90	75.34
7	300	80	3	250.83	152.17	50	90	83.61
8	300	80	3	270.00	133.00	60	90	89.30
9	300	80	3	300.00	103.00	65	90	100
10	300	80	3	298.70	104.3	65	90	99.57
11	300	120	3	278.73	174.27	50	90	92.91
12	300	120	3	286.00	170.00	60	90	95.33
13	300	120	3	297.54	155.46	65	60	99.18
14	300	120	3	300.54	153.00	65	90	100
15	300	160	3	289.10	163.90	60	90	96.37
16	300	160	3	300.00	153.00	65	90	100
17	300	160	3	300.00	153.00	65	60	100
18	300	80	1.5	285.51	115.99	65	90	95.17
19	300	80	4.5	262.08	142.42	65	90	87.36

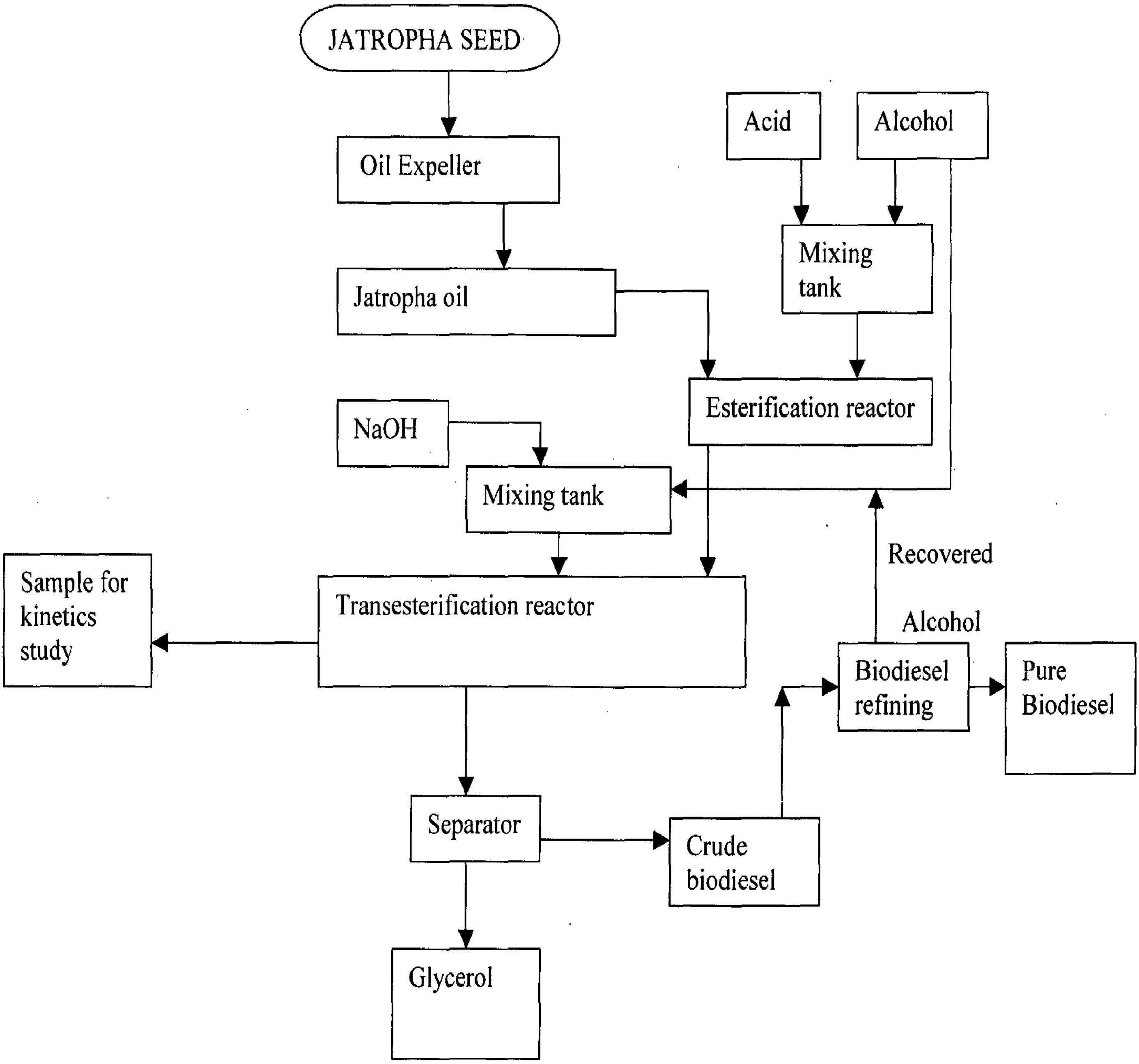
TABLE A1: Concentration of triglyceride

Sl. No	Time (min)	Concentration of triglyceride (g)				
		60 ^{0}C			40^{0}C	50^{0}C
		3:1	6:1	9:1	6:1	
1	0	3	3	3	3	3
2	10	1.04	0.382	0.12	0.951	1.6
3	20	0.964	0.27	0.265	0.945	1.16
4	30	0.936	0.237	0.28	0.930	1.12
5	40	0.924	0.326	0.28	0.911	1.04
6	50	0.924	0.236	0.28	0.893	0.987
7	60	0.924	0.236	0.28	0.875	0.963

Flow chart for the simulation of model



PROCESS FLOW DIAGRAM FOR TRANSESTERIFICATION OF JATROPHA OIL



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