CASTOR OIL TRANSESTERIFICATION-EXPERIMENTAL AND MODELING STUDIES

Ph. D. THESIS

by

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CENTRE FOR TRANSPORTATION SYSTEMS
and
DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE- 247 667 (INDIA)
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A THESIS

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

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in

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INDIAN INSTITUTE OF TECHNOLOGY ROORKEE, ROORKEE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **"Castor Oil Transesterification-Experimental and Modeling Studies"** in partial fulfillment of the requirements for the award of the Degree of Doctor of Philosophy and submitted in the Department of Chemistry of the Indian Institute of Technology Roorkee, Roorkee is an authentic record of my own work carried out at Centre for Transportation Systems (CTRANS) during a period from August, 2008 to July, 2014 under the supervision of Dr. Surendra Kumar, Professor, Department of Chemical Engineering, and Dr. V. K. Gupta, Professor, Department of Chemistry, Indian Institute of Technology Roorkee.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other Institute.

(Payal)

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

(Surendra Kumar) (V. K. Gupta)
Supervisor Supervisor

Date: July, 2014

The Ph.D. Viva-Voce Examination of **Ms. Payal,** Research Scholar, has been held on……………………………………………………………………… .

Signature of Supervisors **Signature of External Examiner**

Chairman, SRC **Head of the Deptt./Centre**

ABSTRACT

Energy demand is growing at a fast pace probably in every country of the word. This is because of increase in population in some parts of the globe and also due to enhanced impetus on the development of infrastructure of all kinds and related human related services. The demand of energy driven sectors, are mostly met by fossil fuels namely Petroleum, Natural Gas and Coal whose reserves are constantly depleting. Use of fossil fuels also results into adverse impact on environment and climatic conditions (Wang et al., 2012). Therefore, there has been a growing interest in searching alternative renewable and eco-friendly sources of energy (Caballero and Guirardello, 2013). It is expected that these alternative sources can replace fossil fuels to a large extent or can at least supplement them. Due to this reason, Biodiesel has become more attractive alternative and sustainable fuel source (Balat and Balat, 2010).

Biodiesel is made from renewable biological sources namely vegetable oils and animal fats (Ma and Hanna, 1999). Biodiesel is a nontoxic, biodegradable and environmental friendly fuel. It also provides lower hydrocarbon and carbon monoxide emissions, higher cetane number, less smoke and particulate matter (Atadashi et al., 2012).Generally, vegetable oils or animal fats can be easily converted to biofuel by transesterification reaction with an alcohol in the presence of a catalyst. The main product is mixture of fatty acid alkyl ester (FAAE), called as biodiesel (Badday et al., 2014), and glycerol is produced as a byproduct (Fayyazi et al., 2013).

Leung et al. (2010) in an excellent review has described various vegetable oil feedstocks, which are used for producing biodiesel. These may be classified as edible vegetable oils, non-edible vegetable oils, and others. Edible oils include Soybean, Rapeseed, Sunflower, Palm, Peanut, Corn, Camelina, canola, cotton, pumpkin, while non-edible oils are Jatropha, Pongamia, Sea mango, Palanga, Tallow, Nile tilapia, poultry, and used cooking oils fall in the category of others. Biodiesel produced from these edible oils is a suitable substitute for diesel fuel. In India as well as in other countries, edible oils are not recommended to be used as raw material for biodiesel. Its use is likely to increase the cost of edible oils, which are used by human beings. Therefore, it is desirable and preferred to use non-edible oils for this purpose.

Leung et al. (2010) have pointed out in their review that significant amount of research work has been done on non-edible oils namely, *Jatropha curcas*, *Pongamia pinnata*, Sea mango, Palanga, Tallow, Nile tilapia etc and used cooking oil. Several excellent reviews have been published recently on Biodiesel from vegetable oils. These are due to Issariyakul and Dalai (2014), Atabani et al. (2013), and Lin et al. (2011). After critical assessment of published work, it has been observed that relatively less amount of research work has been done on the transesterification of castor oil- a non-edible vegetable oil.

About castor oil, Berman et al. (2011) states "Castor oil is one of the most promising non-edible oil crops, due to its high annual seed production and yield, and since it can be grown on marginal land and in semiarid climate". Scholz and Silva (2008) have reviewed the "Prospects and risks of castor oil as a fuel", and recommended that a better option possibly is its transesterification and addition of the product biodiesel to fossil diesel fuel. Similar view point has been expressed by Shrirame et al. (2011). Berman et al. (2011) have evaluated the fuel related properties of castor oil Biodiesel and recommended its use for blending with diesel with a maximum limit of 10 %.

Therefore, it was thought proper to conduct focused review of literature on castor oil transesterification related to process development, property estimation, cost estimation, reaction kinetics and optimization. Main observations are given below.

(i) Most of the research papers are from the year 2010 and onwards.

(ii) Ethanol and methanol both have been used for transesterification. With ethanol several catalysts namely, KOH, NaOH, $KOCH_3$, $NaOCH_3$, H_2SO_4, HCl, K_2CO_3 and $CaCO_3$, have been used. However sodium methoxide, tin (IV) complex, solid potassium and cesium salts of 12-Tunstophosphoric acid have been used as catalyst with methanol.

(iii) In-situ transesterification of castor oil seeds has also been done.

(iv) Transesterification under supercritical conditions has also been investigated.

(v) Transesterification with methanol using basic catalyst (KOH, NaOH, $KOCH_3$, $NaOCH_3$, $NaOC_2H_5$) has been studied.

(vi) Commonly used molar ratio of methanol to oil varies between 4:1 to 12.5:1. Higher molar ratios 50:1, 225:1 and 250:1 have also been used.

(vii) Operating temperature varies from 25° - 65 °C, but in one study, experiments have also been conducted at 80 °C.

(viii) Experimental results have been utilized to obtain kinetic rate constants of kinetic models of first order irreversible, and second order irreversible and reversible reactions. Most of the researchers have assumed pseudo first order kinetics.

(ix) Design of experiment and Response Surface Method (RSM) has been used to obtain optimized conditions of transesterification reaction.

It may be concluded from the above summary that the transesterification of castor oil with methanol in the presence of acid catalyst have not been investigated from the point of view of determining reaction kinetics, and optimized operation conditions, parameters of kinetic models. For using the alkaline catalyst it is desired that the FFA content in the oil should be less than 1% (Tiwari et al., 2007). In case FFA content exceeds this limit, the soap formation may occur which should inhibit the suppression of ester (Canakci and Gerpen, 2001). In the present case FFA content in castor oil is more than 1%, so acid catalyst have been chosen for castor oil transesterification.

In view of the above discussion, experimental studies on castor oil transesterification have been planned to be conducted in this thesis in two types of Lab Reactors, Small Lab Reactor (500 cc) and the Large Lab Reactor (3 L), with sulphuric acid as a catalyst. Main emphasis is on kinetic modeling, use of RSM and Artificial Neural Network (ANN) for determining optimized conditions, and kinetic parameters. The results are summarized below:

Small lab reactor: The operating conditions used for experimental studies were methanol/oil molar ratio = 6:1, catalyst =1 % concentrated H_2SO_4 (% v/v of castor oil), temperature = 35° to 65 °C at an interval of 5 °C, and 600 RPM. Experimental results have been analyzed with respect to three kinetic schemes namely, first order pseudo irreversible reaction, second order irreversible reaction, and the reversible reaction.

(a) By using first order pseudo irreversible reaction kinetics, and experimental data, rate constant k (mm^{-1}) have been computed at various temperatures. This provides the values of activation energy, and Arrhenius constant as given below.

Activation Energy, E = 38.283 kJ/mol ; Arrhenius constant, A= 1461.0345 min^{-1}

(b) Analysis of experimental data by second order irreversible reaction kinetics provides the following values :

Activation Energy, E = 38.611 kJ/mol ; Arrhenius constant = 343836.48 ml/(mol.min)

Fitting of irreversible second order kinetic model is somewhat better than that of irreversible first order reaction with respect to correlation coefficients.

(c) Kinetic model for reversible reaction with forward reaction as pseudo first order, and backward reaction as second order has also been used to analyze the experimental results and the obtained model is as given below:

$$\frac{dX_c}{dt} = k_1\left[(3 - X_c) - \frac{C_{Ao}}{K} X_c^2\right]$$

Where X_c = fractional formation of FAME; $k_1(\text{min}^{-1}) = 216.264 \exp\left(\frac{-32.33}{R\,T}\right)$;

Gas constant, $R = 8.3144 \frac{kJ}{kmol.K}$; Temperature T = K

Equilibrium constant, $K \left(\frac{gmol}{l}\right) = K_{35}\, exp\left[11857\left(\frac{1}{308.15} - \frac{1}{T}\right)\right]$; and

$K_{35} = 0.008895 \left(\frac{gmol}{l}\right)$

This kinetic model is applicable in the temperature range 35° to 60 °C.

(d) This transesterification reaction is endothermic in nature, and its heat of reaction, computed in this work is 23.560 kcal/g mol.

(e) In order to evaluate the usability of FAME (biodiesel) produced, its several properties have been experimentally determined. From these properties, it is concluded that the biodiesel product formed should be used for blending with diesel oil in appropriate quantity to bring its properties within acceptable limits as viscosity of FAME product and its water content both are on higher side. These conclusions are in accordance with pervious similar findings reported in the literature [Canoira et al. (2010)].

Large Lab Reactor: The experimental data taken in this reactor have been analyzed by response surface Methodology (RSM), and Artificial Neural Networks (ANN). Main Conclusions are:

RSM Modeling: The central composite design (CCD) of the RSM was used to decide the number of experiments, to be conducted. Range of operating conditions was: Methanol to oil ratio = 6:1 to 25:1, catalyst amount (vol. %) = 1 to 3, temperature (°C) = 40 to 60. An experiment was conducted up to 4 hours duration. Samples for analysis were taken in between at regular intervals. A RSM model has been developed by using experimental data of all sets at 4 hour time only. The model in terms of coded variables for predicting % FAME yield for given values of methanol to oil molar ratio, catalyst amount, and the temperature. ANOVA has been used to evaluate the adequacy of the RSM model. The model has also been validated with two additional sets of experimental data. The model predictions are within ± 5 % deviation with respect to experimental results.

RSM model has been used to optimize the experimental conditions. These are methanol to oil ratio = 25:1, catalyst amount = 3 vol %, temperature = 60 °C. RSM model yields % FAME yield as 75.67 % while that obtained experimentally is 76.95 %. Using the model, the effects of variation in operating conditions on % FAME yield have also been studied.

ANN Model: The development of ANN model has been done by using fractional formation of FAME (X_c), versus time (t) experimental data. The developed model is a Feed forward Neural Network (FFNN). There are four input neurons corresponding to four input variables namely methanol to oil molar ratio, catalyst amount, temperature, and time, and one output neuron corresponding to the fractional formation of FAME. There is one hidden layer in optimized ANN model consisting of 12 neurons. In this model tangent sigmoid function has been used as the activation function in the hidden layer and linear function has been used as the activation function in the output layer.

ANN model has been validated with two additional sets of experimental data, obtained by conducting separate experiments, and the ANN model predictions are within ± 4 % deviation.

A kinetic model has been developed by using X_c various time t data namely, 9:1, 12:1, 15:1, 18:1, and the experimental data at 25:1. The model is applicable at the optimum temperature = 60 °C and catalyst amount = 3 % v/v. The kinetic model provides the effect of change in the methanol to oil molar ratio on X_c at optimum operating conditions. The model is reproduced below.

$$\frac{dX_c}{dt} = k_1 C_{A0}(3 - X_c)(M - X_c) - k_2 C_{A0} X_c^2$$

With $X_c = 0$ at $t = 0$. Where t = time (min)

C_{A0} = Initial concentration of Castor Oil (gmol/l),

M = Molar ratio of methanol to castor oil

k_1 = 0.000295 (l/gmol.min), k_2 = 0.026775 (l/gmol.min)

The developed kinetic model predicts the fractional formation of FAME within ± 10 % deviation

It is our view that the results of this study may be useful for designing a batch or continuous flow reactor for castor oil transesterification at optimum operating conditions.

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Payal

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NOMENCLATURE

Notations

ANN	Artificial Neural Network
ANOVA	Analysis Of Variance
AC	Acid Value
BSTR	Batch Stirred Tank Reactor
CA	Canonical Analysis
CCD	Central Composite Design
CSTR	Continuous Stirred Tank Reactor
CSR	Closed Steel Reactor
DOE	Design of Experiments
DF	Degree of Freedom
D (%)	Deviation (%)
FAAE	Fatty Acid Alkyl Esters
FAEE	Fatty Acid Ethyl Esters
FAME	Fatty Acid Methyl Esters
FFA	Free Fatty Acid
FID	Flame Ionization Detector
FFNN	Feed Forward Neural Network
GC	Gas Chromatograph
GL	Glycerol
ML-ANN	Multilayer Feed Forward Artificial Neural Network
ML	Methanol
MSE	Mean Square Error
ME	Methyl Esters
NMR	Nuclear Magnetic Resonance
OGR	Open Glass Reactor
RSM	Response Surface Methodology
THF	Tetrahydrofuran

TG	Triglyceride
TPA	12-Tungstophosphoric Acid
VPO	Vapor Pressure Osmometry
WCO	Waste Cooking Oils

Greek letters

α	[-]	axial point of factorial design
β	[-]	constant coefficient of mathematical model
β_o	[-]	Offset regression term in in Eq. (4.1)
β_i	[-]	linear regression coefficient in Eq. (4.1)
β_{ii}	[-]	Quadratic regression coefficient in Eq. (4.1)
β_{ij}	[-]	Second order interaction regression coefficient in Eq. (4.1)
ε	[-]	random error of mathematical model

Abbreviations

A	[-]	Arrhenius constant in Eq. (3.12)
Adj. R^2	[-]	Adjusted value of regression coefficient
C_{A0}		Initial concentration of castor oil (mol/l) in Eq. (3.10)
E		activation energy in Eq. (3.12) (kJ/mol)
K	[-]	Equilibrium constant in Eq. (3.15)
M		Molar ratio of methanol to castor oil in Eq. (3.10)
min		minutes
N		total number of datasets in Eq. (5.1)
Pc		Critical pressure
p-value		smallest level of significance that would lead to rejection of null hypothesis in test statistics

R		Universal gas constant
R^2		Correlation coefficient
T		Temperature (Kelvin)
Tc		Critical temperature
X_k^{exp}		experimental values of % FAME in Eq. (5.1)
X_k^{cal}		calculated value of % FAME in Eq. (5.1)
ΔH	[Kcal/gmol]	Heat of reaction in Eq. (3.16)
$X_{c_{i,j}}$		values obtained experimentally and predicted through ANN in Eq. (5.3)
X_C	[mol/l]	fractional formation of FAME
Y_{Exp}		Experimental value of response

CHAPTER I

INTRODUCTION

Energy demand is growing at a fast pace probably in every country of the word. This is because of increase in population in some parts of the globe and also due to enhanced impetus on the development of infrastructure of all kinds and related human related services. The demand of energy driven sectors, are mostly met by fossil fuels namely Petroleum, Natural Gas and Coal whose reserves are constantly depleting. Use of fossil fuels also results into adverse impact on environment and climatic conditions (Wang et al., 2012). Therefore, there has been a growing interest in searching alternative renewable and eco-friendly sources of energy (Caballero and Guirardello, 2013). It is expected that these alternative sources can replace fossil fuels to a large extent or can at least supplement them. Due to this reason, Biodiesel has become more attractive alternative and sustainable fuel source (Balat and Balat, 2010).

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Leung et al. (2010) in an excellent review has described various vegetable oil feedstocks, which are used for producing biodiesel. These may be classified as edible vegetable oils, non-edible vegetable oils, and others. Edible oils include Soybean, Rapeseed, Sunflower, Palm, Peanut, Corn, Camelina, canola, cotton, pumpkin, while non-edible oils are Jatropha, Pongamia, Sea mango, Palanga, Tallow, Nile tilapia, poultry, and used cooking oils fall in the category of others. Biodiesel produced from these edible oils is a suitable substitute for diesel fuel. In India as well as in other countries, edible oils are not recommended to be used as raw material for biodiesel. Its use is likely to increase the cost of edible oils, which are used by human beings. Therefore, it is desirable and preferred to use non-edible oils for this purpose.

Leung et al. (2010) have pointed out in their review that significant amount of research work has been done on non-edible oils namely, *Jatropha curcas*, *Pongamia pinnata*, Sea mango, Palanga, Tallow, Nile tilapia etc and used cooking oil. Several excellent reviews have been published recently on Biodiesel from vegetable oils. These are due to Issariyakul and Dalai (2014), Atabani et al. (2013), and Lin et al. (2011). After critical assessment of published work, it has been observed that relatively less amount of research work has been done on the transesterification of castor oil- a non-edible vegetable oil. Therefore, it was thought proper to conduct research work on castor oil transesterification. Again, focused review of literature was done in respect of castor oil as described in the following section.

1.1 CASTOR OIL

Castor oil is extracted, from the seed of a plant with *Ricinus communis* botanical name (Ogunniyi, 2006). It is environmental friendly and naturally occurring resource. Castor oil is a viscous, pale yellow, non-volatile and non drying oil. In comparison to other vegetable oils, it can be stored for longer duration, however exposure to excessive heat should be avoided. About castor oil, Berman et al. (2011) states "Castor oil is one of the most promising non-edible oil crops, due to its high annual seed production and yield, and since it can be grown on marginal land and in semiarid climate". Scholz and Silva (2008) have reviewed the "Prospects and risks of castor oil as a fuel", and recommended that a better option possibly is its transesterification and addition of the product biodiesel to fossil diesel fuel. Similar view point has been expressed by Shrirame et al. (2011). Berman et al. (2011) have evaluated the fuel related properties of castor oil Biodiesel and recommended its use for blending with diesel with a maximum limit of 10 %. Table 1.1(a) and 1.1(b) summarizes various types of used feedstocks for the biodiesel production and their properties. Table 1.2 summarizes the various studies related to process development, property estimation, and cost estimation of biodiesel production from castor oil. From this following observations may be made:

(i) Most of the research papers except one at S. No. 2 are from the year 2010 and onwards.

(ii) Ethanol and methanol both have been used for transesterification. With ethanol several catalysts namely, KOH, NaOH, $KOCH_3$, $NaOCH_3$, H_2SO_4, HCl, K_2CO_3 and $CaCO_3$ have been used. However sodium methoxide, tin (IV) complex, solid potassium and cesium salts of 12-Tunstophosphoric acid have been used as catalyst with methanol.

(iii) In-situ transesterification of castor oil seeds has also been done.

(iv) Transesterification under supercritical conditions has also been investigated.

Similarly Table 1.3 concerns with the summary of research on 'kinetics and optimization studies on castor oil transesterification'. Main observations are given below:

(i) Transesterification with methanol using basic catalyst (KOH, NaOH, $KOCH_3$, $NaOCH_3$, $NaOC_2H_5$) has been studied.

(ii) Commonly used molar ratio of methanol to oil varies between 4:1 to 12.5:1. Higher molar ratios 50:1, 225:1 and 250:1 have also been used.

(iii) Operating temperature varies from 25° - 65 °C, but in one study, experiments have also been conducted at 80 °C.

(iv) Experimental results have been utilized to obtain kinetic rate constants of kinetic models of first order irreversible, and second order irreversible and reversible reactions. Most of the researchers have assumed pseudo first order kinetics.

(v) Design of experiment and Response Surface Method (RSM) has been used to obtain optimized conditions of transesterification reaction.

It may be concluded from the summary that the transesterification of castor oil with methanol in the presence of acid catalyst have not been investigated from the point of view of determining reaction kinetics, and optimized operation conditions, parameters of kinetic models. For using the alkaline catalyst it is desired that the FFA content in the oil should be less than 1% (Tiwari et al., 2007). In case FFA content exceeds this limit, the soap formation may occur which should inhibit the suppression

Table 1.1 (a) : Feedstocks for biodiesel production and their physicochemical properties (Leung et al., 2010)

	Type of oil	Species	Density (g/cm^3)	Flash point (°C)	Kinematic viscosity (cst, at 40 °C)	Acid value (mg KOH/g)	Heating value (MJ/kg)	References
A	**Edible Vegetable Oil**							
	i	Soybean	0.90	254	32.9	0.2	39.6	Byun et al. (1995), Jose Alanso et al. (2008), Singh and Singh (2009), Srivastava and Prasad (2000)
	ii	Rapeseed	0.91	246	35.1	2.92	39.7	Azcan and Danisman (2008), Demirbas (2003), Jose Alanso et al. (2008), Singh and Singh (2009)
	iii	Sunflower	0.92	274	32.6	-	39.6	Jose Alanso et al. (2008), Singh and Singh (2009), Winayanuwattikun et al. (2008)
	iv	Palm	0.92	267	39.6[a]	0.1	-	Abreu et al. (2004), Kansedo et al. (2009), Singh and Singh (2009)
	v	Peanut	0.90	271	22.72	3	39.8	Kaya et al. (2009), Rao et al. (2009), Singh and Singh (2009), Winayanuwattikun et al. (2008)
	vi	Corn	0.91	277	34.9[a]	-	39.5	Saraf and Thomas (2007), Singh and Singh (2009)
	vii	Camelina	0.91	-	-	0.76	42.2	Barnardo et al. (2003), Zubr (1997)
	viii	Canola			38.2	0.4		Demirbas (2003), Issariyakul et al. (2008)
	ix	Cotton	0.91	234	18.2		39.5	Saraf and Thomas (2007), Singh and Singh (2009)
	x	Pumpkin	0.92	> 230	35.6	0.55	39	Schinas et al. (2009)

a : Kinematic viscosity at 38 ^{0}C, mm^2/s.

Table 1.1 (b) : Feed stocks for biodiesel production and their physicochemical properties (Leung et al., 2010)

	Type of oil	Species	Density (g/cm^3)	Flash point (^{0}C)	Kinematic viscosity (cst, at 40^{0}C)	Acid value (mg KOH/g)	Heating value (MJ/kg)	References
B	**Non-edible Vegetable Oil**							
	i	Jatropha curcas	0.92	225	29.4	28	38.5	Berchmans and Hirata (2008), Chitra et al. (2005), Tiwari et al. (2007)
	ii	Pongamina pinnata	0.91	205	27.8	5.06	34	Sahoo and Das (2009)
	ii	Sea mango	0.92	-	29.6	0.24	40.86	Kansedo et al. (2009)
	iii	Palanga	0.90	221	72.0	44	39.25	Sahoo and Das (2009)
	iv	Tallow	0.92	-	-	-	40.05	Saraf and Thomas (2007), Goodrum et al. (2003)
	v	Nile tilapia	0.91	-	32.1^b	2.81	-	Santos et al. (2010)
	vi	Poultry	0.90	-	-	-	39.4	Goodrum et al. (2003), Liu et al. (2004)
C	**Others**							
	i	Used cooking oil	0.90	-	44.7	2.5	-	Issariyakul et al. (2008)

b : Kinematic viscosity at 37 ^{0}C, mm^2/s.

Table 1.2 : Transesterification of Castor Oil

S. No	Author	Process conditions	Type of study
1.	Hincapie et al. (2011)	Conventional in-situ transesterification of castor oil seeds; ethanol (molar ratio of alcohol to oil = 60:1) Two step process : Acid catalyzed transesterification(H_2SO_4) and base catalyzed transesterification (KOH)	Process development
2.	Meneghetti et al. (2006)	Transesterification with ethanol; several catalysts, KOH, NaOH, $KOCH_3$, $NaOCH_3$, H_2SO_4, HCl, K_2CO_3 and $CaCO_3$ tried; EtOH:oil:catalyst = 60:10:2 (molar ratio)	Process development
3.	Canoira et al. (2010)	Transesterification with methanol in presence of sodium methoxide catalyst.	Process development and properties estimation
4.	Thomas et al. (2012)	Evaluation of viscosity reduction of castor Methyl and Ethyl Ester blends with diesel	Properties estimation of blends
5.	Barbosa et al. (2010)	Ethanol of mixed castor and soybean oils with potassium hydroxide as catalyst	Process development
6.	Serra et al. (2011)	Methanolysis of castor and soybean oil individually in the presence of tin (IV) complexes	Comparative performance study
7.	Vieitez et al. (2011)	Synthesis of castor oil ethyl esters under supercritical ethanol without catalyst.	Process development
8.	Zieba et al. (2009)	Methanolysis of castor oil with solid potassium and cesium salts of 12-Tunstophosphoric acid as catalyst	Process development
9.	Santana et al. (2010)	Transesterification with ethanol and NaOH as catalyst	Simulation of biodiesel plant by using HYSIS and cost estimation

Table 1.3 : Kinetics and optimization studies of castor oil transesterification

S. No.	Author	Process			Temperature	Remarks
		Alcohol	Catalyst	Molar ratio (Alcohol to oil)		
1.	Madankar et al. (2013)	Methanol	KOH (0.5-2%)	50:1 to 250:1	35-65 ^{0}C	Kinetic study, first order kinetics used: Reaction extraction of castor seeds; Use of Methyl esters as bio-lubricant promising.
2.	Pradhan et al. (2012)	Methanol	KOH (1 wt% of oil)	225:1	55 ^{0}C	Reaction extraction of castor seed to produce biodiesel; Used Response Surface Methodology (RSM) to optimize process parameters
3.	Ramezani et al. (2010)	Methanol	Basic catalyst (0.25, 0.35, 0.50 %) NaOH,$NaOCH_3$, $KOCH_3$,KOH	4:1, 6:1, 8:1	25, 65, 80 ^{0}C	First order irreversible kinetics used: Estimated properties, Kinetic viscosity, Cetane number
4.	Lopez et al. (2011)	Methanol	NaOH catalyst to castor molar ratio 0.10, 0.15, 0.20, 0.25	6:1	25, 65 ^{0}C	Used proton nuclear magnetic response spectroscopy for monitoring the results and outcomes of the transesterification; an irreversible first order step followed by a reversible stage, both of pseudo first order
5.	Jeong and Park (2009)	Methanol	KOH % (w/w))	2.45:1 to 12.55:1	24.8-65 ^{0}C	Optimized operating conditions by using first level, three factor design and Response Surface Methodology
6.	Kilic et al. (2013)	Methanol	Basic catalyst NaOH, KOH etc. 0.5-1.5 (%w)	5:1 to 7:1	25-65 ^{0}C	Used Central Composite Design and RSM to optimize operating conditions
7.	Da Silva et al. (2009)	Ethanol	Sodium Ethoxide 0.5-1.5 (%w)	6:1 to 20:1	30-80 ^{0}C	Experimental design and RSM to optimize operating conditions; first order irreversible kinetic model

of ester (Canakci and Gerpen, 2001). In the present case FFA content in castor oil is more than 1%, so acid catalyst have been chosen for castor oil transesterification.

In view of the above discussion, it was planned to study the castor oil transesterification in presence of H_2SO_4 as catalyst with the objectives given in the following section. Main emphasis is on kinetic modeling, use of RSM and Artificial Neural Network (ANN) for determining optimized conditions, and kinetic parameters.

1.2 OBJECTIVES

In this thesis, experimental studies on castor oil transesterification have been planned to be conducted in two types of Lab Reactors, Small Lab Reactor (500 cc) and the Large Lab Reactor (3 L), with sulphuric acid as a catalyst. Objectives in brief are given below:

[A] Small Lab Reactor

(i) To conduct experimental investigations at the wide range of operating conditions in the reactor. These are methanol to oil molar ratio = 6:1; catalyst concentrated H_2SO_4 1% (v/v of castor oil), temperature = 35° to 65 °C at a interval of 5 °C, rpm = 600.

(ii) (a) To estimate rate constants of pseudo first order irreversible, and second order irreversible reactions.

(b) To estimate activation energy and Arrhenius constant for both the reactions.

(iii) (a) To analyze the experimental data by a reversible reaction with forward reaction as pseudo first order, and the backward reaction as second order.

(b) To estimate forward reaction rate constant and equilibrium constant, and develop equations, which provide their dependency on temperature.

(c) To estimate Heat of Reaction.

(iv) To determine properties of produced castor oil biodiesel (FAMEs) by standard tests.

[B] Large Lab Reactor

(i) To conduct experimental studies in Large Lab Reactor at operating conditions: methanol to oil molar ratio=6:1 to 25:1; catalyst amount (vol.%) = 1 to 3, Temperature (C) = 40 °C to 60 °C, duration of experiments = 4 h.

(ii) To use central composition design (CCD) to decide the number of experiments, which are to be conducted in the range of operating variable, mentioned above in (i).

(iii) (a) To develop RSM (Response Surface Method) model by using all experimental data at 4h time only for predicting % FAME Yield.

(b) To test the adequacy of RSM model by ANOVA.

(c) To validate the RSM model by two sets of additional experimental data, obtained separately, to check the accuracy of RSM model.

(iv) (a) To develop a ANN (Artificial Neural Network) model by using experimental data on fractional formation of FAME versus time, obtained for all sets, and decided by the CCD.

(b) To validate ANN model with two sets of additional experimental data, obtained separately.

(v) To predict fractional formation of FAME (X_c) versus time (t) profile by using ANN model for few molar ratios, 9:1, 12:1, 15:1, and 18:1 at optimized conditions (determined by RSM).

(vi) (a) To develop a kinetic model for optimum operating conditions, which accounts for variation in molar ratio, by taking above four predicted profiles (X_c vs. t), and experimentally obtained profile for 25:1 molar ratio.

(b) To obtain rate constants of the model. The problem becomes parameter estimation of a differential equation model using experimental data.

1.3 ORGANIZATION OF THE THESIS

In this thesis, the research work has been organized in six chapters. Chapter I provides introduction to the transesterification of vegetable oils, edible and non-edible. Emphasis has been given on castor oil transesterification, which is the subject matter of this thesis. Objectives of the thesis have also been outlined. Chapter II provides review of selected literature on issues related to castor oil transesterification. Chapter III reports experimental studies carried out in the small lab reactor at wide range of operating conditions. This chapter also describes the estimation of rate constants for assumed reaction schemes. Physical properties of produced castor biodiesel (or FAME), determined by standard tests, has been mentioned. On the other hand, experimental studies performed on a large lab reactor on several sets of operating conditions decided by the Central Composite Design, has been described in Chapter IV. This chapter also includes development of RSM model, its validation and accuracy of its predictions. Lastly it described the effect of operating variables of fractional formation of FAME, predicted by RSM model. The Chapter V is devoted to the development of a ANN model by using fractional formation of FAME (X_c) versus time data, obtained at all sets of operating conditions, decided by the CCD. This chapter also describes the development of a kinetic model, which explains the effect of methanol to oil molar ratio on X_c at optimized operating conditions, Parameters' estimation of a differential equation model has also been discussed. Finally, Chapter VI highlights the main conclusions of the research work and provides the recommendations for future work.

CHAPTER II

LITERATURE REVIEW

2.0 INTRODUCTION

As the oil demand is increasing, the oil reserves are depleting. The increased consumption is also adding to the higher level of environmental pollution. This crisis has raised the interest of international research communities and governments in other alternative fuels mainly fuels of biological origin in comparison to petroleum based fuels in. The world energy assembly speculated that in less than ten decades deposit based fuels consisting coal and gasoline will become collapsed (Sharma et al. 2008; WEO, 2009). Therefore, it is compulsary to establish unsustainable fuel resources to replace the ancestral fuel. The alternative to diesel fuel must be technically advantages, methodically competitive, environmentally acquired and easily accesible. One of such good alternative fuel is biodiesel produced from vegetable crop oil, animal fat and waste frying oils. Biodiesel means ester based oxygenated biofuel which is equivalent to diesel produced by transesterification reaction from renewable biological materials such as plant oil. It is nontoxic, biodegradable and renewable fuel. The petroleum diesel hydrocarbon does not break easily and they create pollution in air and water resources (Fingas and Fieldhouse, 2012). The biodiesel can be produced by using various techniques such as transesterification, cracking, emulsion and pyrolysis as discussed in Chapter I. Transesterification of vegetable oils has been in use from last few years. Abbaszaadeh et al. (2012) reviewed the techniques that are used for the biodiesel formation. At the present time non-edible oils are preferably used for biodiesel formation because it does not compete with food crop. Therefore, non-edible oils like Jatropha, Castor, Karanja, Mahua, Neem oil etc. can be utilized for biodiesel production. In India, ethanol and biodiesel as a second fuel option to established fuel is gaining importance. As these enhance the energy security and at the same time decrease the environmental concerns. Both these method of fuel production can provide a large scale of employment in rural area, particularly in developing countries like India (MNRE report Govt. of India 2008).

India is the world leader in castor oil production and significant quantity of its produce is used for export purpose. Castor oil has various applications in cosmetics, pharmaceutical industries, used as a non drying oil in paint industries and for the production of biodiesel. The castor oil has a toxin named ricin in its chemical composition hence it cannot be used as cooking oil for human population and not for animals as fodder crop. Since last few years, interest in creation of biodiesel from non-edible oils has increased, as the world is facing fuel crisis. Therefore, in this chapter, production of biodiesel from non-edible castor oil by the use of various types of reaction have been described and reviewed. The aim of review is to shed light on the biodiesel formation from castor oil, its characterization and fuel properties, optimization of reaction parameters, kinetic, and modeling studies related to the objectives of the present research work mentioned in Chapter I. A brief description of various catalysts used in transesterification of vegetable oils in batch reactors with their advantages and effect of various reaction parameters on the process is given for the general understanding of the biodiesel production process. Experimental and optimization studies of biodiesel formation from castor oil are also discussed in this chapter. Borugadda and Goud (2012) reported that India is the largest producer and exporter of castor oil seeds in world, and its yield of production is 200-290 Kg/ha. India produces 8-8.5 million tonnes of castor seeds annually and produces more than 60% of the total world production.

The present work has two main motives :

- To determine the best operating conditions for the transesterification reaction of castor oil with methyl alcohol, use of concentrated H_2SO_4 as an acid catalyst
- And evaluation of rate constants, activation energy and kinetics of transesterification reactions.
- Optimization of reaction variables of transesterification reaction by the use of response surface methodology and Artificial Neural Network.

The castor oil has been selected for this study because it is non-edible, has a high content of oil and it can grow well in tropical environment. Further, the choice of acidic catalyst over alkaline catalyst is made to avoid accumulation of soap as by product. As commercially available crude castor oil has a high FFA amount hence with alkaline catalyst it can produce soaps as by product of the reaction. but the acid catalyst is not concerned by the presence of free fatty acids in the oil feedstock and can esterifies the oil to esters, therefore acid catalyst is a acceptable choice for the biodiesel formation from castor oil.

Gupta et al. (1951) reported that castor plant which has botanical name *Ricinus communis*, related to the family Euphorbiacae and is cultivated in the tropical as well as sub tropical regions of world. Castor seed contains about 45- 55% oil by weight. Castor plant is originally a tree that can grow to about 15 meter height with age 4-5 years and can grow in regions having low humidity and temperature range of 15°-40 °C. Jain et al. (2011) carried out the experimental studies on jatropha oil for the formation of biodiesel and optimized the reaction parameters. The total mehyl esters yield was obtained 90% and kinetic study also has been done. Wang and Lu (1996) reviewed the effect of catalyst selection and their activity, reaction mechanism of carbon dioxide reforming of methane for the production of synthesis gas. According to Knothe (2005), Srivastva and Prasad, (2000) the viscosity of plant oils is 10-20 times greater than the fossil fuel, therefore directly using plant oils as a fuel can create engine issues like injector fouling and accumulation of particles. Therefore, a slight chemical change is needed to ensure the use of vegetable oils in diesel engines. A few methods have been established and these consists of transesterification reaction, blending, micro-emulsification, cracking and pyrolysis. Fukuda et al., (2001) and Singh and Gu (2010) reported that methyl alcohol and ethyl alcohol are most extensively adopted alcohols in biodiesel industries as methyl alcohol is cheap and ethyl alcohol can be originated by using agronomical waste materials (renewable resources). Methanol is commonly used alcohol for transestrification reaction because it has low molecular weight, low cost and is easily available. Balat, (2011) and Gui et al., (2008) reported in their studies that globally more than 90% of biodiesel is originated mainly from cooking oils such as Soybean, Sunflower, Palm tree, Peanut, Mustard oils .However, as per the recent discussions in forums and deliberations a new debate has started on the efficient use of edible oils for biodiesel production. It is observed that use of edible oils have a negative impact in food chain supply and causes environmental desertification and eradication of ecosystem. So, in order to run over these negative impacts investigations have been done to synthesize the biodiesel using inedible oils as substitute to edible oils.

2.1 FEEDSTOCK FOR BIODIESEL PRODUCTION

Currently, the researchers all over the world are focusing on biodiesel synthesis from cheap resource materials, non-edible oils, waste cooking oils, animal fats and algae. The use of plant oils as good alternative fuel to petroleum based diesel has started almost 100 years ago. Rudolph Diesel was the first to invent the compression ignition engine using peanut oil for its operation.

The cost of basic materials, used for the synthesis of biodiesel, constitutes the major portion of biodiesel production cost and on the other hand the cost of raw material is directly linked to its easy availability. (Zhang et al., 2003; Demirbas, 2007) reviewed that the use of refined or high quality feedstock material that is used for biodiesel production constitutes about 80-88% of the overall manufacturing or production cost. The properties of feedstock oil for biodiesel production also have a important impact on the quality of produced esters. The production cost can be reduced by choosing the crop with a higher oil yield. Pandey et al., (2013) investigated the use of nanomaterials for the analysis of biomolecules. (Gui et al., 2008). The feedstocks used for the biodiesel production can be classified into vegetable oil (edible oil and inedible oil), animal fats, and waste cooking oil (Lang et al., 2001; Shrirame et al. (2011) discussed the use of biodiesel formation from vegetable oils as a renewable resource, from both type of edible and non edible in India. The esters obtained from vegetable oils could be used as a diesel substitute in engines of automobiles, generators etc. Santana et al. (2010) carried out the simulation study of the biodiesel formation process from castor oil by using HYSS simulator.

2.1.1 Edible Oil

Nowadays, the edible vegetable oil is dominant raw material for biodiesel production in different countries, and the choice of vegetable oil depends on the soil and climatic conditions (Sharma et al., 2008). For example, rapeseed oil and sunflower oil are commonly adopted in many European countries, soybean oil is used in the United States, palm oils are used in Malaysia for biodiesel production and coconut oil is used in the Philippines (Demirbas, 2006; Meher et al., 2004).

There are mainly four oil crops, rapeseed, soybean, palm and sunflower which dominate the feedstock vegetable oil resources used for biodiesel production worldwide. Other edible vegetable oils like corn, canola have also been used for biodiesel production and are reported as a good diesel substitute (Lang et al., 2001; Freedman et al., 1986). Other types of oil crops that are currently being investigated are peanut seed oil, melon seed oils and safflower oil. However, the demand for food and fuel is increasing as the world population is increasing and it creates the debate of food versus fuel issues (Balat, 2011). Therefore, the most promising alternative to replace edible oils is non-edible feedstock. In India, the national policy on biofuel has been developed by the ministry of New and Renewable Energy (MNRE), which is the governing body of the use of renewable energy resources. MNRE targets for blending of biofuel such as biodiesel and bioethanol with fossil based fuels by 2017.

2.2.2 Non-edible Oil

Presently, the major problem is high cost of raw feedstock material for the biodiesel production on commercial scale. Several studies have been carried out to explore the performance of these non-edible oils as an alternative feedstock sources. (Zhang et al. (2003) reviewed that approximately 70-95% of biodiesel cost comes from the price of raw feedstock. Therefore, the non-edible vegetable oil, waste cooking oils, animal fats could be adopted as an effective raw material to cut down the cost of biodiesel production. For example *Jatropha curcas* (Ratanjyot), *Pongamia pinnata* (Karanja), *Riccinus communis* (Castor), *Madhuca indica* (Mahua), *Hevea brasiliensis* (Rubber), *Calophyllum inophyllum* (Nagchampa) and *Nicotina tabacum* (Tobacco) are non edible oil crops have been for the biodiesel production. Perdomo et al. (2013) investigated the seven mexican castor seed variety and the oil extraction by different procedure. Scholz and Da Silva (2008) discussed the use of castor oil for the biodiesel formation and other industrial applications. Lavanya et al., (2012) reviewed that castor oil production in India is mainly done for the oil export purpose. They evaluated 15 castor genotypes for the higher amount of fatty acids. The genotype DCH-200 in the hybrids, 48-1 and Aruna in the varieties was identified as the most productive for castor oil plantl. Agarwal et al., (2012) have done experimental studies of some inedible oils such as jatropha, ground nut, mustard and sunflower oil as a excellent alternative source for biodiesel production in India.

Martin et al. (2010) investigated the use of many inedible oil seeds for the biodiesel formation. The oil seeds considered were *Jatropha curcas* (Ratanjyot)), *Moringa oleifera* (Moringa), *Ricinus communis* (Castor beans), *Azadiracta indica* (Neem), *Aleurites moluccana* (Candlenut), and *Aleurites trisperma* (Trisperma). Jatropha oil has been identified as a good option for the biodiesel formation. The trisperma plant seeds have the highest oil amount but due to presence of polyunsaturated fatty acids in high amount, this could not be used for the biodiesel formation. The moringa oil and castor oil also have a highamount of oil content as they contain 70.6% of oleic acid and 86.0% of ricinoleic acid respectively. The moringa and neem oil cakes and husk have a high content of cellulose (approximately 30%) and could be used as a good alternative substrate for the bioethanol formation.

Ogunniyi et al. (2006) have discussed the other chemical, domestic and industrial applications of the non edible castor oil. Berman et al. (2011) examine the use of non edible castor oil as a viable recurring crop for the formation of biodiesel. Pure castor methyl esters (B100) and its blend with petroleum diesel (B10) were analyzed for the two properties, kinematic viscosity and distillation temperature. The blend of castor methyl esters with diesel (B10) fulfill all the standards, hence castor plant oil could be considered for the biodiesel formation.

Most of the non-edible oil contain significant amounts of FFA like raw mahua oil contain approximate 13-20% FFA (Ghadge and Raheman, (2006), raw jatropha oil content approximate 12-14% FFA (Srivastava and Prasad, 2000), tobacco seed oil containsabout 17% FFA (Veljkovic et al., 2006). Asian countries like India and Indonesia have started using non edible crops jatropha and karanja, castor oil as the feedstock materials for the synthesis of biodiesel fuels. Jatropha oil contains toxin phorbol and curcin as toxic chemicals while castor seeds have ricin toxin which is poisonous. (Tiwari et al., 2007). Naik et al., (2008) discussed the mechanism of the dual step process adopted for the synthesis of biodiesel from Karanja oil that has high FFA content. This dual step process successfully resulted in a 96.6-97 % yield of biodiesel. Kumar et al. (2012) investigated the complete life cycle of jatropha plant as a good alternative crop for the biodiesel formation.

2.2.3 Waste Oil and Animal Fats

The use of waste cooking oils (WCO), greases and soapstocks (a by-product of vegetable oil refinery) as a cheap low quality feedstocks significantly helps to improve the economic feasibility of biodiesel (Zhang et al., 2006; Canakci, 2007) WCO is generally in the liquid state at optimum temperature, whereas greases and soapstocks are in consolidated state at low temperature. WCO is about 2.5 - 3.5 times economically than pure plant oils depending on the sources and availability (Balat, 2011). The low quality feedstocks are usually directly disposed off into the environment, aggravating the problems of water pollution and human health problems. Canakci (2007) identified that the level of FFA varied from 0.7% to 41.8% and water from 0.01% to 55.38% in feedstock from waste cooking oils, animal fats, and grease restaurant. The high product yields could be achieved by using the two-step process for biodiesel synthesis. In the first step, the pre-treatment step is needed to reduce the amount of the FFA present in the feedstock, which is normally around 12-40 wt% of FFA, and the second step is of using a base catalyst for the biodiesel production. Animal fatty tissues have also been used as the feedstock for biodiesel production.

Biodiesel derived from animal fats has a higher level of saturated fatty acid and thus due to its poor cold temperature properties it causes problems in winter operation. According to researchers the presence of saturated fatty acids lowers the fuel property of biodiesel for example heating value and cetane number.

2.2.4 Algae

A few studies have illustrated the use of algae as a possible resource for biodiesel synthesis (Griffiths and Harrison 2009; Chisti, 2007; Yang, 2011). Algae can convert CO_2 into carbohydrates and protein in the presence of sunlight, but when they are cease for nitrogen, they essentially produce oil. Microalgae are reported to have a higher photosynthetic efficiency, higher biomass production and can grow very fast as compared to other energy crops (Dote et al., 1994). However, in spite of a great interest in algae feedstocks for biodiesel production, only a few studies have been conducted in this area.

Singh and Gu (2010) reviewed microalgae feedstocks as a good alternative resource for biodiesel production in India. Algae grows fast, have a high lipid content, carbohydrate and other nutrient contents and do not compete for land with other food crops. The microalgae have a good potential for production of algal biofuels as compared to biodiesel, bioethanol and other types of renewable fuels. Najafi G. et al. (2011) investigated the use of algae as an alternative source of energy. As the algae does not compete for land, its fast growing attribute and high oil content make it a good choice as a source of future energy fuel. Algae generally give more than 50 % oil yield of its total weigh.

2.3 TRIGLYCERIDES COMPOSITION IN BIODIESEL FUEL

The basic physicochemical properties of the triglycerides are determined by the chemical structure of the fatty acids and their chemical mixtures present in the parent oil. The carbon chain elongation and number of double bonds present in triglyceride molecule determines its chemical characteristics. Dias et al. (2012) describes a method for the assurance of glycerides, free glycerol and total glycerol in ethyl esters biodiesel obtained from castor oil. Berman et al. (2010) carried out a study on the use of a new technique to determine the oil content. The basic fatty acid structure and composition of the feedstock does not change in the transesterification process, hence these structure and compositions are significantly important with respect to several biodiesel parameters such as the pour point, the cold flow properties and the cetane number. The fatty acid chemical structure and composition for different types of vegetable oils are shown in Table 2.1. The fatty acid composition of castor oil has been shown in table 2.2. Lang et al. (2001) reviewed the physicochemical properties of biodiesel as fuel derived from several oil resources (sunflower, canola, rapeseed, and linseed oil) and compared their fuel properties with the conventional diesel fuel. They found that biodiesel is considerably less volatile as compare to the conventional diesel fuel.

Table 2.1: Chemical structures of common fatty acids (Srivastav and Prasad 2004)

Fatty Acid	Systematic name	Chemical Structure	Carbon: Double Bonds
Lauric	Dodecanoic	$CH_3(CH_2)_{10}COOH$	C12:0
Myristic	Tetradecanoic	$CH_3(CH_2)_{12}COOH$	C14:0
Palmitic	Hexadecanoic	$CH_3(CH_2)_{14}COOH$	C16:0
Palmitoleic	Cis–9 Hexadecanoic acid	$CH_3(CH_2)_5CH=CH(CH2)_7$ COOH	C16:1
Stearic	Octadecanoic	$CH_3(CH_2)_{16}COOH$	C18:0
Oleic	Cis-9-Octadecanoic	$CH_3(CH_2)_7CH=CH(CH2)_7COOH$	C18:1
Linoleic	cis-9,cis-12-Octadecadienoic	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$	C18:2
Linolenic	cis-9,cis-12,cis-15-Octadecatrienoic	$C_2H_5CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$	C18:3
Arachidic	Eicosanoic	$CH_3(CH_2)_{18}COOH$	C20:0
Behenic	Docosanoic	$CH_3(CH_2)_{20}COOH$	C22:0
Erucic	Cis-13-Docosenoic	$CH_3(CH_2)_7CH=CH(CH_2)_{11}COOH$	C22:1
Lignoceric	Tetracosanoic	$CH_3(CH_2)_{22}COOH$	C24:0

Table 2.2: Chemical structure of fatty acids in Castor oil

Systematic name	Chemical Structure	FA composition [%]
Palmitic acid	16:0	1.01
Stearic acid	18:0	1.10
Oleic acid	18:1	3.30
Linoleic acid	18:2	4.61
Linolenic acid	18:3	0.48
Eicosenoic acid	20:1	0.29
Lignoceric acid	24:0	0.04
Nervonic acid	24:1	0.01
Ricinoleic	18:1-OH	83.15

2.4 TRANSESTERIFICATION

Freedman et al. (1984) were first to reported the transesterification reaction of soybean oil with methanol, butanol and acid catalyst to examine the effect of different varieties of alcohol on transesterification reaction. Transesterification generally term explained the chemical reaction for the production of biodiesel from the various triglycerides. From the point of view of stoichiometry only 3 moles of methanol are essential to convert one mole of triglyceride into methyl ester. Transesterification is a reversible reaction, consisting of three steps that initially converts the triglycerides into a mixture of fatty acid alkyl esters (FAAE) and glycerine, in the presence of a catalyst with alcohol. Therefore, to obtain maximum methyl ester yield, a greater molar ratio is employed. When methanol and ethanol are used the esters are known as fatty acid methyl esters (FAME) and fatty acid ethyl esters (FAEE) and these methyl/ethyl esters are biodiesel. The overall transesterification reaction of a triglyceride molecule with methyl alcohol in the presence of a catalyst, to give fatty acid methyl esters and glycerin, has been shown in Figure 2.1.

The overall chemical reaction between triglycerides and alcohol to give FAAE is a chain of three sequential steps as depicted in Figure 2.2.

2.4.1 Acid catalyzed Transesterification

The most commonly adopted acid catalysts for esterification reactions are sulphuric acid, hydrochloric acid, or sulfonic acid (Demirbas, 2009). Acid catalysts can be used for free fatty acid (FFA) and high FFA oil feedstock conversions using either methanol or ethanol. However, very little research work have been done till date on the biodiesel production using transesterification reaction method catalyzed using acid (Srivastava and Prasad 2000). The rate of homogeneous acid-catalyzed reaction is generally 4000 times slower as compare to homogeneous base-catalyzed reaction this is the main reason why acid based catalyst reaction is not much in prevalence. But transesterifications reactions using acid catalyst has some great advantages as compared to base catalyzed reactions

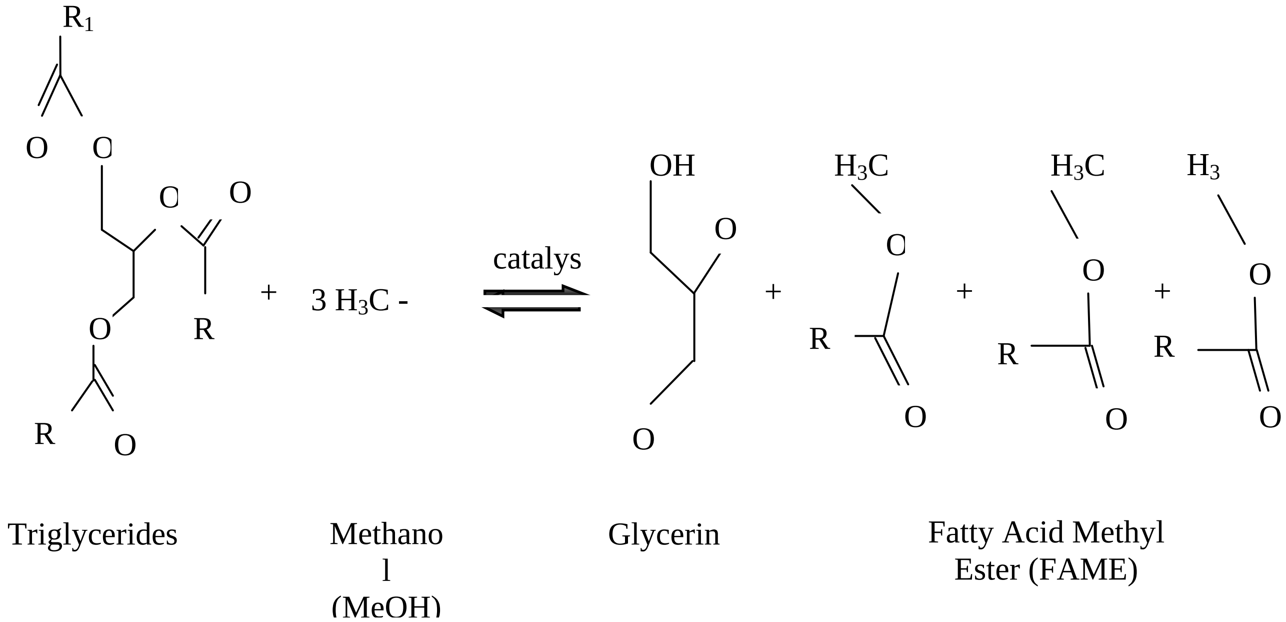


Figure 2.1: Shows step by step conversion of triglycerides with methanol to FAME and glycerin

Triglyceride + ROH ⇄ Diglyceride + $RCOOR_1$

Diglyceride + ROH ⇄ Monoglyceride + $RCOOR_2$

Monoglyceride + ROH ⇄ Glycerine + $RCOOR_3$

Figure 2.2: Step-by-step conversion of triglycerides to FAAE and glycerine. R refers to alkyl group of the alcohol

- The acid catalyst is not affected by the presence of high amount of FFAs in the oil feedstock, and,
- The other very important fact is that the esterification and transesterification reactions both are catalyzed by acid catalyst in the same time.

Therefore acid catalyst could be directly used to produce the biodiesel from high FFAs containing, low cost feedstock.

Freedman et al., (1986) studied the transesterification reaction of soybean oil with butanol and catalyst 1 wt % H_2SO_4, at various temperatures ranges from 77° to 117 °C required. The authors established that a large molar ratio of alcohol/oil 30:1 was needed to obtain higher product yield with a good reaction rate. In this way, to cut down biodiesel production costs, various investigators have been attempting to find ideal molar proportion of alcohol/triglycerides that should be exercised. There are two main parameters which should be considered for optimization of the process

- First, as increase the molar ratio of alcohol/triglycerides will increase the production but increasing the molar ratio also makes the recovery of alcohol difficult this in turn increases the production cost..Therefore, it becomes important to optimize the molar ratio.
- Second, the greater conversions could be obtained with the acid-catalyzed transesterification at high temperature but achieving higher temperature adds to the industrial cost. Hence, it becomes important to optimize the temperature.

Demirbas, (2003) and Fukuda, (2001) investigated use of different alcohols customized in acid-catalyzed transesterification including methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, and amyl alcohol and they concluded that methanol and ethanol are frequently used in both laboratory research and the biodiesel industry. Low cost and easy availability of methanol makes it the first choice for the transesterification reaction. Since ethanol is derived from agriculture products (renewable sources) and is biologically less harmful, it becomes the ideal choice as solvent that should be used for the formation of a fully renewable fuel. However, transesterification reaction with alcohols, like butanol, will give higher product yield as butanol is better miscible with the triglycerides in comparison to smaller alcohols. The higher boiling point of bigger alcohols enables the reaction process to operate at higher temperature and at normal pressure. This is an essential requirement for the acid-catalyzed transesterification reactions required high temperatures to obtain high product yield with faster reaction rates. For systems in which acid catalyst adopted, sulphuric acid has been the most examined catalyst, but other acids, like H_3PO_4, HCl, BF_3, and organic sulfonic acids, have also been adopted by several authors.

Agra et al. (1996) have examined the esterification of castor oil with ethyl alcohol in presence of concentrated sulfuric acid at 80 °C. The experiments were conducted for 60 min and separation of the product from the reactant mixture was done by using separating funnel. In the second stage the product of first step was again esterified by the use of concentrated H_2SO_4 along with methanol as second step of the reaction. In single step reaction of 120 minutes the product yield obtained was 60 % ethyl esters while in two step reaction procedure of 60 minutes each the reaction procedure gave 82 % fatty acid ethyl esters yield. And, the order of the reaction was determined as first order.

Zieba et al. (2009) carried out the investigation on the formation of esters from castor oil by using acid catalyst, concentrated H_2SO_4, basic catalyst KOH and 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$, HPW) as the homogenous catalyst. The salts of HPW were also used to catalyze the reaction of castor oil. The properties of solid acid salts were characterized by the use of BET, SEM, EDS and Laser Diffraction Technique. The potassium doped salts of HPW proved to be the best catalyst for formation of methyl esters. They concluded that the catalytic activity of a catalyst could be determined by the accessibility of reactant molecules to the active sites of catalyst which is due to high surface area and open structure of colloidal form of catalyst.

Canakci and Gerpen (1999) investigated the effect of different amount of H_2SO_4 (1, 3 and 5 wt %) for the esterification of grease by using methanol. They analyzed that as the concentration of catalyst increases the rate of reaction also increased from 72.7 to 95.0%. However, when acid catalyst is used the ester conversion increases by using the low cost feedstock material but during the reaction process water is also produced and this has a negative effect on biodiesel production. The effect is that esters could be hydrolyzed by the amount of water in the reaction system and can reversely produce FFAs. Crabbe et al. (2001) also investigated the consequence of molar ratio, ranging from 3:1-23:1, on transesterification process. They reported that higher molar ratio was essential for complete transesterification using methanol and sulphuric acid and the prescribed range was identified as 35:1 - 45:1. Canakci and Gerpen (2001) investigated for two-step sulphuric acid-catalyzed reaction process for reduction of FFA content to 1 wt%. Kusdiana and Saka (2004) investigated the effect of water on methyl ester formation in the transesterification of rapeseed oil with methanol by using different catalysts. In reaction where acid catalyst adopted, ester formation was decreased to 6% while using 5 wt % water at the start of reaction. But the alkaline catalyzed reaction was less influenced by the existance of water in the reaction system. As mentioned earlier, the acid catalyst is more commonly used for the reduction of the amount of FFA in esterification process of triglycerides. Marchetti and Errazu (2007) studied the use of sulphuric acid as a good alternative catalyst to produce biodiesel by direct esterification of waste oil which contains high amounts of FFA in place of alkaline KOH catalyst.

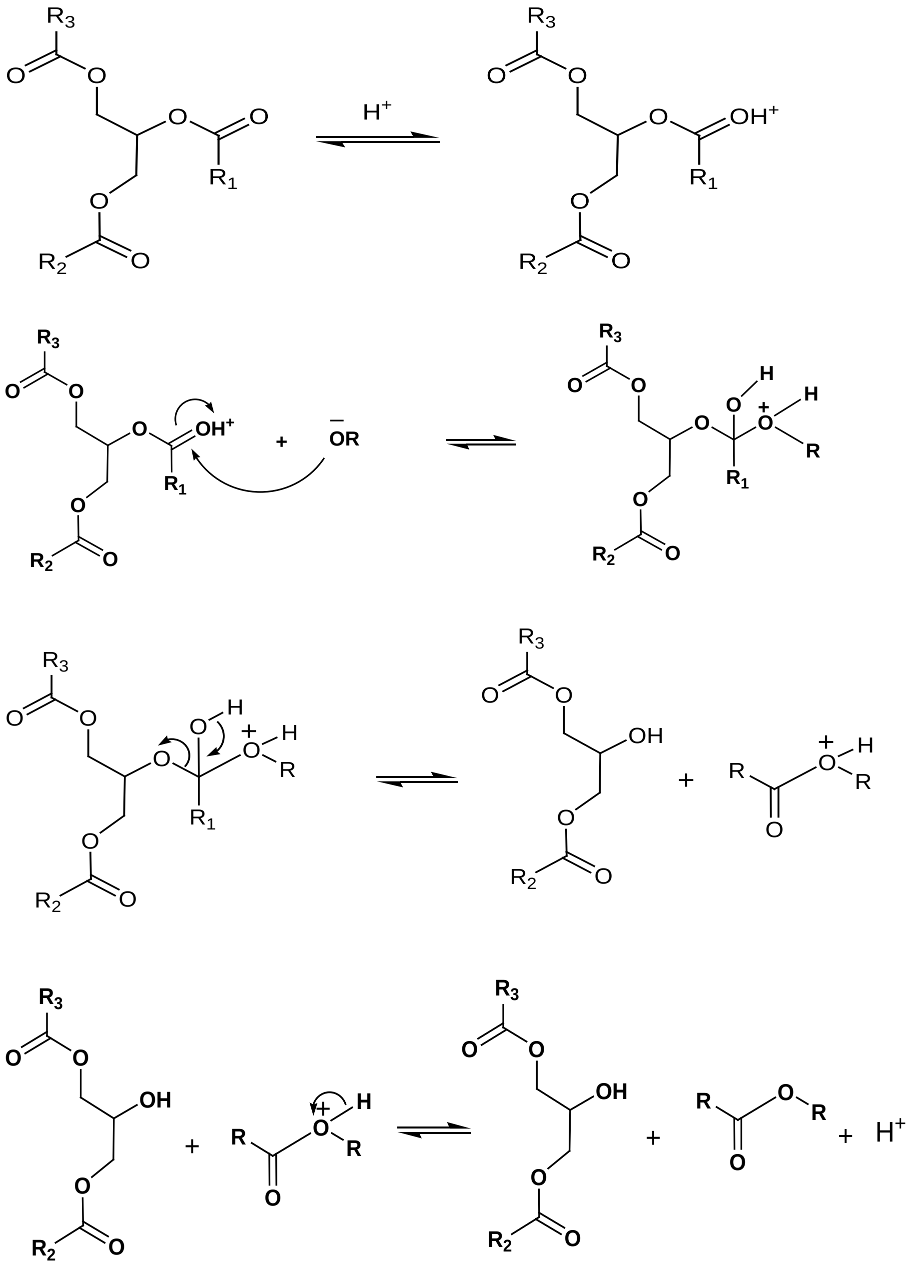


Figure 2.3 : Mechanism of acid catalyzed transesterification of triglycerides with alcohol. (1) Protonation of the carbonyl group by the acid catalyst, (2) nucleophilic attack of the alcohol, forming a tetrahedral intermediate, (3 and 4) proton migration and the breakdown of the intermediate. R1, R2 and R3 refers to carbon chain of the fatty acid where as R refers to alkyl group of the alcohol (Lotero et al., (2005).

The esterification where acid catalyst adopted follows a reaction mechanism analogus to base catalyzed transesterification reaction. In acid catalyzed reaction process, the reaction starts with a free fatty acid molecule, whereas, in transesterification reaction the starting molecule for the reaction is triglyceride as shown in figure 2.3.

In this case, steric hindrance of acid molecule and alcohol is an important factor as it influences the reaction rate of esterification.. However, dehydration of alcohols take place in this process due to use of high amount of acid catalyst as a result of this dehydration ethers are formed., . Also, when a high concentration of sulphuric acid is used as a catalyst at higher temperature it could burn the oil which in turn gives a lower product yield. Liu (1994) investigated the acid catalysts behavior and discussed that it has an important advantage as it can catalyze the esterification and transesterification reactions of triglycerides at the same time. They further advocated that acid catalyst could be used for the production of biodiesel from cheap and easily available lipid feedstocks which have FFAs levels of 6% such as greases, waste cooking oil.In the acid catalyzed process, the protonation of the carbonyl group of the triglyceride molecule leads to the formation of carbocation, and further alcohol attacks on this carbocation as a nucleophilic molecule and consequently a tetrahedral structure is formed as an intermediate compounds in the reaction. Finally, this tetrahedral intermediate compound rearranges itself and a diglyceride molecule and fatty acid alkyl ester is formed. The reaction continues up to the formation of diglycerides and monoglycerides. The main problem is that the formation of carboxylic acids occurs as a by-product if water is present in the reaction medium. The study is suggestive that acid catalyzed transesterification reaction is always preferable for the reduction of the large FFAs content present in the raw material..

In the esterification reaction catalyst has been used and the reduction of free fatty acid content was reported from 10.684% to 0.54% w/w and the reaction shows endothermic behavior. Recently, heterogeneous acid catalysts are used for the transesterification reactions by many researchers as they could be used several times, corrosion problem do not occur, and they are environmentally safe.

Vicente et al. (1998) investigated the use of Amberlyst-15 as heterogenous catalyst for transesterification of sunflower oil. Solid catalysts can be used for the esterification process as they cut out the corrosion problem and environmental issues. Cao et al. (2008) analyzed the formation of biodiesel from waste frying oil by using HPW and they obtained a good product yield. Kulkarni et al. (2006) examined the use of four types of support, silica, alumina, zirconia, and activated carbon for impregnation of 12-Tungstophosphoric acid (TPA) and further use of these as a solid acid catalyst for transesterification of canola oil which contains up to 20 wt % free fatty acids. The highest methyl esters yield was 90 wt% with 9:1 alcohol/oil molar ratio and catalyst loading of TPA supported hydrous zirconia 3 wt% and the same catalyst can be used several times.

Serra et al. (2011) carried out the experimental study for methanolysis of castor oil and soybean oil independently by using the Lewis acid Sn (IV) based catalyst. For the reactions two types of reactors were used namely - open glass reactor (OG) with reflux condensation system and other reactor as a closed steel (CS) reactor. The obtained esters yield was low for the castor oil than soybean oil. It was concluded that ester yield was affected by triglyceride compositions rather than the type of reactor used for the transesterification process. The highest methyl esters yield was obtained with closed steel (CS) reactor as it provides the high methanol concentration and high temperature in the reaction system.

2.4.2 Base Catalyzed Transesterification

Transesterification of triglycerides could be done by the use of alkaline catalysts. Encinar et al. (2007) investigated the four basic catalysts for the ester yield, NaOH, KOH, $NaOC_2H_5$ and KOC_2H_5. The highest ester yield was obtained when ethanol was used as solvent and catalyst potassium hydroxide. Vicente et al. (2004) investigated the comparative study between potassium hydroxide and sodium hydroxide and it was reported that the highest esters yield was obtained with potassium hydroxide catalyst.

De Oliveira et al. (2005) carried out study on the ethyl esters production from castor oil, soybean oil and degummed soybean oil using alkaline catalyst NaOH. The reaction parameters studied were oil/ethanol molar ratio (1:3–1:9), catalyst concentration (0.5-1.5 wt/wt %), temperature (30°- 70 °C) and reaction time (1-3 h). It was found that the ethyl ester conversion was affected by all the variables. As increase in reaction time, oil/ethanol molar ratio and reaction temperature the esters yield also increased. The maximum fatty acid esters conversion for castor oil was 96.2 % obtained at optimized oil/ethanol molar ratio 1:3, reaction temperature 70 °C and catalyst concentration 0.5 wt/wt %. For refined soybean oil best ester yield 94.6 % was attained at optimized conditions, oil/ethanol molar ratio 1:9 and 0.5 wt/wt % catalyst concentration at 30 °C reaction temperature for 1 hour reaction time. For the degummed soybean oil, maximum ethyl esters yield was 93.0 % obtained at optimized variables, 1:9 oil/ethanol molar ratio, and 0.5 wt/wt % catalyst concentration at 70 °C for 3 hour reaction time. All the experimentally obtained values were in good agreement with empirically obtained values by model.

Da Silva et al. (2006) studied the castor oil transesterificationa with bioethanol in the presence of $NaOC_2H_5$ as base catalyst. Castor oil contains ricinoleic acid so it is easily soluble in alcohol.

Deligiannis et al. (2009) have done experimental study by using castor oil for the synthesis of biodiesel. The oil content of castor seed has been reported as high as 40.3 %. The high calorific value and high cetane number has been discussed as an advantage of oil but the high viscosity of castor oil is a major hurdle to use it for the biodiesel production. The reaction variables such as methanol/castor oil molar ratio 6:1, catalyst amount (0.5 – 2 %) and reaction temperature (25° – 65 °C) were used to optimize the maximum yield for esters formation. When experiments were performed with 6:1 methanol/oil molar ratio, 1.5 % catalyst amount at reaction temperature at 25 °C and 65 °C, the esters conversion obtained were 93.8 wt % and 94.2 wt % respectively. The author also suggested that viscosity of castor biodiesel could be reformed by the making of blends with diesel.

Sousa al. (2010) examined the production of biodiesel from castor oil with methanol. The raw castor oil was neutralized with glycerol and it reduces the FFA content of castor oil. The methyl esters yield was 92.5 % obtained with 6:1 methanol/oil molar ratio, 0.5 % w/w of catalyst concentration after 15 minutes of reaction time. They concluded that the glycerol could be used to neutralize the raw castor oil, which was formed as a byproduct during the transesterification reaction. In this work, the transesterification reaction of castor oil with methanol was performed in a batch reactor, using raw castor oil and neutralized castor oil. The methyl esters yield obtained by using neutralized castor oil was high as compare to the yield of raw oil than the yield obtained from raw oil under the same operating conditions.

Barbosa et al. (2010) examined biodiesel production from the mixture of castor oil and soybean oil with ethanol in the presence of alkaline catalyst KOH. They reported that when mixture of castor oil and soybean oil were used for the transesterification reaction, there was no preference about substrate in the reaction. The mixture of the both oils in the reaction yield increases and the efficiencies also increases for the purification of product. Castrol oil could be adopted for biodiesel production. The mixture of oil feedstock could be used for the biodiesel production and the product could be used directly without the need of blending of biodiesel with fuel diesel.

Panwar et al. (2010) carried out the experimental study on the production of biodiesel from castor seed oil by the use of alkaline catalyst, and methanol. The properties of castor biodiesel were studied for engine application. Biodiesel yield of 95.8% was obtained the methyl esters of Castrol obtained were sulfur less and has a good cetane number.It indicates that the ignition quality of resultant methyl esters is good. They concluded that the density, calorific value were much near to that of diesel.

Sreenivas et al. (2011) carried out experimental study on the biodiesel formation from castor oil which was treated with mineral turpentine oil. Castor oil was transesterified by using methanol as a solvent in presence of base catalyst NaOH. The parameters of reaction such as temperature, reaction rate and catalyst amount were optimized. For Biodiesel properties standard values BIS: 15 densities, flashpoint, kinematic viscosity at 40 °C, cetane number, net calorific value, and Iodine value have been studied. Crude castor oil was also transesterified using methanol and basic catalyst NaOH. The resulting total yield of methyl esters was obtained as 92 %. Agarwal et al., (2012) studied the biodiesel formation with alkaline KOH as homogenous catalyst and KOH loaded on alumina as heterogeneous catalyst. They obtained 98.2 % yield with homogenous alkaline catalyst KOH and 96.8 % with heterogeneous catalyst KOH loaded with alumina. They concluded that heterogeneous catalyst could be used for the continuous process of biodiesel formation as it can be easily separated from glycerol, no water washing is required and could be reused for many cycles.

2.4.3 Combination of acid-base catalysts Process

Liu et al. (1994) investigated that acid catalysts has an important advantage as it can catalyze both esterification and transesterification of oil at the same time and they can synthesize biodiesel from low-cost lipid feedstock materials.

Meneghetti et al. (2006) investigated the formation of fatty acid ethyl esters from castor oil and cottonseed oil with different types of catalytic systems. The maximum esters yield could be achieved from castor oil by using acid and methoxide as catalysts. The cottonseed oil has much different chemical composition as compared to castor oil but it has very similar fatty acids composition to the vegetable oils. The maximum esters yield from cottonseed oil can be obtained by using alkaline catalyst.

2.4.4 Enzymatic transesterification

Since the last few decades a number of research papers have been published on the use of enzymes in transesterification reaction. Lipase enzymes have been used as they can catalyze the hydrolysis of ester bonds in long chain triglycerides thereby producing esters and glycerol. The enzymes are lipase enzymes from filamentous fungi and recombinant bacteria, immobilized enzymes have been used for the biodiesel formation. Du et al, (2008) studied the use of enzymes in transesterification reactions. The higher cost, large reaction volume, time and higher concentration of catalyst are the main issues to use e enzymes for transesterification reaction on commercial scale. Even this process is more environmentally friendly in comparison to any other chemical process.

De Oliveira et al. (2004) studied production of biodiesel from castor oil by using two commercial Enzymes, Novozyme 435 and Lipozyne IM. They used Taguchi design method for optimization of the experimental conditions. The reaction variables were taken as oil/ethanol molar ratio (1:3 - 1:10), enzyme concentration (5 - 20 w/w %), temperature (35° – 65 °C), and water amount (0 - 10 w/w%). When enzyme Novozyme 435 with 20 w/w % concentration was used as a catalyst, the ethyl esters yield obtained was 81.4 % at 65 °C temperature, 0 w/w % water concentrations and 1:10 oil to ethanol ratio. The maximum esters yield 98 % was obtained with Lipozyme IM with 20 w/w % concentration at 65 °C temperature with 1:3 oil/ethanol ratio and 0 w/w % of water concentration. Jeong and Park (2008) considered rapeseed oil for transesterification process with methanol in presence of enzyme Novozym 435 and tertiary butanol. The highest conversion of esters, 76.1 % was obtained at 3:1 methanol/oil molar ratio, 5 % (w/w) Novozym 435 catalyst concentration, water weight content 1% (w/w), at reaction temperature 40 °C for reaction time 24 hours. Banerjee and Kishore (2006) studied the lysozyme enzyme and peptides interactions. Atkinson et al. (1979) carried research on the direct use of whole cell biocatalysts, or intracellular enzymes for the formation of methyl esters. The use of whole cell biocatalysts offers the advantage of not requiring purification as the enzyme is formed inside the cells, which can be used directly in the reaction mixture.

2.4.5 Non- catalytic transesterification

The non-catalytic method of transesterification involves the use of supercritical conditions (the highest temperature and highest pressure at which the liquid and vapors can exists) for the process. The supercritical method of transesterfication is also called as non-catalytic transesterification as in this method catalyst is not used for the process of conversion of fatty acids into methyl esters. In industrial process for biodiesel formation the supercritical conditions are generally avoided due to economic reason. The critical temperature for methanol (Tc) is 239 °C and the critical pressure (Pc) for methanol is 8.09 MPa. Kusdiana and Saka, (2001) investigated the formation of biodiesel from rapeseed oil with methanol at 350 °C for 240 seconds. They revealed that a 100% yield was achieved within 4 minutes, at a temperature of 593 K, pressure of 8.4 MPa and 43:1 oil to methanol molar ratio.

Vieitez et al. (2011) investigated the production of ethyl esters from castor oil in a catalyst free reaction system under supercritical conditions. The variables studied for transesterification reaction were reaction temperature, water concentration effect, substrate flow rate and pressure.. The ethyl esters yield 74.2 % obtained with flow rate of substrate 0.8 ml min^{-1}, in 20 MPa pressure, and 5 wt % water concentration at 573 K temperature. The ethyl ester yield increases up to 88.7% with flow rate of substrate 0.8 ml min^{-1} at 648K reaction temperature. They concluded that the castor oil could be used for the formation of esters under supercritical process by using ethanol. But as the castor oil has some unique chemical composition than other oils, so at high temperature due to the formation of some other chemical compounds, the ester yield could be decreased. Sanan and Mahajan (2011) discussed the use of surfactants on the fatty acid chains and its effect on the environment.

Mgudu et al. (2012) analyzed the effect of microwaves for oil extraction from castor seeds. The parameters affecting the oil extraction were FFA, moisture content, refractive index, pH, specific gravity, acid value and total oil yield. They concluded that the highest yield of castor oil was 44.34% obtained in 120 seconds when the castor seeds were treated at 280 W in microwave.

Rodriguez-Guerrero et al. (2013) carried out experimental study of the production of biodiesel from castor oil in supercritical reaction conditions. The reaction parameters studied were ethanol to oil molar ratio, catalyst amount, reaction temperature and total reaction time. The catalyst amount 0.1 % NaOH as alkaline catalyst is sufficient for high yield of esters. The RSM was used to study the optimization of the catalytic and non-catalytic reaction process and the total ester yield was 98.9 % for catalytic and 56.2 % for the non-catalytic process. The kinetic study was also done for the reaction and the rate of reaction was determined as pseudo first order. Some researchers have also stressed on the use of co-solvent such as tetrahydrofuran (THF) and hexane to increase the esters yield. The use of co-solvents decreases the miscibility problem of the reactant and solvent in the reaction mixture and it also increases the methanolysis rate.

Hincapie et al. (2011) examined the biodiesel production from castor oil through conventional process and in situ process by the use of castor seeds directly. Biodiesel was produced from two different varieties of castor seeds - *Riccinus communis* L. red and BRS-149 Nordestina, with ethanol in the presence of alkaline catalyst KOH. Co- solvant n-Hexane was also used and it was found that the presence of n-hextane in the reaction mixture did not significantly affect the biodiesel yield in transesterification reaction. In situ transesterification, biodiesel was produced directly from seeds in presence of solvent and a catalyst. The crude castor oil having a high FFA content was used for ester formation. NMR was used to quantify the ester content in reaction product. Conventional method gave highest esters conversion using very low quality oil in comparison to in situ method. Castor oil as a feedstock remains in huge demand in the chemical and pharmaceutical companies. Due to the presence of ricinoleic fatty acids that consists of both a double bond and a hydroxyl group, has a unique chemical composition, have a good lubricity, high viscosity, lower cloud and pour point. The advantage of this method is the high product yield and pure product obtained in low reaction time and there is no requirement of after-processing of the product. The main disadvantage of this method is the requirement of extreme conditions which lead to the economic problems on industrial scale.

2.4.6 Microwave assisted transesterification

Perin et al. (2008) carried out the biodiesel production from castor oil in the presence of methanol or ethanol by the use of microwave radiation. When solid acid catalyst H_2SO_4/SiO_2 used with 1:6 oil to methanol molar ratio, 10 % w/w of catalyst under microwaves irradiations the best yield was obtained. The best ester yield for basic catalyst was obtained by using basic alumina (Al_2O_3/50 % KOH) catalyst with methanol at 60 °C in microwave radiations for 5 minutes. It was analyzed that solid acid catalyst could be reused for several cycles and by the use of microwave radiation reaction time could also be reduced for the transesterification reaction

Yuan et al. (2011) carried out experimental studies for the formation of biodiesel from castor oil by using microwaves. The microwave radiation could be used for the biodiesel formation. By using $AlCl_3$, $NaHSO_4.H_2O$, and Na_2CO_3 as catalysts thee total esters yield 73%, 74% and 90 % were obtained respectively with 1:18 oil to methanol molar ratio, 7.5 wt % of catalyst in 200 W radiation microwave power for 120 minutes at 338 K temperature.. They concluded that the fluidized bed with high temperature could be used for the drying of castor seeds and castor oil could be used for the formation of biodiesel.

2.5 PROCESS VARIABLES AFFECTING TRANSESTERIFICATION

The transesterification reaction is altered by many process variables such as type of vegetable oil, molar ratio of oil to methanol, amount and type of catalyst, reaction temperature, type of mixing and its intensity, reaction time, amount of FFAs and moisture content in the feedstock. In the following part the effect of foresaid parameters are studied.

2.5.1 Molar ratio

From a stoichiometric point of view only three moles of methanol are compulsoryto convert one mole of triglyceride into methyl ester. Transesterification reaction is a reversible reaction and to obtain a high product yield reaction, forward reaction should dominate in the reaction medium. Therefore, to obtain maximum methyl ester yield, a greater molar ratio is employed. Freedman et al. (1984) analyzed the formation of esters from soybean oil by using acid catalyst with molar ratio 6:1 and 20:1 for 3 and 18 hours, for both cases the methyl esters conversion was not satisfactory. Boocock et al., (1998) explored the transesterification of soybean oil by employing tetrahydrofuran (THF) as a co-solvent for increasing the esters yield.

Madankar et al. (2013) have considered the production of methyl esters by using castor seeds directly and further transestreification reaction was done in the reaction system. They used higher methanol to castor oil molar ratio 1:50-1:250 with catalyst amount 0.5-2 % at temperature 35° - 65 °C with mixing rate 200 - 800 rpm were studied to optimized the reaction conditions. The castor methyl esters yield is 96.01 % with the optimized parameters methanol/oil molar ratio 250:1, reaction temperature 65 °C with 1 % basic catalyst KOH at a stirring rate of 600 rpm after 3 hours. The methanol/oil molar ratio and reaction temperature are the most significant parameters.

2.5.2 Catalysts

For the transesterification reaction mainly two types of catalysts as acid catalyst and base catalyst are used. Acid catalyzed reactions are much slower as compare to the base catalyzed reactions and H_2SO_4, HCl are commonly used for the acid catalysis. Base catalysts like KOH, NaOH, $KOCH_3$, $NaOCH_3$ are generally used for the transesterification reaction.

Sanchez-Cantu et al. (2013) considered the use of hydrated lime and CaO as catalyst for biodiesel formation from castor oil and methanol. Product was characterized was by using NMR and TLC. The highest conversion of methyl esters from raw castor oil has reported by using hydrated lime (HL) and CaO as catalyst. The reaction variables such as oil/methanol molar ratio, catalyst amount, reaction temperature and reaction time has been investigated by using hydrated lime as catalyst. The total methyl esters conversion 98 % was obtained with castor oil after 14 hours.

2.5.3 Temperature

Transesterification reactions using acid catalyst, typically requires high temperature and pressure to obtain the high product yield. Freedman et al., (1986) and Liu et al., (1994) studied the transesterification of soybean oil with butanol by using 1 wt % H_2SO_4 as catalyst, at various temperatures ranges from 77 to 117 °C . The authors have fixed that a considerable molar ratio of alcohol/oil 30:1 was needed to obtain higher product yield with a good reaction rate. The researchers proposed that the transesterifiction reaction is temperature dependent. Freedman et al., (1984) inspected the transesterification reaction of soybean oil using methanol with 1% wt. NaOH and 1:6 oil/methanol molar ratio at three different temperatures 32 °C, 45 °C and 60 °C. They found that at high temperature by using base catalyst, the rate of formation of methyl esters was high.

2.5.4 Types of alcohol

Methyl alcohol and ethyl alcohol are the most commonly adopted alcohols for transesterification of vegetable oils. Methanol is cheaper than any other alcohol and easily available so it is the first choice for transesterification reactions. Whereas the ethanol could be produced from waste cellulosic materials such as agricultural waste and is totally renewable resource of alcohol for transesterification process. The rate of transesterification with butanol has been reported very fast as compared to when methanol was used. Freedman at al., (1984) and (1986) checked the formation of biodiesel from soybean oil by using ethanol and butanol as solvent with a methanol/oil molar ratio of 30:1 by using 1 % concentrated H_2SO_4 and the high esters conversion was obtained after 3, 22, 69 hours of reaction time for butanol, ethanol and methanol respectively. Pandey et al., (2001) explored the use of a modified silicate as a biosensor for ethanol.

2.5.5 Types of mixing

The vegetable oil and solvent phase does not readily mix with each other due to their chemical phase behavior and due to this mixing of both phases are required in the reaction medium. The mixing of reaction mixture could be done by using magnetic stirrer, mechanical stirrer. The ultrasonication is a new method of mixing the reactants and could be used for the conversion of the fatty acids in to esters. This is very efficient and fast method in comparison to other type of mixing of the reaction mixture. Kumar et al. (2010) have used ultrasonication method for the synthesis of biodiesel from coconut oil and ethanol as an alcohol. Colucci et al. (2005) have done experimental study for the production of biodiesel from soybean oil by using ultrasonication as an alternate to conventional mixing.

Encinar J.M. et al. (2012) analyzed the use of ultrasonication method for mixing castor oil, methanol and basic catalyst KOH for the formation of biodiesel. They concluded that high methyl ester yield could be obtained in short reaction time by using ultrasonication method in comparison to magnetic mixing or mechanical mixing at low reaction temperature as compared to conventional method.

2.6 KINETIC STUDIES OF TRANSESTERIFICATION REACTIONS

Freedman and Pryde (1986) investigated the kinetic behaviour of the transesterification reaction of soybean oil. The consequence of reaction variables with molar ratio, type and concentration of catalyst, reaction temperature and type of alcohol on the transesterification reaction has been studied. The reaction mechanism was explained by the use of second order model and rate of reaction also determined. The reaction mechanism with 1:6 oil to methanol molar ratio has been proposed as shunt reaction mechanism. Mittal et al., (2007) have investigated the kinetics of waste water treatment. Noureddini and Zhu (1997) studied the effects of mixing of soybean oil and methanol on kinetics of reaction and reported that initial mass transfer controls kinetics and reaction is second order rate reaction. Banerjee and Kishore (2004) studied the kinetics of thermal denaturation of concanavalin.

Conceicao et al. (2007) have investigated the dynamic kinetics of thermal decomposition of biodiesel obtained from castor oil by employing methanol and ethanol. Kinetic data were obtained by using Coats-Redfern, Madhusudan and Ozawa methods. The highest biodiesel yield was, 97.7% obtained with 6:1 molar ratio, catalyst concentration 1 % KOH at room temperature for 30 minutes. The thermal stability was found in order of castor oil > ethanol biodiesel > methanol biodiesel on the basis of thermogravimetric curves. Methanol biodiesel having good combustion properties as it have less activation energy. They found that the best conditions for calorimetric analysis and TG are heating rate of 10 °C/min within synthetic air atmosphere. Mittal et al., (2007) have investigated the kinetic thermal study of dyes. **Wang and Li (2005)** studied the adsorption of dyes and their kinetic modeling.

Ramezani et al. (2010) considered the transesterification reaction from castor oil by using different basic catalysts $NaOCH_3$, NaOH, $KOCH_3$ and KOH. The best catalyst was found $KOCH_3$. The optimization of parameters such as methanol/oil molar ratio 4:1 - 8:1, catalyst amount 0.25 - 0.5 %, reaction temperature 25° - 80 °C and the mixing intensity 250-600 rpm (revolution per minute) has been done by using Taguchi design method. The two parameters temperature 65 °C and mixing speed 400 rpm were optimized for the highest product yield. Kinetic study was also done and a linear equation was fitted and rate of reaction has been suggested as Pseudo-first order. The total yield was obtained 87 % with molar ratio 8:1, 0.5 % $KOCH_3$ catalyst at 65 °C temperature after two hours. The rate constant was obtained $4.91 \times 10^{-3}(min^{-1})$.

Lopez et al. (2011) analyzed the kinetic behavior of formation of esters from castor oil by the use of NMR technique. The parameters were taken as methanol to oil molar ratio 6:1, stirring speed remains constant, but the catalyst concentration and temperature varied from 0.10 - 0.25 wt % and 25°- 65 °C respectively. The total reaction time for the reaction was 60 minutes. The rate of reaction was determined as a Pseudo-second order. Kaur et al., (2013) studied the kinetics for the adsorption of removal of waste harmful dye chemicals by the use of biologically waste materials. Okoro et al., (2012) studied the blends of kerosene with different alcohols and their energy was determined by the use of calorimetric determination method. Wang and Li (2005) analyzed the kinetic study of adsorption of dyes and the pseudo-second order was determined. Agarwal et al., (2012) have done experimental studies of biodiesel formation with heterogeneous catalysts from vegetable oils and kinetic study of the reaction mechanism was done.

Madankar et al. (2013) carried out the kinetic study of biodiesel formation by using castor oil at temperature 45°, 55° and 65 °C while other parameters molar ratio 250:1, catalyst amount 1 % and mixing speed 600 rpm all remains constant. They concluded that the directly extraction from castor seeds and transesterification gave high product yield and cost effective method for the formation methyl esters.

2.7 PROCESS OPTIMIZATION OF BIODIESEL PRODUCTION

The design of biodiesel production is of critical importance during the development of industrial scale production of biodiesel production process. The reaction parameters such as oil to methanol molar ratio, types of catalyst and its concentration, type of mixing and its intensity, reaction temperature, and reaction time has significant effect on the transesterification reaction of biodiesel production process. The experimental study for the optimization of reaction variables to obtain maximum product yield considering all variables and their interaction is time consuming and laborious because of relatively large number of experiments. For the optimization of process and high product yield, ‘Design of Experiments (DoE)’ approach has been used that integrates the design of experiment and optimization techniques. Many experimental designs such as partial factorial (fractional factorial), full factorial (complete factorial), orthogonal array, central composite (Box and Wilson), Plackett-Burman, and Box-Behenken have been used to improve the process of esters formation (Zafar et al. 2012; Daraei et al. (2014). Similarly various optimization methods such as response surface methodology (RSM), canonical analysis (CA), multiple linear regression, and artificial neural networks and genetic algorithm have been used to estimate the performance of transesterification reactions. Pandey et al. (1998) have discussed the use of biosensors for ethyl alcohol and oxidation of NADH co-enzyme by the electrochemical method.

Several studies have been reported on the optimization of biodiesel formation using various oil resources, different types of catalyst, different alcohols. Few studies related to the optimization of biodiesel production using castor oil as a feedstock material have been discussed here.

Conceicao et al. (2007) analyzed the thermal and oxidative degradation of biodiesel produced from castor oil. The biodiesel was stable up to 150 °C but after that temperature, degradation of esters starts and intermediate compounds were formed. When biodiesel was degraded at 210 °C for 48 hours, the formation of gum was observed and it was suggested that the oxidative polymerization of esters was completed. Bakshi et al., (2006) examined the effect of surfactants on the cloud point measurement. The biodiesel degradation was studied at different temperatures for different times and calorimetric thermogravimetric profiles were obtained. Singh and Kishore (2008) have done calorimetric studies of albumin.

Da Silva et al. (2009) carried out the optimization study of the production of biodiesel from castor oil with bioethanol using sodium hydroxide and sodium ethoxide as catalyst. Factorial scheme method was used to optimize the reaction variables and to obtain the maximum transformation of ethyl esters. The reaction variables were ethanol to oil molar ratio (6:1 – 20:1), catalyst amount (0.5 – 1.5 %wt) and reaction temperature (30° – 80 °C). The catalyst amount was the most significant factor that affects the ethyl ester formation. When 1 % sodium ethoxide was used as catalyst the total 99 % wt of ethyl ester conversion was obtained with 16:1 ethanol to oil molar ratio at 30 °C for 30 minutes of reaction time. The kinetic study was also carried out at 30°, 40°, 50° and 70 °C and rate of the reaction was determined as first order. Scale up of the reaction was also carried out using 1 L batch stirred tank reactor (BSTR) with 19:1 ethanol/oil molar ratio at 1 % wt of sodium hydroxide catalyst. The vapor pressure osmometry (VPO) technique was adopted for the determination of molecular weight of castor oil and it was concluded that VPO could be a fast and low cost alternative method for the determination of molecular weight. Araujo et al. (2009) carried out study on the use of a fast method for the evaluation of oxidation stability of methyl esters obtained from castor oil. They also investigated use of antioxidants for increasing the stability of esters.

Monteiro et al. (2009) carried out the study of blending of biodiesel produced using castor oil and soybean oil. The blends of biodiesel from castor biodiesel and soybean biodiesel were made with different concentration 0.5 – 30% (v/v) with petroleum diesel. The commercially available B_2 blend, castor biodiesel blend and soybean biodiesel blend were studied for quantification by using NMR technique, and it was observed that NMR method could be used to determine the biodiesel blend level with petroleum diesel. Wang and Fingas (1997) have discussed the use of gas chromatography methodfor the estimation of hydrocarbons present in oil and its derivative compounds. Hubbard (2009) investigated the formation of microemulsions, their microstructure, behavior, , and effect of alcohols on the microemulsions properties.

Jeong and Park (2008) have done the optimization study of biodiesel formation form castor oil by using RSM. They use five- level, 3-factor design method. The variable parameters were considered as reaction temperature (35° – 65 °C), oil/ methanol molar ratio (4.5 - 10.5) and catalyst amount (0.5 - 1.5 % w/w). They found that the maximum biodiesel output was obtained at optimized parameters, temperature 35.5 °C, catalyst 1.45 % wt % with 1:8.24 molar ratio at 40 minutes reaction time. The determination coefficient for the model was 0.74 that indicates the model well represented the relationship between the experimental values.

Canoira et al. (2010) investigated the methyl esters formation from castor oil by using methanol and sodium methoxide as basic catalyst. The transesterifiction study was done by using 1.5 L and 50 L with basic catalyst methoxide. The reaction parameters optimized were methanol/oil molar ratio 7.5:1, catalyst 1 wt %, reaction temp 40 °C for 90 minutes in 1.5 L reactor. The yield 96 % was obtained for 1.5 L reactor. For 50 L reactor, the castor oil was used 30 Lt, the catalyst concentration 1 % (wt % of oil) and the temperature was taken 40 °C. The blends of castor biodiesel with petroleum diesel were made and effect of blending on different properties has been studied.

Cavalcante et al. (2010) performed out the biodiesel production from castor oil with ethanol in the presence of base catalyst. The ethyl esters formation was optimized by the use of central composite rotatable design (CCRD). The maximum ethyl esters from castor oil were obtained with ethanol to castor oil molar ratio 1:1, catalyst amount

1.75 % and the reaction time was 90 minutes. Analysis of Variance (ANOVA) was used to find out the significance of proposed model for esters yield from castor oil. The reaction yield was affected by all variables. All the esters properties were within the standard limits but viscosity was very high and it was suggested that the viscosity could be duced by blending the esters with petroleum diesel up to 20 % known as B_{20}. The regression model was significantly explained the data variation and it gives 95 % confidence limit.

Valente et al. (2010) carried out the experimental study to analyze the use of biodiesel blend in generator engine. The biodiesel blends with 5%, 20%, and 35% of castor biodiesel in diesel fuel, and for soybean oil blends 5 %, 20 %, 35 %, 50 % and 85 % in diesel fuel were tested for the consumption of fuel and total emissions of exhaust of a diesel engine. The engine load was varied from 9.6 – 35.7 KW and amount of the carbon monoxide, carbon dioxide, hydrocarbons and specific fuel consumptions were tested. The fuel consumption increase as the biodiesel amount increases in blends of both castor and soybean. When castor biodiesel blend 35 % was used then the carbon monoxide emission increased by 80 % and for 35 % of soybean biodiesel blend the carbon monoxide emission increases up to 80 %. The hydrocarbon emission was 16 % and 18 % for 20 % blend of castor biodiesel and soybean biodiesel.

Valente et al. (2011) investigated the physicochemical properties of mixture biodiesel produced by using waste cooking oil or castor oil biodiesel with diesel fuel oil. The properties assessed were fuel density, kinematic viscosity, cetane index, distillation temperatures, and sulfur content, analyzed applying standard test methods. Fuel blends with up to 20 % waste cooking oil biodiesel or 35% castor oil biodiesel concentration in number 2 diesel fuel. Thomas T.P. et al., (2012) carried out experimental studies with castor biodiesel and safflower biodiesel and their blends with fuel diesel. The viscosity could be reduced by chemical reactions and blending with diesel. Sanghavi et al. (2014) have reviewed the use of nanomaterials for the analysis of drugs.

Kilic et al. (2013) carried out the maximization of biodiesel formation from castor oil by applying full factorial design method. They used many alkaline catalysts such as NaOH, KOH, CH_3ONa and CH_3OK and found CH_3OK as best alkaline catalyst, as it gave the highest fatty esters yield. The variable factors were temperature

(25° - 65 °C), catalyst amount (0.5 - 1.5) wt % and methanol to oil molar ratio (5:1 - 7:1). CCD method was used to optimize the reaction variables. The reaction parameters and optimum values were obtained as methanol to oil molar ratio 7:1, catalyst concentration 1.5 % at 65 °C temperature with 10 minutes reaction time gave 99.81 % maximum biodiesel yield.

Makama et al. (2011) evaluated the use of the mixture of castor oil and olive oil for the formation of biodiesel. The reaction variables range for the optimization of the reaction were selected as molar ratio 5:1 - 15:1, castor to olive ratio 30:70 - 40:60, reaction temperature 45 °C – 75 °C and catalyst amount 0.5 - 1 wt % at constant 400 rpm. The optimum value to obtain the maximum esters yield was found as the methanol to oil molar ratio 6:1, temperature 60°C, catalysts concentration 0.5 wt % NaOH and castor oil to olive oil ratio 45: 55 % at 400 rpm for 120 minutes. The highest esters yield was obtained as 92 %. They concluded that the product yield was higher of the olive oil and castor oil mixture as compared the biodiesel yield obtained from either olive oil or castor oil alone. The viscosity and calorific values increase as the castor oil percent composition in the reaction mixture increases. Hubbard (2011) has reviewed the different properties of emulsions for many uses in industries.

Pradhan S. et al. (2012) have done the optimization of reactive extraction from castor seeds for production of biodiesel by using RSM. Central composite design (CCD) method was used to study the effects of methanol to castor oil molar ratio (100:1 - 350:1), catalyst amount (0.5 - 1.5 %), reaction temperature (45° - 65 °C) and mixing intensity (100 – 600 rpm) on the fatty acid methyl esters yield (FAME). They found that the catalyst amount and methanol to oil molar ratio were the most significant parameters that influence FAME production. Second order quadratic model was fitted and R^2 was obtained 0.998 that means the model was well fitted to the reaction. The interaction of oil to methanol molar ratio, catalyst amount and temperature shows a positive effect on the yield of FAME. The optimized value for methyl esters wasobtained 88.2 % at 225:1 methanol to oil molar ratio, 1 % catalyst amount, 350 mixing intensity at 55 °C temperature. Sanghavi et al. (2013) have reported a simple and easy method for the detection of ATP molecules by using modified electrodes as compared to the use of HPLC or UV method.

Biodiesel production from castor oil has been studied on different scales, in small reactor such as in 500 ml and large reactor as in 50 L (Canoira et al., (2010). The transeserification reaction of blend of castor oil with other type of vegetable oil has also been reviewed. Hubbard (2013) analyzed the behaviour of nanoparticles and their use in biotechnology industries. Sanghavi et al. (2014) investigated detection of neuropeptides by the use of modified electrodes in nanochannel.

Mejia et al. (2013) investigated the fuel properties of the mixtures of biodiesel obtained by using castor oil and palm oil and their blending with petroleum based diesel fuel. The castor oil based biodiesel has high viscosity but low cloud point whereas the palm oil based biodiesel has high cloud point. The fuel properties cloud point, flash point and viscosity of the mixtures of castor biodiesel, palm biodiesel and diesel were analyzed. The blends of castor biodiesel with diesel up to 40 % shows good viscosity and cloud point. They concluded that the blends of castor biodiesel and palm biodiesel with diesel fuel were not a good option for practical use. Okoro et al., (2011) carried out experimental study of blends of biodiesels of cashew nut and olive oil and their viscosity and their thermal behavior were determined. Fingas (2014) studied the predictions of formation of emulsion and water and oil.

Dias et al. (2013) discussed the cultivation of castor crop in brazil. It can grow in Northern Portugal region, with Brazilian seeds and it did not required maintenance. The plant has a good adaptability to the environment. It could be grown as a complimentary oil seed crop on poorly managed lands. Soxhlet extraction method was used to extract the castor oil from seeds and the total yield oil was obtained 54.1 % (w/w). They observed that for production of biodiesel fromunrefined, low quality oil, longer time was required to obtain high conversion as compared to the refined oil. CCD method was considered to optimize the parameters for biodiesel production. They chose the parameters for optimization as product yield (n), acid value (AV), kinematic viscosity (ϑ) and methyl ester content. The time and temperature were the most significant variable parameters those affect the product yield. The best reaction time optimized was 8 hours, reaction temperature 65 $^{\circ}$C, viscosity 17.95 mm^2/sec, 0.92 acid value and the total product yield obtained was 73.62 % (w/w). The blending of castor biodiesel with diesel has been suggested to reduce the viscosity.

Advantages of Biodiesel

Advantages of using biodiesel as a substitute fuel are as follows:

(i) Biodiesel is a green liquid fuel that decomposes easily, free from harmful pollutants emission in to environment.

(ii) Biodiesel does not require any type of engine modification as it can be used directly (B_{100}) or in the form of blends like B_{10}, B_{20}, B_{50} etc.

(iii) Biodiesels makes the vehicle performance good as it has high cetane number (over 100) as a ignition quality parameters.

(iv) Biodiesel energy efficiency is very good.

(v) Biodiesel is cost effective fuel as it can be produced locally where seeds are grown & can be used itself. So it does not require transportation from one place to another place.

(vi) Biodiesel reduces the environmental pollutants; it recues wastes materials because it can be synthesized from waste materials.

Disadvantages of Biodiesel

(i) Biodiesel has low calorific value as compare to diesel fuel.

(ii) Biodiesel could pour point is much higher than diesel.

(iii) Biodiesel recues the GHG emission, S but when it is used in diesel engine it give high NO_x emission & increased the Nitrogen pollutant in atmosphere.

(iv) Biodiesel is corrosive in nature when used in engine as compare to diesel against metals.

2.8 MOTIVATION OF THE PROPOSED STUDY

In this chapter, a review on experimental analysis, optimization of the reaction parameters, scale up of reaction, modeling and simulation studies carried out for the biodiesel production process from castor oil has been presented. The following conclusions have been made from literature survey:

- Biodiesel is a nontoxic, environment friendly and sustainable fuel obtained from renewable resources like plant oils, animal fats. It is technically achievable, economically aggressive, and environmentally acceptable fuel. Currently the use of edible oil is first choice throughout the world but it creates the problem of availability of edible oils for food requirement.

- Biodiesel obtained from castor oil has very similar fuel properties as the diesel fuel. The castor biodiesel has a high viscosity so the blending it with diesel fuel has been suggested.
- Castor is a nonedible oil and is a good alternative source for the biodiesel formation. Several researchers have reported the use of basic catalysts for the biodiesel synthesis but only few studies are related to the use of acid catalyst in transesterification reactions and parameters optimization and modeling study.

With these features in mind, the purpose of the research work, mentioned in Chapter I have discussed for the present work.

2.9 CONCLUDING REMARKS

In this chapter, a literature review has been done on the biodiesel production from castor oil and other renewable resources like vegetable oils, waste cooking oil, animal fats, algae by the using different catalysts, in different reaction processes, fuel properties of biodiesel and properties of their blends with diesel fuel. The motivation for the proposed research work has also been discussed.

CHAPTER III

TRANSESTERIFICATION OF CASTOR OIL IN SMALL LAB REACTOR-EXPERIMENTS AND KINETICS DETERMINATION

3.0 INTRODUCTION

In this thesis, the transesterification of castor oil has been carried out in two types of Lab reactors, small lab reactor (500 c.c.) and large lab reactor (3L). This chapter describes the experimental work done in the small lab reactor at various operating conditions. In the transesterification reactions, sulphuric acid has been used as the catalyst. By using the obtained results in experiments, kinetics of transesterification reaction has been determined. The results have been explained and compared with those available in the literature.

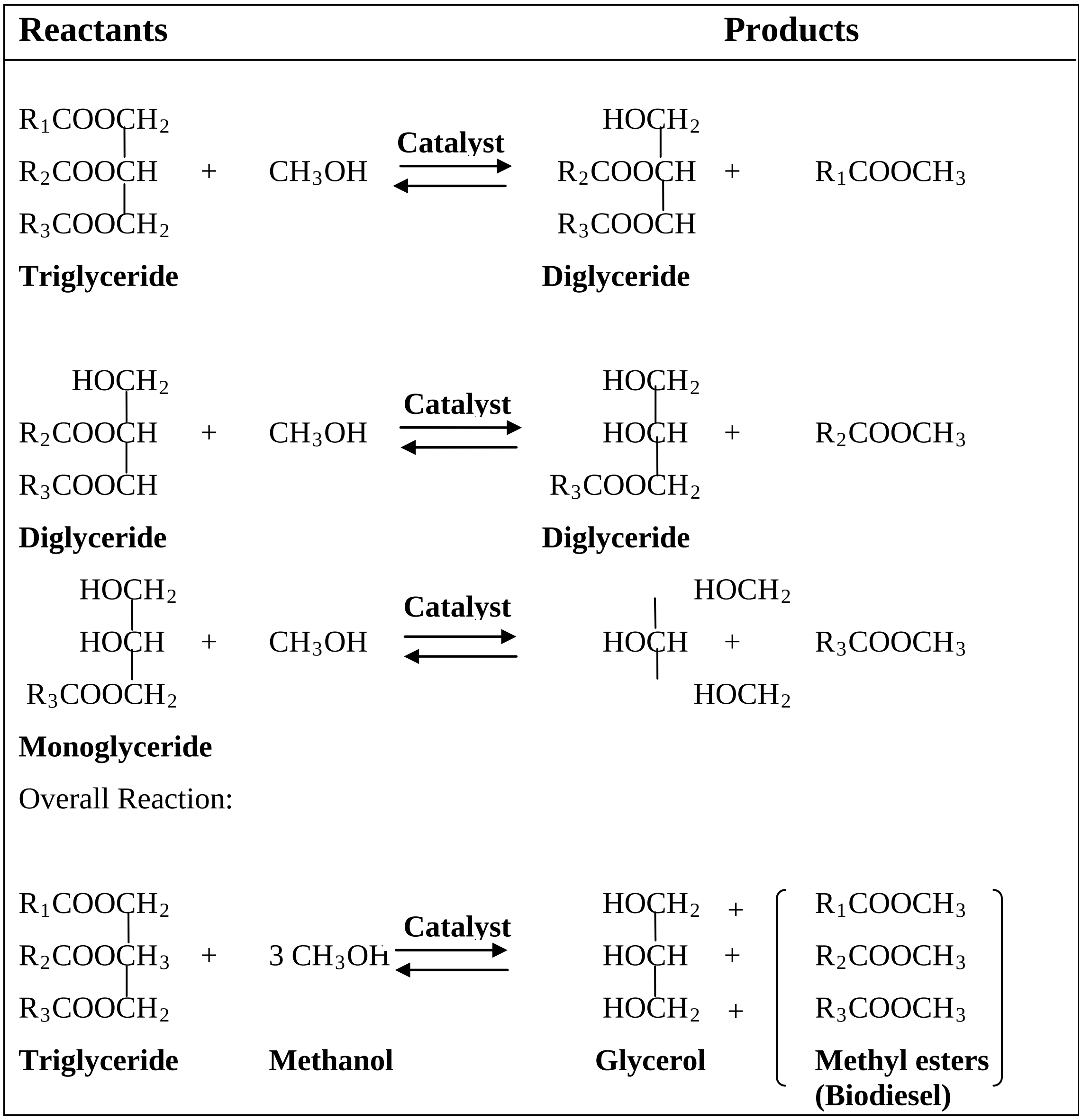
3.1 Materials Used

Pharmaceutical grade Castor oil was purchased from the local market through the authorized standard chemical supplier of the institute. All chemicals H_2SO_4 (97 %), anhydrous methanol, Na_2SO_4 was of analytical grade and were purchased from Merck India and used without further purification. Pure standard of methyl esters was purchased from Sigma Aldrich, U.S.A.

3.2 Transesterification Reactions

The most commonly used technology for the production of biodiesel is the transesterification of oils (triglycerides) with alcohol which provides fatty acid alkyl esters, FAAE (biodiesel) as main product and glycerin as by product. Transesterification (also called alcoholysis) is the reaction of fat or oil with an alcohol to form esters and glycerol. The general transesterification reaction system is illustrated in Figure 3.1. In this reaction network, the first step is conversion of triglycerides into diglycerides, which is followed by the conversion of diglycerides to monoglycerides and conversion of monoglycerides to glycerol, providing one methyl ester molecule from each glyceride at each step.

Figure 3.1 : Transesterification reactions of glycerides with methanol



In present work, the optimum operating conditions for the transesterification reaction of castor oil with methyl alcohol and concentrated sulphuric acid as catalyst are investigated. The effect of reaction temperature is considered which is followed by the kinetic modeling of the production of biodiesel.

The transesterification reactions require a catalyst in order to achieve optimum conversion. Generally, biodiesel is produced by using alkaline catalyst, such as potassium methaoxides, hydroxides, and sodium methaoxides. Sodium hydroxide and potassium hydroxide are most preferable catalyst in industries due to their easy availability and low price. But transesterification consisting base catalyzed process has limitation of feedstock specifications which results into higher prices of biodiesel. For using the alkaline catalyst it is desired that FFA content should be less than 1 % (Tiwari et al., 2007). If the FFA content exceeds this limit, the formation of soap will occur which will inhibit the separation of the ester from the glycerin (Canakci and Gerpen, 2001). Thus, in this process, the main issue is the formation of soap which will result into the formation of gels, increase in viscosity, and increase in product separation cost (Dorado et al., 2004). The methodology related with acid catalyzed reactions is an alternative to overcome this difficulty and lower production cost. So technologies based on acid catalyzed reactions are popular due to their potential for the production of biodiesel because these catalysts do not show measurable susceptibility to free fatty acids. Due to this reason, experimental work on the production of biodiesel using acid catalyst is the main focus in the present research work.

3.3 Experimental Setup and Procedure

FFA contents of the castor oil were determined by using ASTM D5555 - 95 method [ASTM International, Designation: D5555 – 95 (Reapproved 2011)]. Castor oil used in the present research work contains 2.25 % FFA. Therefore, acid catalyst namely, concentrated sulphuric acid was used here. Transesterification reaction was carried out in 4-neck round bottom flask with 500 ml capacity as a small lab reactor, equipped with a reflux condenser, a mechanical stirrer, digital thermometer; water bath was used to maintain the constant temperature.

First, a specific measured volume of castor oil was taken in the reactor and heated up to a pre specified temperature at which transesterification reaction was to be carried out. In this work, seven different temperatures (35°, 40°, 45°, 50°, 55°, 60° and 65 °C) were considered. A mixture of methyl alcohol (25 ml) and catalyst (1% of concentrated H_2SO_4, % v/v of castor oil) was stirred and heated separately at the same temperature specified above for 10 minutes and was slowly added to the heated castor oil (100 ml) in the reactor. The reaction mixture was refluxed and stirred with mechanical stirrer at constant speed 600 rpm (revolution per minute) for 2.5 hour. Sample of about 2 ml. was taken out at predetermined time intervals for analysis to determine the percentage of methyl ester yield (% ME). After the experiment total reaction mixture was poured into the separating funnel and kept for overnight. The schematic diagram of experimental set up is given in Figure 3.2 and the photograph of experimental small lab reactor assembly is shown in the Figure 3.3.

3.3.1 Sample Treatment

To deactivate the catalyst distilled water was added to the sample in the ice bath to lower down its temperature. After this, all samples were centrifuged at least three times after washing the reaction mixture with distilled water. The two layers were formed in the reaction mixture; first upper layer contains methyl esters and the second which is heavier and lower layer as shown in figure 3.4 contain all the impurities and by products. Upper layer was separated and heated to remove moisture and dried over sodium bisulfate. All samples were thus collected and stored in air tight bottles.

3.3.2 Analysis by Gas Chromatograph

Analysis of all samples for fatty acid methyl ester (FAME content) formation were carried out by using the gas chromatograph (GC) (Nucon Gas Chromatograph, 5765, INDIA), equipped with a flame ionization detector (FID) and a capillary column with dimension of 0.55 mm I.D. X 10 m length X 0.50 m thickness. Nitrogen was used as carrier gas. The column temperature was kept at 170 °C for 1 min, heated at 10 °C/min up to 240 °C and then it was maintained constant. The temperature of the injector and detector were set at 220 °C and 240 °C respectively. Methyl heptadecanoate was used as internal standard for GC. The concentration of methyl heptadecanoate was used as 10 mg/ml. The analysis was done by injecting 1 µl sample into the column.

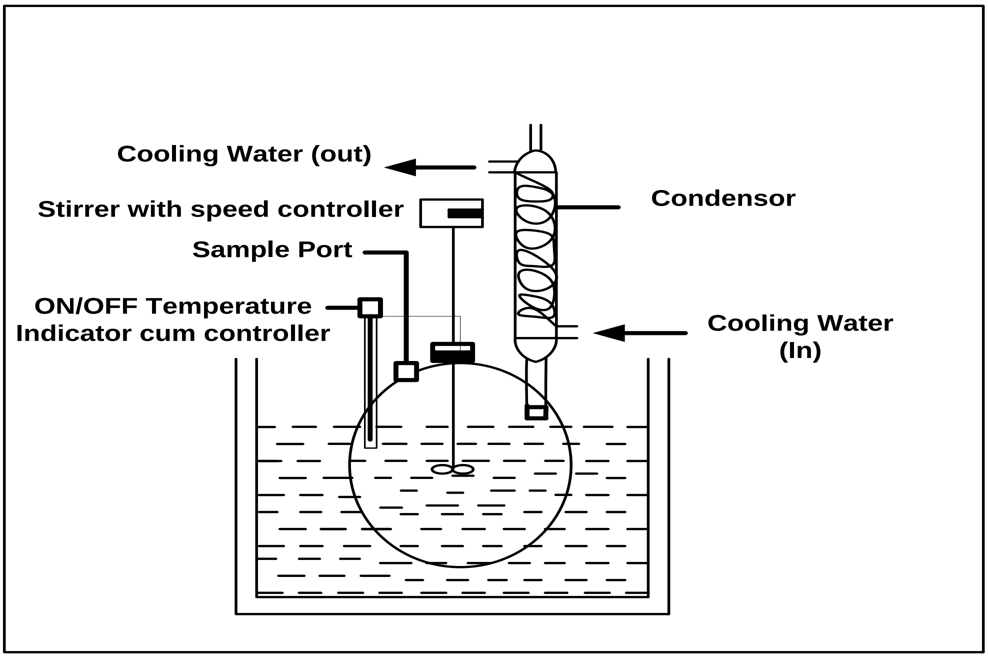
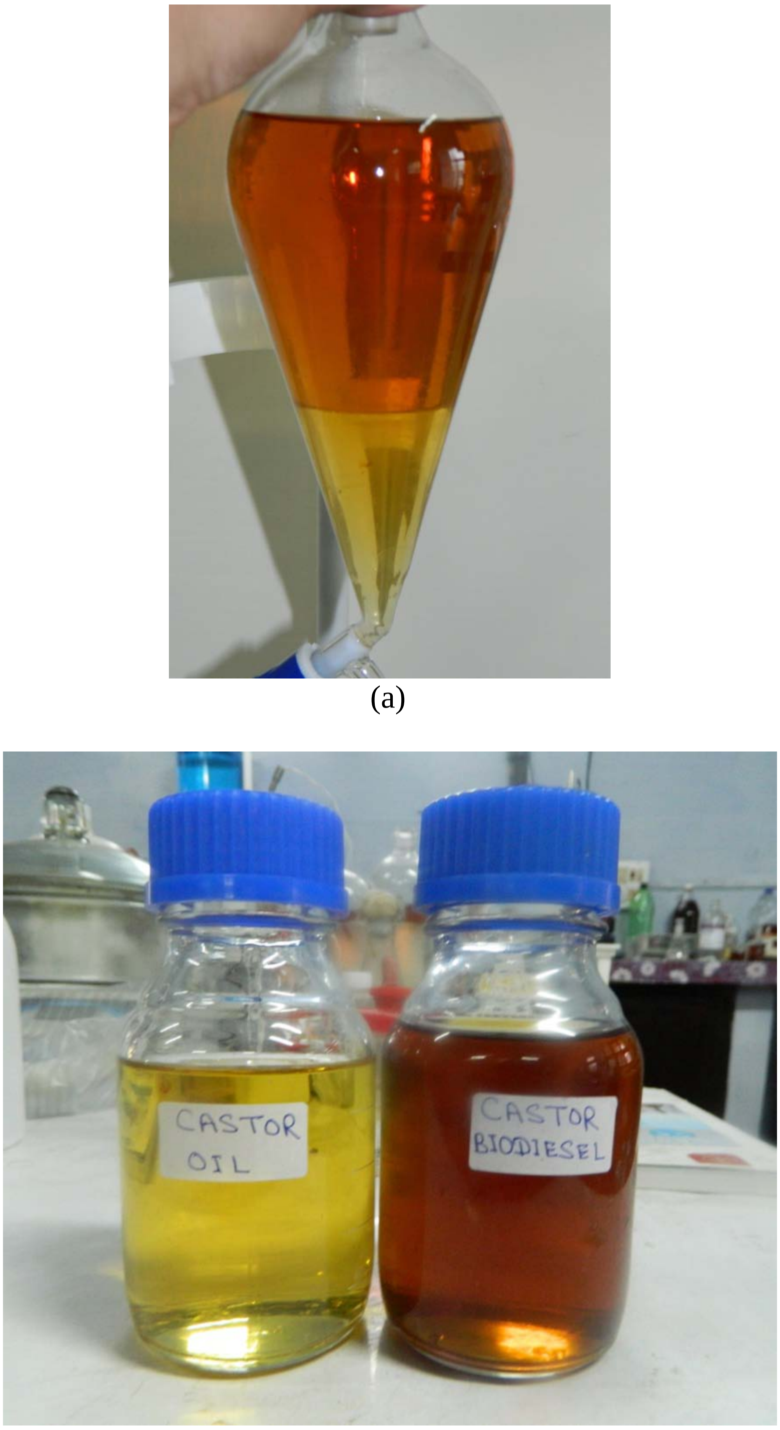


Figure 3.2 : Schematic Diagram of Small Lab reactor

Figure 3.3 : Photograph of Small Lab Reactor Assembly



(a)

(b)

Figure 3.4: (a) shows separation of methyl ester phase, (b) shows raw castor oil and castor biodiesel after transesterification reaction

Quantitative analysis of % ME was done by using European standard EN 14103:2003.The % ME yield (or % FAME yield) was calculated by using equation (3.1), (Ruppel and Hubrighs, 2008-2012):

$$\%\ \text{FAME yield} = \frac{\sum A - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100 \qquad (3.1)$$

Where, $\sum A$ =Total peak area from methyl esters in $C_{14;\,0}$ - $C_{24;\,1}$,

A_{EI} =Peak area corresponding to methyl heptadecanoate,

C_{EI} = Concentration of the methyl heptadecanoate solution (mg/mL),

V_{EI} = Volume of methyl heptadecanoate solution (mL),

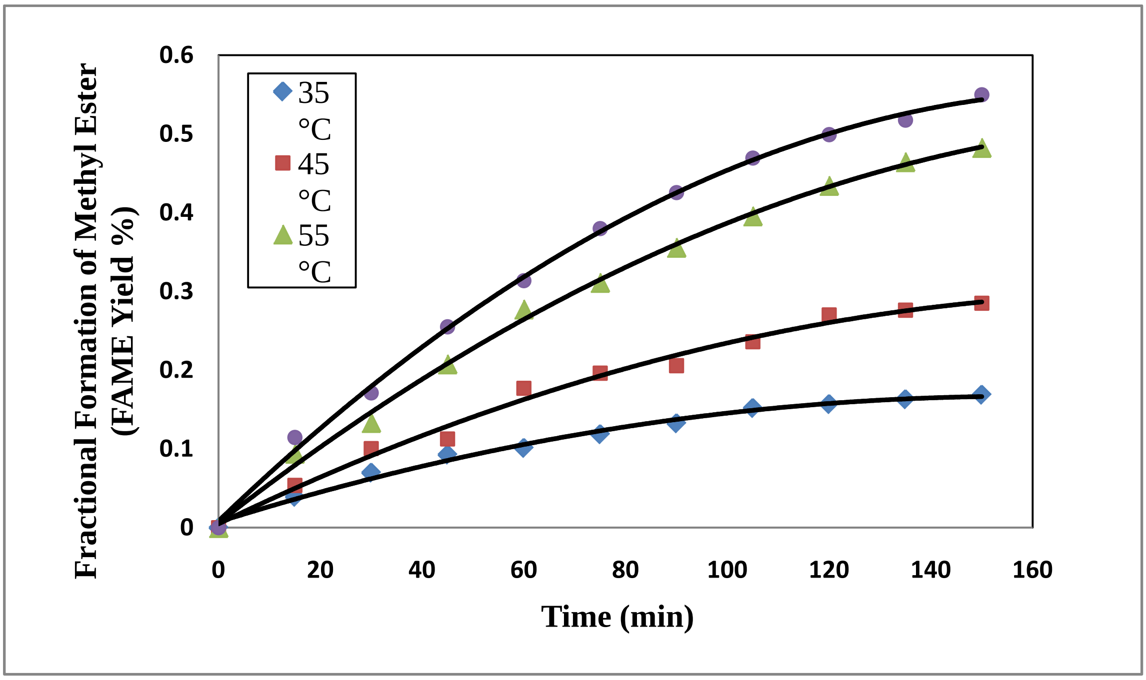
m = Mass of the sample (mg)

3.4 RESULTS AND DISCUSSION

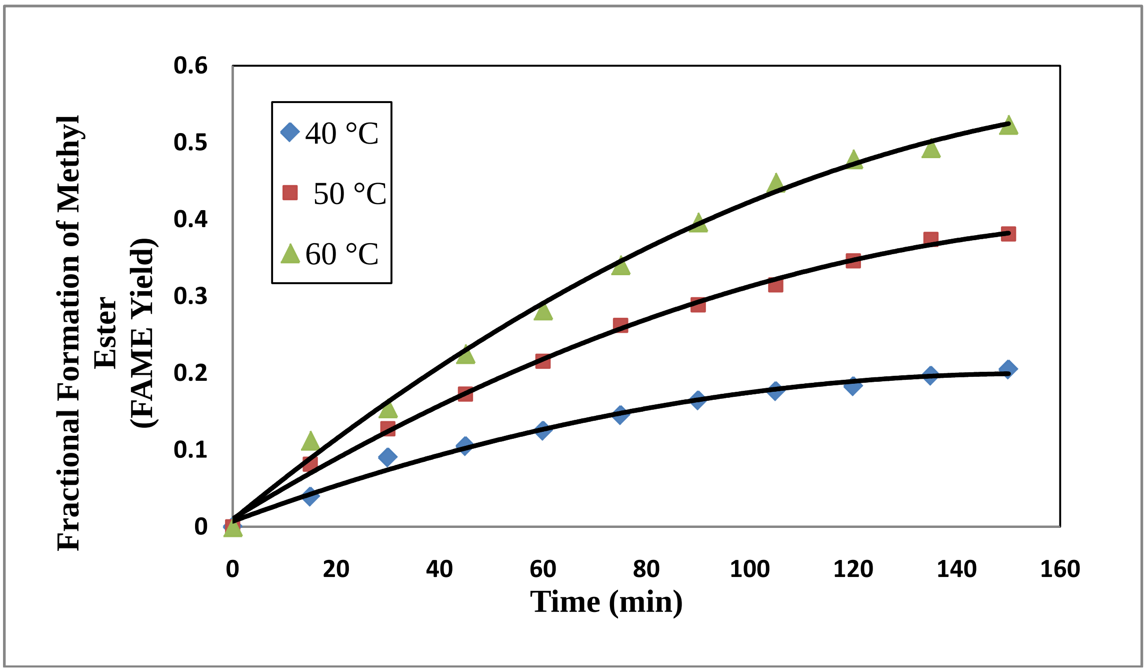
Fractional formation of methyl esters (FAME) has been tabulated in Table 3.1 as a function of time (min) at various temperatures in the range 35 to 65 °C with an interval of 5 °C. These experimental results have also been plotted in Figures 3.5 (a) and (b). From the critical analysis of tabulated results, it is obvious that there is no significant change in fractional methyl ester yields at 60 °C and 65 °C. Due to this reason, optimum reaction temperature has been taken as 60 °C.

Table 3.1 : Fractional Formation of Methyl Esters (FAME) with Time (min) at various Temperatures

Time (min)	Fractional Formation of Methyl Esters at the Temperature						
	35 °C	**40 °C**	**45 °C**	**50 °C**	**55 °C**	**60 °C**	**65 °C**
0	0	0	0	0	0	0	0
15	0.0391	0.0392	0.0537	0.0815	0.0943	0.11252	0.1146
30	0.06985	0.0902	0.1005	0.1276	0.1334	0.15467	0.1712
45	0.09275	0.1049	0.1127	0.1728	0.2078	0.22523	0.2551
60	0.1012	0.1249	0.1771	0.2155	0.2775	0.28203	0.3137
75	0.11865	0.1452	0.1963	0.2621	0.3113	0.34087	0.3799
90	0.1325	0.1644	0.2058	0.2889	0.3559	0.39653	0.4255
105	0.1519	0.1764	0.2362	0.3148	0.3958	0.4483	0.4694
120	0.1569	0.1828	0.2702	0.3461	0.4345	0.4787	0.4992
135	0.16305	0.1965	0.2763	0.374	0.4646	0.4932	0.5175
150	0.1688	0.2046	0.2851	0.3811	0.4827	0.5235	0.5498



(a)



(b)

Figure 3.5 : Plots of Fractional Formation of Methyl Esters (FAME) with Time at Temperatures (a) 35°C, 45°C, 55 °C, 65°C (b) 40°C, 50°C, 60°C

3.5 KINETIC MODELING

Overall transesterification reaction of a triglyceride with methanol can be represented as follows:

$$\text{Triglyceride} + 3\ \text{Methanol} \rightleftarrows 3\ \text{Methyl Ester} + \text{Glycerol.}$$

$$\text{or} \qquad \text{TG} + 3\ \text{ML} \underset{k}{\overset{k}{\rightleftarrows}} 3\ \text{ME} + \text{GL};$$

$$\text{or} \qquad \text{A} + 3\ \text{B} \underset{k_2}{\overset{k_1}{\rightleftarrows}} 3\ \text{C} + \text{D};$$

Where A, B, C, and D represents TG (Triglyceride), ML (Methanol), ME (Methyl Ester) and GL (Glycerol) respectively.

Above reaction is a liquid phase constant density reaction. So rate of reaction with respect to reactant A can be written as

$$(-r_A) = \frac{-dC_A}{dt} = k_1 C_A C_B - k_2 C_C C_D \qquad (3.2)$$

Where, C_i = molar concentration of species i, and i = A, B, C, and D. In equation, it is assumed that the reaction is reversible and order of reaction is 1 with respect to each and every reactant and product.

If, X_A=Fractional conversion of A, and C_{A0}, C_{B0}, C_{C0}, and C_{D0}= Initial Concentrations of A, B, C, D. $C_{C0} = 0$; $C_{D0} = 0$ as no product has been assumed to be present at t = 0. Now equation (3.2) becomes

$$\frac{dX_A}{dt} = k_1 C_{A0}\left[(1 - X_A)\,(M - 3X_A) - 3\frac{1}{K}X_A^2\right] \qquad (3.3)$$

Where, $\frac{k_1}{k_2} = K$

M = C_{B0}/C_{A0} = Molar ratio of methanol to Triglycerides and in a batch reactor experiment, we know that,

$t = 0; X_A = 0$

(3.3a)

Equation (3.3) and (3.3a) describe the increase in fractional conversion of A (triglycerides) with time.

In the experiment, progress of reaction is monitored by measuring the concentration of Methyl ester (C) with time. We know that

$$\frac{(-r_A)}{1} = \frac{(-r_B)}{3} = \frac{(r_c)}{3} = \frac{(r_D)}{1} \quad (3.4)$$

or $\quad (-r_A) = \dfrac{(r_C)}{3}$

So equation (3.3) in terms of X_C (fractional formation of methyl ester) becomes

$$\frac{1}{3}\frac{dX_C}{dt} = k_1 C_{A0}\left[\left(1 - \frac{X_C}{3}\right)(M - X_C) - \frac{1}{K}\frac{X_C^2}{3}\right]$$

$$\frac{dX_C}{dt} = (k_1 C_{A0})\left[(3 - X_C)(M - X_C) - \frac{1}{K}X_C^2\right] \quad (3.5)$$

At $t = 0$; $\quad X_C = 0$

Case I: Reaction is pseudo homogeneous first order irreversible. This assumption is valid when methanol is taken in large excess. Equation (3.5) reduces to

$$\frac{dX_A}{dt} = k(1 - X_A)$$

$$\frac{dX_C}{dt} = k(3 - X_C)$$

or $$\ln\frac{3}{(3 - X_C)} = kt \quad (3.6)$$

Therefore, a plot of $\ln\dfrac{3}{(3 - X_C)}$ verses t gives a straight line and its slope gives rate constant k.

Case II: Reaction is irreversible second order. Under this assumption, equation (3.5) becomes

$$\frac{dX_C}{dt} = (k_1 C_{A0})\,(3 - X_C)\,(M - X_C) \tag{3.7}$$

$$\frac{dX_C}{dt} = k_1^{'}(3 - X_C)\,(M - X_C); \qquad k_1^{'} = k_1 C_{A0}$$

$$\int_0^{X_C} \frac{dX_C}{(3 - X_C)\,(M - X_C)} = k_1^{'} \int_0^t dt$$

or
$$\frac{1}{(M-3)} \int_0^{X_C} \left[\frac{1}{(3 - X_C)} - \frac{1}{(M - X_C)} \right] dX_C = k_1^{'} t \tag{3.8}$$

or
$$\frac{1}{(M-3)} \ln\left[\frac{3(M - X_C)}{M(3 - X_C)} \right] = k_1^{'} t$$

or
$$\ln\left[\frac{3(M - X_C)}{M(3 - X_C)} \right] = k_1^{''} t \tag{3.9}$$

Where, $k_1^{''} = (M-3)k_1^{'} = (M-3)k_1 C_{A0} = (M-3)C_{A0}k_1$ (3.9a)

So, a plot of $\ln\left[\frac{3(M - X_C)}{M(3 - X_C)} \right]$ versus *t* would be a straight line and its slope yields *(M-3)* $C_{A0}k_1$, and k_1 can be easily estimated.

Case III: Reversible Reactions

Equation (3.5) can be written in the following from

$$\frac{dX_C}{dt} = C_{A0}\left[k_1(3 - X_C)\,(M - X_C) - k_2 X_C^2 \right] \tag{3.10}$$

In the beginning reaction proceeds at a fast rate, but with the passage of time, rate of reaction reduces as reactants are depleted and backward reaction rate increases as product’s concentrations are appreciable.

As equilibrium conversion is not known, k_1 and k_2 are proposed to be estimated by using experimental data. Differential method of analysis [Levenspiel, 1999 and Fogler, 2006] may be used, but in this method there is every likelihood of erroneous estimation of derivative *(dX_C/dt)*. So following procedure is adopted.

Let X_{Ci} and t_i; i=1, N represents N experimental data points. X_{Ci}^{p} represents predicted value from assumed model at t_i. Then the estimation of k_1 and k_2 may be stated as follows:

Minimize ϕ to estimate k_1 and k_2, where

$$\phi = \sum_{i=1}^{N} (X_{Ci} - X_{Ci}^{p})^2 \tag{3.11}$$

This problem may now be stated as the estimation of k_1 and k_2 of a differential equation model. For optimization and solution of differential equation, MATLAB tool box have been used.

3.5.1 Determination of Arrhenius Parameters

The Arrhenius equation relates rate constant k with activation energy E of a reaction system as follows:

$$k = Ae^{-\frac{E}{RT}} \tag{3.12}$$

Where, R is the universal gas constant and T is the temperature (in Kelvin). It may be converted into linear equation as given below:

$$\ln k = \ln A - \frac{E}{RT} \tag{3.13a}$$

or

$$\ln\left(\frac{1}{k}\right) = \ln\left(\frac{1}{A}\right) + \frac{E}{RT} \tag{3.13b}$$

Therefore, the plot of ln (1/*k*) versus 1/T is a straight line whose slope is E/R and intercept is $\ln\left(\frac{1}{A}\right)$. Thus, activation energy E and Arrhenius parameter A may be computed.

3.6 ESTIMATION OF KINETIC CONSTANTS

In this work, three kinetic models namely, first order irreversible reaction, second order irreversible reaction and reversible reaction (Forward reaction: pseudo first order and Backward reaction: second order), were fitted to the experimental data to obtain the appropriate kinetic model for the transesterification reaction.

3.6.1 First Order Irreversible Reaction

For every temperature, $\ln[3/(3-X_C)]$ was plotted with time t and a straight line was fitted by regression analysis to obtain the first order rate constant. These estimated values of k with temperature and correlation coefficients are given in Table 3.2.

Figures 3.6 (a) and (b) depict the fitting of straight line to experimental data at two temperatures 55 °C and 60 °C respectively. From the table, it is observed that the correlation coefficients are more than 0.93 for temperatures above 40 °C while the same is of order 0.85-0.86 for temperatures below 45 °C. Though fitting of straight line at temperatures 35 °C and 40 °C is not as good as at higher temperatures but it is still acceptable.

In order to obtain activation energy, a plot of ln (1/k) versus (1/T) was plotted as shown in Figure 3.7; other computational details are shown in Table 3.3. Correlation coefficient, R^2 is high and equals to 0.9638. Therefore, the fitting of straight line by regression analysis is good. For this straight line, the slope E/R = 4604.4, and intercept ln (*1/A*) = -7.2869. As gas constant R = 8.3144 kJ/kmol.K, therefore, E = 38.283 kJ/mol, and A = 1461.0345 min^{-1}. The value of activation energy computed is in agreement with that (38.916 kJ/mol) obtained by Madankar et al. (2013).

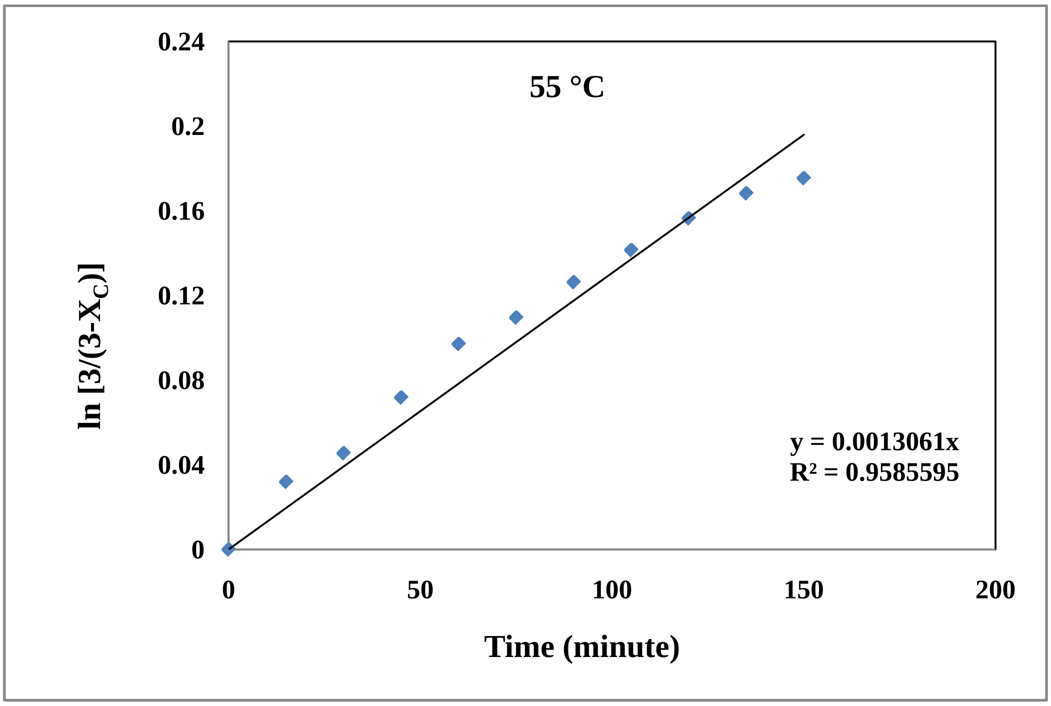
Ramezani et al. (2010) conducted experimental studies on transesterification of castor oil in the presence of basic catalysts namely $NaOCH_3$, NaOH, $KOCH_3$ and KOH at 25, 65 and 80 °C by using methanol in different molar ratios (4:1, 6:1 and 8:1). They also fitted the first order irreversible reaction kinetics and obtained k as 0.00491 min^{-1} at operating conditions (methanol/oil molar ratio = 8:1, temperature = 65 °C, mixing intensity = 400 RPM, catalyst = CH_3OK at 0.5 % concentration). The value of k obtained in the present study at 65 °C is 0.001529 min^{-1}. This value is acceptable as it is known that basic catalysts catalyze transesterification reaction much faster in comparison to acid catalysts.

Table 3.2 : Estimated values of rate constant *k* for first order irreversible reaction at various temperatures

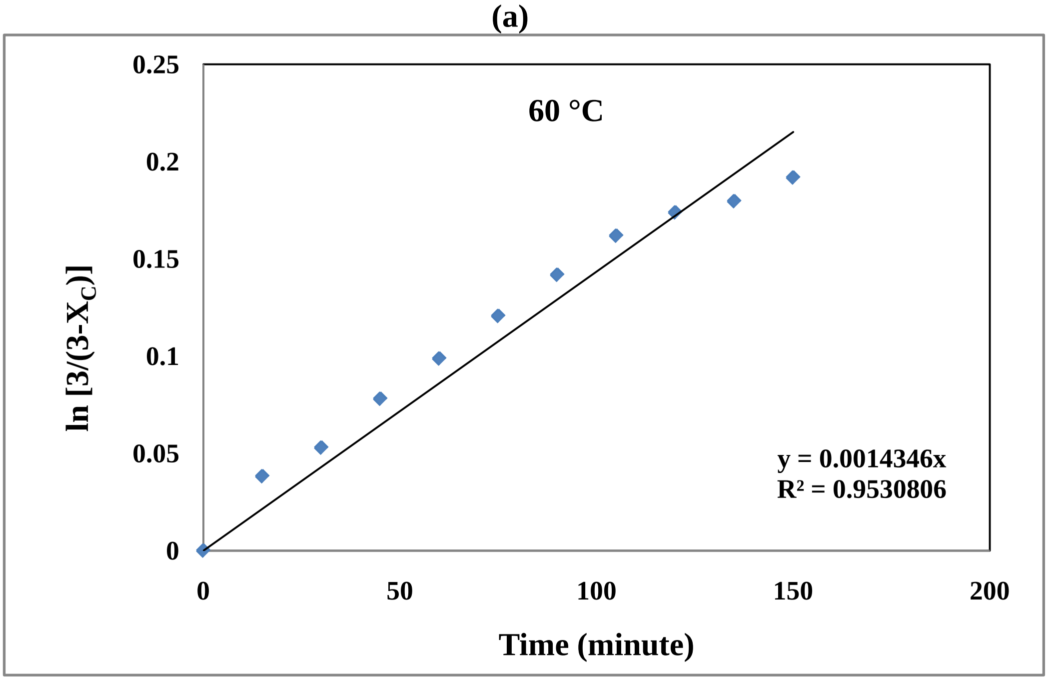
S. No.	Temperature (°C)	Estimated Value of k, min^{-1}	Correlation Coefficient, R^2
1	35	0.000457	0.85
2	40	0.000551	0.86
3	45	0.000763	0.93
4	50	0.001034	0.94
5	55	0.001306	0.96
6	60	0.001435	0.95
7	65	0.001530	0.94

Table 3.3 : Shows ln(*1/k*) versus *1/T* data for first order irreversible reaction

S. No.	Temperature (K)	k	*1/T*	ln*(1/k)*
1.	338	0.001530	0.002959	6.482546
2.	333	0.001435	0.003003	6.546590
3.	328	0.013060	0.003049	6.640710
4.	323	0.001034	0.003096	6.874611
5.	318	0.000763	0.003145	7.178253
6.	313	0.000551	0.003195	7.504320
7.	308	0.000457	0.003247	7.690608



(a)



(b)

Figure 3.6 : Plots of Fractional Formation of Methyl Esters (FAME) with Time at Temperatures (a) 55 °C, (b) 60 °C

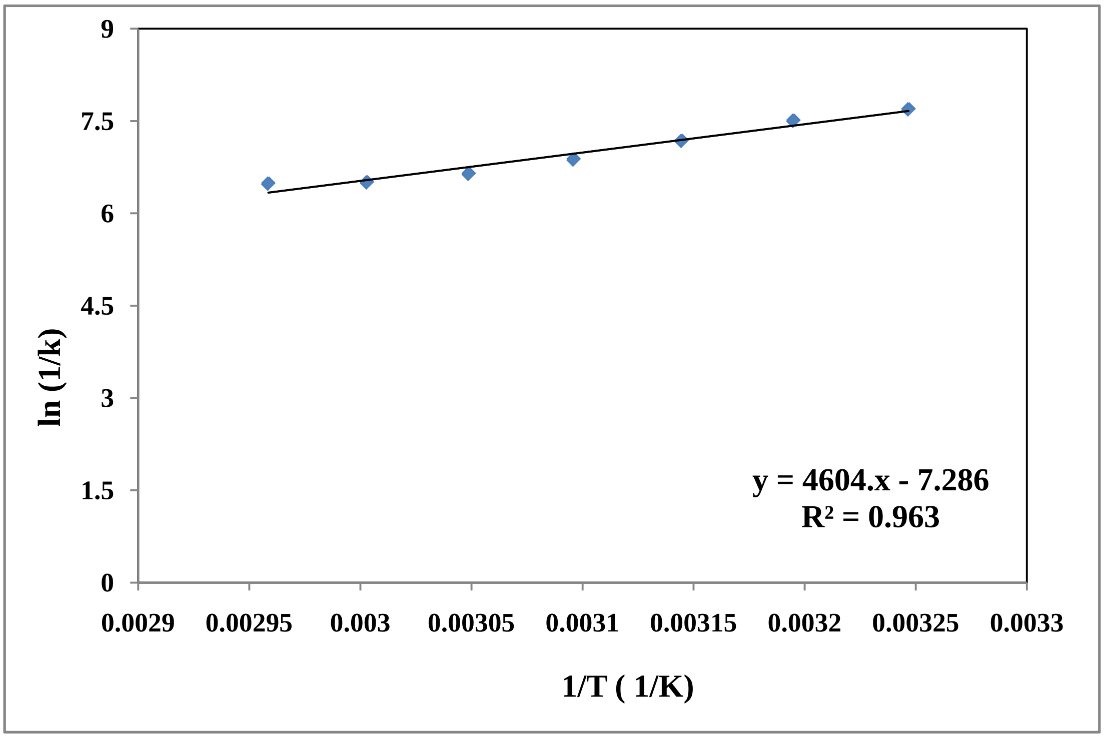


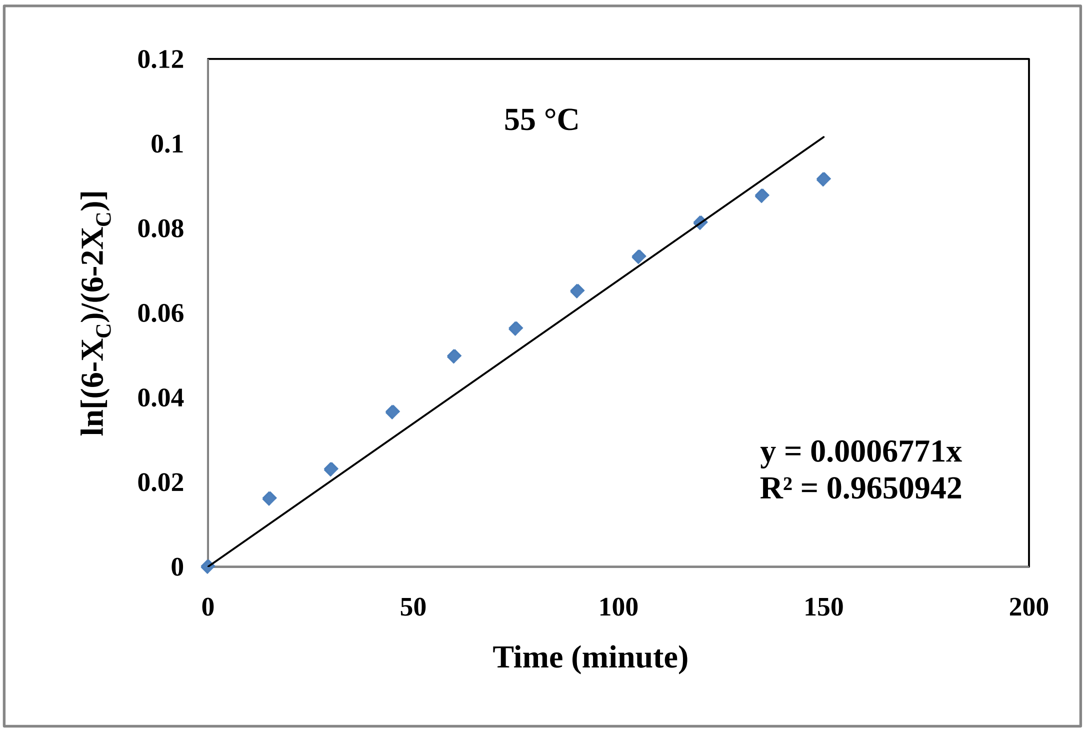
Figure 3.7 : Estimation of activation energy for first order irreversible reaction

3.6.2 Second Order Irreversible Reaction

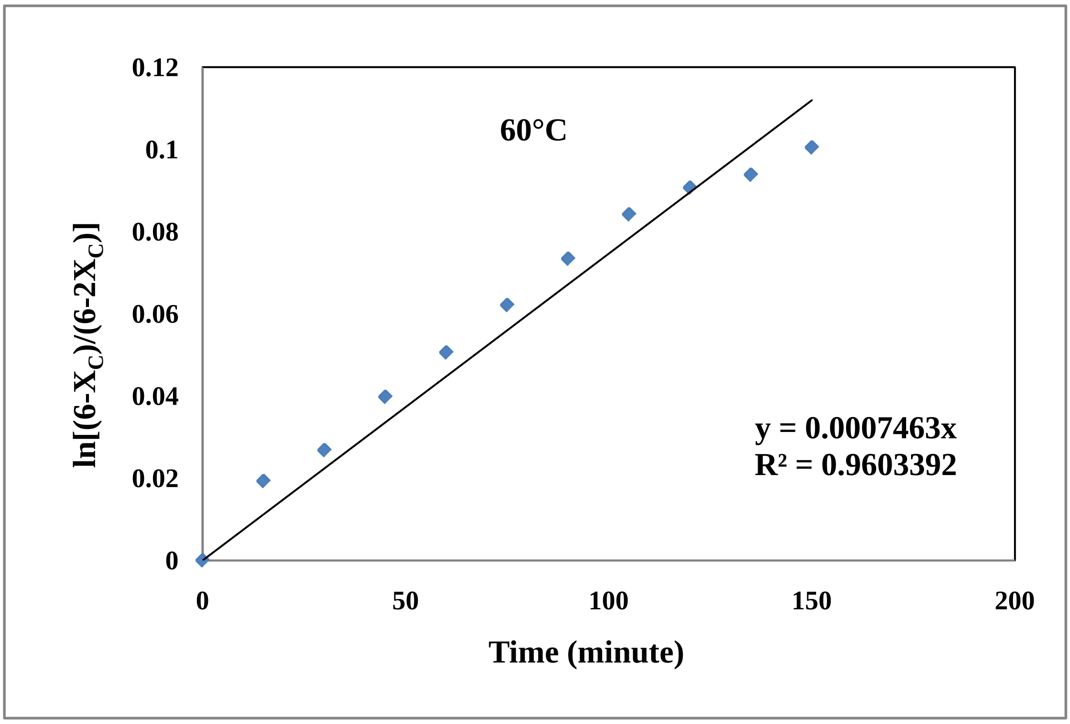
According to case II of section 3.5, plots of $\ln\left[\frac{3(M-X_C)}{M(3-X_C)}\right]$ versus *t* were prepared for every reaction temperature. By using method of least square, a straight line was fitted to the experimental data. The slope of this line provides the value of rate constant. These rate constant values at different temperatures along with correlation coefficients are given in Table 3.4.

Figures 3.8 (a) and (b) provide plot of $\ln\left[\frac{6-X_C}{6-2X_C}\right]$ versus *t* only for temperatures 55° and 60 °C respectively. Such plots prepared for of other temperatures were not given as theses were also similar in nature.

Using estimated values of *k* at different temperatures, the slope and intercept of ln*(1/k)* versus *1/T* straight line (Figure 3.9) were determined as described in section 3.5.1. Table 3.5 provides ln(1/k) versus 1/T data which were used to obtain the activation energy.



(a)



(b)

Figure 3.8 : Plots of $\ln\left[\frac{6-X_C}{6-2X_C}\right]$ with Time at Temperatures **(a)** 55 °C, **(b)** 60 °C

Therefore, fitting of straight line is good with correlation coefficient, R^2 = 0.9651. For this straight line, the slope E/R = 4643.9, intercept ln(1/A) = -12.748. As gas constant R= 8.3144 kJ/kmol.K, therefore, E is equal to 38.611 kJ/mol and A is 343836.48 ml/ (mol.min).

Table 3.4 : Estimated values of rate constant *k* for second order irreversible reaction at various temperatures

S. No.	Temperature (°C)	Estimated Value of k, ml/(mol.min)	Correlation Coefficient, R^2
1	35	0.094500248	0.86
2	40	0.114052024	0.86
3	45	0.158858176	0.93
4	50	0.216698846	0.94
5	55	0.275761501	0.97
6	60	0.303867178	0.96
7	65	0.325048268	0.94

Table: 3.5 ln(*1/k*) versus *1/T* data for second order irreversible reaction

S. No.	Temperature (K)	k	1/T	ln(1/k)
1.	338	0.325048268	0.002959	1.123781589
2.	333	0.303867178	0.003003	1.191164587
3.	328	0.275761501	0.003049	1.288218914
4.	323	0.216698846	0.003096	1.529246697
5.	318	0.158858176	0.003145	1.839743448
6.	313	0.114052024	0.003195	2.171100584
7.	308	0.094500248	0.003247	2.359152815

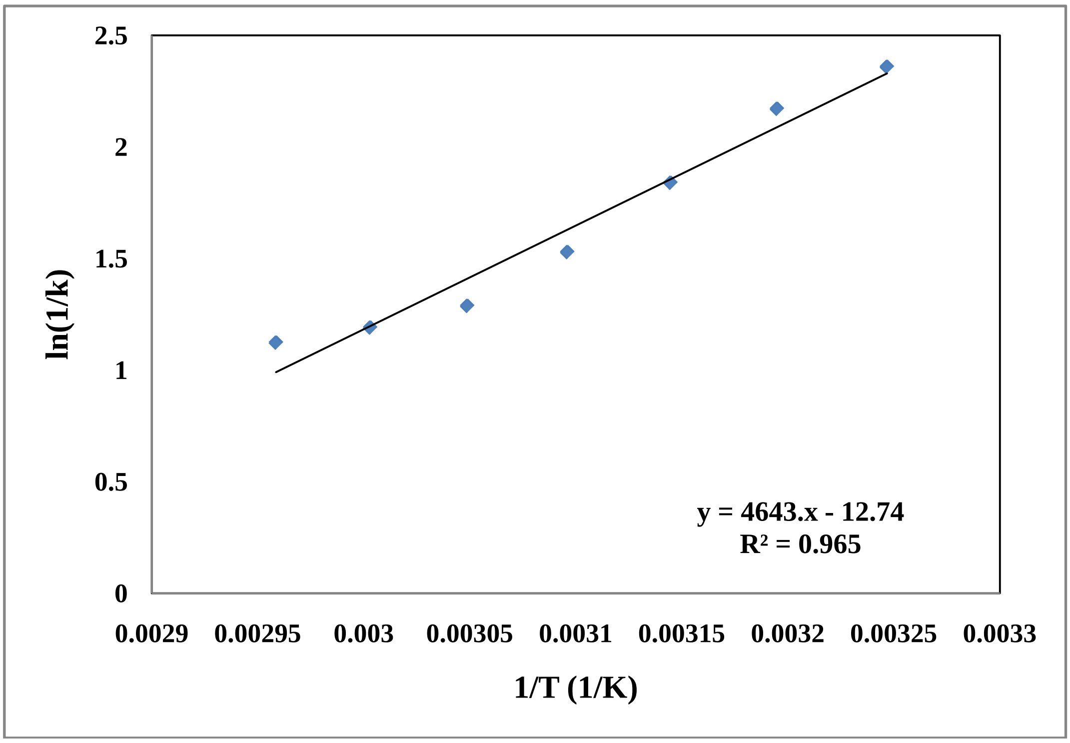


Figure 3.9 : Estimation of activation energy for second order irreversible reaction

3.6.3 Reversible Reaction

In the transesterifcation experiments, molar ratio of methanol to oil is 6:1, while the stoichiometric requirement is 3:1. In the literature use of even higher molar ratio (up to 25:1) is reported (Madankar et al., 2013; Canakci and Van Gerpan, 2001; Freedman et al., 1986). Thus, forward reaction may be considered as pseudo first order with respect to oil, but backward reaction is second order, first order with respect to each of the products. Under these assumptions, equation (3.10) takes the following from:

$$\frac{dX_c}{dt} = k_1(3 - X_c) - k_2 X_c^2 C_{A0} \tag{3.14}$$

With $X_c = 0$ at t = 0.

Berrios et al. (2007) also used similar rate law for studying the kinetics of the esterification of FFA in Sunflower oil. However, their proposed method of estimating rate constants appears to be arbitrary and requires trial and error procedure.

For estimating the values of k_1 and k_2, the procedure described in the section 3.5 case III was used. The values of k_1 and k_2, were estimated by using MATLAB (R2008a) version 7.6. The SUNDIALS (SUitE of Nonlinear and DIfferential / ALgebraic equation Solvers) toolbox version 2.3.0 was installed in MATLAB for use of solvers such as CVODE, CVODES, IDA, IDAS and KINSOL. The toolbox is available from the website: computation.llnl.gov/casc/sundials/main.htm (Swaney and Rawlings, 2011). Estimated values of rate constants are given in table 3.6.

The details have been provided in the table 3.6 for reaction temperature of 60 °C. Values of (rate constants) k_1 and k_2 are 0.00183 min^{-1} and 0.01388 l/mol.min respectively with Correlation coefficient R^2 = 0.9954. Predicted and experimental values of X_c are given in table 3.7 and their comparison is also depicted in figure 3.10

Figure 3.11 shows the 99% level confidence for estimated values of k_1 and k_2 in case of reversible reaction. This also supports the goodness of fit of the model. Further confidence intervals for the parameters k_1 and k_2 are calculated for 99% confidence level. An approximate inexpensive method is used to obtain ellipsoidal confidence regions. Ellipsoidal regions have been proven to be exact in case of linear process models. The principal axes of the ellipsoid indicate the smallest and largest variations in linear combinations of the parameters that lead to equivalent data fitting (Arora and Bieger, 2004). Clearly, the smaller the ellipsoid, the better is the parameter estimation

Further by using procedure outline in the section 3.5.1, activation energy of forward reaction and Arrhenius constants have been determined (Figure 3.12), which is 32.33 kJ/mol and A= 216.264 min^{-1}. Equilibrium constant K ($=k_1/k_2$) has been computed by taking the estimated values of k_1 and k_2 and plotted in the figure 3.13 as a function of temperature. This curve shows that the equilibrium constant increases with the increase in temperature. Thus, transesterfication of castor oil is an endothermic reaction. Similar observations were made by Yusup et al., (2013).

Further, the dependency of equilibrium constant K on the temperature is given by van't Hoff equation (3.15) as given below (Froment and Bischoff, 1990).

$$\frac{d(\ln K)}{dT} = -\frac{\Delta H}{RT^2} \tag{3.15}$$

$$\ln\frac{K_2}{K_1} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] ;\ T_2 > T_1 \tag{3.16}$$

or $\ln\frac{K}{K_0} = \frac{\Delta H}{R}\left[\frac{1}{T_0} - \frac{1}{T}\right]$; $T > T_0$ and T_0 is assumed equal to 35 °C.

Where R is Universal gas constant and ΔH is the Heat of reaction.

On the basis of above relationship, following correlation has been determined by regression analysis of computed results of K verses T. (figure 3.13)

$$K = K_{35}\exp\left[11857\left(\frac{1}{308.15} - \frac{1}{T}\right)\right];\ \ K_0 = K_{35} \text{ and T is in K.} \tag{3.17}$$

So, endothermic heat of reactionΔH is equal to 23559.86 cal/gmol (=23.560 kcal/gmol).

From K vs. T curve (figure 3.13), it is obvious that Equilibrium constant at 65 °C does not lie on the curve and has lesser value than one at 60 °C. This change in the trend was observed and reasoned that at higher reaction temperature (65 °C), there was increased vaporization of the alcohol (methanol) used in the transesterification reaction due to the proximity of the reaction temperature (65 °C) to the boiling point of methanol (64.7 °C) (Abdulkareem et. al, 2012).

Table 3.6 : Estimated values of rate constants for reversible reaction

S. No.	Reaction Temperature (K)	Estimated values of Rate Constants				Normalized Standard Deviation of Model	Regression coefficient	K (=k_1/k_2)
		k_1 (min^{-1})	Standard deviation	k_2 (l/mol.min)	Standard Deviation			
1	308.15	0.00071	0.00013	0.07982	0.03548	0.005755794	0.9889	0.008895014
2	313.15	0.00085	0.00015	0.06641	0.0281	0.0064728	0.9904	0.012799277
3	318.15	0.00102	0.00018	0.03137	0.02005	0.010003391	0.989	0.032515142
4	323.15	0.0014	0.00016	0.02392	0.00943	0.008278243	0.9957	0.058528428
5	328.15	0.00165	0.00016	0.01482	0.00617	0.008920377	0.9969	0.111336032
6	333.15	0.00183	0.00021	0.01388	0.00684	0.011731911	0.9954	0.13184438
7	338.15	0.00206	0.00017	0.01606	0.00458	0.008501177	0.9978	0.128268991

Table 3.7 : Experimental and predicted values of X_c at temperature 60 °C

Fractional formation of methyl esters, X_c		
Time (minute)	**Predicted value X_c**	**Experimental value X_c**
0	0	0
15	0.080915856	0.11252
30	0.157516387	0.15467
45	0.228169386	0.22523
60	0.291789869	0.28203
75	0.347850519	0.34087
90	0.396314722	0.39653
105	0.43752457	0.4483
120	0.472075963	0.4787
135	0.50070436	0.4932
150	0.524193713	0.5235

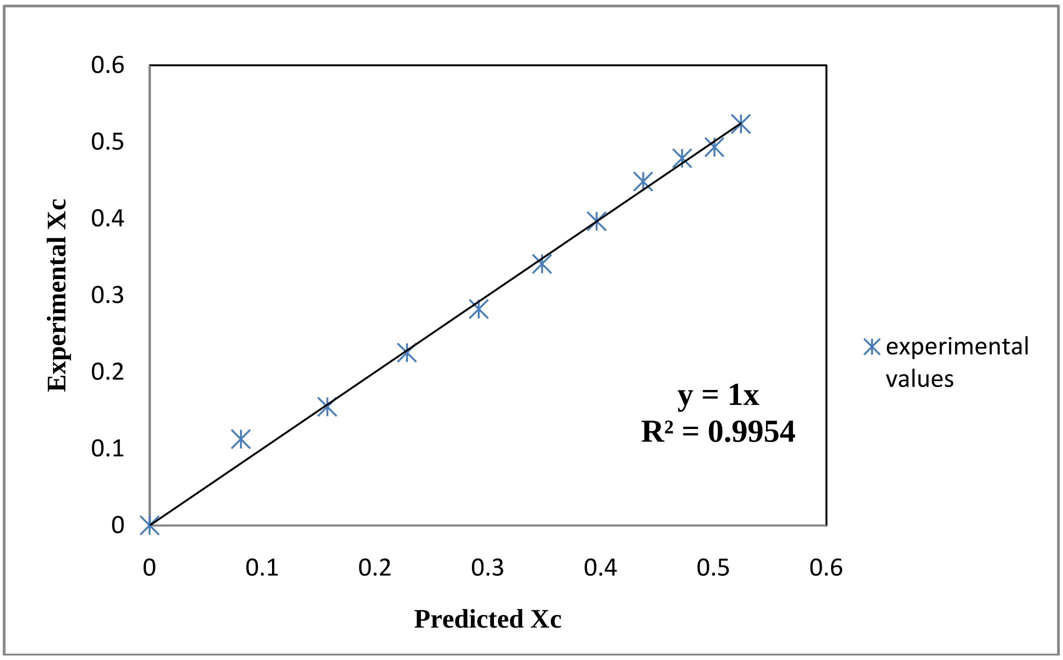


Figure 3.10 : Comparison of experimental and predicted values of X_c at 60 °C.

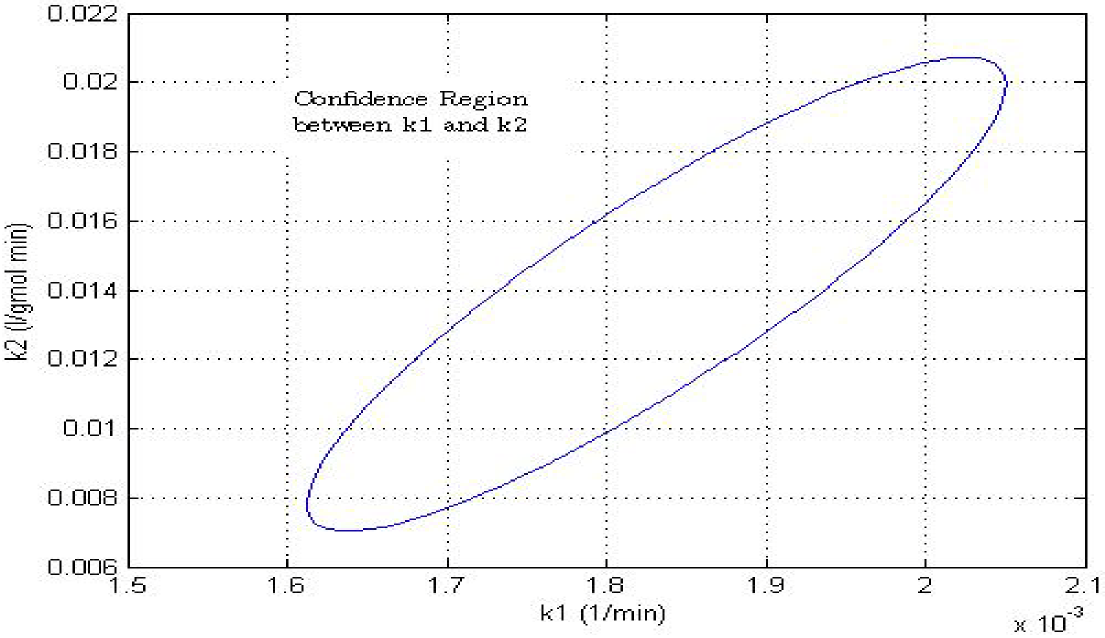


Figure 3.11 : 99% Level confidence interval for k_1 and k_2 for reversible reaction.

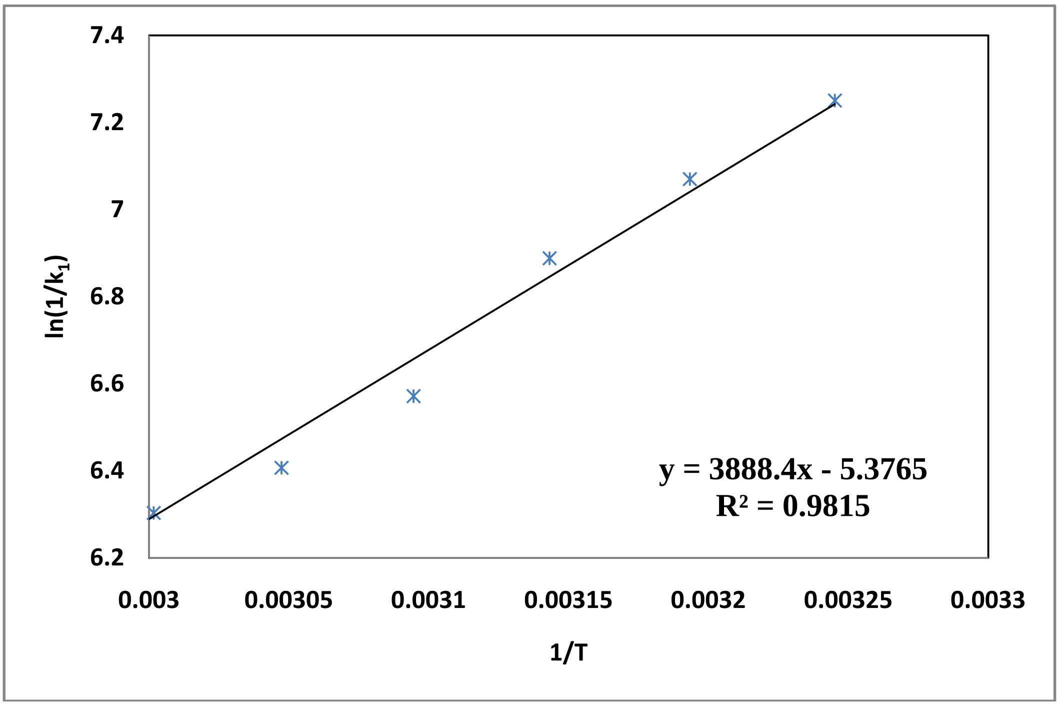


Figure 3.12 : Estimation of activation energy for forward reaction.

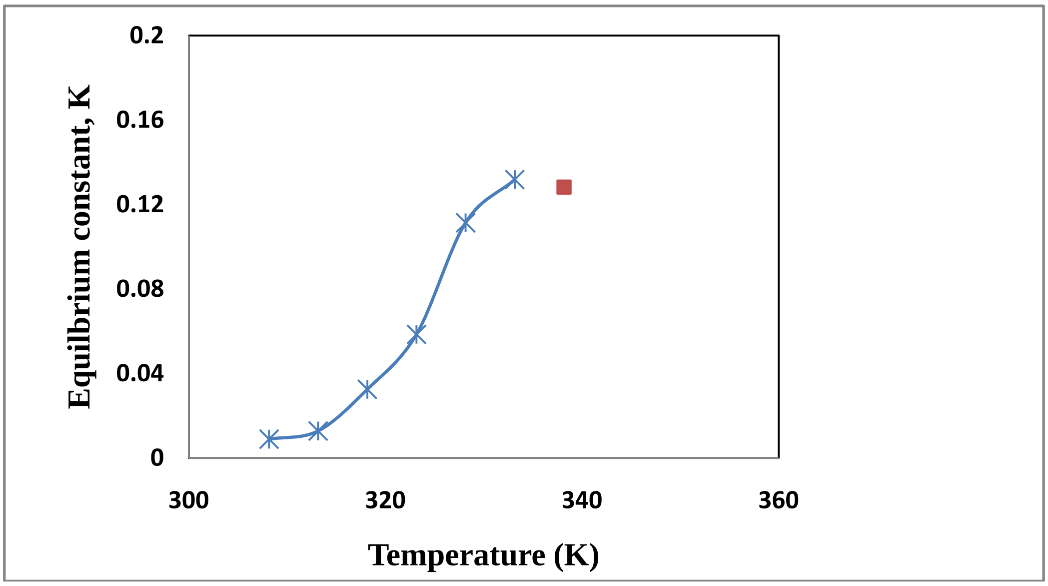


Figure 3.13 : Equilibrium constant for transesterfication reaction as a function of temperature.

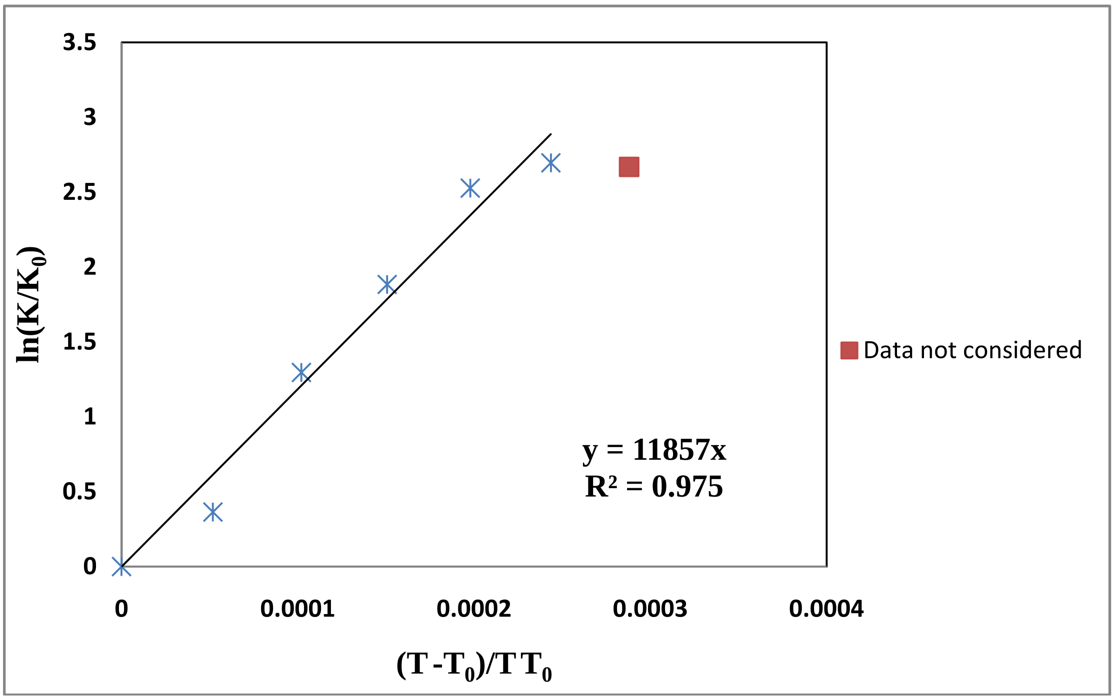


Figure 3.14 : Estimation of heat of reaction by using fitting of Van't Hoff equation.

3.7 PROPERTIES OF CASTOR FAME

In order to assess the quality of FAME produced during transesterification of castor oil, several properties of the FAME product obtained were determined following standard tests. These are summarized in the table 3.8. It is observed that viscosity and water content are on higher side, which is usual characteristics of FAME produced from castor oil (Canoira et al., 2010). Thus the product formed should be used for blending with diesel oil in appropriate proportion to bring the properties within acceptable range or limit. Canoira et al. (2010) rightly commented as, "We intently avoid the name of biodiesel for the FAME obtained from the transesterification of castor oil since the extremely high viscosity and high water content of this FAME discard its use in pure form as a fuel in the internal combustion engines". In the Table 3.8, standard values/ranges of properties are also provided, which are as per EN 14214 norms, given by Canoira et al., (2010).

Table 3.8 : Properties of FAME from Castor Oil

S. No.	Property	Determined in present study	Standard value/range Canoira et al. (2010)
1.	Kinematic viscosity (mm^2/s at 40^0C)	18.55	3.5 - 5.00
2.	Density (kg/m^3)	920.5	860 -900
3.	Acid Value (mg KOH/g)	0.25	< 0.50
4.	Flash point (°C)	170	>120
5.	Water content (%)	0.006	< 0.0005 or < 500 mg/kg
6.	Calorific value (MJ/kg)	39.5	37.27-38.22*
7.	Oxidation stability at 110^0C (hr)	8	> 6.0
8.	Sulfur content (mg/kg)	0.03	<10
9.	Cloud point (^0C)	-8	-
10.	Pour point	-29	_
11.	Copper strip corrosion	1a	Class 1
12.	Elemental analysis % C % H % N	 65.59 12.50 0.15	_

*Values determined experimentally by Canoira et al., (2010)

3.8 CONCLUDING REMARKS

In this chapter, experimental studies on transesterification of castor oil in small lab reactor have been described. Operating conditions used are methanol/oil molar ratio (6:1), catalysts (1% of concentrated H_2SO_4, % v/v of castor oil), temperature from 35° to 65 °C at an interval of 5 °C, and 600 rpm. Experimental results have been analyzed with respect to the kinetics of three reaction schemes namely, first order irreversible reaction, second order irreversible reaction and reversible reaction. Kinetics constants and activation energy have been estimated in all cases by using method of least squares / Regression analysis. Activation energy computed is equal to 38.383 kJ/mol, which is in agreement with that reported in literature. In case of reversible reaction, a correlation describing dependency of equilibrium constant, K on temperature has also been developed. Further, castor oil transesterification reaction is endothermic in nature with heat of reaction equal to 23.560 kcal/gmol. Lastly, properties of FAME produced from castor oil have been experimentally determined and compared with standard values.

CHAPTER IV

TRANSESTERIFICATION OF CASTOR OIL IN A LARGE LAB REACTOR – EXPERIMENTS AND RSM MODELING

4.0 INTRODUCTION

For biodiesel synthesis, the most common method is transesterification, in which the triglycerides react with an alcohol in the presence of a catalyst ((Jeong et al., 2008; Vijay et al., 2005; Canakci and Gerpen, 2001). This study deals with the reaction of castor oil with methanol which was used a solvent in the presence of sulphuric acid as a catalyst (Hassan et al., 2014; Moradi et al., 2013; Liu et al., 2006; Marchetti et al., 2007; Agra et al., 1996). The stoichiometry of methanolysis reaction requires minimum 3 mole of methanol and 1 mole of oil to give 3 mole of fatty acid methyl ester (FAME) and 1 mole of glycerol. While to proceed the reaction in a forward direction or to obtain good yield of esters, the moles of methanol should be greater than 3:1 (Freedman et al., 1986; Ma et al., 1999). The reaction system was influenced by more than one factor at a time and simultaneously their interaction. Generally the reaction parameters like reactant methanol/oil molar ratio, catalyst amount and reaction temperature have a great influence on the reaction system (Jain et al., 2010; Tiwari et al., 2007; Oliveira et al., 2005). So, it is important to optimize these parameters for optimum product yield.

In present study, the biodiesel production process from castor oil has been optimized by the use of response surface methodology (RSM). The regression and graphical analysis of the experimental data was done by using the Design Expert version 9.0 (Stat-Ease., Inc., Minneapolis, MN 55413 USA) software (Jayakumar et al., 2014; Cao et al., 2014; Da Silva et al., 2006). The central composite design (CCD) is a full factorial design which was used for statistical design of experiments and data analysis. CCD helps to analyze the interaction effects of parameters and to optimize the effective parameters by minimizing the total number of experiments (Garba et al., 2014; Oliveira et al., 2004). Effects of the methanol/oil molar ratio (1:1 - 25:1), catalyst amount (1 - 3 vol. %) and reaction temperature (40° - 60 °C) on the reaction system optimized by using 2^3 full factorial central composite design (Kilic et al., 2013). All the experiments were carried out in triplicates to minimize the experimental error using 2 L working volume reactor (DaSilva et al., 2009). The samples obtained after the reaction were analyzed by using gas chromatography technique (Madankar et al., 2013).

4.1 MATERIALS AND METHODS

4.1.1 Chemicals

The chemicals used have been described in the section 3.1, but have been reproduced here for the sake of completeness. Pharmaceutical grade Castor oil was purchased from the local market through the authorized standard chemical supplier of the institute. All chemicals H_2SO_4 (97 %), anhydrous methanol, Na_2SO_4 was of analytical grade and were purchased from Merck India and used without further purification. Methyl heptadecanoate was use as an internal standard with 10 mg/ml concentration. Pure standard of methyl esters was purchased from Sigma Aldrich, USA.

4.1.2 Experimental Setup

A bioreactor (Applikon, Schiedam, The Netherlands, stirred type, capacity: 3 L, ez-control system,) was used for conducting the reaction (Figure 4.1). This reactor was 3 L double jacketed borosilicate glass reactor having 2 L working volume. The temperature was regularly monitored by the display of the system. The reflux system was used to avoid the vaporization of methanol from the reaction system. The temperature of the reaction system was maintained constant by the circulation of water through outer wall of the reactor vessel and controlled by the use of automatic chiller. Mechanical stirring was used for the proper mixing of the reaction mixture in the reactor.

4.1.3 Experimental Procedure

Initially 1 L castor oil was transferred in to the reactor and heated it to the desire temperature. Appropriate quantities of methanol and catalyst (sulphuric acid) were mixed thoroughly at the preset temperature separately. The above mixture of catalyst and methanol was then transferred to the reactor vessel where the mixing was carried out at 800 rpm for the preset reaction temperature and time (4 hrs).The mixing intensity (800 rpm) optimized prior to conducting the experiments at constant methanol/oil molar ratio 6:1, catalyst concentration 1 % and reaction temperature 60 ˚C.

Figure 4.1: Large Lab Reactor Assembly (volume 3 L)

The samples were taken up to 4 hrs regularly at the 20 min time interval and total 12 samples were collected during this time period. The samples were collected in 15 ml centrifuge tubes filled with 5 ml of distilled water. Shaking and quenching of the samples were done immediately, and the centrifuge tubes with the sample were kept in ice bath immediately. The samples were washed and centrifuged at 4000 rpm for 20 minute to separate ester layer. After centrifuging the sample, two separate layers were formed; the bottom one contained the glycerol and catalyst in water phase while the top layer is of ester.

4.1.4 Gas Chromatography Analysis

The FAME content in the reaction product mixture was quantified by using a Gas Chromatograph (Nucon Gas Chromatogarph, 5765, INDIA) equipped with a flame ionization detector (FID), and a capillary column with dimension of 0.55 mm ID. X 10 m length X 0.50 m thickness. The other details have been provided in the section 3.3.2 of the Chapter III.

4.2 EXPERIMENTAL DESIGN

Response Surface Methodology (RSM) is a useful technique for the modeling and analysis of programs in which a response of interest is influenced by several variables and the ultimate objective of RSM is to optimize this response (Kumar and Singh, 2014, Ghadge and Raheman, 2006). Therefore, in this study, to determine the optimum and experimental design matrix, Response Surface Methodology was used.

A Central Composite Design (CCD) of the RSM is the most commonly used in optimization experiments. Central composite designs are a factorial or fractional factorial design with center points, augmented with a group of axial points (also called star points). As the distance of a factorial point from the centre of the design space is defined as $\pm$ 1 unit for each factor, the distance of a star or axial point from the centre of the design is $\pm \alpha$ with $(\alpha) > 1$.

In present study, the CCD was used to optimize three operating parameters (methanol/oil molar ratio, catalyst amount, and temperature of the reaction) for enhancing the % FAME yield. In CCD, the total number of experimental combinations was $2^k + 2k + n$, where ‘k’ is the number of independent variables and ‘n’ is the number of repetitions of experiments at the central axis point to reduce the pure error (Jeong et al., 2009, Yuan et al., 2008). Total 20 experiments were required for this work. Here, the run numbers 18, 19, and 20 were not considered because the experiment was not feasible to perform under these conditions (Kilic et al., 2013) and 6 were repeated experiments. The dependent variables for this study, was % FAME yield Y (%) and the independent variables selected were: methanol/oil molar ratio (x_1), catalyst amount (x_2), and temperature (x_3). The range and levels of individual variable factor were given in Table 4.1. The experimental design with their coded and actual values was given in Table 4.2

Table 4.2 : Central composite rotatable design arrangements with Coded and Actual values of independent variables

Run No.	Actual variables			Coded variables		
	Methanol / Oil molar ratio (M)	Catalyst amount (vol. %)	Temperature (°C)	x_1	x_2	x_3
1	6	3	60	- 1	+ 1	+ 1
2	15.5	2	50	0	0	0
3	15.5	2	50	0	0	0
4	25	3	40	+ 1	+ 1	- 1
5	6	1	40	- 1	- 1	- 1
6	15.5	2	50	0	0	0
7	15.5	2	50	0	0	0
8	6	3	40	- 1	+ 1	- 1
9	6	1	60	- 1	- 1	+ 1
10	15.5	2	66.82	0	0	+ 1.68
11	25	1	40	+ 1	- 1	- 1
12	15.5	3.68	50	0	+ 1.68	0
13	15.5	2	50	0	0	0
14	25	1	60	+ 1	- 1	+ 1
15	25	3	60	+ 1	+ 1	+ 1
16	31.48	2	50	+ 1.68	0	0
17	15.5	2	50	0	0	0
18	15.5	0.32	50	0	-1.68	0
19	15.5	2	33.18	0	0	-1.68
20	-0.48	2	50	-1.68	0	0

Table 4.1 : Independent variables and levels used for CCD

S. No.	Variables	Coded Symbols	Range and Levels		
			-1	**0**	**+1**
1	Methanol /oil molar ratio	x_1	6	15.5	25
2	Catalyst amount (vol. %)	x_2	1	2	3
3	Temperature (°C)	x_3	40	50	60

A mathematical model, describing the relationships among the process dependent variable factors and independent variable factors were developed. Once all the experiments were performed, the response variable (% FAME yield) was fitted in a second order polynomial model to find out the correlation between the response variable to the independent variables. The general form of the second degree polynomial equation (Uzoh et al., 2013) is as follows:

$$Y = \beta_o + \sum_{i=1}^{k} \beta_i \, x_i + \sum_{i=1}^{\mathrm{k}} \beta_{ij} \, {x_i}^2 + \sum_{i_{i>1}}^{k} \sum_{j}^{k} \beta_{ij} \;\; x_i x_j + \varepsilon \qquad (4.1)$$

Where, ‘Y’ is the predicted response; ‘β_o’, ‘β_i’, and ‘β_{ij}’ constant coefficients; ‘x_i’ and ‘x_j’ are the coded independent variables and ‘ε’ is the random error. The predicted values were found out from the derived equations for each of the response. The contour plots and three dimensional plots were determined by *F-test* (Montgomery, 2001). The *p-value* (Probability value) serves as a tool for checking the significance of each of the coefficients and their interaction, which may indicate the patterns of the interactions among the variables. The smaller the *p-value*, the more significant is the corresponding coefficient (Khuri, et al., 1987).

4.3 RESULTS AND DISCUSSION

4.3.1 Development of RSM Model

In the present study, the relationship between response (% FAME yield) and three independent factors (methanol/oil molar ratio, catalyst amount and temperature) were studied. The independent and dependent factors were fitted to the second order model equation and examined in terms of the goodness of fit (Jeong et al., 2007). The predicted values with the second order polynomial equation obtained from the CCD experimental runs were compared with the experimental values (Table 4.3). Figure 4.2 gives the predicted response along with the experimental data. On the basis of ANOVA, as shown in Table 4.4 a second order model was established (equation 4.2) describing the % FAME yield as a function of methanol/oil molar ratio (x_1), catalyst amount (x_2) and temperature (x_3). Based on the large *F-values* and low corresponding *p-values*, all the linear terms had very strong effect on % FAME yield. However, temperature (*F-value* = 262.62) was the most significant variable followed by the methanol/oil molar ratio (*F-value* = 72.86) and lastly, catalyst (*F-value* = 26.22). All the coefficients were considered in the design to minimize the error. Table 4.4 shows the model coefficients and probability values.

The coded model was used to generate response surfaces for the analysis of the variable effects on % FAME yield:

$$Y\ (\%) = 51.67 + 6.89\ x_1 + 4.13\ x_2 + 13.07\ x_3 - 3.04\ x_1^2 + 4.13\ x_2^2 - 3.92\ x_3^2 + 0.44\ x_1x_2 + 4.10\ x_1x_3 - 1.79\ x_2x_3 \quad (4.2)$$

Table 4.3: Observed responses and predicted values

Run No.	Actual response	Predicted response	Residual values
1	55.27	52.83	2.44
2	51.25	51.67	-0.42
3	51.54	51.67	-0.13
4	47.36	44.92	2.44
5	27.92	27.50	0.42
6	52.15	51.67	0.48
7	51.92	51.67	0.25
8	37.71	38.45	-0.74
9	48.29	49.03	-0.74
10	60.18	62.58	-2.40
11	31.45	32.19	-0.74
12	67.89	70.29	-2.40
13	51.98	51.67	0.31
14	72.55	70.11	2.44
15	76.95	75.68	1.27
16	52.25	54.65	-2.40
17	51.58	51.67	0.09

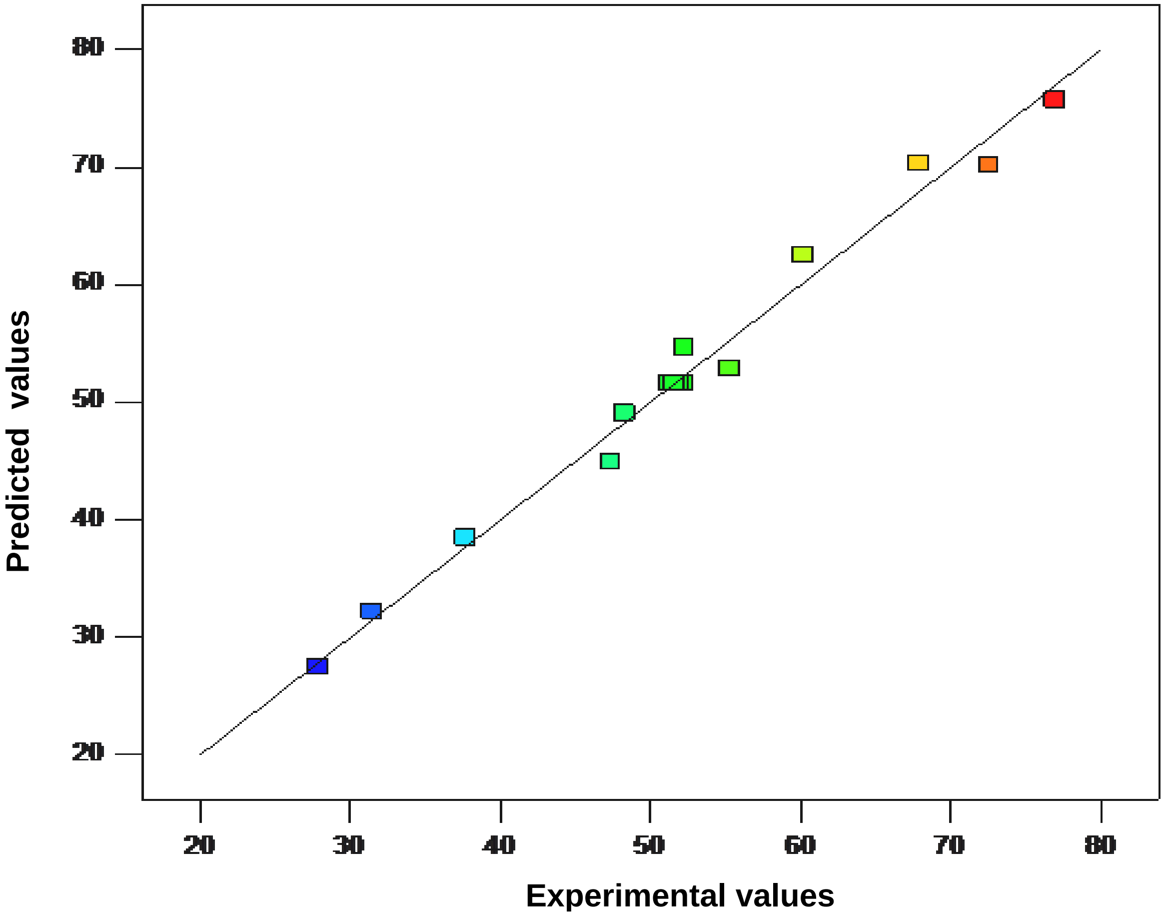


Figure 4.2 : % FAME yield observed in the experiment versus predicted values by the RSM model

The analysis of variance was used to evaluate the adequacy of the fitted model. ANOVA is a statistical technique that subdivided the total variation of a set of data into component associated to specific sources of variation. The regression equation obtained from the ANOVA shows (Table 4.4) that the R^2 was 0.98, indicates a good correlation between the observed and predicted values. This is an estimate of the fraction of overall variation in the data accounted by the model and thus model is capable of predicting the response within 2 % variation. The R^2 value provided a measure of how much of the variability in the observed response values could be explained by the experimental factors and their interactions. The adjusted R^2 (0.96) was also very high which indicates that the model is good.

Normal probability plot of the residuals follows a straight line indicating normal distribution of residuals (Figure 4.3).

4.3.2 Response Surface Analysis

Figure 4.4 shows the effects of reaction temperature, methanol/oil molar ratio and their reciprocal interactions on % FAME yield using a constant catalyst amount of 2 vol. %. As the temperature increases from 40 °C to 60 °C, % FAME yield increases. The responses increase as the methanol/oil molar ratio increases from 6:1 to 21:1 while beyond the molar ratio value of 21:1, there was no significant change in % FAME yield.

Figure 4.5 shows the effect of different reaction temperature and amount of added catalyst on % FAME yield when a constant methanol/oil molar ratio of 15.5:1 was maintained. The % FAME yield increases slowly as the amount of catalyst increases from 1 to 3 vol. %. An increase in temperature enhances the % FAME yield in a linear trend and it shows that influence of temperature on % FAME yield is more significant in comparison to catalyst amount.

Table 4.4 : ANOVA for response surface quadratic model

Source	Sum of squares	df	Mean square	F-value	p-value
Model	2577.36	9	286.37	51.17	< 0.0001
x_1	407.76	1	407.76	72.86	< 0.0001
x_2	146.74	1	146.74	26.22	0.0014
x_3	1469.85	1	1469.85	262.62	< 0.0001
x_1x_2	1.57	1	1.57	0.28	0.6131
x_1x_3	134.15	1	134.15	23.97	0.0018
x_2x_3	25.63	1	25.63	4.58	0.0696
x_1^2	64.69	1	64.69	11.56	0.0114
x_2^2	119.22	1	119.22	21.30	0.0024
x_3^2	107.31	1	107.31	19.31	0.0032
Residual	39.18	7	5.60		
Lack of fit	38.61	2	19.31	171.24	< 0.0001
Pure Error	0.56	5	0.11		
Totals corrected for the mean	2616.53	16			
$R^2 = 0.98$; R^2 (adjacent) = 0.96; Std. Dev. = 2.37 %					

Normal % Probability

Internally Studentized Residuals

Figure 4.3 : Normal probability plots of residuals obtained from % FAME yield data analysis

Figure 4.4 : 3 D response surface plot for the effect of methanol/oil molar ratio and temperature on % FAME yield; catalyst amount = 2 vol.%

Figure 4.5: 3 D response surface plot for the effect of catalyst amount and temperature on % FAME yield at constant methanol/oil molar ratio of 15.5:1

Figure 4.6 shows the effect of different methanol/oil molar ratio and amount of catalyst on % FAME yield at constant reaction temperature of 50 °C. The catalyst amount and methanol/oil molar ratio both effectively influenced % FAME yield. At any amount of catalyst, an increase in the quantity of added methanol/oil molar ratio enhanced the % FAME yield in a linear trend but methanol/oil molar ratio has more significant effect.

The results showed that the two factors temperature and methanol/oil molar ratio were the most significant parameters for influencing the % FAME yield. On the basis of data shown in above figures, we optimized the optimal value of three factors for maximizing the % FAME yield. The optimal values for these factors were determined by resolving the regression equation using Design Expert 9. The optimal conditions were selected from within the designated range of methanol/oil molar ratio 6:1 – 25:1, catalyst amount 1 – 3 vol. % and reaction temperature 40 °C – 60 °C. The optimal conditions for % FAME yield, as estimated by model equation were as follows: x_1 = 25:1, x_2 = 3 vol. % and x_3 = 60 °C (Figure 4.7). Theoretically these conditions should yield a % FAME yield, i.e. Y = 75.67 %. % FAME yield obtained in the experiment was 76.95 %, which was much closer to the theoretically predicted value.

Figure 4.6 : 3 D response surface plot for the effect of catalyst amount and methanol/oil molar ratio on % FAME yield at a constant reaction temperature of 50 °C

Figure 4.7 : 3 D response surface plot representing the effect of catalyst amount and methanol/oil molar ratio on the optimum % FAME yield at constant at 60 °C temperature

4.3.3 Model Validation

In order to validate the RSM model additional two experiments were also conducted at two different sets of operating conditions. The experimentally obtained % FAME yield and that predicted by the model are given in the Table 4.5. From the table it is clear that RSM model predicts the % FAME yield within acceptable accuracy (within a deviation of ± 5%). Therefore, it is concluded that the model may be used to predict the % FAME yield at other values of three operating parameters within pre-specified range.

Table 4.5 : Comparison of model prediction with experimental values obtained additionally at two sets of operating conditions

S. No.	Operating conditions			% FAME yield		% Deviation
	Temp.	Catalyst Amount (vol. %)	Methanol/Oil Molar ratio	Experimental value	Value predicted by model	
1	45	3	12:1	45.15	44.99	-0.3543
2	55	3	18:1	67.56	70.93	+4.988

[% deviation = (Y_{pred}- Y_{exp}/ Y_{exp}) x 100]

4.4 Application of RSM Model

The developed RSM model has been used to study the effect of variation in operating parameters on % FAME yield. Figures 4.8 (a, b, c) shows the variation of % FAME yield with methanol/oil molar ratio 6:1 - 25:1 at varying amounts of catalyst 1 - 3 vol. % at three constant temperatures 40 °C, 50 °C and 60 °C, respectively. At 40 °C, % FAME yield does not change appreciably when the methanol/oil molar ratio is increased beyond 12:1. At higher temperature (50 °C and 60 °C) % FAME yield increases with the increase in molar ratio.

Figures 4.9 (a, b, c) shows the variation of % FAME yield with temperatures 40 °C, 50 °C and 60 °C at varying amounts of methanol/oil molar ratio 6:1 - 25:1 at three constant catalyst amount 1 - 3 vol. % respectively. The % FAME yield increases following the similar trend for all the three catalyst amounts. Further, it is noted that up to 40 °C methanol/oil molar ratio does not show appreciable effect on % FAME yield for all the three catalyst amounts but with further increase in temperature, % FAME yield increases with the increase in molar ratio.

Figures 4.10 (a, b, c, d) shows the variation of % FAME yield with catalyst amount 1-3 vol. % at different temperatures 40 °C, 50 °C and 60 °C at four constant methanol/oil molar ratios 6:1 - 25:1 respectively. In all the four figures, increase in % FAME yield follows the same trend with the increase in catalyst amount. It is interesting to note that at catalyst amount of 2 vol. %, % FAME yield curve passes through minima for all the cases. This phenomenon is more predominant at higher temperatures (50 °C and 60 °C).

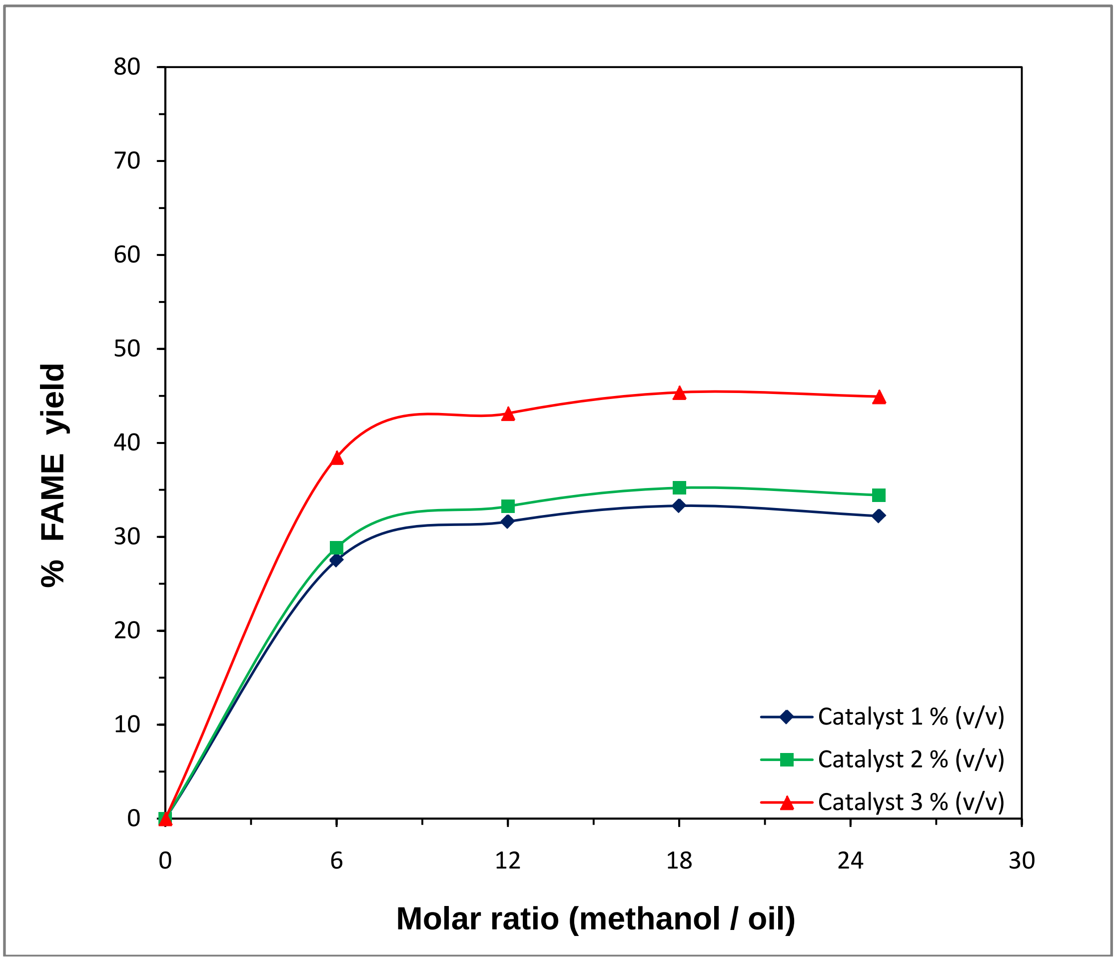


Figure 4.8 (a) : **% FAME yield with varying molar ratio and catalyst amount at constant temperature 40 °C**

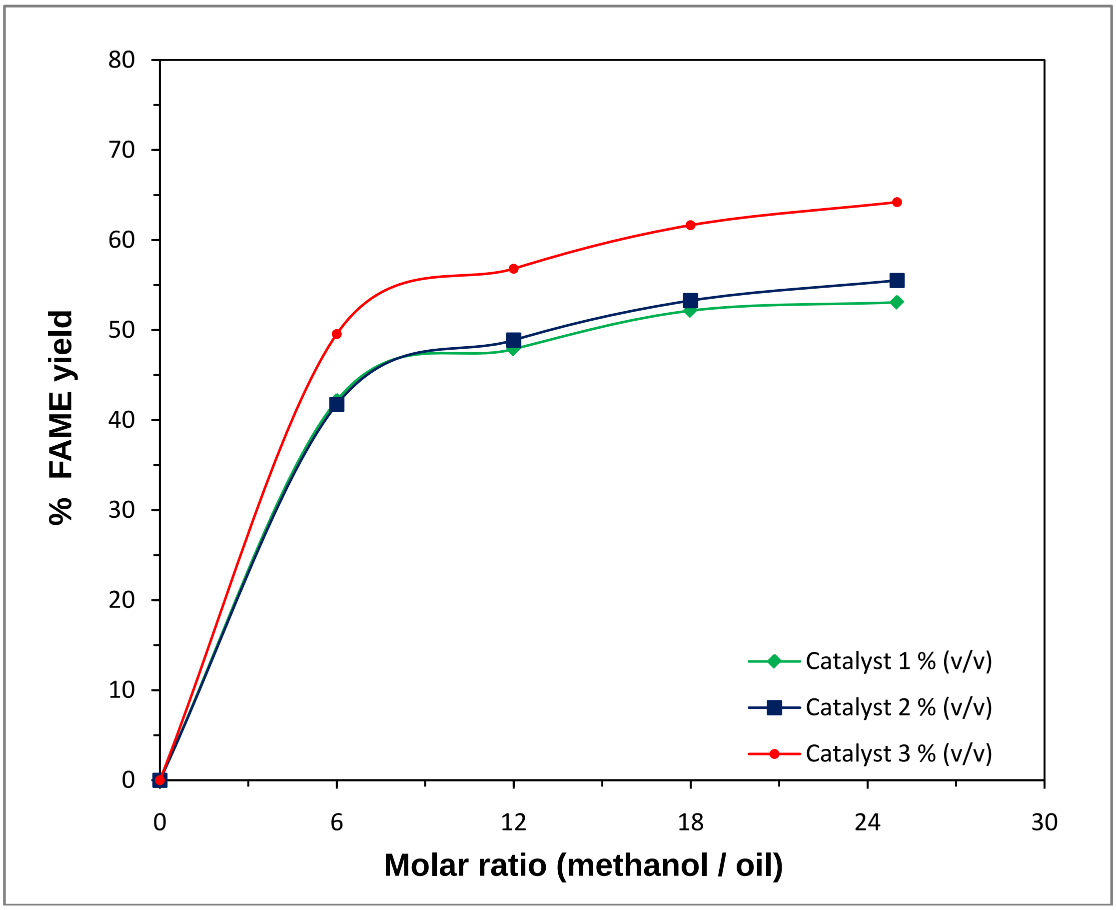


Figure 4.8 (b) : % FAME yield with varying molar ratio and catalyst amount at constant temperature 50 °C

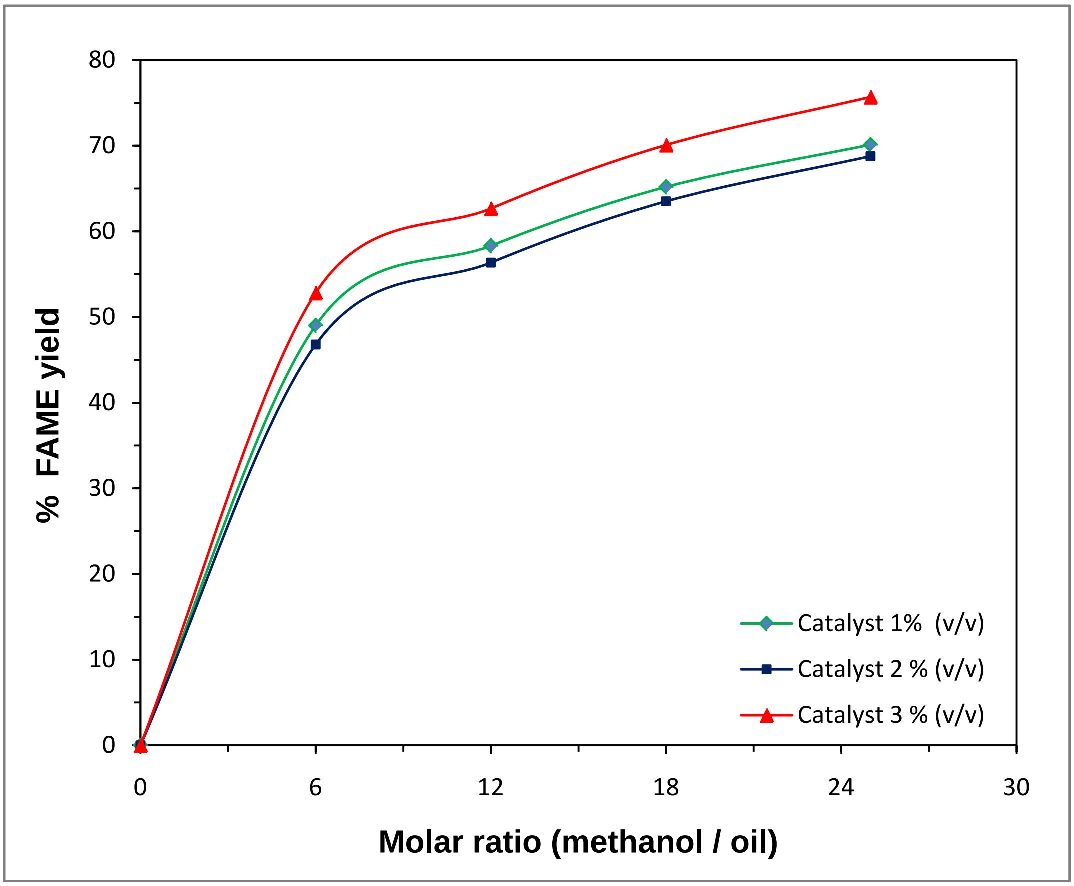


Figure 4.8 (c) : **% FAME yield with varying molar ratio and catalyst amount at constant temperature 60 °C**

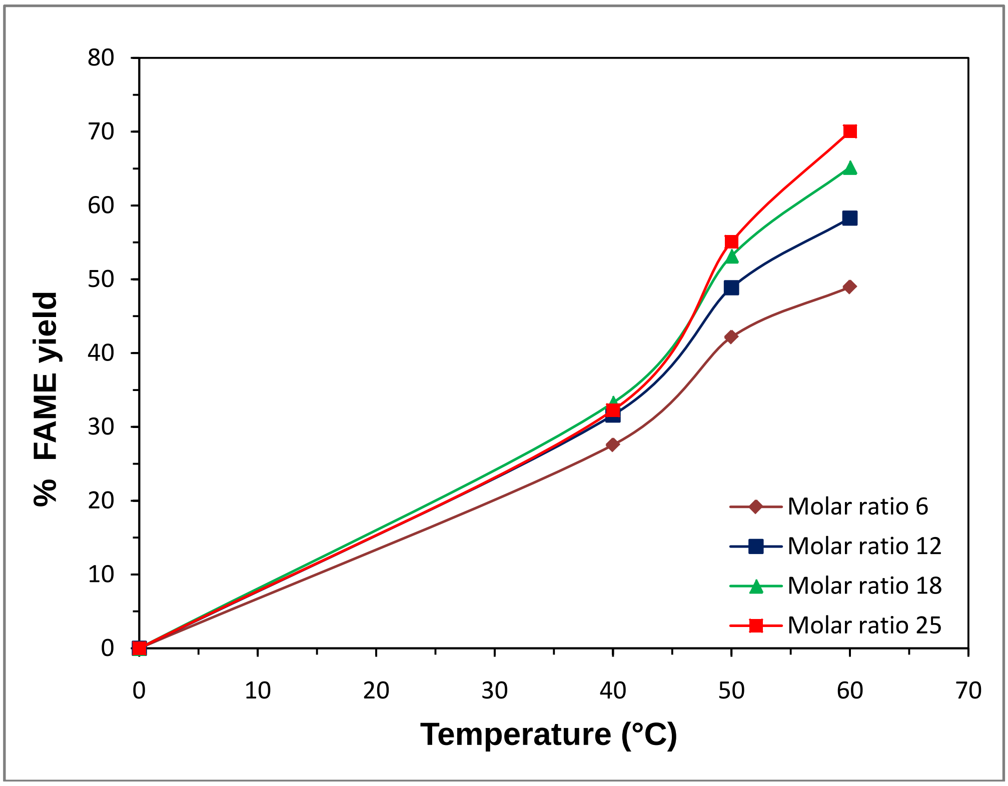


Figure 4.9 (a) : % FAME yield with varying molar ratio and temperature at constant catalyst amount (1 vol. %)

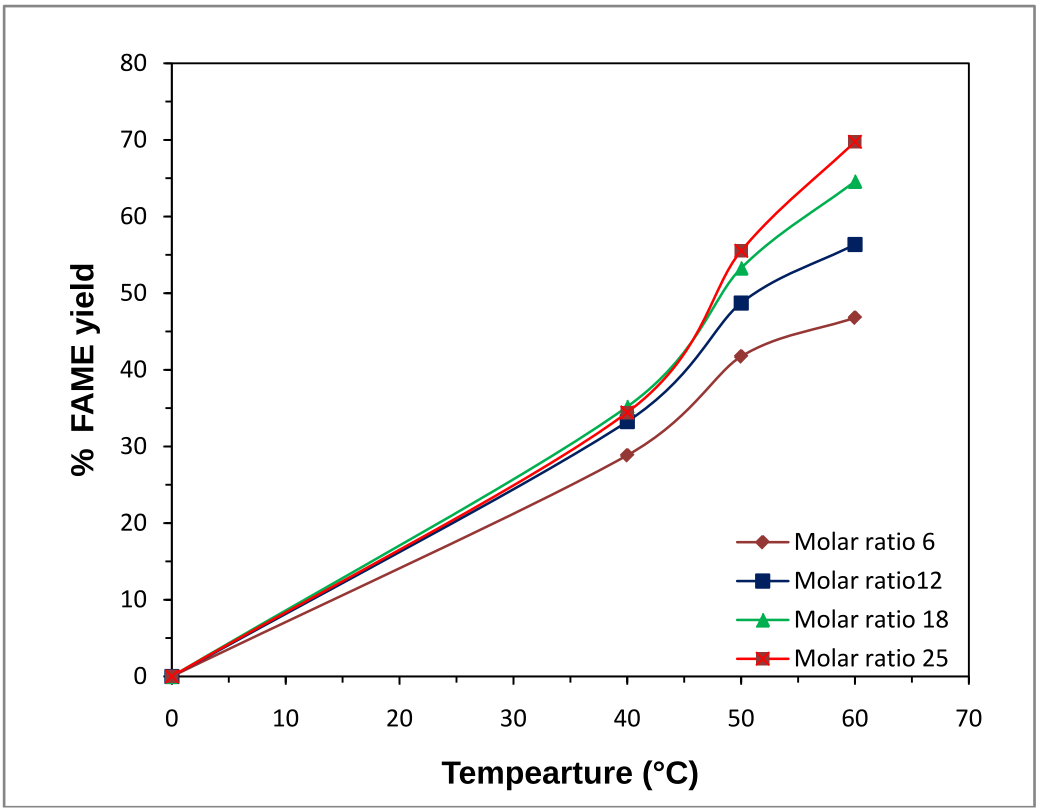


Figure 4.9 (b) : **% FAME yield with varying molar ratio and temperature at constant catalyst amount (2 vol. %)**

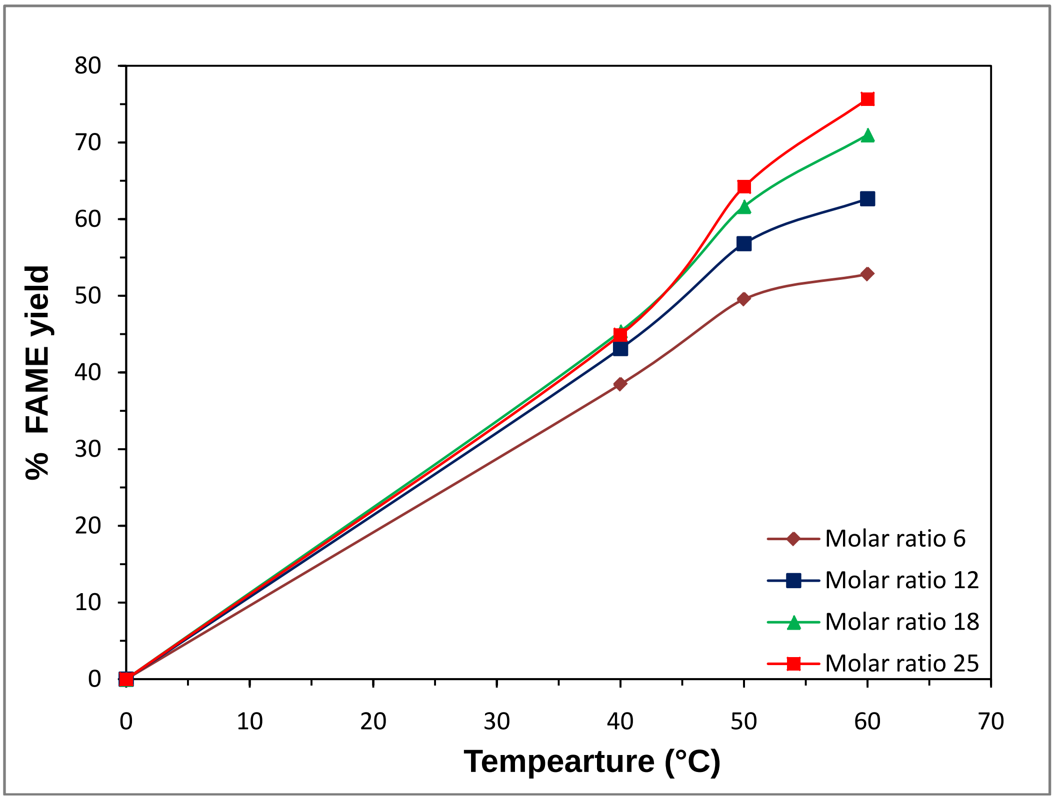


Figure 4.9 (c) : % FAME yield with varying molar ratio and temperature at constant catalyst amount (3 vol. %)

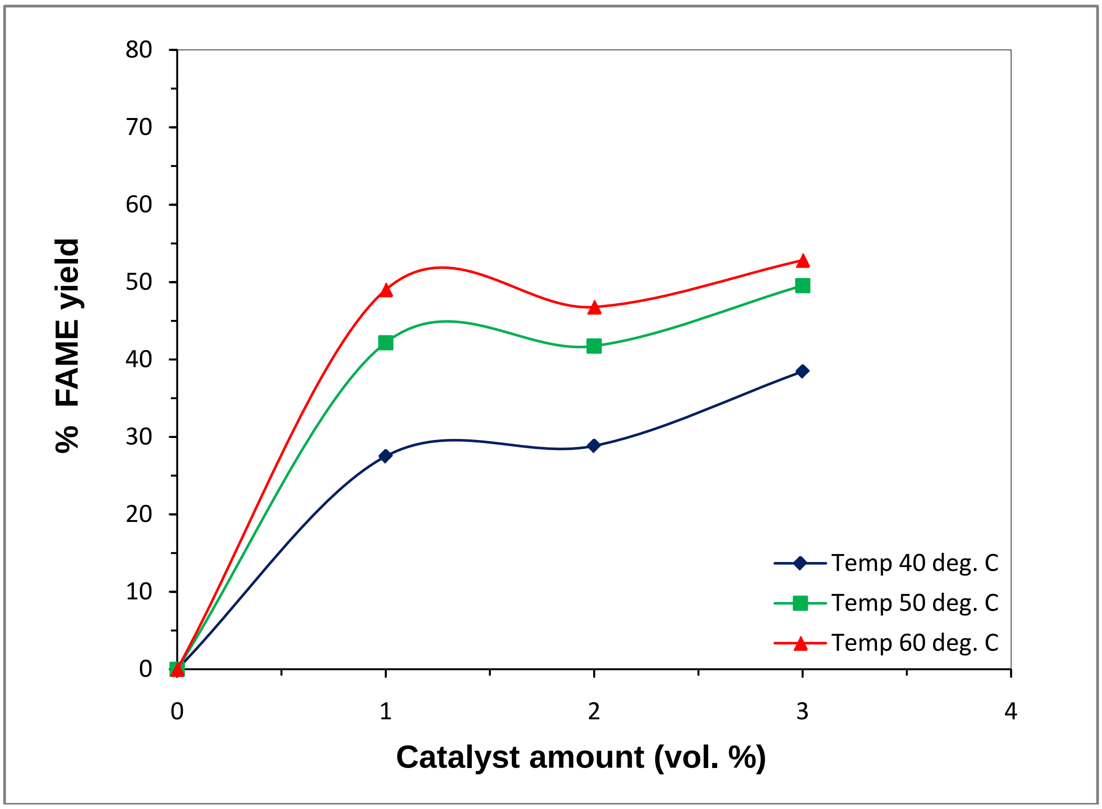


Figure 4.10 (a) : % FAME yield with varying molar ratio and catalyst amount at constant molar ratio 6:1

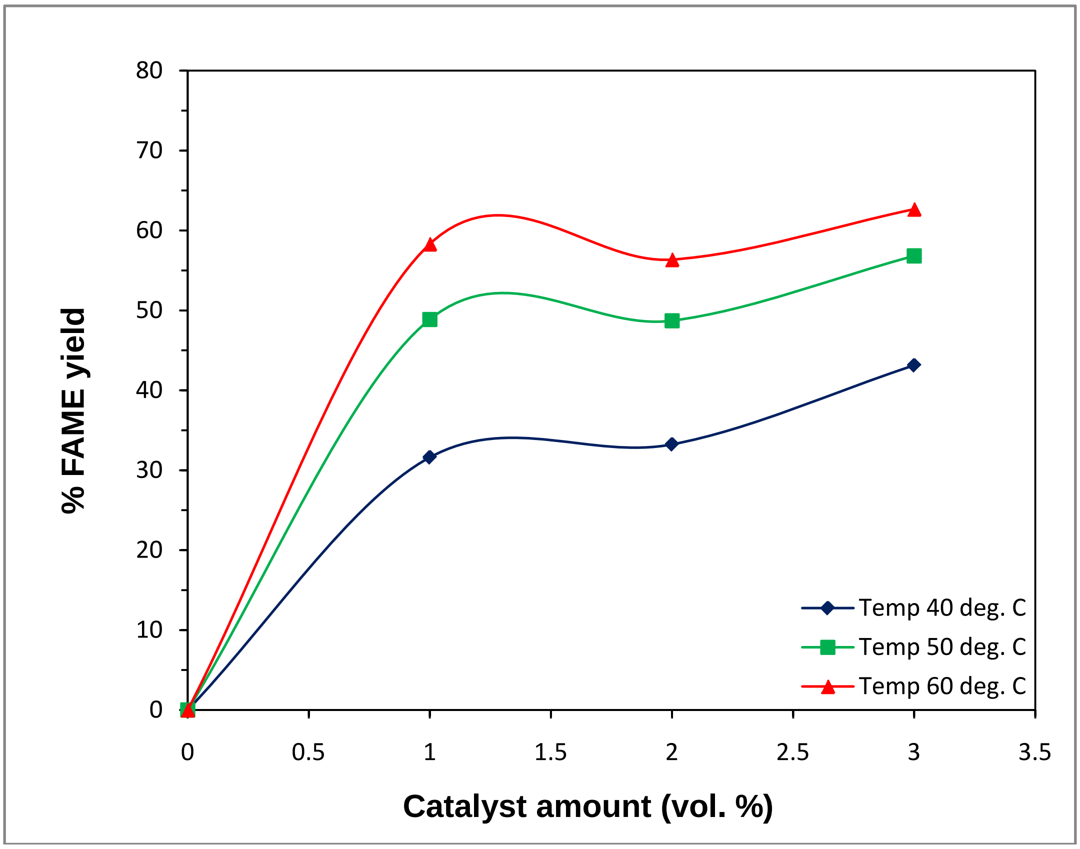


Figure 4.10 (b) : % FAME yield with varying molar ratio and catalyst amount at constant molar ratio 12:1

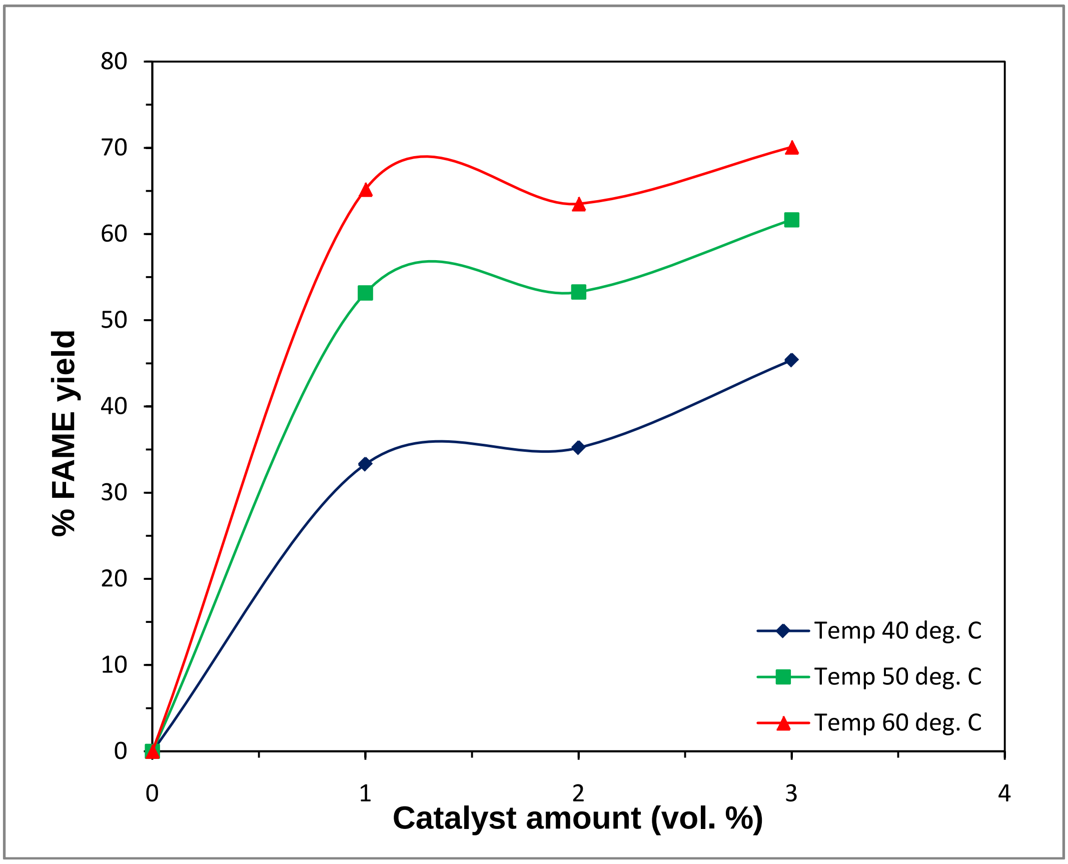


Figure 4.10 (c) : % FAME yield with varying molar ratio and catalyst amount at constant molar ratio 18:1

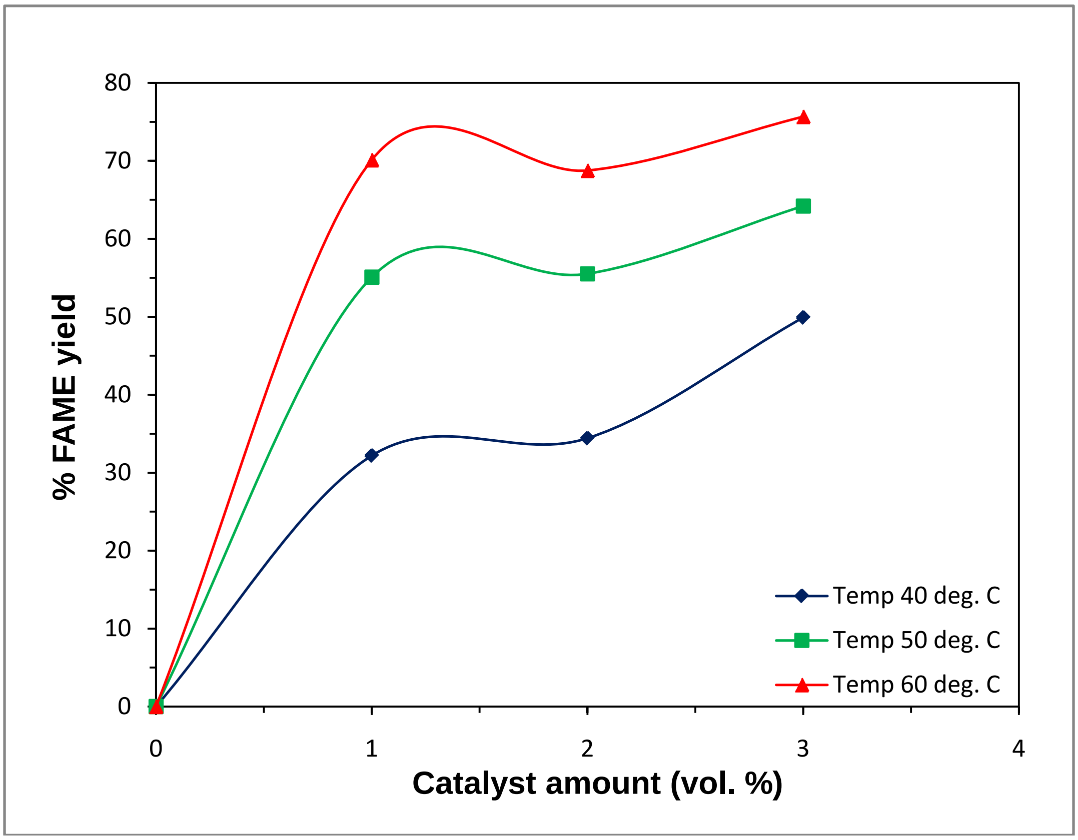


Figure 4.10 (d) : % FAME yield with varying molar ratio and catalyst amount at constant molar ratio 25:1

4.5 CONCLUDING REMARKS

In this Chapter, CCD method was used to find out the optimized operating parameters (reaction temperature, catalyst amount and methanol/oil molar ratio) for transesterification reaction of castor oil in the presence of H_2SO_4 catalyst, and also the optimum value of % FAME yield. The optimum values of these three independent parameters obtained by using CCD were 25:1 methanol/oil molar ratio, 3 vol. % catalyst amount and 60 °C reaction temperature. At these optimum conditions, 76.95 % FAME yield has been observed. Developed RSM model was also validated with the additional two different sets of experimental data and its predictions were found to be within ± 5 % deviation. Using the RSM model, the effect of variation in operating parameters on % FAME yield was also studied as shown in Figures 4.8 (a, b, c), 4.9 (a, b, c) and 4.10 (a, b, c, d).

CHAPTER V

ANN MODELING OF EXPERIMENTAL DATA OBTAINED IN LARGE LAB REACTOR

5.0 INTRODUCTION

As described in the previous chapter, experimental results related to castor oil transesterification were obtained in a large lab reactor. An experimental run was performed up to four hours in the Chapter IV. A RSM model has been developed by using fractional formation of FAME experimental data obtained at 4 hour time only. The present chapter is devoted to the development of ANN (Artificial Neural Network) model, which would utilize X_C (fractional formation of FAME) versus t (time) experimental data obtained for various set of operating conditions (methanol to oil molar ratio, reaction temperature, catalyst concentration). By using the developed model, X_C versus t profiles may be generated for those operating conditions, for which no experimental data are available. In the end, parameter estimation of kinetic model (reversible second order reaction) has been described. This estimation is based upon X_C versus t data (experimentally obtained and generated by the model) for optimum operating conditions.

5.1 EXPERIMENTAL DATA OBTAINED ON LARGE LAB REACTOR

In the section 4.1 Materials and Methods of Chapter IV, chemicals used, experimental set up and procedure for conducting experiments on the large lab reactor have been described. The central composite design (CCD) of the RSM was used to optimize the experiments. Table 4.2 provides twenty sets of actual values of variables, for which experiments were to be conducted. Out of these, number of experiments reduces to only ten as four are repeat experiments, in other six either variable becomes negative or temperature exceeds boiling point of methanol or becomes lower etc. % formation of FAME versus time data are summarized in the Tables 5.1 (a) and (b).

5.2 ANN MODEL DEVLOPMENT

5.2.1 Artificial Neural Networks (ANN)

ANNs are widely used tools for different technical applications such as function approximation, prediction, modeling, clustering etc. They are capable of 'mirroring' or

Table 5.1(a) : Experimental results on % FAME formation with time.

S. No.	Time	% formation of FAME, X_c				
		1/60/25:1	1/60/6:1	3/60/25:1	3/60/6:1	1/40/25:1
1	0	0	0	0	0	0
2	20	7.50	13.81	31.50	16.88	5.32
3	40	9.51	21.46	38.79	20.58	6.95
4	60	12.96	24.93	46.06	24.63	8.45
5	80	16.82	28.81	54.59	26.75	12.23
6	100	21.59	31.92	59.79	29.04	13.94
7	120	32.04	35.96	63.06	31.59	16.94
8	140	36.90	39.79	67.05	37.95	18.45
9	160	40.32	41.71	71.09	44.79	20.18
10	180	46.65	42.05	73.53	48.09	22.65
11	200	53.05	44.19	74.59	50.05	26.94
12	220	62.18	46.63	76.25	52.76	28.42
13	240	72.55	48.29	76.95	55.27	31.45

Table 5.1 (b) : Experimental results on % FAME formation with time.

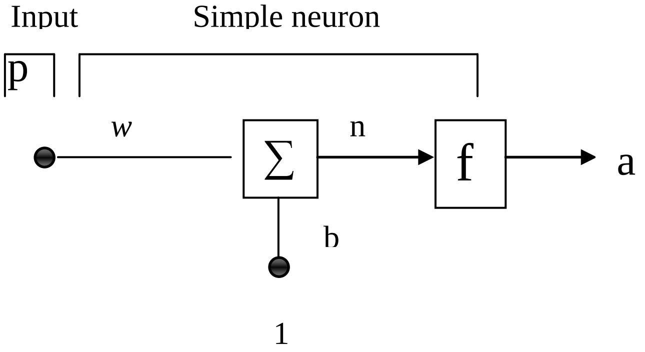
S. No.	Time	% formation of FAME, X_c				
		1/40/6:1	3/40/25:1	3/40/6:1	2/50/15.5:1	3.68/50/15.5:1
1	0	0	0	0	0	0
2	20	5.95	7.23	16.28	9.93	33.45
3	40	7.80	9.59	19.15	14.56	38.56
4	60	9.35	12.81	23.92	21.72	42.69
5	80	10.54	18.12	24.56	26.92	46.44
6	100	12.09	22.42	26.65	30.59	51.56
7	120	15.15	23.59	27.05	34.49	55.69
8	140	18.99	28.65	28.53	38.95	58.91
9	160	21.59	31.95	29.75	43.65	60.08
10	180	24.65	34.03	30.07	45.96	62.15
11	200	26.56	36.95	33.05	47.56	63.95
12	220	28.19	44.15	35.84	49.62	65.67
13	240	29.95	47.36	37.71	52.25	67.89

Note: In above tables, a/b/c means catalyst amount in %v/v, temperature in °C and methanol to oil molar ratio respectively.

'mimicking' arbitrary functional relationships within an acceptable degree of precision (Curry et al., 2002). They are useful for the study of complex phenomena for which we have appropriate data but a poor understanding of the mathematical projection between them (Gorr et al., 1994). Neural networks are powerful in solving problems which are difficult to generalize but for which there is a wide variety of examples available (Mandic and Chambers, 2002). The fundamental building block for any ANN model is the single-input neuron which processes the input-output relationship as shown in Figures 5.1(a) and (b). It takes any scalar or vector input (p) and multiplies it to any scalar or vector weight (w) to form a weighted input (wp). Then, a scalar or vector bias 'b' is added to give the net input 'n' which is the sum of these two elements. This net input passes through a suitable transfer function f, which produces finally a scalar output 'a'. These are named weight function, net input function and transfer function, respectively. It is mentioned that the weight function or synaptic weights (w) and the input bias 'b' are adjustable free parameters associated with the neuron. Suitable transfer functions are chosen to process the neural network. These are often of a hard-limiting nature, which serves the purpose of binding the input signal within permissible limits of [-1, 1] or [0, 1].

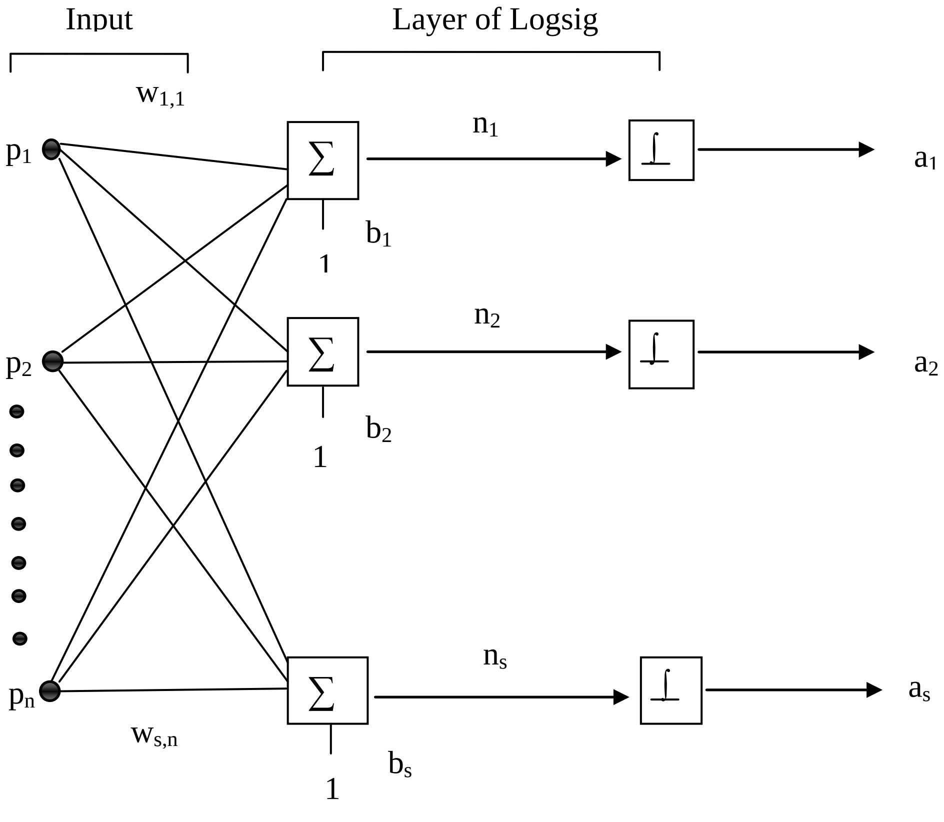
The linear transfer function is mostly used in the output layer of multilayer network models, and sigmoidal functions such as tansig or logsig are applied in the hidden layers of these networks to 'squash' the input into bounded values (Beale et al., 2013). There are several modeling strategies in ANNs, which have various applications in designing and analyzing existing processes (Widrow et al., 1994). In the present work, we have selected a Multilayer Feed Forward Artificial Neural Network (ML-ANN) architecture as our preferred network configuration, owing to its ability to exhibit powerful non-linear mapping between inputs and outputs (Zurada et al., 1992; Haykin et al., 1999).

A typical feed forward neural network consists of an input layer, a single or multiple hidden layers and an output layer. Every node in each layer is connected to all the nodes in the following layer through synaptic weights, which resemble a typical biological neural system



$$a = f(wp + b)$$

Figure 5.1 (a) : Structure of a simple neuron



$$a = \text{logsig}\,(wp + b)$$

Figure 5.1 (b) : A simple feed forward neural network (FFNN)

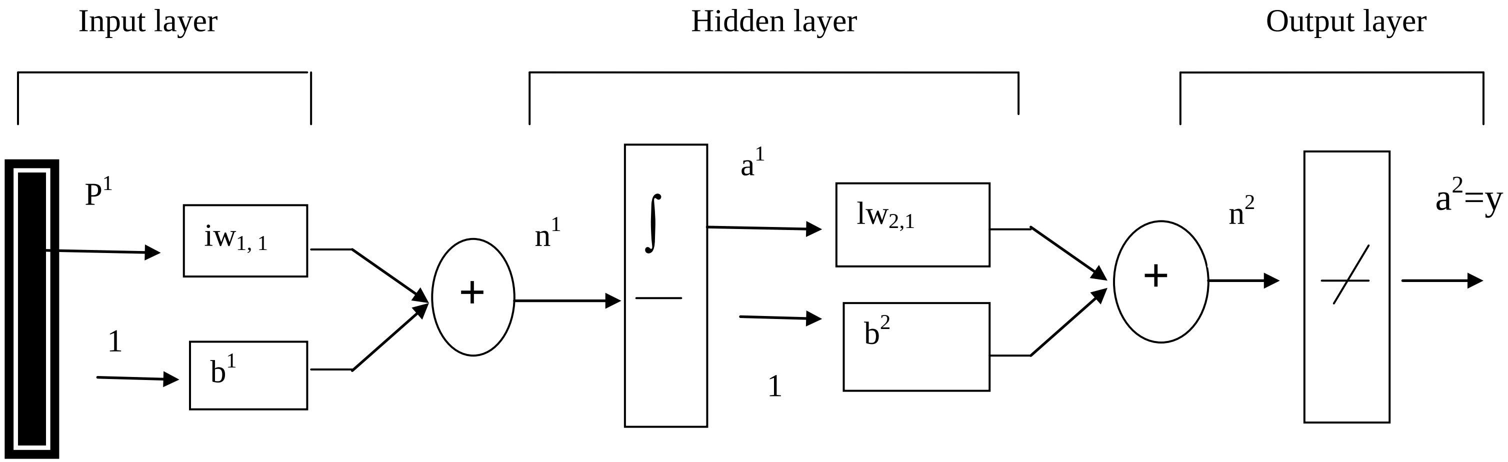
(Pacheco-Vega et al, 2001). Figure 5.2 shows the Feed Forward Neural Network. These kind of networks often have one or more hidden layers of sigmoid neurons which are followed by an output layer of neurons having linear nature. The output layer is often kept linear and used for fitting non-linear functions.

In the present case, the ANN model has been used to first validate and then predict experimental data based on the training of the neural network. A total of 156 experimental data sets were used to train and test the performance of the ANN for the modeling of performance of large size lab reactor used for the production of FAME by transesterification process.

Each experimental data set includes 4 input variables namely, methanol to oil molar ratio (mr), catalyst amount (c) , temperature (T) and time (t), and one output variable, the yield of FAME (X) at a time (t). The ML-ANN structure was therefore constructed as four input neurons, a hidden layer and a single output neuron. The topology of the ML-ANN architecture has been chosen to describe the reaction process in the large lab reactor. It consists of an input layer consisting of 4 input neurons, a hidden layer consisting of a given number of sigmoidal neurons and an output layer having a single neuron.

Performance of neural networks are affected by a number of factors such as noise corruption, spatial distribution and data size which are used to construct and train the ANN model as well as the characteristics of the model, i.e. number of neuron layers, hidden nodes, architecture, etc (Kramer and Leonard,1990). Niyogi and Girosa (1990) demonstrated that upper bounds on errors due to training data and ANN size cannot be reduced at the same time. Therefore, an adequate training set has to be provided to the network for obtaining satisfactory performance.

Scaling of the input and output variables is usually recommended (Hojjat et al., 2001). In the present work, the inputs (molar ratio, catalyst amount, temperature and time) and output (% Formation of FAME) were scaled in the range [0, 1] by dividing each variable by their maximum values (Table 5.2). All the scaled variables are identified with a bar over each one of them. The exact configuration of the neural network used in the present modeling studies is shown in the Figure 5.3.



a^1= tansig (iw ^{1,1} $p^1 + b^1$), a^2= purelin ($lw^{2,1}a^1 + b^2$)

Figure 5.2 : Hidden layer in ML-ANN having sigmoidal

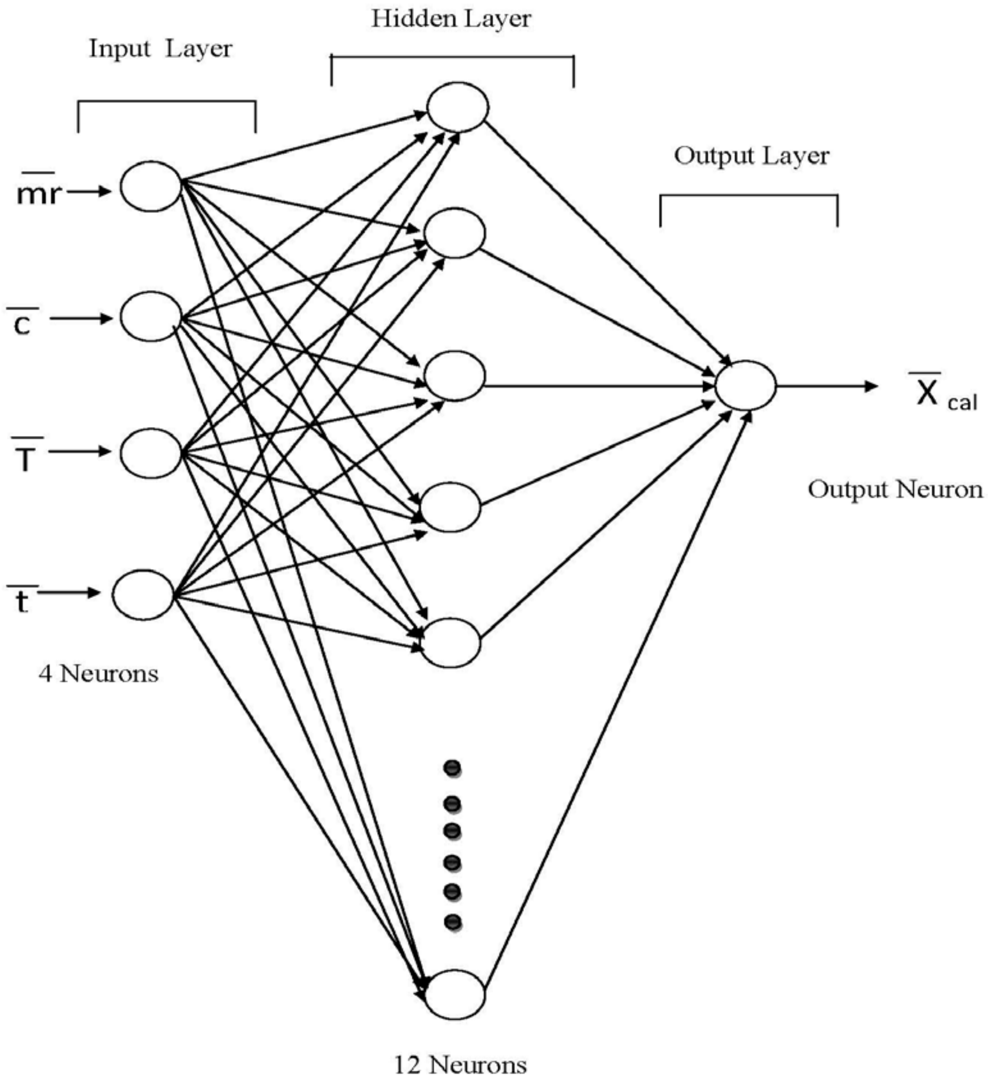


Figure 5.3 : Neural Network structure used in the present work.

A total of 130 samples of static data were scaled and fed to the input layer of the network for the training process. The Levenberg-Marquardt training algorithm was applied to the neural network structure which works on the principle of error back-propagation (Hagen and Menhaj, 1994). The 130 training datasets were distributed into three separate subsets, namely, 70% of the data into training set, 15% as the validation set and the remaining 15% as the test set.

Table 5.2 : Maximum values of input and output variables

S. No.	Variable	Maximum Value
1	Molar Ratio (-)	25:1
2	Catalyst Amount (% v/v)	3.68
3	Temperature (^{0}C)	60
4	Time (min)	240
5	FAME yield (%)	100

In all the computational experiments, tangent sigmoid function was preferred as the activation function in the hidden layer and linear function has been used as the activation function in the output layer as it passes the activation level from the hidden layer to the output layer directly (Cavas et al., 2011).

Optimal architecture of the ANN model was determined by training the network with one and two hidden layers with different number of neurons. Mean square error (MSE) was chosen as the performance function for observing the deviations between the experimental and predicted values of the required output. The MSE was calculated for all architecture with different weight initializations to prevent the network from converging to a local minimum which gives erroneous results.

A decreasing behaviour was observed for the MSE with respect to the increasing hidden layer size (Figure 5.4). When hidden neurons are increased beyond a certain level, overfitting occurs and network adapts to the noisy training data (Cavas et al., 2011). The optimal value of the number of hidden neurons in a single layer was set at 12 as our training and testing error start to diverge uncontrollably on further increase in the number of neurons.

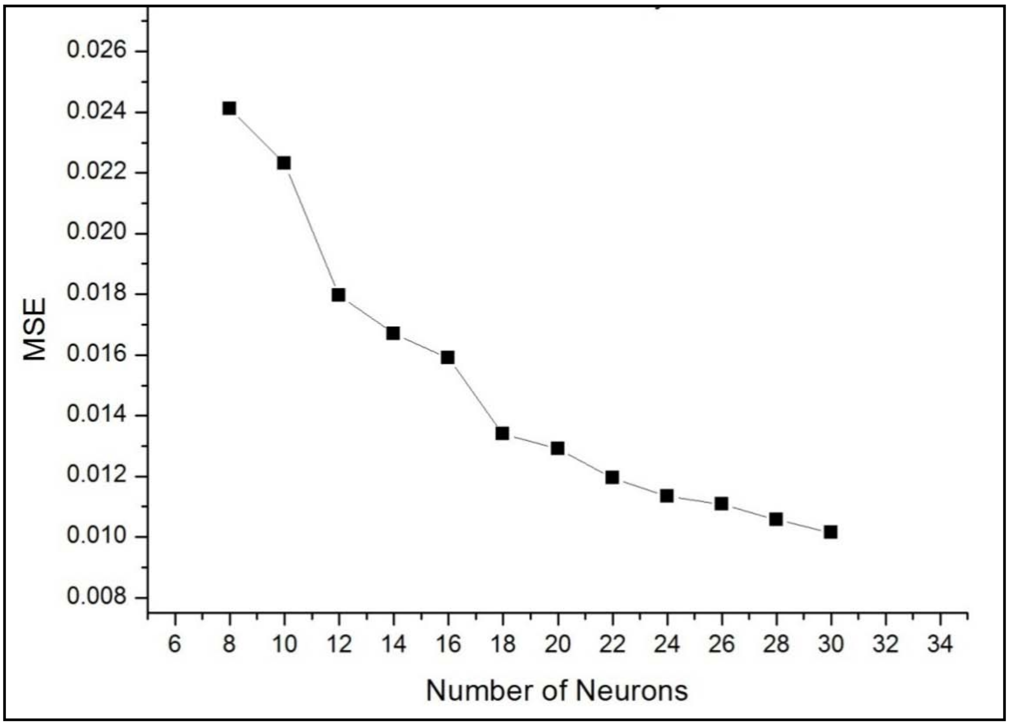


Figure 5.4 : MSE with increasing number of neurons in hidden layer

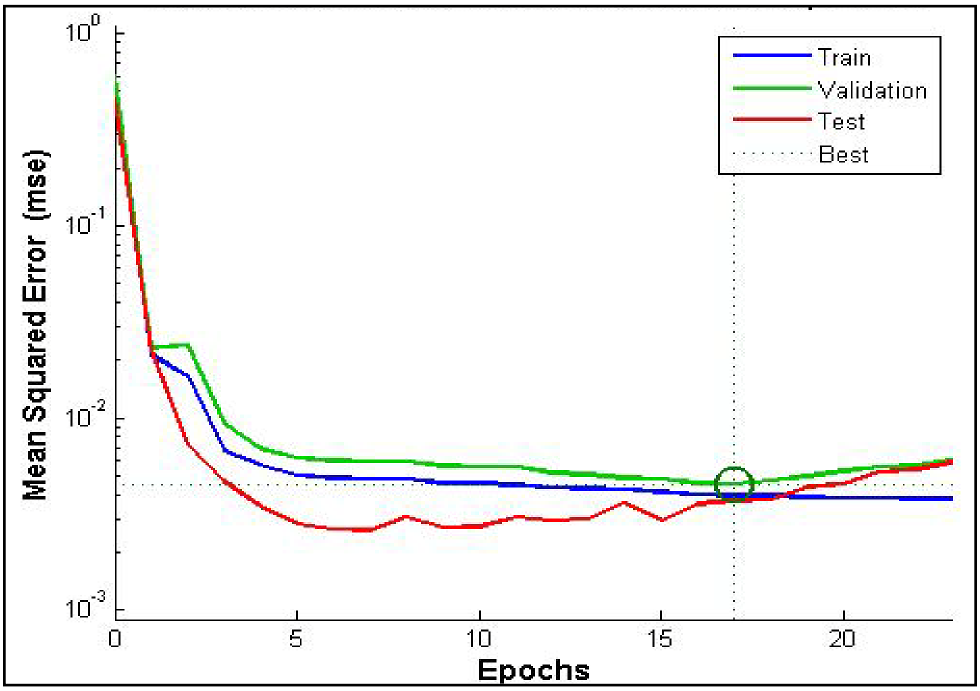


Figure 5.5 Performance plot for the neural network

The differences between predicted and experimental data are probably caused by sampling and measurement errors in the experimental data (Herink et al., 2007). The performance characteristics of the trained network are given by the training error, validation error and test error. Best validation MSE for the network was reported as 0.0045476 after which the validation gradient started to increase as the training progressed (Figure 5.5). For the present study, the MSE was expressed as follows:

$$\mathrm{MSE} = \frac{\sum_{k=1}^{N}\left(\frac{X_k^{exp}}{100}-\frac{X_k^{cal}}{100}\right)^2}{N} \tag{5.1}$$

Where, N represents the total number of datasets, X_k^{exp} and X_k^{cal} are the experimental and calculated values of the % formation of FAME for the k^{th} input.

A regression coefficient of 0.958 was obtained between targets and outputs for the network which showed that the network had been satisfactorily trained for the further testing and prediction process (Figure 5.6). A few outliers were observed which are common in any neural network development due to various factors such as experimental errors, observational error etc.

5.2.2 ANN Model Validation

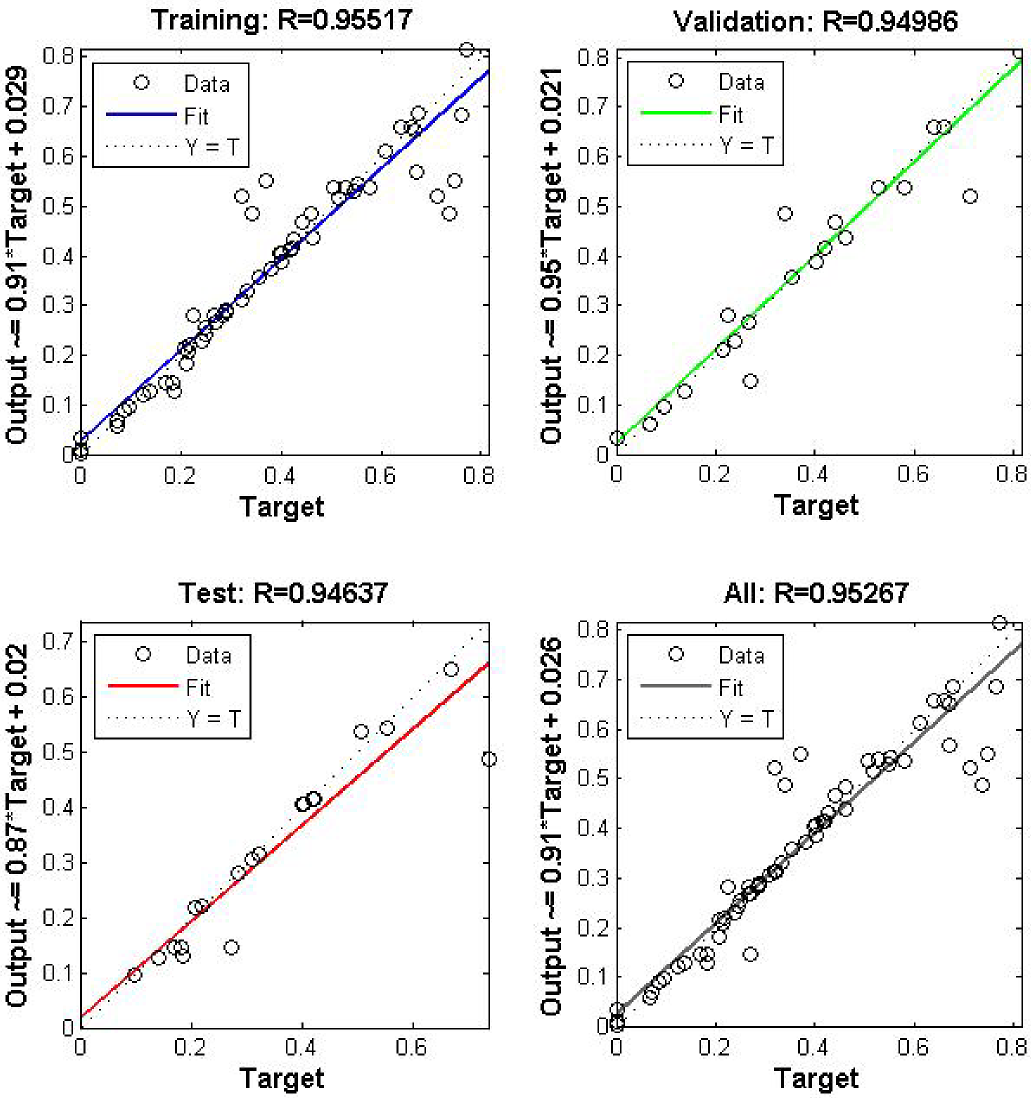
After the training process, data samples other than the training set were used to assess the performance of the modeled ANN. In the present study the developed optimized ANN model was validated by using two different sets of experimental data (other than those used in the section 5.2.1) having 13 data points each; for this purpose MATLAB Neural network tool box was used. These additional data were obtained by conducting actual experiments on the lab reactor at 45 °C and 55 °C respectively. The scaled data used for validating the present neural network are given in the Table 5.3. The ANN model predictions for these two validation sets along with results obtained from the actual experiments are given in the Table 5.4 in terms of scaled variables. These results are also shown in parity plots in Figures 5.7 (a) and (b). It is obvious from these figures that all the model predictions are within ± 4 % deviation.

Table 5.3 : Scaled experimental data used for validation

Time($\bar{t}=\frac{t}{240}$)	**FAME Yield**	
	Validation Set-I $\overline{mr}=\frac{mr}{25}=0.48$, $\bar{c}=\frac{c}{3.68}=0.8152$, $\bar{T}=\frac{T}{60}=0.75$	**Validation Set-II** $\overline{mr}=\frac{mr}{25}=0.72$, $\bar{c}=\frac{c}{3.68}=0.8152$, $\bar{T}=\frac{T}{60}=0.9167$
0	0	0
0.0833	0.1841	0.208
0.1667	0.2395	0.3216
0.2500	0.2649	0.4015
0.3333	0.2885	0.4596
0.4167	0.3091	0.5055
0.5000	0.3318	0.5472
0.5833	0.3539	0.5786
0.6667	0.3798	0.6098
0.7500	0.4018	0.6385
0.8333	0.4259	0.6597
0.9167	0.4419	0.6689
1.0000	0.4615	0.6756

Table 5.4 : Comparison between experimental data and ANN model predictions

Time	**Fractional Formation of FAME**			
	Validation Set I (45 ^{0}C)		**Validation Set II (55 ^{0}C)**	
	Obtained From Experiments	**Predicted by ANN Model**	**Obtained From Experiments**	**Predicted by ANN Model**
0	0	0	0	0
0.083333	0.1841	0.168443101	0.208	0.182670973
0.166667	0.2395	0.22930315	0.3216	0.313190837
0.25	0.2649	0.280608363	0.4015	0.406677523
0.333333	0.2885	0.290487416	0.4596	0.485338157
0.416667	0.3091	0.30460737	0.5055	0.536617358
0.5	0.3318	0.330657084	0.5472	0.530663182
0.583333	0.3539	0.357032044	0.5786	0.536748616
0.666667	0.3798	0.373759829	0.6098	0.610963753
0.75	0.4018	0.387803057	0.6385	0.659510442
0.833333	0.4259	0.432028336	0.6597	0.658434111
0.916667	0.4419	0.467919308	0.6689	0.650330853
1	0.4615	0.438074122	0.6756	0.687219747



Training: R=0.95517

Validation: R=0.94986

Test: R=0.94637

All: R=0.95267

Figure 5.6 : Regression plot for the ANN model

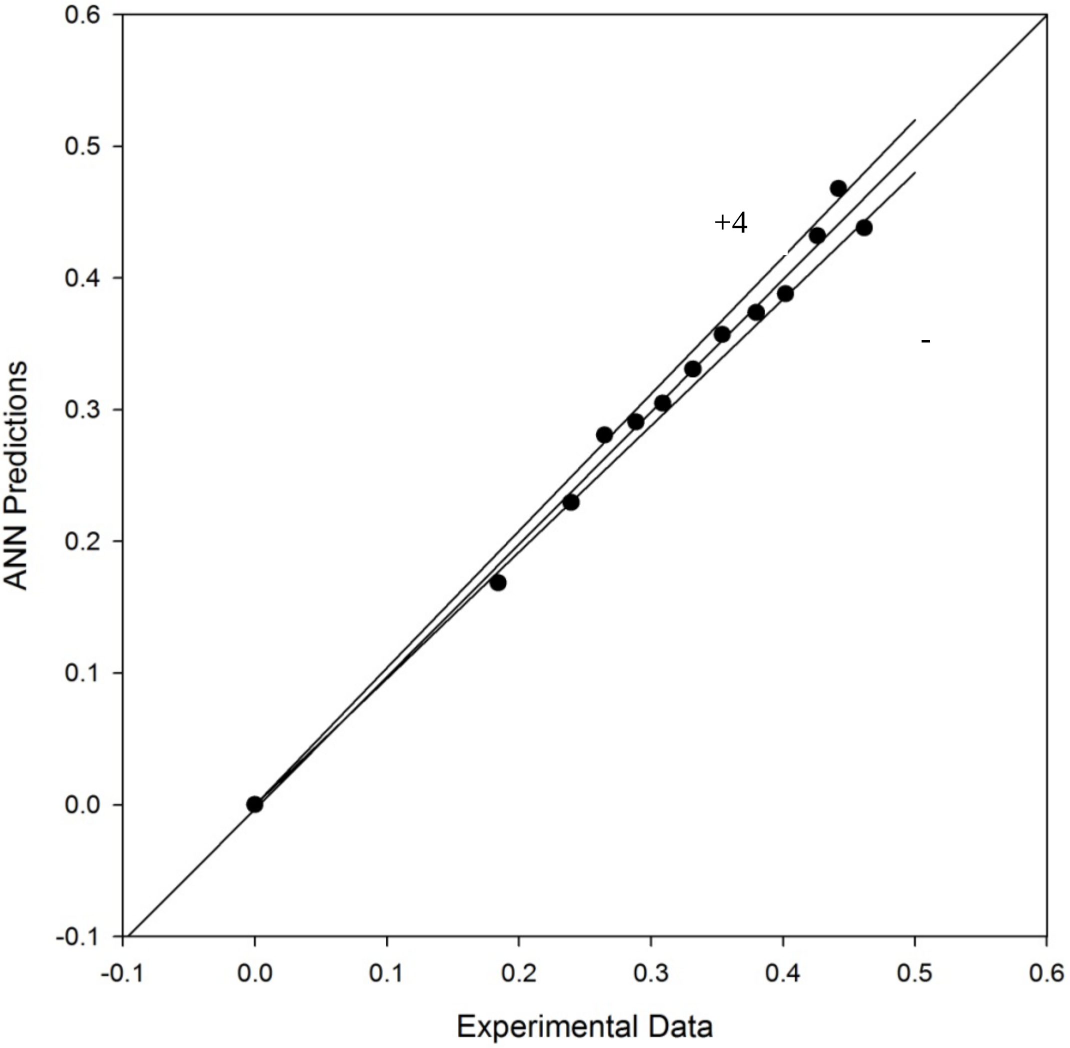


Figure 5.7 (a) : Comparison between experimental data and ANN predictions at 45 °C
(Molar ratio = 12:1, Catalyst Amount = 3 % v/v)

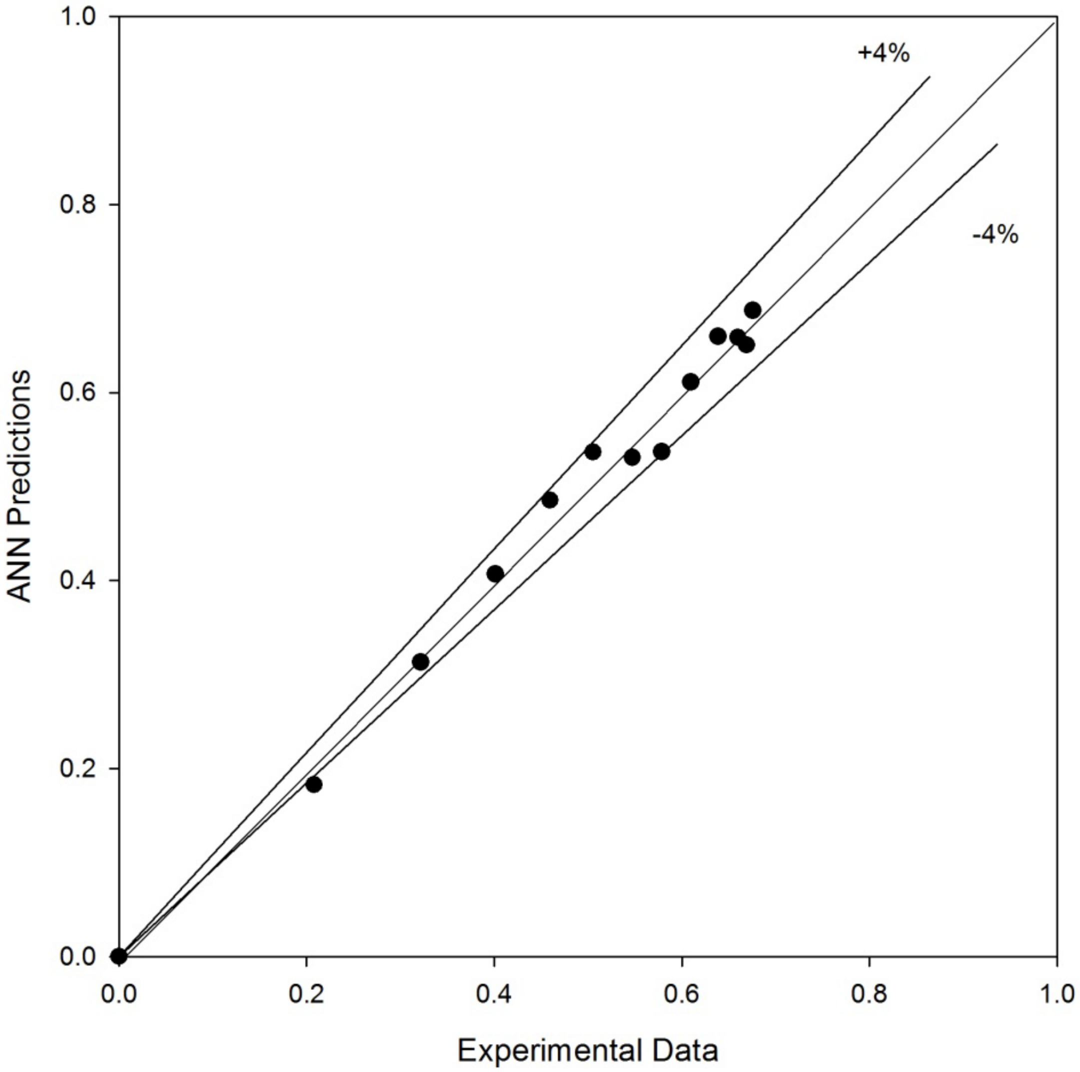


Figure 5.7: (b) Comparison between experimental data and ANN predictions at 55 °C

(Molar ratio = 18:1, Catalyst Amount = 3 % v/v)

From the above investigation, it may be concluded that the developed ANN model can be successfully applied to predict the FAME yield at the conditions other than experimental ones in the range of considered variables.

5.2.3 Predictions using ANN Model

In the Chapter IV optimum operating conditions were found by using RSM. These are methanol to oil molar ratio = 25:1, Catalyst amount = 3% v/v, and temperature = 60 °C. It was considered appropriate to develop a kinetic model at this temperature and catalyst amount, which takes into account the variation in methanol to oil molar ratio. This model may be used to study the effect of molar ratio on FAME yield. Therefore, predictions have been made using the developed ANN model for molar ratios, 9:1, 12:1, 15: 1 and 18:1, and are shown in Figure 5.8. These results have been used in the following section to develop the kinetic model.

5.3 KINETIC MODEL AND PARAMETER ESTIMATIOM

In the preceding section, profiles for fractional formation of FAME with time have been obtained by using developed ANN model for methanol to oil molar ratios namely, 9:1, 12:1, 15: 1 and 18:1, and experimental profile for molar ratio 25:1 is already available, for optimum catalyst amount and temperature. This section concerns the development of suitable kinetic model on the basis of these five profiles so that effect of change in molar ratio on fractional formation of FAME can be studied.

5.3.1 Kinetic Model

In section 3.6.3, values of kinetic constants k_1 and k_2 were estimated using experimental data of small lab reactor and the kinetic model, given by the equation (3.14). This equation corresponds to a reversible reaction in which forward reaction is pseudo first order, and backward reaction is second order, first order with respect to each of the two products. First, efforts have been made to fit this model, but goodness of fit and regression coefficient was not acceptable. Therefore, it is logical to fit the general reversible reaction model, in which both forward and backward reactions are second order, first order with respect to each of the reactants and products. Thus equation (3.10) as given below has been used to estimate the kinetics constants.

$$\frac{dX_c}{dt} = k_1 C_{A0}(3 - X_c)(M - X_c) - k_2 C_{A0} X_c^2 \qquad (3.10)$$

With $X_c = 0$ at $t = 0$. Where

$C_{A0} = Initial\ concentration\ of\ Castor\ Oil\ (mol/l)$

$X_c = Fractional\ Formation\ of\ FAME$

$M = Molar\ ratio\ of\ methanol\ to\ castor\ oil$

$k_1, k_2 = Kinetic\ constants\ (l/mol.min)$

The values of k_1 and k_2 were estimated using MATLAB (R2008a) version 7.6 code. The MATLAB code consists of optimization tool 'fminsearch'. As mentioned above, the data computed for different molar ratios at temperature 60 °C and 3% v/v catalyst concentration have then been used to estimate the kinetic parameters with the optimization tool. The differential equation was solved symbolically using 'dsolve' command in Matlab to determine a functional relationship between X_c and other variables as follows:

$$X_{c_{i,j}} = g(t_{i,j}, k_1, k_2, C_{A0_i}, M_i) \qquad (5.2)$$

Therefore, the function which has been minimized is as follows:

$$\sum_{i=1}^{N} \sum_{j=1}^{M} [X_{c_{i,j}} - g(t_{i,j}, k_1, \quad k_2, C_{A0_i}, M_i)]^2 \qquad (5.3)$$

Where

$X_{c_{i,j}} =$ values obtained experimentally and predicted through ANN,

M = number of data points, and N = number of molar ratios.

'fminsearch' finds the minimum of a scalar function of several variables, starting at an initial estimate. This is generally referred to as unconstrained nonlinear optimization. 'fminsearch' uses the simplex search method. This is a direct search method that does not require numerical or analytic gradients. If n is the length of x, a simplex in n-dimensional space is characterized by the n+1 distinct vectors that are its vertices. In two-space, a simplex is a triangle; in three-space, it is a pyramid. At each step of the search, a new point in or near the current simplex is generated. The function value at the new point is compared with the function's values at the vertices of the simplex and, usually, one of the vertices corresponding to worst value of function is

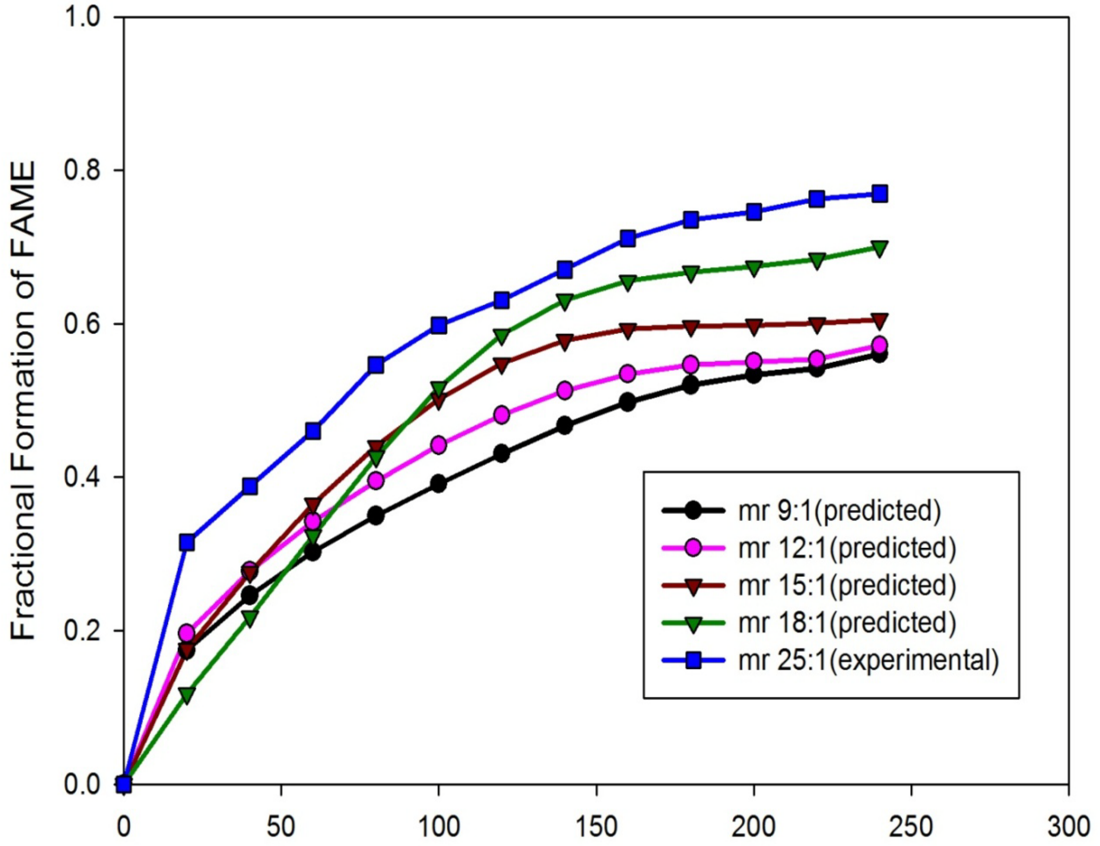


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Figure 5.8 : Predicted profiles of Fractional formation of FAME with time at different molar ratio (catalyst amount = 3% v/v, and temperature = 60 °C)

replaced by the new point, giving a new simplex. This step is repeated until the size of the simplex is less than the specified tolerance. The C_{A0} values corresponding to different molar ratios are given in the Table 5.5.

Table 5.5 : C_{A0} values corresponding to different molar ratios

S.No.	Molar Ratio (M)	C_{A0} (gmol/l)	Catalyst (% vol/vol)
1	9:1	0.733668	3%
2	12:1	0.67393	3%
3	15:1	0.622769	3%
4	18:1	0.57927	3%
5	25:1	0.49771	3%

Following the procedure outlined above, the values of k_1 and k_2 have been estimated which are 0.000295 (l/gmol.min) and 0.026775 (l/gmol.min) respectively. The Table 5.6 describes the correlation coefficients of fitted kinetic model corresponding to various molar ratios.

Table 5.6 : Regression coefficients obtained for different molar ratios during estimation

Molar Ratio	9 :1	12:1	15:1	18 :1	25 :1
R^2 (Regression Coefficient)	0.9754	0.9850	0.9959	0.9471	0.9631

For molar ratio 25:1, experimental and predicted values are mentioned in Table 5.7. This comparison is also depicted in the Figure 5.9. Both the comparisons testify the goodness of fit of the kinetic model.

In order to ensure the accuracy of model further, all the predicted and used values (experimental and generated) have been plotted in the Figure 5.10 for all five molar ratios. From this Figure, it can be concluded that the about 88 % of predictions lie within ±10 % deviation; the remaining ones fall just outside the ±10 % deviation line except one point.

It is important to mention here that the kinetic constants, k_1 and k_2, estimated in this Chapter cannot be compared with those estimated in the Chapter III, because the catalyst concentrations used in both the cases are different. Besides, forward reaction in kinetic model fitted in the Chapter III is pseudo first order while here it is second order.

Table 5.7 : Comparison of predicted and experimental data for M= 25:1

Time, min	X_c predicted	X_c experimental
0	0	0
20	0.207331067	0.315
40	0.379085196	0.3879
60	0.509119147	0.4606
80	0.601013862	0.5459
100	0.662839891	0.5979
120	0.703071851	0.6306
140	0.728686779	0.6705
160	0.7447694	0.7109
180	0.754778774	0.7353
200	0.76097432	0.7459
220	0.764796218	0.7625
240	0.767148934	0.7695

Further, this ANN model has been used to compute X_c versus time t profiles for four molar ratios, 9:1, 12:1, 15: 1 and 18:1, at optimum temperature 60 °C and catalyst amount, 3 % v/v. These computed profiles and experimental profile at molar ratio 25:1, have been used to estimate kinetic constants of the kinetic model given by the equation (3.10). For this purpose, ‘fminsearch’ has been used to minimize the objective function to estimate the kinetic constants. The estimated kinetic constants are k_1= 0.000295 (l/gmol.min) and k_2 = 0.026775 (l/gmol.min). The developed kinetic model predicts the fractional formation of FAME within ± 10 % deviation.

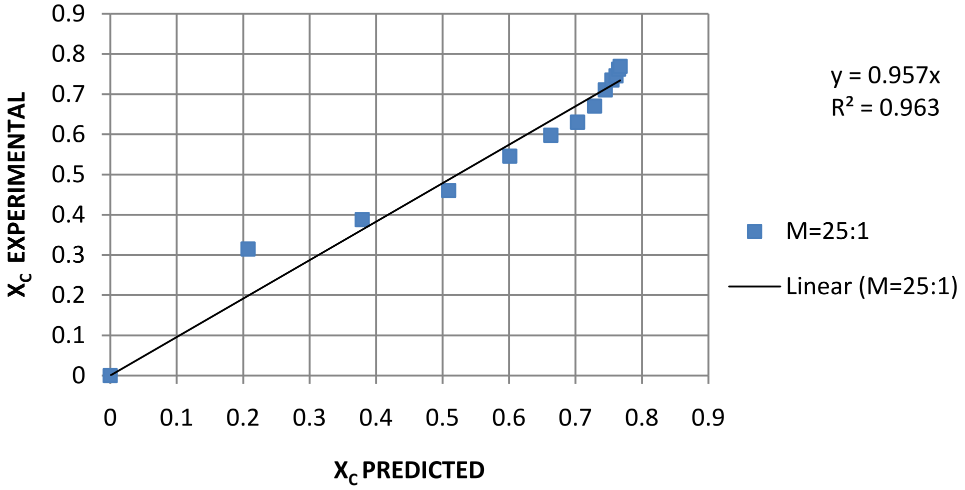

Figure 5.9 : Comparison of predicted and experimental values of X_c for M=25:1

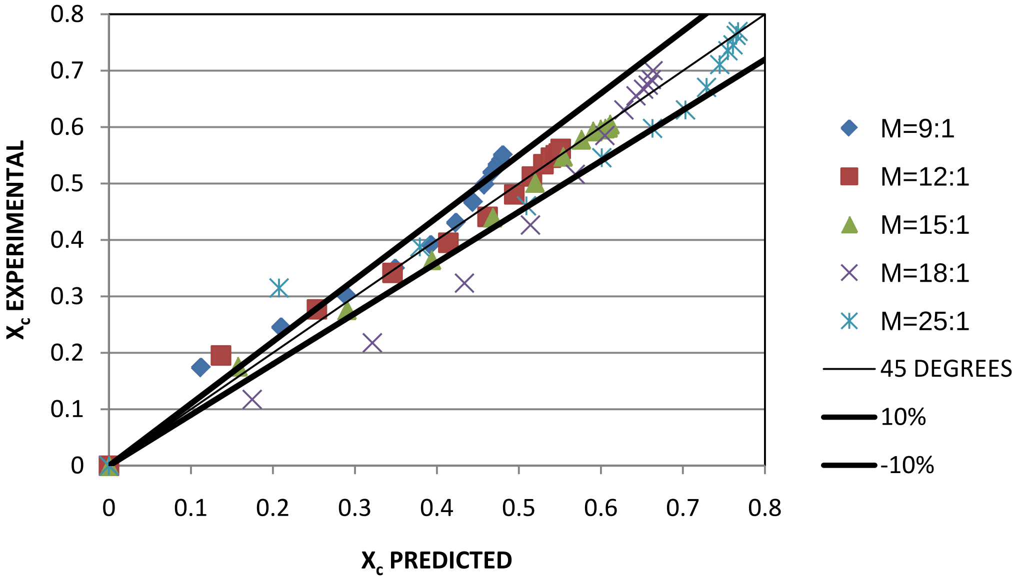

Figure 5.10 : Comparison of Predicted and Experimental and generated values of X_c for all the five molar ratios

5.4 CONCLUDING REMARKS

In this Chapter, an ANN Model has been developed to describe batch reactor experiments in large lab reactor. The model has been checked for its accuracy with reference to various criteria. Besides, this model has also been validated with two additional sets of experimental data, and its predictions have been found to be within ± 4 % deviation. This developed model has been used to compute data for those conditions for which no experimental data were available.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

In this thesis, investigations on the transesterification of castor oil have been done in two types of lab reactors, small lab reactor (500 cc) and the large lab reactor (3 L); sulphuric acid has been used as a catalyst. The investigations include experimental and modeling work. This chapter summarizes the main conclusions of the research work along with the recommendations for future work.

6.1 CONCLUSIONS

Conclusions of the research work are described section wise as follows:

6.1.1 Small Lab Reactor

(i) The operating conditions used for experimental studies are methanol/ oil molar ratio = 6:1, catalyst = 1 % concentrated H_2SO_4 (% v/v of castor oil), temperature = 35° to 65 °C at an interval of 5 °C, and 600 rpm. Experimental results have been analyzed with respect to three kinetic schemes namely, first order pseudo irreversible reaction, second order irreversible reaction, and the reversible reaction.

(ii) By using first order pseudo irreversible reaction kinetics, and experimental data, rate constant k (mm^{-1}) have been computed at various temperatures. This provides the values of activation energy, and Arrhenius constant as given below.

Activation Energy, E = 38.283 kJ/mol

Arrhenius constant, A= 1461.0345 min^{-1}

(iii) Analysis of experimental data by second order irreversible reaction kinetics provides the following values:

Activation Energy, E = 38.611 kJ/mol

Arrhenius constant = 343836.48 ml/(mol.min)

Fitting of irreversible second order kinetic model is somewhat better than that of irreversible first order reaction with respect to correlation coefficients.

(iv) Kinetic model for reversible reaction with forward reaction as pseudo first order, and backward reaction as second order has also been used to analyze the experimental results and the obtained model is as given below:

$$\frac{dX_c}{dt} = k_1\left[(3 - X_c) - \frac{C_{Ao}}{K}\, X_c^2\right]$$

Where X_c = fractional formation of FAME

k_1(min^{-1}) = 216.264 exp$\left(\frac{-32.33}{R\,T}\right)$;

Gas constant, R = $8.3144\ \frac{kJ}{kmol.K}$; Temperature T = K

Equilibrium constant,

$$K\left(\frac{gmol}{l}\right) = K_{35}\, exp\left[11857\left(\frac{1}{308.15} - \frac{1}{T}\right)\right] \text{; T is in K} \tag{3.17}$$

and K_{35} = 0.008895 $\left(\frac{gmol}{l}\right)$

This kinetic model is applicable in the temperature range 35° to 60 °C.

(v) This transesterification reaction is endothermic in nature, and its heat of reaction, computed in this work is 23.560 kcal/gmol.

(vi) In order to evaluate the usability of FAME (biodiesel) produced, its several properties have been experimentally determined. From these properties (Table 3.8) it is concluded that the biodiesel product formed should be used for blending with diesel oil in appropriate quantity to bring its properties within acceptable limits as viscosity of FAME product and its water content both are on higher side. These conclusions are in accordance with pervious similar findings reported in the literature (Canoira et al., 2010).

6.1.2 Large Lab Reactor

The experimental data taken in this reactor have been analyzed by response surface Methodology (RSM), and Artificial Neural Networks (ANM). Therefore, conclusions have been also been divided in two sections A and B.

[A] RSM Modeling

The central composite design (CCD) of the RSM was used to decide the number of experiments, to be conducted. Range of operating conditions was: Methanol to oil ratio = 6: 1 to 25:1, catalyst amount (vol. %) = 1 to 3, temperature (°C) = 40 to 60 °C.

An experiment was conducted up to 4 hours duration. Samples for analysis were taken in between at regular intervals.

(i) RSM Model

A RSM model has been developed by using experimental data of all sets at 4 hour time only. The model in terms of coded variables for calculating % FAME yield (Y) is given in the equation (4.2).

ANOVA has been used to evaluate the adequacy of the RSM model. The model has also been validated with two additional sets. The model predictions are within ± 5 % deviation with respect to experimental results.

RSM model has been used to optimize the experimental conditions. These are methanol to oil ratio = 25:1, catalyst amount = 3 vol %, temperature 60^0 C. RSM model yields % FAME yield as 75.67 % while that obtained experimentally is 76.95 % . Using the model, the effects of variation in operating conditions on % FAME have also been studied.

[B] ANN Model

(i) The development of ANN model has been done by using fractional formation of FAME (X_c) versus time (t) experimental data. The developed model is a Feed Forward Neural Network (FFNN). There are four input neurons corresponding to four input variables namely methanol to oil molar ratio, catalyst amount, temperature, and time, and one output neuron corresponding to the fractional formation of FAME. There is one hidden layer in optimized ANN model consisting of 12 neurons. In this model tangent sigmoid function has been used as the activation function in the hidden layer and linear function has been used as the activation function in the output layer.

ANN model has been validated with two additional sets of experimental data, obtained by conducting separate experiments. It is obvious from the Figures 5.7 (a) and (b) that the ANN model predictions are within ± 4 % deviation.

(ii) In chapter IV optimum operating conditions for castor oil transesterification have been obtained, and are given in preceding section above. By using ANN model, X_c versus t profiles were obtained for few molar ratios, 9:1, 12:1, 15:1, 18:1 ; for these molar ratios no experimental data were taken.

(iii) A kinetic model has been developed by using X_c versus time t data namely, 9:1, 12:1, 15:1, 18:1, and the experimental data at 25:1. The model is applicable at the optimum temperature = 60 °C and catalyst amount = 3 % v/v. The kinetic model provides the effect of change in the methanol to oil molar ratio on X_c at optimum operating conditions. The model is reproduced below.

$$\frac{dX_c}{dt} = k_1 C_{A0}(3 - X_c)(M - X_c) - k_2 C_{A0} X_c^2 \tag{3.10}$$

With $X_c = 0$ at $t = 0$. Where t = time (min)

$C_{A0} =$ Initial concentration of Castor Oil (gmol/l)

$X_c =$ Fractional Formation of FAME

$M =$ Molar ratio of methanol to castor oil

k_1 = 0.000295 (l/gmol.min)

k_2 = 0.026775 (l/gmol.min)

The developed kinetic model predicts the fractional formation of FAME within ± 10 % deviation (Figure 5.10).

Remarks

It is our view that the results of this study may be used to design a batch or continuous flow reactor for castor oil transesterification at optimum operating conditions.

6.2 RECOMMENDATIONS FOR FUTURE WORK

(i) As methanol boiling point is close to 65 °C, therefore kinetic experiments be conducted at higher temperature and higher pressure (> 1 atm), and optimum conditions for maximum FAME production be obtained.

(ii) Due to formation of glycerol, problem in mixing the reaction mixture may be experienced. Therefore, kinetic studies of this reaction be performed in hydro-cavitation reactor or sonicaton reactor. It is felt that this mixing arrangement would reduce the methanol to oil molar ratio without effecting the optimum FAME production.

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APPENDICES

A1 GC CURVES OF PRODUCED FAMEA1.1

A1.1 GC Curve of Produced FAME

The peak areas of produced methyl esters determined by gas chromatograph (GC) using internal standard methyl heptadecanoate with FID detector to determine the total fatty acid composition of oil [for detail methodology see section 3.3.2]

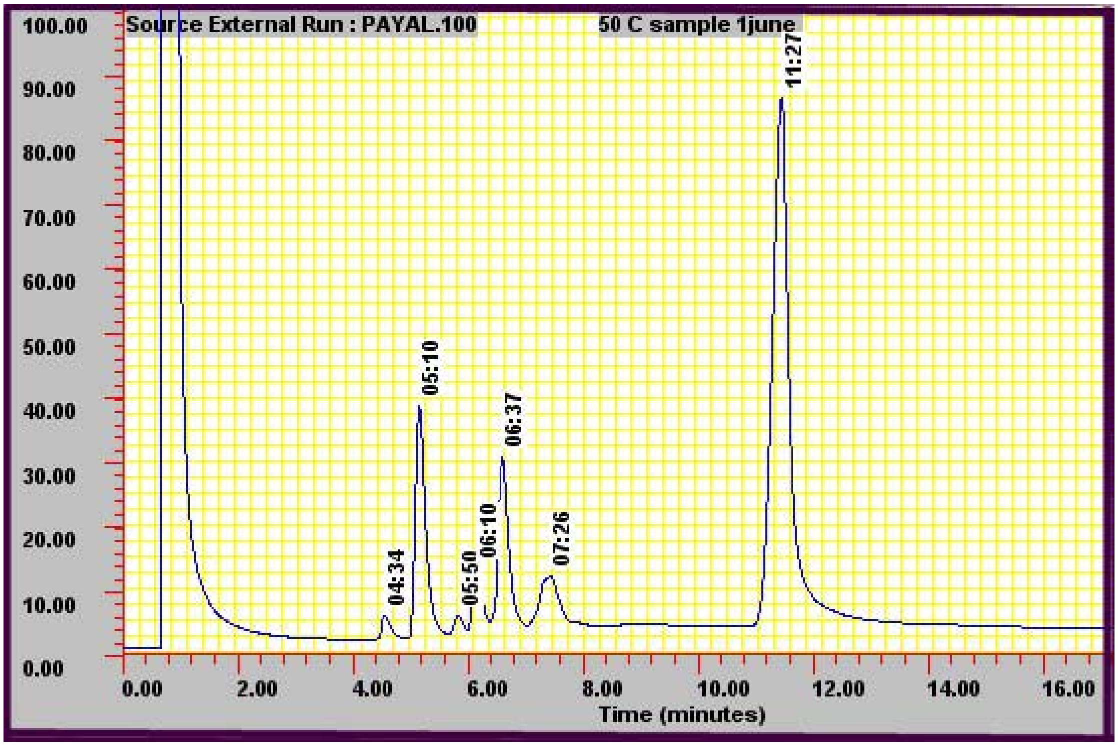

Figure A1.1 : FAME quantification and characterization by Gas Chromatograph

A1.2 Effect of rpm on % FAME yield

The effect of mixing intensity on the production of methyl esters with 6:1 molar ratio, 1% catalyst amount at 60 ^{o}C temperature has been studied. The values of rpm were varied from 400 – 1000 rpm. FAME % yield has been analyzed by gas chromatography. It was observed that the maximum FAME yield % of 46.63 % has been achieved at 800 rpm (Figure 4.11). [for detail methodology see section 4.1.3]

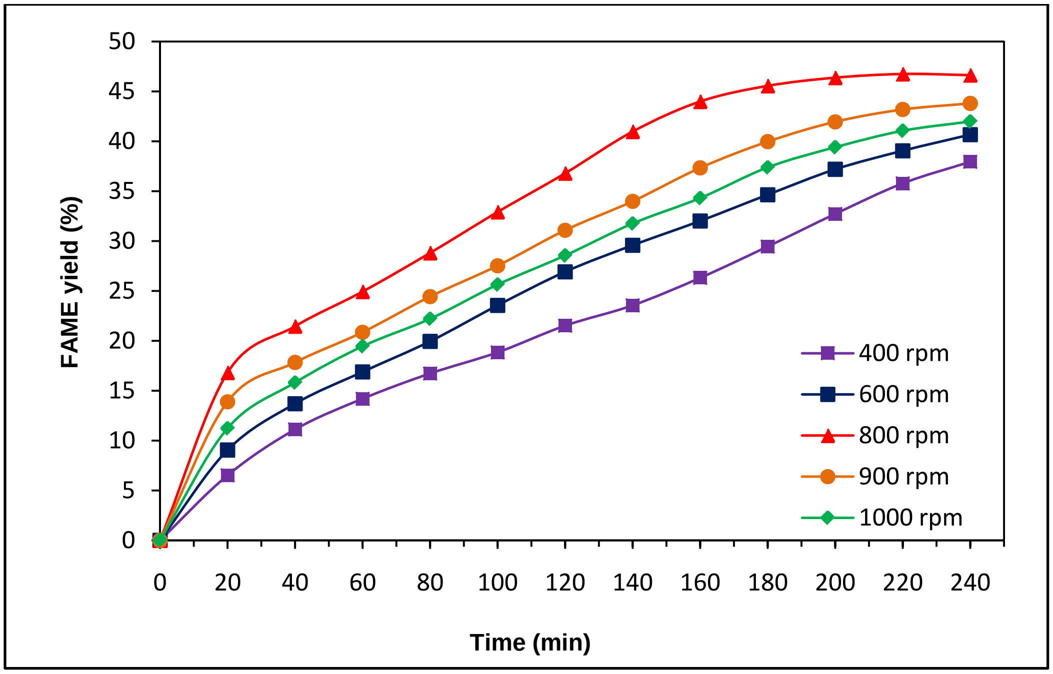

Figure A1.2: FAME yield (%) with varying rpm at constant catalyst amount 1%, methanol/oil molar ratio 6:1 and temperature 60 °C

A2.1 : (a) Table shows the % FAME yield with constant amount of catalyst 3 %, at temperature 40 °C molar ratio of 6:1 and 25:1 for 4 hours time duration

Temp – 40 °C Catalyst = 3 % (vol/vol) Time = 4 hrs			
S. No.	**Time (min)**	**FAME% Yield at molar ratio of Methanol: oil**	
		6	**25**
1.	20	7.25	16.28
2.	40	9.59	19.15
3.	60	12.81	23.92
4.	80	18.12	24.56
5.	100	22.42	26.65
6.	120	23.59	27.05
7.	140	28.53	29.85
8.	160	29.53	31.95
9.	180	30.07	34.03
10.	200	33.05	36.95
11.	220	35.84	44.15
12.	240	37.71	47.36

A2.1 : (b) Table shows the % FAME yield with constant amount of catalyst 1 %, at temperature 40 °C molar ratio of 6:1 and 25:1 for 4 hours time duration

Temp – 40 °C Catalyst = 1 % (vol/vol) Time = 4 hrs			
S. No.	**Time (min)**	**FAME% Yield at molar ratio of Methanol: oil**	
		6	**25**
1.	20	4.32	5.95
2.	40	6.95	7.8
3.	60	8.45	9.35
4.	80	10.23	11.54
5.	100	12.24	13.09
6.	120	14.15	15.95
7.	140	16.99	18.45
8.	160	18.59	21.18
9.	180	22.65	24.65
10.	200	25.56	26.94
11.	220	27.19	29.42
12.	240	28.55	32.95

A2.2 : (a) Table shows the % FAME yield with constant amount of catalyst 2 %, at temperature 50 °C molar ratio of 15.5 for 4 hours time duration

Temp – 50 °C Catalyst = 2 % (vol/vol) Time = 4 hrs		
S. No.	**Time (min)**	**FAME% Yield at molar ratio of Methanol: oil**
		15.5
1.	20	9.93
2.	40	14.56
3.	60	21.72
4.	80	26.92
5.	100	30.59
6.	120	34.49
7.	140	38.95
8.	160	43.65
9.	180	45.96
10.	200	47.56
11.	220	49.62
12.	240	52.25

A2.2 : (b) Table shows the % FAME yield with constant amount of catalyst 3.68 %,at temperature 50 °C molar ratio of 15.5:1 for 4 hours time duration

Temp – 50 °C Catalyst = 3.68 % (vol/vol) Time = 4 hrs		
S.No.	**Time (min)**	**FAME% Yield at molar ratio of Methanol: oil**
		15.5
1.	20	28.45
2.	40	36.56
3.	60	41.69
4.	80	46.44
5.	100	51.56
6.	120	54.69
7.	140	57.91
8.	160	60.08
9.	180	62.15
10.	200	63.95
11.	220	65.67
12.	240	67.89

A2.3 : (a) Table shows the % FAME yield with constant amount of catalyst 1 %, at temperature 60 ^{o}C molar ratio of 6:1 and 25:1 for 4 hours time duration

Temp – 60 °C Catalyst = 1 % (vol/vol) Time = 4 hrs			
S. No.	**Time (min)**	**FAME% Yield at molar ratio of Methanol: oil**	
		6	**25**
1.	20	6.52	13.81
2.	40	10.51	19.46
3.	60	12.96	23.93
4.	80	16.82	28.81
5.	100	20.59	31.92
6.	120	27.04	36.96
7.	140	32.92	40.42
8.	160	38.32	46.32
9.	180	42.05	51.65
10.	200	44.19	57.05
11.	220	46.63	65.18
12.	240	47.29	72.55

Table A2.3 : (b) shows the % FAME yield with constant amount of catalyst 3 %, at temperature 60 ^{o}C molar ratio of 6:1 and 25:1 for 4 hours time duration.

Temp – 60 °C Catalyst = 3 % (vol/vol) Time = 4 hrs			
S. No.	**Time (min)**	**FAME% Yield at molar ratio of Methanol: oil**	
		6	**25**
1.	20	15.88	31.5
2.	40	20.58	38.79
3.	60	24.63	46.06
4.	80	26.75	54.59
5.	100	29.04	59.79
6.	120	32.59	63.06
7.	140	37.95	67.05
8.	160	43.79	69.09
9.	180	48.09	71.35
10.	200	50.05	73.53
11.	220	52.76	75.59
12.	240	55.27	76.85

A3.2.4: (b) Table shows the % FAME yield with constant amount of catalyst 2%, at temperature 64 ^{o} C molar ratio of 15.5 for 4 hours time duration

Temp – 64 °C Catalyst = 2 % (vol./vol.) Time = 4 hrs		
S. No.	**Time (min)**	**FAME% Yield at molar ratio of Methanol: oil**
		15.5
1.	20	12.78
2.	40	22.25
3.	60	29.52
4.	80	34.26
5.	100	38.72
6.	120	41.69
7.	140	46.81
8.	160	47.95
9.	180	51.51
10.	200	53.09
11.	220	57.52
12.	240	60.18