STUDIES ON TRANSESTERIFICATION OF VEGETABLE OIL FOR GLYCEROL FREE SYNTHESIS OF BIODIESEL

By

VIVEK RATHORE

DEPARTMENT OF CHEMICAL ENGINEERING

Under the Guidance of

DR. R. P. BADONI
(DISTINGUISHED PROFESSOR, UPES)
&
DR. BHARAT NEWALKAR
(CHIEF MANGAER, BPCL)

Submitted

IN PARTIAL FULFILLMENT OF THE REQUIREMENT OF THE DEGREE OF DOCTOR OF PHILOSOPHY

TO

UNIVERSITY OF PETROLEUM & ENERGY STUDIES
DEHRADUN 248 007 (INDIA)
JULY, 2014

DECLARATION

I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which has been accepted for the award of any other degree or diploma of the university or other institute of higher learning, except where due acknowledgment has been made in the text.

Vivek Rathore
Date:

THESIS COMPLETION CERTIFICATE

*This is to certify that the thesis entitled "***Studies on Transesterification of Vegetable Oil for Glycerol Free Synthesis of Biodiesel"** *submitted by* **Vivek Rathore** *to* **University of Petroleum & Energy Studies** *in partial completion of the requirements for the award of the Degree of Doctor of Philosophy is a bona fide record of the research work carried out by him under our supervision and guidance.*

It is also to certify that the content of the thesis, in full or parts have not been submitted to any other Institute or University for the award of any other degree or diploma.

Research Supervisors

Dr. R. P. Badoni	*Dr. Bharat Newalkar*
(UPES)	*(BPCL)*

Place:
Date:

UPES & BPCL RESEARCH ARCHIVE

e-Theses Repository

ACKNOWLEDGEMENT

I am deeply indebted to my guides, **Dr. Bharat Newalkar (Chief Manager, Corporate R&D Centre, BPCL) & Dr. R.P. Badoni (Distinguished Professor, UPES)** *for their excellent guidance, encouragement and support throughout my research work. Their profound theoretical knowledge as well as vast experimental experience that they have shared readily during research work, helped me to overcome many difficulties. I can't forget the innumerable time and efforts to teach me for conducting the research and in writing it, that my work will never be able to match. Their constant support, encouragement, never-ending enthusiasm, and confidence in me have been a source of motivation for me.*

I am extremely thankful to **BPCL Management** *and* **Dr. P.S. Viswanathan, (Head/DGM, Corporate R&D Centre, BPCL***) for providing me with necessary facilities for this project. In addition, I am thankful to BPCL (HRD, Mumbai Refinery) for my candidature in their Employee Professional Education Scheme to encourage staff for higher education.*

I am grateful to Dr. Sudha Tyagi (manager, Corporate R&D Centre, BPCL), to for extend her support for analytical facilities. Also, I am thankful to Dr. Kamal Bansal, Dr. Anjali Midha and Ms. Rakhi Ruhal from UPES/CCE for their support and encouragement.

I would like to thank my CRDC colleagues, Mr. Prashant Parihar, Ms. Sayanti Ghosh and Dr. Shivanand Pai for their support and help. I must concede that there were lot more who helped me directly or indirectly in the completion of this work, whose name I could not mention.

Finally, I express my deepest gratitude to my family for their constant love and support.

Vivek Rathore

ABSTRACT

Transesterification of non-edible vegetable oils namely Jatropha and Pongamia is investigated with DMC in presence of base catalyst *viz.* potassium hydroxide (KOH). The optimization study is carried out to comprehend the effects of reaction parameters such as catalyst amount, reactant molar ratio, temperature and reaction time on conversion into respective biodiesel of Jatropha and Pongamia oil. Furthermore, transesterification reaction kinetics is investigated in the temperature range of 60-80 ^{o}C. Based on the obtained results, the optimized reaction conditions have been zeroed in w.r.t. aforementioned parameters. Typically, maximum conversion of 94.0% and 96.0% have been achieved for Jatropha oil and Pongamia oil, respectively, at 9% (based on oil wt) of catalyst amount, 10:1 DMC to oil molar ratio at 80^{o}C in the 8 h reaction time. The activation energy (Ea) and the pre-exponential factor (k_o) are found to be, 66.4 ±2 KJ/mol and $3.7x10^{7}$ min^{-1} and 54.5 ±2 KJ/mol and $6.8x10^{5}$ min^{-1} for transesterification of Jatropha and Pongamia oil, respectively, using pseudo-first order kinetics. Furthermore, DMC-biodiesel samples are characterized for its fuel properties and are found to be in good agreement vis-à-vis ASTM D6751/EN 14214/IS 15607 specifications. In view of this, glycerin free DMC-biodiesel process is conceptualized for its development and possible implementation.

Likewise, Glycerin free synthesis of biodiesel from non-edible oils *viz.* Jatropha and Pongamia oil under supercritical conditions has been investigated using dimethyl carbonate (DMC) and diethyl carbonate (DEC) as methylating agent without employing the catalyst. Typically, supercritical conditions w.r.t. reactants to oil molar ratio, reaction temperature and time have been optimized. Accordingly, the supercritical conditions with 40:1 molar ratio of DMC / DEC to oil at 325°C /150 bar individually, have been found to be adequate to achieve nearly complete conversion in 40 min. Furthermore, reaction kinetics has been investigated under supercritical condition of DMC and DEC in the temperature range of 250-350 °C at 150 bar. The estimated activation energies (Ea) are of the order of 38.0 ±2 and 35.5 ±2 kJ/mol for DMC, and 40.4 ±2 and 38.2 ±2 kJ/mol for DEC, for conversion of Jatropha and Pongamia oil, respectively, using pseudo-first order kinetics. The prepared biodiesel samples have been characterized w.r.t. their distillation characteristics, normal boiling points and fuel properties. The obtained results demonstrated a good agreement with ASTM D6751/EN 14214/IS 15607 specifications. In view of this, non-catalytic glycerin free supercritical biodiesel process is conceptualized for its development and possible implementation to overcome the problems associated with purification of biodiesel and by product *viz.* glycerin in conventional homogeneous catalytic process for biodiesel production.

In addition, to understand the complete design aspect of glycerol free process for biodiesel production, the conceptualized catalytic and non-catalytic process for capacity (~1000 Kg/h) are simulated and compared with conventional methanol process in ASPEN PLUS simulation software. The process flow diagrams are developed using Aspen Plus simulation software and verified through laboratory experimental results. Process conditions are attuned until a glycerol-free biodiesel was produced to meets the international standard. By avoiding the glycerol moiety within the final product, similar yields were obtained in novel route by employing minimal unit operation and ease of separation followed by purification steps for product/byproduct. In addition, complete mass balance, energy loads and design specifications were obtained and operating parameters were zeroed at efficient operating condition using simulation studies.

TABLE OF CONTENTS

CHAPTER 1.....1

INTRODUCTION.....1

CHAPTER 2.....19

SCOPE OF THE THESIS.....19

2.1 Context.....19

2.2 Purpose.....20

2.3 Research Overview.....21

CHAPTER 3.....23

LITERATURE SURVEY.....23

3.1 Conventional routes for vegetable oil processing for biodiesel production.....23

  3.1.1 Biodiesel through homogeneously catalyzed transesterification of vegetable oil.....24

  3.1.2. Biodiesel through heterogeneously catalyzed transesterification of vegetable oil.....32

3.2 Non-Conventional routes for vegetable oil processing for biodiesel production.....40

  3.2.1 Enzyme-catalyzed transesterification.....40

  3.2.2 Transesterification under supercritical methanol phase.....47

  3.2.3 Microwave assisted transesterification.....53

  3.2.4 Cavitation / Ultrasonic irradiation assisted transesterification.....59

  3.2.5 Membrane assisted transesterification.....64

  3.2.6 Static mixture assisted transesterification.....68

3.3 Commercial process features of transesterification vegetable oil.....70

3.4 An alternative: Glycerin free routes.....71

  3.4.1 Hydroprocessing.....71

  3.4.2 Substitution of methanol.....84

3.5 Summary......90

CHAPTER 4......91

JATROPHA AND PONGAMIA OIL DERIVED DMC-BIODIESEL SYNTHESIS: A KINETICS STUDY 91

4.1 Introduction 91

4.2 Experimental Section......95

4.2.1 Materials......95

4.2.2 Method: DMC-Biodiesel synthesis and its kinetics 95

4.2.3 GC Analysis......96

4.3 Results and discussion......97

4.3.1 Fatty acid composition for Jatropha and Pongamia oil 97

4.3.2 DMC-Biodiesel synthesis......98

4.3.3 Optimization of reaction parameters for DMC-Oil system......100

4.3.3.1 Effect of KOH amount 100

4.3.3.2 Effect of reactant molar ratio......101

4.3.3.3 Effect of temperature......103

4.3.3.4 Effect of reaction time......104

4.3.4 Kinetics of the reaction and its modeling......105

4.3.5 Biodiesel Characterization......109

4.4 Conceptualization of process......111

4.5 Conclusions 112

CHAPTER 5......114

GLYCERIN FREE SYNTHESIS OF JATROPHA AND PONGAMIA BIODIESEL IN SUPERCRITICAL DIMETHYL AND DIETHYL CARBONATE......114

5.1 Introduction 114

5.2 Experimental section 117

5.2.1 Materials 117

5.2.2 Synthesis 118

5.2.3 GC Analysis 119

5.3 Results and discussion 120

5.3.1 Fatty acid (FA) composition for Jatropha and Pongamia oil 120

5.3.2 Optimization of reaction parameters 122

5.3.2.1 Effect of molar ratio of DMC / DEC to oil 122

5.3.2.2 Effect of temperature 124

5.3.3 Reaction Kinetics 129

5.3.4 Thermal stability of biodiesel in supercritical condition 134

5.3.5 Distillation characteristics, estimation of normal boiling point and fuel properties 137

5.4 Conceptualization of process 142

5.5 Conclusions 145

CHAPTER 6 146

SIMULATION OF GLYCEROL FREE BIODIESEL SYNTHESIS UNDER CATALYTIC AND NON-CATALYTIC SUPERCRITICAL PROCESS CONDITIONS 146

6.1 Introduction 146

6.2 Materials and Methods 147

6.3 Process development and downstream separation strategy 152

6.4 ASPEN simulation 158

6.4.1 Feedstock composition 158

6.4.2 Transesterification reaction 159

6.4.3 DMC recovery 161

6.4.4 Separation of KOH and its neutralization 162

6.4.5 Separation of byproduct GDC from FAME/Unreacted oil 162

6.5 Mass balances 163

6.6 Energy balance and Heat integration 165

6.7 Conclusions 170

CHAPTER 7 172

SUMMARY AND WAY FORWARD 172

7.1 Summary 172

7.2 Way Forward 177

REFERENCES 182

LIST OF PUBLICATIONS 222

BIODATA OF AUTHOR 223

LIST OF TABLES

Table 3.1 Summary of some studies for biodiesel synthesis using homogeneous base catalysts 26

Table 3.2 Summary of some studies for biodiesel synthesis using homogeneous acid catalysts..29

Table 3.3 Summary of some studies for biodiesel synthesis using two step homogeneous acid/base catalysts 31

Table 3.4 Summary of some studies for biodiesel synthesis using heterogeneous catalysts 34

Table 3.5 Summary of some studies for biodiesel synthesis using two step homogeneous and heterogeneous catalysts 38

Table 3.6 Summary of some studies for enzymatic biodiesel synthesis..................42

Table 3.7 Summary of some studies for enzymatic biodiesel synthesis in supercritical carbon dioxide 45

Table 3.8 Summary of some studies for biodiesel synthesis in supercritical condition..49

Table 3.9 Summary of some studies for biodiesel synthesis in microwave 54

Table 3.10 Summary of some studies for biodiesel synthesis in Cavitation / Ultrasonic irradiation..61

Table 3.11 Summary of some studies for biodiesel synthesis using membrane.......66

Table 3.12 Summary of some studies for biodiesel synthesis using static mixer.....69

Table 3.13 Summary of some studies for green diesel synthesis through hydro treatment 75

Table 3.14 Summary of some studies for glycerin free synthesis of biodiesel through substituting methanol 86

Table 4.1 Fatty acid composition (% wt) of Jatropha and Pongamia oil used in this study........98

Table 4.2 Physical property characterization of Jatropha and Pongamia oil used in this study 98

Table 4.3 Characterization of Jatropha and Pongamia oil derived DMC-Biodiesel from this study vis-a vis international standards........110

Table 5.1 Physical and thermodynamic properties of DMC and DEC........117

Table 5.2 Fatty acid composition (% wt) of Jatropha and Pongamia oil used in this study 121

Table 5.3 Process parameter comparison for glycerin free synthesis of biodiesel vis-à-vis present study 128

Table 5.4 Comparison of predicted and measured normal boiling point of Jatropha and Pongamia biodiesel 140

Table 5.5 Characterization of Jatropha and Pongamia oil derived DMC/DEC-biodiesel........141

Table 6.1 Description of operating conditions of main equipment in catalytic glycerin free biodiesel process 149

Table 6.2 Description of operating conditions of main equipment in non-catalytic glycerin free biodiesel supercritical process........151

Table 6.3 Feed composition for the ASPEN Plus simulation in catalytic and non-catalytic supercritical route 159

Table 6.4 Product composition of the RStoic reactor used for yield reactor product specification 160

Table 6.5 Product composition of the Rstoic reactor used for yield reactor product specification 161

Table 6.6 Simulated yield and purity of product stream in catalytic and non-catalytic supercritical route 164

Table 6.7 Simulated yield and purity of byproduct stream in catalytic and non-catalytic supercritical route 164

Table 6.8 Percent increase in yield in new biodiesel production process compared to the conventional process. 165

Table 6.9 Energy requirement based on the simulated operation for the catalytic and non-catalytic process 166

Table 6.10 Detail heat exchanger design for catalytic route 168

Table 6.11 Utility requirements from HEN network for catalytic route 168

Table 6.12 Detail heat exchanger design for non-catalytic supercritical route 169

Table 6.13 Utility requirements from HEN network for non-catalytic supercritical route 169

LIST OF FIGURES

Figure 1.1 Estimated production of crude glycerol in different countries...............11

Figure 1.2 Change of trend for glycerin supply driver 12

Figure 1.3 Supply and demand of crude glycerol in different regions 13

Figure 1.4 Price trend of glycerin 14

Figure 3.1 Simplified process flow diagram for conventional homogeneous process 24

Figure 3.2 Simplified process diagram flow of conventional heterogeneous process 33

Figure 3.3 Process for hydrotretment of vegetable oil for Green diesel production...73

Figure 4.1 Reaction mechanism of glycerin free and convention synthesis of biodiesel...93

Figure 4.2 Effect of diverse nature of reactants and KOH presence in oil-DMC /methanol system 99

Figure 4.3 Effect of catalyst amount on conversion for synthesis of biodiesel from Jatropha and Pongamia oil with DMC under reflux condition for 8 h reaction time 101

Figure 4.4 Effect of molar ratio of DMC to oil on conversion for synthesis of biodiesel from Jatropha and Pongamia oil with DMC at 9% catalyst amount, 8 h reaction time and under reflux condition..102

Figure 4.5 Effect of temperature on conversion for synthesis of biodiesel from Jatropha and Pongamia oil with DMC, at 10:1 molar ratio of DMC to oil, 9% catalyst amount and 8 h reaction time 103

Figure 4.6 Effect of reaction time on the conversion for synthesis of biodiesel from Jatropha and Pongamia oil with DMC, at 9% catalyst amount, 10:1 molar ration of DMC to oil and under reflux condition 104

Figure 4.7 Kinetics of Jatropha DMC-biodiesel and Pongamia DMC-biodiesel synthesis at various temperatures using 9% catalyst amount and 10:1 molar ratio of DMC to oil 106

Figure 4.8 Envisaging the rate constant for synthesis of Jatropha DMC-biodiesel and Pongamia DMC-biodiesel through ln $[1/(1-X_{TG})]$ as a function of reaction time t, at various temperatures based on 10:1 molar ratio of DMC to oil, 9% KOH as catalyst amount 107

Figure 4.9 Variation of the rate coefficient, k with temperature for the synthesis Jatropha DMC-biodiesel and Pongamia DMC-biodiesel 108

Figure 4.10 Conceptualized process flow diagram for glycerol free DMC-Biodiesel synthesis 111

Figure 5.1 Experimental setup of autoclave for supercritical synthesis of biodiesel. 118

Figure 5.2 Effect of molar ratio on conversion for synthesis of biodiesel at 325°C in 40 min under supercritical DMC and DEC.. 123

Figure 5.3 Effect of temperature and reaction time for synthesis of biodiesel in supercritical DMC/DEC. 126

Figure 5.4 Reaction mechanism for glycerin free synthesis of biodiesel 130

Figure 5.5 Envisaging the rate constant for synthesis of Jatropha/Pongamia Biodiesel through ln [1/(1-X_{TG})] as a function of reaction time at 40:1 molar ratio of reactants to oil under various temperatures in supercritical DMC/DEC conditions. 132

Figure 5.6 Variation of the rate coefficient, (k), with temperature for supercritical synthesis of biodiesel in DMC/DEC 133

Figure 5.7 Thermal stability of biodiesel under various temperatures at 150 bar in supercritical condition of DMC and DEC. 136

Figure 5.8 Distillation Characteristics (by ASTM D1160 unit) of biodiesel synthesized in supercritical condition of DMC and DEC 138

Figure 5.9. Conceptualized process flow diagram for non-catalytic glycerin free supercritical process for biodiesel synthesis 142

Figure 6.1 ASPEN plus simulated process flow schematic of Catalytic process for DMC-biodiesel production 153

Figure 6.2 ASPEN plus simulated process flow schematic of non-catalytic supercritical process for DMC-biodiesel production 154

Figure 6.3 The concentration of DMC in the biodiesel samples after water washing 156

Figure 6.4 Grid diagram for catalytic route from heat integration stream method 167

Figure 6.5 Grid diagram for non-catalytic supercritical route from heat integration stream method 167

Figure 7.1 Conceptualized process for microwave method 178

Figure 7.2 Conceptualized process for non-catalytic glycerin free supercritical DMC/DEC method..179

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials	GDC	glycerin dicarbonate
EN	European Committee for Standardization	GC	gas chromatography
IS	Indian Standard	E_a	activation energy
TGs	triglycerides	MOC	material of construction
FAAE	fatty acid alkyl ester	FA	fatty acid
FAMEs	fatty acid methyl esters	ACDG	alkyl carbonate diglyceride
FAESs	fatty acid ethyl esters	DACMG	dialkyl carbonate mono-glyceride
FFA	free fatty acid	AET	atmosphere equivalent temperature
SCF	supercritical fluid	T_{nb}	normal boiling point
DAC	dialkyl carbonate	bp	boiling point
DMC	dimethyl carbonate	DEC	diethyl carbonate
CSTR	continuous stirred tank reactor	PFR	plug flow reactor
NRTL	non-random two liquid model	UNIFAC	universal functional activity coefficient

CHAPTER 1

INTRODUCTION

Today, stringent environmental norms and depletion of oil reserves have added impetus for development of eco-friendly and sustainable fuel options. This has resulted into emergence of biofuels from sustainable bio-resources. In this context, fuels of bio-origin, such as bio-alcohols, biodiesel, biogas, green diesel, Bio-aviation turbine fuel (Bio-ATF) are found to be potential alternatives and are increasingly becoming important. Among these, vegetable oil based biofuel options i.e. biodiesel, green diesel and bio-ATF have become more attractive in recent time because of their ease of production from available vegetable oil feedstock options.

The direct use of vegetable oil as an alternative for diesel has been attempted in the past due to its portability, heat content (80% of diesel fuel), ready availability and renewability. However, its major disadvantages namely high viscosity, lower volatility and presence of unsaturated hydrocarbon have hampered its direct use as a diesel fuel [Pryde, 1983]. Therefore, different ways have been evolved to transform vegetable oil to compatible diesel fuel option. This has led to development of (a) dilution, (b) micro emulsions, (c) pyrolysis, (d) catalytic processing and (e) transesterification approaches to convert vegetable oil to viable biofuel option [Ma and Hanna, 1999]. Among all these alternatives, transesterification of vegetable oil with methanol leads to fatty acid methyl esters (biodiesel) formation having the physical characteristics that are very close to the diesel fuel [Selmi and Thomas, 1998; De, et al., 1999].

Conventionally, transesterification of vegetable oils with methanol is performed in the presence of homogeneous or heterogeneous alkali / acid as catalysts [Serdari et al., 1999; Aksoy et al., 1990]. The selection of alkali or acid catalysts mostly depends on the impurities like water content and free fatty acid (FFA) content of the oil. The alkaline catalysts are preferred for feedstock having FFA content of less than 0.5 wt% and consumption of catalyst is reported when FFA found to be more than 0.5% [Helwani et al., 2009]. The preferred alkaline homogeneous catalyst such as sodium hydroxide (NaOH), potassium hydroxide (KOH), and sodium methoxide (CH_3ONa) has been reported and successfully commercialized for production of biodiesel [Qian et al., 2010; Sharma et al., 2008]. This process is highly complex in nature due to the downstream separation and purification steps to produce biodiesel of requisite quality. Typically, downstream treatments involve separation of reaction product *viz.* biodiesel and glycerin from contaminants i.e. excess alcohol, soap formed (due to the presence of free fatty acid, FFA, in vegetable oil) and catalyst. Although the removal of the excess alcohol from both phases are achieved by distillation, but the removal of catalyst and soap is more complicated, time consuming, and often leads to lower biodiesel yields [Fukuda et al., 2001].

On the other hand, homogeneous acid catalyst is preferred for high FFA content where shows their ability to catalyze reactions like FFA esterification and transesterification of vegetable oil simultaneously. [Kulkarni and Dalai, 2006, Canakci and Van Gerpen, 1999]. The preferred catalysts are sulfuric acid (H_2SO_4) and hydrochloric acid (HCl), but are corrosive in nature, create handling issue during the operation. In addition, reaction kinetics is reported to be slow , requiring higher molar ratio of methanol to oil (12:1) and high reaction temperatures compared to conventional base catalytic process [Leung and Guo, 2006]. Therefore, basic catalytic processes are more commercially acceptable on the industrial scale over acidic catalytic process [Ma et al., 1998].

To overcome the limitations of the individual homogeneous process for both alkali and acid catalysts, two-step processes have been developed for biodiesel production for high FFA content feed stock. The two-step process consists of feed preparation (acid catalyzed FFA esterification to reduce the FFAs <0.5 %) followed by transesterification (base catalyzed) for achieving high biodiesel yield within a short reaction time at mild reaction conditions [Canakci and Van Gerpen, 2003]. The soap formation is eliminated in first step to produce esters which improves the product yield and reduces the complexities involved in the base catalyzed transesterification followed by downstream purification steps. Unfortunately, both the acid as well as alkali catalyzed transesterification routes of vegetable oil lead to poor quality of glycerin formation, which in turn demand complex purification steps leading to economic off balance of the process on sustainable basis. Therefore, to easy the separation and purification steps and improving the quality of product/byproduct, alternate heterogeneous alkali/acid routes are also developed for processing vegetable oil to produce biodiesel [Dossin et al., 2006; Mbaraka and Shanks, 2006].

The solid heterogeneous catalyst can handle high FFA (>0.5 %), avoid soap formation, offers regeneration and reusability, and provides eco-friendly option for easier separation /purification steps in downstream processing for biodiesel synthesis [Leung et al., 2010; Dossin et al., 2006; Mbaraka and Shanks, 2006]. The most commonly used basic catalysts are alkaline metals carbonates (Na_2CO_3, K_2CO_3), alkaline earth metal carbonates ($CaCO_3$), alkaline earth metal oxides (CaO, MgO, SrO, BaO) and transition metal oxides (ZnO) [Dossin et al., 2006; Fukuda et al., 2001; Liu et al., 2007; Lotero et al., 2005; Ma and Hanna, 1999; Verziu et al., 2008]. On the other hand, heterogeneous acid catalysts such as Nafion-NR50 (perfluorinated alkane sulfonic acid resin), sulfated zirconia-alumina (SZA), and tungstated zirconia–alumina (WZA), have also been investigated for biodiesel production [Lopez et al., 2007; Chai et al., 2007]. In addition, solid acids such as tungstated zirconia and sulfated zirconia can significantly promote the transesterification of vegetable oils as well as the esterification of FFAs [Kouzu et al., 2008; Furuta et al., 2004].

Based on heterogeneous catalyst, commercial processes namely Esterfip-H (using alkali catalyst, Zn/Al_2O_3) and ENSEL^{TM} (using acid catalyst, double metal cyanide complex) been demonstrated by M/s. Axens, France and M/s. Benefuel respectively [Bournay et al., 2005; Srinivas et al., 2009]. The pre-treatment of feed stock, high alcohol to oil molar ratio, elevated pressure and temperature conditions are recommended in both the transesterification process. Even though, such processes are envisaged to offer better overall economics for biodiesel production in view of the superior quality of glycerin produced compared to homogeneous catalyzed processes.

On the other hand, the commercial turnkey plants are reported to offer by M/s Lurgi, M/s Desmet Ballestra and M/s Pacific Biodiesel based on the homogeneous catalytic process [Pacific Biodiesel, 1996; GmbHL1996; Desmet Ballestra, 2008; Oh et al., 2012]. The offered commercial plants are using pre-treatment steps prior to transesterification with flexibility to handle variety of feed stocks. Here in the conventional process , pre-treatment of vegetable oil feedstock is highly recommended to overcome the problems associated with downstream processing. The overall performance of conventional process is mainly governed by impurity levels present in the vegetable oil as well as in the processed product. Therefore, to optimize the product yield and meet desired purity, process advances are made over the period in vegetable oil processing. Such advancement involves the use of pre-treatment steps, modified reactor designs and integration of non-conventional process intensification steps. This has resulted into development of various processing technologies for biodiesel production, which have been widely adopted [Serio et al., 2007; Bournay et al, 2005, Gogate and Kabadi, 2009; Ahmad et al., 2012]. In this context, use of supercritical conditions, enzymatic catalyzed, cavitation, membrane and microwave assisted transesterification have been explored [Saka and Kusdiana, 2001; Du et al., 2004; Refaat et al., 2008; Georgogianni et al., 2009; Cao et al., 2007].

To promote the reaction at very mild operating condition and ease of separation of catalyst/reactants/products, the bio-catalytic routes as "*Enzymatic process*" is very promising. Enzymatic transesterification of triglycerides offers an environmentally more attractive option to the conventional process. Biological reactions are similar to other chemical process, except that they are catalyzed by variety of biological catalysts mainly lipase [triacylglycerol acylhydrolase, EC (3.1.1.3)] such as Candida antarctica, Pseudomonas cepacia, Rhizopus oryzae, Candida rugosa, Rhizomucor miehei, Thermomyces lanuginosus, and Pseudomonas fluorescens [Moreira et al., 2007]. The enzymes are economically viable when employed in immobilized form for biodiesel production to enable the stability and reusability in the process of transesterification [Ranganathan et al., 2008]. Several researchers have investigated the transesterification reaction of vegetable oils with methanol by employing immobilized Novozym 435 (commercially available C. antarctica lipase) [Shimada et al., 1999]. However, it is also reported that deactivation of enzyme by methanol (0.5 M equivalent) and generation of viscous byproducts viz. glycerin simultaneously [Marchetti et al, 2008]. Therefore, researches have suggested the enzymatic transesterification in presence of chemical co-solvent, supercritical carbon dioxide and substituting methanol [Ha et al., 2007; Chen et al., 2006; Rathore et al., 2007]. Nevertheless, still it has fair share of constraints especially when implemented in industrial scale such as slow reaction rate, high cost of enzyme, and enzyme deactivation. Thus, development research need to adopt the approach to reduce the cost either using new immobilization techniques or extended robust nature of lipase through innovative reaction systems for larger scale commercialization in near future.

On the other hand, the disadvantages resulting from the use of a catalyst and its removal from the products, a non-catalytic process has been developed using supercritical condition of reactant s such as methanol [Saka and Kusdiana, 2001]. It is well know that the supercritical fluids (SCFs) are fluids above their critical temperature and pressure with gas like diffusivities and a liquid like viscosities. Typically, various types of reactions co-exist in the method for biodiesel production: transesterification of triglycerides, hydrolysis of triglycerides in presence of water and esterification of fatty acids. Thus, presence of water and FFA does not have any adverse effect on the conversion/yield compared to conventional methods [Kusudiana and Saka, 2001; 2004]. Typically, non-polar triglycerides are solvated with supercritical methanol to form a single phase oil/alcohol mixture followed by easy of separation and purification which is very unlike in conventional acid or alkali catalytic process [Bunyakiat et al., 2006; Saka and Kusdiana, 2001]. Thus, offers higher conversion and yield than that to conventional alkaline-catalyzed method. The merits are very short reaction time, simple separation followed by purification and easy tenability of processing parameters. On the contrary, the major demerits of supercritical reaction are; requirement of very high pressure and temperature, excessive molar ratio of alcohol to oil followed by its recovery, the degradation of biodiesel at an extremely high temperature with exposure of time and extremely high cost of the apparatus [Juan et al., 2011]. Therefore, their applicative potential at commercial level is yet to be established.

To intensify the transesterification reaction, the microwave assisted route has been envisaged where heating can be provided through electromagnetic energy namely “microwave irradiation” [Corsaro et al., 2004; Lertsathapornsuk et al., 2008]. Utilization of microwave process for the biodiesel can be explained on the basis of polarity of alcohol along with non polar triglyceride molecule, and base catalyst. Microwave induces the small degree of variance in polar molecules and ions, followed by in situ heat generation due to molecular friction to initiate the transesterification reactions [Azcan and Danisman, 2007; Saifuddin and Chua, 2004]. Therefore, comparing to conventional synthesis, a microwave transesterification is efficiently accelerated in a short reaction time due to instantaneous localized superheating which able to achieve similar biodiesel conversion [Refaat et al., 2008]. In sum, microwave heating is environmentally benign, more energy-efficient and favorably over conventional methods. Nevertheless, commercial scalability from laboratory level needs special attention due to penetration depth of microwave radiation and safety aspect.

In recent years another type of process intensification method, cavitation is a new, more efficient mixing method to enhance mass transfer rate in biodiesel production, compared to conventional method [Gogate and Kabadi, 2009; Pal et al., 2010]. Typically, transesterification is reported to be a mass transfer limited reaction due to the immiscible reactants, triglycerides and alcohol/methanol where mixing is important factor for increasing biodiesel yield/conversion. Cavitation can be classified as hydrodynamic and acoustic cavitation (ultrasonic irradiation) [Qiu et al., 2010]. Both the type of cavitation, induces high local energy densities, temperature and pressure within the reaction mass through generation of cavities followed by their growth and subsequently violent collapsing of the cavities, thereby delimiting the mass transfer and enhancing the reaction kinetics [Gogate and Kabadi, 2009; Qiu et al., 2010]. Thereby, all these effects provides sufficient activation energy to initiate the reaction which improves the reaction rate, yields and decreases the reaction time and energy consumption [Singh et al., 2007; Ji et al., 2006]. Recently, various cavitation based technologies for biodiesel production have been reviewed [Oh et al., 2012]. In this context, the patented hydrodynamic cavitation reactor i.e. Bioforce 9000 Nano developed by Cavitation Technologies Inc., has been successfully commercialized for biodiesel production and adopting with major oil plant engineering supplier, M/s Desmet Ballestra in Brazil [Gordon et al., 2011; Voegele E, 2009; Cavitation Technologies Inc., 2013].

In the continuation of process intensification, membrane assisted transesterification provides innovative efficient process solutions to biodiesel production [Sanchez Marcano and Tsotsis, 2002]. In recent year, application of membrane in biodiesel production has received attention owing to its operating principle which simultaneously offers the equilibrium of reversible transesterification reaction towards product formation and selective separation for improving the biodiesel quality [Cao et al., 2007]. Typically, membrane process integrate reaction and separation steps into a single step, thereby reducing separation costs and recycle requirements, and an enhancement of thermodynamically limited or product inhibited reactions resulting in higher conversions per pass [Reyes et al. 2012; Dubé et al., 2007]. Fundamentally, membranes restrict the flow large oil droplets, which form upon mixing and reaction of oil and methanol [Cao et al., 2008a, 2008b]. The membrane assisted biodiesel synthesis requires higher molar ratios of methanol to oil, low reaction temperature and ultralow catalyst concentration compared to conventional synthesis using stirred batch reactor [Cao et al., 2008a; Cheng et al., 2010]. Hence, offers the low capital and operating cost due to mild operating condition as well as elimination of intermediate processing step.

Another PI technique, specially designed stationary geometric helical elements fixed within a pipe called "Static mixers" which offers intense agitation with minimal energy consumption compared to conventional mechanical agitation. This type of rector comers under the plug flow type of reaction system. These elements promote micro-mixing through radial mixing and very effective in the mass transfer limited chemical reactions for immiscible liquids [Thompson et al., 2007]. They are widely used in the chemical, pharmaceutical, petroleum, waste treatment, and food processing industries. The continuous biodiesel production in presence of homogenous sodium hydroxide as catalyst is reported using static mixer reactor systems at much mild reaction conditions [Peterson et al., 2002; Thompson et al., 2007]. However, the mixing process relies mainly on slow, unforced molecular inter-diffusion in the laminar regime. This type of reactor operation is also reported for efficient biodiesel separation from emulsified reactants [Boucher et al., 2009].The advantages of such reactor are mainly, no moving parts, low space requirement, and low maintenance and operating cost. The utilization of static mixer/plug flow reactor in commercial scale has been demonstrated by M/s ENERGEA, Austria and M/s Spec Engineers India [SPEC, 2010]. The reactor offers less reaction time (20 sec), maximum yield and conversion using minimal energy [SPEC, 2010]. This technology is continuous evolving in combination of other PI options to produce biodiesel in more economically viable and environmental friendly manner.

Fundamentally, most of these process technologies increase the rate of reaction by intensifying mass and energy transport process and mixing between alcohol and oil. In sum, all methods hold merit over conventional process in terms of energy efficiency, eco-friendliness, very short reaction time, and high yield.

As discussed, in spite of conventional/non-conventional transesterification of vegetable with alcohol particularly methanol, ethanol etc. produces glycerol as byproduct. It is almost 10 % by weight of the oil and recovery of this crude glycerol along with methanol, water and residues of the alkaline catalyst leads to purification difficulties. This makes the price of purified glycerol, 10 times higher than the un-purified one. Furthermore, plenty of glycerol stock is anticipated to be available in the world market with increased production of biodiesel thereby forcing drop in crude glycerol pricing [McCoy, 2005; 2006]. Therefore, the overall economic viability of biodiesel production has been in question due to inferior glycerin quality and its oversupply.

In last decades, biodiesel have drawn serious attention as a renewable, biodegradable, and non-toxic fuel. Biodiesel is widely being commercialized and it has recently experienced a major surge worldwide. Figure 1 shows the clear estimated crude glycerol production resulting from biodiesel production in different countries and It is evident that the estimated production of glycerol would reach 5.8 billion pounds in 2020 [ABG Inc., 2007]. This is due to increase in demand of biodiesel that is projected at 8 billion gallons in 2020. Subsequently, the production of glycerol rapidly increased and many other countries like USA, Indonesia, Malaysia, China and India started to produce glycerol. The projected data suggest that the glycerol production will attain 4 billion lbs in 2015 if its production increases at the same pace. The estimated quantity will touch to 6 billion lbs after 2020 and majorly contributed from EU and then USA. The other countries those will boost glycerol production in future are Malaysia, India, China, Indonesia, Brazil, Argentina and Colombia.

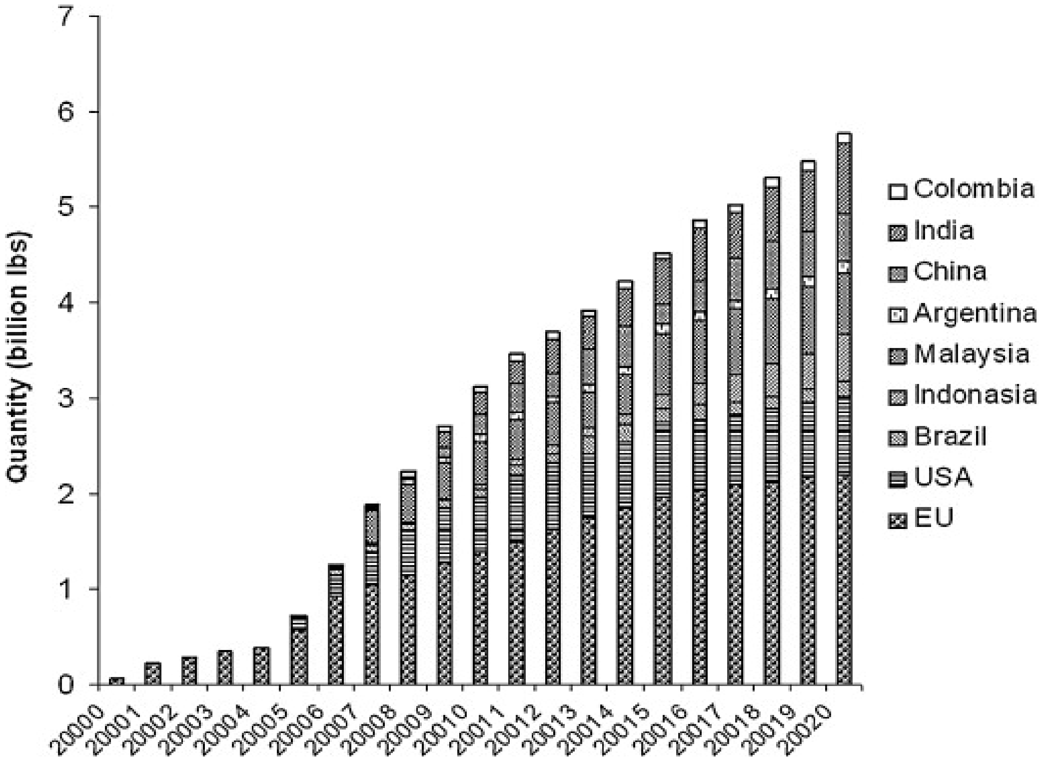


Figure 1.1 Estimated production of crude glycerol in different countries [ABG Inc., 2007].

An enormous change was observed between supply drivers of glycerol in the last 10 years. The source of glycerol was shifted from one of the most popular supply drivers, i.e. the fatty acids industry to biodiesel industry. It is also clear from this figure 2 that fatty acids and soap manufacturing were two main sources for glycerol production before biodiesel industry boosted up during past few years [Bogaart, 2009]. In 1999, the sources for production of glycerol were fatty acids, soap manufacturing process, fatty alcohols process and biodiesel process. The production ratio for these sources was at 47%, 24%, 12% and 9%, respectively. In 2009, these sources of glycerol were completely changed and they at 21%, 6%, 8% and 64%, respectively. Hence, biodiesel industry jumped up for biggest change in glycerol supply driver from 9% to 64% and fatty acid dropped from 47% to 21% during the same period. It can be summarized that quick changes in supply drivers and production of glycerol after 2006 was attributed to biodiesel industry. Hence, commercial production of biodiesel is going to create a glut of glycerol as a co-product; it will cause market prices of glycerol to be plummeting.

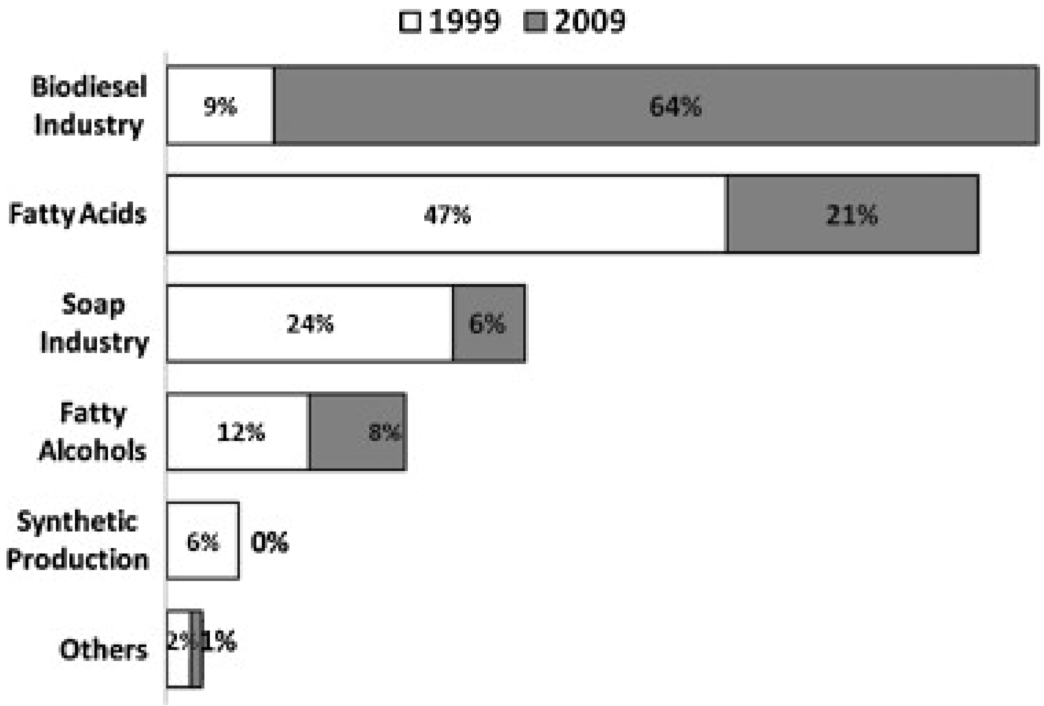


Figure 1.2 Change of trend for glycerin supply driver [Bogaart, 2009]

Currently, the global glycerol market is uncertain, there is strong gap in the demand and supply, world wide due to the shifting of supply derivers from soap and fatty acids to mostly biodiesel process.. However, oversupply problem is driving down the prices of crude glycerol globally. The crude glycerol prices dropped from 25 cents/lb in 2004 to 2.5–5 cents/lb in 2006 because the U.S. demand for glycerol was not large enough for all of this excess glycerol in 2007 [Yazdani and Gonzalez, 2007; Johnson and Taconi, 2007]. Figure 1.3 shows the supply and demand of crude glycerol during 2009 in different regions where crude glycerol played a vital role to their economy [Bogaart, 2009]. The glycerol supply during 2009 mostly originated from Europe, ASEAN, US and Latin America. In the same year, the supply of glycerol from these countries was 4 times less than its demand in China. It might be possible that the fluctuation in demand and supply is due to development of some new industries in ASAEN regions.

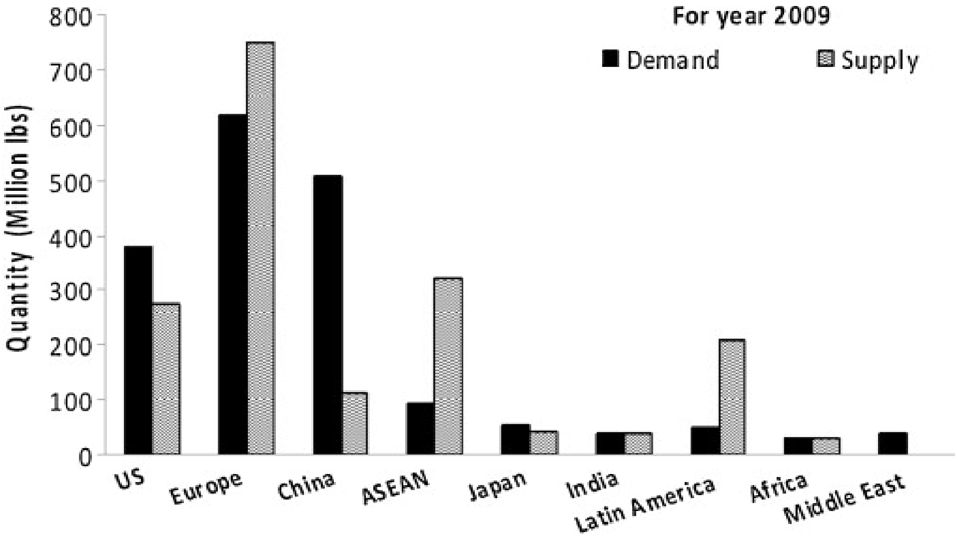


Figure 1.3 Supply and demand of crude glycerol in different regions during 2009 [Bogaart, 2009].

Currently, biodiesel production results in a rapid increase in the availability of crude glycerol worldwide and now refineries have hit the limits of their capacity. The prices for crude glycerol have fallen through the floor, falling down to zero and even negative as producers of glycerol (especially biodiesel) are forced to pay to have it taken away from their plants and incinerated [Miller, 2007]. On the other hand, the prices for refined glycerol have not varied inversely and price was stable from about \$1200 per ton to \$1800 per ton with biodiesel production till 2000. But 2000 onwards, both glycerol market became tight and significantly affected by supply from biodiesel market. Figure 1.4 shows that the down fall in price trends of all type of glycerol, even refine glycerol decreased from 2005 to first quarter of 2007 and making high in the start of year 2008. After that prices started to decline sharply till the end of year 2008 and then again became stable at their lowest prices in year 2009.

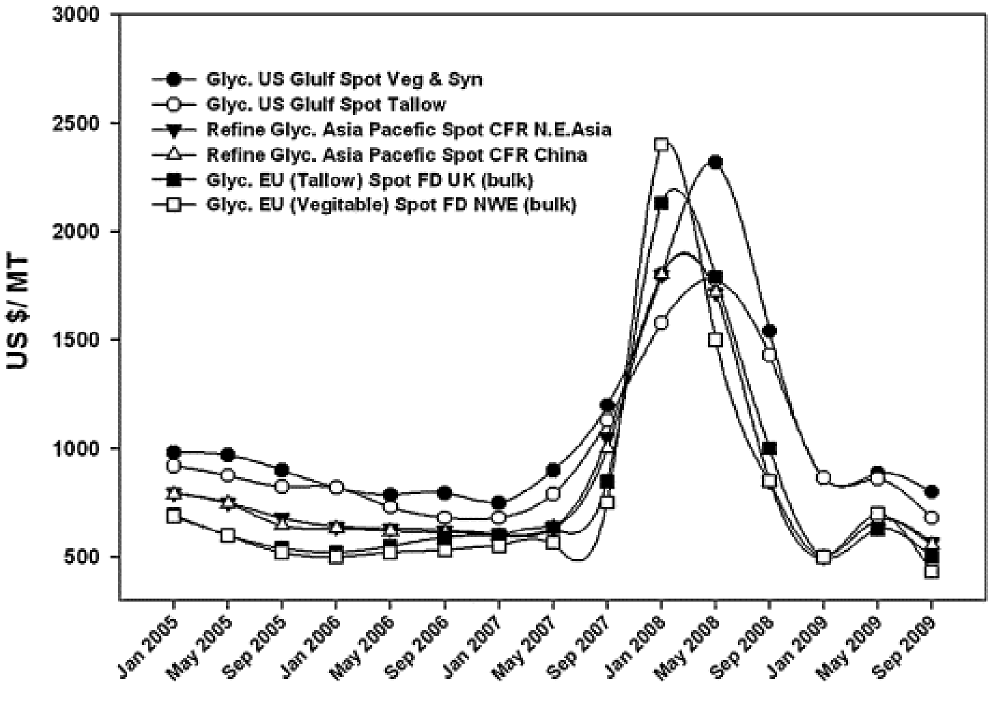


Figure 1.4 Price trend of glycerin during 2005–2009 [Bogaart, 2009].

Therefore, fluctuation in glycerol pricing is due to oversupply of glycerol resulting from biodiesel production process. The fluctuation in price of glycerol from 1995 to 2006 may primarily be attributed to the slowly increasing production of biodiesel. The increasing price of glycerol during 2007–2008 was due to an imbalance between supply and demand of glycerol in global market while the drop in prices after 2008 was due to oversupply of glycerol. This may also be caused by the global economic recession and the excess production of biodiesel in those years.

In the context of biodiesel market, the low value of glycerol plays a vital role because it is a major by-product in the formation of biodiesel. The market for crude glycerol has been relatively depressed due to a larger supply of crude than the ability to turn it into a refined product while the market for refined glycerol is still reasonably good. Unfortunately, conversion of crude glycerol into refined is not economically viable and does not support the biodiesel economics. Therefore, biodiesel total production cost is directly depends to the cost of oil feedstock and inversely proportional to glycerol credit. According to this scenario and viewing other factors like glycerol market it can be concluded that biodiesel may not be economically feasible any more under these circumstances. Hence, it is utmost important to balance glycerin's availability, quality and demand. Therefore, attempts have been reported either to valorize glycerin stream by converting it to fuel additives (glycerin ethers), specialty chemicals (propane diols, succinic acid, polyesters, lactic acid, and polyglycerins), hydrogen production or to eliminate glycerin formation during biodiesel process [Leoneti et al., 2012; García et al., 2008; Fabbri et al., 2007]. Furthermore, the efficiency of such processes are often found to be limited due to handling of feedstock containing high free fatty acids (FFAs) and moisture. However, it is superior if glycerol free biodiesel production could be achieved.

Hence forth, alternate to the existing conventional and non-conventional methods of biodiesel production other potential glycerin free biodiesel is conceptualized through two pathways namely hydroprocessing route and replacement of methanol as a reactant. The development hydroprocessing route has added impetus for integration of vegetable oil processing in existing oil refining processes. The hydrotreatment/hydroprocessing of triglycerides i.e. mainly vegetable oil or its blend with petroleum feedstock involves the cracking of larger molecules and hydrofining of derived products with hydrogenation in presence of catalyst. This process leads to produce a renewable liquid hydrocarbon mixture specially C_{15}-C_{18} hydrocarbons within the boiling range of petro-diesel. Such route offers platform for production of diesel and jet fuel fraction namely “Green Diesel” and “Bio-ATF”, respectively. The green diesel fuel fraction produced is found to have excellent cetane number vis-à-vis mineral oil based diesel fraction [Choudhary et al., 2011; Lestari et al., 2009]. In recent years, several refiners have had an increasing interest in producing renewable liquid fuels from the hydroprocessing of various triglycerides feedstocks, and commercially develop the process called as “Ecofining process” [Choudhary et al., 2011]. This complete process integrated with two-stage hydrorefining using two separate reaction mechanism, specially hydrodeoxygenation and hydroisomerisation. This first stage process produces hydrodeoxygenated paraffin rich diesel has high cetane number (>70) but poor cold flow properties (freezing point in between 20 and 28 °C). Therefore, second stage i.e. catalytic hydroisomerisation process is required additional hydrogen to convert long chain hydrocarbon into branched paraffin rich diesel to meet the cold flow properties [Bezergianni et al., 2009; Kovacs et al., 2011].

Typically, hydroconversion of triglycerides is reported performed in two schemes; hydroprocessing of triglycerides only and the co-processing of triglycerides with existing petroleum derived vacuum gas oil [Corma et al., 2007; Stern et al., 2000]. Implementation of the process scheme is not required additional facilities for refiners and can easily integrate with the existing infrastructure at refinery [Huber and Corma, 2007]. The operation costs can be reduced by using the existing installations and also would offer flexibility in the production scheme and a very good alternative to the production of mixed petro-biodiesel. The salient features of this route include, flexibility, ease of optimization to accommodate changes in feedstock, and integration with refinery operation. Nevertheless, there is limitation for blending vegetable oil into diesel pool and refineries are hesitating due to third party assurance on catalyst performance guaranty and commitment from process licensor.

On the other hand, alternatives of alcohols have been researched in recent years and substitution of methanol with dimethyl carbonate (DMC) and methyl acetate has been reported [Fabbri et al., 2007; Huang and Yan, 2008]. Therefore, this alternative novel process with potential reactants produces biodiesel (fatty acid methyl esters) and by products namely triacin [Isayama and Saka, 2007] and or glycerol carbonates [Ilham and Saka, 2009; 2010] instead of low valued glycerin from triglyceride with methyl acetate and DMC, respectively. The mixture of fatty acid methyl esters with triacin or glycerol carbonate can be used entirely as biofuel due to their miscibility, enhanced lubricity and improved combustion properties [Tundo and Selva, 2002; Delledonne et al., 2001]. Another merit of this method is that the mutual solubility of oil and DMC, which does not require any solvent, and act as a solvent to overcome the mass transfer limitation in the conventional method. However, catalytic DMC based transesterification synthesis is reported to have prolonged reaction time and high amount of catalyst owing to polarity difference between reactants and catalyst [Fabbri et al., 2007]. Therefore, non-catalytic supercritical DMC process using vegetable oil as a feedstock has been attempted [IIham and Saka, 2009 and 2010]. It is worthwhile to note that the reported process is a non-catalytic process, which offers the elimination of several cumbersome separation and purification steps as compared to conventional process. In addition, the by-products in supercritical synthesis such as glycerin carbonate (GC), glycerin dicarbonate (GDC), citramalic acid, glyoxal (if FFA is present), are highly valuable adducts [Ilham and Saka, 2009]. Hence, the discussed route is investigated for some of the edible oils which are not available in India. Therefore, the relevant work is sparse in literature and promising compared to other alternative route in terms of handle moisture and FFA content, offers more environment friendly reactant compared to methanol, nullify mass transfer resistance, generate valuable by product and avoid cumbersome downstream separation/purification steps. In view of the above, it is utmost important to investigate the glycerin-free synthesis route for non-edible oil from Indian context to develop glycerin free biodiesel process for successful implementation of biofuel program.

CHAPTER 2

SCOPE OF THE THESIS

2.1 Context

The over growing environmental concerns worldwide have added impetus for development and implementation of biofuel programs. This has led to implementation of biodiesel program, in many part of the world, to offer eco-friendly substitute in terms of sulfur free fuel for existing fossil fuels. Moreover, the implementation of such program has envisaged to offer better fuel economy in terms of lubricity and cetane number as compared to diesel fuel derived from crude oil. Thus, various process options, involving transesterification of triglycerides (TGs), sourced from vegetable oils or animal fats, with methanol to produce biodiesel i.e. fatty acid methyl esters (FAME) and by-product glycerin, have been evolved. Typically, processes based on homogeneous / heterogeneous catalytic route have been developed and commercialized. However, their sustainability is yet to be proven due to the market dynamics and cost involved in purification of by-product glycerin which constitute about 10% of the reaction product. This is mainly because of involvement of high capital and energy intensive steps involved in purification of crude glycerin formed in the process for its valorization in other applications. Therefore, commercial production of biodiesel is going to create a glut of glycerol which cause market prices of glycerin to be plummet. Thus, situation demands alternate route where could be no glycerin produced.

Henceforth, alternate reaction pathways were adapted substituting methylating agent like DMC/DEC instead of conventionally used methanol. Thus, high value co-products like glycerin carbonate (GC) and dicarbonate (GDC) were produced along with improved quality of biodiesel. This plat forms offers complete support to the entire biodiesel value chain for their economic sustainability in near future.

2.2 Purpose

The purpose of the study is to investigate the glycerin free synthesis of biodiesel using non-edible oil viz. Jatropha and Pongamia. The glycerin free biodiesel synthesis is carried out with DMC/DEC to address. Both reactants are neutral, non-toxic, non-corrosive, odorless, economical, and exhibits excellent solvent properties and considered to be versatile compound due to their eco-friendliness, chemical reactivity and physical properties. Synthesis was performed by two different routes; catalytic (using KOH) and non-catalytic supercritical phase of DMC/DEC. The produced DMC/DEC-biodiesel meets international standards with better lubricity, improved oxidation stability and high oxygen content. The ultimate objective is to conceptualize the catalytic and non-catalytic process for DMC/DEC-biodiesel synthesis and performed modeling and simulation studies. Therefore, the present work aims to investigate;

1. Glycerin free synthesis of biodiesel with and without catalyst under supercritical conditions of DMC/DEC using Jatropha and Pongamia oil, respectively
2. Optimizations of glycerin free biodiesel synthesis parameters *viz.* catalyst concentration, reactant molar ratio, temperature and reaction time.

3. Comparison of the kinetics studies and its parameters namely reaction rate constants (k) at different temperatures, activation energy (Ea) with the pre-exponential factor (k_o)
4. Establish the thermal stability of biodiesel fuel at high temperature *w.r.t.* the exposure time.
5. Evaluation of distillation characteristics and determination of boiling points
6. Characterization of produced biodiesel as per ASTM D6751/EN14214/IS15607 specifications
7. Conceptualization of process flow diagram for glycerin free synthesis of biodiesel using Jatropha and Pongamia oil as feedstock.
8. Process optimization, design and simulation studies using ASPEN Plus

2.3 Research Overview

The objective of this research is to scrutinize various conventional, non-conventional and glycerin free biodiesel production to economically balance the biodiesel process. Thus, the innovative options for glycerin free biodiesel process have been studied. Hence, a brief organization summary of the thesis is as follows.

Chapter 3 is a literature survey in the area of biodiesel/biofuel synthesis using convention and un-conventional routes which forms the basis of present study to explore the route for glycerin free synthesis. Chapter 4 deals with the synthesis of DMC-biodiesel from non-edible oils viz. Jatropha and Pongamia in presence of catalyst followed by optimization and kinetic study, where all parameters affect the conversion are investigated. Chapter 5 deals with study of synthesis of DMC/DEC-biodiesel from Jatropha and Pongamia in non-catalytic supercritical DMC/DEC followed by investigation of process parameters, optimization study, and kinetic study. In addition, degradation study of alkyl esters is also performed to further optimized the synthesis condition in supercritical DMC/DEC. Chapter 6 deals with the process simulation study of the proposed process scheme for catalytic and non-catalytic super critical route to investigate the economic viability. The summary and way forward is outlined in Chapter 7.

CHAPTER 3

LITERATURE SURVEY

This chapter summarizes the literature on various methods for conversion of vegetable oil (VO) into biofuels through conventional routes, non-conventional routes, process intensification routes and recently developed glycerol free biofuel production. The most common conventional transesterification routes are by employing either homogeneous or heterogeneous catalyst. The unconventional routes viz. enzymatic process, supercritical synthesis and, inclusion of process intensification by employing microwave, cavitation/ultrasonication, membrane, static mixers to maximize the yield, conversion and ease of separation and purification of product/byproduct. This chapter also focuses on the merit/demerit of the available commercial process for biodiesel production. Also, reviews on the newly developed glycerin free biofuel/biodiesel process technology viz. hydrotreatment and substitution of methanol.

3.1 Conventional routes for vegetable oil processing for biodiesel production

Transesterification route is the most common method of processing vegetable oil into biodiesel and it is practiced by employing either homogeneous or heterogeneous catalyst. The salient features of this process are discussed below.

3.1.1 Biodiesel through homogeneously catalyzed transesterification of vegetable oil

Transesterification of vegetable oil is performed by employing either acidic or alkaline types of homogeneous catalysts. The selection of alkali or acid catalysts mostly depends on the water content and free fatty acid (FFA) content of the oil which depends on the factors like source of oil, cultivation type and storage mechanism. The alkaline catalysts are preferred for feedstock having FFA content of less than 0.5 wt% [Helwani et al., 2009]. Thus, use of alkaline homogeneous catalyst such as sodium hydroxide (NaOH), potassium hydroxide (KOH), and sodium methoxide (CH_3ONa) has been reported and successfully commercialized for production of biodiesel [Qian et al., 2010; Sharma et al., 2008]. A simplified process flow diagram for conventional homogeneous process is depicted in Figure 3.1.

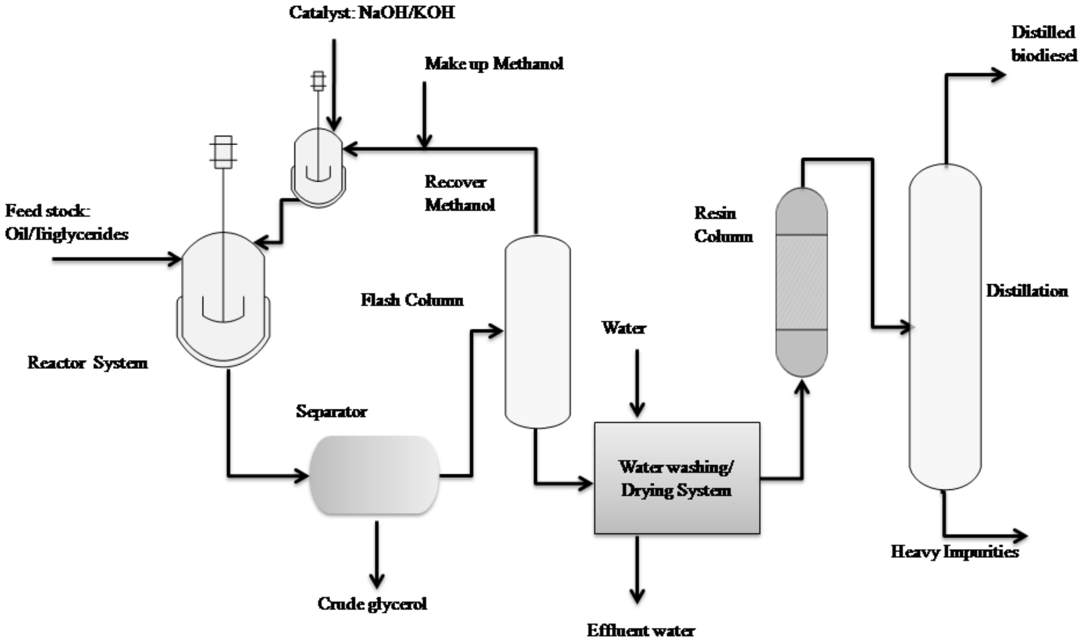


Figure 3.1 Simplified process flow diagram for conventional homogeneous process

The merits of homogeneous alkaline catalysed biodiesel production process are (1) lower reaction temperature (60-65 ^{o}C) and atmospheric pressure; (2) simple operation due to which it is widely preferred for biodiesel production at commercial level [Lotero et al., 2006].

However, alkaline catalyst under performs when applied over feedstock containing high FFA *i.e.* >0.5 wt %. This is mainly due to the neutralization of alkaline catalyst with FFA to produce sodium/potassium soaps [Marchetti and Errazu, 2008] which leads to prolonged reaction time. The formed soaps are miscible in by-product glycerin and subsequently demand their removal through the neutralization in presence of strong-concentrated inorganic acids (i.e. sulphuric, hydrochloric and phosphoric) or an organic acid (i.e. acetic acid). A brief summary of some studies for biodiesel synthesis using homogeneous alkali catalysts are compiled in Table 3.1.

Table 3.1 Summary of some studies for biodiesel synthesis using homogeneous base catalysts

Feedstock	Catalyst	Catalyst, wt.%	Temperature, ^{o}C	Reaction time, h	Yield/Conversion, %	References
Soybean	KOH	0.8	40	1	95^{a}	Zagonel et al., 2002
Sunflower	NaOH	1	60	2	97.1^{a}	Dias et al., 2008
Cottonseed	CH_3ONa	0.75	65	1.5	96.9^{a}	Rashid et al., 2009b
Rice bran	CH_3ONa	0.88	55	1	83.3^{a}	Rashid et al., 2009a
Palm	NaOH	1	60	0.5	95^{a}	Lubes & Zakaria et al., 2009
Palm kernel	KOH	1	60	1	96^{a}	Alamu et al., 2007
WFO	KOH	1.2	60	2	95.8^{a}	Dias et al., 2008
Jatropha	KOH	1	65	1	97.6^{a}	El et al., 2009
Jatropha	NaOH	1	60	1	98^{a}	Chitra et al., 2005
Jatropha	NaOH	3.3	65	2	55^{a}	Berchmans & Hirata, 2008
Jatropha	NaOH	0.8	45	0.5	96.3^{b}	Tapanes et al., 2008
Jatropha	KOH	1	50	2	97.1^{a}	Berchmans et al., 2010
Pongamia	KOH	1	60	1.5	92^{b}	Karmee & Chadha, 2005

Neem	NaOH	0.7	60-75	6.5-8	88–94 [a]	Nabi et al., 2008
Castor	NaOH, KOH, CH_3ONa, CH_3OK	0.2 (molar ratio)	60	1	85 [a]	Meneghetti et al., 2006
Castor	C_2H_5ONa	1	30	0.5	93.1 [a]	`Silva et al., 2009
Mahua	KOH	1	45	3	95 [a]	Kumar et al., 2011

[a] Yield

[b] Conversion

On the other hand, acid catalyst has low susceptibility to the FFA in the feedstock, and simultaneously has ability to catalyze reactions both the reaction like FFA esterification and transesterification of vegetable oil [Kulkarni and Dalai, 2006, Canakci and Van Gerpen, 1999]. The ssummary of few studies for biodiesel synthesis using homogeneous acid catalysts is presented in the Table 3.2. However, homogeneous acidic catalytic process suffers on the slow kinetics vis-a-vis alkali catalyst thus requiring higher molar ratio of methanol to oil (12:1) and high reaction temperatures (80–100 °C) [Leung and Guo, 2006]. Furthermore, the acid catalyzed process is reported to be very sensitive to water content [Leung and Guo, 2006]. Among acidic catalysts, sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) are the most-used catalysts in acid catalyzed transesterification processes [Man et al., 2010]. In addition, economic analysis has proven that acid catalyzed procedure, being a one-step process, is more economical than the base-catalyzed process which requires an extra step to convert FFA to methyl esters [Zhang et al., 2003a, b]. However, acidic catalyst are corrosive in nature, creates handling issue during the operation. Therefore, basic catalytic processes are more commercially acceptable on the industrial scale over acidic catalytic process [Ma et al., 1998].

Table 3.2 Summary of some studies for biodiesel synthesis using homogeneous acid catalysts

Feed stock	Catalyst	Catalyst, wt.%	Temperature, °C	Reaction time, h	Yield/Conversion, %	References
Soybean	H_2SO_4	1	65	69	>90[a]	Freedman et al., 1984
Soybean	HCl	10	70	45	65 [a]	Rachmaniah et al., 2004
Rice bran	HCl	10	70	6	>90 [a]	Rachmaniah et al., 2004
Corn	p-TsOHa	4	80	2	97.1 [a]	Guan et al., 2009
Canola	$AlCl_3$	5	110	18	98 [a]	Soriano et al., 2009
Mahua	H_2SO_4	6	65–70	5	92 [a]	Saravanan et al., 2010
Castor	H_2SO_4	0.2[c]	60	8	85 [a]	Meneghetti et al., 2006
	HCL	0.2 [c]	60	4	75 [a]	Meneghetti et al., 2006

[a] Yield

[b] Conversion

[c] Molar ratio

To overcome the limitations of the individual homogeneous process for both alkali and acid catalysts, two-step processes have been developed for biodiesel production using high FFA content vegetable oils. The two-step process consists of feed preparation (acid catalyzed FFA esterification) followed by transesterification (base catalyzed transesterification) to reduce the FFAs (below 1%) for achieving high biodiesel yield within a short reaction time at mild reaction conditions [Canakci and Van Gerpen, 2003]. By using an acid catalyst (mainly sulfuric acid) in the first step of the process, the soap formation is eliminated which improves the product yield and reduces the complexities involved in the downstream purification steps. However, higher amount of acid catalyst is required in the first step due to slow rate of FFA esterification reaction [Jain and Sharma, 2010; Lakshmi et al., 2011]. A summary of some studies for biodiesel synthesis using two step homogeneous acid - base catalysts is presented in Table 3.3.

Table 3.3 Summary of some studies for biodiesel synthesis using two step homogeneous acid/base catalysts

Feed stock	Catalyst	Catalyst, wt.%	Temperature, ^{o}C	Reaction time, h	Yield/Conversion, %	References
Jatropha	H_2SO_4	0.5	45	2	93^{b}	Patil et al., 2009
	KOH	2	60	2	95^{a}	
Jatropha	H_2SO_4	1	65	3	95^{b}	Jain & Sharma, 2010
	NaOH	1	50	3	90.1^{a}	
Jatropha	H_2SO_4	0.4	60	0.5	92^{b}	Wang et al., 2011
	KOH	1	60	0.5	86.2^{a}	
Pongamia	H_2SO_4	1	50	0.75	94^{b}	Patil et al., 2009
	KOH	0.5	50	0.5	80^{a}	
Pongamia	H_2SO_4	1	60	-	95^{b}	Lakshmi et al., 2011
	KOH	1	60	1	97^{b}	

^{a}Yield
^{b}Conversion

The sustainability of the aforementioned processes is mainly governed by the quality of the feedstock and by product i.e. glycerin formed during the process. Typically, both the acid as well as alkali catalysed transesterification routes of vegetable oil lead to poor quality of glycerin formation, which in turn demand complex purification steps leading to economic off balance of the process on sustainable basis. This has added a quest for development alternate routes to process vegetable oil for biodiesel production. The efforts made in this regard are listed below.

3.1.2. Biodiesel through heterogeneously catalyzed transesterification of vegetable oil

The use of solid heterogeneous catalyst offers eco-friendly option for biodiesel synthesis due to its ease of regeneration and reusability [Dossin et al., 2006; Mbaraka and Shanks, 2006]. In addition, solid catalysts also offer ease of operation and efficiencies to handle high FFA (>0.5 %) as well as low quality feed stocks for production of biodiesel [Leung et al., 2010]. Moreover, heterogeneous catalyzed biodiesel production does not face the obstacle of soap formation and as a result offers platform for easier separation and purification steps in downstream processing. This in turn often leads to ease formation of better quality of glycerin during the process [Nakagaki et al., 2008].

Typically, literature reports the investigation on both acidic and basic heterogeneous catalysts and their combination for processing of vegetable oil for biodiesel production. The most commonly used basic catalysts are alkaline metals carbonates (Na_2CO_3, K_2CO_3), alkaline earth metal carbonates ($CaCO_3$), alkaline earth metal oxides (CaO, MgO, SrO, BaO) and transition metal oxides (ZnO) [Dossin et al., 2006; Fukuda et al., 2001; Liu et al., 2007; Lotero et al., 2005; Ma and Hanna, 1999; Verziu et al., 2008]. On the other hand, heterogeneous acid catalysts such as Nafion-NR50 (perfluorinated alkane sulfonic acid resin), sulfated zirconia-alumina (SZA), and tungstated zirconia–alumina (WZA), have been investigated for biodiesel production [Lopez et al., 2007; Chai et al., 2007]. In addition, solid acids such as tungstated zirconia and sulfated zirconia can significantly promote the transesterification of vegetable oils as well as the esterification of FFAs [Kouzu et al., 2008; Furuta et al., 2004]. A simplified process diagram based on heterogeneous process is presented in Figure 3.2.

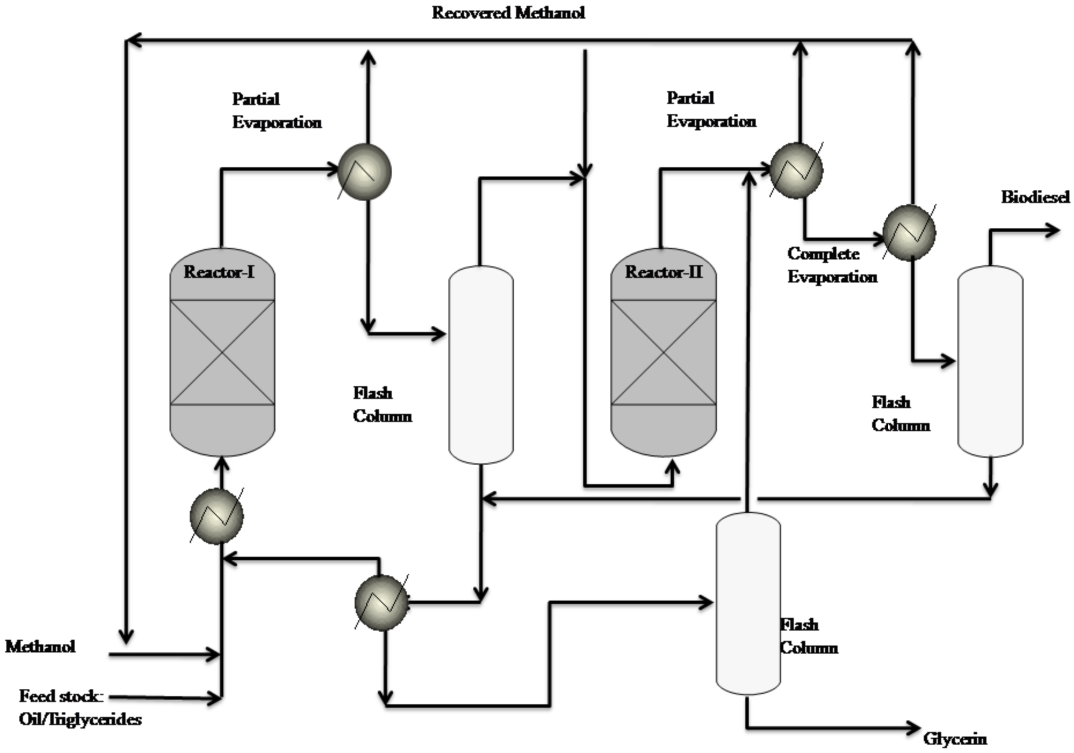


Figure 3.2 Simplified process diagram flow of conventional heterogeneous process

A typical overview of different solid catalysts employed for vegetable oil processing to produce biodiesel is given in Table 3.4.

Table 3.4 Summary of some studies for biodiesel synthesis using heterogeneous catalysts

Feed stock	Catalysts	Molar Ratio, Methanol/Oil	Reaction time, h	Temperature, °C	Yield/ Conversion, %	References
Soybean	MgO, ZnO, Al2O3	55	7	70, 100, 130	82^{b}	Antunes et al., 2008
Soybean	Cu and Co	5	3	70		Wang et al., 2006
Soybean	WO_3/ZrO_2, zirconia–Alumina and sulfated tin oxide	40	20	200–300	90^{b}	Furuta et al., 2004
Soybean	Calcined LDH (Li–Al)	15	1–6	65	71.9^{b}	Shumaker et al., 2008
Soybean	La/zeolite beta	14.5	4	160	48.9^{b}	Shu et al., 2007
Soybean	MgO MgAl2O4	3	10	65	57^{b}	Wang, et al., 2008
Soybean	CaO, SrO	12	0.5–3	65	95^{b}	Liu et al., 2008/Liu et al., 2007
Soybean	ETS-10	6	24	120	94.6^{b}	Suppes et al., 2004
Sunflower	CaO/SBA-14	12	5	160	95^{b}	Albuquerque et al., 2008
Jatropha Curcas	CaO	9	2.5	70	93^{b}	Huaping et al., 2006
VO	Cs-hetero poly acid,	19.4	1	75	70^{b}	Park et al., 2008

	SO_4^{2-}/ZrO_2, SO_4^{2-}/Al2O3, SO_4^{2-}/SiO_2, WO_3/ZrO_2					
Rape seed	Mg–Al HT	6	4	65	90.5 [b]	Zeng et al., 2008
Sunflower	NaOH/alumina	6–48	1	50	99 [b]	Arzamendi et al., 2007
Palm	Mg–Al–CO3 (hydrotalcite)	30	6	100	86.6 [b]	Xie et al., 2006/Trakarnpruk et al., 2008
Cotton seed	Mg–Al–CO3 HT	6	12	180–210	87 [b]	Barakos et al., 2008
Blended VO	Mesoporous silica loaded with MgO	8	5	220	96 [b]	Li & Rudolph, 2008
Jatropha	Montmorillonite KSF	12	6	160	68[a]	Zanette et al., 2011
Jatropha	Amberlyst 15	16	3	65	59 [a]	Supamathanon et al., 2011
	K/NaY zeolite	16	6	65	73 [a]	
Jatropha	CaMgO	15	3	65	83[b]	Taufiq-Yap et al., 2011
Jatropha	CaO $Fe_2(SO_4)_3$	9	3	70	100 [a]	Endalew et al., 2011
	Li–CaO+ $Fe_2(SO_4)$	9	3	70	100 [a]	
Pongamia	Li/CaO	12	1	65	>99 [a]	Kaur and Ali, 2011
Pongamia	ZnO	10	24	120	83 [a]	Karmee and Chadha,

						2005
Castor	$Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$	29	3	60	20 [a]	Zieba et al., 2010
Castor	TiO_2/ SO_4^{2-}	6	1	120	25 [a]	Almeida et al., 2008
Cottonseed	TiO_2- SO_4^{2-}	12	8	230	>90 [a]	Chen et al., 2007
Cottonseed	KF-Al_2O_3	12	3	65	>90 [a]	Lingfeng et al., 2007

[a] Yield

[b] Conversion

Interestingly, the combination of homogeneous and heterogeneous catalyst system has also been investigated for biodiesel synthesis [Corro et al., 2010; Deng et al., 2011; Sharma et al., 2010]. The summary of few studies reported on biodiesel synthesis using two-step homogeneous and heterogeneous catalysts is compiled in Table 3.5 wherein heterogeneous catalysts are used either to catalyze FFA esterification or transesterification of vegetable oil.

Table 3.5 Summary of some studies for biodiesel synthesis using two step homogeneous and heterogeneous catalysts

Feed stock	Catalysts	Molar Ratio, MeOH/Oil	Reaction time, h	Temperature, °C	Yield/ FFA Conversion, %	References
Jatropha	$SiO_2{\cdot}HF$	12	60	1	96[b]	Corro et al., 2010
	NaOH	6	60	2	99.6[a]	
Jatropha	H_2SO_4	40(methanol to FFA)	60	1	88 [b]	Deng et al., 2011
	Hydrotalcite with Mg/Al molar ratio	4	45	1.5	95[a]	
Mahua	H_2SO_4	6	55	1	91 [b]	Singh et al., 2011
	CaO	8	65	2.5	95[a]	
Pongamia	H_2SO_4	6	65	1	91 [b]	Sharma et al., 2010
	CaO	8	65	2.5	95[a]	
Neem	SO_4^{2-}/ZrO_2	9	65	2	94 [b]	Muthu et al., 2010
	KOH	6	60	2	95y	

[a] Yield

[b] Conversion

Owing to the aforementioned distinct advantages of heterogeneous catalyst systems, M/s Axens, France, using proprietary solid catalyst (Zn/Al2O3), has developed a continuous biodiesel production process viz. Esterfip-H. The Esterfip-H process consists of two fixed bed catalytic reactors producing biodiesel by transesterification of oils such as sunflower, soybean and rapeseed with methanol under high temperature and pressure conditions [Bournay et al., 2005]. The excess methanol is removed after each of the two reactors by a partial flash vaporization. The salient features of this process include production of biodiesel with minimum purification steps along with high quality glycerin. However, such process demands utmost control on moisture level during the feedstock processing to avoid hydrolysis of formed biodiesel phase under reaction conditions. On similar lines, a process *viz.* ENSEL^{TM} based on solid acid catalyst *viz.* double metal cyanide complex has been developed wherein esterification of FFA present in vegetable oil and transesterification of vegetable oil is performed at elevated temperature (150-200 ^{o}C) and pressure to produce biodiesel [Srinivas et al., 2009**]**. Such processes are envisaged to offer better overall economics for biodiesel production in view of the superior quality of glycerin produced compared to homogeneous catalyzed processes.

On similar lines, efforts are also been made to improve the cost benefit for homogeneous route by applying non-conventional approaches for vegetable oil processing to develop rapid, energy efficient and cost effective processes keeping in view of the enhancement of the quality of by-product. The efforts made in this context are discussed in the following section.

3.2 Non-Conventional routes for vegetable oil processing for biodiesel production

3.2.1 Enzyme-catalyzed transesterification

In recent years, enzymes have gained importance due to their ability to catalyze reactions for biofuel production by offering ease of separation while comparing with conventional method of production [Robles-Medina et al., 2009]. Typically, enzymes are biocatalyst, principally naturally occurring lipases which are isolated from a number of bacterial species such as Candida antarctica, Pseudomonas cepacia, Rhizopus oryzae, Candida rugosa, Rhizomucor miehei, Thermomyces lanuginosus, and Pseudomonas fluorescens [Moreira et al., 2007]. The enzymes are typically employed in immobilized form for biodiesel production to enable the stability and reusability of enzyme in the process of transesterification. Immobilization can be provided by several methods viz. adsorption, covalent bonding, entrapment, encapsulation, and cross-linking, by embedding the enzyme on solid support. These methods provide the stability and option of recycling the enzyme in the process of transesterification, and reduce the overall cost of the enzyme which is considered to be the biggest hurdle in commercialization.

Several researchers have investigated the transesterification reaction of vegetable oils with methanol by employing immobilized Novozym 435 (commercially available C. antarctica lipase) [Shimada et al., 1999]. This immobilized enzyme found to slightly economically viable for transesterification of vegetable oil [Ranganathan et al., 2008].

Typically, enzymatic catalysis proceeds at mild reaction conditions viz. near to stoichiometry molar ratio of alcohol to vegetable oil (3:1), mild temperature (40-

50^{o}C), stirring speed of about 200 rpm, enzyme concentrations in the range of 12.5–25%, with reaction time of 4–8 h. Furthermore, it offers high quality products and by-product (glycerin), ease of product recovery, and also insensitive to FFA content present in oil [Kulkarni and Dalai, 2006]. Hence, these facts proves that enzyme catalyzed biodiesel production has immense potential to be an eco-friendly and a promising alternative to the chemical process. Thus, attempts have been made to investigate the potential of various enzymes for transesterification reaction of vegetable oils using methanol (Table 3.6).

Table 3.6 Summary of some studies for enzymatic biodiesel synthesis

Feed stock	Catalyst	Catalyst, wt.%	Reaction time, h	Temperature, °C	Yield/ Conversion, %	References
Soybean	Candida antarctica	4	30	48	93.8[a]	Van Gerpen et al., 2004
Soybean	Lipozyme RMIM	7	50	4	60 [a]	Lv et al., 2009
Sunflower	Candida antarctica	3	45	50	>99 [a]	Reyes-Duarte et al., 2005
Olive pomace	Thermomyces lanuginosus lipase	5	25	24	93 [a]	Yücel, 2011
Jatropha	Burkholderia cepacia lipase	5	40	12	95 [a]	Kawakami et al., 2011
Rapeseed	Candida antarctica	5	40	24	76.1 [a]	Watanabe et al., 2002
Jatropha	Pseudomonas cepacia	5	50	8	98 [a]	Shao et al., 2008

WCO	Novozym 435	15	44.5	12	100 [a]	Azócar et al., 2010a
Castor	Novozym 435 and Lipozyme IM	20	65	6	81.4–98.0 [a]	Oliveira et al., 2004
Grease	Pseudomonas cepacia (PS30)	13.7	38.4	2.47	96 [a]	Wu et at., 1999
WCO	Novozym 435	4	30	50	90.9 [a]	Watanabe et al., 2001
	Rhizopus oryzae	30	40	30	88–90 [a]	Chen et al., 2006

---

[a] Yield
[b] Conversion

However, it is also reported that enzyme activity suffers significantly by addition of methanol (0.5 M equivalent) in the beginning of the reactions and also generation of byproducts viz. glycerin simultaneously [Marchetti et al, 2008]. Therefore, researches have suggested the stepwise addition of methanol, substitution of acyl acceptor (viz. methyl acetate, acetate ethyl) to avoid formation of glycerin and addition of high concentration of chemical co-solvent (viz. t-butanol, 1,4-dioxane, ionic liquid) to improve the solubility [Ha et al., 2007; chen et al., 2006]. Nevertheless, additions of chemical solvents are being discouraged due to environmental concerns.

To overcome this aspect, enzymatic transesterification of vegetable oil has been attempted under supercritical carbon dioxide ($SCCO_2$) conditions. The use of supercritical carbon dioxide phase offers distinct advantages in enhancing solubility of non-polar organics (vegetable oil) in polar phase (methanol) with extremely high diffusivities. A simultaneous use of $SCCO_2$ and enzymatic catalysis is reported to favour eco-friendly transformation of vegetable oil into biodiesel (Table 3.7). However, owing to the slow reaction kinetics, this route is not preferred at industrial scale.

Table 3.7 Summary of some studies for enzymatic biodiesel synthesis in supercritical carbon dioxide

Feed stock	Catalyst	Catalyst, wt.%	Reaction time, h	Temperature, °C	Conversion, %	References
Sunflower	Novozym 435 Supercritical methanol/ethanol in supercritical CO2	30	45	12	23^a, 27^b	Giridhar et al., 2004
Sesame	Novozym 435 Candida Supercritical methanol/ethanol in supercritical CO2	10	50	24	60^a, 51^b	Varma et al., 2010
Mustard	Novozym 435 Candida Supercritical methanol/ethanol in supercritical CO2	10	50	24	71^a, 71^b	Varma et al., 2010
Soybean	Candida antartica lipase Supercritical methanol in supercritical CO2		45	6	58^a	Lee et al., 2009
Olive					65.8^a	
Sunflower					50^a	

Rapeseed					60 [a]	
Palm					59	
Groundnut		30	45	15	~65 [a], 75[b]	Rathore et al., 2010
Palm	Novozym 435 Supercritical methanol/ethanol in supercritical CO2	30	45	15	~65 [a], 75[b]	
Pongamia pinnata		30	45	24	~47 [a], 52 [b]	
Jatropha curcas		30	45	24	~47 [a], 56 [b]	

---

[a] Conversion into methyl ester
[b] Conversion into ethyl ester

3.2.2 Transesterification under supercritical methanol phase

Transesterification of vegetable oil in supercritical methanol phase is one of the non-catalytic method for biodiesel production [Saka and Kusdiana, 2001]. It is well known that the supercritical fluids (SCFs) are fluids above their critical temperature and pressure with gas like diffusivities and a liquid like viscosities. Thus, high solubility of vegetable oil in supercritical methanol phase leads to form a single phase, thus allowing rapid formation of biodiesel phase with highly pure glycerin phase. Unlike, conventional catalytic process, such reaction approach is found to be insensitive to moisture content as well as FFA content of vegetable oil and offers ease of separation and purification of biodiesel phase [Bunyakiat et al., 2006; Saka and Kusdiana, 2001]. Conversely, the supercritical method simultaneous promotes the hydrolysis of triglyceride (TG) in presence of moisture, esterification in presence of FFA and largely transesterification which in sum turns into a positive effect on fatty acid methyl ester yield [Saka and Kusdiana, 2001, Kusudiana and Saka, 2001; 2004]. In contrast, moisture and presence of FFA are unacceptable in conventional industrial method of biodiesel production due to formation of soap and deactivation of the catalyst. Furthermore, reaction is supercritical alcohol is much faster due to reduction in diverse polarity behaviours of TG and alcohol, which provide high conversion and high yield. Reported studies claims that the complete conversion is achieved within 10 min of reaction at high molar ratio of alcohol to oil (40:1), high pressure (20–40MPa), high temperature (250–400°C) [Saka and Kusdiana, 2001; Kawashima et al., 2009].

The literature reports the investigation on effect of the process parameters like reaction temperature, pressure, alcohol to oil molar ratio, and reaction time on supercritical transesterification [Demirbas, 2009; Hawash et al., 2009; Rathore and Madras, 2007; Valle et al., 2010]. Typically, an increase in the reaction temperature and pressure is reported to have favourable effect on the conversion and biodiesel yield, which attributes to the supercritical properties of alcohol [Campanelli et al., 2010; Rathore and Madras, 2007]. In addition, a very high molar ratio (40:1) is also reported to drive the reaction equilibrium in the forward direction for achieving almost complete conversion [Campanelli et al., 2010]. The yield of fatty acid methyl esters is found to be increased with increasing the molar ratio of methanol to oil, perhaps due to the increased contact area between alcohol and triglycerides [Hawash et al., 2009, Rathore and Madras, 2007]. The optimal condition is zeroed at temperature (300^{O}C), pressure (9 MPa) and reaction time (15 min) in which biodiesel yield is reported to be more than 97% [Saka and Kusdiana, 2001]. The studies pertaining to aforementioned reaction parameters on biodiesel synthesis under supercritical methanol medium are compiled Table 3.8.

However, the use of supercritical approach suffers major disadvantage due to requirement of very high pressure and temperature, excessive molar ratio of alcohol/methanol to oil and probable degradation of biodiesel at an extremely high temperature with exposure of time [Juan et al., 2011]. Thus, their applicative potential at commercial level is yet to be established.

Table 3.8 Summary of some studies for biodiesel synthesis in supercritical condition

Feed stock	Alcohol	Molar ratio, Alcohol/oil	Temperature, Pressure	Reaction time, min	Yield/ Conversion, %	References
Rapeseed	Supercritical methanol	42:1	350 °C, 19 Mpa	4	95^{a}	Kusdiana and Saka, 2001
Rapeseed	Supercritical methanol	42:1	350 °C, 30 Mpa	4	95^{b}	Saka and Kusdiana, 2001
Rapeseed	Supercritical methanol	42:1	350 °C, 35 Mpa	4	98.5^{b}	Saka & Kusdiana, 2002
Rapeseed	Supercritical methanol	42:1	350 °C,14 Mpa	4	35^{a}	Kusdiana & Saka, 2001
Rapeseed	Subcritical acetic acid	54:1	300 °C, 20 MPa	30	92^{a}	Saka et al., 2010
	Supercritical methanol	14:1	270 °C, 17 MPa	15	97^{a}	
Rapeseed	Supercritical methanol +metal oxide catalysts (ZnO)	40:1 % 1 (wt) ZnO	250 °C, 105 bar	10	95.2^{a}	Yoo et al., 2010
Rapeseed	Subcritical water+Two-step supercritical methanol	1:1 (v/v) 1.8:1 (v/v)	270 °C, 20 MPa 320 °C, 20 MPa	60 10	90^{a}	Minami & Saka, 2006
	Supercritical methanol	1.8:1 (v/v)	380 °C, 20 MPa	15	80^{a}	

Purified palm	Supercritical methanol	40:1	372 °C, 29.7 MPa	16	81.5 [a]	Tan et al., 2010c
	Supercritical ethanol	33:01:00	349 °C, 26.2 MPa	29	79.2 [a]	
Palm	Supercritical methanol	30:1	360 °C, 22 MPa	20	72 [a]	Tan et al., 2009
Refined, bleached and deodorized palm	Supercritical methanol	45:1	350 °C, 40 MPa	5	90 [a]	Song et al., 2008
Soybean	Supercritical methanol	40:1	310 °C, 35 MPa	25	96 [a]	He et al., 2007
Refined soybean	Supercritical methanol	42:1	350 °C, 20 MPa	10	95 [a]	Yin et al., 2008
	Supercritical methanol+hexane (co-solvent)		300 °C	30	85.5 [a]	
	Supercritical methanol+CO2 (co-solvent)		300 °C	30	90.6 [a]	

	Supercritical methanol+ KOH		160 °C, 10 MPa	30	98 [a]	
Sunflower	Supercritical methanol + calcium oxide (%3 wt)	41:1	525 K, 24 Mpa	6	100 [a]	Demirbaş, 2007
Jatropha	Supercritical methanol	40:1	350 °C, 200 bar	40	>90 [b]	Rathore & Madras, 2007
Jatropha	Supercritical methanol	5:1	563 K, 11 Mpa	15	100 [b]	Chen et al., 2010
Jatropha	Supercritical methanol + propane	43:1	593 K, 8.4 Mpa	4	100 [a]	Hawash et al., 2009
Wet algae	Supercritical methanol	9:1	255 °C, 1200 psi	25	90 [a]	Patil et al., 2010b
Cottonseed	Supercritical methanol	41:1	523 K	8	98 [a]	Demirbaş, 2008
	Supercritical ethanol	41:1	503 K	8	70 [a]	
Rice bran	Supercritical methanol	27:1	300 °C, 30 Mpa	5	51.28 [a]	Kasim et al., 2009
Dewaxed /degummed rice bran					94.84 [a]	

WCO	Supercritical methanol	10:1-50:1	300 °C, 1450 psi	10-30	80 [a]	Patil et al., 2010a
WCO	Supercritical methanol	41:1	560 K	30	100 [a]	Demirbaş, 2009
Chicken fat	Supercritical methanol	6:1	400 °C, 41.1 Mpa	6	88 [a]	Marulanda et al., 2010
Linseed	Supercritical methanol	41:1	523 K	8	98 [a]	Demirbaş, 2009
	Supercritical ethanol	41:1	523 K	8	89 [a]	
	Supercritical methanol	41:1	503 K	8	70 [a]	
	Supercritical ethanol	41:1	503 K	8	65 [a]	
Hazelnut kernel	Supercritical methanol	41:1	350 °C	5	95[b]	Demirbaş, 2002
Coconut and palm kernel	Supercritical methanol	42:1	350 °C, 19 Mpa	6.7	95-96 [b]	Bunyakiat et al, 2006
R. sativus L.	Supercritical ethanol	42:1	590.5 K, 12.5 MPa	29	95.5 [a]	Valle et al., 2010
	Supercritical methanol	39:01:00	590 K, 14.1 MPa	27	99.8 [a]	

[a] Yield

[b] Conversion

3.2.3 Microwave assisted transesterification

The microwave-assisted transesterification is an energy efficient route for rapid biodiesel production. Microwaves assisted transesterification has gain research interest for their direct mode of energy transfer to the reactant molecules [Corsaro et al., 2004; Lertsathapornsuk et al., 2008]. This non-ionizing radiation influences the molecular motions such as ion migration or dipole moment, and does not affect the molecular structure [Fini and Breccia, 1999; Refaat et al., 2008]. Typically, induced molecular friction generates in situ heat for the reaction by employing continuous magnetic field on polar molecules and ions [Azcan and Danisman, 2007; Saifuddin and Chua, 2004]. It employs microwave frequency of 2.45 GHz and 900 MHz, which are permissible for use at domestic and industrial level, respectively. Such route encompasses the advantage of volumetric heating of polar reaction mass (methanol) under the influence of microwaves [Corsaro et al., 2004; Lertsathapornsuk et al., 2008]. Therefore, transesterification is efficiently accelerated in a short reaction time due to instantaneous localized superheating thereby enhancing the reaction kinetics [Refaat et al., 2008; Azcan and Danisman, 2007]. Such energy efficient approach has been employed for processing of various vegetable oil feedstocks (Table 3.9).

Table 3.9 Summary of some studies for biodiesel synthesis in microwave

Feed stock	Catalyst	Catalyst amount, wt%)	Molar ratio, Alcohol/ oil	Microwave conditions	Reaction time, min	Temperature, °C	Yield/ Conversion, %	References
Soybean	NaOH	1	6:1	900 W	1	30	97.7[b]	Hsiao et al., 2011
Soybean	NaOH	1	6:1	600 W (Ultrasonic) 900 W (Microwave)	1 2	60	97.7 [b]	Hsiao et al., 2010
Soybean	Nano CaO (heterogeneous catalyst)	3	7:1	-	60	65	96.6 [b]	Hsiao et al., 2011
Soybean	NaOH	0.6	5:1[c]	-	10	73	99.25 [b]	Terigar et al., 2010
Soybean	NaOH	1.30	18:1	300 W	1	60	97[a] , 95[a]	Hernando et al., 2007

Soybean and Oleic acid	Sulfated zirconia	5	20:1	-	20	60	90 ^{b}	Kim et al., 2011
Soybean Corn	Diphenyl ammonium salts: DPAMs (Mesylate) DPABs (Be nzenesulfonate) DPATs (Tosylate) DPAMs DPABs	20 (molar) 10 (molar) 10 (molar) 10 9	5 g methenol / 2 g oil	-	20	150	100 ^{b}, 96 ^{b}, 100 ^{b} 92 ^{b}, 97 ^{b}	Majewski et al., 2009
Sunflower	H_2SO_4	0.05	10:1	400W	45		96.2 ^{b}	Han et al., 2008
Sunflower	TiO_2/SO_4	0.02	12:1	300W	25		94.3 ^{a}	Kong et al., 2009
Neat vegetable virgin sunflower	KOH	1	6:1	500 W	60	65	96.15 ^{a}	Refaat et al., 2008
Safflower seed	NaOH	1	10:1	300 W	6	60	98.4 ^{b}	Düz et al., 2011

Crude palm	KOH	1.50	8.5:1 ^{c}	70 W	5	70	85 ^{a}, 98.1 ^{b}	Suppalakpanya et al., 2010
Cotton seed	KOH	1.5	6:1	21% of 1200 W	7	60	92.4 ^{a}	Azcanand Danisman, 2007
Rice bran	NaOH	0.6	5:1 ^{c}	-	10	73	99.34 ^{a}	Terigar et al., 2010
Rapeseed	KOH NaOH	1	6:1	67 % of 1200 W	5 3	50 40	93.7 (yield) 92.7 ^{a}	Azcan and Danisman, 2008
Rapeseed	-	-	2.5:1	-	240/80bar	310	91 ^{b}	Geuens et al., 2008
Maize	NaOH	1.5	10:1	-	-	-	98 ^{b}	Öztürk et al., 2010
Canola	$ZnO/La_2O.2CO_3$ (heterogeneous catalyst)	< 1	1:1 (w/w)		< 5	<100	> 95 ^{a}	Jin et al., 2011
Camelina sativa	Heterogen eous metal oxide catalysts	1.5 2	9:1	800 W	-	-	94 ^{a}, 80 ^{a}	Patil et al., 2009

	(BaO, SiO)							
Macauba	Novozyme 435	2.5	9:1 ^{c}	-	15	30	45.2 ^{b}	Nogueira et al., 2010
	Lipozyme IM	5			5	40	35.8 ^{b}	
Castor	H_2SO_4 / C	5	1:12	200 W	60	65	94 ^{a}	Yuan et al., 2009
Castor	Al2O3 / 50% KOH	1	1:6	40 W	5	-	95 ^{b}	Perin et al., 2008
	SiO_2 / 50% H_2SO_4	1		40 W	30		95 ^{b}	
	SiO_2 / 30% H_2SO_4	1		220 W	25		95 ^{b}	
Jatropha	KOH	1.50	7.5:1	-	2	65	97.4 ^{b}	Shakinaz et al., 2010
Jatropha curcas	NaOH	4	30:1	-	7	55	86.3 ^{b}	Yaakob et al., 2008
Crude Pongamia	KOH	1.33	%33.4 (w/w)	180 W	2.5	-	89.9 ^{b}	Venkatesh et al., 2011
Dry micro algae	KOH	2	9:1	800 W	6	-	80.13 ^{b}	Patil et al., 2011

WFO	NaOH	3	12:1 [c]	800 W	0.5	-	97 [b]	Lertsathaporn suk et al., 2008
WFO	NaOH	1	6:1	600 W	5	64	93.36 [a]	Yücel et al., 2010
FO	NaOH	0.5	1:6	50% of 750 W	4	60	87 [b]	Saifuddin and Chua, 2004
Domestic WCO	KOH	1	6:1	500 W	60	65	95.79 [a]	Refaat et al., 2008
Restaurant WCO	KOH	1	6:1	500 W	60	65	94.51 [a]	Refaat et al., 2008
Triolein	KOH NaOH	5	1:6	25 W	1	50	98 [b]	Leadbeater and Stencel, 2006
Yellow horn	Heteropol yacid (HPA)	1	12:1	500 W	10 min	60	96.22 [a]	Zhang et al., 2010b

[a] Yield

[b] Conversion

[c] Ethanol to oil

In sum, microwaves induced transesterification reaction offer high yield of purified product, minimizes the separation and purification time (Nuechter etal., 2000; Hernando et al., 2007]. Therefore, microwave heating is environmentally benign, energy-efficient and favorable over conventional methods, where heating is relatively slow and inefficient as heat transfer depends on convection currents, thermal conductivity, specific heat and density of the reaction mixture [Refaat et al., 2008; Groisman and Gedanken, 2008]. Although, microwave processing is well established route in ceramic industry, its integration with vegetable oil processing route is yet to be carefully examined at commercial level for biodiesel production.

3.2.4 Cavitation / Ultrasonic irradiation assisted transesterification

Cavitation has been recognized as an effective method to enhance mass transfer rate between immiscible liquids within a heterogeneous liquid reaction system. Such concept has been applied for biodiesel production [Gogate and Kabadi, 2009; Pal et al., 2010; Qiu et al., 2010]. Typically, cavitation is broadly classified into two types: hydrodynamic cavitation and acoustic cavitation [Qiu et al., 2010]. It aids in achieving high local energy densities, temperature and pressure within the reaction mass through generation of cavities followed by their growth and subsequently violent collapsing of cavities, thereby delimiting the mass transfer and enhancing the reaction kinetics [Gogate and Kabadi, 2009; Qiu et al., 2010].

Hydrodynamic cavitation can be generated by using an orifice plate/throttling valve/venture across the direction of a liquid flow [Gogate and Kabadi, 2009]. The mixing efficiency of a hydrodynamic cavitation is reported to be 160–400 times higher which consumes half of the energy compared to the conventional mixing method especially in case of immiscible liquids [Pal et al., 2010; Qiu et al., 2010]. On the other hand, acoustic cavitation is induced by means of ultrasound to achieve the similar features as to hydrodynamic cavitation [Qiu et al., 2010]. Ultrasonic waves are energy application of sound waves, which lies between 20 kHz and 100 MHz , are beyond human hearing limits (16 and 18 kHz) [Vyas et al., 2010]. Ultrasonic irradiations are generated through piezoelectric material with the help of power converter (transducer). This high frequency sound wave compresses and stretches the molecular spacing of a medium in which it passes through to create localized high energy densities within reaction mass.

Ultrasonic irradiation holds three major effects; (1) variation of sonic pressure, (2) cavitation, and (3) acoustic stream mixing which causes solvent compression and rarefaction cycle, liquid will break down and cavities / bubble formation followed by disrupting the interfacial boundary layers respectively [Colucci et al., 2005; Kumar et al., 2010b]. In total, theses effects improves mass transfer, creates high local pressure (up to 1000 atm) and temperatures (~5000 K), increased catalytic surface areas, and thus finally accelerate the rate of reaction [Gogate and Kabadi, 2009; Kelkar et al., 2008; Pal et al., 2010; Qiu et al., 2010]. Accordingly, the use of ultrasound during transesterification of vegetable oil leads to improvement in the heat and mass transfer by generating small cavities and vigorous mixing between immiscible reactants. Thus, provides sufficient activation energy to initiate the reaction which improves upon the reaction rate and yields, and thereby shorter the reaction time and energy consumption [Singh et al., 2007; Ji et al., 2006]. Attempts have studied the effect of catalyst, type of alcohol, ultrasonic power and frequency on ultrasonic assisted biodiesel production [Refaat and El Sheltawy, 2008, Wang et al., 2007]. A brief summary of few studies for biodiesel synthesis in the presence of Cavitation / Ultrasonic irradiation is presented in Table 3.10

Table 3.10 Summary of some studies for biodiesel synthesis in Cavitation / Ultrasonic irradiation

Feed stock	Catalyst	Catalyst Amount, ,wt %	Alcohol	Molar Ratio, Alcohol /oil,	Reaction temperature, °C	Reaction time, min	Reaction Condition	Yield/ Conversion, %	References
Refined soybean oil	KOH	1.5	Methanol	6:1	40	15	20 kHz, 14.49 W	>99.4^{b}	Colucci et al., 2005
Soybean	NaOH	1	Methanol	6:1	45	10	197 kHz, 150W	99^{a}	Ji et al., 2006
Soybean	KOH	0.5	Methanol	6:1	26 -45	30 <	611 kHz, 139 W	>90 ^{b}	Mahamuni and Adewuyi, 2009
Soybean	Na or K methoxide	0.15	Methanol	6:1	45	60	21.5 kHz, 600 W	100 ^{b}	Cintas et al., 2010
Soybean	Ti(Pr)4 Al(Pr)3	3	Methanol	6:1	60	120	-	64^{a}	Ye et al., 2007
Soybean	Novozym 435	6	Methanol	6:1	40	240	40 kHz, 500 W	96^{a}	Yu et al., 2010

Palm	KOH	-	Methanol	6:1	38–40	20	45 kHz,600 W	95 ^{a}	Stavarache et al., 2007
Palm	CaO SrO BaO	3	Methanol	9:1	65	60	30 kHz	77.3 ^{a} 95 ^{a} 95 ^{a}	Mootabadi et al., 2010
Palm	BaO SrO	2.8	Methanol	9:1	65	50 <	20 kHz, 200 W	>92 ^{a}	Salamatinia et al., 2010
Canola	KOH	0.7	Methanol	5:1	25	50	20 kHz, 1000 W	>95 ^{b}	Thanh et al., 2010a
Canola Soybean Corn	KOH	1	Methanol	6:1	55	30	450 W	95 ^{a} 95 ^{a}	Lee et al., 2011
Neat vegetable oil	NaOH KOH	0.5	Methanol	6:1	25	20	Ultrasonic cleaner20 kHz 40 kHz 1200 W	98 ^{a} 96 ^{a}	Stavarache et al., 2005
Coconut	KOH	0.75	Ethanol	6:1	-	7	24kHz, 200 W	>92 ^{a}	Kumar et al., 2010a
WCO	KOH	1	Methanol	6:1	45	40	20 kHz, 200 W	89 ^{b}	Hingu et al., 2010

WCO	KOH	0.7	Methanol	2.5:1 (mol)	20-25	10	20 kHz, 1000W (at each step)	81 [a]	Thanh et al., 2010b
		0.3		1.5:1		20		99 [a]	
Triolein	KOH	1	Methanol	6:1	25	30	Ultrasonic cleaner 40 kHz, 1200 W	~99 [a]	Hanh et al., 2008
Triolein	NaOH	1	Methanol	6:1	25	25	Ultrasonic cleaner 40 kHz, 1200 W	>95 [b]	Hanh et al., 2009
	KOH		Ethanol						
Beef Tallow	KOH	0.5	Methanol	6:1	60	1.16	40 kHz, 1200 W	>92 [b]	Teixeira et al., 2009

[a] Yield
[b] Conversion

Owing to the advantages of cavitation in influencing the degree of reactant mixing and reaction kinetics, a commercial scale process for transesterification of vegetable oil using homogeneous catalyst system has been developed [Gordon et al.,2011; Oh et al., 2012]. In this context, the patented hydrodynamic cavitation reactor i.e. Bioforce 9000 Nano for commercial biodiesel production is developed by Cavitation Technologies Inc. (CTI) [Gordon et al., 2011; Voegele E, 2009]. Major plant, engineering and equipment supplier in the field of oil and fats, M/s Desmet Ballestra in Brazil is adopting this technology, where biodiesel production is envisaged to grow enormously [Cavitation Technologies Inc., 2013], On similar lines, M/s SRS Engineering installed 10 MMgpy turnkey biodiesel plant using hydrodynamic cavitation technologies at Moberly, Missouri, USA. The facility is targeted to process multiple feedstocks like soybean , WVO and animal fats with an option of high FFA feedstocks [Cavitation Technologies Inc., 2013]. Furthermore, M/s SRS Engineering has claimed substantial savings in capital and production costs with cavitation based technology while comparing with existing conventional technologies. On the other hand, ultrasonic based cavitation approach is yet to be exploited at commercial level due to possible erosion of ultrasonic source and high surface energy intensity [Gogate and Kabadi, 2009, Qiu et al., 2010].

3.2.5 Membrane assisted transesterification

Membrane assisted transesterification provides platform for clean, energy efficient and cost effective continuous biodiesel production [Sanchez Marcano and Tsotsis, 2002]. Typically, membrane reactor simultaneously offers shifting equilibrium to reversible transesterification reaction towards product formation and selective separation, which improves the quality of biodiesel [Cao et al., 2007]. The transesterification of vegetable oil is performed in membrane reactor by exploiting the immiscibility of the oil and methanol, which posed the major mass transfer limitation to conventional biodiesel production. Typically, membrane process integrate reaction and separation steps into a single step, thereby reducing separation costs and recycle requirements, and an enhancement of thermodynamically limited or product inhibited reactions resulting in higher conversions per pass [Dubé et al., 2007]. Therefore, the application of membrane in biodiesel production has received attention in recent years [Reyes et al. 2012; Cao et al., 2008b]. This process is a unique combination for simultaneous steps viz. phase solubility, oil droplet separation and product separation at lower reaction temperatures [Saleh et al., 2010; Baroutian et al., 2011; Dubé et al., 2007, Böddeker, 2008]. The process uses cross-flow filtration through micro-porous inorganic membranes for selective removal of biodiesel, methanol and glycerin during transesterification. Fundamentally, membranes restrict the flow large oil droplets, which form upon mixing and reaction of oil and methanol [Cao et al., 2008 a,b]. Additionally, the presence of two phases in the reactor also ensures product quality by creating a barrier which prevents the movement of un-reacted oil into the product stream [Böddeker, 2008].The employed membranes are either organic in nature (i.e. polymeric) or inorganic where the thermal stability of the latter is better than the former. The pore size of the membrane is the crucial parameter and the effects of the pore size have been investigated for the biodiesel production [Cao et al., 2007]. The membrane assisted biodiesel synthesis requires higher molar ratios of methanol to oil and ultralow catalyst concentration compared to conventional synthesis [Cao et al., 2008a; Cheng et al., 2010]. A Summary of reported studies for biodiesel synthesis using membrane reactor is presented in Table 3.11.

Table 3.11 Summary of some studies for biodiesel synthesis using membrane

Feed stock	Catalyst	Mixture	Membrane	Temperature, °C	System Pressure, KPa	Trans-membrane Pressure, KPa	FAME content in Permeate	References
Palm	KOH	Crude biodiesel from KOH-trans-esterification of refined palm oil	Ceramic tube	60	not reported	150	> 90	Wang et al., 2009
Palm	KOH (heterogeneous)	Crude biodiesel from heterogeneous KOH-trans-esterification of refined palm oil	Ceramic tube	70	100	not reported	95	Baroutian et al., 2011
Canola	H_2SO_4	Emulsion (commercial Canola oil/methanol/H2SO4 FAME, glycerin)	Carbon tube	65	138	not reported	96	Dubé et al., 2007
Canola	H_2SO_4	Emulsion (commercial canola oil/methanol/	Ceramic tube	65	275,8	173.4	93	Cao et al., 2008b

		H2SO4 FAME, glycerin mixture) with recirculation of phase methanol/ H2SO4						
Canola	NaOH	Crude Biodiesel from NaOH-transesterification of canola oil	Ceramic tube	55	41	not reported	79	Reyes et al., 2012
Canola	NaOH	Biodiesel from NaOH-transesterification of canola oil	Ceramic disc	40	not reported	66.7	60	Cheng et al., 2009
Soybean	PTSA/MCM-41	Mixture of soyabean oil, MeOH	Ceramic membrane tube	80		80	84.1	Xu et al., 2014
Soybean	KF/Ca−Mg−Al hydrotalcite solid base	Mixture of soyabean oil, MeOH	Membrane tube	70		50	91	Xu et al., 2013
Palm	KOH	Mixture of palm oil, MeOH, KOH	Ceramic membrane	40	Not reported	2 00	98.32	Atadashi et al., 2012

3.2.6 Static mixture assisted transesterification

Static mixers are known to promote radial mixing in the mass transfer limited chemical reactions for immiscible liquids [Thompson et al., 2007]. This special type of reactor system consists of specially designed motionless helical mixing elements within a hollow cylindrical geometry and offers intense agitation with minimal energy consumption compared to conventional mechanical agitation. The advantages of such reactor are mainly, no moving parts, low space requirement, and low maintenance and operating cost. The continuous biodiesel production in presence of homogenous sodium hydroxide as catalyst is reported using static mixer reactor systems which are in integration with other equipments [Peterson et al., 2002; Thompson et al., 2007]. This type of reactor system is also reported for efficient biodiesel separation from emulsified reactants. [Boucher et al., 2009]. Table 3.12 summaries some studies for biodiesel synthesis using static mixer. The reaction condition is zeroed for 99% conversion and simultaneous removal of 70–99% of the glycerol at 60 ◦C temperature, 1.5% sodium hydroxide catalyst concentration and 30 min reaction time [Thompson et al., 2007].

The utilization of static mixer/plug flow reactor in commercial scale has been demonstrated by M/s ENERGEA, Austria and M/s Spec Engineers India, for the production of biodiesel [SPEC, 2010]. The reactor dimensions are reported to be 1500mmx700mmx2000mm for 50 Ton/day capacity with less reaction time (20 sec), maximum yield and conversion using minimal energy have been achieved [SPEC, 2010].

Table 3.12 Summary of some studies for biodiesel synthesis using static mixer

Feed stock	Type of mixing element	Catalyst , wt.%	Molar ratio, MeOH/oil	Temperature, °C	Residence time, s	Yield, %	References
Canola	Helical mixing element	KOH, 1.5	6	60	1800	97.6[a]	Thompson et al., 2007
Soybean	Metal foam	KOH, 1	6	60	196	95.2[a]	Yu et al., 2010
Soybean	Stainless steel wool	KOH, 2	6	60	180	97[a]	Santacesaria et al., 2011; Santacesaria et al., 2012 (a,b)
Soybean	Stainless steel sphere						Santacesaria et al., 2011
	Uniform spheres Φ = 2.5 mm, Channels ≈ 1000 μm	KOH, 1	6	60	80	82[a]	
	Two sizes spheres Φ_1 = 2.5 mm, Φ_2 = 1 mm, Channels ≈ 500 μm	KOH, 2	6	60	60	98.2[a]	
	Two sizes spheres Φ_1 = 2.5 mm, Φ_2= 0.39 mm, Channels ≈ 300 μm	KOH, 1	6	60	20	80.5[a]	

[a]Yield [b]Conversion

3.3 Commercial process features of transesterification vegetable oil

Owing to the aforementioned developments, the commercial turnkey plant reported to offer by M/s Lurgi, M/s Desmet Ballestra and M/s Pacific Biodiesel based on the homogeneous catalytic process [Pacific Biodiesel, 1996; GmbHL1996; Desmet Ballestra, 2008; Oh et al., 2012]. The offered commercial technology claims multi-feedstock flexibility with FFA content up to 15 % using pre-treatment steps prior to main transesterification reaction. Typically, M/s Lurgi and Desmet Ballestra offer simultaneous separation of products / by-products to drive the reversible transesterification reaction towards forward direction. The two and three stage rector cum separator type of system offered by both the process licensors whereas M/s Pacific biodiesel uses the batch operation for easy of handling feed stock, chemicals and manage the quality [Pacific Biodiesel, 1996; GmbHL1996; Desmet Ballestra, 2008; Oh et al., 2012]. The produced biodiesel has been claimed to meet desired fuel specifications with glycerin purity up to 90% depending on the purification steps involved in the process. On the other hand, the commercial plant based on heterogeneous catalyst process, Esterfip-H offers ease of products separation, high quality of biodiesel and glycerin, but suffers on battery limit of the FFA and water content which cannot tolerate impurities above the 0.25% and 1000 ppm, respectively [Melero et al., 2009]. This continuous process consists of two fixed bed reactors, which sequentially handle oil and methanol [Bournay et al., 2005]. The complete conversion is reached within two successive fixed-bed stages with glycerin separation in each stage to shift the equilibrium towards the product formation [Ondrey et al., 2004]. The produced biodiesel claimed to have a higher purity (>99%) with production yield (~100%) without involving purification steps. In addition, the directly produced by-product glycerin is claimed to have purity level of at least 98% without any contaminants. These aspects eliminate the products purification and refining steps, and ultimately, reduce the total production costs. Nevertheless, this process still have drawbacks such as close window for feedstock selection, higher methanol to oil ratio, higher temperature and pressure compared to conventional homogeneous alkali catalytic process.

3.4 An alternative: Glycerin free routes

3.4.1 Hydroprocessing

The search for diesel fuel, from renewable source, with excellent oxidation stability and fuel quality in terms of improved cetane number has led to development of vegetable oil glycerin free hydroprocessing route. The hydroprocessing of vegetable oil or its blend with petroleum feedstock involves hydrodeoxygenation of triglycerides and hydrofining of derived products in the presence of catalyst and hydrogen environment. This process leads to formation of a liquid hydrocarbon mixture specially C_{15}-C_{18} n-paraffins within the boiling range of mineral oil based diesel, which is commonly called “green diesel”, “renewable diesel”, “bio-hydrogenated diesel”, and second-generation biodiesel and ATF [Choudhary et al., 2011].

Typically, hydrodeoxygenation process is performed over Ni/Co-Mo-Al_2O_3 type of catalyst to produce long chain n-paraffins whereas hydroisomerization step is carried out using proprietary catalyst to tailor the cold flow properties by converting n-paraffins to iso-paraffins. The hydroisomerization step is reported to be the most critical step because cold flow properties of green diesel produced needs to be improved to meet cold flow plugging point (CFPP) without much compromise on cetane number whereas pour point for bio-ATF fraction needs to be achieved < - 47 °C as per the aviation industry norms [IS, 2008]. It may be noted that n-paraffins have higher cetane number than corresponding branched isomers whereas increase in degree of branching improves cold flow properties. Hydrotreatment process is robust in nature can handle varieties of feed stock ranging from edible vegetable oil (soybean, rapeseed , palm), non-edible vegetable oil (Jatropha and algal) , acid oil/waste cooking oil (WCO) and extremely lower-cost stock such as tallow oil and waste greases. The hydrogen requirement during the process is found to be highly dependent on the nature of feedstocks. For example, the less unsaturated feedstock, such as palm and tallow oils requires lower hydrogen consumption vis-à-vis feedstock with higher olefin content, such as soybean and rapeseed oils. Similar to conventional process, pre-treatment of feedstock is mandatory for employing hydroprocessing route as presence of gum and metal content in the feedstock severely hampers the activity of the hydrotreating catalysts. Furthermore, the type of catalyst and temperature are the most important factors to determine the yield and composition of liquid products, such as green naphtha (C_5-C_{10}), green jet fuel (C_{11}-C_{13}), and green diesel (C_{14}-C_{20}), and even green liquid petroleum gas (LPG) [Bezergianni et al., 2009, Table 12]. Here, the severity of process depends on the quality of feedstock and operating conditions. The salient features of this route include, flexibility, ease of optimization to accommodate changes in feedstock, and integration with refinery operation.

In recent years, several refiners have had an increasing interest in producing renewable liquid fuels from the hydroprocessing of various triglycerides feedstocks. This has led to successful development of commercial processes, which are now offered by M/s UOP and M/s Halder Topse [Kalnes et al., 2008; Egeberg et.al., 2010]. A simplified process sketch is shown in Figure 3.3.

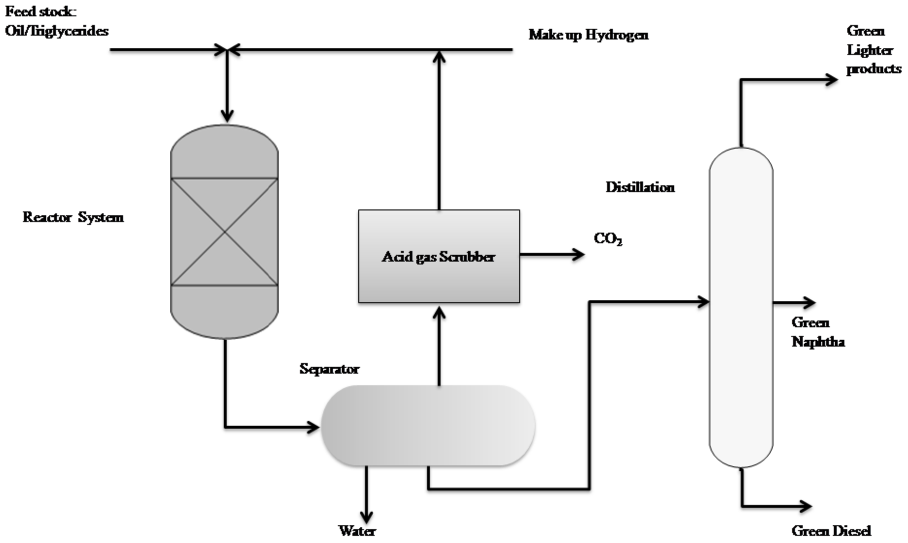


Figure 3.3 Process for hydrotretment of vegetable oil for Green diesel production

In this process, hydrogen is mixed with feedstock at predefined pressure (~ up to 100 bar) and processed over a multi-stage adiabatic reactors at each stage. In the first catalytic hydrodeoxygenation reactor, alkanes generates along with by-products like carbon dioxide, water and propane from fatty acid chain. This first stage process produces diesel boiling-range paraffins, and also has shown complete conversion with very high selectivity towards desired products. The deoxygenated product can be separated by distillation, and the heavier fractions are further hydrotreatment. The obtained hydrodeoxygenated n-paraffin rich diesel (is mainly composed of C_{15} and C_{18} n-paraffins) has high cetane number (> 70) but poor cold flow properties (freezing point in between 20 and 28 °C). Therefore, additional mixing of hydrogen is required through an integrated catalytic hydro-isomerisation process in which produces branched paraffin rich diesel to meet the cold flow properties. Implementation of the above process scheme does not required additional facilities for refiners and can easily integrate with the existing infrastructure at refinery. Even, vegetable oils can be mixed with straight run gas oil (VO) and/or vacuum gas oil (VGO) for hydroprocessing in existing conventional hydrotreaters (diesel hydrodesulfurization units) used in refineries [Corma et al., 2007; Huber and Corma, 2007; Stern et al., 2000]. By doing this, operation costs can be reduced by using the existing installations and also would offer flexibility in the production scheme and a very good alternative to the production of mixed petro-biofuel. In this setup, two main reactions would occur, e.g. hydrodeoxygenation of triglycerides and hydrodesulfurization of gas oil. Both reactions are carried out over the same hydrotreating catalyst. The deoxygenated products are stable in nature and completely compatible with petro-diesel fuels, and exhibit high cetane number [Senol et al., 2005; Ferrari et al, 2001a; Kubicˇkova et al., 2001; Snåre et al., 2008]. Literature summary of such work with oil sources and their blend with mineral oil diesel, reactor type, reaction conditions, catalysts, and main products are shown in Table 3.13.

Recently, several petroleum related companies such as UOP/ENI (Ecofining process) [UOP, 2012], The Neste Oil Co. (NExBTL process) [Neste Oil, 2012], Tyson Foods Inc. and Syntroleum Corporation [Environmental Leader. Tyson foods, 2012], Valero Energy Corporation [New Orleans Net., 2012], ConocoPhillips [Conocophillips renewable diesel, 2012], Nippon Oil Corporation [Second Generation Renewable Diesel., 2012], have shown their interest in producing renewable green liquid fuels based on hydroprocessing of various types of triglyceride feedstocks.

Table 3.13 Summary of some studies for green diesel synthesis through hydro treatment

Feed Stock	Reactor type	Reaction conditions	Catalyst	Main products	Conversion/ Yield, % wt	References
Neat oil as feedstock						
Jatropha	Fixed bed	T=350°C P=4 MPa LHSV=7.6 h-1 H2/oil ratio=800 Nm^3/m^3	$NiMo/Al_2O_3$-SiO_2	LPG C_{15}-$C1_8$ n- paraffins	$100^b/83.5^a$	Liu et al., 2011
			$NiMo/SiO_2$	C_{11}-C_{20}		
			NiMo/γ-Al_2O_3	C_{11}-C_{20}		
			NiMo/H-Y	C_{11}-C_{20}		
			NiMo/H-ZSM-5	C_5-C_{10}		
Jatropha	Batch	T=270°C P=6.5 MPa t=12 h Catalyst/oil wt ratio=1	Pt/H-ZSM-5	C_{10}-C_{20} n-paraffins	$83.8^b/67.7^a$	Murata et al., 2010
			Pt/USY	C_{10}-C_{20} n-paraffins	$100^b/90^a$	

Soybean	Batch	T=400°C P=9.2MPa t=1 h Catalyst/oil wt ratio=0.044, 0.088	NiMo/γ-Al_2O_3	C_{15}-C_{18} n-paraffins	$92.9^b/64.5^a$	Veriansyah et al., 2011
			Pd/ γ-Al_2O_3	C_{15}-C_{17} n-paraffins	$91.9^b/79.2^a$	
			CoMo/ γ-Al_2O3	C_{15}-C_{17} n-paraffins	$78.9^b/33.7^a$	
			Ni/Al2O3-SiO_2	C_{15}-C_{17} n-paraffins	$60.8^b/39.2^a$	
			Pt/ γ-Al_2O_3	C_{15}-C_{17} n-paraffins	$50.8^b/37.7^a$	
			Ru/ γ-Al_2O_3	C_{15}-C_{17} n-paraffins	$39.7^b/32.0^a$	
Soybean	Batch	T=350°C P=0.7 MPa N_2 t=4 h Stirring rate=1000	Ni/Al_2O_3	$\geq C_{18}$	$68^b/51.2^a$	Morgan et al., 2012

		rpm	NiAl/LDH	C_8-C_{17}	74[b]/52.9[a]	
			MgAl/LDH	C_8-C_{17}	72[b]/47.8[a]	
Rapeseed	Fixed bed	T=340°C P=4.0 MPa LHSV=1 h-1 H2/oil ratio=500-1000 Nm^3/m^3	NiMo/γ-Al_2O_3	C_{15}-C_{18} n-paraffins	93[b]/54.5[a]	Mikulec et al., 2010
			NiW/TiO_2			
			NiMo/TiO_2			
			NiW/ZrO_2			
			NiW/NaY			
Rapeseed	Batch	T=300-400°C P=5-11 MPa t=3 h	NiMo/Al_2O_3	C_7-C_{18} n-paraffins	70-80[a]	Sotelo-Boyás et al., 2011
			Pt/H-Y Pt/H-ZSM-5	C_5-C_{22} n- and iso-paraffins	20-40[a]	

Sunflower	Fixed bed	T=360-420°C P=18 MPa Oil flow=49 g/h H2flow=0.049 Nm^3/h	Sulfided catalyst (not specified)	C_{15}-C_{20}n- and iso-paraffins	64.7[a] (360 °C)	Simacek et al., 2011
			NiMo/Al_2O_3		81.8-97.4[b]/ 42-51.9[a]	
			NiW/Al_2O_3		86.7-95.6[b]/ 9.4-49.3[a]	
Sunflower	Fixed bed	T=350-370°C P=2-4 MPa LHSV=1.0 h^{-1} H2/oil ratio=500 Nm^3/m^3	NiMo/Al_2O_3-F	C_{15}-C_{18} n-paraffins	73.2-75.6[a]	Kovacs et al., 2011
Sunflower	Fixed bed	T=380°C P=4-6 MPa LHSV=1.0 h-1 H2/oil ratio=500-600 Nm^3/m^3	CoMo/Al_2O_3	C_{14}-C_{19} n-paraffins	100[b]/73.7-73.9[a]	Krár et al., 2010

Sunflower	Fixed bed	T=310-360°C P=2 MPa LHSV=0.9-1.2 h-1 H2/oil ratio=1000 Nm^3/m^3	Pd/SAPO-31	C_{16}-C_{18} n-and iso-paraffins	89.3-73.4[a]	Kikhtyanin et al., 2010
			Triflic acid/SBA-15	C_{15}-C_{23} n-paraffins	99[b]	
Palm	Fixed bed (pilot plant)	T=350°C P=4-9 MPa LHSV=2 h-1 TOS=0-14 days	$NiMo/Al_2O_3$	C_{16}-C_{18} n-paraffins	100[a], molar	Guzman et al., 2010
Palm	Batch	T=300-320°C Atm. pressure t=1-2 h Catalyst/oil wt ratio=0.0133	NiMo/zeolite (klinoptilolite type)	C_8-C_{19} n-paraffins	11.93 [a], vol.	Nasikin et al., 2009
Waste cooking oil	Fixed bed	T=350°C P=2 MPa LHSV=15.2 h-1	Ru/Al13-montmorillonite	C_{15}-C_{18} n-paraffins	100[b]/82.1-84[a]	Liu et al., 2012

		H2/oil ratio=400 Nm^3/m^3				
Blend of mineral-gas oil + vegetable oil as feedstock						
Rapeseed	Fixed bed	T=300°C P=4.5 MPa LHSV=1.5 h^{-1} H2/oil ratio=250 Nm^3/m^3	NiMo/Al$_2$O$_3$	C$_{15}$-C$_{20}$ n-paraffins	97[b]	Donnis et al., 2009
Rapeseed	Fixed bed	T=400-420°C P=18 MPa WHSV=1 h^{-1} H2/oil ratio=1000 Nm^3/m^3	NiMo/Al$_2$O$_3$	C$_{15}$-C$_{20}$ n-paraffins	55.4[a] (420 °C)	Simacek and Kubicka, 2010
Palm	Fixed	T=310-350°C P=3.3 MPa WHSV=0.7-1.4 h^{-1} H2/oil ratio=1500 Nm^3/m^3	CoMo/Al$_2$O$_3$	Diesel-range paraffins	100[b]	Templis et al., 2011

Palm	Fixed	T = 300-320 ºC, P = 1 atm	NiMo/zeolite klinoptilolite type	Diesel-range paraffins	11.9[a]	Nasikin et al., 2009
Sunflower	Fixed	T=360-380°C P=8 MPa LHSV=1 h^{-1} H2/oil ratio=600 Nm^3/m^3	NiMo/Al2O3	C_{11}-C_{22} n-paraffins	82-90[a]	Tóth et al., 2011
Sunflower	Fixed bed	T=350°C P=13.8 MPa LHSV=1.5 h^{-1} H2/oil ratio=1060 Nm^3/m^3	Hydrotreating catalyst (not specified)	Diesel-range paraffins	85[b]/42[a]	Lappas et al., 2009
Sunflower	Fixed bed	T=350°C P=6.9 MPa LHSV=1.5 h^{-1} H2/oil ratio=1068 Nm^3/m^3	Hydrocracking commercial catalysts (not specified)	Naphtha, kerosene, and diesel-range paraffins	64[b] (catalyst B) 37.5[b] (catalyst C)	Bezergianni et al., 2009

Sunflower	Fixed bed	T=300-450°C P=5 MPa LHSV=4.97 h^{-1} H$_2$/oil ratio=1600 Nm^3/m^3	NiMo/Al$_2$O$_3$	C$_{15}$-C$_{18}$ n-paraffins	54 – 75^a	Huber et al., 2007
Sunflower	Fixed bed	T=320-350°C P=3-6 MPa LHSV=1.4 h^{-1} H$_2$/oil ratio=1068 Nm^3/m^3	NiMo/ Al$_2$O$_3$-β-zeolite	C$_{17}$-C$_{18}$ n-paraffins	/>90^b	Sankaranarayanan et al., 2011
Soybean	Fixed bed	T=340-380°C P=5 MPa LHSV=2.4 h^{-1} H$_2$/oil ratio = 1500 Nm^3/m^3	NiW/Al$_2$O$_3$-SiO2 NiMo/ Al$_2$O$_3$	C$_{15}$-C$_{20}$ n-paraffins	85-95^a	Tiwari et al., 2011
WCO	Batch	T=325°C P=2 MPa Stirring=900 rpm t=1, 2, 5, 20 h	Pt/ γ-Al$_2$O3		100^b/60^a	Madsen et al., 2011
			Ni/ γ- Al$_2$O3		76.8^b	

			Pt/γ- Al_2O3		100^b	
WCO	Fixed bed	T=330-398°C P=8.3 MPa LHSV=1 h-1 H_2/oil ratio=710 Nm^3/m^3	Hydrotreating catalyst (not specified)	$C_{8-}C_{29}$n- and iso-paraffins	$72.62^b/71^a$ (at 350°C)	Bezergianni et al., 2010

---

[a] Yield
[b] Conversion

3.4.2 Substitution of methanol

The need for biodiesel process economic improvement w.r.t. glycerin glut, has led to development of methanol free route of transesterification for biodiesel production. Therefore, to alter the reaction path ways for avoiding the formation of glycerin, alternatives of alcohol/methanol as methyl acetate and dimethyl carbonate (DMC) have been explored [Huang and Yan, 2008; Fabbri et al., 2007; Su et al., 2009].

The difference in reaction pathway for transesterification of vegetable oil with methanol *vis-à-vis* DMC as reported elsewhere [Fabbri et al., 2007] in which glycerin-adduct, glycerin dicarbonate (GDC), is co-produced with DMC-biodiesel instead of low value glycerin. Interestingly, DMC based biodiesel is reported to have better lubricating properties *vis-à-vis* conventional biodiesel due to miscibility of formed by-product GDC in the DMC-biodiesel phase. In addition, the characteristics of produced DMC-biodiesel have been reported to be in good agreement with conventional methanol based biodiesel [Fabbri et al., 2007]. In this method, the mutual solubility of oil and DMC does not require any solvent, and act as a solvent to overcome the mass transfer limitation between oil and alcohol as in the conventional method. However, DMC based transesterification synthesis is reported to have prolonged reaction time and high amount of catalyst owing to polarity difference between reactant and catalyst [Fabbri et al., 2007]. Therefore, non-catalytic supercritical DMC process using vegetable oil as a feedstock has been attempted [IIham and Saka, 2009 and 2010]. It is worthwhile to note that the reported process is a non-catalytic process, which offers the elimination of several cumbersome separation and purification steps as compared to conventional process.

In addition, the by-products in supercritical synthesis such as glycerine carbonate (GC), glycerin di-carbonate (GDC), citramalic acid, glyoxal (if FFA is present), obtained in this process are highly valuable adducts for biodiesel and diesel fuel instead low value glycerin in the conventional process [Ilham and Saka, 2009]. A brief summary of the efforts made on glycerin free biodiesel synthesis via transesterification route is listed in Table 3.14.

On similar lines, the lipase-catalyzed transesterification has been reported using vegetable oil and DMC in presence of immobilized lipase Novozym 435 [Su et al. 2007; Tian et al. 2009]. However, the high cost of the enzyme has limited the commercial exploitation of the process. Furthermore, supercritical methyl acetate method has been investigated to produce glycerin free biodiesel and triacetin [Saka and Isayama, 2009]. As a result, the mixture of biodiesel and triacetin can be used entirely as a kind of biofuel due to their miscibility and similar improved fuel properties like DMC-biodiesel [Saka and Isayama, 2009]. The two step biodiesel production process has also been investigated based on the hydrolysis of triglycerides in sub-critical water and followed by esterification of fatty acids in supercritical dimethyl carbonate in catalyst free route [IIham and Saka, 2010]. Although, these methods could produce the by-products with higher values, the severe reaction conditions may become a major concern in commercial applicat

Table 3.14 Summary of some studies for glycerin free synthesis of biodiesel through substituting methanol

Feed stock	Reactant	Catalyst	Molar ratio, Reactant/oil	Temperature, Pressure	Reaction time, min	Yield/ Conversion, %	References
Palm	DMC	KOH as heterogeneous catalyst, 8.5 % wt of oil	9:1	60-75 °C, 1 atm	480	96.2^{a}	Zhang et al., 2010a
Soybean	DMC	Heterogeneous: 5% wt of oil, Homogeneous: 5% mol of oil	2042 gm oil, 782 gm DMC and 632 gm DMC with cat.	90 °C, 1 atm	300		Fabbri et al., 2007
		Sodium methoxide (30% in methanol)				$>99.5^{b}$	
		Na$_2$PEG (300)				$>98^{b}$	
		Sodium hydride				$<5^{b}$	

		1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD)				>99.5 [b]	
		1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU)				<5 [b]	
		1,4-Diazabicyclo[2.2.2]octane (DABCO)				<5 [b]	
		4-Dimethylaminopyridine				<5 [b]	
		Hydrotalcite Pural Mg70				<5 [b]	
		13X Zeolite				<10 [b]	
		Titanosilicate ETS 10				<5 [b]	
Rapseed	Supercritical	No catalyst	42:1	300 °C, 20 Mpa	20	97.4 [a]	Ilham and Saka,

	DMC						2012
Palm	Supercritical DMC	No catalyst	39:1	380 ^{o}C	30	91[a]	Tan et al., 2010b
Canola	DMC	TBD, 2.5 % wt oil	3:1	60 ^{o}C, 1 atm	360	99.92[b], 99.45[a]	Kurle et al., 2013
Pongamia pinnata	DMC	KOH catalyst , 4 % wt	3:1	60 ^{o}C, 1 atm	360	96[a]	Panchal et al., 2013
Soybean /Waste soybean /Sunflower /Jatropha curcas	Supercritical methyl acetate	No catalyst	42:1/42:1/42:1/42:1	345 °C, 20 Mpa/345 °C, 20 Mpa/ 345 °C, 20 Mpa/345 °C, 20 MPa	50 / 50 / 50 / 50	100[a] / 100[a] / 100[a] / 100[a] ,	Campanelli et al., 2010
Rapeseed Oleic acid	Supercritical methyl acetate	No catalyst	42:1	350 °C, 20 MPa	45	91[a]	Saka and Isayama, 2009
Purified palm	Supercritical methyl acetate	No catalyst	30:1	399 °C	59	97.6[a]	Tan et al., 2010a

Jatropha curcas	Sub-critical water+ supercritical DMC	No catalyst	217:1 /14:1	270 °C, 27 MP/300 °C, 9 MPa	25 /15	> 97 [a]	Ilham and Saka, 2010
Rapeseed /Oleic acid	Supercritical DMC/Supercritical DMC	No catalyst	42:1/ 42:1	350°C, 20MPa/300°C,9 MPa	12 /9	94[a]/90[a]	Ilham and Saka, 2009

[a] Yield
[b] Conversion

3.5 Summary

This literature survey indicates that most of the methods for synthesis of biodiesel has been demonstrate by conventional technology using homogeneous and heterogeneous catalyst. Some of the process intensification options have been developed and their implementation at commercial level is being under developmental stage.

Glycerin, being the main by-product, of the biodiesel process and its production almost equivalent to approximately 10 wt.% of the TG, its separation and purification is challenging for making biodiesel process completely economically viable due to involvement of capital and high energy intensive several steps of treatment to make commercial grade glycerin. Therefore, hydroprocessing and substitution of methanol routes have been investigated. However, hydroprocessing route requires high capital as well as operating cost; and also limits the throughput in the existing units. Hence, the substituting methanol by altering the synthesis chemistry to produce glycerine free biodiesel would be highly effective to counter the economic imbalance of conventional biodiesel synthesis. Few attempts have been made in the literature to investigate the glycerin free biodiesel synthesis. However, such attempts have not been reported using Jatropha and Pongamia oil as a feedstock. Therefore, the preset study investigates the novel biodiesel synthesis by employing catalytic and non-catalytic supercritical route, optimization of process parameters followed by detailed kinetic study, characterisation of laboratory-synthesised biodiesel, and process design and simulation studies. The detailed work performed on these aspects is decribed in the following chapters.

CHAPTER 4

JATROPHA AND PONGAMIA OIL DERIVED DMC-BIODIESEL SYNTHESIS: A KINETICS STUDY

4.1 Introduction

Today, the need for alternate fuels is becoming increasingly important due to diminishing petroleum reserves and the stringent environmental norms [Ma and Hanna, 1999; De et al., 1999]. In this context, biodiesel (Fatty acid methyl esters; FAMEs) has emerged as first generation biofuel option which led to implementation of B5, B10, B20 and B100 fuel specifications in Europe and North America. However, its process economic viability is yet to be established worldwide due to the market dynamics of feedstock and by-product glycerol.

In current scenario, multiple process options, based on homogeneous transesterification route, have been developed for production of biodiesel using vegetable oil and methanol as reactants [Barnwal and Sharma, 2005; Bautista et al., 2009]. However, the economic feasibility of the available options is often limited due to quality of by product; glycerol; produced and cost involved in purification process for its utilization. Typically, during the process, glycerol, which accounts 10% of the feedstock, is recovered together in reaction mixture consisting of FAME, methanol, water and spent alkaline catalyst. Thus, several purification steps are required to recover the pure glycerol which imbalances the overall process economics of biodiesel production [Huber et al., 2006]. To overcome the glycerol purification problem, a capital and energy intensive heterogeneous catalyst assisted biodiesel production processes, leading to formation of pure glycerol, have also been developed [Marchetti et al., 2008].

In spite of aforementioned biodiesel production options, the fear of glycerol glut creation is anticipated with implementation of biodiesel program worldwide. This is envisaged to plummet glycerol market prices which would inturn affect the deployment of biodiesel value chain. In fact, especially in Europe, glycerol price has decreased tremendously due to surplus supply in the market with implementation of biofuel program by European Union [McCoy, 2005and 2006]. Thus, it is utmost important to handle glycerol innovatively for economic feasibility of homogeneous catalyst based biodiesel production process.

To balance glycerol's availability and demand, attempts have been reported for glycerol valorization [Zheng et al., 2008; Behr et al., 2008]. For example, glycerol ethers are reported to be cetane improvers and can be utilized as fuel additives [García et al., 2008; Jaecker-Voirol et al., 2008]. On the other hand, the use of glycerol is found to be good source for hydrogen production [Adhikari et al., 2007]. However, such utilization often demands purification of crude glycerol. On the other hand, attempts have been made for glycerol free synthesis of biodiesel using eco-friendly reactant such as methyl acetate and dimethyl carbonate (DMC) [Huang et al., 2008; Su et al., 2009; Tundo and Selva, 2002]. Interestingly, DMC-based biodiesel is reported to have better lubricating properties vis-à-vis conventional biodiesel due to miscibility of formed by- product glycerol dicarbonate (GDC) in the DMC-biodiesel phase [Fabbri et al., 2007].

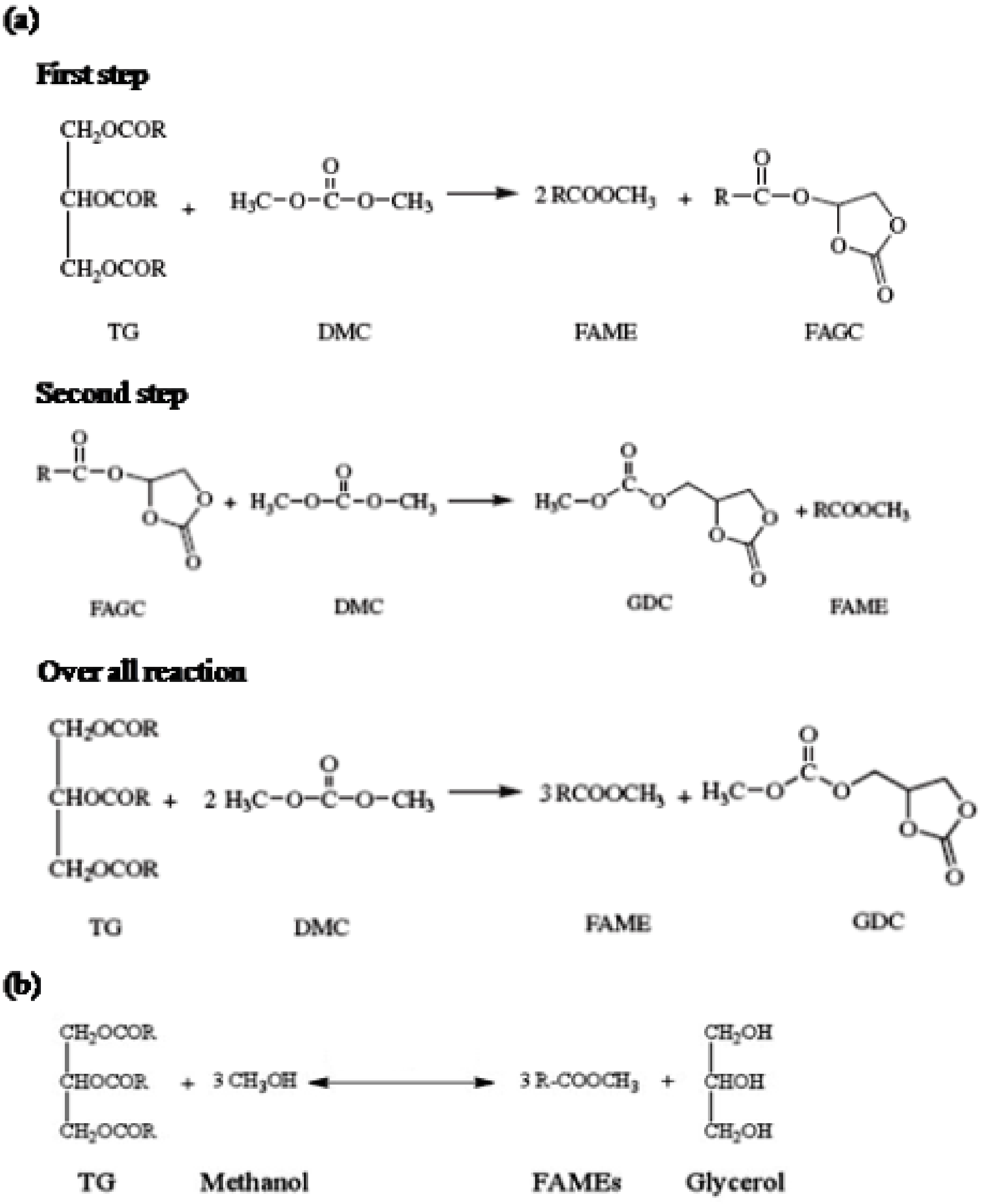


Figure 4.1 Reaction mechanism (a) Glycerin free (b) Convention synthesis of biodiesel

The formation of GDC is ascribed to the difference in reaction pathway for transesterification of vegetable oil with methanol vis-à-vis DMC. As presented in the Figure 4.1 (a), triglyceride reacts with DMC in the two consecutive steps wherein two moles of FAME is produced along with intermediate i.e. fatty acid glycerol carbonate (FAGC) in the first step and subsequently in the second step, FAGC converts into one more mole of FAME and GDC in excess of DMC. In the overall reaction, each mole of vegetable oil (Triglyceride) stoichiometry requires two moles of DMC to produce three moles of biodiesel and one mole of GDC which is miscible with biodiesel phase. On the other hand in Figure 4.1(b), conventional biodiesel synthesis with low molecular weight alcohol such as methanol requires 3 moles of methanol to produce same amount of FAME and one mole of crude glycerol. Thus, it is noteworthy that DMC assisted biodiesel synthesis offers two distinct advantages over conventional process in terms of better lubricating fuel property and ease of product purification owing to miscibility of formed glycerol-adduct (GDC), Furthermore, it can avoid tedious post synthesis purification steps which inturn is anticipated to offer platform for cost effective operational route for biodiesel process. In view of this, it is important to investigate the transesterification of non-edible oils, like Jatropha and Pongamia oil, with DMC as both the oils are the targeted backbone for development of biodiesel value chain.

Therefore, the present work aims to investigate and compare the kinetics of glycerol free synthesis of biodiesel route using Jatropha and Pongamia oil with DMC as feed stock in presence of KOH as a catalyst. Typically, biodiesel synthesis parameters viz. catalyst concentration, reactant molar ratio, temperature and reaction time have been investigated. Based on the evaluation, optimal synthesis conditions have been zeroed in and kinetic parameters have been estimated. The reaction rate constants (k) at different temperatures are determined and the activation energy (Ea) with the pre-exponential factor (k_o) is reported for Jatropha and Pongamia oil DMC-biodiesel synthesis. Furthermore, fuel characteristics of Jatropha and Pongamia oil derived DMC-biodiesel have been evaluated vis-a-vis standard ASTM D6751/EN 14214/IS 15607 biodiesel specifications, and simplified process flow is proposed for glycerin free production of biodiesel.

4.2 Experimental Section

4.2.1 Materials

Crude Jatropha oil and Pongamia oil samples were obtained from the respective seeds by mechanical pressing. Other reactants namely KOH (MERCK, India) and DMC (technical grade, S.D. Fine Chem. Ltd., India) were used as received. The GC standards, namely methyl heptadecanoate (as internal standard, minimum purity 99%), fatty acids (Myristic, C14:0; Plamitic, C16:0; Palmitoliec, C16:1; Margaric, C17:0; Steric, C18:0; Oleic, C18:1, Linoleic, C18:2; Linolenic, C18:3; Arachidic, C20:0; Eicosenoic, C20:1; Behenic, C22:0; Lignoceric, C24:0) and their respective methyl esters were procured from Sigma-Aldrich, and employed for determination of oil composition and its conversion level w.r.t. FAME formation.

4.2.2 Method: DMC-Biodiesel synthesis and its kinetics

Transesterification of Jatropha and Pongamia oil was carried out in a 500 ml three-neck round bottom glass flask under stirred conditions in the temperature range of 60-80 ^{o}C for predetermined time. Typically, oil and DMC were mixed in the predefined molar ratio *w.r.t.* oil and reaction was carried out by employing KOH (on the basis of wt% of the oil) as catalyst. After the reaction time, the glass flask was quenched in the ice-water to arrest the reaction and subsequently the catalyst was removed *via.* filtration. Subsequently, reaction mixture was washed with dilute acid to neutralize trace amount of KOH present in the reaction mass. The excess DMC was separated using vacuum distillation unit (HERZOPPAC, Germany; Model: HDV 632). All reactions were conducted in triplicate to ensure reproducibility *w.r.t.* oil conversion within the error limit of ± 2%. The extent of reaction was followed by means of gas chromatography (GC) technique. For this purpose, conversion was estimated by recovering oil phase from the reactant mixture as per the purification steps reported elsewhere [Felizardo et al., 2006].

The kinetic study of DMC-Biodiesel reaction was investigated under optimized condition, having molar ratio of DMC to oils (molar ratio: 10:1) and KOH (9 wt %) which is derived from the present study. The total reaction volume was regarded as constant during kinetic study considering that the volume of samples withdrawn was not more than 1% of the total reaction volume. While performing the study, reaction samples (approximate 0.5 mL) were withdrawn from the reaction mixture through 0.25 µm syringe filter at pre-specified time intervals, and subsequent quenched to arrest the reaction. The extent of reaction was followed by means of GC technique using methyl heptadecanoate as internal standard and n-heptane as solvent.

4.2.3 GC Analysis

The reaction samples were analyzed by gas chromatography technique (Perkin Elmer, USA; Model: Claurus 580) using a Elite-Wax ETR capillary column (30m length,0.32 mm ID), having 0.5 µm film of polyethylene glycol and a flame ionization detector. Helium was used as the carrier gas at a flow rate of 2.0 mL/min. The flow rates of oxygen and hydrogen were 2 and 4 mL/min, respectively. Temperature of injector and detector was individually maintained at 250 ^{o}C while the oven temperature was maintained at 230 ^{o}C. The methyl esters (C_{14}-C_{24}) samples were used to construct the standard calibration curve for GC analysis. The oil and reaction samples were accurately weighed, then mixed with predetermined amount of known concentration of internal standard solution (methyl heptadecanoate). Ester composition was determined by integration of area under the peak using internal standard method.

4.3 Results and discussion

The reaction conditions for glycerol free DMC-biodiesel synthesis have been investigated. The obtained results are discussed in the following sections.

4.3.1 Fatty acid composition for Jatropha and Pongamia oil

Fatty acid composition of both Jatropha and Pongamia oil is determined through GC technique as reported elsewhere in the literature [Meher et al., 2006]. The fatty acid compositions of the oils are listed in Table 1. As presented, Pongamia oil has more saturated (26.39%) and mono-unsaturated (54.37%) fatty acids compared to Jatropha oil where theses fatty acids content is 21.6 % and 45.4 % respectively. On the other hand, higher poly-unsaturated (di and tri) fatty acid content is observed in Jatropha (33%) compared to Pongamia oil (19.24%). In addition, physical properties of both oils are evaluated and listed in Table 2.

Table 4.1 Fatty acid composition (% wt) of Jatropha and Pongamia oil used in this study

Fatty acid	Structure[a]	Formula	Jatropha oil	Pongamia oil
Myristic	14:0	$C_{14}H_{28}O_2$	0.1	-
Plamitic	16:0	$C_{16}H_{32}O_2$	14.2	11.65
Palmitoliec	16:1	$C_{16}H_{30}O_2$	0.7	-
Margaric	17:0	$C_{17}H_{34}O_2$	0.1	-
Steric	18:0	$C_{18}H_{36}O_2$	7	7.5
Oleic	18:1	$C_{18}H_{34}O_2$	44.7	53.27
Linoleic	18:2	$C_{18}H_{34}O_2$	32.8	16.64
Linolenic	18:3	$C_{18}H_{30}O_2$	0.2	2.6
Arachidic	20:0	$C_{20}H_{40}O_2$	0.2	1.7
Eicosenoic	20:1	$C_{20}H38O_2$	-	1.1
Behenic	22:0	$C_{22}H_{44}O_2$	-	4.45
Lignoceric	24:0	$C_{24}H_{48}O_2$	-	1.09

[a] The former number represents the number of the carbons in the hydrocarbon chain while thelatter represents the number of the double bond in the respective fatty acid

Table 4.2 Physical property characterization of Jatropha and Pongamia oil used in this study

Vegetable oil	Density @ 15^0C ,gm/cm^3	Viscosity @ 40^0C, cSt	Moisture content, % wt
Jatropha	0.9195	35.62	ND[b]
Pongamia	0.9353	43.02	ND[b]

[b] ND, not detectable

4.3.2 DMC-Biodiesel synthesis

Conventionally, biodiesel synthesis is mass transfer limited reaction due to repeal polarity of the reactants like non-polar vegetable oil i.e. triglycerides and polar low molecular weight alcohols [Guan et al., 2009]. Conversely, DMC and triglyceride (oil) are completely miscible, and hence mass transfer limitations are envisaged to be negligible. In order to establish this aspect, transesterification reactions were performed in the absence of KOH catalyst under reflux conditions for 6 h to evaluate the thermal effect and influence of polarity on conversion.

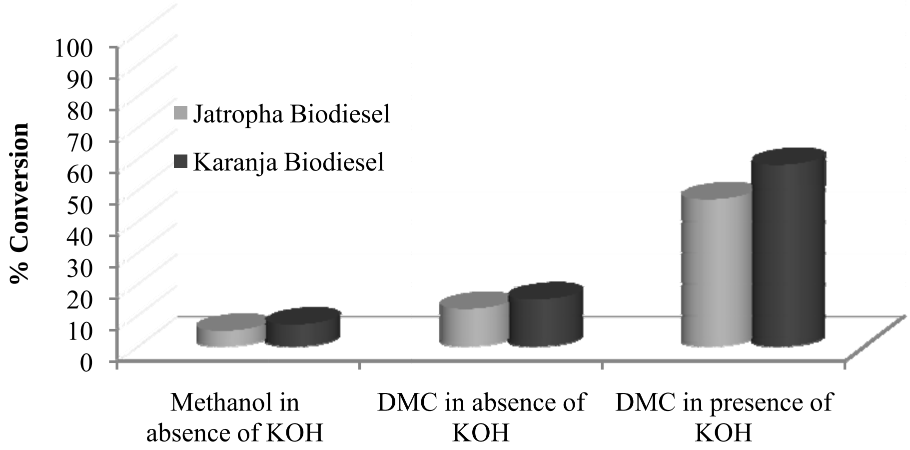


Figure 4.2 Effect of diverse nature of reactants and KOH presence (as catalyst) in oil-DMC /methanol system

As shown in Figure 4.2, the conversion of both the feedstock was in the range of 5-7% and 10-15 % with diverse polar natured reactant like methanol and DMC, respectively. Such trend demonstrates ease of reaction progression due to reduction in the mass transfer resistance while using DMC as a reactant. In order to further increasing the conversion, the reaction is carried out in the presence of catalyst (KOH) wherein about 47-58 % conversion was achieved within 6 h. Even though, KOH solubility in reaction media; oil-DMC; is found to be limited due to non-polar nature of reactants, but the KOH presence has positive effect to drive the reaction in the forward direction towards completion [Zhang et al., 2010]. Thus, experimental studies are performed to optimize the KOH concentration and other reaction parameters such as reactant ratio, temperature, and time to maximize conversion. The obtained results are given in following section.

4.3.3 Optimization of reaction parameters for DMC-Oil system

4.3.3.1 Effect of KOH amount

The effect of KOH concentration, in the range of 2.0–12.0% (based on the oil wt), is investigated under reflux conditions for 8 h with reactant ratio of 12:1 (DMC:oil ratio) and the results are depicted in Figure 4.3. Typically, the conversion increased from 20% to 95% with an increase in amount of KOH concentration from 2 to 12% for Jatropha and Pongamia oil, respectively. However, it is worthwhile to note that the conversion remained almost constant beyond 9 % of the KOH concentration thus indicating that the optimum concentration of 9% is essential to achieve almost complete conversion (≥ 95%) for the transesterification of Jatropha and Pongamia oil with DMC.

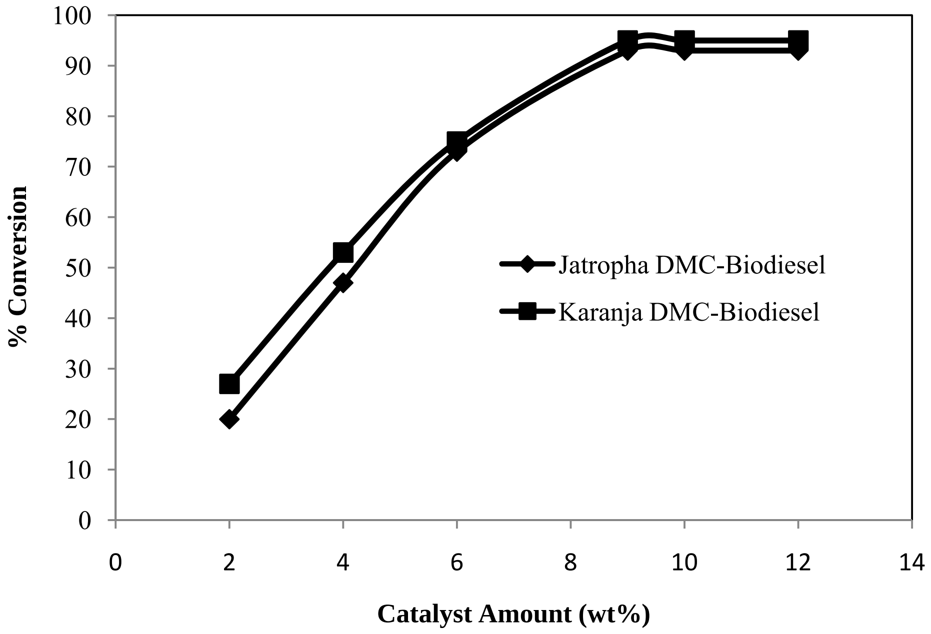


Figure 4.3 Effect of catalyst amount (wt %) on conversion for synthesis of biodiesel from Jatropha and Pongamia oil with DMC under reflux condition for 8 h reaction time

As the KOH solubility is limited in the reaction mass, most of the KOH content is found to form a precipitate after the reaction. This in turn indicates its possible option of reuse upon recovery and ease of downstream separation cum purification process. However, a mild acid treatment is essential to neutralize traces of KOH present in the reaction mass. This confirms the partial leaching of KOH in reaction phase to facilitate the conversion of oil.

4.3.3.2 Effect of reactant molar ratio

The molar ratio of DMC to oil is one of the most important variables influencing the conversion of oil into biodiesel. Typically, Figure 4.1 (a) depicts the transesterification of each mole of oil requires two moles of DMC and reaction is reversible in nature. Thus, it is essential to employ excess of DMC concentration to shift the reaction towards product formation i.e. biodiesel. Therefore, the molar ratio of DMC to oil was varied from 3:1 to 12:1 at constant KOH concentration 9% (based on oil content) under reflux conditions for 8 h (Figure 4.4).

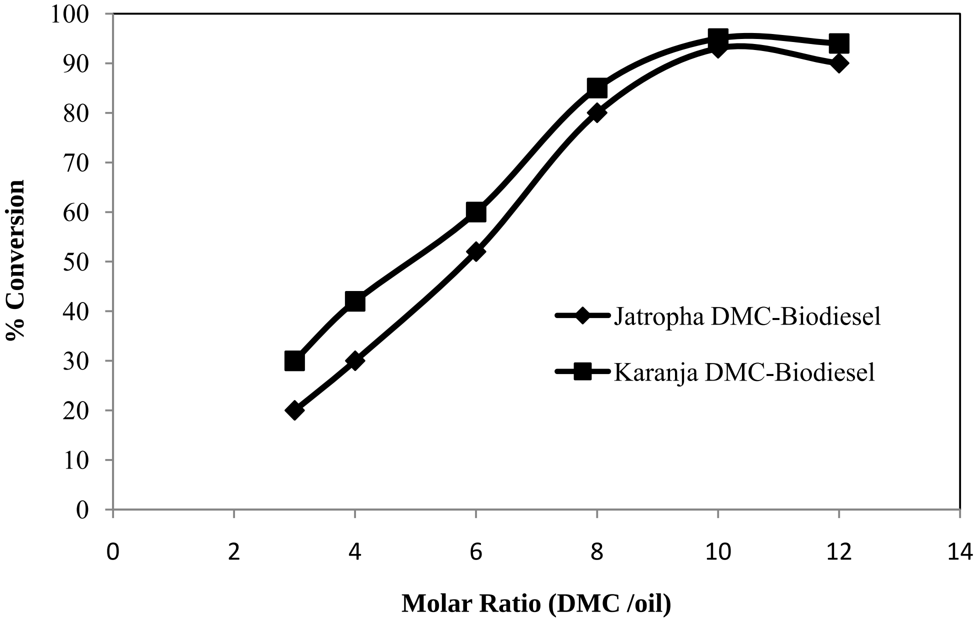


Figure 4.4 Effect of molar ratio of DMC to oil on conversion for synthesis of biodiesel from Jatropha and Pongamia oil with DMC at 9% catalyst amount, 8 h reaction time and under reflux condition

Typically, the conversion level continued to increase from 20% to 94% and 30 % to 96% with an increase the molar ratio of DMC to oil from 3:1 to 12:1 for both the oils. The maximum conversion 94% and 96% was obtained at a molar ratio of 10:1 for Jatropha and Pongamia oil respectively. Further increase in molar ratio did not influence the conversion significantly. Therefore, the reactant molar ratio of 10:1 (DMC:oil) is found to be optimum to achieve the best possible yield for DMC-biodiesel.

4.3.3.3 Effect of temperature

The effect of temperature on transesterification reaction was studied in the range of 60-80 ^{o}C for 8h by employing optimal reactant molar ratio (10:1) and KOH concentration (9 % wt).

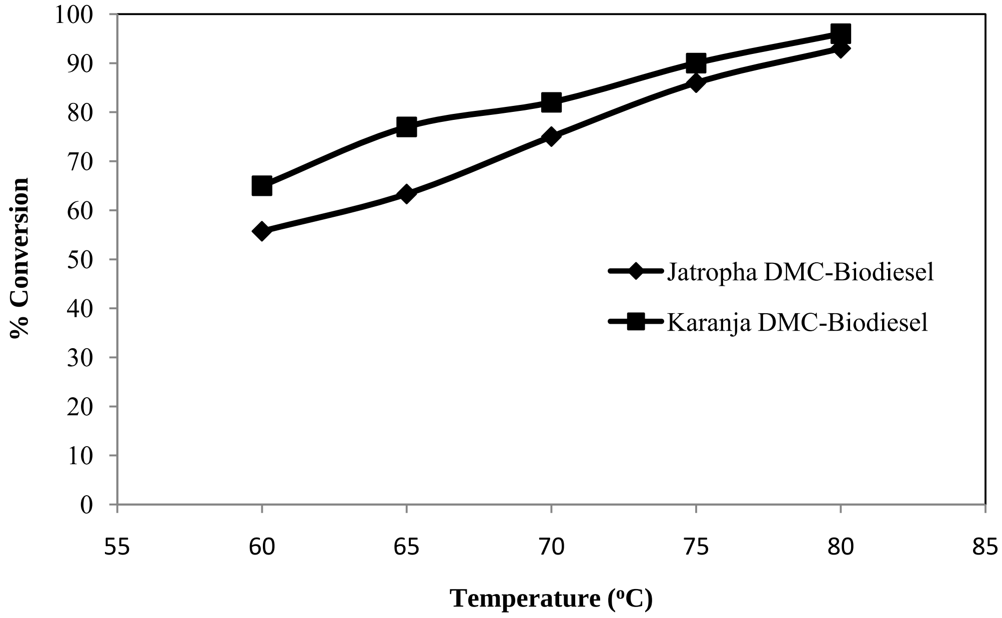


Figure 4.5 Effect of temperature on conversion for synthesis of biodiesel from Jatropha and Pongamia oil with DMC, at 10:1 molar ratio of DMC to oil, 9% catalyst amount and 8 h reaction time

Figure 4.5 depicts the temperature dependency of the reaction wherein conversion increased from 55 % to 94 % and 65 % to 96 % with rise in temperature from 60 ^{o}C to 80 ^{o}C for Jatropha and Pongamia oil respectively. Thus, the optimum temperature is found to be 80 ^{o}C at which reaction mass is observed to be in near reflux conditions during reaction.

4.3.3.4 Effect of reaction time

In order to optimize the reaction time, the DMC-biodiesel synthesis has been investigated at 80° C by employing optimized conditions as defined in the aforementioned sections and conversion levels have been estimated in the time duration of 2-12 h.

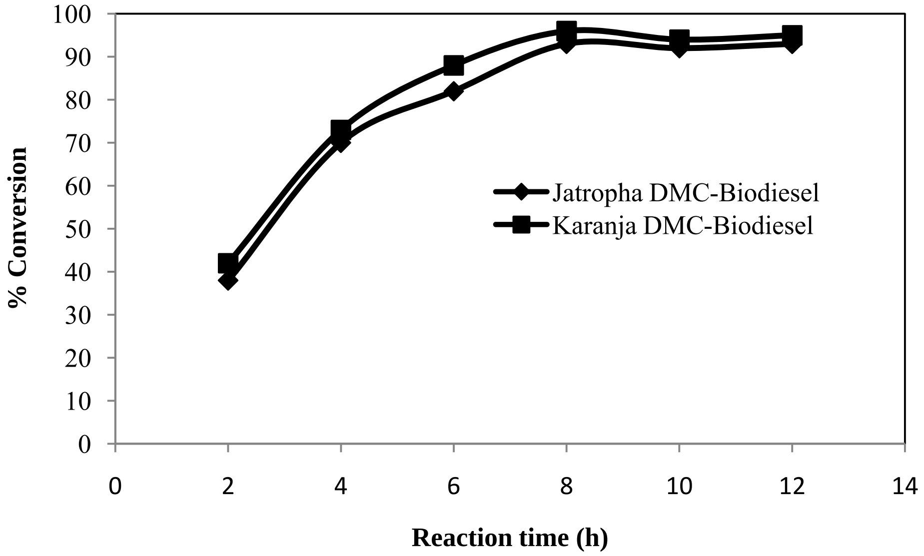


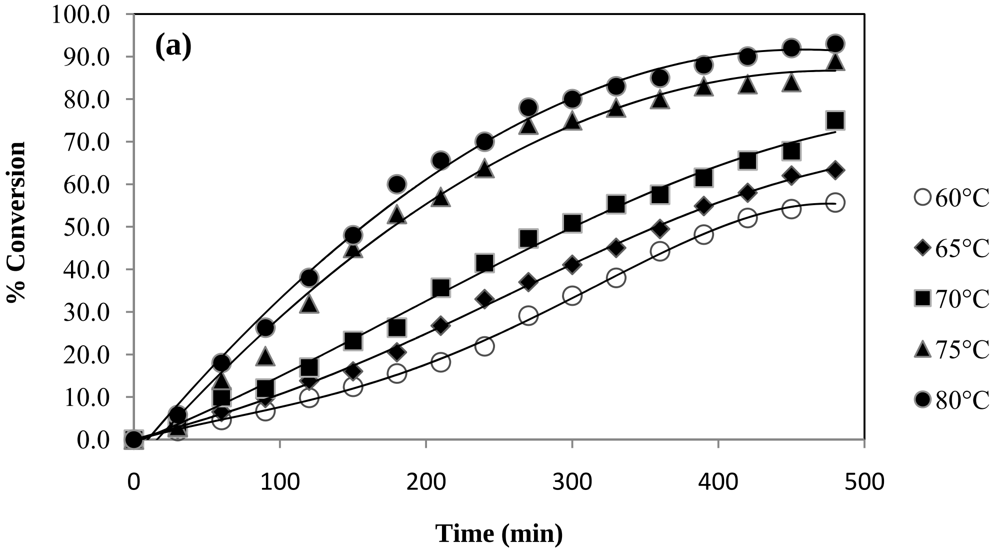
Figure 4.6 Effect of reaction time on the conversion for synthesis of biodiesel from Jatropha and Pongamia oil with DMC, at 9% catalyst amount, 10:1 molar ration of DMC to oil and under reflux condition

Figure 4.6 illustrates the obtained trend *w.r.t.* conversion. The conversion levels are found to increase with an increase in time from 2 h to 8 h and almost complete conversion of vegetable oil into DMC-biodiesel is achieved within 8 h. Further increase in time did not affect the conversion levels. Typically, conversion levels of approximately 94% and 96.0 % for Jatropha and Pongamia oil respectively, are noticed within 8 h of reaction time.

In view of the above, the kinetics of DMC-Biodiesel formation has been investigated under optimized reaction conditions. The results so obtained are discussed in the following section.

4.3.4 Kinetics of the reaction and its modeling

The formation of DMC-biodiesel has been investigated under optimized conditions (reactant ratio; DMC:oil = 10:1, KOH: 9%) in the temperature range of 60-80 oC. Typically, glycerol free transesterification reaction of vegetable oil (Triglycerides; TG) with DMC is comprised of two steps and the detailed reaction mechanism is reported elsewhere [Zhang et al., 2010]. The overall glycerol free transesterification reaction as depicted in Figure 4.1(a) is considered for kinetic study. Furthermore, each reaction step is assumed to be of first order with respect to each reacting component and irreversible due to excess amount of DMC. Therefore, the complete reaction system can be simplified into a single step assuming the whole reaction as a pseudo first-order reaction with respect to oil concentration, zero order for DMC concentration.



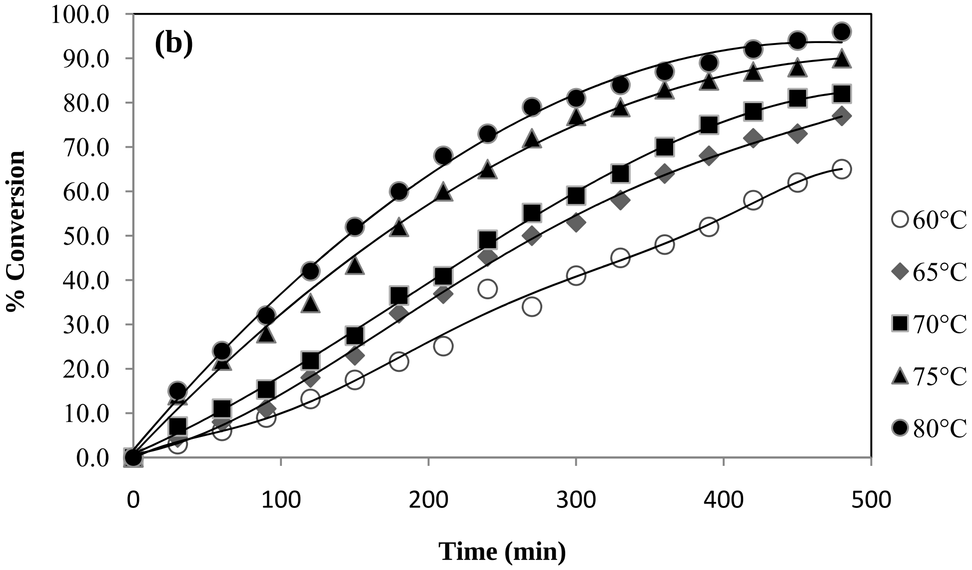
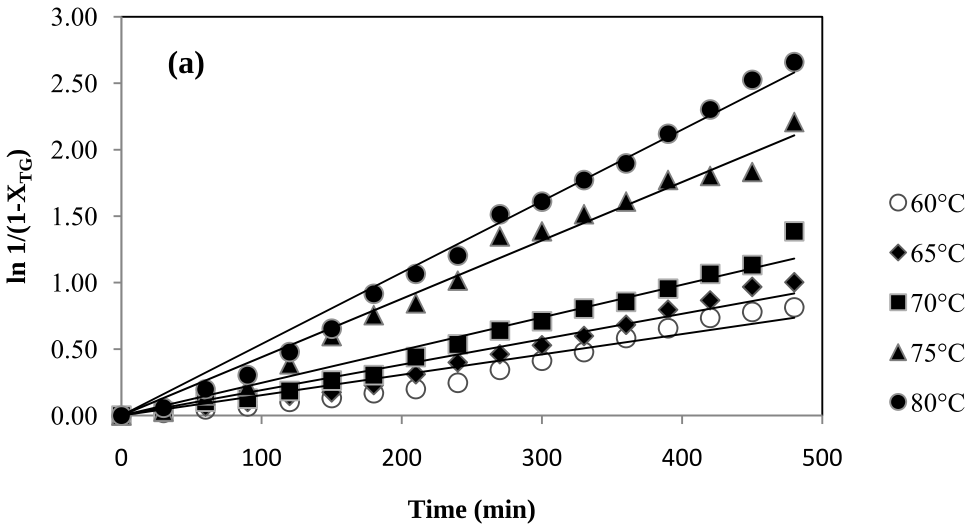


Figure 4.7 Kinetics of (a) Jatropha DMC-biodiesel and (b) Pongamia DMC-biodiesel synthesis at various temperatures using 9% catalyst amount and 10:1 molar ratio of DMC to oil

Figure 4.7 (a & b) illustrate the continuous increment in the conversion of TG into FAMEs as a function of time at various temperatures for the synthesis of DMC-biodiesel using Jatropha and Pongamia oil as feedstocks. From the measured kinetics data, it is evident that the rate of conversion into FAMEs is slow in the initial stage of the reaction, then increased and finally reached to the maximum level (> 90%) in about 480 min.

Furthermore, a good linear relation between ln [1/(1-X_{TG})] (where X_{TG} represents concentration of triglyceride *w.r.t.* time) and reaction time is observed which reinforced pseudo first-order reaction kinetic pathway during formation of DMC-biodiesel (Figure 4.8 a, b). The rate coefficient and the order of the reaction have been obtained from the intercept and slope of a semi log plot of the reaction rate with TG concentration.



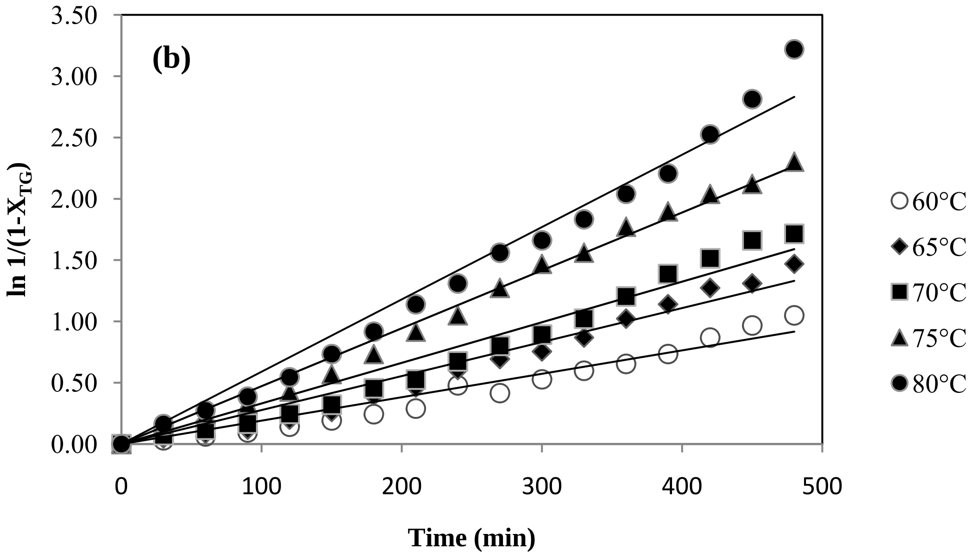


Figure 4.8 Envisaging the rate constant for synthesis of (a) Jatropha DMC-biodiesel and (b) Pongamia DMC-biodiesel through ln [1/(1-X_{TG})] as a function of reaction time t, at various temperatures based on 10:1 molar ratio of DMC to oil, 9% KOH as catalyst amount

Using reaction rate constants at different temperatures, the activation energy for the transesterification reaction is estimated by the Arrhenius Eq. (Figure 4.9 a, b). The estimated activation energies (E_a), are in the order of 66.4 ±2 and 54.6 ±2 kJ/mol for the synthesis of biodiesel from Jatropha and Pongamia oils with DMC respectively. These results are found to be in good agreement with literature data reported for DMC-Jatropha based biodiesel [Zhang et al., 2010; Darnoko and Cheryan, 2000; Freedman et al., 1986; Noureddini and Zhu, 1997]. Likewise, the pre-exponential factors (k_o) are found to be 3.7×10^7 min^{-1} and 6.8×10^5 min^{-1} for transesterification of Jatropha and Pongamia oils with DMC.

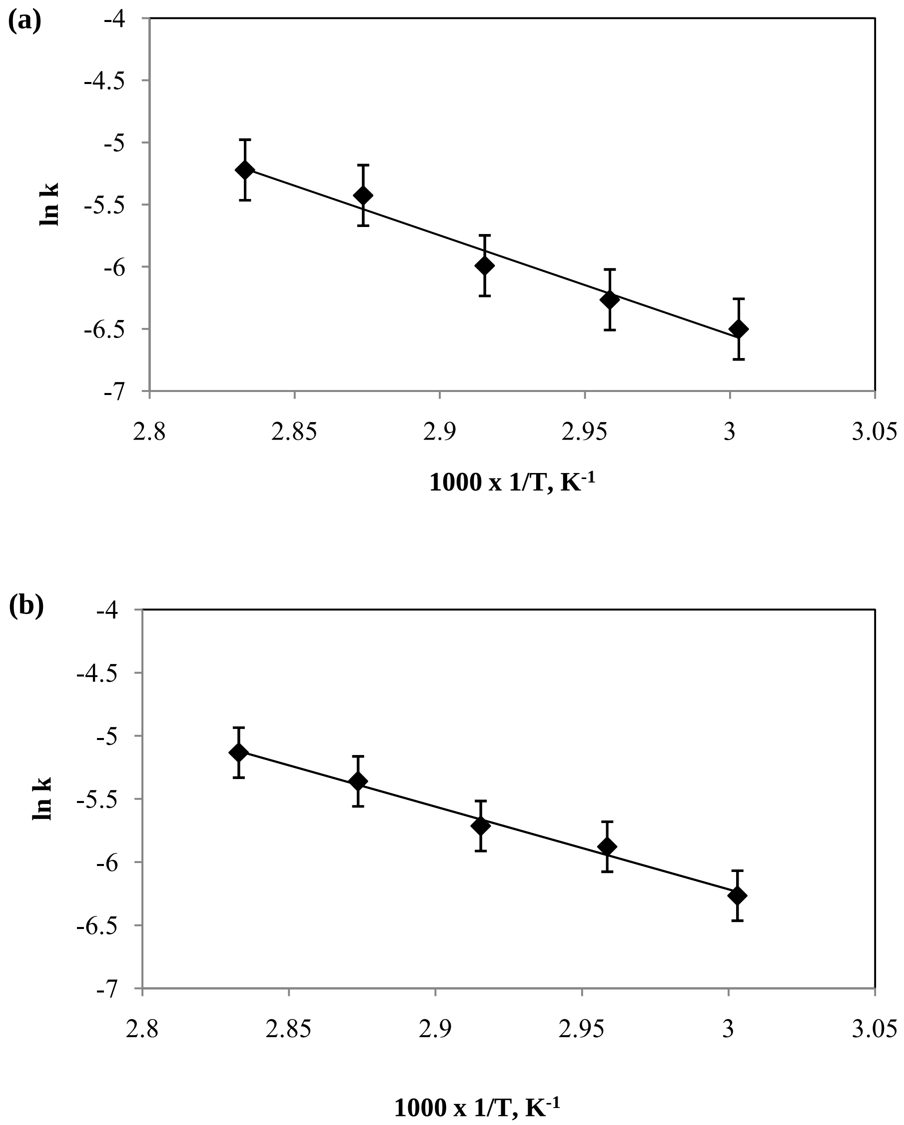


Figure 4.9 Variation of the rate coefficient, k with temperature for the synthesis (a) Jatropha DMC-biodiesel and (b) Pongamia DMC-biodiesel

It is worthwhile to note that the activation energy for transesterification of Jatropha oil is higher compared to that of Pongamia oil which can be attributed to the dissimilarity in the composition of neat oils [Rathore and Madras, 2007]. Typically, Pongamia oil has high content of mono-unsaturated and saturated fatty acids followed by low content of poly-unsaturated fatty acids compared to Jatropha oil fatty acid composition with respect to these acids as presented in the Table 4.1 of this study. This clearly shows that the transesterification reaction rate is the highest for the triglycerides of mono-unsaturated and saturated fatty acids followed by triglycerides of poly-unsaturated acids. On the other hand, the rate of reaction for oils containing poly-unsaturated fatty acids is expected to be slow vis-à-vis oils with of mono-unsaturated or saturated fatty acids. This further reinforces the obtained reaction kinetics trend for Pongamia and Jatropha oil in this study.

4.3.5 Biodiesel Characterization

Synthesized DMC-biodiesel samples are purified and further characterized as per standard methods ASTM D6751/EN 14214/IS 15607. The essential fuel properties are compared and presented in Table 4.3. The measured fuel properties are found to be in good agreement with the prescribed fuel specifications in various countries.

Table 4.3 Characterization of Jatropha and Pongamia oil derived DMC-Biodiesel from this study vis-a vis international standards

Property	Test Method	Unit	Specifications[a]			Synthesised DMC-Biodiesel	
			ASTM D 6751-2007	EN 14214:2008	IS 15607:2005	Jatropha	Pongamia
Density at 15^{0}C	ASTM D4052	gm/cm^3	-	0.860-0.900	0.860-0.900	0.8815	0.8850
Kinematic Viscosity at 40^{0}C	ASTM D445	cSt	1.9-6.0	3.5-5.0	3.5-5.0	4.02	5.6
Total acid number (TAN)	ASTM D664	mg/KOH	0.0-0.5.0	0.0-0.5	0.0-0.5	0.32	0.42
Moisture content	ASTM D2709	% wt	0.0-0.05	0.0-0.05	0.0-0.05	0.01	0.02
Flash point	ASTM D93	^{0}C	130 min	101 min	120 min	185	144
Copper strip corrosion	ASTM D30	rating	No. 3 max	Class 1	Class 1	Class 1	Class 1
Sulphur	ASTM D5453	% wt	0.0-0.05	0.0-0.001	0.0-0.001	0.0014	0.0018
Ester Content	EN 14103	% wt	-	96.5 min	96.5 min	96.8	97.2
Carbon Residue (10% bottom)	ASTM D4530	% wt	0.0-0.05	0.0-0.30	0.0-0.05	0.025	0.015
Alkaline Metals (Na+K)	EN 14108	mg/Kg	-	0.0-5.0	0.0-5.0	2.6	1.8
Phosphorus content	ASTM D4951	mg/Kg	0-10	0.0-4.0	0.0-10.0	4	5
Oxidation stability at 110^{0}C	EN 14112	hr	-	6 hr, min	6 hr, min	6.5[b]	6.8[b]

[a] ASTM (D 6751-2007); EN (14214:2008) ; IS (15607:2005)

[b] with additive i.e. butylated hydroxytoluene as antioxidant

4.4 Conceptualization of process

In view of the good agreement in fuel properties of DMC-biodiesel *vis-à-vis* conventional biodiesel, it is important to develop process for continuous production of DMC-biodiesel from commercial point of view. Thus, based on the present study, a batch process package is conceptualized for the productions of glycerol free DMC-biodiesel, and is presented in the Figure 4.10.

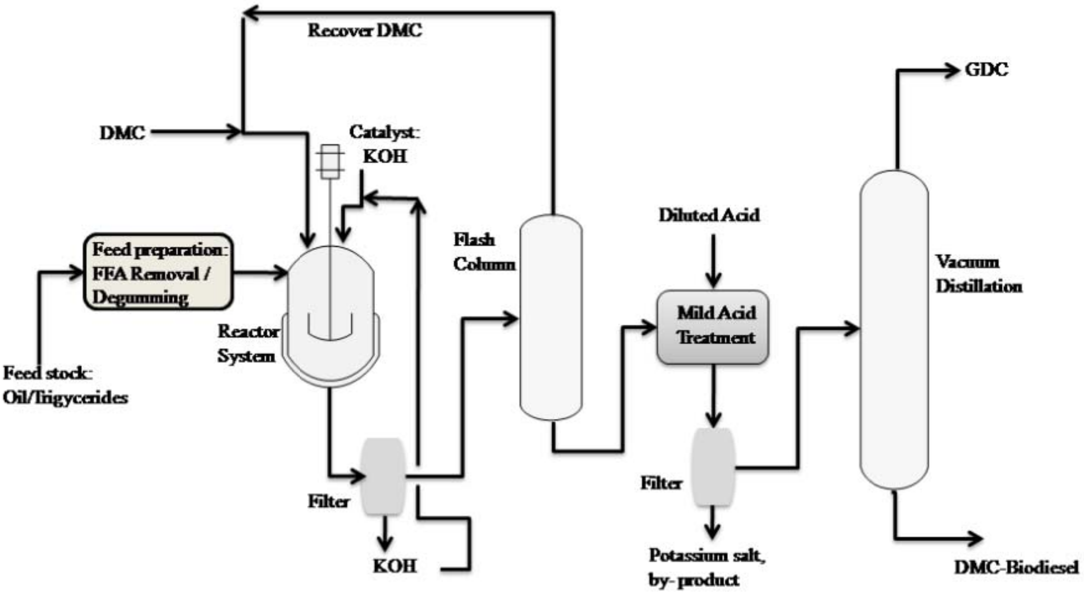


Figure 4.10 Conceptualized process flow diagram for glycerol free DMC-Biodiesel synthesis

Typically, feed preparation unit is proposed prior to transesterification reaction to avoid downstream operational problems associated to gums and free fatty acid (FFA) present in crude vegetable oil. The proposed process scheme consists of three sections i.e. feed preparation section, reaction section and product separation cum purification section. Thus, FFA free and degummed oil can be subjected to reaction with DMC in reactor section under stirred conditions using optimized conditions derived in the present study. The excess DMC recovery can be achieved via. flash column operation for its recycle from the formed product. Likewise, KOH can be recovered from reaction mixture for its reuse through filtration. Finally, the so obtained reaction mass can be subjected to product purification step by neutralizing (using dilute acid) the trace amount of KOH in form of insoluble potassium salt followed by separation through filtration. Subsequently, recovery of lighter component such as GDC can be envisaged based on the economic feasibility from the mixture of DMC-biodiesel and GDC. In sum, the key features of the proposed process are envisaged in terms of recovery of a) major amount of KOH which is not practiced in conventional biodiesel synthesis and can be recycled thereby reducing the load on effluent treatment process and b) optional recovery of by-product GDC based on market demand for its derivatives.

4.5 Conclusions

Transesterification of non-edible oils viz. Pongamia and Jatropha oil with DMC in presence of base catalyst*viz.* potassium hydroxide (KOH) has been investigated. Owing to glycerin market dynamics, glycerin free synthesis of biodiesel is offer platform for sustainable process development of for biofuel production and its implementation. The optimization study is carried out to comprehend the effects of reaction parameters such as catalyst amount, reactant molar ratio, temperature and reaction time on conversion into respective biodiesel of Jatropha and Pongamia oil. Furthermore, transesterification reaction kinetics is investigated in the temperature range of 60-80 ^{o}C. Based on the obtained results, the optimized reaction conditions have been zeroed in *w.r.t.* aforementioned parameters. Typically, maximum conversion of 94.0% and 96.0% have been achieved for Jatropha oil and Pongamia oil, respectively, at 9% (based on oil wt) of catalyst amount, 10:1 DMC to oil molar ratio at 80^{o}C in the 8 h reaction time. The activation energy (Ea) and the pre-exponential factor (k_o) are found to be, 66.4 ±2 KJ/mol and 3.7x10^{7} min^{-1} and 54.5 ±2 KJ/mol and 6.8x10^{5} min^{-1} for transesterification of Jatropha and Pongamia oil, respectively, using pseudo-first order kinetics. The obtained results, based on optimized parameters, demonstrate the feasibility of glycerin free synthesis of biodiesel. The kinetics data suggest DMC-biodiesel formation is more facile with Pongamia oil compared to Jatropha oil. Furthermore, properties for DMC-biodiesel of Jatropha and Pongamia oil are found to meet ASTM D6751/EN 14214/IS 15607 standards. In view of this, an eco-friendly glycerin free biodiesel process is conceptualized for its development and possible implementation.

CHAPTER 5

GLYCERIN FREE SYNTHESIS OF JATROPHA AND PONGAMIA BIODIESEL IN SUPERCRITICAL DIMETHYL AND DIETHYL CARBONATE

5.1 Introduction

The over growing environmental concerns worldwide have added impetus for development and implementation of biofuel programs. This has led to implementation of biodiesel program, in many part of the world, to offer eco-friendly substitute in terms of sulfur free fuel for existing fossil fuels [Ma and Hanna, 1999]. Moreover, the implementation of such program has envisaged to offer better fuel economy in terms of lubricity and cetane number as compared to diesel fuel derived from crude oil [Barnwal and Sharma, 2005]. Thus, various process options, involving transesterification of triglycerides (TGs), sourced from vegetable oils or animal fats, with methanol to produce biodiesel i.e. fatty acid methyl esters (FAME) and by-product glycerin, have been evolved [Ma and Hanna, 1999; Barnwal and Sharma, 2005]. Typically, processes based on homogeneous / heterogeneous catalytic route have been developed and commercialized [Anastasia et al., 2010]. However, their sustainability is yet to be proven due to the market dynamics and cost involved in purification of by-product glycerin which constitute about 10% of the reaction product. This is mainly because of involvement of high capital and energy intensive steps involved in purification of crude glycerin formed in the process for its valorization as fuel additives [García et al., 2008], hydrogen production [Adhikari, et al., 2008], methanol or ethanol production [Goetsch et al., 2008; Oh et al., 2011, varieties of fine chemicals specially 1,2- propanediol, 1,3-

propanediol, succinic acid, polyesters, lactic acid, and polyglycerins [Leoneti et al., 2012]. Furthermore, the efficiency of such processes are often found to be limited due to handling of feedstock containing high free fatty acids (FFAs) and moisture [Huber et al., 2006].

In order to capture the aforementioned issues, novel non-catalytic route i.e. supercritical synthesis of biodiesel has been developed [Saka and Kusdiana, 2001; Kusdiana and Saka, 2004]. The supercritical fluid (SCF) is a phase of fluid which exists above their critical temperature and pressure and has gas like diffusivities and liquid like viscosities, thereby offering a unique medium for synthesis and processing. This novel synthesis offers improve solvency of alcohols in the non-polar TGs and not affected by presence of free fatty acids and water in the feed stock as suffered by conventional synthesis processes [Kusdiana and Saka, 2004].

Conversely, attempts have been made for glycerin free synthesis of biodiesel using eco-friendly reactant such as methyl acetate and dimethyl carbonate (DMC) [Saka and Isayama, 2009; Fabbri et al., 2007]. The difference in reaction pathway for transesterification of vegetable oil with methanol *vis-à-vis* DMC as reported elsewhere in which glycerin-adduct, glycerin dicarbonate (GDC), is co-produced with DMC-biodiesel instead of low value glycerin. Interestingly, DMC based biodiesel is reported to have better lubricating properties *vis-à-vis* conventional biodiesel due to miscibility of formed byproduct GDC in the DMC-biodiesel phase [Fabbri et al., 2007]. In addition, the characteristics of produced DMC-biodiesel have been reported to be in good agreement with conventional methanol-biodiesel. However, DMC based transesterification synthesis is reported to have prolonged reaction time and high amount of catalyst owing to polarity difference between reactant and catalyst [Fabbri et al., 2007]. Therefore, non-catalytic supercritical

DMC process using vegetable oil as a feedstock have been attempted [Ilham and Saka, 2009; Ilham and Saka, 2009]. However, studies pertaining to use of non-edible oil such as Jatropha and Pongamia oil as a feedstock under supercritical conditions are sparse in the literature.

Therefore, the present work aims to investigate a) the glycerin free synthesis of biodiesel in supercritical phase of DMC and diethyl carbonate (DEC, for the first time to the best of our knowledge) using Jatropha and Pongamia oil as feed stock in absence of a catalyst and b) the kinetics of the reaction *vis-à-vis* non-catalytic supercritical methanol route. Typically, studies *w.r.t.* optimization of DMC/DEC-biodiesel synthesis parameters viz. (a) reactant to oil molar ratio; (b) temperature and (c) reaction time have been carried out. Based on the evaluation, optimal synthesis conditions have been determined and kinetic parameters have been estimated. The reaction rate constants (k) at different temperatures are determined and the activation energy (Ea) is reported for Jatropha and Pongamia biodiesel, individually with DMC and DEC. Also, to establish the thermal stability of biodiesel fuel at high temperature *w.r.t.* the exposure time, degradation study is also carried out at 325°C, 350 °C and 375 °C. Furthermore, distillation characteristics have been investigated for produced biodiesel and fuel characteristics have been evaluated *vis-a-vis* standard ASTM D6751/EN14214/IS15607 biodiesel specifications. Finally a simplified process flow is conceptualized for glycerin free supercritical process for production of DMC/DEC-biodiesel.

5.2 Experimental section

5.2.1 Materials

Crude Jatropha oil and Pongamia oil samples were obtained from the respective seeds by mechanical pressing. The reactants namely DMC and DEC (Technical grade) were purchased from S.D. Fine Chem. Ltd., India and used as received. Detailed physical and thermodynamic properties of DMC and DEC are shown in Table 5.1. The requisite GC standards namely methyl heptadecanoate (as internal standard, min purity 99%), fatty acids (Myristic, C14:0; Plamitic, C16:0; Palmitoliec, C16:1; Margaric, C17:0; Steric, C18:0; Oleic, C18:1, Linoleic, C18:2; Linolenic, C18:3; Arachidic, C20:0; Eicosenoic, C20:1; Behenic, C22:0; Lignoceric, C24:0) and their respective methyl esters were procured from Sigma-Aldrich, and employed for determination of oil composition and its conversion level as esters.

Table 5.1 Physical and thermodynamic properties of DMC and DEC

Properties	Unit	DMC[a]	DEC[b]
Density at 20°C	g/ml	1.07	0.975
Viscosity at 20°C	cP	0.625	0.827
Molecular wt.	g/mol	90.08	118.13
Solubility in water	g/100g	13.9	negligible
Vapour pressure at 20°C	mbar	53	11
Critical pressure, Pc	MPa	4.63	3.39
Critical temperature, Tc	°C	274.9	302.85
Melting temperature	°C	4.6	-43
Boiling temperature	°C	90.3	126.8
Flash point	°C	18	31
Dielectric constant		3.09	
Dipole moment	l, D	0.91	1.10
ΔH_{vap}	kcal/mol	8.03	8.83
Refractive index		1.3682	1.383

[a] [Tundo and Selva, 2002] [b] [ChemSpider, http://www.chemspider.com]

5.2.2 Synthesis

Transesterification of Jathropha and Pongamia in supercritical DMC and DEC was carried out in a custom designed 700 mL, four-necked batch type auto clave reactor (MOC: Hastelloy C-276, Amar Equipments, India) equipped with a cooling coil, magnetic drive coupling, turbine stirrer, external electrical ceramic band heater, condenser, thermocouple, pressure gauge and a sampling port. The simplified design sketch of the auto clave reactor used in this study is shown in Figure 5.1.

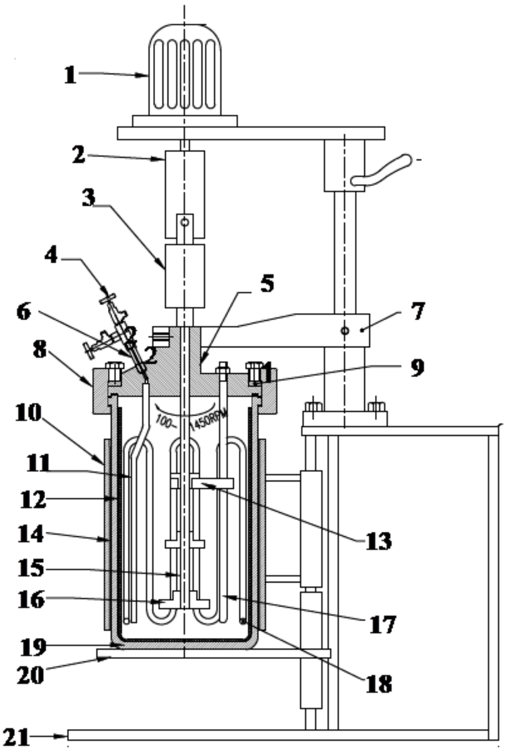


Figure 5.1 Experimental setup of autoclave for supercritical synthesis of biodiesel.

Legends: (1) stirrer motor; (2) coupling; (3) magnetic drive; (4) needle valve and sparger; (5) head; (6) adapter; (7) fixed head bracket; (8) body clamp; (9) compression ring; (10) removable electric ceramic band heater; (11) dip tube; (12) beaker ; (13) stirrer clamp; (14) heater shell; (15) stirrer shaft; (16) turbine impeller; (17) thermowell; (18) cooling coil; (19) auto clave body; (20) body lift arrangement; (21) table top arrangement

The reaction path was monitored through data logging software and variation of temperature in the system was controlled through PID controller (Model: DC1010, Honeywell, India) with ± 1 °C. A pre calibrated thermocouple and pressure gauge were employed to monitor the reaction temperature and pressure, respectively.

The kinetic study of biodiesel synthesis under supercritical DMC/DEC was investigated under optimized molar ratio of DMC/DEC to oils (molar ratio: 40:1) individually which is derived from the present study. This study is performed under stirred conditions in the temperature range of 250-350 °C for predetermined reaction time at 150 bar. Typically, reactants were introduced in the reactor at predefined molar ratio without any prior mixing. After reaching the desired reaction conditions, the reactor was quenched in to the ice-water bath. Subsequently, the reaction mass was taken out from the reactor and the excess DMC/DEC was separated using vacuum distillation unit (HERZOP PAC, Germany; Model: HDV 632). All reactions were conducted in triplicate to ensure reproducibility *w.r.t.* oil conversion within the error limit of ±2%. The extent of reaction was followed by means of gas chromatography (GC) technique using methyl heptadecanoate as internal standard and n-heptane as solvent. For this purpose, conversion was estimated by recovering oil phase from the reactant mixture as per the purification steps reported elsewhere [Meher et al., 2006].

5.2.3 GC Analysis

Fatty acid composition of both Jatropha and Pongamia oil was determined through GC technique (Perkin Elmer, USA; Model: Claurus 580) as reported elsewhere [Meher et al., 2006]. The reaction samples were analyzed by gas chromatography technique using a Elite-Wax ETR capillary column (30m length, 0.32 mm ID), having 0.5 µm film of polyethylene glycol and a flame ionization detector. Helium was used as the carrier gas at a flow rate of 2.0 mL/min. The flow rates of oxygen and hydrogen were 2 and 4 mL/min, respectively. Temperature of injector and detector was individually maintained at 250 °C while the oven temperature was maintained at 230 °C. The methyl esters (C_{14}-C_{24}) samples were used to construct the standard calibration curve for GC analysis. The oil and reaction samples were accurately weighed then mixed with predetermined amount of known concentration of internal standard solution (methyl heptadecanoate). Ester composition was determined by integration of area under the peak using internal standard method.

5.3 Results and discussion

The reaction conditions for glycerin free biodiesel synthesis in supercritical DMC and DEC have been investigated. The obtained results are discussed in the following sections.

5.3.1 Fatty acid (FA) composition for Jatropha and Pongamia oil

The estimated FA composition for Jatropha and Pongamia oils is compiled in Table 5.2. Likewise, physical properties of these oils used in the present study are listed in Table 4.2

Table 5.2 Fatty acid composition (% wt) of Jatropha and Pongamia oil used in this study

	Jatropha oil		Pongamia oil	
	Fatty acid constituents[n]	Composition (wt %)	Fatty acid constituents[n]	Composition (wt %)
Saturated acid (sat)	14:0; 16:0; 17:0; 18:0; 20:0	21.6[a]	16:0; 18:0; 20:0; 22:0; 24:0	26.39[b]
Mono-unsaturated acid (mono-unsat)	16:1; 18:1	45.4[c]	18:1; 20:1	54.37[d]
Di-unsaturated acid	18:2	32.8	18:2	16.64
Tri-unsaturated acid	18:3	0.2	18:3	2.60
Poly- unsaturated acid (poly-unsat)	18:2; 18:3	33.0[e]	18:2; 18:3	19.24[e]

[n] The former number represents the number of the carbons in the hydrocarbon chain while thelatter represents the number of the double bond in the respective fatty acid

[a] ∑ sat = C14:0+C16:0+C17:0+C18:0+C20:0 ; [b] ∑ sat = C16:0+C18:0+ C20:0+C 22:0+C24:0 ;
[c] ∑ mono-unsat = C16:1+C18:1 ; [d] ∑ mono-unsat = C18:1+C20:1; [e] ∑ ploy-unsat = C18:2+C18:3

Based on the estimated FA content in Jatropha oil, the distribution of FA is observed to be as myristic (C14:0; 0.1 %), plamitic (C16:0; 14.2%), palmitoliec (C16:1; 0.7%), margaric (C17:0; 0.1%), stearic (C18:0; 7.0%), oleic (C18:1; 44.7%), linoleic (C18:2; 32.8%), linolenic (C18:3; 0.2%) and arachidic (C20:0; 0.2%). Conversely, Pongamia oil has plamitic (C16:0; 11.65%), stearic (C18:0; 7.5%), oleic (C18:1; 53.27%), linoleic (C18:2; 16.64%), linolenic (C18:3; 2.6%), arachidic (C20:0; 1.7%), eicosenoic (C20:1; 1.1%), behenic (C22:0; 4.45%), and lignoceric (C24:0; 1.09%). Overall, Pongamia has more saturated (26.39%) and mono-unsaturated (54.37%) fatty acids compared to Jatropha oil where these fatty acids content is found to be 21.6 % and 45.4 % respectively. On the other hand, higher poly-unsaturated (di and tri) fatty acid content is determined in Jatropha (33%) compared to Pongamia oil (19.24%).

Fatty acid (FA) composition specially mono-unsaturated content and non-edible characteristics of Jatropha and Pongamia oil plays vital role for utilization in biodiesel production. Typically, mono-unsaturated acid content of oil are the ideal constituents for deriving biodiesel to meet fuel properties [Knothe, 2005; Moser and Vaughn, 2012]. These constituents provide a satisfactory balance between cold flow and oxidative stability as well as between kinematic viscosity (kV) and cetane number [Knothe, 2005; Moser and Vaughn, 2012]. Hence, the investigated oils used in this study, are provides better option as a feedstock for biodiesel synthesis and in between them, Pongamia has better perspective over Jatropha due to high oleic (mono-unsaturated) content.

5.3.2 Optimization of reaction parameters

5.3.2.1 Effect of molar ratio of DMC / DEC to oil

In supercritical synthesis of fatty acid methyl esters / ethyl esters (FAME / FAEE) i.e. biodiesel, the molar ratio of reactants (DMC and DEC) to oil is one of the most important variables due to reversible nature of the reactions. Stoichiometrically, 2 moles of DMC / DEC are required for 1 mole of triglycerides to accomplish the reaction and in practice, has to be present in plenty [Ilham and Saka, 2012]. Usually, the excess amount of DMC / DEC is needed for more interaction with bulky TGs molecule, to shift the equilibrium of the reaction towards in favor of the product. Therefore, the molar ratio of DMC and DEC to oil was investigated individually in the present study.

The effect of molar ratio was investigated under supercritical condition i.e. 325 °C, 150 bar for 40 min using Jatropha and Pongamia oil with DMC and DEC, individually. Figure 5.2 shows the effect of the molar ratio on the conversion into methyl and ethyl esters for Jatropha and Pongamia oil in supercritical DMC and DEC.

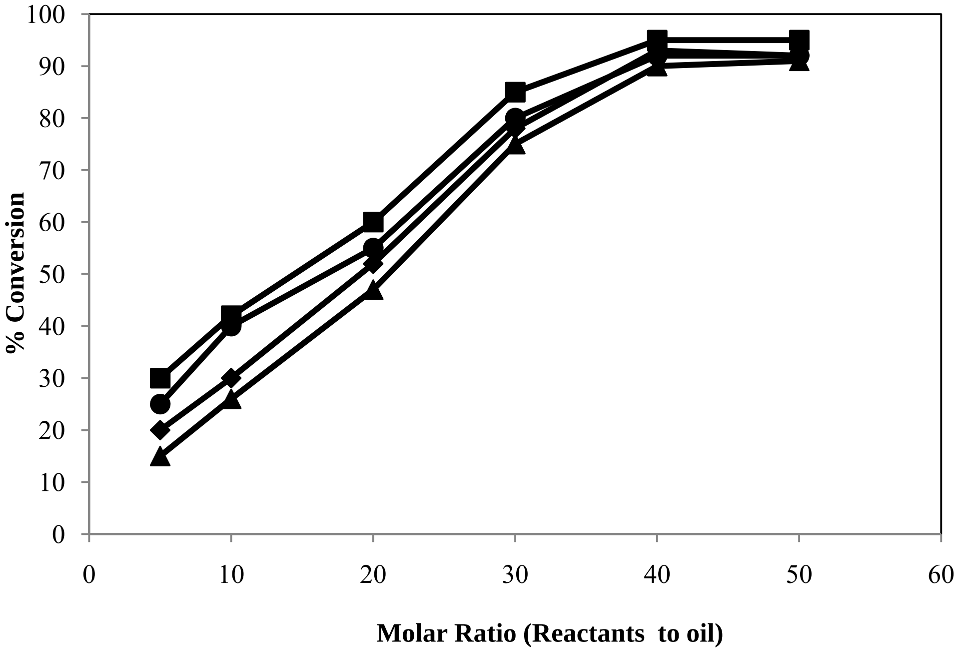


Figure 5.2 Effect of molar ratio on conversion for synthesis of biodiesel at 325°C in 40 min under supercritical DMC and DEC. Legends: (♦) Jatropha DMC-Biodiesel, (■) Pongamia DMC-Biodiesel, (▲) Jatropha DEC-Biodiesel, (●) Pongamia DEC-Biodiesel.

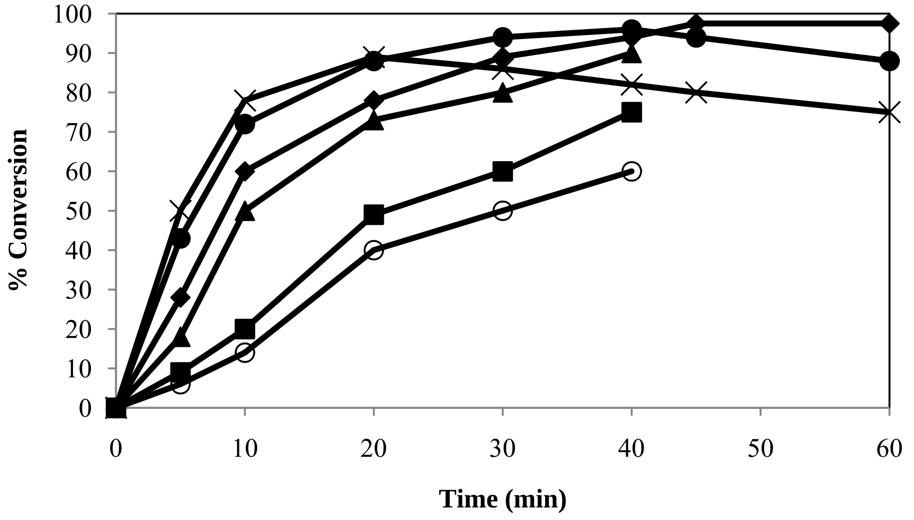
The conversion increases from 15 to 30% at a molar ratio of 5 to 90–95% at a molar ratio of 50 (Figure 5.1). This indicates that the higher molar ratio of DMC/DEC results in better reactivity for reaction, perhaps due to the increased contact area between DMC or DEC and TGs similarly as using supercritical methanol [Saka and Kusdiana, 2001]. In supercritical synthesis process, DMC and

DEC are expected to behave like fluids, have density like liquids and diffusivity like gases which helps to facilitate the batch and flow-type supercritical processes. Therefore, the conversion improves with higher amount of DMC/DEC in reaction media, and a saturation level is attained at 40 molar ratio. Afterwards conversion does not improve significantly and reaction rate is just in the plateau region when more of DMC/DEC introduced in the reaction. This phenomenon can be explained on formation of homogeneous phase which is influenced by lower molar ratio and remain unaffected at high molar ratio due to no change in homogeneity [He et al., 2007]. Hence, the optimum molar ratio of DMC/DEC to oil is found to be 40. These results are in good agreement with reported studies on DMC-biodiesel system [Ilham and Saka, 2009] and the depicted trends are similar to supercritical methanol based biodiesel synthesis [Saka and Kusdiana, 2001; Kusdiana and Saka, 2004; Saka and Kusdiana, 2001].

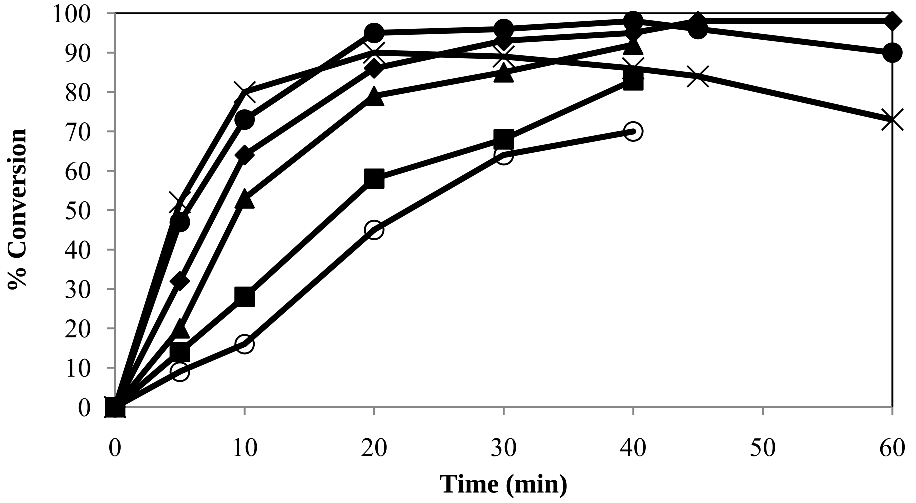
5.3.2.2 Effect of temperature

The effect of temperature was investigated by carrying out experiments with an optimum molar ratio of 40:1 at 150 bar for both the oils in the low temperature range 250-300 ^{o}C and higher temperature range 325-375 ^{o}C with variation in time up to 40 min and 60 min respectively. Figures 5.3 a,b and c,d depict the plot of conversion at different temperatures with time for the formation of methyl and ethyl esters, respectively.

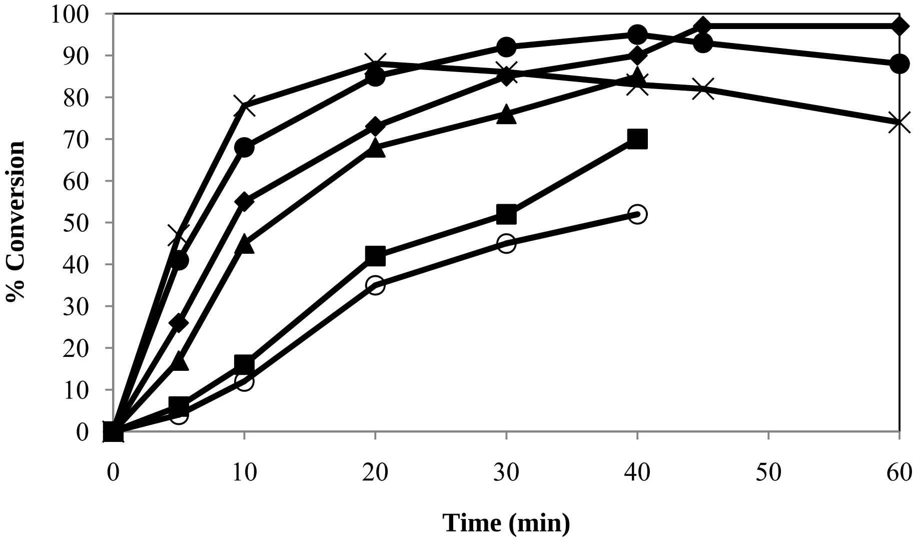
(a)


100
90
80
70
60
50
40
30
20
10
0
% Conversion
0
10
20
30
40
50
60
Time (min)

(b)


100
90
80
70
60
50
40
30
20
10
0
% Conversion
0
10
20
30
40
50
60
Time (min)

(c)


100
90
80
70
60
50
40
30
20
10
0
% Conversion
0
10
20
30
40
50
60
Time (min)

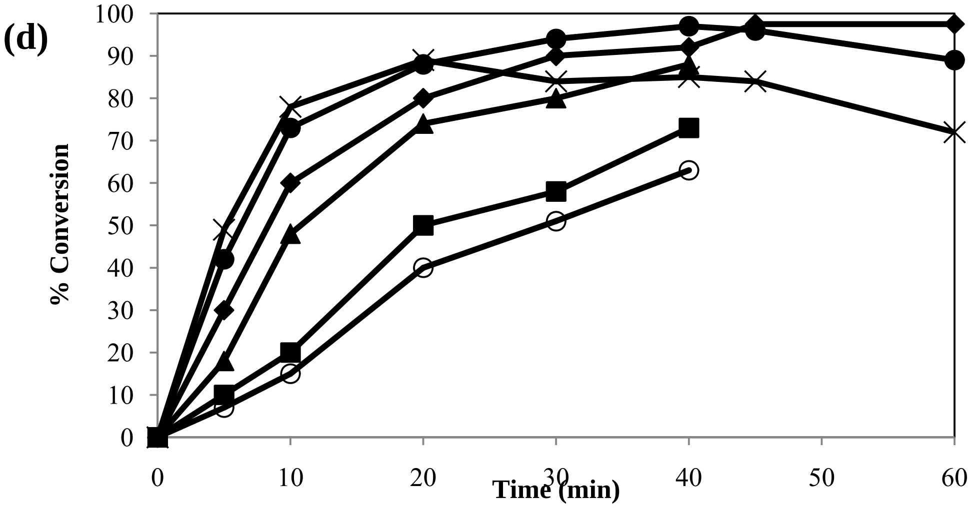


Figure 5.3 Effect of temperature and reaction time for synthesis of biodiesel. (a) Jatropha DMC-Biodiesel, (b) Pongamia DMC-Biodiesel, (c) Jatropha DEC-Biodiesel, (d) Pongamia DMC-Biodiesel. Legends: (○) 250°C, (■) 275°C, (▲) 300°C, (♦) 325°C, (●) 350°C, (x) 375°C

At 250°C and 275°C, the relatively low conversion of TGs into fatty acid alkyl ester (FAAE) is evident due to the subcritical state of DMC and DEC respectively. The range of maximum conversion lies in between 70-83% for DMC and 63-73 % for DEC at 250 °C and 275 °C, respectively. The obtained results are in good agreement with the trend reported elsewhere [Demirbas, 2002]. The conversion levels were found to be higher in case of Pongamia oil compared to Jatropha oil as a function of time. This could be due to their inherent FA composition w.r.t. mono-unsaturation leading to higher reactivity of Pongamia oil over Jatropha oil.

However, it was observed that conversion continues to improve with higher temperature and it reaches to its maximum level i.e. 92 % for DMC and 88% for DEC at 300°C/150 bar in 40 min of reaction time. Hence, temperature plays vital to achieve the desire level of conversion in non-catalytic supercritical synthesis.

Therefore, higher temperature range 325-375 °C was also investigated at 150 bar with longer reaction time i.e. up to 60 min (Figure 5.3).

The conversion level is found to further improve at 325°C/150 bar for both DMC and DEC. Typically, the conversion was obtained in the range of 28-32% for DMC; 26-30% for DEC in 5 min and it found to reach near completion to about 98-99 % in 45 min for DMC/DEC. Similarly, at higher temperature i.e. 350 °C, conversion improved from 43-47% for DMC; 41-42% for DEC in 5 min and 96-98% for DMC; 95-97% for DEC in 40 min. However, further increase the reaction time led to drop in conversion level. Likewise, further increase in reaction temperature to 375 °C favored increase in conversion level up to 20 min and subsequently led to drop in conversion level with an increase in reaction time. The observed trend can be ascribed to the thermal decomposition of DMC/DEC-biodiesel at 150 bar as discussed in section 3.4. Hence, the obtained results have demonstrated the better conversion at lower pressure and temperature condition i.e. 325°C / 150 bar in single step process. Therefore, the optimum supercritical has been zeroed in at 325°C / 150 bar, 45 min for DMC and DEC, individually to avoid the thermal decomposition of the reactant/product. The obtained results were further compared with reported studies on glycerin free synthesis of biodiesel (Table 5.3).

Table 5.3 Process parameter comparison for glycerin free synthesis of biodiesel vis-à-vis present study

Oil	Reactant	Reaction pathway	Optimal reaction parameters			% Ester yield	Reference
			Temperature (°C)	Pressure (bar)	Time (min)		
Rapeseed	DMC	Transesterification	350	200	15	94	[Ilham and Saka, 2009]
Jatropha	DMC	Hydrolysis Esterification	Step I 270 Step II 300	200 90	20 15	97	[Ilham and Saka, 2010]
Rapeseed	DMC	Transesterification	350-380	200	<30	97	[Ilham and Saka, 2012]
Rapeseed	Methyl acetate	Transesterification	350	200	45	97	[Saka and Isayama, 2009]
Jatropha	DMC/DEC	Transesterification	325	150	45	98-99	Present study
Pongamia	DMC/DEC	Transesterification	325	150	45	98-99	Present study

Typically, reported studies on rapeseed oil based biodiesel synthesis using methyl acetate as methylating agent under supercritical conditions demands process parameters of 350 °C and 200 bar with optimum time of 45 min to achieve 97% conversion level [Saka and Isayama, 2009]. Furthermore, the successful formation of rapeseed-DMC biodiesel under supercritical conditions is reported to demand high pressure conditions. On the other hand, two stage conversion process is reported to bring down the severity of the reaction for Jatropha based biodiesel synthesis wherein TGs are converted to FAs via hydrolysis route at 200 bar followed by their esterification with DMC. In view of the reported studies, it is evident from the present study that Jatropha/Pongamia-DMC/DEC biodiesel demands lower reaction pressure and temperature (150 bar / 325 ^{o}C) as compared to rapeseed-DMC biodiesel. It may be noted that the rapeseed oil contains less amount of saturated, higher amount of mono-unsaturated and poly-unsaturated FA compared to Jatropha and Pongamia oils. This trend in turn reinforces the influence of FA composition of feedstock in optimization of reaction parameters under supercritical conditions.

5.3.3 Reaction Kinetics

The reaction kinetics is performed for subcritical and supercritical state of DMC/DEC at 150 bar, temperature ranging 250-350 ^{o}C for 40 min of reaction time. The higher temperatures 375 ^{o}C and longer reaction time beyond 40 min for 350 ^{o}C were not considered due to thermal decomposition of reactants/products. The conversion into alkyl esters with time at various temperatures (250^{o}C-350^{o}C) is depicted in Figure 5.3 (a,b,c,d). From the measured kinetics data (Figure 5.2), it is evident that the rate of conversion into biodiesel is slow in subcritical state (250^{o}C for DMC; 275^{o}C for DEC) compared to supercritical state of DMC and DEC, and improves with time. As per the proposed reaction mechanism under supercritical conditions, the formation of FAAE is ascribed to the difference in reaction pathway compared to conventional synthesis of biodiesel using methanol. Here, TGs react with supercritical di-alkyl carbonate (DAC) molecule (DMC and DEC) to form intermediates viz. alkyl carbonate di-glycerides (ACDG), and then di-alkyl carbonate mono-glycerides (DACMG). This further reacts to form FAAE, intermediate fatty acid glycerol carbonate (FAGC) and by product GDC [Ilham and Saka, 2009].

As presented in Figure 5.4, 2 mole of FAAE form along with intermediate i.e. FAGC in the first step and subsequently in the second step, FAGC again converts into one more mole of FAAE and by product like GDC wherein, each reaction step is considered to be of first order with respect to each reacting component and irreversible due to excess amount of DAC. Therefore, the complete reaction system can be simplified into a single step assuming the whole reaction as a pseudo first-order reaction with respect to oil concentration, zero order for DMC and DEC concentration individually.

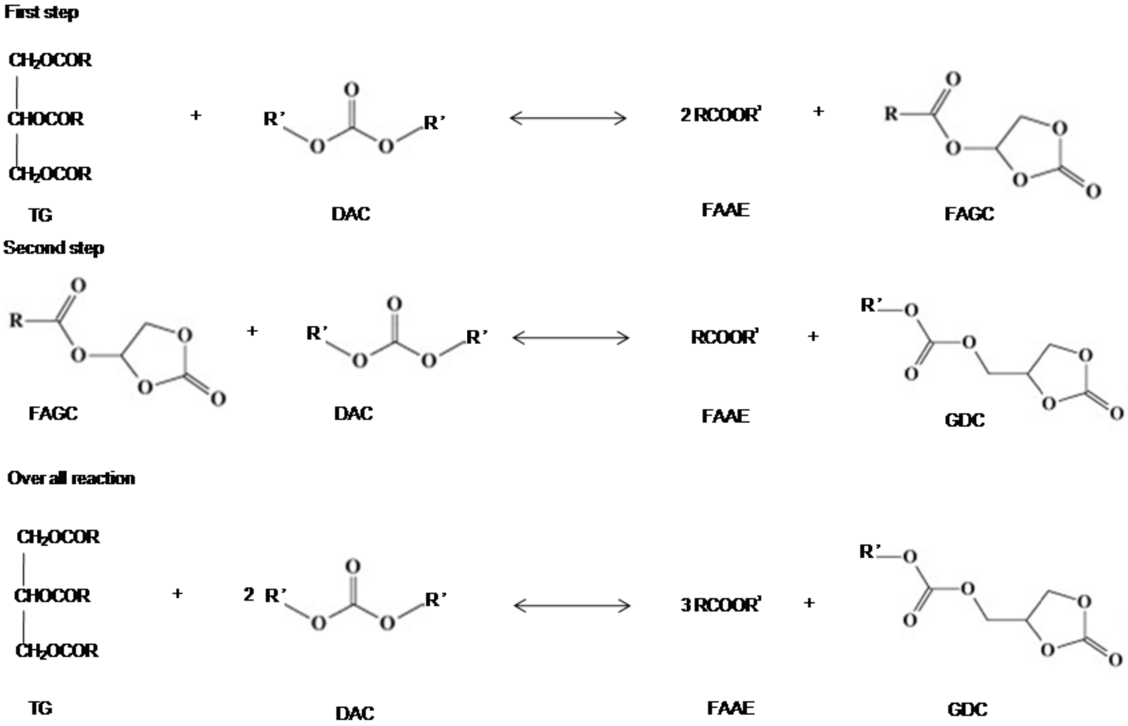
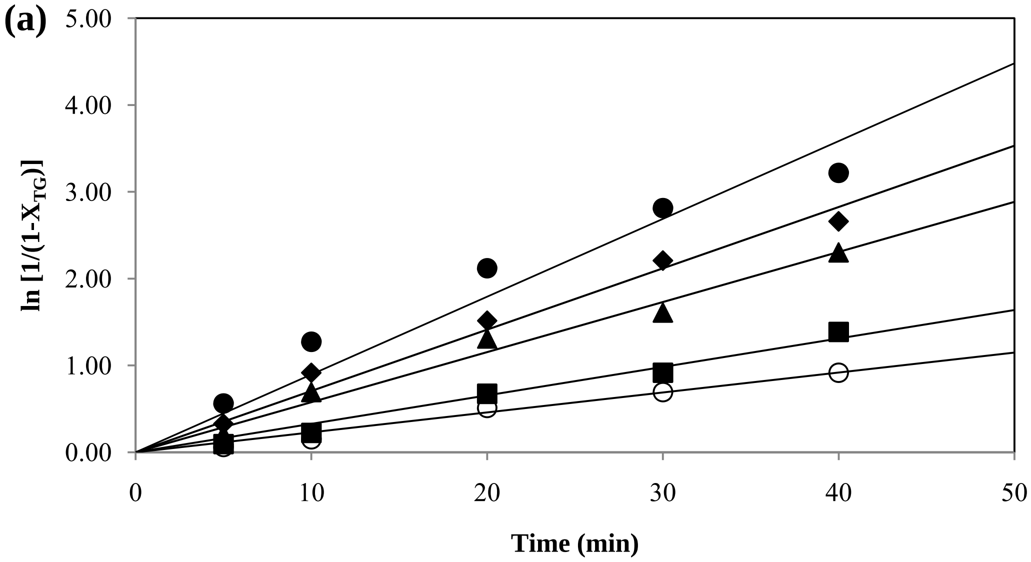
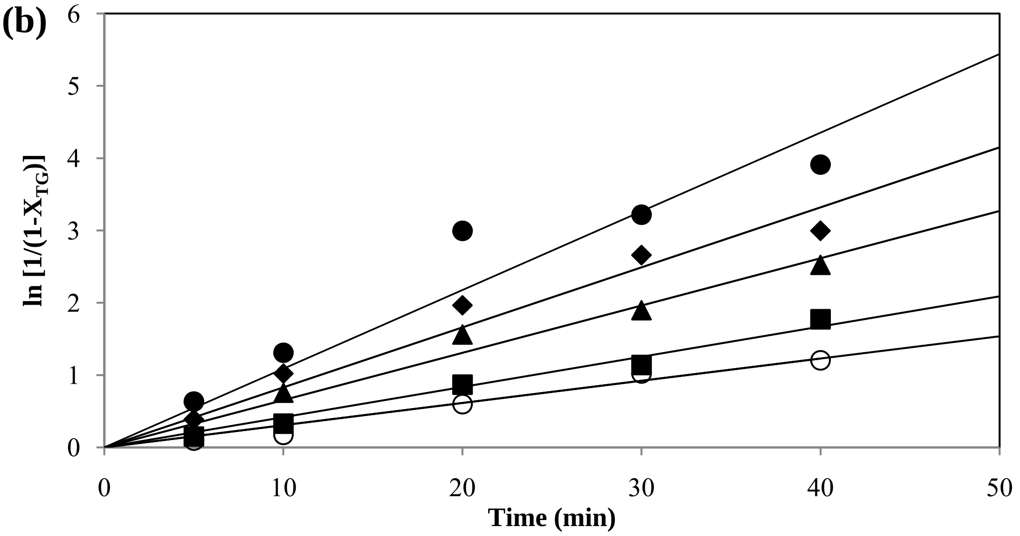


Figure 5.4 Reaction mechanism for glycerin free synthesis of biodiesel. Legends: R', CH_3 for DMC, C_2H_5 for DEC

The rate coefficient, the order of the reaction and the rate coefficient of the reaction can be directly obtained from the intercept and slope of a semi-log plot of the reaction rate with oil concentration [Demirbas, 2002; Madras et al., 2004]. A good linear relation between ln $[1/(1-X_{TG})]$ (where X_{TG} represents concentration of triglyceride *w.r.t.* time) and reaction time is observed which reinforced pseudo first-order reaction kinetic pathway during formation of biodiesel in supercritical DMC and DEC (Figure 5.5 a,b,c,d). The rate coefficient and the order of the reaction have been obtained from the intercept and slope of a semi log plot of the reaction rate with TGs concentration.





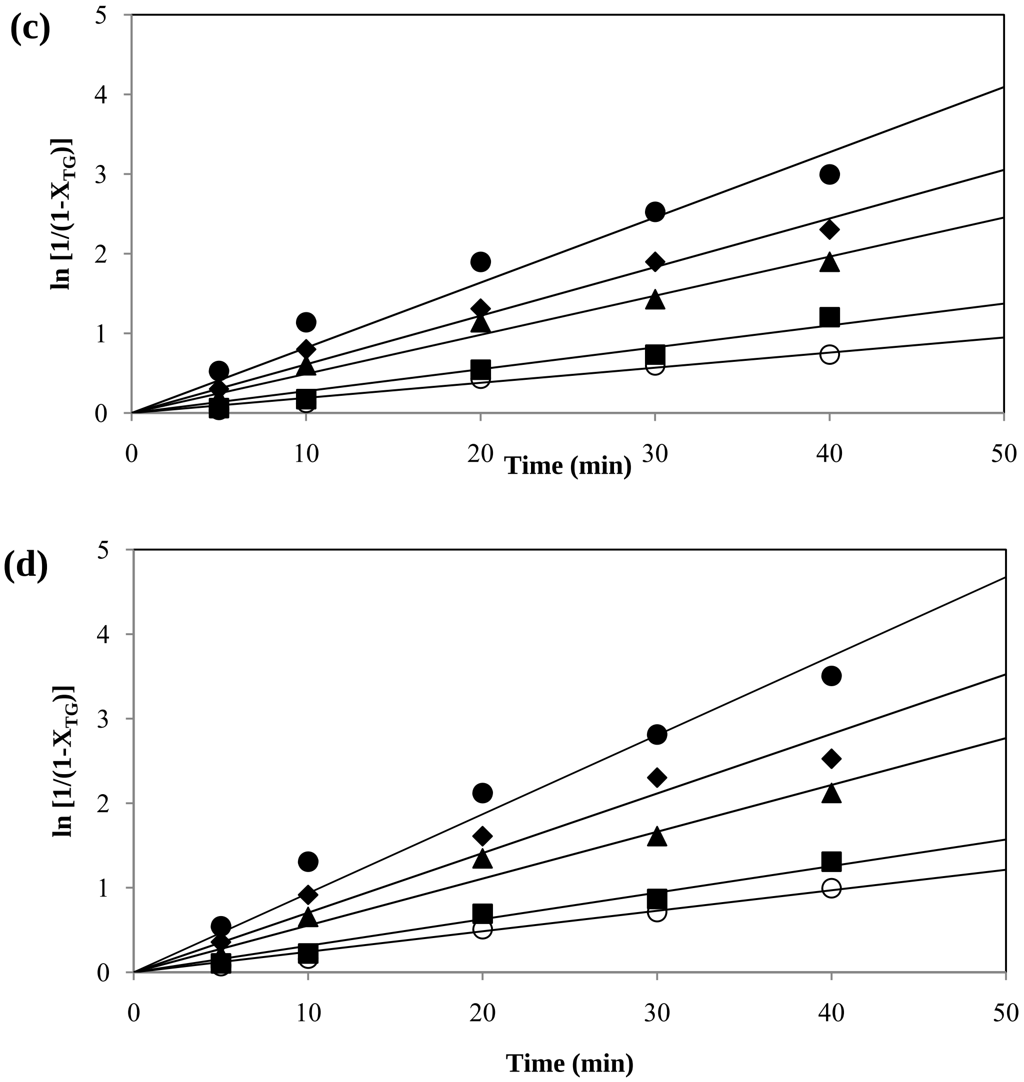


Figure 5.5 Envisaging the rate constant for synthesis of (a) Jatropha DMC-Biodiesel, (b) Pongamia DMC-Biodiesel, (c) Jatropha DEC-Biodiesel, (d) Pongamia DMC-Biodiesel through ln [1/(1-X_{TG})] as a function of reaction time at 40:1 molar ratio of reactants to oil under various temperatures in supercritical conditions. Legends: (○) 250°C, (■) 275°C, (▲) 300°C, (♦) 325°C, (●) 350°C.

Using reaction rate constants at different temperatures, the activation energy for the reaction is estimated by the Arrhenius Eq. (Figure 5.6 a, b). The estimated activation energies (E_a), are in the order of 38.0 ±2 and 35.5 ±2 kJ/mol for the synthesis of biodiesel in supercritical DMC from Jatropha and Pongamia oil, respectively. These activation energies are lesser than the reported for palm oil with DMC in presence of catalyst [Zhang, et al., 2010]. While in supercritical DEC, estimation activation energies are in the order of 40.4 ±2 and 38.2 ±2 kJ/mol for conversion of Jatropha and Pongamia oil, respectively. The presented study is found to be in a good agreement with literature data reported for synthesis of biodiesel in supercritical methanol using rapeseed oil as a feedstock [Saka and Kusdiana, 2001].

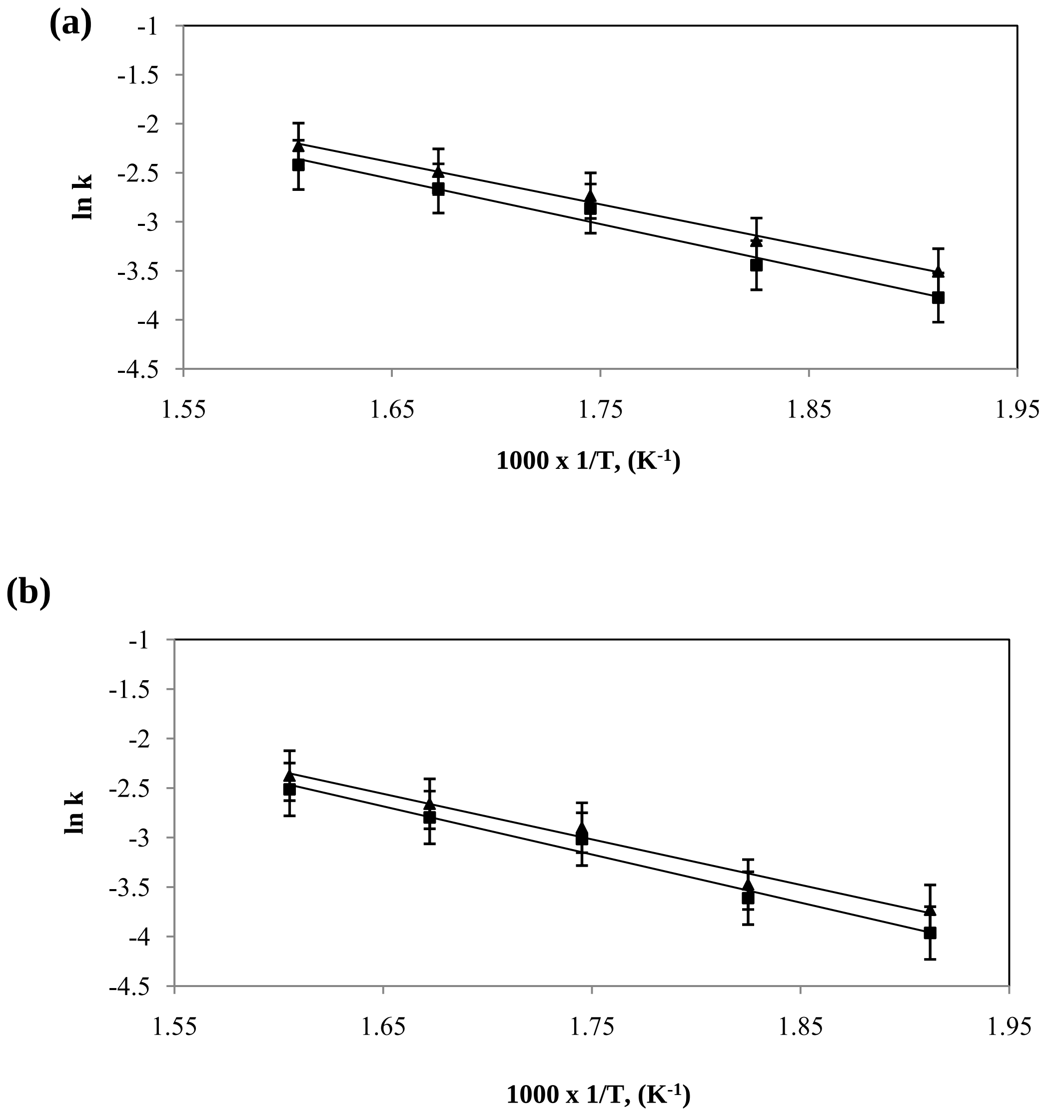
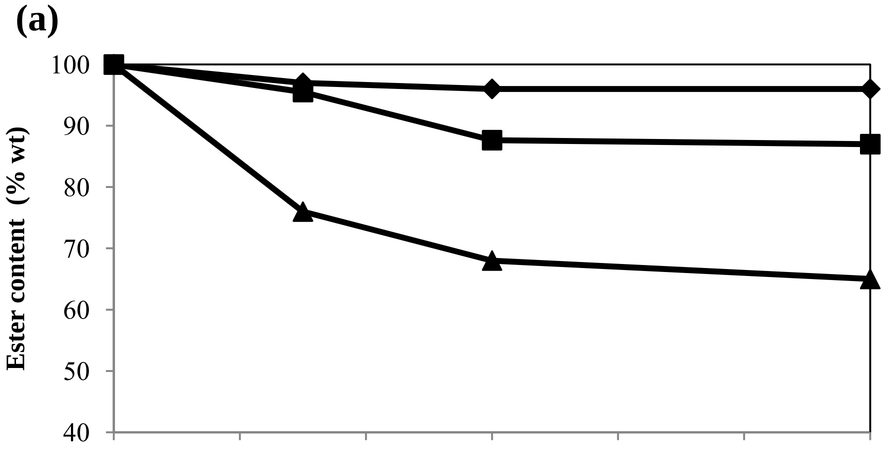


Figure 5.6 Variation of the rate coefficient, (k), with temperature for supercritical synthesis of biodiesel. (a) DMC-Biodiesel, (b) DEC-Biodiesel. Legends: (■) Jatropha oil , (▲) Pongamia oil.

It is worthwhile to note that the activation energy in supercritical DMC is slightly lower than the supercritical DEC. Hence, reaction in supercritical DMC is faster than the supercritical DEC, and it is perhaps due to greater molecule interactions and easy of cleavage with DMC compared to DEC. In addition, rate of reaction is high for Pongamia oil compared to that of Jatropha oil which can be attributed to the dissimilarity in the composition of neat oils (Table 5.2) [Rathore and Madras, 2007]. Typically, Pongamia oil has high content of mono-unsaturated and saturated fatty acids followed by low content of poly-unsaturated fatty acids as compared to Jatropha oil as presented in the Table 5.2 of this study. This clearly shows that the transesterification reaction rate is the highest for the triglycerides of mono-unsaturated and saturated fatty acids followed by triglycerides of poly-unsaturated acids. On the other hand, the rate of reaction for oils containing poly-unsaturated fatty acids is expected to be slow vis-à-vis oils with of mono-unsaturated or saturated fatty acids. This further reinforces the obtained reaction kinetics trend for Jatropha and Pongamia oil in this study.

5.3.4 Thermal stability of biodiesel in supercritical condition

The thermal stability of Jatropha and Pongamia biodiesel formed under supercritical condition of DMC and DEC, was investigated by performing thermal treatment of the biodiesel product in the temperature range of 325-375 °C at 150 bar by varying exposure time. Figure 5.7 depicts that the severity of biodiesel degradation increases with temperature and time. At 325 °C, the biodiesel content is found to be 96.5-98.6 % in 15 min which remained unaltered even after 60 min of exposure time. Hence, the prepared DMC/DEC-biodiesel is observed to be stable at 325 °C. However, further rise in temperature showed onset of thermal degradation of prepared biodiesel samples. Typically, the biodiesel content is dropped in the range of 94-96.5% and 73-77% in 15 min of exposure at 350 and 375 °C, respectively and reached to 85-87 % and 62-69 % in 60 min due to increment in the exposure time. While comparison, effect of thermal degradation was more pronounced with Jatropha oil derived biodiesel samples compared to Pongamia oil biodiesel. It is perhaps due to inherent dissimilarity of the FA composition and presence of lower degree of saturation (Table 5.2). The obtained results is also good agreement with the previous study [Ilham and Saka, 2012; Imahara et al., 2008] and confirms that poly-unsaturated biodiesel contents are especially vulnerable to thermal decomposition when compared with mono-unsaturated and saturated ones. In view of this, supercritical synthesis has been carried out in the vicinity of supercritical region (325 °C / 150 bar for DMC / DEC) to avoid onset of thermal degradation of the formed product.



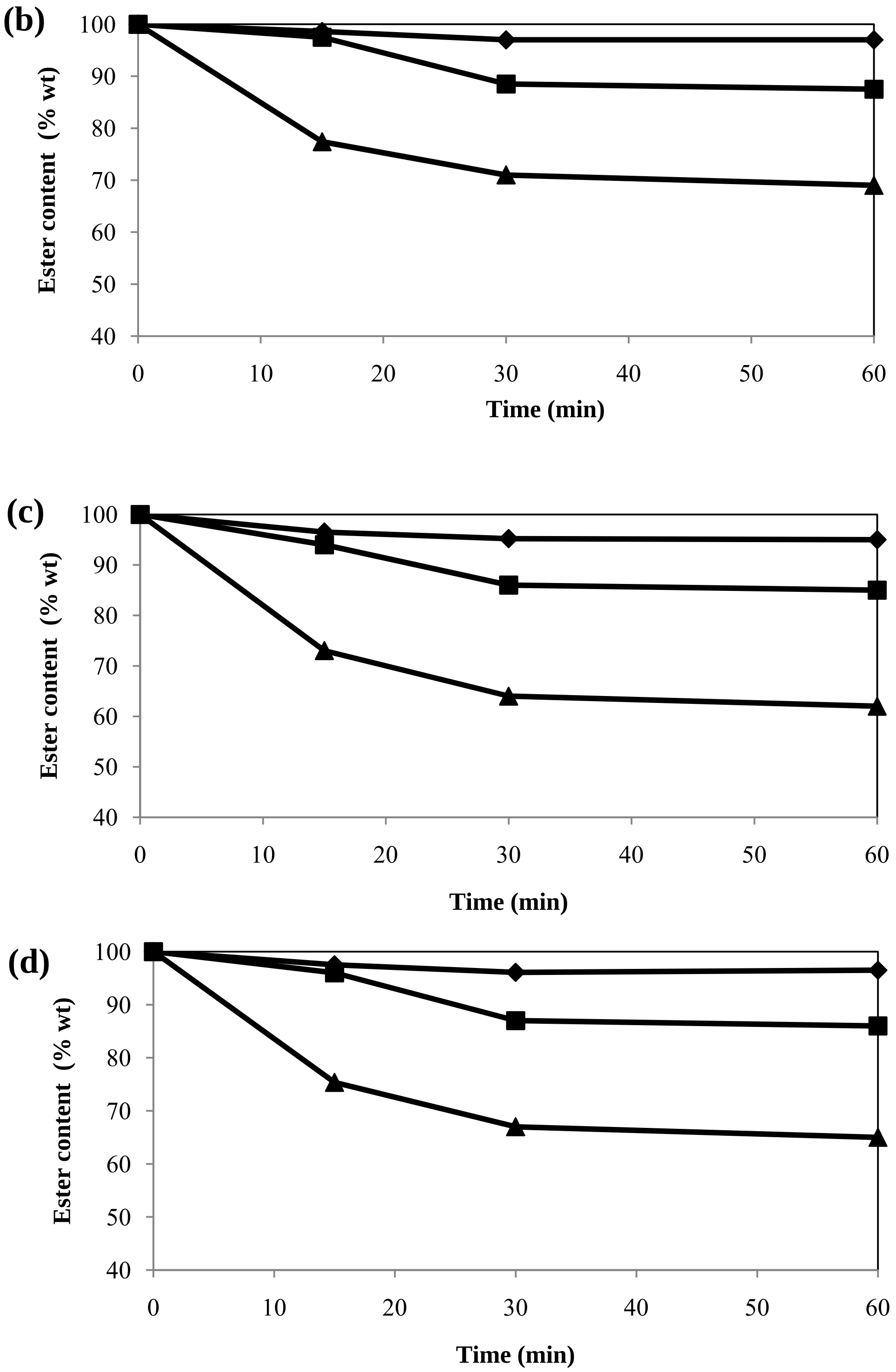


Figure 5.7 Thermal stability of biodiesel under various temperatures at 150 bar in supercritical condition of DMC and DEC. (a) Jatropha DMC-Biodiesel, (b) Pongamia DMC-Biodiesel, (c) Jatropha DEC-Biodiesel, (d) Pongamia DMC-Biodiesel. Legends: (♦) 325°C, (■) 350°C, (▲) 375°C.

5.3.5 Distillation characteristics, estimation of normal boiling point and fuel properties

The biodiesel is a mixture of fatty acid alkyl esters which is having a narrow boiling range (~325 and 350 °C) compared to commercial diesel fuel [Graboski et al., 1998]. The distillation characteristics of DMC/DEC-Jatropha /Pongamia biodiesel have been evaluated in the present study and are reported for the first time, to the best of our knowledge. The distillation characteristics are reported in atmospheric equivalent temperature (AET), were determined by ASTM D1160 method at 1.32 mbar. Figure 5.8a depicts that the Jatropha and Pongamia DMC-biodiesel has a boiling range of 295-373 ^{o}C and 310-375 ^{o}C respectively. Likewise, Figure 5.8b depicts that Jatropha and Pongamia DEC- biodiesel has boiling range of 305-385 ^{o}C and 312-386 ^{o}C, respectively. Hence, it is observe that boiling range of DEC-biodiesel is slightly higher compared to DMC-biodiesel. Furthermore, the reported distillation range for biodiesel samples is found to be slightly higher compared to biodiesel prepared using methanol (Figure 5.8a). This could be due to the presence of glycerin carbonate formed during the reaction along with DMC/DEC-biodiesel product.

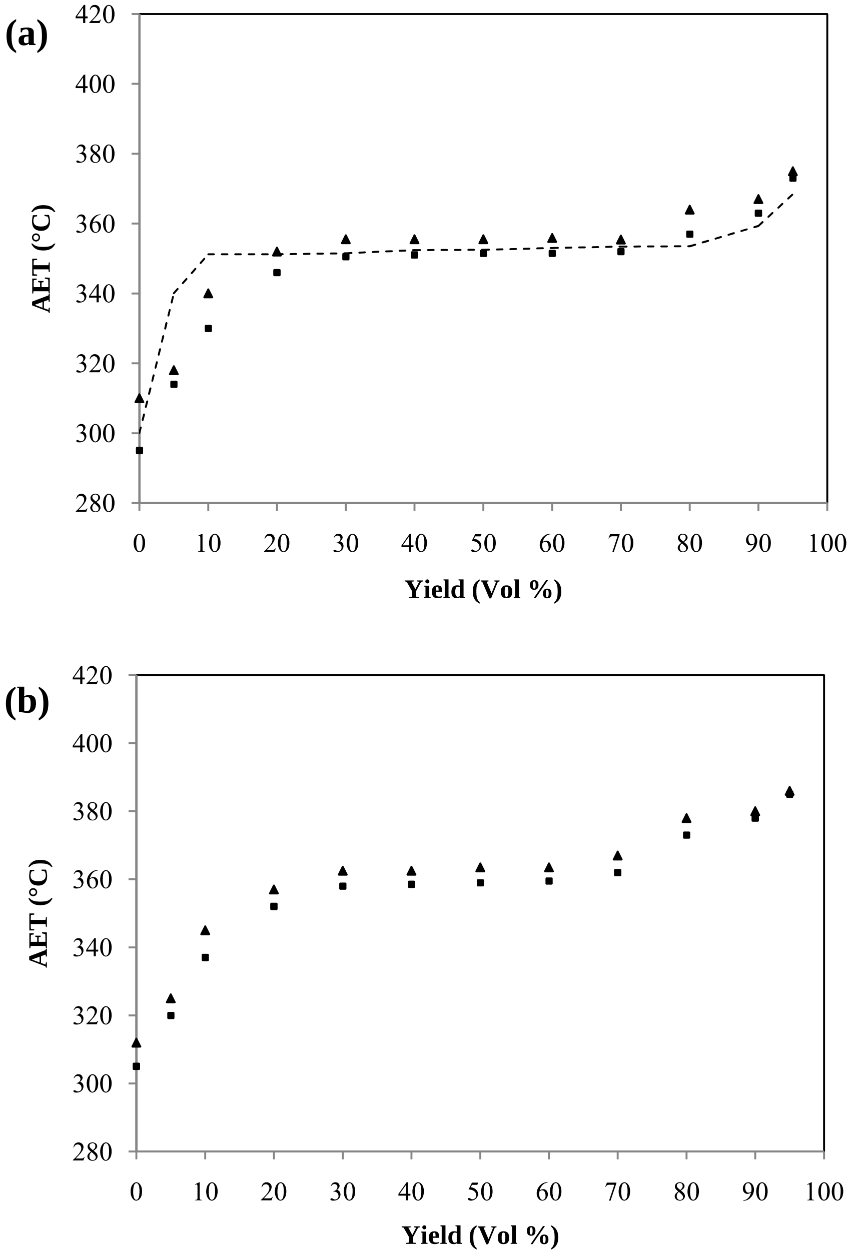


Figure 5.8 Distillation Characteristics (by ASTM D1160 unit) of biodiesel synthesized in supercritical condition of DMC and DEC. (a) DMC-Biodiesel, (b) DEC-Biodiesel. Legends: (■) Jatropha, (▲) Pongamia, (--) Conventional Jatropha – Methanol biodiesel

Biodiesel quality should be consistent and needs to be ensured while its distribution and utilization. Therefore, biodiesel characterization is required based on density, viscosity, boiling points and other properties. In which, boiling point especially at atmospheric pressure, called normal boiling point T_{nb}, is a vital fuel property for controlling the quality in petroleum industry. This property is crucial for the prediction of critical parameters and temperature-dependent properties such as density, viscosity, vapor pressure, latent heat of vaporization, and surface tension of biodiesel [Yuan et al., 2005]. In the present study, T_{nb} is measured experimentally using thermal method and also estimated through correlation as reported earlier [Yuan et al., 2005; Goodrum, 1997]. While estimating the bp for biodiesel, 3°C difference is considered based on fully saturated and mono-unsaturated bond present in fatty acid [Graboski et al., 1998]. In addition, the reported T_{nb} value of 366.2 °C has been accepted for C18:2 on absent of data for alkenes with more than one double bond [Graboski et al., 1998]. Furthermore, the same value of T_{nb} also assigned to C18:3 based on the assumption that normal boiling points are nearly independent of the degree of unsaturation of the fatty acid [Graboski et al., 1998; Goodrum, 1997].

In this study, it can be seen from Table 5.4 that the predicted T_{nb} of the four biodiesel fuels are in good agreement with the experimental values within an error range 0.22-0.41 %. The measured error T_{nb} could be due to uncertainty in the aforementioned assumption made for unsaturated pure fatty esters (C18:2 and C18:3). The relative error for Pongamia DMC/DEC-biodiesel is found to be lower than Jatropha one. The possible reason is that the Pongamia has less poly unsaturated fatty esters (C18:2 and C18:3; 19.24 % in total mass) compared to Jatropha where this content is 33% (Table 5.2). It may be noted that variation in the process parameters, feed treatments and feedstock source also influence the fatty acid content which in turn affects the boiling point and distillation characteristics of formed biodiesel [Graboski et al., 1998; Goodrum, 1997].

Table 5.4 Comparison of predicted and measured normal boiling point of Jatropha and Pongamia biodiesel

	Normal boiling Point (T_{nb}), K		Absolute error, K	Relative error, %
	Predicted	Measured		
Jatropha DMC-Biodiesel	624.5	622.8	1.7	0.27
Pongamia DMC-Biodiesel	625.6	624.2	1.4	0.22
Jatropha DEC-Biodiesel	635.0	632.4	2.6	0.41
Pongamia DEC-Biodiesel	637.2	635.2	2.0	0.31

Synthesized biodiesel in supercritical DMC/DEC from Jatropha and Pongamia, are purified and further characterized as per standard methods ASTM D6751/EN 14214/IS 15607 [ASTM D6751, 2007; EN 14214, 2003; IS 15607, 2005]. The essential fuel properties are compared and presented in Table 5.5. The measured fuel properties are found to be in good agreement with the prescribed fuel specifications. Furthermore, the produced DMC/DEC biodiesel has slightly high kinematic viscosity, better lubricity for engine performance, high flash for safer transportation, good oxidation stability for storage, high oxygen content for better combustion characteristic and thermally stable compared to conventionally produced biodiesel. The oxidation stability tests were performed with and without additive (butylated hydroxytoluene: BHT, 2ppmw concentration) for DMC/DEC-biodiesel vis-à-vis conventional biodiesel. Based on the obtained results, DMC/DEC-biodiesel samples are found to be more stable as compared to conventional biodiesel which could be due to higher oxygen content in DMC/DEC-biodiesel. Thus, DMC/DEC-biodiesel can be envisaged as an ideal blend stock for ultra low sulfur diesel owing its improved oxidation stability and lubricity.

Table 5.5 Characterization of Jatropha and Pongamia oil derived DMC/DEC-biodiesel

Property	Test Method	Unit	Specifications[a]			Synthesised DMC-Biodiesel		Synthesised DEC-Biodiesel	
			ASTM D 6751-2007	EN 14214:2008	IS 15607:2005	Jatropha	Pongamia	Jatropha	Pongamia
Density at 150C	ASTM D4052	gm/cm3	-	0.860-0.900	0.860-0.900	0.8799	0.8830	0.8817	0.8870
Kinematic Viscosity at 40^{0}C	ASTM D445	cSt	1.9-6.0	3.5-5.0	3.5-5.0	3.9	4.5	4.2	4.9
Total acid number (TAN)	ASTM D664	mg/KOH	0.5 Max	0.5 Max	0.5 Max	0.09	0.08	0.08	0.07
Moisture content	ASTM D2709	mg/Kg	500 Max	500 Max	500 Max	70	60	50	60
Flash point	ASTM D93	0C	130 min	101 min	120 min	165	170	168	175
Copper strip corrosion	ASTM D30	rating	No. 3 max	Class 1	Class 1	Class 1	Class 1	Class 1	Class 1
Sulphur	ASTM D5453	% wt	0.05 Max	0.001 Max	0.001 Max	0.0017	0.0012	0.0016	0.0015
Ester Content	EN 14103	% wt	-	96.5 min	96.5 min	96.9	97.5	97.0	97.7
Carbon Residue (10% bottom)	ASTM D4530	% wt	0.05 Max	0.30 Max	0.05 Max	0.012	0.013	0.015	0.018
Alkaline Metals (Na+K+)	EN 14108	mg/Kg	-	5.0 Max	5.0 Max	3.2	2.2	3.4	2.6
Phosphorus content	ASTM D4951	mg/Kg	0-10	4.0 Max	10.0 Max	4	5	4	5
Oxidation stability at 110^{0}C	EN 14112	hr	-	6 hr, min	6 hr, min	5.8	6.0	5.9	6.2
						6.0[b]	6.2[b]	6.1[b]	6.7[b]
						2.9[c]	3.1[c]		

[a] ASTM (D 6751-2007)[32]; EN (14214:2008)[33]; IS (15607:2005)[34]

[b] with additive i.e. butylated hydroxytoluene (BHT) as antioxidant

[c] Conventional Jatropha/Pongamia biodiesel sample prepared using methanol

5.4 Conceptualization of process

In view of the good agreement in fuel properties of DMC/DEC-biodiesel synthesized in supercritical process *vis-à-vis* conventional biodiesel, it is important to develop supercritical process for continuous production of biodiesel from commercial point of view. Thus, based on the present study, a continuous process package is conceptualized for the production of glycerin free biodiesel in supercritical conditions, and is presented in the **Figure 5.9**.

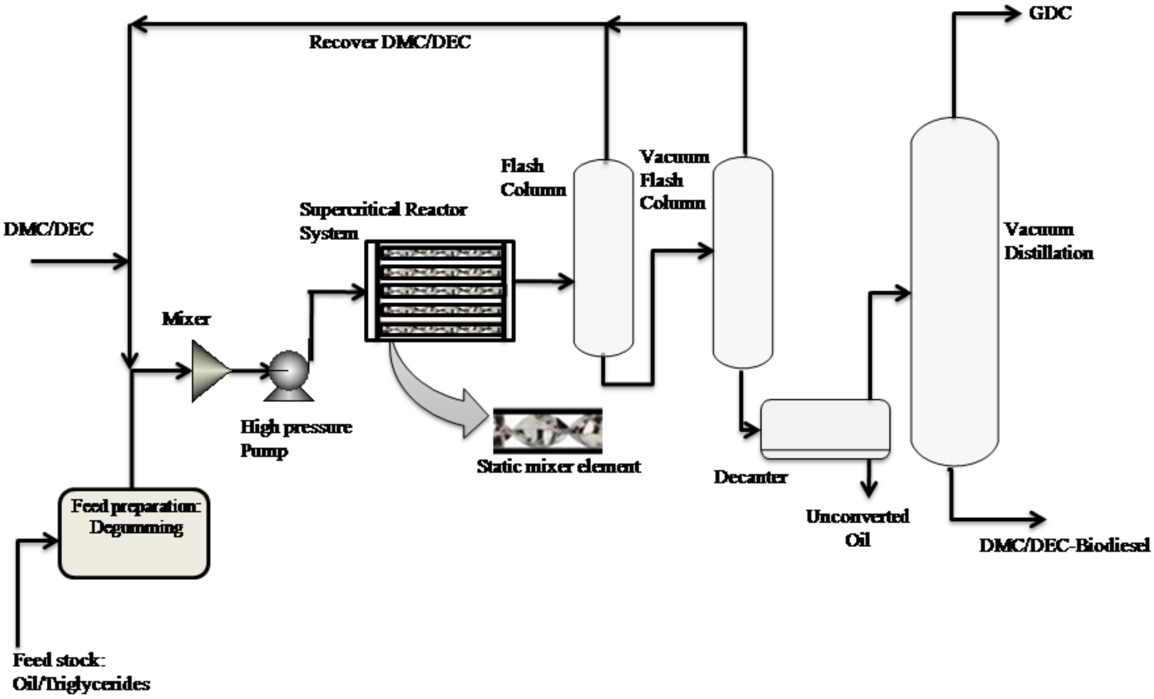


Figure 5.9. Conceptualized process flow diagram for non-catalytic glycerin free supercritical process for biodiesel synthesis

Typically, feed preparation unit is proposed prior to reaction to avoid downstream operational problems associated to gums and un-saponified matter presented in crude vegetable oil. The proposed process scheme consists of three sections i.e. feed preparation section, reaction section and product separation cum purification section. Thus, degummed oil can be subjected to supercritical attained reaction section where TGs enter with DMC/DEC in pre-determined molar ratio obtained from this study. The reactor section is proposed to consist of multiple continuous plug flow type reactor, having static mixer element to promote vigorous mixing where supercritical pressure can be achieved through high pressure pump and under vigorous stirred conditions by static mixer elements. The pre-determined reactants ratio and optimized conditions derived in the present study can be utilized for production of glycerin free biodiesel in supercritical condition. The excess DMC/DEC recovery can be achieved via. flash column operation for its recycle from the formed product. Subsequently, reacted mass can be left for settlement in a decanter where two layers of reaction mass will be formed where upper layer consists of biodiesel as well as GDC and lower layer consists of unconverted oil, if any. The separated biodiesel can be used directly or further purified through reduced pressure distillation. The recovery of lighter component such as GDC from biodiesel can be envisaged based on the economic feasibility of the process. The hydrolysis of GDC produces more versatile and more economic valuable glycerol carbonate compared to other byproduct viz. triacetin which is co-produced through another glycerin free route using acetic acid or methyl acetate as alkylating agent [Ang et al., 2014]. In addition, no downstream purification steps are required in the proposed process compared to conventional process which often imbalances the overall process economics due to involvement of various purification steps. Typically, conventional synthesis demands glycerin purification for removal of catalyst impurities and methanol recovery through acid neutralization and distillation process, respectively. Furthermore, requirement of effluent treatment adds up to the overall process cost. On the other hand, the present route is non- catalytic and is free of glycerin production. Hence, the overall process is envisaged to be less complicated as compared to conventional processes. Also, the formed DMC/DEC-biodiesel product is expected to be superior in quality in terms of lubricity, oxidation stability and density vis-à-vis conventional biodiesel which would offer advantage in terms of fuel blending aspects with diesel.

In the proposed process, proposed reactor design which is capable to cope the higher production capacity and lower operating costs can ensure the long term supply of biodiesel and overall economy. Though, the supercritical fluid technology requires high temperature and high pressure can provide the distinct advantage in comparison to conventional process. In fact, the key operating parameters such as oil concentration and the density of the mixture (depending on temperature, pressure and composition) in the supercritical phase, can be easily controlled and optimized under flow conditions.

In sum, the key features of the proposed process are envisaged in terms of recovery of (a) excess DMC/DEC using flash column and its recycling into the process without any treatment, (b) non-catalytic route and no discrete operation *viz.* catalyst neutralization and separation is required, (c) no production of low value glycerin and, (d) optional recovery of valuable by-product, GDC based on market demand for its derivatives. In view of the above mentioned facts, the proposed scheme can be envisaged to offer economic advantages for biodiesel production due to its flexibility on GDC recovery.

5.5 Conclusions

To overcome the fear of glycerin glut formation based on biodiesel production process, the present study is investigated glycerin free biodiesel process under non-conventional synthesis conditions. Accordingly, glycerin free synthesis of biodiesel from non-edible oils *viz.* Jatropha and Pongamia oil under supercritical conditions has been investigated using dimethyl carbonate (DMC) and diethyl carbonate (DEC) as methylating agent, individually. Typically, supercritical conditions with 40:1 molar ratio of DMC / DEC to oil at 325°C/150bar individually, have been found to be adequate to achieve nearly complete conversion in 45 min. Furthermore, reaction kinetics has been investigated under supercritical condition of DMC and DEC in the temperature range of 250-350°C at 150bar. The estimated activation energies (Ea), are of the order of 38.0 ±2 and 35.5 ±2 kJ/mol for DMC, and 40.4 ±2 and 38.2 ±2 kJ/mol for DEC, for conversion of Jatropha and Pongamia oil, respectively, using pseudo-first order kinetics. The kinetics data suggest DMC/DEC-biodiesel formation is more facile with Pongamia oil compared to Jatropha oil. In addition, thermal stability chrematistics of DMC/DEC-biodiesel of Pongamia oil found to be better than the Jatropha oil under supercritical conditions. The prepared biodiesel samples have been found to align with ASTM D6751/EN 14214/IS 15607 specifications. In view of this, non-catalytic glycerin free supercritical biodiesel synthesis process is an eco-friendly continuous process with no cumbersome operation, improved yield, and high purity of products/byproducts, can be evolved to its commercialization in near future.

CHAPTER 6

SIMULATION OF GLYCEROL FREE BIODIESEL SYNTHESIS UNDER CATALYTIC AND NON-CATALYTIC SUPERCRITICAL PROCESS CONDITIONS

6.1 Introduction

Worldwide energy demand has steady increased which is continuously widening the gap between the supply and demand of petroleum oil, and raising environmental concerns about the endless consumptions of fossil fuels [De et al., 1999]. Alternate to fossils fuels, biodiesel has gained boosting attention as alternative fuels.

Biodiesel is a mixture of fatty acid alkyl esters which are commonly derived from triglycerides and alcohol through transesterification reaction [Barnwal and Sharma, 2005]. Feedstocks for biodiesel are mainly source of TG such as edible/non-edible vegetable oils, waste/used vegetable oils, fats etc. Edible vegetable oils are not economically viable in view of their trade price as well as concern of food vs. fuel. However, the cost of biodiesel is still high as feedstock accounts for 80% of the production cost, creation of low valued glycerin glut and inefficient process [Behr et al., 2008]. Thus, biodiesel production is only feasible with non-edible vegetable oil or other alternate resources, alternate utilization or no production of glycerin moiety or and efficient process.

In view of the above, the present study is aimed at developing glycerol-free biodiesel process based on; catalytic and non-catalytic supercritical routes using experimental data as illustrated in chapter 4 and 5. In this context, the process flow diagrams were developed by Aspen Plus simulation software and verified through experimental work. Typically, the process simulation conditions were adjusted to meet the product specifications as per ASTM D6751 and EN 14214 standards. Thus, key parameters were explored to determine the optimal transesterification conditions, determined the complete mass and energy balance, and tuned the process parameters to develop most efficient process in view of energy minimization and reduction in downstream processing steps for separation and purification of products/byproducts. In addition, simplified process design of a biodiesel plant is described here based on experimental results which are integrated in rigorous simulations performed using AspenTech Aspen Plus as a computer aided process engineering tool (Aspen Technology, Aspen Plus V7.3). This work also helps in the economic assessment of the glycerol free process routes in near future.

6.2 Materials and Methods

In this study, the ASPEN Plus software package (Licensing version 7.3 to BPCL) is used. The simulation is carried out in two conceptualized glycerol free routes, catalytic and non-catalytic supercritical process. In the catalytic process, KOH functions as heterogeneous catalyst wherein its utilization depends on the recovery and recycle in to the process based on the process economics. Where as in non-catalytic process where no catalyst is used and supercritical conditions are achieved by providing the pre-determined molar ratio of the reactants.

Also, the non-random two-liquid (NRTL) thermodynamic property package is used according to Aspen Plus property method. This selection was made on the basis of reactants nature and reaction parameters, such as polar/non polar molecule, non-electrolyte, no liquid–liquid equilibrium and reaction pressure. Although the thermodynamic data for some triglycerides (trioline as model compound), fatty acids, DMC, DEC and methyl esters are available in ASPEN Plus, but GDC and FAGC are not found in the databanks. Therefore, thermodynamic properties are estimated by ASPEN Plus upon providing the molecular structure of the compounds. The molecular structure of triglycerides, FAGC, GDC, and FAME can be either created by ChemSketch molecular modeling program or downloaded from the NIST database)\ as.mol files and subsequently imported into the ASPEN simulation. Thermo data engine (TDE) is used to estimate all missing thermochemical properties of the compounds involved.

Thus, a plant having annual capacity of producing 8.3×10^6 Kg yr^{-1} biodiesel is simulated based on 330 days as stream days in year. Therefore, a basis of ~1000 kg h^{-1} of Jatropha/Pongamia oil is considered for processing with optimized amount of DMC. The main processing units included mixers, heat exchangers, reactor, filter, pumps and distillation column. A simple stoichiometric reactor model is use to describe catalyzed transesterification reactions with obtained conversion into FAME by experimental studies (this was the conversion determined from preliminary assessment). Triolein is considered as major triglycerides with reference to pre-treated oil to react with DMC in simulation studies.

In simulation process, the unit operation specifications such as feedstock, reactants, required catalysts and separation strategies are predefined based on the experimental studies. Accordingly, process aspects envisaged for glycerine-free biodiesel synthesis for simulation studies are listed below:

- Reaction temperature of 80 ^oC for catalytic process at atmosphere pressure due to limited limited solubility of KOH (in case of catalytic process)

- Trace catalyst separation by inclusion of inline filter followed by resin column operation
- Separation of excess DMC from from product mixture and its recycle prior to acid wash due to mutual solubility of DMC and water, to avoid the formation of azeotrope due to their close boiling point and experimental study.
- Vaccum distillation upto maximum 280 ^{o}C in the downstream process to separate FAME (in view of its thermal stability) from by product such as GDC, unreacted oil and excess of amount of DMC .
- Catalyst separation/recycle operation
- Optimization of blending ratio of biodiesl containing GDC with mineral oil based diesel till the composition meets the international standards.
- Separation of GDC owing to its economic valuability

The process parameters for the major unit operations are listed for catalytic and non-catalytic supercritical glycerin free biodiesel process in Table 6.1 and Table 6.2, respectively.

Table 6.1 Description of operating conditions of main equipment in catalytic glycerin free biodiesel process

Main process equipment	ID	Parameter	Value
Transesterification	REACTOR	Temp., °C	80
		Pressure, bar	1
Neutralization	ACIDTREA	Temp., °C	25
		Pressure, bar	1
Separation	FILT1	Temp., °C	80

		Pressure, bar	1
	FILT2	Temp., °C	25
		Pressure, bar	1
	DMCFRAC	Temp., °C	30 max
		Pressure, bar	0.001
		Total number of theoretical stages	10
		Feed stage	6
		Reflux ratio (mass)	0.95
	GDCFRAC	Temp., °C	258 max
		Pressure, bar	0.001
		Total number of theoretical stages	14
		Feed stage	7
		Reflux ratio (mass)	0.95
	BIODIFRA	Temp., °C	184 max
		Pressure, bar	0.001
		Total number of theoretical stages	38
		Feed stage	18
		Reflux ratio (mass)	0.95
Heater/Cooler	HX1	Temp., °C	60
		Pressure, bar	0.001
	HX2	Temp., °C	60
		Pressure, bar	1.1
	HX3	Temp., °C	258

		Pressure, bar	0.1
	COOLER1	Temp., °C	30
		Pressure, bar	1
	COOLER2	Temp., °C	30
		Pressure, bar	1

Table 6.2 Description of operating conditions of main equipment in non-catalytic glycerin free biodiesel supercritical process

Main process equipment	ID	Parameter	Value
Transesterification	REACTOR	Temp., °C	325
		Pressure, bar	150
Separation	DMCFRAC	Temp., °C	26.5 max
		Pressure, bar	0.001
		Total number of theoretical stages	10
		Feed stage	6
		Reflux ratio (mass)	0.95
	GDCFRAC	Temp., °C	258 max
		Pressure, bar	0.001
		Total number of theoretical stages	14
		Feed stage	7
		Reflux ratio (mass)	0.95
	BIODIFRA	Temp., °C	184 max
		Pressure, bar	0.001
		Total number of theoretical stages	60
		Feed stage	28

		Reflux ratio (mass)	0.95
Heater/Cooler	HX1	Temp., °C	-40
		Pressure, bar	0.001
	HX2	Temp., °C	258
		Pressure, bar	0.1
	COOLER1	Temp., °C	30
		Pressure, bar	1
	COOLER2	Temp., °C	30
		Pressure, bar	1

6.3 Process development and downstream separation strategy

In this work, the Jatropha/Pongamia oil was transesterified to a DMC-biodiesel by two different route: catalytic (KOH) and non-catalytic (supercritical condition of DMC) in a continuous batch process. Typically, the catalytic biodiesel production in the current studies consists of five sections (Figure 6.1): (1) feed preparation (not considered in simulation) (2) transesterification reaction, (3) KOH **r**emoval and recycle, (4) DMC recovery and (5) separation of by-products GDC from FAME. Whereas non-catalytic supercritical route consists of four sections (Figure 6.2): viz. (1) feed preparation (not considered in simulation) (2) transesterification reaction, (3) DMC recovery and (4) separation of byproduct GDC from FAME As reported, presence of water in any of the feedstock components forms CO_2 [Kurle et al., 2013]. Therefore, oil was stored in the nitrogen environment and traces of water were removed by applying vacuum. Hence, formation of side products can be avoided to improve the overall yield and conversion in the conceptualized process.

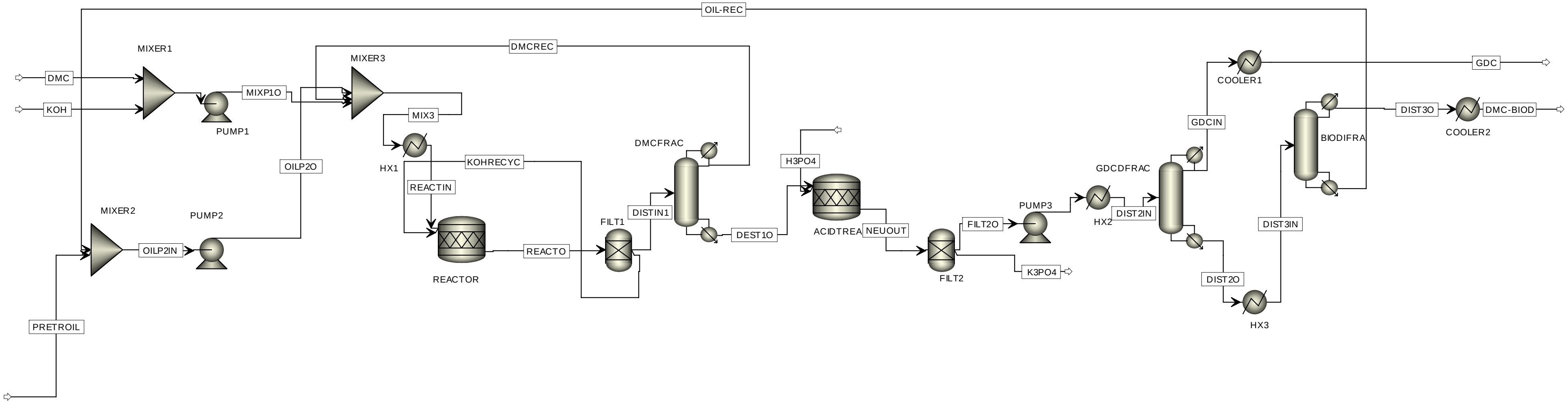


Figure 6.1 ASPEN plus simulated process flow schematic of Catalytic process for DMC-biodiesel production

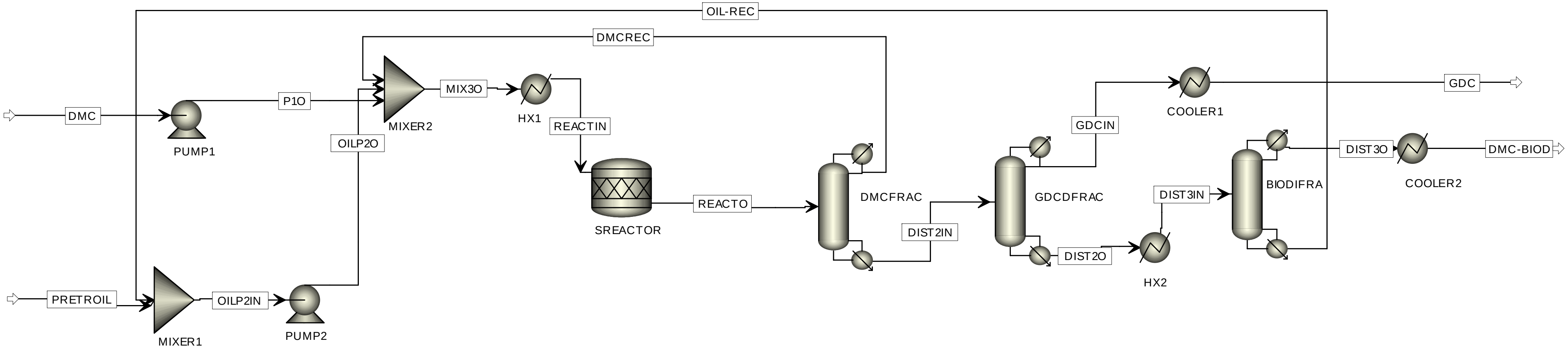


Figure 6.2 ASPEN plus simulated process flow schematic of non-catalytic supercritical process for DMC-biodiesel production

To develop the conceptualized catalytic process, different separation methods for the separation of KOH and purification of the biodiesel were considered. Preliminarily, filtration, centrifuge and crystallization were considered for KOH separation/removal followed by drying for recycle whereas water washing, distillation, and flash were considered for DMC separation. Among possible options mentioned above the described below potential possible separation scenarios are considered to separate KOH and DMC from the product mixtures: filtration, crystallization and drying of KOH, water washing of DMC, dilute/mild acid treatment of DMC, distillation of DMC, flash of DMC, water wash of biodiesel and dilute/mild acid treatment of biodiesel mixture etc.

It is also observed that KOH, DMC, and GDC are soluble in water and could be separated from the product mixture by water washing. However, further separation of the individual compounds from aqueous phase would be difficult. In addition, the separation of DMC from water is difficult due to close boiling points (90 °C and 100 °C, respectively at 101.3 kPa) and affinity to form an azeotrope. From the laboratory experimental results and reported elsewhere [Kurle et al., 2013], it was found that even after several water-washing steps, a significant amount of DMC remained in the product mixture (Figure 6.3). Nevertheless, water is the cheapest option for washing the sample but not the preferred one. On the other side, ion exchange resin can be used to provide the dry wash to the biodiesel sample based on the economic viability of the process.

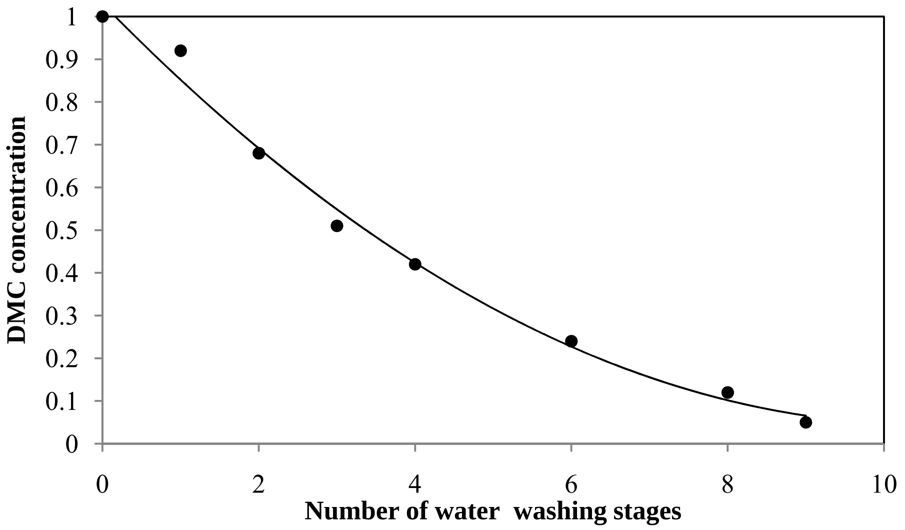


Figure 6.3 The concentration of DMC in the biodiesel samples after water washing

The laboratory experimental results also indicated that the solubility of KOH in DMC and DMC-Oil mixture is limited due to diverse nature of polarity. Hence, KOH separation was simpler compared to conventional process. Even though, KOH has very limited solubility even at high temperatures; therefore, complete recovery of KOH would be easy by crystallization. Furthermore, the temperature of the mixture could not be lowered below the 40 °C). Thereafter, the removal of KOH catalyst would be unfavourable. Even by lowering the reaction/product mixture temperature, the KOH makes the whole reaction mass viscous and creates separation issues. Therefore, it is proposed to remove KOH in hot condition from reaction mass using filter. Filtration was chosen as it is simple and consumes less energy. However, by looking at the solubility data obtained from the experimental studies and analytical methods. It is also observed that the KOH concentration was in 10 -15 ppm in final biodiesel product mixture. Therefore, this trace amount of KOH can be eliminated either by mild/dilute acid treatment or by using ion exchange column. While using phosphoric acid 9 H_3PO_4), separation was in the form of potassium phosphate (K_3PO_4) which can easily separate by filtration; whereas ion exchange resin neutralize the potassium ions and can be regenerate by standard regenerating procedure prescribed by the resin supplier. In addition, it can be concluded that based on our laboratory study that DMC should not be separated by distillation unless KOH was removed first at temperatures above 40 °C. In sum, KOH removal and acid treatment was performed for the catalytic route where as no KOH was used in the non-catalytic supercritical route.

The difference in boiling points of DMC and other chemicals in the mixture is sufficiently large and therefore distillation is attempted to separate DMC. Because of the relatively higher volatility of DMC in product mixture, it could be evaporated at low temperature and low pressure. This would also avoid undesired reactions that might occur at higher temperatures. DMC is separated using distillation under vacuum at 80 ^{o}C and upon cooling recycled into reactor. The low pressure at which the maximum amount of DMC could be recovered with minimum duty on the reboiler, was determined by ASPEN Plus simulation. The methodology is similar for conceptualized both the route after separation of DMC and KOH. Now, the reaction/product mixture (FAME and GDC) is left with unreacted oil (if any).

Hence, before using distillation operation, ASPEN Plus was also used to estimate the boiling points of GDC and found 281 °C at atmospheric pressure. The range of boiling points for major FAME is 300 °C to 410 °C was obtained by experimental study as well as estimation method proposed elsewhere [Graboski et al., 1998; Goodrum, 1997; Kurle et al., 2013] . Therefore, distillation method is considered for the separation of GDC from the reaction product mass. The distillation can be applied in the two stages to separate GDC in first stage and unreacted oil (if any) in the second stage. The second stage distillation depends on the complete economic viability of the process to meet the purity of biodiesel in final product for application apart from fuel. As in the proposed process, unreacted triglycerides and total glycerin content were within the ASTM specifications; therefore, there was no need of their separation from the FAME and GDC mixture.

6.4 ASPEN simulation

The Aspen plus simulation is performed for both the conceptualized catalytic and non-catalytic supercritical route on created process flow sheets. Depicts from Figure 6.1 and Figure 6.2, separation strategies for GDC/FAME and unreacted oil is similar in both the available option. In catalytic option, KOH was used as heterogeneous catalyst, which subsequently separated after the reaction through filter and recycled. Thereafter, DMC is separated using vacuum distillation as standard separation method due to difference in boiling point with other product/reactants. The traces of KOH in product mixture were treated with diluted H_3PO_4, which subsequently removed as K_3PO_4, by filtration. In non-catalytic process, no catalyst used thereby no separation/treatment was given to product/reaction mixture. The DMC removal was performed similar to the catalytic process. The section/stage wise description is discussed in the following section.

6.4.1 Feedstock composition

In catalytic synthesis, KOH is used as catalyst which is premixed with predetermined DMC ratio as form of slurry. This slurry is again mixed with pre-treated oil before fed into reactor directly. The flow rate of DMC and oil was set at experimentally determined molar ratio so that the required molar ratio is attained in the reactor. The optimized molar ratio was found from experimental studies, which was 10:1 and 40:1 for catalytic and non-catalytic supercritical methods, respectively. Excess DMC resulted in high conversion making the reaction essentially irreversible. For simulation purpose, triolein was chosen as components of Jatropha/Pongamia oil, which appear in largest proportion in the oil [Shahidi, 1991]. The compositions of reactant fed into the reactor are shown in Table 6.3 for catalytic and non-catalytic supercritical methods.

Table 6.3 Feed composition for the ASPEN Plus simulation in catalytic and non-catalytic supercritical route

Constituents	Catalytic route		Non-catalytic supercritical route	
	Mass Flow, Kg/h	Mass Fraction	Mass Flow, Kg/h	Mass Fraction
Jatropha/Pongamia oil	1050	0.470	1060	0.199
DMC	1081	0.483	4274	0.801
KOH	105	0.047	-	-
Total	2236	1	5334	1

6.4.2 Transesterification reaction

Initially, RStoic is used, for the simulation since the reaction stoichiometry and conversion is available for the main reaction as studied in the present laboratory work. Intermediate reaction and other side reactions which forms fatty acid glycerol carbonate (FAGC) and decomposition of GDC are not considered due to which absence of conversion [Fabbri et al., 2007]. From the experimental results, it is observed that almost 95-96% conversion was obtained in catalytic KOH route; whereas almost near to complete conversion is achieved in the non-catalytic supercritical route.

Reaction is specified for simulation as shown below:

Oil + 2DMC → 3FAME + GDC

However, gas chromatography (GC) analysis confirms the formation of FAME and GDC. However, DMC was removed completely before the GC analysis, thus the injected sample contained only oil as a reactant and mixture of FAME. Therefore, the conversion of Jatropha/Pongamia oil during the transesterification reaction is calculated on the basis of formed product in the reaction.

The reaction parameters for RStoic reactor are: conversion, 96%; Temperature, 80 °C; Pressure, 1 bar for catalytic route; whereas reaction parameters are: conversion, 99%; Temperature, 325 °C; Pressure, 150 bar in non-catalytic supercritical route. Using the mentioned condition, simulated yield and mass fraction of RStoic feed and product composition are presented in Table 6.4 and Table 6.5 for catalytic and non-catalytic route, respectively. In addition, the heat of reaction for the transesterification reaction was found to be 19 and 88 kJ/mol, for catalytic and non-catalytic route, respectively.

Table 6.4 Product composition of the RStoic reactor used for yield reactor product specification

	RStoic feed composition		RStoic product composition	
Constituents	Mass flow, Kg/h	Mass fraction	Mass flow, Kg/h	Mass fraction
OIL	1093.73	0.022	43.75	0.001
DMC	48671.07	0.976	48457.44	0.952
KOH	1143.45	0.002	1143.45	0.022
Biodiesel	0.10	0.0	1054.86	0.022
GDC	0.02	0.0	208.88	0.004

Table 6.5 Product composition of the Rstoic reactor used for yield reactor product specification

Constituents	RStoic feed composition		RStoic product composition	
	Mass flow, Kg/h	Mass fraction	Mass flow, Kg/h	Mass fraction
OIL	1061.91	0.017	10.61	0.0
DMC	61094.12	0.983	60880.43	0.979
Biodiesel	0.08	0.0	1055.17	0.017
GDC	0.023	0.0	208.94	0.003

6.4.3 DMC recovery

Excess DMC can be removed either using flash drum or vacuum distillation in both the routes, except filtration for KOH was performed in the catalytic route before separation of DMC from reactant mixture. However, vacuum (reduced pressure) distillation offers better separation efficiency compared to the flash drum in view of the purity of product stream. Hence, maximum recovery of DMC will also ensure better separation of unreacted DMC from product stream. By applying design specification, 0.1 and 1 m bar, DMC recovery obtained to be 99.9% and 99.79%, respectively. Therefore, the less energy intensive 1 m bar reduced pressure operation was chosen where vapour stream of the flash was at 80 °C and 1 m bar. To recycle the DMC, the vapor stream can passed through a multistage compressor to bring it to 1.20 bar and 60 °C.

6.4.4 Separation of KOH and its neutralization

Separation of KOH and subsequently its neutralization is validated only for catalytic route. The KOH is removed from product mixture after the transesterification and upon crystallization recycled in the reactor. Based on the experimental study, KOH present in the reaction mass as heterogeneous catalyst. Even though, it has very limited solubility in the DMC, its presence in the biodiesel phase confirms the leaching at trace level. Hence, the produced biodiesel required neutralization treatment either using ion exchange resin or diluted acid treatment. Thus, its removal was performed on separation K_3PO_4 which was separated using filter. In simulation study, 99.1% recycle was consider after transesterification reaction and thereafter, 0.9% recovery was performed as K_3PO_4 in the subsequent filter prior to GDCFRAC column.

6.4.5 Separation of byproduct GDC from FAME/Unreacted oil

Strategies are similar for separation of byproduct GDC from FAME/unreacted oil in catalytic and non-catalytic route. Two stage vacuum distillations are used to separate GDC, FAME and unreacted oil. First stage GDC is removed from FAME and unreacted oil (if any) and second stage unreacted is removed and recycled to main reactor. The second stage operation is depending on the economic feasibility in view of quality of FAME produces. GDC may find versatile utilization as additives or chemical intermediates [Pagliaro et al., 2007]. The distillation cut was given between heaviest of light key components and lightest of heavy key components. First stage, GDC is light key and FAME/Unreacted oil is heavy key where as in the second stage FAME is light key and unreacted oil as heavy key, used in ASPEN simulation. Considering the boiling point, if distillation performed at atmospheric pressure then bottom temperature would be in between boiling points, of GDC and methyl ester (methyl palmitate) (i.e. 281 and 311 °C). Then, there is chance of thermal cracking of the desired products. Therefore, it was necessary to maintain the process temperature strictly below auto ignition temperature and smoke point of the compounds in the reaction. The ASTM D 1160 profile helps in the simulation to fix the operation temperature below 280 °C. Simulation also indicated that 258 °C bottom temperature was achieved at 1 mbar column pressure. Thus the distillation column was operated at 1 mbar to achieve the target temperature. The design parameters viz. number of trays, reflux ratio, feed tray location, distillate to feed ratio were obtained from DSTWU column with specification of 99.9% GDC and FAME recovery in distillates. The optimum feed temperature was decided based on minimum possible energy consumption by the distillation column in Figure 6.1 and Figure 6.2 for catalytic and non-catalytic supercritical route, respectively. Similarly, the mass fraction and temperature profile at all stages in the column and variation of temperature were decide on the minimum energy consumption as function of the feed temperature in the distillation column.

6.5 Mass balances

Mass balance is determined based on 1050-1060 kg of Jatropha/Pongamia oil according to the process flow shown in Figure 6.1 and Figure 6.2 for both the process. There are several major operational steps in the process flow diagram such as transesterification, recycle of DMC, recovery of KOH (catalytic route), and purification of the products. In total, 1055 Kg/h of biodiesel with 99.9% purity (Table 6.6 and Table 6.7) was produced from 1050-1060 Kg of Jatropha/Pongamia oil. The product contained the trace amount of GDC which improves the essential physical properties and also provides the better combustion characteristics to biodiesel. In addition, based on a theoretical calculation (Table 6.8), a higher biodiesel yield (19.97 wt %) could be obtained when compared to the conventional methanol synthesis route by avoiding the formation of low valued glycerol moiety. Slight loss was found in DMC, which was insignificant. In addition, impurity like moisture promotes the side reaction which generates methanol and affect the overall yield of the product in this process.

Table 6.6 Simulated yield and purity of product stream in catalytic and non-catalytic supercritical route

Constituents	Catalytic route		Non-catalytic supercritical route	
	Yield, Kg/h	Purity	Yield, Kg/h	Purity
DMC-Biodiesel	1054.67	99.99	1054.93	99.99
GDC	0	Trace	0	Trace
Jatropha/Pongamia oil	0.004	4 ppm	0.001	938 ppm
DMC	0	Trace	0	Trace

Table 6.7 Simulated yield and purity of byproduct stream in catalytic and non-catalytic supercritical route

Constituents	Catalytic route		Non-catalytic supercritical route	
	Yield, Kg/h	Purity	Yield, Kg/h	Purity
GDC	208.85	0.977	208.92	0.972
DMC-Biodiesel	0.011	49 ppm	0.011	49 ppm
Jatropha/Pongamia oil	0.012	56 ppm	0.003	12 ppm
DMC	4.846	0.023	6.088	0.028

Table 6.8 Percent increase in yield in new biodiesel production process compared to the conventional process.

Conventional route	Oil + 3Methanol → 3FAME + Glycerol
Mass (Kg)	1000 (basis) 108.9 1004.6 104.3
Quantity of fuel	Quantity of FAME = 1.004 Kg/Kg of oil
Novel route	Oil + 2DMC → 3 FAME + GDC
Mass (Kg)	1050 (basis) 213.6 1055.0 209.0
Quantity of fuel	Quantity of FAME + quantity of GDC = 1.204 Kg/Kg of oil

Thus, % Extra fuel obtained in novel route = (difference in production/quantity from conventional process) * 100 = 19.90 %.

6.6 Energy balance and Heat integration

In this process conceptualization and simulation, energy requirement for various operations were determined and presented in Table 6.9 for both the routes. In addition, it is challenge to identify the optimal heat load, which needs to be removed and added from the hot and cold streams, respectively. Therefore, heat integration options are emphasized for the minimal energy requirements, which are presented as grid diagram in Figure 6.4 and Figure 6.5 for catalytic and non-catalytic route respectively. Here, the heat exchangers are shown in circle along with the heat duty provided underneath. The heat duty required in two different routes are shown in table 6.8 and table 6.9 for catalytic and non-catalytic process, respectively.

Table 6.9 Energy requirement based on the simulated operation for the catalytic and non-catalytic process

Main process equipment	ID	Heat duty, KW	
		Catalytic route	Non-catalytic supercritical route
Transesterification	REACTOR/SREACTOR	2734.56	15312.4
Neutralization	ACIDTREA	-2.727	-
Heater/Cooler	HX1	0	0.0
	HX2	22.075	0.0
	HX3	0	
	COOLER1	1.582	1.732
	COOLER2	-96.5186	-96.522
Pump, Break power	PUMP1	0.4197	0.2956
	PUMP2	0.4557	0.4386
	PUMP3	0.0115	-

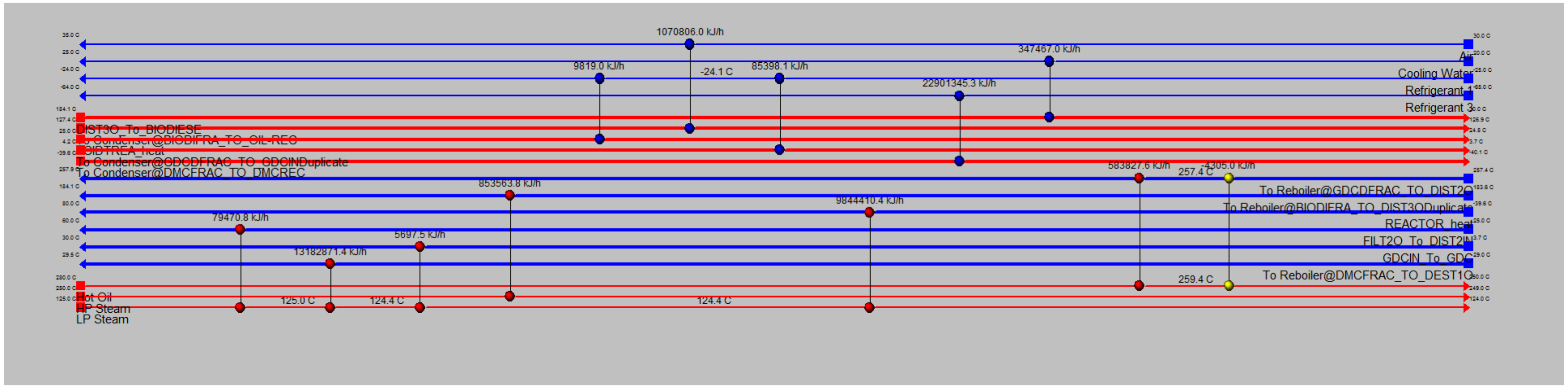


Figure 6.4 Grid diagram for catalytic route from heat integration stream method

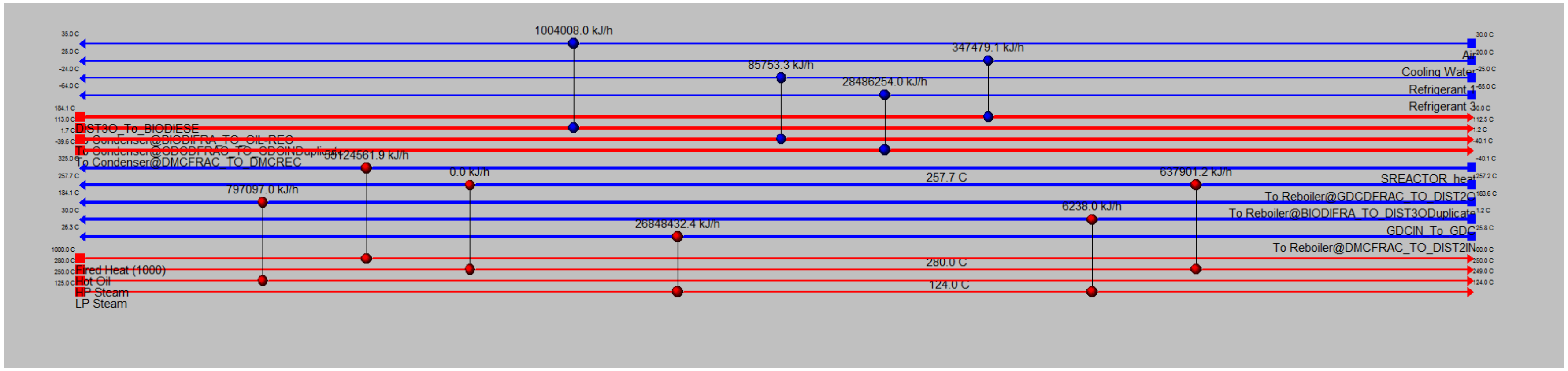


Figure 6.5 Grid diagram for non-catalytic supercritical route from heat integration stream method

Table 6.10 Detail heat exchanger design for catalytic route

Heat Exchanger	Type	Cost index, Cost/s	Area, m^2	Shell	Load, KW
Condenser@BIODIFRA	COLD	2.65E+04	44.02	1	297.45
Condenser@GDCDFRAC	COLD	1.28E+04	4.81	1	23.72
Condenser@DMCFRAC	COLD	3.54E+05	1490.29	3	6361.48
ACIDTREA_heat_Exchanger	COLD	1.03E+04	0.32	1	2.73
Reboiler@BIODIFRA	HOT	1.83E+04	18.65	1	237.10
HX2	HOT	1.06E+04	0.73	1	22.08
Reboiler@DMCFRAC	HOT	6.50E+04	198.15	1	3661.91
COOLER2	COLD	1.19E+04	2.98	1	96.52
COOLER1	HOT	1.01E+04	0.08	1	1.58
Reboiler@GDCDFRAC	HOT	6.29E+04	188.67	1	162.17
HX3	HOT	0.00E+00	-5.51	1	-1.20
REACTOR_heat_Exchanger	HOT	5.52E+04	154.70	1	2734.56

Table 6.11 Utility requirements from HEN network for catalytic route

Utility	Type	Cost Index, Cost/s	Load, KW
Air	COLD	0	297.4
Refrigerant 1	COLD	7.24E-05	26.4
Refrigerant 3	COLD	3.74E-02	6361.5
HP Steam	HOT	5.93E-04	237.1
LP Steam	HOT	1.22E-02	6420.1
Cooling Water	COLD	2.05E-05	96.5
Hot Oil	HOT	8.25E-04	235.7

Table 6.12 Detail heat exchanger design for non-catalytic supercritical route

Heat Exchanger	Type	Cost Index , Cost/s	Area, m^2	Shells	Load, KW
Condenser@BIODIFRA	COLD	2.79E+04	48.71	1	278.89
Condenser@GDCDFRAC	COLD	1.31E+04	5.535	1	23.88
Condenser@DMCFRAC	COLD	4.70E+05	1989	4	8488.89
Reboiler@BIODIFRA	HOT	1.79E+04	17.42	1	221.39
HX2	HOT	0.00E+00	0	-	0.00
Reboiler@DMCFRAC	HOT	1.09E+05	412.3	1	7961.11
COOLER2	COLD	1.19E+04	2.981	1	96.53
COOLER1	HOT	1.01E+04	8.58E-02	1	1.80
Reboiler@GDCDFRAC	HOT	1.08E+05	344.6	2	177.92
REACTOR_heat_Exchanger	HOT	2.45E+06	484.7	1	16391.67

Table 6.13 Utility requirements from HEN network for non-catalytic supercritical route

Utility	Type	Cost Index , Cost/s	Load, KW
Air	COLD	0	278.89
Refrigerant 1	COLD	6.54E-05	23.88
Refrigerant 3	COLD	4.99E-02	8488.89
HP Steam	HOT	5.54E-04	221.39
Hot Oil	HOT	8.29E-04	236.81
LP Steam	HOT	1.51E-02	7961.11
Cooling Water	COLD	2.05E-05	96.53
Fired Heat (1000)	HOT	6.97E-02	16391.93

To compare the energy consumption of the conceptualized process with the contemporary methanol based processes for biodiesel production; these processes were optimized with heat integration method to reduce the overall energy usage.

Special attention was given to the heat integration within the proposed plant. The maximum energy was utilized in reboiler in distillation column. Using heat integration, it was found that the process required .0017 and 0.004 kWh of energy to produce 1 kg of the biofuel using catalytic and non-catalytic supercritical route respectively.. From the energy comparisons with other processes, we can conclude that both the conceptualized processes are efficient and competitive albeit the process utilizes medium vacuum (1 mbar) and high compression.

6.7 Conclusions

Current study opens the possibility for production of glycerin free biodiesel having high purity products through minimizing and simplifying the purification compared to convention production process. Catalytic and non-catalytic routes present an alternative strategy to produce improved quality biodiesel by altering the synthesis chemistry using DMC as methylating agent.

Both the processes have been investigated and simulated in ASPEN Plus for a biodiesel production of 8.3×10^6 kg yr^{-1}. The optimized reaction parameters obtained from laboratory experiments are considered in simulation studies. Zeroed optimization parameters were 10:1 DMC to oil molar ratio / 9 % catalyst loading / 80 ^{o}C / 8 h and 40:1 DMC to oil molar ratio / 325 ^{o}C/ 45 min in catalytic and non-catalytic supercritical routes, respectively. Furthermore, downstream separation strategy is developed from laboratory results and simulated using ASPEN Plus. The new conceptualized processes have the following advantages over the conventional process:

- The yield of diesel is similar to conventional process and co-produced GDC, a highly economically favorable substitute in place of low valued glycerin.
- The consumption of KOH in catalytic process is minimal and can be recycled upon recovery through easy filtration step. Very dilute acid wash or neutralization through acid resin column can be envisaged in industrial level production; whereas, no catalyst is required in non-catalytic supercritical process.
- There are no significant byproducts other than GDC. This high value by product supports the complete biodiesel economic value chain. In addition, their presence in ppm level improves the quality of biodiesel. Hence, separation level from FAME depends on the overall economics.
- Both the downstream separation strategies are found to be easier and viable option for the separation of the desired products.
- The conceptualized processing options are required comparatively less number of unit operations while comparison to conventional production process.
- As per the alternate reaction chemistry, yield is not affected by presence of FFA content in the feed stock in the conceptualized processes.

In sum, both the routes offers high yield, high purity of product/byproducts, ease of reactant/product recovery, operational simplicity, user friendliness, and environmental propriety will commend these processes for commercial implementation in economically viable biodiesel production.

CHAPTER 7

SUMMARY AND WAY FORWARD

7.1 Summary

In recent years, alternative fuels are becoming increasingly important due to diminishing petroleum reserves and the environmental hazards. Among them biodiesel has become more attractive to replace petroleum fuel because of its environmental benefits. Therefore, biodiesel fuel program is adopted in the various parts of the world such as Brazil, US, Europe. Unfortunately, owing to the high cost of the fees stock and abundant value of by-product glycerin, process economic viability is yet to be established worldwide. Thus, it is utmost important to support and handle economic feasibility of bio-diesel production process innovatively. Henceforth, novel ways and means have been searched for glycerin free synthesis of biodiesel to balance economic viability. In addition, glycerin free biodiesel synthesis from crude non-edible oils like Jatropha curcas and Pongamia have been opted to provide the consistent supply of feed stock especially Pongamia in Indian scenario.

The present study investigated the glycerin free synthesis of biodiesel from non-edible oils (Jatropha curcas and Pogamia pinnata) by catalytic (using KOH) and non-catalytic supercritical routes. Here, DMC and DEC were selected as green, renewable reagents for their health and environmental inertness for exploring novel route of synthesis glycerin free biodiesel. DMC/DEC are found to be most competitive substitute by altering the reaction path ways to yield valuable by products viz. GDC, GC instead of glycerin in conventional transesterification synthesis route.

In catalytic route, both reactants (Oil and DMC) were non-polar in nature while KOH was polar in nature and studied reaction system was heterogeneous compared to conventional homogeneous system. Therefore, the presence of KOH as heterogeneous catalyst was investigated with DMC as methylating reagent and compared with methanol based biodiesel synthesis. It was observed that the presence of KOH as positive effect on conversion and yield of DMC-Biodiesel. In addition, the used KOH has option to recycle upon recovery and further utilization in the reaction medium as prevails in conventional heterogeneous catalyst reaction system. The optimization study was carried out to comprehend the effects of reaction parameters such as catalyst amount, reactant molar ratio, temperature and reaction time on conversion into respective biodiesel of Jatropha and Pongamia oil. Typically, optimal conditions which have been zeroed in at maximum conversion of 94.0% and 96.0% for Jatropha oil and Pongamia oil, respectively, are 9% (based on oil wt) of catalyst amount, 10:1 DMC to oil molar ratio at 80^{o}C in the 8 h reaction time. Furthermore, transesterification reaction kinetics has been investigated in the temperature range of 60-80 ^{o}C. The activation energy (Ea) and the pre-exponential factor (k_o) have been found to be, 66.4 ±2 KJ/mol and 3.7×10^{7} min^{-1} and 54.5 ±2 KJ/mol and 6.8×10^{5} min^{-1} for transesterification of Jatropha and Pongamia oil, respectively, using pseudo-first order kinetics. Furthermore, DMC-biodiesel samples are characterized for its fuel properties and are found to be in good agreement vis-à-vis ASTM D6751/EN 14214/IS 15607 specifications. The DMC-biodiesel has better oxidation stability, high oxygen content, and high flash point. In view of this, glycerin free DMC-biodiesel process is conceptualized for its development and possible implementation where minimal downstream separation, treatment and purification steps were required.

Even though, the base catalyzed DMC-biodiesel transesterification route offer better platform compared to conventional commercially available process for biodiesel production. However, this route still have drawbacks, such as: synthesis reaction undergo on longer reaction time, presence of catalyst followed by separation and still requires lesser tedious separation and purification steps for solubilize potassium species compared to conventional process. Therefore, non-catalytic supercritical process have also been developed to lessen the reaction time considerably and making easy of separation and purification procedures. Thus, the developed novel process has been proven a promising and competitive route to produce biodiesel and valuable adducts which could conquer the creation of deprived glycerol glut and imbalance biodiesel economics.

Likewise, in non-catalytic supercritical route, glycerin free biodiesel synthesis was investigated under supercritical conditions using dimethyl carbonate (DMC) and diethyl carbonate (DEC) as methylating agent without employing any catalyst. This novel synthesis offers improve solvency of alcohols in the non-polar TGs and not affected by presence of free fatty acids and water in the feed stock as suffered by conventional synthesis processes. However, the presence of water affected positively the formation of alkyl esters in supercritical condition. Furthermore, it is found that at a subcritical state of DMC/DEC, the reaction rate is low and the rate gradually increases as temperature rises. It was also observed that increasing the reaction temperature, especially to supercritical conditions, had a favorable influence on ester yield. Typically, supercritical conditions w.r.t. reactants to oil molar ratio, reaction temperature and time have been optimized. Accordingly, the supercritical conditions having 40:1 molar ratio of DMC / DEC to oil at 325^{o}C

/150 bar individually, have been found to be adequate to achieve nearly complete conversion in 45 min. Furthermore, reaction kinetics has been investigated under supercritical condition of DMC and DEC in the temperature range of 250-350 ^{o}C at 150 bar. The estimated activation energies (Ea) are of the order of 38.0 ±2 and 35.5 ±2 kJ/mol for DMC, and 40.4 ±2 and 38.2 ±2 kJ/mol for DEC, for conversion of Jatropha and Pongamia oil, respectively, using pseudo-first order kinetics. The activation energy investigated in supercritical condition of DMC/DEC, found lesser than the catalytic DMC route as well as conventional methods. In addition, pre-exponential factors ($k_{o,}$ min^{-1}) were also found to be 144.9 and 104.5 for DMC; 208.3 and 153.0 for DEC, for conversion of Jatropha and Pongamia oil, respectively. Rate constants were also determined in the present study and found good agreement with reported studies. Furthermore, the thermal stability of Jatropha and Pongamia biodiesel formed under supercritical condition of DMC and DEC, was investigated by performing thermal treatment of the biodiesel product in the temperature range of 325-375 ^{o}C at 150 bar by varying exposure time. It was found that the severity of thermal degradation increases with increasing temperature and exposure of time, and synthesis in supercritical conditions has to performed in the vicinity of supercritical region (325 ^{o}C / 150 bar for DMC / DEC) to avoid onset of thermal degradation of the formed product. The prepared biodiesel samples have been characterized w.r.t. their distillation characteristics, normal boiling points and fuel properties. The obtained results demonstrated a good agreement with ASTM D6751/EN 14214/IS 15607 specifications. The DMC/DEC-biodiesel holds the better lubricity for engine performance, high flash for safer transportation, good oxidation stability for storage, high oxygen content for better combustion characteristic and thermally stable compared to conventionally produced biodiesel. In view of this, non-catalytic glycerin free supercritical biodiesel process is conceptualized for its development and possible implementation to overcome the problems associated with purification of biodiesel and by product viz. glycerin in conventional homogeneous catalytic process for biodiesel production. Also, the conceptualize process has incorporated the idea of process intensification while using static mixer to attain near to complete conversion in lesser time, and reduction in capital and operating cost.

To develop the better understanding for the conceptualized, catalytic and non-catalytic supercritical process, the process flow diagrams are developed using Aspen Plus simulation software and verified through laboratory experimental results. Simulation has carried out for plant capacity (1000 Kg/h) where process conditions have been attuned until a glycerol-free biodiesel meets the international standard. Furthermore, complete mass balance, energy loads and design specification were obtained. Also, operating parameters were zeroed at efficient operating conditions by employing minimal unit operations in the designed process. Design of reactors, distillation columns, mixers, pump and duty of heat exchangers were caluated for scaleup studies for successful commercialization of technolgy.

Between, catalytic and non-catalytic supercritical routes, higher conversion was obtained in supercritical DMC/DEC route in shorter reaction time. However, high conversions have been obtained when the reaction was conducted with DMC in both the routes, and it is perhaps due to greater molecule interactions and easy of cleavage with DMC compared to DEC. In addition, conversion of Pongamia oil is found to be high, compared to Jatropha oil irrespective of DMC/DEC and presence of a catalyst. Hence, it is worthwhile to note that the activation energy in supercritical DMC is slightly lower than the supercritical DEC. Similarly, activation energy for transesterification of Jatropha oil is higher compared to that of Pongamia oil which can be attributed to the dissimilarity in the composition of neat oils. This clearly illustrate that the transesterification reaction rate is the highest for the triglycerides of mono-unsaturated and saturated fatty acids followed by triglycerides of poly-unsaturated acid. Some of the characteristics viz. oxidation stability, flash point, lubricity and high oxygen content of the DMC/DEC-biodiesel, are found to be better than the conventional biodiesel. Thus, process scheme conceptualized for catalytic and non-catalytic supercritical route. The success of this alternative routes can be improved further in near future while apoting other process intensification technologies as described in the following section.

7.2 Way Forward

Owing to stringent environmental norms, the implementation of biofuel programs is expected to increase worldwide, which is expected to add fuel growth of energy efficient and cost effective new commercial processes for vegetable oil processing from varied sourced options. Till date, the developed routes based on transesterification of vegetable oil forbiodiesel production offer limitation *w.r.t.* feedstock impurity (i.e. FFA and gum) level and hence demand pre treatment steps to counter impurity levels. Such steps coupled with glycerin purification steps are expected to lead to expensive proposition for vegetable oil processing for production of biodiesel. In view of this, glycerin free synthesis of biofuel production through vegetable oil could offer better option from commercial point of view. Thus, glycerin free biodiesel production through transesterification of vegetable oil can be integrated with non-conventional options such as supercritical /microwave /

cavitation / static mixture assisted processing to enhance the kinetics of reaction. For example, microwave coupled with static mixture approach assisted DMC-glycerin process can significantly enhance the reaction kinetic. This is mainly because of localized heating of microwaves can favour better dissolution of catalyst which coupled with increased efficiency of reactant mixing in the presence of static mixture is expected to reduce the reaction time significantly. A conceptualize process is depicted in Figure 7.1.

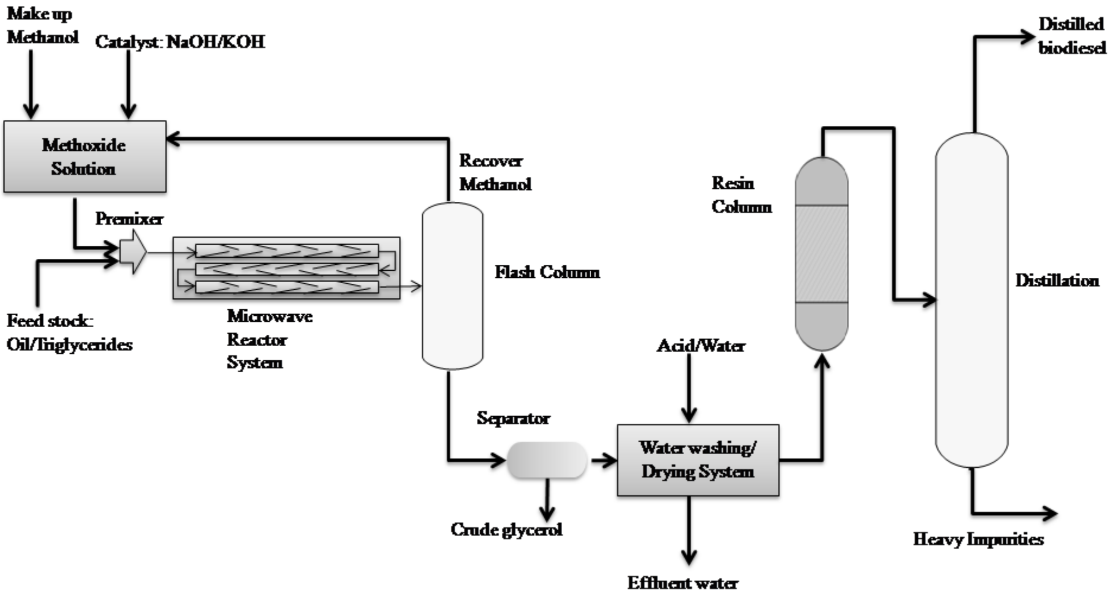


Figure 7.1 Conceptualized process for microwave method

In this proposed process, combination of microwave heating system is coupled static mixer with for simultaneously getting the benefit of localized heating and intense mixing to propagate the fast reaction kinetics. The design of proposed reaction system required to have multiple static mixer element in series, made of microwave non absorber material where thickness of the holding concentric pipe is specially designed to avoid the loss of microwave penetration. The optimum frequency needs to be zeroed in for safety purpose and optimal performance of the process. The pre-mixer, acid neutralization, washing and resin column are essential part of the process for overall plant efficiency.

Likewise, supercritical process coupled with static mixture feature for continuous production of Dimethyl carbonate/Diethyl carbonate (DMC/DEC)-biodiesel from commercial point of view can be envisaged (Figure 7.2). The salient features of the proposed process are listed below:

- Simultaneously utilization of process intensification method viz. supercritical condition and static mixers
- Fast reaction kinetics thereby less reaction time
- No catalyst recovery, treatment owing to non-catalytic process
- Low space requirement due to size of reactor
- Less maintenance in absence of mechanical moving assemblies

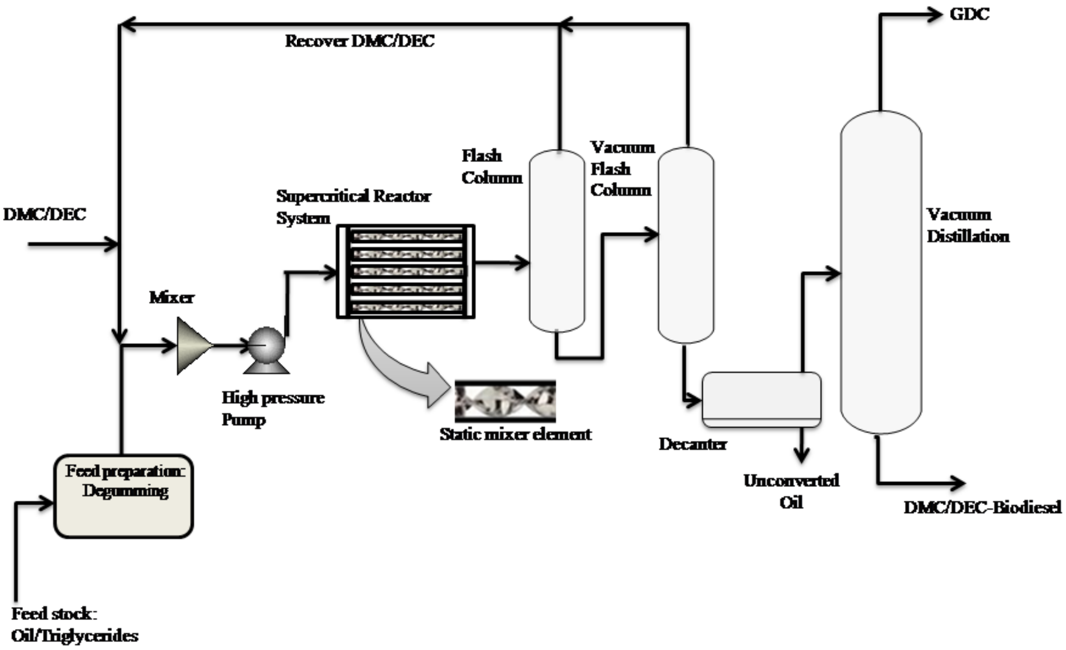


Figure 7.2 Conceptualized process for non-catalytic glycerin free supercritical DMC/DEC method

Typically, feed preparation unit is proposed prior to reaction to avoid downstream operational problems associated to gums and un-saponified matter presented in crude vegetable oil. The proposed process scheme consists of three sections i.e. feed preparation section, reaction section and product separation cum purification section. Thus, degummed oil can be subjected to supercritical attained reaction section where TGs enter with DMC in pre-determined molar ratio obtained from this study. The reactor section is proposed to consist of multiple continuous plug flow type reactor, having static mixer element to promote vigorous mixing where supercritical pressure can be achieved through high pressure pump and under vigorous stirred conditions by static mixer elements. The pre-determined reactants ratio at optimized reaction conditions can be utilized for production of glycerin free biodiesel in supercritical condition. The excess DMC recovery can be achieved via. flash column operation for its recycle from the formed product. Subsequently, reacted mass can be left for settlement in a decanter where two layers of reaction mass will be formed where upper layer consists of biodiesel as well as GDC and lower layer consists of un-reacted oil, if any. The separated biodiesel can be used directly or further purified through reduced pressure distillation. The recovery of lighter component such as GDC from biodiesel can be envisaged based on the economic feasibility of the process. In the proposed process, proposed reactor design which is capable to cope the higher production capacity and lower operating costs can ensure the long term supply of biodiesel and overall economy. Though, the supercritical fluid technology requires high temperature and high pressure can provide the distinct advantage in comparison to conventional process. In fact, the key operating parameters such as oil concentration and the density of the mixture (depending on temperature, pressure and composition) in the supercritical phase, can be easily controlled and optimized under flow conditions.

The key features of the proposed process are envisaged in terms of recovery of (a) excess DMC/DEC using flash column and its recycling into the process without any treatment, (b) non-catalytic and no discrete operation *viz.* catalyst neutralization and separation is required, (c) no production of low valued glycerin and, (d) optional recovery of valuable by-product, GDC based on market demand for its derivatives. In sum, glycerine free biofuel generation via. vegetable oil processing can be integrated with non-conventional routes for economic competitiveness as the demand for biofuel increases in coming years. For this purpose, life cycle assessment is a critical aspects which needs to be carefully examined prior to process commercialization.

REFERENCES

Abbaszaadeh A, Ghobadian B, Omidkhah MR, Najafi G. Current biodiesel production technologies: A comparative review. Energ Convers Manag 2012;63:138–148.

ABG Inc. Company. Glycerin market analysis. 2007. Available at: http://www. asasea.com/download doc.php. Last accessed on 20 March 2014.

Adhikari S, Fernando SD, Gwaltney SR, To SDF, Bricka RM, Steele PH, Haryanto A. A thermodynamic analysis of hydrogen production by steam reforming of glycerol. Int J Hydro Energy 2007;32:2875–80.

Adhikari S, Fernando SD, Haryanto A. Hydrogen production from glycerin by steam reforming over nickel catalysts. Renewable Energy 2008, 33 (5), 1097-1100.

Aksoy HA, Becerik I, Karaosmanoglu F, Yatmaz HC, Civelekoglu H. Utilization prospects of Turkish raisin seed oil as an alternative engine fuel. Fuel 1990;69:600–603.

Alamu OJ, Waheed MA, Jekayinfa SO, Akintola TA. Optimal transesterification duration for biodiesel production from Nigerian palm kernel oil. Agri Eng Int CIGR E J 2007;11:1–11.

Albuquerque MCG, Jimenez-Urbistondo I, Santamarıa-Gonzalez J, Merida–-Robles JM, et al. CaO supported on mesoporous silicas as basic catalysts for transesterification reactions. Appl Catal A: Gen 2008;334:35–43.

Almeida RMD, Noda LK, Gonc¸ alves NS, Meneghetti SMP, Meneghetti MR. Transesterification reaction of vegetable oils, using superacid sulfated TiO2–base catalysts. Appl Catal A: Gen 2008;347:100–105.

Anastasia M, Girolamo G, Barbara O, Donato C, Antonio T, Maria GA. Biodiesel production process by homogeneous/heterogeneous catalytic system using an acid–base catalyst. Applied Catalysis A 2010, 378, 160-168.

Ang GT, Tan KT, Lee KT. Recent development and economic analysis of glycerol-free processes via supercritical fluid transesterification for biodiesel production. Renew. Sust. Energ Rev. 2014, 31, 61-70.

Antunes WM, Veloso CO, Henriques CA. Transesterification of soybean oil with methanol catalyzed by basic solids. Catal Today 2008;133(135):548–554.

Arzamendi G, Campoa I, Arguinarena E, Sanchez M, Montes M, Gandia LM. Synthesis of biodiesel with heterogeneous NaOH/alumina catalysts: comparison with homogeneous NaOH. Chem Eng J 2007;134:123–130.

ASTM D6751. Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate. American Society for Testing and Materials; 2007.

Atadashi IM, Aroua MK, Abdul Aziz AR, Sulaiman NMN. High quality biodiesel obtained through membrane technology. Journal of Membrane Science 2012; (421–422):154–164.

Ayoub M, Abdullah AZ. Critical review on the current scenario and significance of crude glycerol resulting from biodiesel industry towards more sustainable renewable energy industry Renew Sustain Energ Rev 2012;16(5): 2671‑2686.

Azcan N, Danisman A. Alkali catalyzed transesterification of cottonseed oil bymicrowave irradiation. Fuel 2007;86:2639–2644.

Azcan N, Danisman A. Microwave assisted transesterification of rapeseed oil. Fuel 2008;87: 1781–1788.

Azócar L, Ciudad G, Heipieper HJ, Muñoz R, Navia R. Improving fatty acid methyl ester production yield in a lipase–catalyzed process using waste frying oils as feedstock. J Biosci Bioeng 2010 a;109: 609–614.

Bajaj A, Lohan P, Jha PN, Mehrotra R. Biodiesel production through lipase catalyzed transesterification: an overview. J Mol Catal B Enzym 2010;62:9–14.

Barakos N, Pasias S, Papayannakos N. Transesterification of triglycerides in high and low quality oil feeds over an HT2 hydrotalcite catalyst. Biosour Technol 2008;99:5037–5042.

Barnard TM, Leadbeater NE, Boucher MB, Stencel LM, Wilhite BA. Continuous-flow preparation of biodiesel using microwave heating. Energy Fuels 2007;21:1777–1781.

Barnwal BK, Sharma MP. Prospects of biodiesel production from vegetable oils in India. Renew Sust Energ Rev 2005;9:363–78.

Baroutian S, Aroua MK, Raman AAA, Sulaiman NMN. A packed bed membrane reactor for production of biodiesel using activated carbon supported catalyst. Bioresour Technol 2011;102: 1095–1102.

Barrón AE, Melo-Banda JA, Dominguez JM, Hernández E, Silva R, Reyes AI, Meraz MA. Catalytic Hydrocracking of Vegetable Oil for Agrofuels Production using Ni-Mo, Ni-W, Pt and TFA Catalysts Supported on SBA-15. Catal Today 2011;166:102–110.

Bautista LF, Vicente G, Rodríguez R, Pacheco M. Optimisation of FAME production from waste cooking oil for biodiesel use. Biomass Bioenergy 2009;33:862–72.

Behr A, Eilting J, Irawadi K, Leschinski J, Lindner F. Improved utilisation of renewable resources: new important derivatives of glycerol. Green Chem 2008;10:13–30.

Berchmans HJ, Hirata S. Biodiesel production from crude Jatropha curcas L. seed oil with a high content of free fatty acids. Bioresour Technol 2008;99:1716–1721.

Berchmans HJ, Morishita K, Takarada T. Kinetic study of hydroxide–catalyzed methanolysis of Jatropha curcas waste food oil mixture for biodiesel production. Fuel 2010;89:2815–2821.

Bezergianni S, Dimitriadis A, Kalogianni A, Pilavachi PA. Hydrotreating of Waste Cooking Oil for Biodiesel Production. Part I: Effect of Temperature on Product Yields and Heteroatom Removal. Bioresour Technology 2010;101:6651–6656.

Bezergianni S, Kalogianni A, Vasalos IA. Hydrocracking of vacuum gas oil-vegetable oil mixtures for biofuels production. Bioresour Technol 2009;100 (12):3036-3042.

Böddeker KW. Liquid separations with membranes. Berlin: Springer–Verlag Berlin Heidelberg 2008;34.

Bogaart V. Glycerin Marke Brief, Croda Oleochemicals – new ideas in natural ingredients; 2009. Available at: http://www.npt.nl/vereniging/images/stories/Verslagen/Presentatie Bogaart Croda 15042010.pdf Last accessed on 20 March 2014.

Boucher MB, Weed C, Leadbeater NE, Wilhite BA, Stuart JD, Parnas RS. Pilot scale two-phase continuous flow biodiesel production via novel laminar flow reactor-separator. Energy Fuels 2009;23:2750–2756.

Bournay L, Casanave D, Delfort B, Hillion G, Chodorge JA. New heterogeneous process for biodiesel production :a way to improve the quality and the value of the crude glycerin produced by biodiesel plants. Catal Today2005;106:190–192.

Bunyakiat K, Makmee S, Sawangkeaw R, Ngamprasertsith S. Continuous production of biodiesel via transesterification from vegetable oils in supercritical methanol. Energy Fuels 2006;20; 812–817.

Campanelli P, Banchero M, Manna L. Synthesis of biodiesel from edible, non–edible and waste cooking oils via supercritical methyl acetate transesterification. Fuel 2010;89:3675–3682.

Canakci M, Gerpen JV. A pilot plant to produce biodiesel from high free fatty acid feedstocks. Trans Autom Sci Eng 2003;46:945–955.

Cao P, Dubé MA, Tremblay AY. High–purity fatty acid methyl ester production from canola, soybean, palm, and yellow grease lipids by means of a membrane reactor. Biomass Bioenergy 2008a;32:1028–1036

Cao P, Dubé MA, Tremblay AY. Methanol recycling in the production of biodiesel in a membrane reactor. Fuel 2008b;87:825–833.

Cao P, Tremblay AY, Dube´ MA, Morse K. Effect of membrane pore size on the performance of a membrane reactor for biodiesel production. Ind Eng Chem Res 2007;46(1):52–58.

Cavitation Technologies Inc. Desmet to install CTI Nano Reactor in Brazilian soy oil refinery. October 15, 2013. http://www.biodieselmagazine.com/articles/9366/desmet-to-install-cti-nano-reactor-in-brazilian-soy-oil-refinery. Last Accessed : April 3, 2014.

Chai F, Cao F, Zhai F, Chen Y, Wang X, Su Z. Transesterification of vegetable oil to biodiesel using a heteropolyacid solid catalyst. Adv Synth Catal 2007;349:1057–1065.

Charusiri W, Yongchareon W, Vitidsant T. Conversion of used vegetable oils to liquid fuels and chemicals over HZSM-5, sulfated zirconia and hybrid catalysts. Korean J Chem Eng 2006;23 (3):349–355.

ChemSpider, http://www.chemspider.com: Last accessed on March 1, 2014.

Chen CH, Chen WH, Chang CM J, Lai S–M, Tu CH. Biodiesel production from supercritical carbon dioxide extracted Jatropha oil using subcritical hydrolysis and supercritical methylation. J Supercrit Fluids 2010;52:228–234.

Chen G, Ying M, Li W. Enzymatic conversion of waste cooking oils into alternative fuel biodiesel. Appl Biochem Biotechnol 2006;132:911–921.

Chen H, Peng B, Wang D, Wang J. Biodiesel production by the transesterification of cottonseed oil by solid acid catalysts. Front Chem Sci Eng 2007;1:11–15.

Cheng LH, Cheng YF, Yen SY, Chen J. Ultrafiltration of triglyceride from biodiesel using the phase diagram of oil–FAME–MeOH. J Membr Sci 2009;330:156–165.

Cheng LH, Yen SY, Su LS, Chen J. Study on membrane reactors for biodiesel production by phase behaviors of canola oil methanolysis in batch reactors. Bioresour Technol 2010;101:6663–6668.

Chitra P, Venkatachalam P, Sampathrajan A. Optimization of experimental conditions for biodiesel production from alkali–catalysed transesterification of Jatropha curcus oil. Energy Sustain Dev 2005;9:13–18.

Choudhary TV, Phillips CB. Renewable fuels via catalytic hydrodeoxygenation. Appl Catal A: General 2011;397(1–2):1–12.

Cintas P, Mantegna S, Gaudino EC, Cravotto G. A new pilot flow reactor for high–intensity ultrasound irradiation. Application to the synthesis of biodiesel. Ultrason Sonochem 2010;17:985–989.

Colucci JA, Borrero EE, Alape F. Biodiesel from an alkaline transesterification reaction of soybean oil using ultrasonic mixing. J Am Oil Chem Soc 2005;82:525–530.

Conocophillips renewable diesel. http://www.biodieselmagazine.com/articles/1481/conocophillips-begins-production-of-renewable-diesel. Last accessed: April 12th , 2014.

Corma A, Huber GW, Sauvanaud L, O'Connor P. Processing biomass-derived oxygenates in the oil refinery: catalytic cracking (FCC) reaction pathways and role of catalyst. J Catal 2007;247 (2):307-327.

Corro G, Tellez N, Ayala E, Marinez–Ayala A. Two–step biodiesel production from Jatropha curcas crude oil using SiO2•HF solid catalyst for FFA esterification step. Fuel 2010;89:2815–2821.

Ctinanotech http://ctinanotech.com/technology/biodiesel–transesterification : Last accessed on April 17, 2014

Darnoko D, Cheryan M. Kinetics of palm oil transesterification in a batch reactor. J Am Oil Chem Soc 2000;77:1263–67.

De BK, Bhattacharyya DK, Bandhu C. Enzymatic synthesis of fatty alcohol esters by alcoholysis. J Am Oil Chem Soc 1999;76:451–453.

Delledonne D, Rivetti F, Romano U. Developments in the production and applications of dimethylcarbonate. Appl Catal A 2001;221:241–251.

Demirbas A. Biodiesel from sunflower oil in supercritical methanol with calcium oxide. Energ Convers Manag 2007;48: 937–941.

Demirbas A. Biodiesel from vegetable oil via transesterification in supercritical methanol. Energy Convers. Mgmt. 2002, 43, 2349-2356.

Demirbaş A. Biodiesel from vegetable oils via transesterification in supercritical methanol. Energ Convers Manag 2002;43:2349–4356.

Demirbas A. Biodiesel from waste cooking oil via base–catalytic and supercritical methanol transesterification. Energ Convers Manag 2009;50:923–927.

Demirbas A. Progress and recent trends in biodiesel fuels. Energ Convers Manag 2009;50(1):14–34.

Demirbas A. Studies on cottonseed oil biodiesel prepared in non–catalytic SCF conditions. Bioresour Technol 2008;99:1125–1130.

Deng X, Fang Z, Liu YH, Chang LY. Production of biodiesel from Jatropha oil catalyzed by nanosized solid basic catalyst. Energy 2011;36:777–784.

Desmet Ballestra, 2008. http://www.desmetballestra.com/what-industry/biodiesel Last Accessed: April 3, 2014.

Dias JM, Alvim–Ferraz MCM, Almeida MF. Comparison of the performance of different homogeneous alkali catalysts during transesterification of waste and virgin oils and evaluation of biodiesel quality. Fuel 2008;87: 3572–3578.

Diwani EG, Attia NK, Hawash SI. Development and evaluation of biodiesel fuel and by–products from jatropha oil. Int J Environ Sci Technol 2009;6:219–224.

Donnis B, Gottschalck R, Blom EP, Knudsen KG. Hydroprocessing of Bio-Oils and Oxygenates to Hydrocarbons. Understanding the Reaction Routes. Topics in Catalysis 2009;52:229–240.

Dossin TF, Reyniers M–F, Berger RJ, Marin GB. Simulation of heterogeneously MgO–catalyzed transesterification for fine–chemical and biodiesel industrial production. Appl Catal B: Environ 2006;67:136–148.

Du W, Xu YY, Liu DH, Zeng J. Comparative study on lipase catalyzed transformation of soybean oil for biodiesel production with different acyl acceptors. J Mol Catalysis B – Enzymatic 2004;30:125–129.

Dubé MA, Tremblay AY, Liu J. Biodiesel production using a membrane reactor. Bioresour Technol 2007;98:639–647.

Düz MZ, Saydut A, Öztürk G. Alkali catalyzed transesterification of safflower seed oil assisted by microwave irradiation. Fuel Process Technol 2011;92:308–313.

Egeberg R, Michaelsen N, Skyum L, Zeuthen P. Hydrotreating in the production of green diesel. PTQ 2010;Q2or http://www.topsoe.com/business_areas/refining/~/media/PDF%20files/Refining/novel_hydrotreating_technology_for_production_of_green_diesel.ashx

EN 14214. European Standard for Biodiesel. European Committee of Standardization; 2003.

Endalew AK, Kiros Y, Zanzi R. Heterogeneous catalysis for biodiesel production from Jatropha curcas oil. Energy 2011;36:2693–2700.

Environmental Leader. Tyson Foods, Syntroleum Partner to Turn Grease into Fuel.http://www.environmentalleader.com/2010/11/09/tyson-foods-syntroleum-partner-to-turn-grease-into-fuel/ Last accessed: April 12th , 2014.

Fabbri D, Bevoni V, Notari M, Rivetti F. Properties of a potential biofuels obtained from soybean oil by transmethylation with dimethyl carbonate. Fuel 2007;86:690–697.

Felizardo P, Correia MJ, Raposo I, Mendes JF, Berkemeier R, Bordado JM. Production of biodiesel from waste frying oils. Waste Manag. 2006;26(5):487-94.

Ferrari M, Bosmans S, Maggi R, Delmon B, Grange P. CoMo/Carbon hydrodeoxygenation catalysts: influence of the hydrogen sulfide partial pressure and of the sulfidation temperature. Catal Today 2001;65:257–264.

Fini A, Breccia A. Chemistry by microwaves. Pure Appl Chem 1999;71(4): 573–579.

Freedman B, Butterfield RO, Pryde EH. Transesterification kinetics of soybean oil. J Am Oil Chem Soc 1986;63:1375–80.

Freedman B, Pryde EH, Mounts TL. Variables affecting the yields of fatty esters from transesterified vegetable oils. J Am Oil Chem Soc 1984;61:1638–1643.

Fukuda H, Konda A, Noda N. Biodiesel fuel production by transesterification of oils. J Biosci Bioeng 2001;92:405–416.

Furuta S, Matsuhasbi H, Arata K. Biodiesel fuel production with solid superacid catalysis in fixed bed reactor under atmospheric pressure. Catal Commun 2004;5:721–723.

García E, Laca M, Pérez E, Garrido Á, Peinado J. New class of acetal derived from glycerin as a biodiesel fuel component. Energy Fuel 2008, 22, 4274-4280.

Georgogianni KG, Katsoulidis AP, Pomonis PJ, Kontominas MG. Transesterification of soybean frying oil to biodiesel using heterogeneous catalysts. Fuel Process Technol 2009;90:671–676.

Geuens J, Kremsner JM, Nebel BA, Schober S, Dommisse RA, Mittelbach M,Tavernier S, Kappe CO, Maes BUW. Microwave–assisted catalyst–free transesterification of triglycerides with 1-butanol under supercritical conditions. Energy Fuels 2008; 22(1): 643–645.

Giridhar M, Kolluru C, Kumar R. Synthesis of biodiesel in supercritical fluids. Fuel 2004;83: 2029–2033.

GmbHL1996. /http://www.lurgi.com/website/Biodiesel.57.0.html?&L=1S; Last accessed, April 15, 2014.

Goetsch D, Machay IS, White LR. Production of methanol from the crude glycerin by-product of producing biodiesel. United States Patent 2008, US7388034B1.

Gogate PR, Kabadi AM. A review of applications of cavitation in biochemical engineering/ biotechnology. Biochem Eng J 2009;44:60–72.

Goodrum JW. Rapid measurements of boiling point and vapor pressure of short-chain triglycerides by thermo gravimetric analysis. J. Am. Oil Chem. Soc. 1997, 74(8), 947–950.

Gordon R, Gorodnitsky I, Grichko V. Process for producing biodiesel through lower molecular weight alcohol–targeted cavitation US Patent: US 20110151524 A1, Jun. 23, 2011

Graboski MS, McCormick RL. Combustion of fat and vegetable oil derived fuels in diesel engines. Prog. Energy Combust. Sci. 1998, 24, 125-164.

Groisman Y, Gedanken A. Continuous flow, circulating microwave system and its application in nanoparticle fabrication and biodiesel synthesis. J Phy Chem 2008;112:8802–8808.

Guan G, Kusakabe K, Sakurai N, Moriyama K. Transesterification of vegetable oil to biodiesel fuel using acid catalysts in the presence of dimethyl ether. Fuel 2009:88: 81-86.

Guan G, Kusakabe K, Sakurai N, Moriyama K. Transesterification of vegetable oil to biodiesel fuel using acid catalysts in the presence of dimethyl ether. Fuel 2009;88:81–86.

Guzman A, Torres JE, Prada LP, Nunez ML. Hydroprocessing of crude palm oil at pilot plant scale. Catal Today 2010;156 (1-2):38–43.

Ha SH, Lan MN, Lee SH, Hwang SM, Koo YM. Lipase catalyzed biodiesel production from soybean oil in ionic liquids. Enzyme Microb Technol 2007;41:480–483.

Hancsók J, Kasza T, Kovacs S, Solymosi P, Holló A. Production of Bioparaffins by the Catalytic Hydrogenation of Natural Triglycerides. J Cleaner Prod 2012; 34:76–81.

Hanh HD, Dong NT, Okitsu K, Nishimura R, Maeda Y. Biodiesel production through transesterification of triolein with various alcohols in an ultrasonic field. Renew Energ 2009;34:766–768.

Hanh HD, Dong NT, Starvarache C, Okitsu K, Maeda Y, Nishimura R. Methanolysis of triolein by low frequency ultrasonic irradiation. Energ Convers Manag 2008;49:276–280.

Hawash S, Kamal N, Zaher F, Kenawi O, El DG. Biodiesel fuel from Jatropha oil via non–catalytic supercritical methanol transesterification. Fuel 2009;88:579–582.

He H, Wang T, Zhu S. Continuous production of biodiesel fuel from vegetable oil using supercritical methanol process. Fuel 2007, 86, 442–447.

Helwani Z, Othman MR, Aziz N, Fernando WJN, Kim J. Technologies for production of biodiesel focusing on green catalytic techniques: a review. Fuel Process Technol 2009;90:1502–1514.

Hernando J, Leton P, Matia MP, Novella JL, Alvarez–Builla J. Biodiesel and FAME synthesis assisted by microwaves. Homogeneous batch and flow processes. Fuel 2007;86(10–11):1641–1644.

Hingu SM, Gogate PR, Rathod VK. Synthesis of biodiesel from waste cooking oil using sonochemical reactors. Ultrason Sonochem 2010;17:827–832.

Hsiao MC, Lin CC, Chang YH, Chen LC. Ultrasonic mixing and closed microwave irradiation assisted transesterification of soybean oil. Fuel 2010;89(12):3618–3622.

Hsiao MC, Lin CC, Chang YH. Microwave irradiation assisted transesterification of soybean oil to biodiesel catalyzed by nano powder calcium oxide. Fuel 2011; 90(5):1963-1967.

Huang Y, Yan Y. Lipase-catalyzed biodiesel production with methyl acetate as acyl acceptor. Zeitschrift Fur Naturforschung C – A J Bio Sci 2008;63:297–302.

Huaping Z, Zongbin W , Yuanxiao C, Ping Z, Shije D, Xiaohua L, Zongqiang M. Preparation of biodiesel catalyzed by solid super base of calcium oxide and its refining process. Chinese J Catal 2006;27(5):391–396.

Huber GW, Corma A. Synergies between bio- and oil refineries for the production of fuels from biomass. Angew Chem Int Ed 2007;46:7184–7201.

Huber GW, Iborra S, Corma A. Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. Chem. Rev. 2006, 106, 4044-4098.

Huber GW, O'Connor P, Corma A. Processing biomass in conventional oil refineries: production of high quality diesel by hydrotreating vegetable oils in heavy vaccum oil mixtures. Appl Catal A: Gen 2007;329:120–129.

Ilham Z, Saka S. Dimethyl carbonate as potential reactant in non-catalytic biodiesel production by supercritical method. Bioresour Technol 2009;100:1793–1796.

Ilham Z, Saka S. Optimization of supercritical dimethyl carbonate method for biodiesel production. Fuel 2012;97:670–677.

Ilham Z, Saka S. Two-step supercritical dimethyl carbonate method for biodiesel production from Jatropha curcas oil. Bioresour. Technol. 2010, 101, 2735-2740.

Imahara H, Minami E, Hari S, Saka S. Thermal stability of biodiesel in supercritical methanol. Fuel 2008, 87 (1), 1–6.

IS 15607. Specifications of Bio-diesel (B 100) blend for diesel fuel. Indian standard for biodiesel; 2005.

IS SPECIFICATION FOR AVIATION TURBINE FUEL (IS 1571 - 2008) http://www.bis.org.in/ Last accessed, April 15, 2014.

Jaecker-Voirol A, Durand I, Hillion G, Delfort B, Montagne X. Glycerine for new biodiesel formulation. Oil Gas Sci Technol 2008;63:395–404.

Jain S, Sharma MP. Biodiesel production from Jatropha curcas oil. Renew Sustain Energy Rev 2010;14:3140–3147.

Ji J, Wang J, Li Y, Yu Y, Xu Z. Preparation of biodiesel with the help of ultrasonic and hydrodynamic cavitation. Ultrasonics 2006;44:411–414.

Jin L, Zhang Y, Dombrowski JP, Chen C, Pravatas A, Xu L, Perkins C,Suib SL. ZnO/La2O2CO3 layered composite: A new heterogeneous catalyst for the efficient ultra–fast microwave biofuel production. Applied Catalysis B: Environ 2011; 103(1):200–205.

Johnson DT, Taconi KA. The glycerin glut: options for the value-added conversion of crude glycerol resulting from biodiesel production. Environ Progress 2007;26:338–48.

Juan JC, Kartika DA, Wub TY, Hin TYY. Biodiesel production from jatropha oil by catalytic and non–catalytic approaches.BioresourTechnol 2011;102:452–460

Kalnes TN, Marker T, Shonnard DR, Koers KP. Green diesel production by hydrorefining renewable feedstocks. Biofuels 2008;4/http://www.uop.com/?document=uop-hydrorefining-green-diesel-tech-paper&download=1

Karmee SK, Chadha A. Preparation of biodiesel from crude oil of Pongamia pinnata. Bioresour Technol 2005;96:1425–1429.

Kasim NS, Tsai TH, Gunawan S,Ju YH. Biodiesel production from rice bran oil and supercritical methanol. Bioresour Technol 2009;100:2399–2403.

Kaur M, Ali A. Lithium ion impregnated calcium oxide as nano catalyst for the biodiesel production from Pongamia and jatropha oils. Renew Energy 2011;36:2866–2871.

Kawakami K, Oda Y, Takahashi R. Application of a Burkholderia cepacia lipase–immobilized silica monolith to batch and continuous biodieselproduction with a stoichiometric mixture of methanol and crude Jatropha oil. Biotechnol Biofuels 2011;4:42–52.

Kawashima A, Matsubara K, Honda K. Acceleration of catalytic activity ofcalcium oxide for biodiesel production. Bioresour Technol 2009;100:696–700.

Kikhtyanin OV, Rubanov AE, Ayupov AB, Echevsky GV. Hydroconversion of sunflower oil on Pd/SAPO-31 catalyst. Fuel 2010;89 (10):3085–3092.

Kim D, Choi J, Kim G, Seol SK, Ha YC, Vijayan M, Jung S, Kim BH, Lee GD, Park SS. Microwave–accelerated energy–efficient esterification of free fatty acid with a heterogeneous catalyst. Bioresour Technol 2011;102:3639–3641.

Knothe G. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. Fuel Process. Technol. 2005, 86, 1059-1070.

Kouzu M, Kasuno T, Tajika M, Sugimoto Y, Yamanaka S, Hidaka J. Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production. Fuel 2008;87:2798–2806.

Kovacs S, Kasza T, A. T, Horbath IW, Hancsók J. Fuel production by hydrotreating of triglycerides on NiMo/Al2O3/F catalyst. Chem Eng J 2011; 176–177:237–243.

Krár M, Kovacs S, Kalló D, Hancsók J. Fuel Purpose Hydrotreating of Sunflower Oil on CoMo/ Al2O3. Catalyst. Bioresour Technol 2010;101:9287–9293.

Kubickova I, Snare M, Eranen K, Maki-Arvela P, Murzin D. Hydrocarbons for diesel fuel via decarboxylation of vegetable oils. Catal Today 2001;106:197–200.

Kulkarni MG, Dalai AK. Waste cooking oil - an economical source for biodiesel: a review. Ind Eng Chem Res 2006;45:2901–2913.

Kumar D, Kumar G, Singh, PCP. Fast, easy ethanolysis of coconut oil for biodiesel production assisted by ultrasonication. Ultrason Sonochem 2010a;17:555–559.

Kumar D, Kumar G, Singh PCP. Ultrasonic–assisted transesterification of Jatropha curcus oil using solid catalyst, Na/SiO2. Ultrason Sonochem 2010b;17:839–844.

Kumar GR, Ravi R, Chadha A. Kinetic studies of base–catalyzed transesterification reactions of non–edible oils to prepare biodiesel: the effect of co–solvent and temperature. Energy Fuels 2011;25:2826–2832.

Kurle YM, Islam MR, Benson TJ. Process development and simulation of glycerol-free biofuel from canola oil and dimethyl carbonate. Fuel Process Technol 2013;114: 49–57.

Kusdiana D, Saka S. Effects of water on biodiesel fuel production by supercritical methanol treatment. Bioresour. Technol. 2004, 91, 289-295.

Kusdiana D, Saka S. Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol. Fuel 2001;80:693–698.

Lakshmi CV, Viswanath K, Venkateshwar S, Satyavathi B. Mixing characteristics of the oil–methanol system in the production of biodiesel using edible and non–edible oils. Fuel Process Technol 2011;92:1411–1417.

Lam MK, Lee KT, Mohamed AR. Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review. Biotechnol Advan 2010;28:500–518.

Lappas AA, Bezergianni S, Vasalos IA. Production of biofuels via co-processing in conventional refining processes. Catal Today 2009;145 (1-2):55–62.

Leadbeater NE, Stencel LM. Fast, easy preparation of biodiesel using microwave heating. Energy Fuels 2006;20(5): 2281–2283.

Lee JH, Kwon CH, Kang JW, Park C, Tae B, Kim SW. Biodiesel production from various oils under supercritical fluid conditions by Candida antarctica lipase B using a stepwise reaction method. Appl Biochem Biotechnol 2009;156:454–464.

Lee SB, Lee JD, Hong IK. Ultrasonic energy effect on vegetable oil based biodiesel synthetic process. J Ind Eng Chem 2011;510:1–6.

Leoneti AB, Leoneti VA, Oliveira SVWB. Glycerin as a by–product of biodiesel production in Brazil: Alternatives for the use of unrefined glycerin. Renew Energy 2012;45:138–145.

Lertsathapornsuk V, Pairintra R, Aryusuk K, Krisnangkur K. Microwave assisted in continuous biodiesel production from waste frying palm oil and its performance in a 100 kW diesel generator. Fuel Process Technol 2008;89:1330–1336.

Lestari S, Mki–Arvela P, Bernas H, Simakova O, Sjholm R, Beltramini J, Lu GQM, Myllyoja J, Irina Simakova I, Murzin DY. Catalytic Deoxygenation of Stearic Acid in a Continuous Reactor over a Mesoporous Carbon–Supported Pd Catalyst. Energy & Fuels 2009;23(8):3842–3845.

Leung DYC, Guo Y. Transesterification of neat and used frying oil: Optimization for biodiesel production. Fuel Process. Technol. 2006;87:883–890.

Leung DYC, Wu X, Leung MKH. A review on biodiesel production using catalyzed transesterification. Appl Energy 2010;87:1083–1095.

Li E, Rudolph V. Transesterification of vegetable oil to biodiesel over MgO functionally mesoporous catalysts. Energy Fuels 2008;22:143–149.

Lingfeng C, Guomin X, Bo X, Guangyuan T. Transesterification of cottonseed oil to biodiesel by using heterogeneous solid basic catalysts. Energy Fuels 2007;21:3740–3743.

Liu X, He H, Wang Y, Zhu S. Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. Fuel 2008;87:216–221.

Liu X, He H, Wang Y, Zhu S, Piao X. Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. Catal Commun 2007;8:1107–1111.

Liu Y, Sotelo-Boyás R, Murata K, Minowa T, Sakanishi K. Hydrotreatment of Vegetable Oil to Produce Bio-hydrogenated Diesel and Liquefied Petroleum Gas Fuel over Catalysts Containing Sulfided Ni-Mo and Solid Acids. Energy Fuels 2011;25:4675–4685.

Liu Y, Sotelo-Boyás R, Murata K, Minowa T, Sakanishi K. Production of Biohydrogenated Diesel by Hydrotreatment of High-Acid-Value Waste Cooking Oil over Ruthenium Catalyst Supported on Al-polyoxocation-Pillared Montmorillonite. Catalysts 2012;2(1):171–190.

Lopez DE, Goodwin Jr JG, Bruce DA. Transesterification of triacetin with methanol on Nafion–acid resins, J Catal 2007;245:381–391.

Lotero E, Goodwin JG, Bruce DA, Suwannakarn K, Liu Y, Lopez DE. The catalysis of biodiesel synthesis. Catalysis 2006;19:41–83.

Lotero E, Liu Y, Lopez DE, Suwannakarn K, Bruce DA, Goodwin JrJG. Synthesis of biodiesel via acid catalysis. Ind Eng Chem Res 2005;44:5353–5363.

Lu H, Liu Y, Zhou H, Yang Y, Chen M, Liang B. Production of biodiesel from Jatropha curcas L. oil. Comput Chem Eng 2009;33:1091–1096.

Lubes ZIZ, Zakaria M. Analysis of parameters for fatty acid methyl esters production from refined palm oil for use as biodiesel in the single–and two stage processes. Malay J Biochem Mol Biol 2009;17:5–9.

Lv P, Wang X, Yuan Z, Tan T. Conversion of soybean oil to biodiesel fuel with immobilized candida lipase on textile cloth. Energy Source Part A 2008;30:872–879.

Ma F, Clements LD, Hanna MA. Biodiesel from animal fat. Ancillary studies on transesterification of beef tallow. Ind Eng Chem Res 1998;37:3768–3771.

Ma F, Hanna MA. Biodiesel production: a review. Bioresour Technol 1999;70(1):1–15.

Madras G, Kolluru C, Kumar R. Synthesis of biodiesel in supercritical fluids. Fuel 2004, 83 (14), 2029-2033.

Madsen AT, Ahmed EH, C.H. C, Fehrmann R, Riisager A. Hydrodeoxygenation of waste fat for diesel production: Study on model feed with Pt/alumina catalyst. Fuel 2011; 90(11):3433–3438.

Mahamuni NN, Adewuyi YG. Optimization of the synthesis of biodiesel via ultrasound–enhanced base–catalyzed transesterification of soybean oil using a multifrequency ultrasonic reactor. Energy Fuels 2009;23:2757–2766.

Majewski MW, Pollack SA, Curtis-Palmer VA. Diphenyl ammonium salt catalysts for microwave assisted triglyceride transesterification of corn and soybean oil for biodiesel production. Tetrahedron Letters 2009;50:5175–5177.

Marchetti JM, Errazu AF. Techno economic study of supercritical biodiesel production plant. Energy Convers Manage 2008;49:2160–2164.

Marchetti, JM, Errazu AF. Techno economic study of supercritical biodiesel production plant. Energy Conv Manage 2008;49:2160–64.

Marulanda VF, Anitescu G, Tavlarides LL. Biodiesel fuels through a continuous flow process of chicken fat supercritical transesterification, Energy Fuels 2010;24(1):253–260.

Mbaraka IK, Shanks BH. Conversion of oils and fats using advanced mesoporous heterogeneous catalysts. J Am Oil Chem Soc 2006;83:79–91.

McCoy M. An unlikely impact. Chem. Eng News 2005; 83(Feb. 21):19–20.

McCoy M. Glycerin surplus. Chem Eng News 2006;84:7-8.

Meher LC, Dharmagadda VSS, Naik SN. Optimization of alkali catalyzed transesterification of pongamia pinnata oil for production of biodiesel. Bioresour. Technol. 2006, 97, 1392-1397.

Melero JA, Iglesias J, Morales G. Heterogeneous acid catalysts for biodiesel production: current status and future challenges. Green Chemistry 2009;11:1285–308.

Meneghetti SMP, Meneghetti MR, Wolf CR, Silva EC, Lima GES, Silva LL, et al. Biodiesel from castor oil: a comparison of ethanolysis versus methanolysis. Energy Fuels 2006;20:2262–2265.

Mikulec J, Cvengroš J, Joríková L, Banic M, Kleinová A. Second Generation Diesel Fuel from Renewable Sources. J Cleaner Prod 2010;18:917–926.

Miller K. Impact of biodiesel production on the glycerol market; 2006. Available at: http://www.ruralsementes.com.br/produtos/Impact of Biodiesel Production on the Glycerol Market.pdf Last accessed on 20 March 2014.

Minami, E, Saka S. Kinetics of hydrolysis and methyl esterification for biodiesel production in two–step supercritical methanol process. Fuel 2006;85:2479–2483.

Mootabadi H, Salamatinia B, Bhatia S, Abdullah AZ. Ultrasonic–assisted biodiesel production process from palm oil using alkaline earth metal oxides as the heterogeneous catalysts. Fuel 2010;89:1818–1825.

Moreira ABR, Perez VH, Zanin GM, Castro HF. Biodiesel synthesis by enzymatic transesterification of palm oil with ethanol using lipases from several sources immobilized on silica–PVA composite. Energy Fuels 2007;21:3689–3694.

Morgan T, Santillan-Jimenez E, Harman-Ware AE, Ji Y, Grubb D, Crocker M. Catalytic Deoxygenation of Triglycerides to Hydrocarbons over Supported Nickel Catalysts. Chem Eng J 2012;189–190:346–355.

Moser BR, Vaughn SF. Efficacy of fatty acid profile as a tool for screening feedstocks for production of biodiesel. Biomass Bioenergy 2012, 37, 31-41.

Murata K, Liu Y, Inaba M, Takahara I. Production of Synthetic Diesel by Hydrotreatment of Jatropha Oils Using Pt-Re/H-ZSM-5 Catalyst. Energy Fuels 2010;24(4):2404–2409.

Nabi MdN, Hustad JE, Kannan D. First generation biodiesel production from non–edible vegetable oil and its effect on diesel emissions. In: Proceedings of the 4th BSME–ASME international conference on thermal engineering. 2008.

Nakagaki S, Bail A, Santos VC, Souza VHR, Vrubel H, Nunes FS, Ramos LP, Use of anhydrous sodium molybdate as an efficient heterogeneous catalyst for soybean oil methanolysis. Appl Catal A: Gen. 2008;351;267– 274.

Nasikin M, Susanto BH, Hirsaman A, Wijanarko A. Biogasoline from Palm Oil by Simultaneous Cracking and Hydrogenation Reaction over NiMo/zeolite. Catalyst. World Appl Sci J 2009;5:74–79.

Nasikin M, Susanto BH, Hirsaman A, Wijanarko A. Biogasoline from Palm Oil by Simultaneous Cracking and Hydrogenation Reaction over NiMo/zeolite. Catalyst. World Appl Sci J 2009;5:74–79.

Neste Oil. NExBTL Diesel http://www.nesteoil.com/default.asp?path=1,41,11991,12243,12335. Last accessed: April 12th , 2014.

New Orleans Net. New renewable diesel plant headed to Norco with federal backing. http://www.nola.com/politics/index.ssf/2011/01/new_biodiesel_plant_headed_to.html. Last accessed: April 12th, 2014.

Nogueira BM, Carretoni C, Cruz R, Freitas S, Melo PA, Costa–Felix R, Pinto JC, Nele M. Microwave activation of enzymatic catalysts for biodiesel production. Journal of Molecular Catalysis B: Enzymatic 2010;67:117–121.

Noureddini H, Zhu D. Kinetics of transesterification of soybean oil. J Am Oil Chem Soc 1997:74:1457–63.

Nuechter M, Ondruschka B, Jungnickel A, Mueller U. Organic processes initiated by non–classical energy sources. J Phy Orgc Chem 2000;13:579–586.

Oh BR, Seo JW, Heo SY, Hong WK, Luo LH, Joe MH, Park DH, Kim CH. Efficient production of ethanol from crude glycerin by a Klebsiella pneumoniae mutant strain. Bioresour. Technol. 2011, 102 (4), 3918-3922.

Oh PP, Lau HLN, Chen J, Chong MF, Choo YM. A review on conventional technologies and emerging process intensification (PI) methods for biodiesel production. Renew Sust Energ Rev 2012; 16:5131–5145.

Oleo DB Biodiesel Technologies: generating clean&sustainableenergy.2004. /http://www.desmetballestrarosedowns.com/brochures.htmlS; Last accessed, April 15, 2014.

Oliveira D, Luccio MD, Faccio C, Rosa CD, Bender JP, Lipke N, Menoncin S, Amroginski C, Oliveira JV. Optimization of enzymatic production of biodiesel from castor oil in organic solvent medium. Appl Biochem Biotechnol 2004;113–116:771–780.

Ondrey G. Biodiesel production using a heterogeneous catalyst. Chementator: Chem Engineering 2004;30.

Öztürk G, Kafadar AB, Duz MZ, Saydut A, Hamamcı C. Microwave assisted transesterification of maize (Zea mays L.) oil as a biodiesel fuel. Energy, Exploration& Exploitation 2010;28(1):47–58, ISSN 0144–5987

Pacific Biodiesel, 1996. http://www.biodiesel.com/technologies/process-technology/ Last Accessed: April 3, 2014.

Pagliaro M, Ciriminna R, Kimura H, Rossi MM, Pina CD, From glycerol to value-added products, Angewandte Chemie International Edition 2007;46:4434‑4440.

Pal A, Verma A, Kachhwaha SS, Maji S. Biodiesel production through hydrodynamic cavitation and performance testing. Renew Energy 2010;35:619–624.

Panchal BM, SB Dhoot, Deshmukh SA, Sharma MR. Production of DMC-BioD from Pongamia pinnata seed oil using dimethyl carbonate. Fuel 2013;109:201–205.

Park YM, Lee DW, Kim DK, Lee JS, Lee KY. The heterogeneous catalyst system for the continuous conversion of free fatty acids in used vegetable oils for the production of biodiesel. Catal Today 2008;13:238–243.

Patil P, Deng S, Rhodes JI, Lammers PJ. Conversion of waste cooking oil to biodiesel using ferric sulfate and supercritical methanol processes. Fuel 2010a;89:360–364.

Patil PD, Gude VG, Mannarswamy A, Cooke P, Munson–McGee S, Nirmalakhandan N, Lammers P, Deng S. Optimization of microwave–assisted transesterification of dry algal biomass using response surface methodology. Bioresour Technol 2011;102:1399–1405.

Patil PD, Gude VG, Mannarswamy A, Deng S, Cooke P, Munson–McGee S, Rhodes I, Lammers P, Nirmalakhandan N. Optimization of direct conversionof wet algae to biodiesel under supercritical methanol conditions. Bioresour Technol 2010b;102:188–122.

Patil PD, Gude VG, Mannarswamy A, Deng S. Biodiesel Production from Jatropha Curcas, Waste Cooking, and Camelina Sativa Oils. Ind Eng Chem Res 2009; 48(24):10850–10856.

Perin G, Alvaro G, Westphal E, Viana LH, Jacob RG, Lenardao EJ, D'Oca MGM. Transesterification of castor oil assisted by microwave irradiation. Fuel 2008;87:2838–2841.

Peterson CL, Cook JL, Thompson JC, Taberski JS. Continuous flow biodiesel production. Appl Eng Agric 2002;18:5–11.

Pryde EH. Vegetable oil as diesel fuel: overview. J Am Oil Chem Soc 1983;60:1557–1558.

Qian J, Yun Z, Shi H. Cogeneration of biodiesel and nontoxic cottonseed meal from cottonseed processed by two–phase solvent extraction. Energy Convers Manag 2010;51:2750–2756.

Qiu Z, Zhao L, Weatherley L. Process intensification technologies in continuous biodiesel production. Chem Eng Process 2010;49:323–330.

Rachmaniah O, Ju YH, Vali SR, Tjondronegoro I, Musfil AS. A study on acid catalyzed transesterification of crude rice bran oil for biodiesel production. In: youth energy symposium, 19th World energy congress and exhibition, Sydney (Australia), September 5–9; 2004.

Ranganathan SV, Narasimhan SL, Muthukumar K. An overview of enzymatic production of biodiesel. Bioresour Technol 2008;99:3975–3981.

Rashid U, Anwar F, Ansari TM, Arif M, Ahmad M. Optimization of alkaline transesterification of rice bran oil for biodiesel production using response surface methodology. J Chem Tech Biotechnol 2009a;84:1364–1370.

Rashid U, Anwar F, Knothe G. Evaluation of biodiesel obtained from cottonseed oil. Fuel Process Technol 2009b;90:1157–1163.

Rathore V, Madras G. Synthesis of biodiesel from edible and non-edible oils in supercritical alcohols and enzymatic synthesis in supercritical carbon dioxide. Fuel 2007, 86, 2650-2659.

Refaat AA, El Sheltawy ST, Sadek KU. Optimum reaction time, performance and exhaust emissions of biodiesel produced by microwave irradiation. Int J Enviornm Sci Technol 2008 ;5(3): 315–322.

Refaat AA, El Sheltawy ST. Comparing three options for biodiesel production from waste vegetable oil. WIT Trans Ecol Environ 2008:133–40.

Reyes I, Ciudad G, Misra M, Mohanty A, Jeison D, Navia D. Novel sequential batch membrane reactor to increase fatty acid methyl esters quality at low methanol to oil molar ratio. Chem Eng J 2012;197:459–467.

Reyes–Duarte D, Lopez–Cortes N, Ferrer M, Plou JF, Ballesteros A. Parameters affecting productivity in the lipase–catalysed synthesis of sucrose palmitate. Biocatal Biotransfor 2005;23:19–27.

Saifuddin N, Chua KH. Production of ethyl ester (biodiesel) from used frying oil: Optimization of transesterification process using microwave irradiation. Malay J Chem 2004;6(1),77–82.

Saka S, Isayama Y, Ilham Z, Jiayu X. New process for catalyst–free biodiesel production using subcritical acetic acid and supercritical methanol. Fuel 2010;89:1442–1446.

Saka S, Isayama Y. A new process for catalyst-free production of biodiesel using supercritical methyl acetate. Fuel 2009; 88:1307–1313.

Saka S, Kusdiana D. Biodiesel fuel from rapeseed oil as prepared insupercritical methanol. Fuel 2001;80:225–231.

Saka S, Kusdiana D. Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol. Fuel 2001, 80, 693-698.

Salamatinia B, Mootabadi H, Bhatia S, Abdullah AZ. Optimization of ultrasonic–assisted heterogeneous biodiesel production from palm oil: A response surface methodology approach. Fuel Process Technol 2010;91:441–448.

Saleh J, Tremblay AY, Dubé MA. Glycerol removal from biodiesel using membrane separation technology. Fuel 2010;89:2260–2266.

Sang OY, Twaiq F, Zakaria R, Mohamed AR, Bhatia S. Biofuel Production from Catalytic Cracking of Palm Oil. Energy Sources 2003;25:859–869.

Sankaranarayanan TM, Banu M, Pandurangan A, Sivasanker S. Hydroprocessing of Sunflower Oil-Gas oil Blends Over Sulfided Ni-Mo-Al-Zeolite Beta Composites. Bioresour Technol 2011;102:10717–10723.

Santacesaria E, Serio MD, Tesser R, Tortorelli M, Turco R, Russo V. A simple device to test biodiesel process intensification. Chem Eng Process 2011a;50:1085–1094.

Santacesaria E, Serio MD, Tesser R, Tortorelli M, Turco R, Russo V. Biodiesel process intensification in a very simple microchannel device. Chem Eng Process: Process Intensification 2012a;52: 47-54.

Santacesaria E, Turco R, Tortorelli M, Russo V, Serio MD, Tesser R. Biodiesel process intensification by using static mixers tubular reactors. Ind Eng Chem Res 2012b;51(26):8777–8787.

Saravanan N, Puhan S, Nagarajan G, Vedaraman N. An experimental comparison of transesterification process with different alcohols using acid catalysts. Biomass Bioenergy 2010;34:999–1005

Second Generation Renewable Diesel. http://www.greencarcongress.com/tests_of_hydrog.html Last accessed: April 12th , 2014.

Selmi B, Thomas D. Immobilized lipase–catalyzed ethanolysis of sunflower oil in a solvent–free medium. J. Am. Oil Chem. Soc. 1998;75:691–695.

Senol OI, Viljava TR, Krause AOI. Hydrodeoxygenation of methyl esters on sulphided NiMo/c-Al2O3 and CoMo/c-Al2O3 catalysts. Catal Today 2005;100:331–335.

Serdari A, Lois E, Stournas S. Impact of esters of mono- and dicaboxylic acids on diesel fuel quality. Ind Eng Chem Res 1999;38:3543–3548.

Serio DM, Cozzolino M, Giordano M, Tesser R, Patrono P, Santacesaria E. From homogeneous to heterogeneous catalysts in biodiesel production. Ind Eng Chem Res 2007;46:6379–6384.

Shahidi F. Canola and rapeseed: production, chemistry, nutrition and processing technology, 1st ed. Avi Book, New York, 1991.

Shakinaz AES, Refaat AA, Shakinaz TES. Production of biodiesel using the microwave technique. J Adv Res 2010;1(4):309–314.

Shao P, Meng X, He J, Sun P. Analysis of immobilized Candida rugosa lipase catalyzed preparation of biodiesel from rapeseed soap stock. Food Bioprod Proces 2008;86:283–289.

Sharma YC, Singh B, Korstad J. Application of an efficient nonconventional heterogeneous catalyst for biodiesel synthesis from Pongamia pinnata oil. Energy Fuels 2010;24:3223–3231.

Shimada Y, Watanabe Y, Samukawa T, Sugihara A, Noda H, Fukuda H, et al. Conversion of vegetable oil to biodiesel using immobilized candida antarctica lipase. J Am Oil Chem Soc 1999;76:789–793.

Shu Q, Yang B, Yuan H, Qing S, Zhu G. Synthesis of biodiesel from soybean oil and methanol catalyzed by zeolite beta modified with La3+. Catal Commun 2007;8:2159–2165.

Shumaker JL, Crofcheck C,Tackett SA, Santillan–Jimenez E, Morgan T, Ji Y, Crocker M, Toops TJ. Biodiesel synthesis using calcined layered double hydroxide catalysts. App Catal B: Env 2008;82:120–130.

Silva DNL, Batistella CB, Filho RM, Maciel MRW. Biodiesel production from castor oil: optimization of alkaline ethanolysis. Energy Fuels 2009;23:5636–5642.

Simacek P, Kubicka D, Kubicková I, Homola F, Pospisil M, Chudoba J. Premium quality renewable diesel fuel by hydroprocessing of sunflower oil. Fuel 2011;90 (7):2473–2479.

Simacek P, Kubicka D. Hydrocracking of petroleum vacuum distillate containing rapeseed oil: Evaluation of diesel fuel. Fuel 2010; 89(7):1508–1513.

Singh AK, Fernando SD, Hernandez R. Base–catalyzed fast transesterification of soybean oil using ultrasonication. Energy Fuels 2007;21:1161–1164.

Singh B, Bux F, Sharma YC. Comparison of homogeneous and heterogeneous catalysis for synthesis of biodiesel from Madhuca indica oil. Chem Ind Chem Eng Q 2011;17:117–124.

Snåre M, Kubicková I, Mäki-Arvela P, Chichova D, Eränen K, Murzin D. Catalytic deoxygenation of unsaturated renewable feedstocks for production of diesel fuel hydrocarbons. Fuel 2008;87:933–945.

Song ES, Lim JW, Lee HS, Lee YW. Transesterification of RBD palm oil using supercritical methanol. J Supercrit Fluids 2008;44: 356–363.

Soriano Jr NU, Vendittia R, Argyropoulos DS. Biodiesel synthesis via homogeneous Lewis acid catalyzed transesterification. Fuel 2009;88:560–565.

Sotelo-Boyás R, Liu Y, Minowa T. Renewable Diesel Production from the Hydrotreating of Rapeseed Oil with Pt/Zeolite and NiMo/Al2O3 Catalysts. Ind Eng Chem Res 2011;50 (5):2791–2799.

SPEC 2010. http://www.specengineers.com/bio_diesel_manufacturing_process.htm : Last accessed, April 12, 2014.

Srinivas, D., Srivastava, R. Ratnasamy, P. Process for the preparation of hydrocarbon fuel US patent 7,482,480 2009.

Starvarache C, Vinatoru M, Nishimura R, Maeda Y. Fatty acids methyl esters from vegetable oil by means of ultrasonic energy. Ultrason Sonochem 2005;12:367–372.

Stavarache C, Vinatoru M, Maeda Y, Bandow H. Ultrasonically driven continuous process for vegetable oil transesterification. Ultrason Sonochem 2007;14:413–417.

Stern R, Hillion G, Rouxel JJ. US Patent 6,147,196. 2000.

Su E, You P, Wei D. In situ lipase-catalyzed reactive extraction of oilseeds with short-chained dialkyl carbonates for biodiesel production. Bioresour Technol 2009;100:5813–5817.

Su EZ, Zhang MH, Zhang JG, Gao JF, Wei DZ. Lipase-catalyzed irreversible transesterification of vegetable oils for fatty acid methyl esters production with dimethyl carbonate as the acyl acceptor. Biochem Eng J 2007;36:167–173.

Supamathanon N, Wittayakun J, Prayoonpokarach S. Properties of Jatropha seed oil from Northeastern Thailand and its transesterification catalyzed by potassium supported on NaY zeolite. J Ind Eng Chem 2011;17:182–185.

Suppalakpanya K, Ratanawilai SB, Tongurai C. Production of ethyl ester from esterified crude palm oil by microwave with dry washing by bleaching earth. Applied Energy 2010; 87(7):2356 –2359.

Suppes GJ, Dasari MA, Doskocil EJ, Mankidy PJ, Goff MJ. Transesterification of soybean oil with zeolite and metal catalysts. Appl Catal A: Gen. 2004;257:213–223.

Tan KT, Lee KT, Mohamed AR. A glycerol-free process to produce biodiesel by supercritical methyl acetate technology: An optimization study via Response Surface Methodology. Bioresour Technol 2010a;101:965–969.

Tan KT, Lee KT, Mohamed AR. Optimization of supercritical dimethyl carbonate (SCDMC) technology for the production of biodiesel and value-added glycerol carbonate. Fuel 2010b;89:3833–3839.

Tapanes NCO, Aranda DAG, Carneiro JWDM, Antunes OAC. Transesterification of Jatropha curcas oil glycerides: theoretical and experimental studies of biodiesel reaction. Fuel 2008;87:2286–2295.

Taufiq–Yap YH, Lee HV, Hussein MZ, Yunus R. Calcium–based mixed oxide catalysts for methanolysis of Jatropha curcas oil to biodiesel. Biomass Bioenergy 2011;35:827–834.

Teixeira LSG, Assis JCR, Mendonça DR, Santos ITV, Guimarães PRB, Pontes LAM, Teixeira JSR. Comparison between conventional and ultrasonic preparation of beef tallow biodiesel. Fuel Process Technol 2009;90:1164–1166.

Templis C, Vonortas A, Sebos I, Papayannakos N. Vegetable oil effect on gasoil HDS in their catalytic co-hydroprocessing. Appl Catal B: Environ 2011;104 (3-4):324–329.

Terigar BG, Balasubramanian S, Lima M, Boldor D. Transesterification of soybean and rice bran oil with ethanol in a continuous-flow microwave-assisted system: yields, quality, and reaction kinetics. Energy Fuels 2010;24(12):6609–6615.

Thanh LT, Okitsu K, Sadanaga Y, Takenaka N, Maeda Y, Bandow H. A two–step continuous ultrasound assisted production of biodiesel fuel from waste cooking oils: A practical and economical approach to produce high quality biodiesel fuel. Bioresour Technol 2010b;101:5394– 5401.

Thanh L T, Okitsu K, Sadanaga Y, Takenaka N, Maeda Y, Bandow H. Ultrasound–assisted production of biodiesel fuel from vegetable oils in a small scalecirculation process. Bioresour Technol 2010a;101: 639–645.

Thompson JC, He BB. Biodiesel production using static mixers. Trans. ASABE 2007;50:161–165.

Tiwari R, Rana BS, Kumar R, Verma D, Kumar R, Joshi RK, Garg MO, Sinha AK. Hydrotreating and Hydrocracking Catalysts for Processing of Waste Soya-Oil and Refinery-Oil Mixtures Catal commun 2011;12:559–562.

TOPSOE Renewable Fuels. http://www.topsoe.com/business_areas/refining/Renewable_fuels.aspx). Last accessed: April 12th , 2014.

Tóth C, Baladincz P, Kovács S, Hancsók J. Producing Clean Diesel Fuel by Cohydrogenation of Vegetable Oil with Gas Oil. Clean technol environ Policy 2011;13:581–585.

Trakarnpruk W, Porntangjitlikit S. Palm oil biodiesel synthesized with potassium loaded calcined hydrotalcite and effect of biodiesel blend on elastomer properties. Renew Energy 2008;33:1558–1563.

Tundo P, Selva M. The chemistry of dimethyl carbonate. Acc Chem Res 2002;35:706–716.

UOP. Green Diesel. http://www.uop.com/processing-solutions/biofuels/green-diesel/. Last accessed: April 12th , 2014.

Valle P, Velez A, Hegel P, Mabe G, Brignole EA. Biodiesel production using supercritical alcohols with a non–edible vegetable oil in a batch reactor. J Supercrit Fluids 2010;54:61–70.

Van Gerpen J, Shanks B, Pruszko R, Clements D, Knothe G. Biodiesel analytical methods: August 2002 – January 2004. National renewable energylaboratory, NREL/SR–510–36240, Colorado; July 2004.

Varma MN, Deshpande A, Madras G. Synthesis of biodiesel in supercritical alcohols and supercritical carbon dioxide. Fuel 2010;89:1641–1646.

Venkatesh H, Requpathi I, Saidutta MB. Optimization of two step Pongamia biodiesel synthesis under microwave irradiation. Fuel Process Technol 2011; 92:100–105.

Veriansyah B, Han JY, Kim SK, Hong SA, Kim YJ, Lim JS, Shu YW, Oh SG, Kim J. Production of Renewable Diesel by Hydroprocessing of Soybean Oil: Effect of Catalysts. Fuel 2011;94: 578–585.

Verziu M, Cojocaru B, Hu J, Richards R, Ciuculescu C, Filip P, Parvulescu VI. Sunflower and rapeseed oil transesterification to biodiesel over different nano crytalline MgO catalysts. Green Chem 2008;10:373–381.

Voegele E. Cavitation sells biodiesel reactor system Biodiesel Magazine. January 01, 2009 http://www.biodieselmagazine.com/articles/3098/cavitation-sells-biodiesel-reactor-system. Last Accessed: April ,3 2014.

Vyas AP, Verma JL, Subrahmanyam N. A review on FAME production processes. Fuel 2010;89:1–9.

Wang JX, Huang QD, Huang FH, Wang JW, Huang QJ. Lipase–catalyzed production of biodiesel from high acid value waste oil using ultrasonic assistant. Chin J Biotechnol 2007;23:1121–1128.

Wang LY, Yang JC. Transesterification of soybean oil with nano-MgO or not in supercritical and subcritical methanol. Fuel 2007;86(3):328–333.

Wang Y, Xingguo W, Yuanfa L, Shiyi O, Yanlai T, Shuze T. Refining of biodiesel by ceramic membrane separation. Fuel Process Technol 2009;90:422–427.

Wang Y, Zhang F, Yu S, Yang L, Li D, Evans DG, Duan X, Preparation of macrospherical magnesia–rich magnesium aluminate spinel catalysts for methnolysis of soybean oil. Chem Eng Sci 63 2008;17:4306–4312.

Wang YD, Shemmeri AT, Eames P, McMullan J, Hewitt N, Huang Y, et al. An experimental investigation of the performance and gaseous exhaust emissions of a diesel engine using blends of a vegetable oil. Appl Thermal Eng 2006;26:1684–1691.

Watanabe Y, Shimada Y, Sugihara A, Tominaga T. Conversion of degummed soybean oil to biodiesel fuel with immobilized Candida antarctica lipase. J Mol Catal B: Enzym 2002;17:151–155.

Watanabe Y, Shimada Y, Sugihara A, Tominaga Y. Enzymatic conversion of waste edible oil to biodiesel fuel in a fixed-bed bioreactor. J Am Oil Chem Soc 2001;78:703–707.

Wu WH, Foglia TA, Marmer WN, Phillips JG. Optimizing production of ethyl esters of grease using 95% ethanol by response surface methodology. J Am Oil Chem Soc 1999;76: 517–521.

Xie WL, Peng H, Chen LG. Calcined Mg–Al hydrotalcites as solid base catalysts for methanolysis of soybean oil. J Mol Catal A: Chem 2006;246:24–32.

Xu W, Gao LJ, Wang SC, Xiao GM. Biodiesel production from soybean oil in a membrane reactor over hydrotalcite based catalyst. An optimization study. Energy Fuels 2013;27:6738–6742.

Xu W, Gao LJ, Wang SC, Xiao GM. Biodiesel production in a membrane reactor using MCM–41 supported solid acid catalyst. Bioresour Technol 2014;159:286–291.

Xu Y, Du W, Liu D, Zeng J. A novel enzymatic route for biodiesel production from renewable oils in a solvent–free medium. Biotechnol Letter 2003;25:1239–1241.

Yaakob Z, Sukarmani IS, Kamarudini SK, Abdullah SRS, Mohamed F. Production of biodiesel from Jatropha curcas by microwave ırradiation.2ndWSEAS/IASME International Conference on renewable energy sources (RES'08), Corfu Greece, October 26–28, 2008.

Yazdani SS, Gonzalez R. Anaerobic fermentation of glycerol: a path to economic viability for the biofuels industry. Curr Opin Biotechnol 2007;18:213–9.

Ye X, Fernando S, Wilson W, Singh A. Application of amphiphilic catalysts, ultrasonication, and nanoemulsions for biodiesel production process. Chem Eng Technol 2007;30(11):1481–1487.

Yin JZ, Xiao M, Song JB. Biodiesel from soybean oil in supercritical methanol with co–solvent. Energ Convers Manag 2008;49: 908–912.

Yoo SJ, Lee HS, Veriansyah B, Kim J, Kim JD, Lee YW. Synthesis of biodiesel from rapeseed oil using supercritical methanol with metal oxide catalysts. Bioresour Technol 2010;101: 8686–8689.

Yu D, Tian L, Wu H, Wang S, Wang Y, Ma D, Fang X. Ultrasonic irradiation with vibration for biodiesel production from soybean oil by Novozym 435. Proce Biochem 2010;45:519–525.

Yu X, Wen Z, Liu Y, Tu ST, Wang Z, Yan J. Intensification of biodiesel synthesis using metal foam reactors. Fuel 2010;89:3450–3456.

Yuan H, Yang BL, Zhu, GL. Synthesis of biodiesel using microwave absorption catalysts. Energy Fuels 2009;23:548–552.

Yuan W, Hansen AC, Zhang Q. Vapor pressure and normal boiling point predictions for pure methyl esters and biodiesel fuels. Fuel 2005, 84, 943-950.

Yücel S, Rahmanlarİ,Özçimen D. The production of methyl esters from wastefrying oil with microwave method. Proceedings of Second International Symposium on Green Chemistry for Environment and Health, Mykonos September 2010.

Yücel Y. Biodiesel production from pomace oil by using lipase immobilized onto olive pomace. Bioresour Technol 2011;102:3977–3980.

Zagonel GF, Peralta–Zamora PG, Ramos LP. Production of ethyl esters from crude soybean oil: optimization of reaction yields using a 23 experimental design and development of a new analytical strategy for reaction control. Preprints Symp: Am Chem Soc Div Fuel Chem 2002;47:363–364.

Zanette AF, Barella RA, Pergher SBC, Treichel H, Oliveira D, Mazutti MA, et al. Screening, optimization and kinetics of Jatropha curcas oil transesterification with heterogeneous catalysts. Renew Energy 2011;36:726–731.

Zeng HY, Feng Z, Deng X, Li YQ. Activation of Mg–Al hydrotalcite catalysts for transesterification of rape oil. Fuel 2008;87(13–14):3071–3076.

Zhang L, Sheng B, Xin Z, Liu Q, Sun S. Kinetics of transesterification of palm oil and dimethyl carbonate for biodiesel production at the catalysis of heterogeneous base catalyst Bioresour Technol 2010a;101:8144–8150.

Zhang S, Zu YG, Fu YJ, Luo M, Zhang DY, Efferth T. Rapid microwave assisted transesterification of yellow horn oil to biodiesel using a hetero poly acid solid catalyst. Bioresour Technol 2010b;101: 931–936.

Zhang Y, Dube MA, McLean DD, Kates M. Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis. Bioresour Technol 2003a;90(3):229–240.

Zhang Y, Dube MA, McLean DD, Kates M. Biodiesel production from waste cooking oil: 1. Process design and technological assessment. Bioresour Technol 2003b ;89:1–16.

Zheng Y, Chen X, Shen Y. Commodity chemicals derived from glycerol, an important biorefinery feedstock. Chem Rev 2008;108:5253–77.

Zieba A, Pacuza A, Drelinkiewicz A. Transesterification of triglycerides with methanol catalyzed by heterogeneous zinc hydroxy nitrate catalyst. Evaluation of variables affecting the activity and stability of catalyst. Energy Fuels 2010;24:634–645.

LIST OF PUBLICATION

Article no.	Title	Journal	Status
1	“Jatropha and Pongamia oil derived DMC-Biodiesel Synthesis: A Kinetics Study”	Fuel	Manuscript Number: JFUE-D-13-02185
2	“Glycerin free synthesis of Jatropha and Pongamia biodiesel in supercritical dimethyl and diethyl carbonate”	Industrial & Engineering Chemistry Research	Published, Volume 53 (26), 2014, Pages 10525–10533
3	“Processing of vegetable oil for biofuel production through conventional and non-conventional routes: A Review”	Energy for Sustainable Development	Manuscript Number, ESD-D-14-00271
4	“Simulation of Glycerol Free Biodiesel in Catalytic and Non-Catalytic Supercritical Process”	-	Under submission

BIODATA OF AUTHOR

VIVEK RATHORE

Deputy Manager
Bharat Petroleum Corporation Limited
Corporate R&D Centre
Plot - 2A, Udyog Kendra, Surajpur
Greater Noida - 201306 (U.P.)

Office: 0120-2354186
Cell: +91 9910801508
Email: vivekrathore@bharatpetroleum.in

Professional Experience

07/2011 - Present

- Deputy Manager, CRDC, Bharat Petroleum Corporation Limited, G'Noida

08/2007 – 06/2011

- Sr. Research Scientist, CRDC, Bharat Petroleum Corporation Limited, G'Noida

08/2006 – 07/2007

- Research Scientist, CRDC, Bharat Petroleum Corporation Limited, G'Noida

Education

07/2011 – Presently Pursuing Ph. D. (Chemical Engg.), University of Petroleum & Energy Studies (UPES), Department of Chemical Engineering, India

2004 – 2006 MS (Chemical Engg.), Indian Institute of Science (IISc), Bangalore, India

1999 – 2003 B.E. (Chemical Engg., Hons.), Pt. R. S. U. Raipur, India

Area of Expertise

- Crude Oil distillation (TBP/Vacuum)followed by generation of Crude Assay
- Crude evaluations studies to improve the distillation yields and data analysis for distillate yield, specification and physicochemical properties etc.
- Generation of simulated distillation profile through ASPEN simulation/Crude manager for crude oil/blends for comparative analysis of distillation yield
- Crude Oil Compatibility/Blending studies through in-house developed methods and development of correlation with properties of neat crude oil
- Strategies for Processing Opportune Crude Oils/blends in Indian Refineries
- Optimization of Crude Oil blends to minimize Crude Pre-Heat train fouling in heat exchangers
- LPG/Gasoline/Kero Sweetening Process
- Resid Upgradation technology like Solvent Deasphaltene, Delayed coker & Visbreaker Units
- Alternative Fuels (Biodiesel), Bioluricant & Glycerol valorization
- Reaction in Supercritical Fluids, Enzymatic reactions
- Modeling of chemical reactions & Simulation studies

Instruments/Pilot Plant Experience

- Crude Oil Atmospheric/ Vacuum Distillation Unit (TBP ASTM D2892/5236)
- Vacuum Distillation Unit (ASTM D 1160)
- Designed Manual Distillation unit with automation and completed distillation of more than 25 crude oil
- Designed & Conceptualize the Biodiesel Plant based on Homogeneous /Heterogeneous catalyst
- Preparation of Technical Specifications include details of hardware, instrumentation; control command etc., with PFD and P&ID for the procurement of SDA unit
- Operation of High Pressure & High Temperature Reactors

- Hands on experience on various instruments like GC, HPLC, FTIR, hot liquid process simulator (HLPS), Density meter, Viscometer, RI
- Software Package: ASPEN plus, Crude Manager

Significant Achievements

At BPCL

- Worked as a Team Leader for Crude Oil Compatibility project with M/s Cairn Energy for studying the compatibility of Rajasthan crude (RJ) with distillates. Above service has generated as significant revenue for R&D during 2007-2008.
- Actively involved during commercialization of IIP-BPCL developed LPG sweetening Merox catalyst (THOXCAT ES) at MRPL, Mangalore during Jun 2008.
- Address the issue of oxidizer nozzle plugging problem of Merox unit at MR during run with IIP-BPCL developed sweetening Catalyst. Suggestion and recommendation communicated to Mumbai Refinery & technology. After words plant is running smoothly without facing such problems.
- Designed/Modified a cooling system for Bitumen packaging plant at Mumbai Refinery during 2007-2008.
- Delivered a Technology review on ‘Recent advances in Bottom of barrel technology for Mumbai Refinery’ during Refinery forum meet on visbreaker and coker held at CRDC in May 2008.
- Presented the idea title “Development and commercialization of IIP-BPCL LPG sweetening catalyst” in IDEA -2008 competitions at shanti Bhavan Mumbai Dec’08.
- Suggested the opportune crude oil blends to supply chain (SCO) & International Trade (IT) for processing in BPC refineries 2009-2010.
- Prepared a comprehensive report on ‘Processing of Opportune Crude Blends at BPC Refineries’ in July 2010 based on research work conducted at CRDC.
- Presented the idea title “A Novel Route for Oxidation of Sulfidic Spent Caustic Streams by Homogenous catalysis Route for Refineries” in IDEA - 2010 competitions at Mumbai.

During Academic

2004: Qualified in Graduate Aptitude Test in Engineering (GATE)

2003: Qualified in Graduate Aptitude Test in Engineering (GATE)

2003: Bachelor of Engineering (B.E.) with Hons. in Chemical from Pt. Ravishankar University, Raipur (C.G.) and Secured 3rd rank in the University

2002: Won the first Prize for Technical Model Category in "Ritofest- 2002"

2001: Won the first Prize for Technical Model Category in "National technological Meet-2001" at Pt. R. S. U. Raipur (C.G.)

1998: Secured 4th rank in the district for Senior Secondary School (10+2, 12th Class) Certificate Examination

1997: Scholarship awarded by "Ministry of Human Resource Development (MHRD)" Govt. of India

1996: Secured 31st rank in Madhya Pradesh and 2nd rank in district for High School (10th Class) Certificate Examination

Honors and Awards

- Received the token of recognition in IDEA -2008 competitions at Shanti Bhavan Mumbai on "Development and commercialization of IIP-BPCL LPG sweetening catalyst"
- Received the token of recognition in IDEA -2011 competitions at Bharat Bhavan Mumbai on "A Novel Route for Oxidation of Sulfidic Spent Caustic Streams by Homogenous catalysis Route for Refineries"

Refinery Forums/Technology Meet

2009: Delivered a talk on *"Processing of Opportune crude Oil in Indian Refineries"* from BPCL (R&D) at CHT MEET held on "Sharing best operational practices on DISTILLATION for Refinery performance improvement" at NRL, Numaligrah.

2012: Presented strategies for *"Enlargement of the Crude Processing Slate in Refinery"* at CHT meet on "Best practices on Distillation" at CPCL, Chennai on 19th & 20th April 2012.

Both the presentation was well taken by all the groups of distillation experts from various refineries.

Computational Skills

- Programming Languages: C, FORTRAN
- Software Packages : Aspen Plus, Crude Manager, Matlab, Mathematica, MS Office

Other accomplishments

- Core-committee member of Chemical Engineering Association (CEA) - 2002, IISc, Bangalore.
- Treasure of Chemical Engineering Student Association (CEASA)-2001-2003 at RIT, Department of Chemical Engineering, Raipur.

Patent filed

US Patent Filed for MULTILAYER FILM FOR PACKAGING, (WO/2011/021219)

> *RAY Saptarshi, RAWAT Jaya, THORAT Tushar Sudhakar,* **RATHORE Vivek,** *PEDDY Venkat Chalapathi, Rao. NETTEM Venkateswarlu Choudary, SIDDIQUI Mohammad Amir*

Papers Published in Journals and Conferences

1. Glycerin free synthesis of Jatropha and Pongamia biodiesel in supercritical dimethyl and diethyl carbonate
   Vivek Rathore*, Sudha Tyagi, Bharat Newalkar and R P Badoni*
   Industrial & Engineering Chemistry Research, Volume 53 (26), 2014, Pages 10525–10533

2. An Approach towards Commercially Viable Proposition on Biodiesel Value Chain
   Tushar S. Thorat, Renny Andrew, ***Vivek Rathore****, Rajeev Kumar, Sudha Tyagi, Sanjeev Gangurde, Nitin Somkuwar, Gokak D.T., Janardan Sharma, Viswanthan P.S.*
   XVIII Refinery Technology Meet, Nov 2013

3. Crude Oil Blends Compatibility – Enlargement of the Crude Processing Slate in Refinery
   Vivek Rathore*, Tushar S Thorat, Dhaneesh VS, Jaya Rawat, Rajiv Brahma, P.S. Viswanathan*

The International Symposium on Fuels and Lubricants (ISFL), March 2012

4. Development of IIP-BPCL Catalyst, Thoxcat ES for Sweetening of LPG
   Vivek Rathore*, PVC Rao, V Suresh, Gautam Das, Sunil Kumar and M O Garg*
   Journal of the Petrotech society, July-Sep 2011

5. Oxidation of Sulfidic Spent Caustic Streams for Refineries: A Catalytic Approach
   Vivek Rathore*, Shalini Gupta, T.S. Thorat, P.V.C. Rao and NV Choudary*
   Petroleum Technology Quarter, Q4 Sep 2011

6. Assessment of Crude Oil Blends – Enlargement of the Crude Processing Slate in Refinery
   Vivek Rathore*, Rajiv Brahma, Tushar S Thorat, P V C Rao and N V Choudary*
   Petroleum Technology Quarter, Q3 July 2011

7. A Novel Route for Oxidation of Sulfidic Spent Caustic Streams by Homogenous catalysis Route for Refineries
   Vivek Rathore, *Shalini Gupta, Biju G., T.S. Thorat, P.V.C. Rao & NV Choudary*
   XV Refinery Technology Meet, Feb 2011

8. Resid Up-gradation Option: Utilization of Petroleum Pitch from SDA Process for Gasifier - A Model Approach
   Vivek Rathore*, Sahil Gupta, Tushar S Thorat, P V C Rao and N V Choudary*
   The International Symposium on Fuels and Lubricants (ISFL), March 2010

9. Prediction of Crude Blend Compatibility way to enlarge the Crude Processing Slate
   Vivek Rathore*, Tushar S Thorat, P V C Rao and N V Choudary*
   Journal of the petrotech society, volume 4, June 2009

10. Processing Opportune Crude Oils: A Catalytic Process for HAC
    Rajeev Kumar, ***Vivek Rathore,*** *Chithra Viswanath, Tushar S. Thorat, P.V.C. Rao and N.V. Choudary*
    Petro-Tech, January 2009

11. Studies on Valorization of Glycerol for its application in petroleum industries
    Vivek Rathore, *Rajeev Kumar, Tushar S. Thorat, P.V.C. Rao and N.V. Choudary*
    Petro-Tech, January 2009

12. Studies on Compatibility of Crude Oil Blends for Enlargement of Crude Processing Slate
    Vivek Rathore, *Tushar S Thorat, P V C Rao and N V Choudary*
    XIV Refinery Technology Meet, Sep 2007

13. Synthesis of biodiesel from edible and non-edible oils in supercritical alcohols and enzymatic synthesis in supercritical carbon dioxide
    Rathore Vivek, *Madras Giridhar*
    Fuel, Volume 86, Issues 17-18, December 2007, Pages 2650-2659

Personal information

DOB : 6th August, 1981

Marital status: Married