



Faculty of Engineering

**Production, Optimization and Performance Analysis of Jatropha
Biodiesel using Nano CaO Catalyst Synthesized from *Polymesoda
erosa* Seashells**

Amaranadha Reddy. Manchuri

**Doctor of Philosophy
2018**

Production, Optimization and Performance Analysis of Jatropha Biodiesel
using Nano CaO Catalyst Synthesized from *Polymesoda erosa* Seashells

Amaranadha Reddy. Manchuri

A thesis submitted

In fulfillment of the requirements for the degree of Doctor of Philosophy

(Mechanical and Manufacturing)

Faculty of Engineering
UNIVERSITI MALAYSIA SARAWAK
2018

DECLARATION

I hereby declare that this thesis is my original writing. This is a true copy of the thesis including any required final revisions, as accepted by my examiners. I understand that my thesis may be made electronically available to the public. The thesis has not been accepted for any degree and is not concurrently submitted in candidature for any other degree.

Name of Student : Amaranadha Reddy. Manchuri

Student Matric : 15010114

Degree : Doctor of Philosophy

Department : Mechanical and Manufacturing

Faculty : Faculty of Engineering

Thesis Title : Production, Optimization and Performance Analysis of
Jatropha Biodiesel using Nano CaO Catalyst Synthesized
from *Polymesoda erosa* Seashells

Amaranadha Reddy. Manchuri

Date:

DEDICATION

With high esteem this humble work is dedicated to

My parents' Sri. Krishna Reddy and Smt. Rukminamma who nurtured me.

My brother Sri. Praveen Kumar Reddy who enshrined me.

Loving Smt. Jyoshna, Smt. Spandana, Pawan Krishna Reddy and Abhi Ram Reddy
who vitalized my intuition.

Sages Sri. Subramanyam Arikatla and Sri. Narayanan Kulathuramaiyer who fortified
absolute virtues in me.

-o0o-

ACKNOWLEDGEMENT

I offer salutations to the Supreme Being goddess ‘Ādi Parāshakti’, divine pure eternal consciousness. Mother, all the time You empowered me to pursue my passions.

I would like to express my sincere gratitude to my supervisor Associate Professor Dr. Abu Saleh Ahmed for his continuous support in my Ph.D. I could not have imagined having a better supervisor for my study. Besides, I would like to thank my co-supervisors Professor Dr. Sinin Hamdan, Dr. Md Rezaur Rahman and Dr. Md Saiful Islam, for their insightful scientific discussions and reinforcement. My sincere thanks also goes to the technical staff and fellow researchers for their indispensable support in experimental investigations.

I would greatly acknowledge UNIMAS, for awarding graduate Scholarship, Zamalah Siswazah UNIMAS award 2015 for the period February-August 2015. I would like to express my highest gratitude towards Ministry of Higher Education (MOHE), Malaysia for awarding prestigious Malaysian International Scholarship, MIS-2015; KPT.B.600-4/1/12 (60) since September 2015. MOHE has fully funded my tuition fees and allowances. Also, my sincere thanks to UNIMAS for sanctioning an internal grant, *Dana Pelajar*, PhD (DPP) F02(DPP45)/1260/2015/60.

Last but not the least, I would like to thank all my family members and well-wishers for their everlasting socio spiritual support throughout this thesis.

Thank you all for being part of my life.

ABSTRACT

In sustainable biodiesel production, both catalyst and feedstock are considered as essential features. Various heterogeneous catalysts are often used to produce biodiesel from non-edible crude oils. In this research, nano calcium oxide (CaO) heterogeneous catalyst was synthesized from indigenous aquatic seashells, *Polymesoda erosa*, through calcination–hydration–dehydration technique. The nano CaO catalyst spectral and structural characteristics were evaluated utilizing spectrographic techniques that include Fourier transform infrared (FT-IR) spectroscopy, transmission electron microscope (TEM), X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET). A nano CaO with a surface area of 90.61 m²/g in spherical or rod-shapes with diameters of 66.2nm and 548.7nm measured. The nano CaO catalysis efficiency was investigated in a two-step transesterification of triglycerides from crude Jatropha oil (CJO) as Jatropha biodiesel (JB). A JB yield of 98.54 % was reported at optimal parametric conditions i.e., 0.02:1 (w/w) catalyst concentration, 133.1 min reaction time and 5.15:1 mol. of methanol to the pre-treated oil. An average of 95.8% JB yield was obtained from the catalyst reusability and leaching study up to the sixth cycle. The fatty acid composition (FAC) of a feedstock influences biodiesel physicochemical properties. The impact of FAC on biodiesel produced using CJO originated from the east and west Malaysian regions was investigated. The physicochemical fuel properties of biodiesel and blends were investigated according to ASTM D6751/ EN 14214 standards. The investigations revealed that the FAC of biodiesel can influence physicochemical properties of the JB due to variant degrees of saturated and unsaturated fatty acid levels. A mathematical model, response surface methodology based on central composite design, coupled with desirability approach was utilized to predict the engine performance and emissions. The engine operating parameters that include engine speed (1700 rpm – 2100

rpm), using JB - PD fuel blends of (B5 – B25) and torque (28 N.m – 36 N.m) were utilized as input parameters. At a collective desirability of 0.969, both engine performance and exhaust gas emissions were resulted as optimal. The engine speed of 1900 rpm, JB – PD fuel blend of B13 and torque of 33 N.m were obtained as optimal parameters. Hence, this research recommends use of B13 biodiesel blends.

Keywords: Biodiesel; transesterification; Jatropha; heterogeneous catalyst; nano catalyst; fatty acid composition; fuel properties; engine performance; exhaust emissions; optimization.

Kajian ke atas Pengeluaran, Pengoptimuman dan Prestasi Biodiesel Jatropha Melalui Sintesis Pemangkin Kalsium Oksida (CaO) Nano daripada Kulit Kerang Polymesoda erosa

ABSTRAK

Bagi kemampunan pengeluaran biodiesel, pemangkin dan bahan mentah dianggap sebagai ciri yang penting. Pelbagai pemangkin heterogen sering digunakan bagi menghasilkan biodiesel daripada minyak mentah bukan makanan. Dalam kajian ini, pemangkin heterogen nano kalsium oksida (CaO) nano telah disintesis daripada kerang akuatik asli iaitu Polymesoda erosa, melalui teknik penalaan-penghidratan-penyahhidratan. Ciri-ciri spektral dan struktur pemangkin CaO nano dinilai dengan menggunakan teknik spektroskopi yang merangkumi Inframerah (FT-IR), Mikroskop Transmisi Elektron (TEM), Sinar Pembelauan-X (XRD) serta teknik Brunauer-Emmett-Teller (BET). CaO nano dengan luas permukaan 90.61 m²/g dalam bentuk sfera atau rod dengan diameter 66.2nm dan 548.7nm telah diukur. Kecekapan katalitik CaO diuji dalam dua fasa trans-esterifikasi trigliserida dari Minyak Jatropha Mentah (CJO) atau disebut sebagai Biodiesel Jatropha (JB). Penghasilan JB mentah sebanyak 98.54% dilaporkan pada keadaan parametrik optimum iaitu 0.02: 1 (w/w) untuk kepekatan pemangkin, 133.1 min. untuk masa tindak balas dan 5.15: 1 mol untuk nisbah metanol kepada minyak sebelum dirawat. Hasil purata sebanyak 95.8% JB mentah telah diperolehi daripada pemangkin yang dikitar-semula, diikuti dengan pengalihan pemangkin sehingga kitaran ke-enam. Komposisi asid lemak (FAC) dari bahan mentah akan mempengaruhi sifat fizikokimia biodiesel. Kesan FAC terhadap biodiesel yang dihasilkan menggunakan CJO yang berasal dari kawasan timur dan barat Malaysia telah diuji. Ciri-ciri bahan bakar fizikokimia biodiesel dan campuran telah dikaji mengikut piawaian ASTM D6751 / EN 14214. Hasil kajian menunjukkan bahawa FAC biodiesel boleh mempengaruhi sifat fizikokimia JB kerana kepelbagaian suhu asid

lemak tepu dan tidak tepu. Model matematik, tindakbalas metodologi permukaan berdasarkan rekabentuk komposit berpusat, beserta dengan pendekatan 'desirability' telah digunakan untuk meramalkan prestasi enjin dan pelepasan. Parameter operasi enjin termasuk kelajuan enjin (1700 rpm - 2100 rpm), dengan menggunakan campuran bahan api JB - PD (B5 - B25) dan 'tork' (28 N.m - 36 N.m) digunakan sebagai parameter input. Secara kolektif, pada nilai 'desirability' 0.969, kedua-dua prestasi enjin dan pelepasan gas ekzos yang dihasilkan adalah optimum. Juga pada kelajuan enjin setinggi 1900 rpm, campuran bahan api JB - PD B13 dan tork 33 N.m diperolehi sebagai parameter optimum. Justeru, kajian ini telah mengesyorkan penggunaan biodiesel B13.

Kata kunci: biodiesel; transesterifikasi; *Jatropha*; pemangkin heterogen; pemangkm nano; komposisi asid lemak; sifat bahan api; prestasi enjin; pelepasan ekzos; pengoptimuman.

TABLE OF CONTENTS

	Page
DECLARATION	i
DEDICATION	ii
ACKNOWLEDGEMENT	iii
ABSTRACT	iv
ABSTRAK	vi
TABLE OF CONTENTS	viii
LIST OF TABLES	xiv
LIST OF FIGURES	xvi
LIST OF ABBREVIATIONS	xx
CHAPTER 1: INTRODUCTION	1
1.1 Introduction	1
1.2 Problem statement	4
1.2.1 Advantages and challenges of biodiesel	7
1.3 Scope of research	8
1.4 Research hypothesis	9
1.5 Objectives	10
1.6 Organization of the thesis	10
CHAPTER 2: LITERATURE REVIEW	12
2.1 Background	12
2.2 Biodiesel worldwide	15
2.3 Biodiesel prospects in Malaysia	16
2.4 Feedstocks for biodiesel	19

2.5	Characteristics of biodiesel	24
2.6	Biodiesel production via transesterification	32
2.7	Effect of transesterification reaction parameters on biodiesel yield	35
2.7.1	Catalyst loading	35
2.7.2	Methanol to oil ratio	36
2.7.3	Transesterification reaction time	37
2.7.4	Heating temperature	37
2.7.5	Stirring speed	38
2.8	Heterogeneous catalyzed transesterification	38
2.9	Synthesis of calcium based heterogeneous catalysts from renewable sources	43
2.9.1	Methods of catalyst synthesis from shells	48
2.9.2	<i>Polymesoda erosa</i> : A potential raw material source for catalyst synthesis	51
2.10	Jatropha as a biodiesel feedstock	52
2.11	Feedstock fatty acid composition influence on physicochemical properties of biodiesel	55
2.11.1	Cetane number	55
2.11.2	Oxidation stability	56
2.11.3	Calorific value	57
2.11.4	Iodine value	57
2.11.5	Acid value	58
2.11.6	Water content	58
2.11.7	Kinematic viscosity	60

2.11.8	Density	61
2.11.9	Cloud point	61
2.11.10	Pour point	62
2.11.11	Flash point	63
2.11.12	Cold filter plugging point	63
2.12	Mathematical modeling based optimization	64
2.13	Diesel engine performance and exhaust emissions	68
2.13.1	Advantages and disadvantages of diesel engines	71
2.14	Summary of literature review and research gap	71
CHAPTER 3: METHODOLOGY		73
3.1	Materials	73
3.2	Synthesis of nano CaO catalyst	73
3.3	Characterization of nano CaO catalyst	74
3.4	Biodiesel production	75
3.4.1	Acid pretreatment	76
3.4.2	Transesterification using nano CaO catalyst	77
3.4.3	Design of experiments for maximum JB yield	77
3.4.4	Model fitting and statistical analysis	78
3.5	Transesterification with reference catalyst	79
3.6	Reusability experiments of <i>P. erosa</i> synthesized nano CaO and commercial CaO	79
3.7	Biodiesel characterization and fuel physicochemical properties analysis	80

3.8	Preparation of Jatropha biodiesel - petro diesel blends and analysis of physicochemical properties	81
3.9	Optimization of biodiesel fueled diesel engine performance and exhaust emissions	84
3.9.1	Mathematical modelling of engine performance and exhaust emissions	84
3.10	Summary of methodology	85
CHAPTER 4: RESULTS AND DISCUSSION		87
4.1	Characteristic analysis of nano CaO catalyst	87
4.1.1	IR spectra analysis of nano CaO catalyst	87
4.1.2	TEM analysis of nano CaO catalyst	89
4.1.3	BET and BJH analysis of nano CaO catalyst	89
4.1.4	Particle size analysis of nano CaO catalyst	90
4.1.5	XRD analysis of nano CaO catalyst	91
4.2	Jatropha biodiesel production and yield analysis	92
4.2.1	CJO Acid pretreatment	92
4.2.2	CCD analysis for transesterification and prediction of JB yield	94
4.2.3	Regression model analysis for optimal JB yield	98
4.2.4	ANOVA for biodiesel yield	100
4.2.5	Impact analysis of transesterification parameter - interaction	101
4.3	Optimization of transesterification parameters for maximum JB yield	103
4.4	Biodiesel yield analysis using commercial CaO catalyst	103
4.5	Reusability analysis of nano CaO catalyst	104

4.6	IR spectrum analysis of Jatropha biodiesel	108
4.7	Analysis of Jatropha biodiesel feedstock fatty acid profile	110
4.8	Analysis of physicochemical properties of Jatropha biodiesel and blends	115
4.8.1	Cetane number of JB-PD biodiesel blends	115
4.8.2	Oxidation stability of JB-PD biodiesel blends	116
4.8.3	Calorific value of JB-PD biodiesel blends	117
4.8.4	Iodine value of JB-PD biodiesel blends	119
4.8.5	Acid value of JB-PD biodiesel blends	120
4.8.6	Water content of JB-PD biodiesel blends	121
4.8.7	Kinematic viscosity of JB-PD biodiesel blends	122
4.8.8	Density of JB-PD biodiesel blends	123
4.8.9	Cloud point of JB-PD biodiesel blends	124
4.8.10	Pour point of JB-PD biodiesel blends	125
4.8.11	Flash point of JB-PD biodiesel blends	126
4.8.12	Cold filter plugging point of JB-PD biodiesel blends	127
4.9	Jatropha biodiesel - petro diesel blends for performance analysis.	128
4.10	Optimization of engine performance parameters	129
4.10.1	Brake power	132
4.10.2	Brake specific fuel consumption	134
4.10.3	Brake thermal efficiency	137
4.10.4	Exhaust gas temperature	140
4.11	Optimization of exhaust gas emissions	143
4.11.1	Nitrogen oxides	146

4.11.2	Hydrocarbon	149
4.11.3	Carbon dioxides	152
4.11.4	Carbon monoxide	155
4.11.5	Smoke opacity	158
4.12	Optimization of engine performance and exhaust emissions parameters	161
4.13	Summary of results and discussion	163
CHAPTER 5: CONCLUSION AND RECOMMENDATIONS		164
5.1	Conclusion	164
5.2	Recommendations	166
REFERENCES		168
APPENDICES		191

LIST OF TABLES

		Page
Table 2.1	Major feedstocks used for biodiesel production across the world	22
Table 2.2	Percentage oil content in non-edible feedstocks for biodiesel production	23
Table 2.3	Advantages of non-edible oil produced biodiesels	24
Table 2.4	Biodiesel properties and specification of the ASTM D6751 and EN 14214 standards	27
Table 2.5	Physicochemical properties of biodiesel synthesized from different feedstocks	29
Table 2.6	Selected physicochemical properties of pure fatty acids	31
Table 2.7	Summary of primary parameters impact on biodiesel production via heterogeneous catalyzed transesterification	45
Table 2.8	Summary of calcium based catalysts synthesized from renewable wastes for biodiesel production	47
Table 2.9	Fatty acid composition (wt %) of Jatropha biodiesels from Thailand and China	54
Table 3.1	Factors and levels for transesterification process	78
Table 3.2	Jatropha biodiesel and blends fuel properties analysis equipment	82
Table 3.3	Diesel engine operating parameters and constraints for optimization	85
Table 4.1	CCD matrix for prediction of Jatropha biodiesel yield	96
Table 4.2	Estimated regression coefficients for biodiesel yield	99
Table 4.3	ANOVA for Jatropha biodiesel yield	101

Table 4.4	Comparison of biodiesel yield and transesterification reaction parameters using <i>P. erosa</i> synthesized nano CaO and commercial CaO catalysts	104
Table 4.5	Leaching results of <i>P. erosa</i> synthesized nano CaO catalyst in reuse cycle	107
Table 4.6	Fatty acid composition (wt %) and categorization of Jatropha biodiesels from East and West Malaysian geographic regions	111
Table 4.7	Physicochemical fuel properties of Jatropha biodiesels from East and West Malaysian regions and Petro diesel	113
Table 4.8	Physicochemical fuel properties of Jatropha biodiesel - petro diesel blends	114
Table 4.9	Biofuel properties of Jatropha biodiesel and petro diesel blends B5-B25	129
Table 4.10	Predicted results of engine performance	130
Table 4.11	ANOVA and regression results of predicted engine performance	131
Table 4.12	Predicted results of exhaust gas emissions	144
Table 4.13	ANOVA and regression results of predicted exhaust gas emissions	145
Table 4.14	Optimization of engine performance and exhaust emissions	162

LIST OF FIGURES

	Page
Figure 2.1 Hubbert’s prediction curve for global crude-oil production over 1850-2200	12
Figure 2.2 World total energy consumption history and projections (quadrillion Btu) over 2012-2040	13
Figure 2.3 Global energy consumption (quadrillion Btu): Present status and projections by source, 1990-2040	14
Figure 2.4 Global top 15 countries in biodiesel production during 2015	17
Figure 2.5 Biodiesel export, consumption, on-road use, production capacity and blending rate in Malaysia during 2008-2017	18
Figure 2.6 Classification of biofuels	20
Figure 2.7 Chemistry of high FFA oils transesterification to biodiesel	32
Figure 2.8 Chemistry of biodiesel synthesis via transesterification	33
Figure 2.9 Classification of biodiesel production methodologies via transesterification	34
Figure 2.10 Catalysts global market share	39
Figure 2.11 General mechanism of base heterogeneous catalyzed transesterification reaction	41
Figure 2.12 Metal oxide surface structure	41
Figure 2.13 General characteristics of a few in situ characterization techniques	42
Figure 2.14 Seashell potential zones of Malaysian coastal areas	51
Figure 2.15 Jatropha curcas plantations across the globe	53
Figure 3.1 Jatropha biodiesel production via two step transesterification	75

Figure 4.1	IR spectrum of CaO catalyst as synthesized from <i>P. erosa</i> shells	88
Figure 4.2	TEM images of nano CaO catalyst (a) Rod shape (b) Spherical shape	89
Figure 4.3	Particle size distribution of nano CaO catalyst synthesized from <i>P. erosa</i> shells	90
Figure 4.4	XRD pattern of nano CaO catalyst as prepared from <i>P. erosa</i> shells	91
Figure 4.5	Reduction of free fatty acid percentage from crude Jatropha oil using H ₂ SO ₄ catalyst	93
Figure 4.6	Effect of Methanol to oil ratio (mol.) and Reaction time (hr.) on ester yield	94
Figure 4.7	Comparative graph between experimental and predicted yield percentage of Jatropha biodiesel	95
Figure 4.8	Contour and surface plots of (a) catalyst concentration and reaction time interactions impact on JB yield % (b) methanol to pretreated oil ratio and catalyst concentration interactions impact on JB yield % (c) methanol to pretreated oil ratio and reaction time interactions impact on JB yield %	102
Figure 4.9	SEM micrographs of nano CaO catalyst showing changes on the catalyst surface structure in nine catalyst reuse cycles	105
Figure 4.10	JB yield% using nano CaO and commercial CaO catalyst reusability cycle analysis at optimal transesterification reaction conditions	106
Figure 4.11	Infrared spectra of Jatropha biodiesel	109
Figure 4.12	Cetane number results of JB-PD biodiesel blends	115
Figure 4.13	Oxidation stability results of JB-PD biodiesel blends	117
Figure 4.14	Calorific value results of JB-PD biodiesel blends	118

Figure 4.15	Iodine value results of JB-PD biodiesel blends	119
Figure 4.16	Acid value results of JB-PD biodiesel blends	120
Figure 4.17	Water content results of JB-PD biodiesel blends	121
Figure 4.18	Kinematic viscosity (at 40°C) results of JB-PD biodiesel blends	122
Figure 4.19	Density (at 15°C) results of JB-PD biodiesel blends	124
Figure 4.20	Cloud point results of JB-PD biodiesel blends	125
Figure 4.21	Pour point results of JB-PD biodiesel blends	126
Figure 4.22	Flash point results of JB-PD biodiesel blends	127
Figure 4.23	Cold filter plugging point results of JB-PD biodiesel blends	128
Figure 4.24	Brake power (kW) variations in contrast to the interactions of engine speed, JB-PD blending ratio and torque	133
Figure 4.25	Comparative graph showing predicted and reference results of brake power	134
Figure 4.26	Brake specific fuel consumption (g/kWh) variations in contrast to the interactions of engine speed, JB-PD blending ratio and torque	136
Figure 4.27	Comparative graph showing predicted and reference results of brake specific fuel consumption	137
Figure 4.28	Brake thermal efficiency (%) variations in contrast to the interactions of engine speed, JB-PD blending ratio and torque	139
Figure 4.29	Comparative graph showing predicted and reference results of brake thermal efficiency	140
Figure 4.30	Exhaust gas temperature (°C) variations in contrast to the interactions of engine speed, JB-PD blending ratio and torque	142

Figure 4.31	Comparative graph showing predicted and reference results of exhaust gas temperature	143
Figure 4.32	NOx exhaust emission (ppm vol.) variations in contrast to the interactions of engine speed, JB-PD blending ratio and torque	147
Figure 4.33	Comparative graph showing predicted and reference results of NOx emissions	149
Figure 4.34	Hydrocarbons exhaust emission (ppm vol.) variations in contrast to the interactions of engine speed, JB-PD blending ratio and torque	151
Figure 4.35	Comparative graph showing predicted and reference results of hydrocarbon emissions	152
Figure 4.36	Carbon dioxide exhaust emission (%vol.) variations in contrast to interactions of engine speed, JB-PD blending ratio and torque	154
Figure 4.37	Comparative graph showing predicted and reference results of carbon dioxide emissions	155
Figure 4.38	Carbon monoxide exhaust emission (%vol.) variations in contrast to the interactions of engine speed, JB-PD blending ratio and torque	157
Figure 4.39	Comparative graph showing predicted and reference results of carbon monoxide emissions	158
Figure 4.40	Smoke opacity (%HSU) variations in contrast to the interactions of engine speed, JB-PD blending ratio and torque	160
Figure 4.41	Comparative graph showing predicted and reference results of carbon dioxide emissions	161

LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrometer
ANN	Artificial neural networks
ANOVA	Analysis of variance
ASTM	American Society for Testing and Materials
AV	Acid value
B1.3	BD 1.3% + PD 98.7%
B2	BD 2% + PD 98%
B5	(BD 5% + PD 95%)/ (JB 5% + PD 95%)
B7	BD 7% + PD 93%
B8	BD 8% + PD 92%
B10	(BD 10% + PD 90%) / (JB 10% + PD 90%)
B13	JB 13% + PD 87%
B15	JB 15% + PD 85%
B20	(BD 20% + PD 80%)/ (JB 20% + PD 80%)
B25	JB 25% + PD 75%
B30	(BD 30% + PD 70%)/ (JB 30% + PD 70%)
B100	(JB 100% + PD 0%)/ Pure biodiesel
BD	Biodiesel
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
BP	Brake power
BSFC	Brake specific fuel consumption

BTE	Brake thermal efficiency
CaO	Calcium oxide
CAS No.	Chemical Abstracts Service Number
CCD	Central composite design
CCRD	Central composite rotatable design
CFPP	Cold filter plugging point
CJO	Crude Jatropha oil
CN	Cetane number
CO	Carbon monoxide
CP	Cloud point
CPP	Clean Power Plan
CV	Calorific value
DE	Density
DECC	Department of Energy and Climate Change of U.K.
DG	Diglycerides
DI-CI	Direct injection compression ignition
DU	Degree of unsaturation
EIA	Energy Information Administration of U.S.
EN	European Standards
FAC	Fatty acid composition
FAME	Fatty acid methyl ester
FFA	Free fatty acids
FP	Flash point
FT-IR	Fourier Transform Infrared

GA	Genetic algorithm
GB/T 20828-2007	China biodiesel standard
GC	Gas chromatograph
HC	Hydrocarbon
IV	Iodine value
JB	Jatropha biodiesel
JB _{EM}	Jatropha biodiesel East Malaysia
JB _{WM}	Jatropha biodiesel West Malaysia
JCL	<i>Jatropha curcas</i> Linnaeus
KV	Kinematic viscosity
LCSF	Long chain saturated factor
ME	Methyl ester
MeOH	Methyl alcohol
MG	Monoglyceride
MPOB	Malaysian Palm Oil Board
MUFAs	Monounsaturated fatty acids
M_w	Molecular weight
NO _x	Oxides of nitrogen
OECD	Organization for Economic Cooperation and Development
ON	Octane number
OS	Oxidation stability
<i>P. erosa</i>	<i>Polymesoda erosa</i>
PD	Petro diesel
PM	Particulate matter

PP	Pour point
PUFAs	Polyunsaturated fatty acids
R^2	Coefficients of determination
R_{adj}^2	Coefficients of correlation
RSM	Response surface methodology
SEM	Scanning electron microscopy
SFAs	Saturated fatty acids
SIRIM	Scientific and Industrial Research Institute of Malaysia
TEM	Transmission Electron Microscope
TG	Triglycerides
UNFCCC	United Nations Framework Convention on Climate Change
USFAs	Unsaturated fatty acids
WC	Water content
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Introduction

The growing fossil fuel consumption in the road transportation and other commercial sectors has explicit impact on environment, global warming and human life due to their excessive combustive exhaust gas emissions (Kessler & Sperling, 2016). Besides, the natural fossil reserves have been diminishing exponentially and hence, escalation in their market prices. The predictions over oil production in the 1950s in the USA by M. K. Hubbert, U.S. geologist, have come to reality in 1970 (Hubbert, 1956). Many real-time and forecast analytics of oil predictions have concurrently agreed with Hubbert's predictions in the year 2000 (Gautier, 2008), and emphasize a precise attention towards energy security as well as search for alternative fuels to mitigate the scarcity of fossil fuels over the year 2025 (Dhamodaran et al., 2017). These critical phenomenon enforces the scientists, researchers, policymakers and engineers to accelerate and emphasis their efforts in search of alternative and renewable fuels. As a result, many leading edge studies reported on several forms of fuel sources and their usage.

Fatty acid methyl ester (FAME),- known as biodiesel, comprises mono alkyl esters of long chain fatty acids, produced by the transesterification using biological feedstocks such as vegetable oils, animal fats and microalgae oils (Qian et al., 2010). In recent years, biodiesel has attained a considerable attention as an alternative renewable fuel for diesel engines due to the fuel's reduced exhaust emissions as well as performance compared to the petro diesel. At first, peanut oil fueled diesel engine was demonstrated by diesel engine inventor, Rudolf

Diesel, at Paris in 1900 (Altın et al., 2001; Sahoo & Das, 2009). However, in the 1980's the biodiesel has been brought into usage in diesel engines as a green fuel (US-EPA, 2010). Additionally, vegetable oils feedstock are highly recommended in attaining the decarbonization targets of 2050 (DECC, 2012; Fries & Cook, 2011). Malaysia is one of the top 10 global biodiesel producer during 2015 (REN21, 2016). The federal government of Malaysia initiated 'National Biofuel Policy-2006' and 'Biofuel Industry Act-2007' to develop indigenous knowledge (Wahab, 2016). Subsequently, The Malaysian palm oil board (MPOB) and Scientific and Industrial Research Institute of Malaysia (SIRIM) principally engaged in developing resources and infrastructure such as feedstocks, technology and biodiesel standards (Mofijur et al., 2013).

Biodiesel is typically produced using oil feedstocks in the presence of methyl alcohol (MeOH) and a suitable catalyst (Meher et al., 2013; Qian et al., 2010). The biodiesel synthesis via transesterification largely governed by reaction parameters that involves catalyst loading, methanol to oil ratio, reaction time, heating temperature, and the stirring rpm (ANR et al., 2016; Goyal et al., 2012; Okullo et al., 2010; Pradhan et al., 2012; Rashid et al., 2008). In catalyzed biodiesel production both homogeneous and heterogeneous catalysts were widely experimented (Lam et al., 2010; Tan, Abdullah, & Nolasco-Hipolito, 2015). However, heterogeneous catalysis revealed many advantages over homogeneous catalysts for instance, improved reaction kinetics, catalyst reusability and stability etc. (Bravo-Suárez et al., 2013). Among all, divalent heterogeneous base metal oxide catalysts such as CaO, MgO, SrO and BaO etc. and their derivatives demonstrated notable catalytic activity in biodiesel production. It is also reported that the transesterification reaction kinetics increased substantially due to presence of acidic and basic active sites also the covalent nature of metal oxides along with better surface morphology (Chouhan & Sarma, 2011). Heterogeneous catalysts specially

fabricated on calcium in pure or mixed oxide forms revealed advantages over homogeneous ones using various feedstocks (Hwa et al., 2014; Joshi et al., 2015; Kawashima et al., 2008; Taufiq-Yap et al., 2011; Teo et al., 2014). On the other hand, synthesis of calcium catalysts using renewable sources such as waste shells, bones etc., gained researcher's attention phenomenally (Chouhan & Sarma, 2011).

The biodiesel standards EN 14214 and American Society for Testing and Materials (ASTM) primarily adopted to test the physicochemical fuel properties of biofuels (Barabás & Todorut, 2011; Knothe, 2006; Sajjadi et al., 2016; Silitonga et al., 2013). Though, many nations have had developed customized biodiesel standards in accordance with the environment and automobile engine standards in place. The biodiesel fueled diesel engines performance and exhaust gas emissions principally relies on the engines combustion cycle as well as physicochemical properties of the fuel. Though, studies on the applicability of biofuel properties and their impact on diesel engine performance and emissions characteristics are insignificant (Chattopadhyay & Sen, 2013; Ong et al., 2014; Rao, 2011; Rizwanul et al., 2014; Shojaeefard et al., 2012; Sivaramakrishnan & Ravikumar, 2013). Furthermore, these investigations include a multi objective and interdisciplinary approach both in design of experiments as well as results analysis. In addition, the research problems that comprises multiple objective functions involves simultaneous multi response optimization approaches. Hence, the design of experiments approaches that consist of mathematical modelling techniques such as response surface methodology (RSM) and desirability approach facilitates a scientific approach both in experimental design as well as results analysis. Moreover, these approaches would enable to analyse impact of input parameters on the out-put or response functions provide statistically (Khoobakht et al., 2016; Sivaramakrishnan & Ravikumar, 2013).

Across the world, mandates have begun to enforce on blending of biodiesel (BD) with petro diesel (PD) over B2 (BD 2% + PD 98%) to B10 (BD 10% + PD 90%) in a phased manner (De Oliveira & Coelho, 2016). Moreover, a few countries have implemented higher blends include Brazil 'B8' (BD 8% + PD 92%), the USA ($\leq$ B10 in some states), Argentina (B10), Colombia (B10) and Indonesia 'B20' (BD 20% + PD 80%) (Hanim, 2016). In Malaysia since 2011 government has initiated B1.3 (BD 1.3% + PD 98.7%) blending of biodiesel with petro diesel in the national central provinces include Negeri Sembilan and Selangor (Wahab, 2016). Then B2 blend in 2012, in southern provinces Johore and Malacca. Subsequently B5 (BD 5% + PD 95%) and B7 (BD 7% + PD 93%) blending mandates were effected nationwide in 2014 and 2015 respectively (Hanim, 2016). However, utilization and demand for biodiesel blends continue to be fairly less. Yet, the legislations and strategic policies reported on growing scenario of green economies due to production of biodiesel and bioenergy's using vegetable oil feedstocks. Besides, this phenomenon safeguards the sustainability by addressing various socioeconomic and environmental concerns (Fries & Cook, 2011).

1.2 Problem statement

In biodiesel production, both catalyst and feedstock are considered as decisive factors. Acid or base catalyzed biodiesel synthesis has been reported extensively in literature (Aransiola et al., 2014), but many studies conclude that an interaction of homogeneous acid catalysts (Meher et al., 2013) and free fatty acids (FFA) present in fatty acid methyl esters (FAME's) during transesterification leading to reduced catalyst availability for the reaction and thus homogeneous catalysts are not recommended (Gübitz et al., 1999).

The particle size of the catalyst is one of the most important factors for their catalytic activity (Thiele, 1939). When the particle is small the chemical reaction rate is increased since the diffusion forces would only be able to carry the product away from the surface of the catalyst particle. Many studies have confirmed that catalysts with a lower particle size and higher surface area accelerate reaction rates (Buasri 2013b; Teo et al., 2015) due to an increased number of molecules that have the minimum required energy for the reaction to occur. Several researchers have explored calcium based heterogeneous catalysts in pure (Choudhury et al., 2014a; Hwa et al., 2014; Kawashima et al., 2009; Tan, et al., 2015; Taufiq-Yap et al., 2011) or mixed oxides (Hwa et al., 2014; Joshi et al., 2015; Kawashima et al., 2008; Taufiq-Yap et al., 2011; Teo et al., 2014) for *Jatropha* biodiesel production and reported that heterogeneous CaO catalysts have advantages over homogeneous ones. These studies signifies that CaO can be a promising catalyst for biodiesel production since catalysts with lower particle sizes and a higher surface area contributes to enhancing the transesterification reaction rate. Very scant work, however, has been devoted to the synthesis of CaO as a nano-catalyst that focuses on reducing the particle size and increasing the surface area for biodiesel production (Goyal et al., 2013; Kumar et al., 2007; Mansourpoor, 2012; Noshadi et al., 2012; Pradhan et al., 2012; Vicente et al., 1998; Yee et al., 2011) especially from the largely available sustainable waste resources such as seashells.

Jatropha curcas (Linnaeus) is a fast growing plant in marginal and non-agriculture fields and is fully adaptable to tropical and subtropical climates (Koh & Mohd, 2011) and, moreover, the oil content of the *Jatropha* seed is about 27%-40% which has been reported as one of the best suited feedstocks for biodiesel production (Achten et al., 2008; Gübitz et al., 1999; Koh & Mohd, 2011). Several state-of-the-art research has been experimented on diesel engines fueled with biodiesels derived from dissimilar ranges of feedstocks (Melo-Espinosa

et al., 2015). The fuel properties that include higher cetane and oxygen, lower sulphur contents reveals biodegradable, cleaner combustion, and relatively less exhaust emission profiles (Altun et al., 2010; Chauhan et al., 2012). The biofuel fueled diesel engine performance investigations for both short and long durations indicates their potential. However, a few critical problems were reported for the long duration engine endurance experiments (Shehata & Razek, 2011). According to investigations by Chuah et al., (2015), Gerhard Knothe et al., (2003), Saraf & Thomas, (2007) and Borhanipour et al., (2014) fatty acid composition (FAC) of a biodiesel feed stock like long chain saturated factor (LCSF), degree of unsaturation (DU), unreacted glycerides and non-fatty acid fractions significantly influences their physicochemical properties. A few scientific investigations have analyzed the relevance of biofuel properties and their impact on diesel engine performance, efficiency and emissions (Chattopadhyay & Sen, 2013; Ong et al., 2014; Rao, 2011; Rizwanul et al., 2014; Shojaeefard et al., 2012; Sivaramakrishnan & Ravikumar, 2013). Further, the design of experimental protocols would offers a scientific basis for analyzing relation between various operating parameters and attain optimal results. Therefore mathematical modelling and statistical analysis embraced optimization approaches provides a comprehensive study basis for engine performance and emission analysis together with fuel properties.

As an alternative diesel engine fuel biodiesel has both advantages and challenges with respect to their production, physicochemical characteristics, storage, logistics, usage, engine compatibility, and emissions (Atabani et al., 2012; Balat & Balat, 2010; Hassan & Kalam, 2013; Janaun & Ellis, 2010; Jena et al., 2010; Gerhard Knothe, 2010; Krishna Reddy et al., 2010; Saxena et al., 2013; Williams, 2012; Yusuf et al., 2011). Summary of advantages and challenges of biodiesel fuel are listed as below.

1.2.1 Advantages and challenges of biodiesel

Biodiesel is sustainable, biodegradable, renewable, eco-friendly, sulfur free, non-igneous, easy to transport and hence ideal for use, hence the biodiesel can be used as an alternative energy fuel aids in climatic changes. On lifecycle basis biodiesel contributes in lessening of 78% net CO₂ exhaust emissions and free from soot. Superior lubricity of biodiesel improves diesel engine's efficiency and minimizes wear and tear of dynamic parts in fuel injector and pump units. The conventional diesel engines can be fueled with biodiesel blends up to B20 without any modifications. Nevertheless a minor engine alterations would facilitate usage of higher blends too. Biodiesel fuels aids in reducing ambient air toxicity through clean fuel combustion. Additionally, these fuels minimizes particulate emission contents which are primarily cause's hazardous health risks such as cancer.

Biodiesels shows superior combustion characteristics owing to 10–11% of oxygen content and cetane number (60-65 based on feedstock oil) compared to petrol diesel (53) as a result ignition delays are minimized. Also biodiesels possesses high flash point values (>100-170°C) relative to petro diesel (60-80°C) which ensures higher safety standards for utilization, transportation and distribution. Biodiesel production using waste oils and lards would reduce their effects on environment and sustainability. The ease in production of biodiesel fuels locally/ regionally minimizes heavy costs involved in non-renewable fossil crude oil extraction, refining and logistics, besides strengthens economy by saving tax and overhead tariffs. All these significant benefits contributes in sustainable rural development by employment growth as well as restoration of degraded landscapes.

Biodiesel volatility is low and viscosity is comparatively 11-18 times higher than petro diesel which lead to incomplete fuel combustion therefore require higher fuel injector

pressure. Oxidation stability of biodiesel is lesser than that of diesel. During combustion of biodiesel fuel in presence of air it can be oxidized into fatty acids then causes corrosion over fuel tank, connecting pipe and injectors. Similarly the corrosion evokes seal failures, blockage of fuel system and filter clogging. The combustion of biodiesel in diesel engine causes polymerization and redundant carbon deposition which effects flow channels also contaminates fuel.

In addition to above, a few complications that include diesel engine compatibility, high operating costs and engine wear, piston ring sticking, injector cocking, poor engine performance, and filter plugging constrained the usage of biodiesel in IC engines. Since the energy content of biodiesel is 12% lesser than petro diesel, causes about 2% - 10% increase in biofuel consumption. Owing to superior characteristics include higher oxygen content, cloud point and pour point in biodiesel spreads up the fuel injection timing causes early start of fuel combustion, as a result biodiesel produces about 10-14% of higher NO_x than diesel. Biodiesel production via transesterification involves use of expensive catalysts, which lead to increase gross fuel cost. Further transesterification of triglycerides to biodiesel require huge amount of water for washing, produces environment hazardous wastes. Large scale production of biodiesel for commercial usage by means of edible oils may disrupt human food cycle leading to socio-economic problems.

1.3 Scope of research

Current research aims at synthesis of heterogeneous nano CaO catalyst heterogeneous nano CaO catalyst besides, production of biodiesel utilizing a non-edible feedstock i.e. crude *Jatropha* oil. The nano CaO catalyst is proposed to synthesize from a tropical biodiversity originated new local seashell species *Polymesoda erosa* (*P. erosa*) following a laboratory

scale protocol ‘calcination–hydration–dehydration’. The newly synthesized nano CaO catalyst would be characterized by evaluating their morphological features. The nano CaO catalytic activity would be investigated in a two-step transesterification of triglycerides from CJO as a biodiesel. Besides nano CaO leaching, catalyst reusability and stability will be studied. To investigate the influence of Jatropha biodiesel FAC on their physicochemical fuel properties, the CJO originated from east and west Malaysian geographic zones was proposed to utilize to produce the JB_{EM} and JB_{WM}. The resulting fuel properties of JB – PD blends were then investigated to compare with EN 14214 biodiesel standards. Further the JB blends fueled diesel engine performance and exhaust emissions were proposed to predict and compare the results with published experimental results from engine research group, Department of Mechanical Engineering, University Malaya (UM), Malaysia.

1.4 Research hypothesis

Present research work was carried out in accordance with the following specific research hypothesis

- i. Natural or renewable indigenous materials such as seashells are highly potential sources for synthesis of solid heterogeneous nano catalysts.
- ii. The catalytic activity of a solid heterogeneous catalyst primarily influenced by its particle size, pore volume, pore diameter and average surface areas. Hence, synthesis of a catalyst with smaller particle size, highly pores would significantly improve its catalytic activity.
- iii. The fatty acid composition of the feedstock utilized to produce biodiesel influences the fuel properties of a biofuel.

- iv. The engine performance and exhaust gas emission profiles can be determined by fractions of biodiesel blends and engine operating parameters. Therefore, modelling of diesel engine performance and emissions would provide scope for optimization of biodiesel blends as well as primary engine operating parameters.

1.5 Objectives

This research focuses on the following objectives

- i. To synthesize heterogeneous nano CaO catalyst from tropical biodiversity indigenous aquatic seashells.
- ii. To produce Jatropha biodiesel from crude Jatropha oil via optimization of transesterification reaction parameters using newly synthesized nano CaO catalyst. Also, to analyze the stability, reusability and leaching characteristics of newly synthesized nano CaO catalyst in Jatropha biodiesel production.
- iii. To study the impact of Jatropha feedstock fatty acid composition on physicochemical properties of Jatropha biodiesel and petro diesel blends.
- iv. To optimize the biodiesel blends usage and diesel engine operating parameters by predicting the engine's performance and exhaust gas emissions using mathematical modelling techniques.

1.6 Organization of the thesis

This thesis is structured in five correlated chapters in following order.

Chapter 1 provides introduction to the thesis, objectives of research and necessary scientific basis and justification.

Chapter 2 discusses state of the art literature review in accordance with present research work. The literature review include feedstocks for biodiesel, chemistry of biodiesel production, heterogeneous catalyzed transesterification, synthesis and characterization of CaO using renewable wastes, correlation between FAC of a feedstock and fuel properties, transesterification reaction kinetics besides, biodiesel blends fueled diesel engine performance and exhaust emissions are comprehensively discussed.

Chapter 3 describes catalyst and biodiesel synthesis as well as characterization methodology as well as the experimental protocols followed in current research. Also, presented on laboratory procedure for biodiesel blends preparation, optimization of biodiesel blends and engine operating parameters and to predict the diesel engine performance and exhaust gas emissions using mathematical modelling techniques

Chapter 4 interprets the as obtained results from the laboratory experiments and predictions of mathematical modelling. The research results are discussed together with experimental and predicted validations and specific scientific justifications.

Chapter 5 concludes the research and presents summary of research findings.

CHAPTER 2

LITERATURE REVIEW

2.1 Background

Ever since the discovery of petroleum by Colonel Drake, its usage in every sphere of human development in the world society is remarkable and hence inevitable dependency on supply of fossil fuels for growing needs. According to the global crude oil production estimations by M. King Hubbert, a U.S. geologist in 1956, as shown in Figure 2.1, the peak of crude oil production is about year 2000 (Hubbert, 1956). These predictions were ascertained with fossil fuel production data (Hook & Tang, 2013) in addition this phenomenon significantly indicates finite availability of fossil reserves and search for sustainable alternative energy sources (De Oliveira & Coelho, 2016).

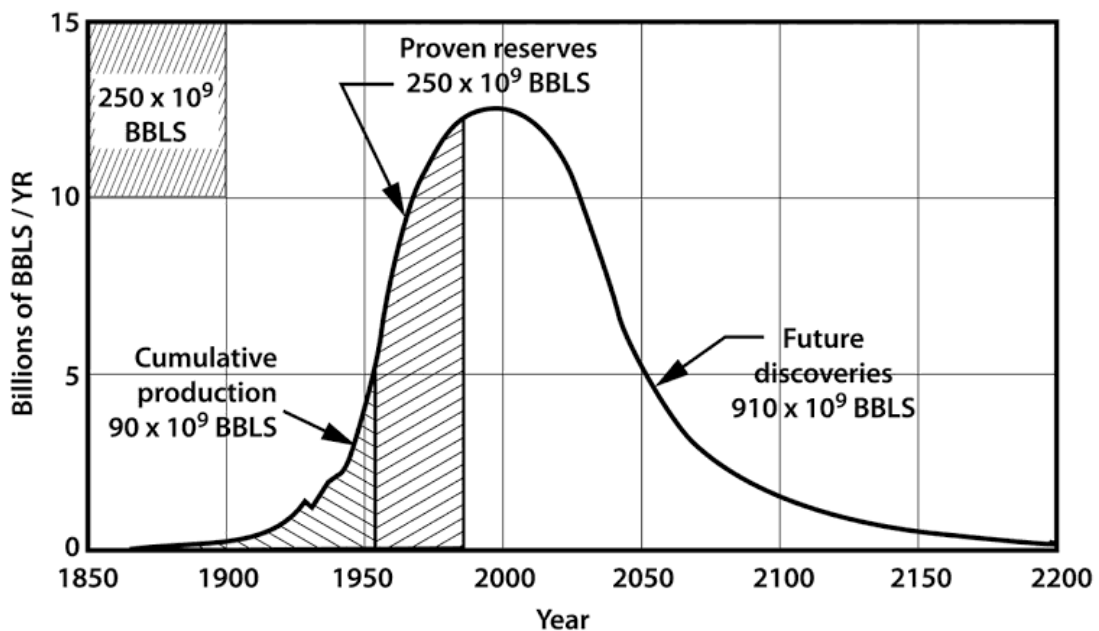


Figure 2.1: Hubbert's prediction curve for global crude-oil production over 1850-2200 (Hubbert, 1956).

According to the U.S. Energy Information Administration (EIA) report ‘International Energy Outlook 2016’ the total world’s energy consumption increases by 48% i.e. 815 quadrillion Btu, over the period 2012-2040, as indicated in Figure 2.2. However, the rise in total energy use among the Organization for Economic Cooperation and Development (OECD) group countries is 18% whereas the non-OECD group countries is 71%. Consequently, carbon dioxide (CO₂) emissions across the world are projected an increase of 34% (43.2 billion metric tons) by 2040 (EIA, 2016).

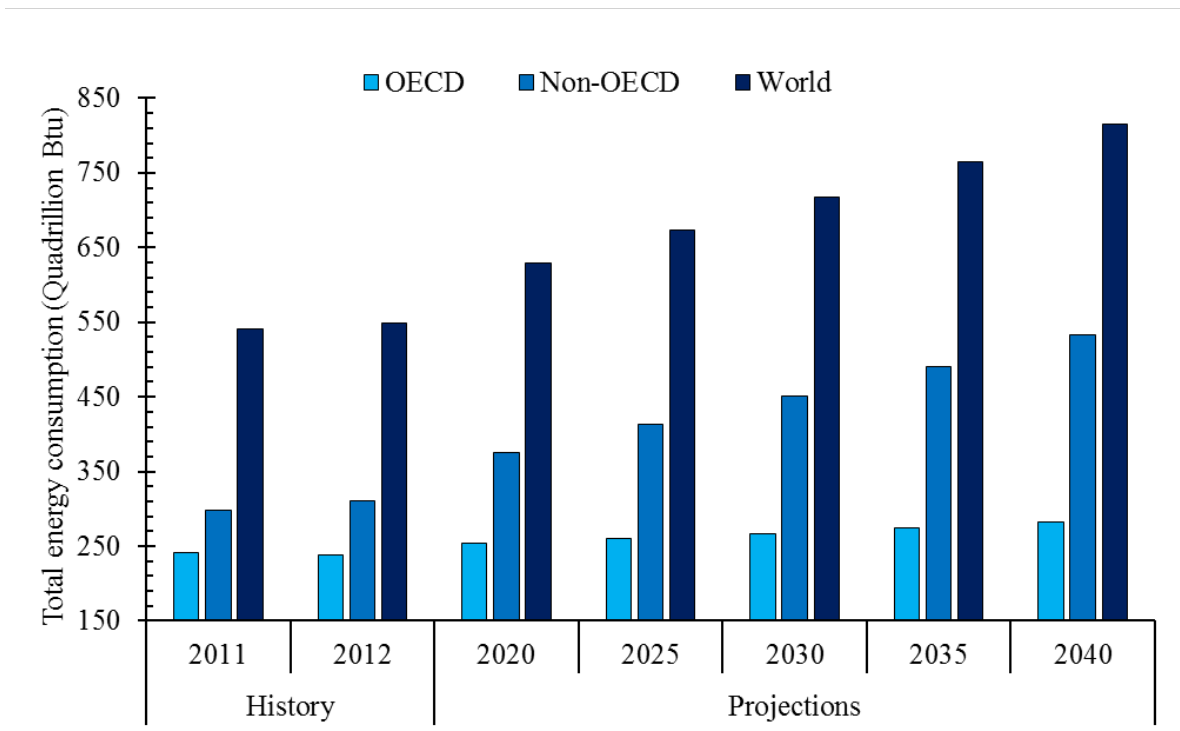


Figure 2.2: World total energy consumption history and projections (quadrillion Btu) over 2012-2040 (EIA, 2016).

Referring to EIA’s global energy consumption status and projections as illustrated in Figure 2.3. In 2040 the amount of fossil fuels that include liquid, natural gas and coal are up to 78% of global use. This analytical estimation designates fossil fuels continue to hold major

share of world's energy source. However, the Clean Power Plan (CPP) in U.S. would result in reducing the coal consumption and phenomenally increases renewable energy usage share.

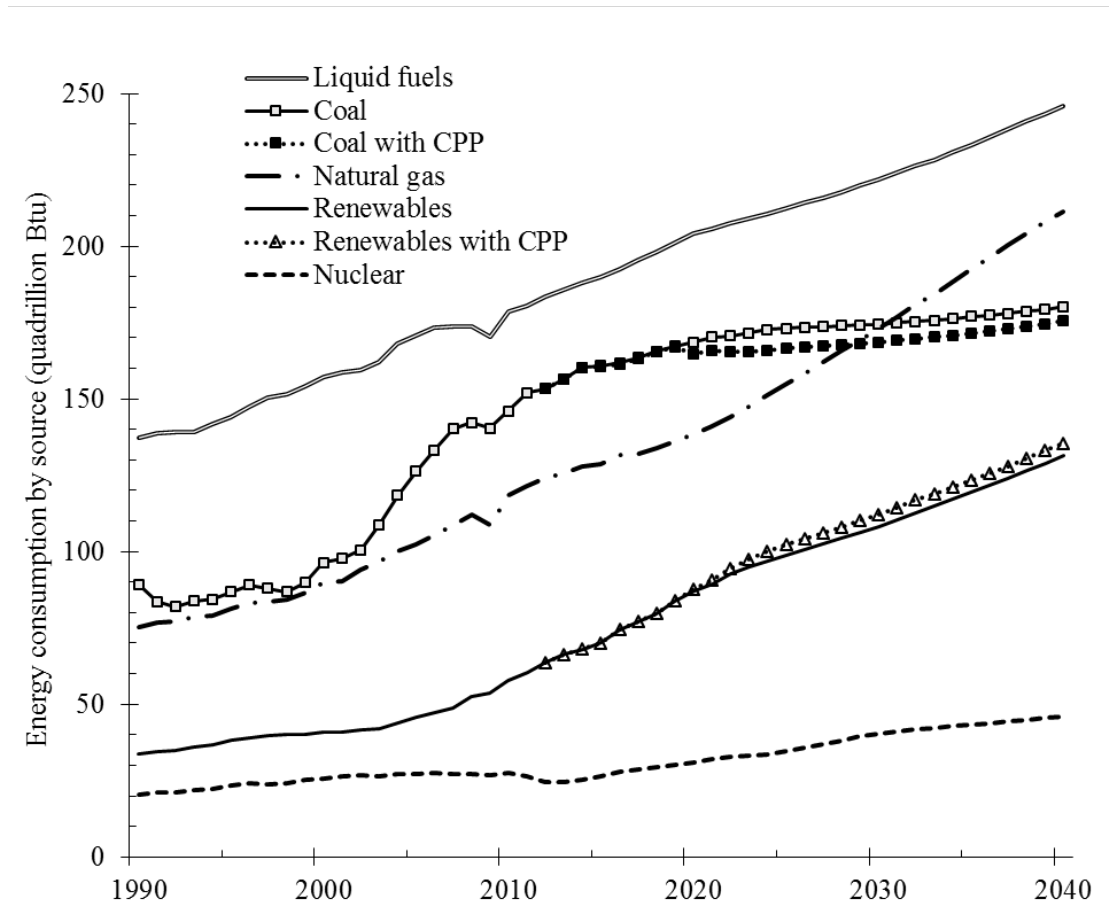


Figure 2.3: Global energy consumption (quadrillion Btu): Present status and projections by source, 1990-2040 (EIA, 2016).

In recent years, worldwide, organized efforts are originated to meet energy demands through policy frameworks, strategies and research initiatives utilizing renewable energy as a sustainable alternative and thereby bioenergy's share increased in most countries (Sven et al., 2015). During last half of 20th century human-contributions to the climate change problem was accepted globally. As a consequence, the United Nations Framework Convention on Climate Change (UNFCCC) was assumed during Rio Earth summit in 1992, and then Kyoto Protocol in 2005 (Erbach, 2016). The Paris agreement has built a constructive effort and spirit

on climate change along with global warming policies. As a result, among the 197 Parties to 'Marrakech climate change convention 2016', held during November 2016, 122 Parties have ratified to implement the strategic proposals of the Paris Agreement (UNFCCC, 2016). In this multilateral pact, the ratified party countries would embedded policy efforts to holding the climate temperature below 2°C as a long term goal to achieve (Bodle et al., 2016).

The biodiesel production has been evolved to confront growing global environmental concerns besides fossil fuel reserves depletion and market price fluctuations (De Oliveira & Coelho, 2016). According to strategic analytics and central assumptions of department of energy and climate change, U.K. (DECC), use of vegetable oil based feedstocks for biodiesel production would be economical by the year 2030. Further, these efforts would contribute in attaining the decarbonization targets of 2050 (DECC, 2012; Fries & Cook, 2011).

2.2 Biodiesel worldwide

The gradual depletion of the world's petroleum reserves and impact of fuel combustion exhaust emissions on the environment and human health, has therefore led to the search for substantial, environmentally friendly alternative energy sources such as biodiesel (Götz et al., 2014; A. F. Lee et al., 2014; Lippke et al., 2011; Westphal et al., 2013). The renewable energy sector is reaching a cost-competitive zone with traditional fossil fuels in the worlds markets. Notably, regardless of major fluctuations and decline in supply and market prices of fossil fuel, renewable energy production capacities continuing to supporting the global energy demands (Balogh et al., 2015; Maniatopoulos et al., 2015). Globally, transportation has raised as a primary liquid fuel consumption sector about 28% and raising drastically, among which the road transport estimated for 67% of demand. However, in 2015, 4% of

transport fuel needs are shared by renewable fuels (100% ethanol or biodiesel, blends, or gaseous biofuels) (REN21, 2016).

According to the 'Renewables 2016 Global Status Report' the U.S., Brazil, Germany, France and Argentina are the major biodiesel yielding countries in 2015 (REN21, 2016). Figure 2.4 indicates top 15 biodiesel producing countries in the world during 2015. In the North American region, during 2015 biodiesel production marginally decreased as compared to 2014. While, biodiesel production in the Latin America region, both Argentina and Colombia reported a slight fall due to a constrained world's fuel market. Conversely, Brazil has risen to 2nd major biodiesel producer in the world. Among the Asian countries Indonesia, Thailand, Malaysia, China and India produce 1.5, 1.2, 0.7, 0.4, and 0.1 billion liters of biodiesel respectively. The reasons for higher biodiesel production in countries like Indonesia and Thailand refer to, apart from policies and geopolitical reasons, availability and utilization of multiple feedstocks for biodiesel production as compared to Malaysia (Nigam & Singh, 2011). In 2014, the USA (4.7 billion liters) and Germany (3.4 billion liters) were the biggest global biodiesel producers. Whereas in 2010 Argentina marked above 50% of world's biodiesel exports, while 85 million gallons exports by the USA.

2.3 Biodiesel prospects in Malaysia

Malaysia is one of the pioneering biodiesel producers in the Asia Pacific region, other non-OECD Asia as well as in the world. Referring to 'Renewables 2016 Global Status Report' in 2015 Malaysia ranked 7th largest biodiesel producer in the world with an average produce of 0.7 billion liters (REN21, 2016).

In March 2006, the Malaysia's 'National Biofuel Policy' was introduced with a global view of developing sustainable and environment friendly alternative energy sources subsequently 'Biofuel Industry Act' was ratified in 2007 (Wahab, 2016). These enabled the Malaysian government to emphasis on development of sustainable technologies for biofuel production and to ensure their utilization in industries and transportation sectors as well as global export (Mofijur et al., 2013).

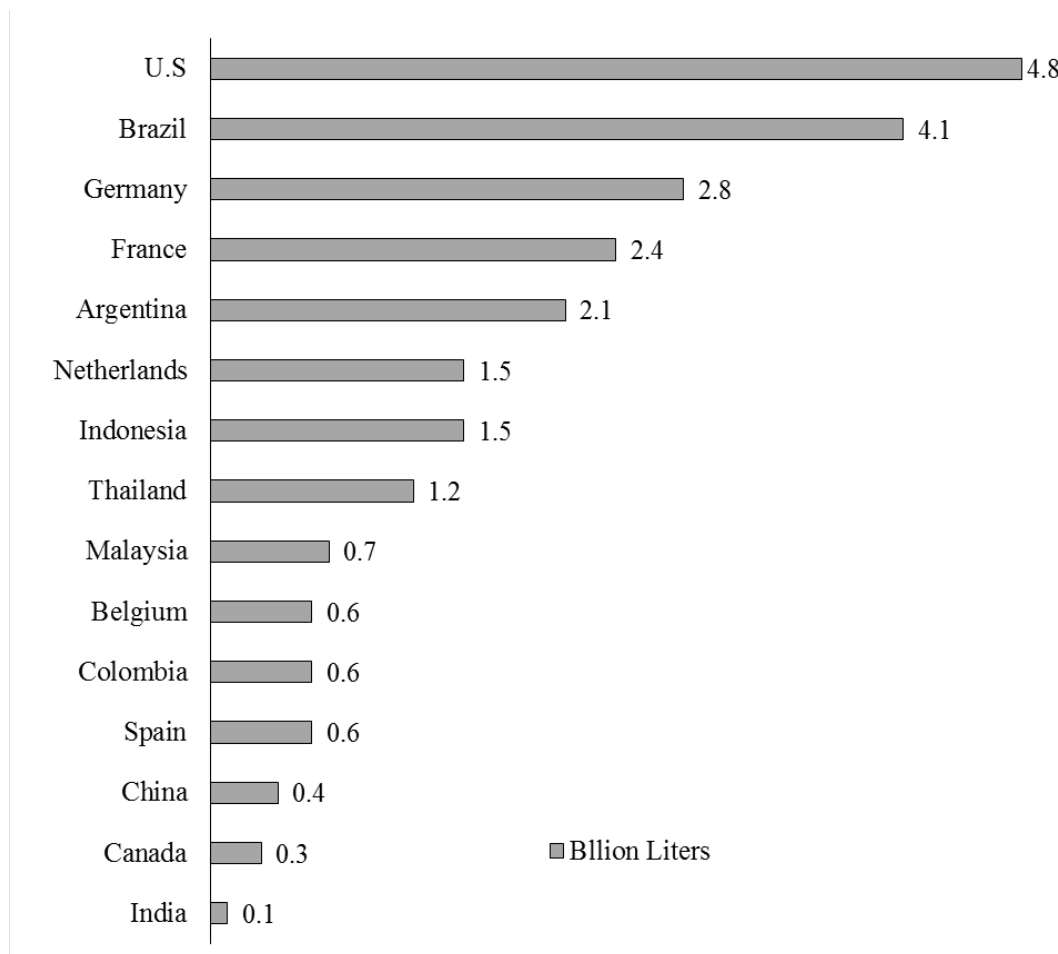


Figure 2.4: Global top 15 countries in biodiesel production during 2015 (REN21, 2016).

Malaysia is one of the largest producer and exporter of palm oil in the world. The Malaysian palm oil board (MPOB) increasingly promoting oil palm plantation, palm oil

oriented technology and industry innovations to support national economy at large. Hence, it is obvious the crude palm oil is a primary feedstock for biodiesel production (Balat & Balat, 2010). However, MPOB has devoted constructive efforts to develop alternative, sustainable and substantial vegetable oil feedstocks such as *Jatropha* plantation (Mofijur et al., 2013).

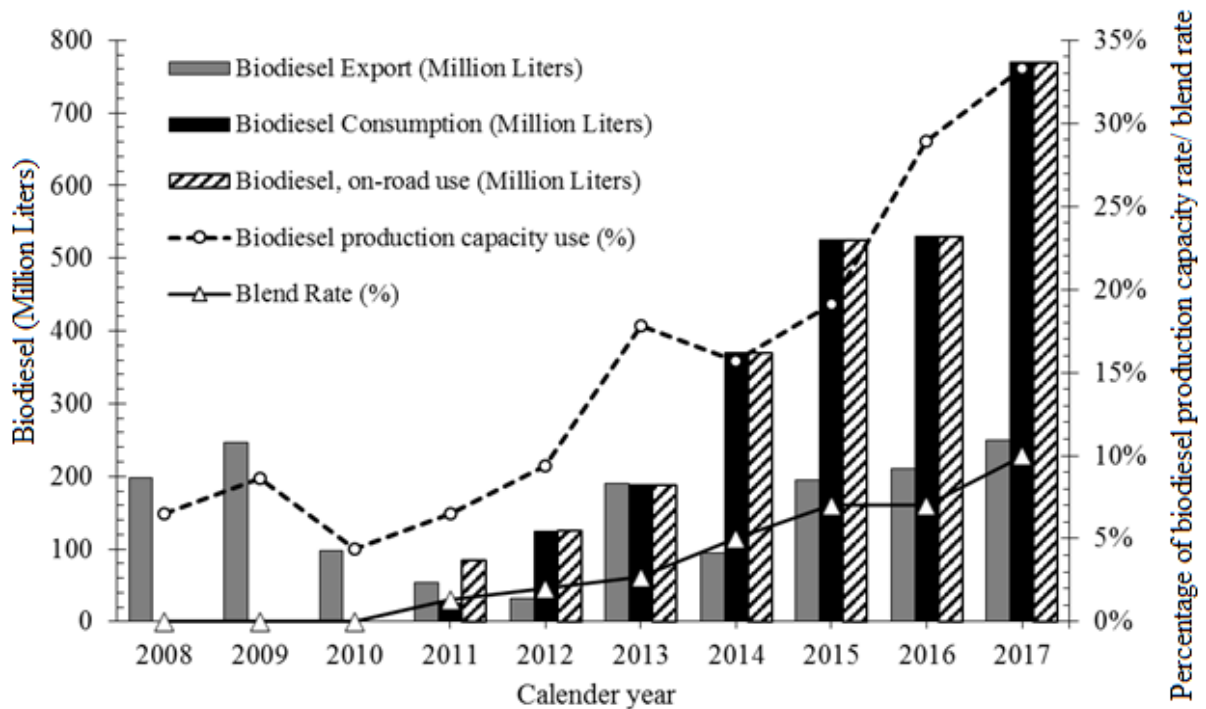


Figure 2.5: Biodiesel export, consumption, on-road use, production capacity and blending rate in Malaysia during 2008-2017 (Wahab, 2016).

The Ministry of Plantation Industries and Commodities of Malaysia is the primary enforcing and stakeholder in fulfilling the biodiesel blend mandates in position. Figure 2.5 summarizes biodiesel export, consumption, on-road use, production capacity and blending rate in Malaysia during 2008-2017. Since 2011 government of Malaysia has initiated B1.3 blending of biodiesel with petro diesel in the national central provinces include Negeri Sembilan and Selangor (Wahab, 2016). Then B2 blend was implemented in 2012, in southern

provinces of Johore and Malacca. Subsequently B5 and B7 blending mandates were effected nationwide in 2014 and 2015 respectively (Hanim, 2016).

2.4 Feedstocks for biodiesel

The biofuels are principally categorized as primary and secondary groups according to the feedstocks utilized for their production and application (Nigam & Singh, 2011). Figure 2.6 presents broad classification of biofuels. The unprocessed feedstocks include wood chips, crop residues, pellets and fire wood are used for production of primary biofuels. These biofuels are mainly intended for cooking, heating or production of electricity.

The green fuels include ethanol, dimethyl ether, biodiesel etc. are called secondary biofuels which are produced using various biomass. The secondary fuels are basically utilized for various domestic and industrial applications. According to the type of feedstock and production technology adopted, these biofuels are further classified into 1st, 2nd and 3rd generations (Figure 2.6). The 1st generation fuels are derived from sugars (bioethanol), vegetable seed oils (biodiesel). While the 2nd generation fuels utilizes lignocellulosic based biomass for bioethanol, dimethyl ether or bio-methanol. The 3rd generation biofuels essentially make use of algae or sea weeds for biodiesel, bioethanol or hydrogen (Nigam & Singh, 2011).

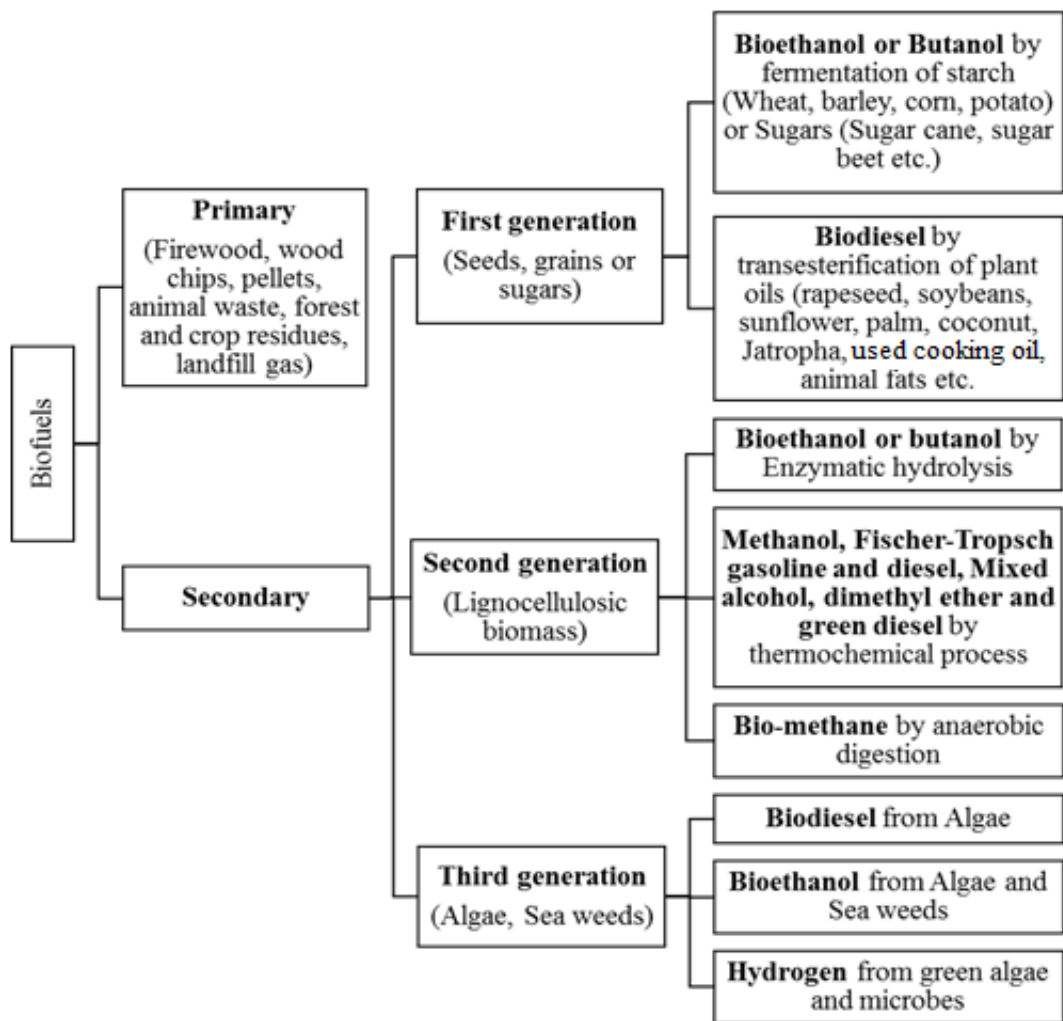


Figure 2.6: Classification of biofuels (Nigam & Singh, 2011).

Biodiesels are largely produced utilizing vegetable oils (edible and non-edible), used or recycled cooking oils and animal fats in general (Atabani et al., 2012). Many state-of the art published literature indicated use of various feedstocks for biodiesel production (Atabani et al., 2013; Banković-Ilić et al., 2012; Bhuiya et al., 2014). Table 2.1 summarizes major feedstocks used for biodiesel production across the world. Among which many countries are producing biodiesels from edible oil feedstock such as Coconut (Indonesia, Thailand, Philippines, Brazil), Palm oil (Thailand, Malaysia, Singapore, Indonesia, Brazil), Soybean (India, Argentina, USA, Brazil, Canada) and Sunflower (Italy, France, Spain, India) etc.

However, use of edible vegetable oils would impact the human food cycle besides concern market prices and economy. Hence, many researchers, policy makers as well as non-governmental organizations emphasize on use of non-edible feedstocks or other alternatives for biofuels (Lam et al., 2009; Mofijur et al., 2013).

The non-edible oils, subsequently, have attained the researcher's and government's attention as an alternative potential feedstock. The Non-edible oil feedstocks commonly used for biodiesel production with botanical and regional names and percentage of oil content in seed and kernel are shown in Table 2.2 (Banković-Ilić et al., 2012). From the tabulation values it can be observed that Yellow oleander kernel contains 67 wt. %, both rubber tree, *Jatropha curcas* can yield a maximum oil content about 40–60 wt. %, while the Castor 45–50 wt. %, Mahua 50 wt. %, and the sea mango seed 54 wt. % oil. However, the percentage of oil content in a seed or kernel varies according to the breed, geographical region and many more conditions.

Table 2.1: Major feedstocks used for biodiesel production across the world.

Feedstock	Country(s) used for biodiesel production
Animal fat	Mexico, Canada, Ireland
Castor	Brazil
Coconut	Indonesia, Thailand, Philippines, Brazil
Cottonseed	Greece
Flax	Canada
Frying oil	Ireland
Jatropha	Philippines, India, China, Indonesia, Thailand
Linseed oil	Spain
Mustard	Canada
Palm oil	Thailand, Malaysia, Singapore, Indonesia, Brazil
Peanut	USA, India
Karanja	India
Rapeseed	Germany, Sweden, China, Canada, Italy, France, UK, India
Soybean	India, Argentina, USA, Brazil, Canada
Sunflower	Italy, France, Spain, India
Tallow	New Zealand, Canada
Waste cooking oil	Japan, UK, New Zealand, China, Mexico, USA
Yellow grease	Canada

Source: (Nigam & Singh, 2011)

Table 2.2: Percentage oil content in non-edible feedstocks for biodiesel production.

Non-edible oil feedstock		Oil content	
Botanical name	Regional name	Seed (wt. %)	Kernel (wt. %)
<i>Argemone mexicana</i>	Mexican prickly poppy	22–36	
<i>Azadirachta indica</i>	Neem	20–30	25–45
<i>Cerbera odollam</i>	Sea mango	54	6.4
<i>Gossypium sp.</i>	Cotton	17–25	
<i>Hevea brasiliensis</i>	Rubber tree	40–60	40–50
<i>Jatropha curcas</i>	Jatropha, ratanjyot	20–60	40–60
<i>Linum usitatissimum</i>	Linseed	35–45	
<i>Madhuca indica</i>	Mahua	35–50	50
<i>Melia azedarach</i>	Persian lilac	10	
<i>Moringa oleifera</i>	Moringa	33–41	2.9
<i>Nicotiana tabaccum</i>	Tobacco	36–41	17
<i>Pongamia pinnata</i>	Karanja, pungam	25–50	30–50
<i>Ricinus communis</i>	Castor	45–50	
<i>Schleichera triguga</i>	Kusum	10.65	
<i>Simmondsia chinensis</i>	Jojoba	45–55	
<i>Thevetia peruviana</i>	Yellow oleander	8.41	67
<i>Thlaspi arvense</i>	Field pennycress	20–36	
<i>Euphorbia lathyris</i>		48	
<i>Sapium sebiferum</i>		12–29	
<i>Pistacia chinensis</i>		30	
<i>Datura stramonium</i>		10.3–23.2	

Source: (Banković-Ilić et al., 2012)

Table 2.3: Advantages of Non-edible oil produced biodiesels.

Nonedible Feedstock	Biodiesel advantages
Jatropha	Greater diffusion combustion, Lesser emissions of particulate matter (PM)
Karanja	Lesser NO _x exhaust emissions
Mahua	Lesser exhaust emissions (NO _x , hydrocarbon (HC), carbon monoxide (CO) and smoke)
Neem	Lesser exhaust emissions (NO _x , CO and smoke)
Rubber	Lesser smoke

Source: (Banković-Ilić et al., 2012)

The use of non-edible oil feedstock for biodiesel not only backings the human-food cycle but also greatly provides numerous advantages with produced biodiesels such as lesser exhaust emissions like NO_x, HC, CO, PM and smoke. Table 2.3 presents advantages of various non-edible oil produced biodiesel fuels used in diesel engines (Banković-Ilić et al., 2012).

2.5 Characteristics of biodiesel

The biodiesel's physicochemical properties are determined by many factors such as the amount of feedstock FAC, fatty acid chain length, and degree of saturation, branching, and biodiesel production methodologies as well as reaction operating conditions at large. However, quality of the biodiesel may vary as a result of residual pollutants from either unreacted glycerides in the feedstock, non-fatty acid fraction, or side reactions during transesterification (Saraf & Thomas, 2007). For instance, according to Knothe et al. (2003)

higher fatty acid chain length aids in producing a higher cetane number biodiesel and thereby less NO_x emissions (Gerhard Knothe et al., 2003). Different international standards were in place for ascertaining use of biodiesel as a diesel fuel. Table 2.4 interprets ASTM D6751 and EN 14214 biodiesel standard limits and testing specifications. While the fuel properties of biodiesel's produced from various feedstocks were summarized in Table 2.5.

The biodiesel feedstocks contain different proportions of saturated fatty acids (SFAs) and unsaturated fatty acids (USFAs). SFA fractions contains only 'C–C' single bonds which are chemically less reactive and hence more stable. USFA fractions which contain only one *cis* configured 'C=C', double bond are termed as monounsaturated fatty acids (MUFAs) and the USFAs with two or more C=C', double bonds in *cis* configuration are termed as polyunsaturated fatty acids (PUFAs). Most vegetable oils contains SFAs fractions include palmitic acid (C16:0) and stearic acid (C18:0); MUFAs of palmitoleic acid (C16:1) and oleic acid (C18:1); and PUFAs fractions of acid (C18:2) and linolenic acid (C18:3) (Wang et al., 2011). A few important properties of various pure fatty acids are shown in Table 2.6.

According to Wang et al. (2011) the feedstocks which encompass higher MUFA fractions, lower SFAs and controlled amount of PUFAs contributes to good biodiesel fuel properties (Wang et al., 2011). Besides, a particular vegetable oil originated from diverse geographic regions reveals distinct proportions of SAFs, MUFAs and PUFAs and hence variations in their fuel properties (Fernandes et al., 2015; Saraf & Thomas, 2007; Silitonga et al., 2013).

Chuah et al. (2015) comprehensively studied seven different non-edible vegetable oils fatty acid structural influence on biodiesel properties which include iodine value (IV) cetane number (CN), oxidation stability (OS) and cold filter plugging point (CFPP) (Chuah

et al., 2015). The biodiesels CFPP was analyzed correlating their fatty acid, long chain saturated factor (LCSF) whereas IV, CN and OS properties were investigated through correlating with fatty acid degree of unsaturated (DU). Borhanipour et al. (2014) studied impact of Jatropha and Palm biodiesels fatty acid DU on their physical properties such as acid value, density, viscosity, iodine value, calorific value, cloud point, flash point, pour point and water content (Borhanipour et al., 2014). They have concluded that, higher DU would significantly rises biodiesel's viscosity whereas higher fatty acid saturation increases density of the fuel. The OS affects and blending of biodiesel with petro diesels on fuel properties were studied.

Chattopadhyay & Sen (2013) investigated cottonseed biofuel properties that includes density, kinematic viscosity at 40°C, acid value, flash point, calorific value (CV) together with their blends B10 (10% BD + 90% PD) and B20 (20% BD + 80% PD) (Chattopadhyay & Sen, 2013). The biodiesel was produced by enzymatic transesterification green process. Comparable diesel engine efficiency and significant reduction exhaust emissions CO₂, HC, CO, smoke and a marginal rise in NO_x level were noted. However, cottonseed oil FAC was not accounted for investigating the biofuel properties and their intricate impacts on engine performance and emissions. Li-bing et al. (2012) evaluated biodiesel fuel properties, produced from ten woody species, mainly CN according to China biodiesel standard (GB/T 20828-2007) IV, following European standard EN 14214 and OS (Li-bing et al., 2012). Among the ten woody oils studied, high quality biodiesel was resulted from the feedstocks which contain high MUFAs.

Table 2.4: Biodiesel Properties and specification of the ASTM D6751 and EN 14214 standards.

Property	Unit	ASTM D6751		EN 14214	
		Limit(s)	Test	Limit(s)	Test
Density at 15°C	kg/m ³	–	–	860–900	EN ISO 3675/ 12185
Calorific value	MJ/kg	–	–	35 min	EN 14214
Ester content	% (m/m)	–	–	96.5 min	EN 14103
Kinematic viscosity at 40°C	mm ² /s	1.9–6.0	D445	3.5–5.0	EN ISO 3104/ 3105
Acid value	mg KOH/g	0.50 max	D664	0.5 max	EN 14104
Carbon residue (Rams bottom)	% mass	0.1	D4530	–	–
Cetane number	–	47 min	D613	51 min	EN ISO 5165
Copper strip corrosion	–	No. 3 max	D130	Class 1	EN ISO 2160
Flash point	°C	130.0 min	D93	101.0 min	EN ISO 3679
Methanol content	% (m/m)	–	–	0.2 max	EN 14110
Oxidation stability at 110°C	H	–	–	6 min	EN 14112
Group I Metals (Na + K)	mg/kg	–	–	5 max	EN 14108/ 14109
Group II Metal (Ca+Mg)	mg/kg	–	–	5 max	EN 14538
Monoglyceride content	% (m/m)	–	–	0.8 max	EN 14105
Total glycerol	% (m/m)	0.240 max	D6584	0.25 max	EN 14105
Triglyceride content	% (m/m)	–	–	0.2 max	EN 14105

Table 2.4 continued

Carbon residue	% (m/m)			0.30	EN ISO 10370
Water and sediment	%vol.	0.050 max	D2709	–	–
Water content	mg/kg	–	–	500 max	EN ISO 12937
Cloud point	°C	Report customer	D2500	–	Country specific
Pour point	°C	-15 to 16	D 97		
Diglyceride content	% (m/m)	–	–	0.2 max	EN 14112
Distillation T90 AET	°C	360 max	D1160	–	–
Free glycerol	% (m/m)	0.020 max	D6584		EN 14105/ 14106
Iodine value	–	–	–	120 max	EN 14111
Phosphorous content	% (m/m)	0.001 max	D4951	0.01 max	EN 14107
Polyunsaturated (P4 double bonds) methyl esters	% (m/m)	–	–	1 max	ISO 3987
Sulfur (S 15 Grade)	ppm	0.0015 max	D5453	–	–
Sulfur (S 500 Grade)	ppm	0.05 max	D5453	–	–
Sulfur content	mg/kg	–	–	10 max	EN ISO 20846/ 20884
Sulphated ash content	% (m/m)	0.020 max	D874	–	–
Total contamination	mg/kg	–	–	24 max	EN 12662

Data adapted from (Barabás & Todorut, 2011; Knothe, 2006; Sajjadi et al., 2016; Silitonga et al., 2013)

Table 2.5: Physicochemical properties of biodiesel synthesized from different feedstocks.

Fuel property	Coconut	Coffee	Corn	Jatropha	Karanja	Micro algal	Neem	Palm	Soybean	Sunflower
Acid value (mg KOH/g)	0.106	0.076	0.283	0.4	0.42	0.022	0.649	0.24	0.266	0.027
Ash content % (m/m)	–	–	–	0.012	0.001	–	–	–	–	–
Calorific value (MJ/kg)	–	–	–	39.23	43.42	–	39.81	–	39.76	
CCR 100% (mass %)	0.01	0.004	0.02	0.025	0.781	0.007	0.105	<0.01	0.038	0.035
Cetane number	–	–	–	51.6	55	–	–	54.6	37.9	49
Cloud point (°C)	0	0.2	–2.8	2.7	7	–5.2	9	16	0.9	3.4
Cold filter plugging point (°C)	–4	–4	–3	0	–	–7	11	12	–4	–3
Density 15 °C (kg/m ³)	807.3	–	–	879.5	931	–	868	864.42*	913.8	880
Diglyceride % (m/m)	0.04	0.175	0.08	0.104	–	0.078	0.474	–	0.088	0.092
Flash point (°C)	114.8	>160	>160	135	95	>160	76	135	254	>160
Free glycerin % (m/m)	0.025	0.001	0.001	0.006	0.015	0.009	0	0.01	0.012	0.007
Iodine number	–	–	–	104	–	–	–	54	128–143	–

Table 2.5 continued

Monoglyceride % (m/m)	0.13	0.575	0.197	0.291	–	0.265	0.338	–	0.473	0.387
Oxidation stability (h,110 °C)	35.5	8.1	2.2	2.3	–	8.5	7.1	10.3	2.1	0.9
Phosphorus (ppm)	<0.1	<0.1	<0.1	<0.1	–	<0.1	<0.1	<0.001	<0.1	<0.1
Pour point (°C)	–	–	–	2	3	–	2	15	–	–
Sulfated ash % (m/m)	0.006	<0.005	<0.005	0.009	–	<0.005	<0.005	0.002	<0.005	<0.005
Sulfur % (ppm)	3.2	9.7	4.6	1.2	5	5.1	473.8	0.003	0.8	0.2
Total glycerin % (m/m)	0.065	0.178	0.66	0.1	0.0797	0.091	0.158	0.01	0.149	0.121
Triglyceride % (m/m)	0	0.022	0.021	0.022	–	0.02	0	–	0.019	0
Viscosity at 40 °C (mm ² /s)	2.726	4.852	4.382	4.8	6.13	4.519	5.213	4.5	4.039	4.439
Water and sediment (vol. %)	<0.005	<0.005	<0.005	<0.005	–	<0.005	<0.005	–	<0.005	<0.005

*Measured at 25°C

Data adapted from (Atabani et al., 2012)

Table 2.6: Selected physicochemical properties of pure fatty acids.

Fatty acid	Molecular weight ^a (g./mol.)	Melting point ^a (°C)	Density ^b at 15°C (kg/m ³)	Kinematic viscosity ^b (mm ² /s)	Cetane number ^b	Calorific value ^b (MJ/kg)	Flash point (°C) ^a
C12:0	200.32	43.8	853.9	2.4331	61.99	37.97	> 113
C14:0	228.38	54.4	852.2	3.3381	69.48	38.43	110
C16:0	256.43	62.5	850.8	4.4136	81.17	39.45	206
C16:1	254.41	-0.1	853.8	3.0642	53.80	39.29	132
C18:0	284.48	69.6	849.8	5.8675	88.57	40.10	113
C18:1	282.47	13.5	859.5	4.5728	62.39	40.09	113
C18:2	280.45	-5	871.5	3.7028	42.10	39.69	112
C18:3	278.44	-11	887	3.2980	32.20	39.34	113
C20:0	312.54	75.5	861.3 ^c	7.00 ^c	100.00	40.61 ^c	169.7

^a (Sajjadi et al., 2016), ^b (Barabás & Todorut, 2011), ^c (Ramírez-Verduzco et al., 2012)

Ramos et al. (2009) examined the transesterification of ten different vegetable oils using KOH as catalyst in Spain (Ramos et al., 2009). Important parameters like CN, OS, IV and CFPP were evaluated and correlated according to DU and LCSF. The vegetable oils containing PUFA fractions (C18:2 and C18:3) have low CN and high IV. Biodiesels comprising high PUFAs showed low OS; where as poor CFPP values are associated with rich long carbon chain SFA feed stocks. Nevertheless other critical fuel physicochemical properties need to be investigated.

2.6 Biodiesel production via transesterification

Biodiesels typically produced by the transesterification of oil feedstocks in the presence of MeOH and a suitable catalyst (Meher et al., 2013; Qian et al., 2010). The amount of FFA exist in a feedstock oil is one of the major decisive factor in base catalyzed transesterification (Encinar et al., 2011). The reaction between FFA and base catalyst lead to soap formation besides loss of catalyst active sites besides interrupts the production, quality and costs (Ong et al., 2014). Therefore, biodiesel production using high FFA is a sensitive reaction thence, acid esterification or pre-transesterification using a strong acid catalyst is necessary. The chemical reaction involves treatment of high FFA shown in Figure 2.7 (Encinar et al., 2011). Consequently, biodiesel production with feedstocks comprise high FFA processed following two-step transesterification first acid esterification followed by base catalyzed transesterification.

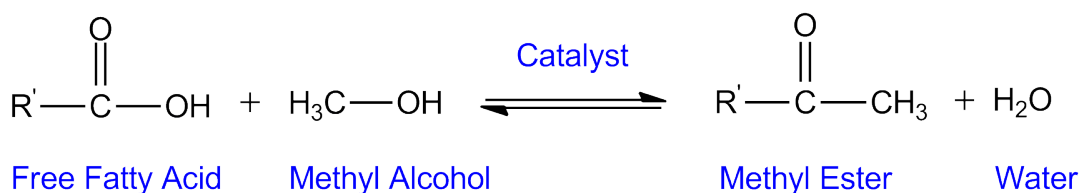


Figure 2.7: Chemistry of high FFA oils transesterification to biodiesel (Encinar et al., 2011).

The chemistry of transesterification is shown in Figure 2.8 (Chouhan & Sarma, 2011). The complete transesterification reaction is a combination of three sequential catalyzed reactions Eq.(1-3) in which triglycerides (TG) of an oil were transformed to diglycerides (DG), monoglyceride (MG) and finally as glycerol and methyl ester (ME) known as biodiesel (Noshadi et al., 2012).

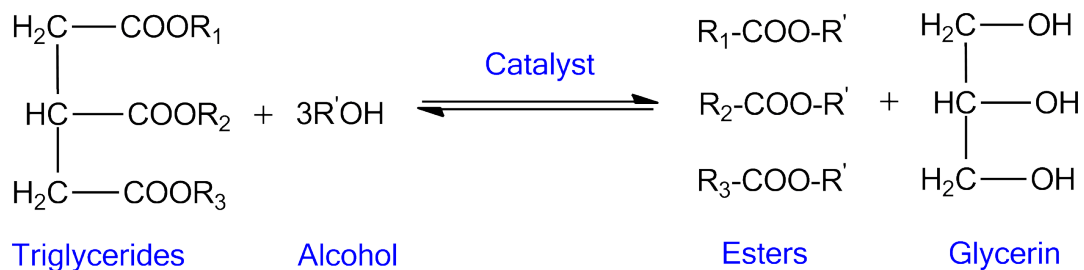
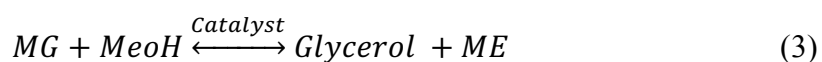


Figure 2.8: Chemistry of biodiesel synthesis via transesterification (Chouhan & Sarma, 2011).



Transesterification reaction depends on various reaction variables and conditions. The general reaction parameters that influences transesterification kinetics, biodiesel yield and quality of biodiesel produced are listed as below. Each of these parameters have to be optimized for optimal biodiesel yield and analyse their impact on biodiesel fuel properties as a whole.

- i. FFA percentage of a feedstock oil
- ii. Extent of water and moisture contents in feedstock oil.
- iii. Type of alcohol
- iv. Molar ratio of alcohol
- v. Nature and form of catalyst
- vi. Catalyst loading.
- vii. Reaction temperature

- viii. Type of heating
- ix. Reaction time
- x. Rate of agitation
- xi. Type of stirring.
- xii. Purification methods.
- xiii. Specific gravity of feedstock oil.

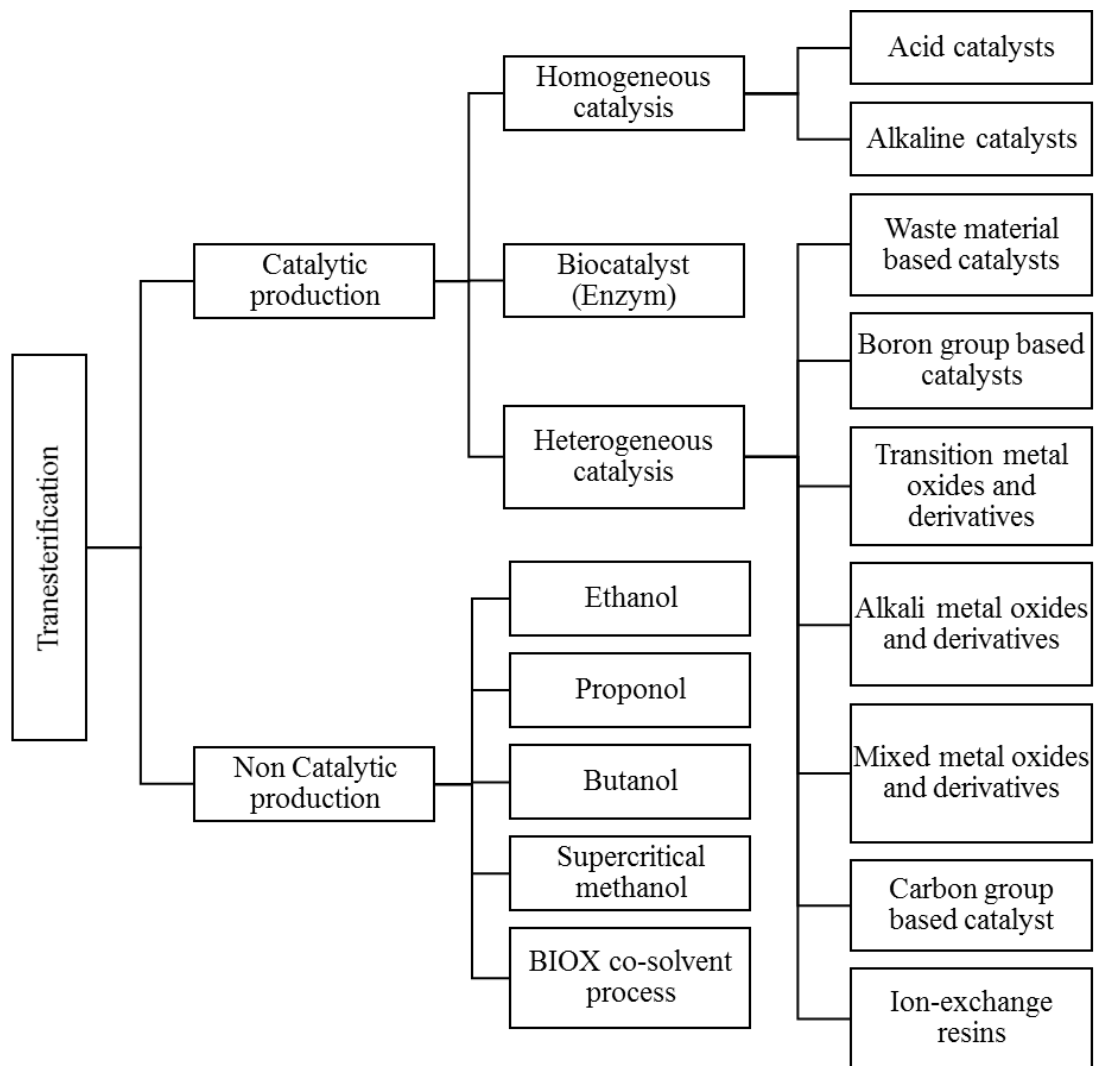


Figure 2.9: Classification of biodiesel production methodologies via transesterification. (Atabani et al., 2012).

Transesterification process kinetics in biodiesel production primarily depends on type of catalyst employed. As seen from Figure 2.9, largely the biodiesel production via transesterification is classified under catalytic and non-catalytic processes (Atabani et al., 2012). The non-catalytic transesterification employed for Ethanol, Propanol, Butanol, Supercritical methanol and BIOX so- solvent process. The catalyzed transesterification performed in the presence of homogeneous, enzyme or heterogeneous catalysts. Acid or base catalyzed transesterification has been reported extensively in literature (Aransiola et al., 2014), but many studies conclude an interaction of homogeneous acid catalysts (Meher et al., 2013) and FFA present in FAME's during transesterification leading to reduced catalyst availability for the reaction and thus homogeneous catalysts are not recommended (Gübitz et al., 1999).

2.7 Effect of transesterification reaction parameters on biodiesel yield

The biodiesel production via transesterification significantly influenced by reaction parameters that includes catalyst loading, methanol to oil ratio, reaction time, heating temperature, and the stirring rpm (ANR et al., 2016; Goyal et al., 2012; Okullo et al., 2010; Pradhan et al., 2012; Rashid et al., 2008).

2.7.1 Catalyst loading

Catalyst loading is one of the key parameters that influence the production of biodiesel both in terms of yield percentage as well as its quality (Chouhan & Sarma, 2011; Joshi et al., 2015; Verma et al., 2016). It was noted that, the lower catalyst loading does not result in a productive FAME yield. Furthermore, the higher catalyst loading leads to the catalyst secondary reactions with other reactants which result in the reduction of biodiesel yield

(Sánchez et al., 2015). The Calcium based catalysts have demonstrated leaching tendency to the biodiesels during transesterification (Deng et al., 2011; Hwa et al., 2014; Lee et al., 2014). According to EN 14214:2008, the biodiesel standards group-I (Na+K) and group- II (Ca+Mg) metals allowable concentration is max. 5.0 mg/kg in the biodiesel samples, the residues of excess metal oxides act as impurities in the biodiesel fuel produced (G Knothe, 2006).

2.7.2 Methanol to oil ratio

Methanol to oil ratio is a primary reactant parameter in the transesterification of vegetable oils. According to the stoichiometric estimations, 30:1 mole/mole % methanol to vegetable oil ratio is required (Ma & Hanna, 1999), however, in actual esterification experiments a critical methanol to oil ratio ranges 30:1 to 210:1 mol./mol. % was reported to carry out complete reaction i.e., transformation of vegetable oil triglycerides into FAME and glycerin. Although many experiments were performed over a range $30 \leq M(\text{mol./mol.}\%) \leq 70$, lower FAME yield % results were noted for < 50 mol./mol. % of methanol to oil ratio, this may be due to the insufficient amount of methanol under the reaction conditions set forth. While, 50-60mol./mol. % methanol maximum transformation was achieved relatively than the molar ratio was 60-70 mol./mol. % which indicates keeping the excessive amount of methanol hampers in achieving the reaction equilibrium as well as biodiesel cost economics (Verma et al., 2016). The methanol to oil ratio interaction with the stirring speed results in positive FAME yield. This may be due to increase in the catalytic and transesterification kinetics as a whole with the stirring speed and hence there is a proportional increase in the % FAME yield together with methanol to oil ratio. On the other hand, methanol interactions with parameters heating temperature and reaction time were marked as highly negative on FAME yield. This is due to the reason, as the reactant heating temperatures are close to the

methanol boiling point (64.7 °C) leading to continuous and rapid evaporation of methanol and hence lesser availability of the methanol for completing the transesterification (Leung et al., 2010).

2.7.3 Transesterification reaction time

The requisite duration of reaction time for catalyzed transesterification is governed by factors such as catalyst type, degree of temperature and also reactants mixing rpm (Leung & Guo, 2006; Leung et al., 2010). In general, at the beginning of the transesterification, a passive rate of reaction phase was observed due to the gradual dispersion of methanol into the glycerides in vegetable oils (Freedman et al., 1984; Leung et al., 2010). As the reaction time increases, the amount of triglycerides conversion into mono glycerides besides FAME yield % also raises. Normally, across the operational reaction time, the '110±5 min.–150±5 min' transesterification iterations results revealed a higher FAME yield. Beyond these reaction duration levels a notable decline in FAME yield % was noted. This may be due to the fact that extended reaction timings lead to reversible reactions Eq.(1-3) which results in continual ester content fall besides soap and diglyceroxide formation (Kouzu et al., 2008; Leung et al., 2010; Prasertsit et al., 2014). Both methanol to oil ratio and temperature shows an unfavorable interactions with reaction time. Hence, an appropriate reaction time was maintained.

2.7.4 Heating temperature

The transesterification reaction kinetics were significantly affected by the reactants heating temperature (Qian et al., 2010). Both higher and lower temperature ranges shown distinct negative impacts on the reaction process. Higher temperatures are considered to be

accelerating the reaction kinetics by minimizing vegetable oil viscosity and hence lead to lowering the FAME yield by soap formation (Qian et al., 2010). In addition, if the operating temperature range approaches the boiling point of reactants specifically methanol (boiling point 64.7 °C) despite the fact that a proper water cooling condenser attachment, methanol gets on accelerated evaporation mode (Freedman et al., 1984; Leung et al., 2010). All these predominantly indicate that an increase in heating temperature does not appreciate the FAME yield rather than reduces the whole reaction activity. Therefore, the heating temperature ranges are lower than methanol boiling point which minimizes its exponential vaporization and allows maintaining sufficient methanol levels during the transesterification.

2.7.5 Stirring speed

Stirring speed of reactants is one of the key reaction parameters in the biodiesel production through heterogeneous catalyzed transesterification process (Boey et al., 2009; Qian et al., 2010; Roy et al., 2014). Further, it's observed that specifically in solid catalyzed transesterifications, the stirring speed interactions on the reaction time and methanol to oil ratio significantly influences FAME yield. This emphasizes that a stirring speed is a productive reaction parameter in achieving a maximum FAME yield.

2.8 Heterogeneous catalyzed transesterification

Design of a stable catalyst is a primary challenge in catalyzed chemical processing's. Even though many research reports are experimented on homogeneous catalyzed transesterification of triglycerides and concluded with many disadvantages (Lam et al., 2010; Tan et al. 2015a). On the other hand, Bravo-Suárez et al., (2013) reviewed on potential of heterogeneous catalysis in biofuel applications (Bravo-Suárez et al., 2013). Several

researchers have explored calcium based heterogeneous catalysts in pure (Choudhury et al., 2014b; Hwa et al., 2014; Kawashima et al., 2009; Tan, et al., 2015; Taufiq-Yap et al., 2011) or mixed oxides (Hwa et al., 2014; Joshi et al., 2015; Kawashima et al., 2008; Taufiq-Yap et al., 2011; Teo et al., 2014) for Jatropha biodiesel production and reported advantages of heterogeneous CaO catalysts over homogeneous ones.

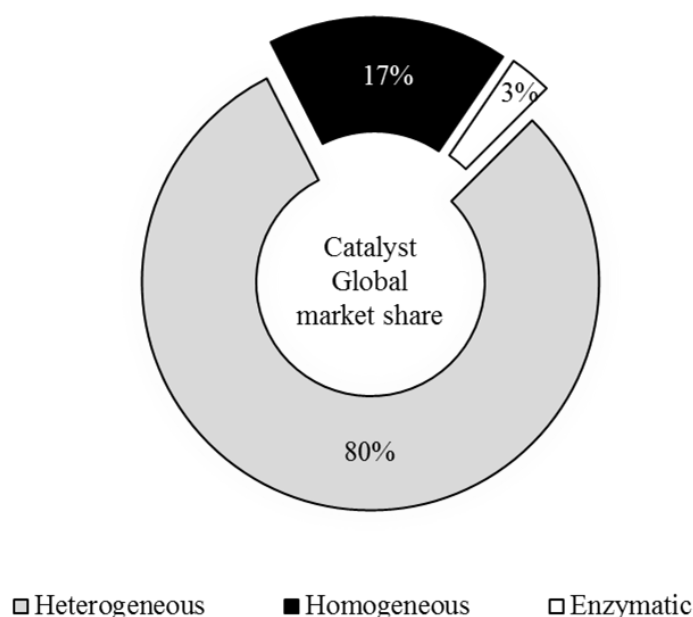


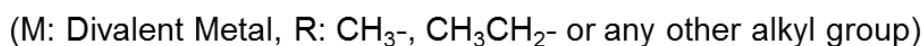
Figure 2.10: Catalysts global market share (Bravo-Suárez et al., 2013).

Immense literature reports explored in the aspects of heterogeneous catalyst design suitable for diverse chemical processing. Classification of biodiesel production methodologies via transesterification according to the catalysts used shown in Figure 2.9. According the catalyst usage in industry across the globe, heterogeneous catalysts are extensively used 80%, compared to homogeneous (17%) and biological or enzymatic (3%) (See Figure 2.10) (Bravo-Suárez et al., 2013). The approaches for heterogeneous catalyst

design and research takes place at three levels specifically 1. Macroscopic, 2. Mesoscopic, and 3. Microscopic. Apart from this many combinational and novel approaches are in place.

However, catalytic kinetics, stability and suitability of a heterogeneous catalyst subject to factors listed below:

- i. Active sites on catalyst
- ii. Acidic/ basicity
- iii. Adsorption onto catalyst surface
- iv. Average surface area
- v. Catalyst synthesis and activation conditions
- vi. Desorption from catalyst surface
- vii. Mobility of catalyst particles
- viii. Pore volume
- ix. Porous particles
- x. Rate of diffusion between intra particles
- xi. Rate of diffusion to external surfaces
- xii. Rate of diffusion while phase transformation
- xiii. Reaction conditions
- xiv. Shape of particles
- xv. Texture of particles
- xvi. Valence state


$$\text{M}^{\delta+}-\text{O}^{\delta-}-\text{M}^{\delta+}-\text{O}^{\delta-}-\text{M}^{\delta+}$$

$\begin{array}{c} \text{H} \quad \text{CH}_3 \\ | \quad | \\ \text{O} \quad \text{O} \end{array}$

(M: Divalent Metal)

41

together with surface structure are presented in Figure 2.12. The covalent nature of metal oxide expedites transesterification reaction kinetics substantially (Chouhan & Sarma, 2011).

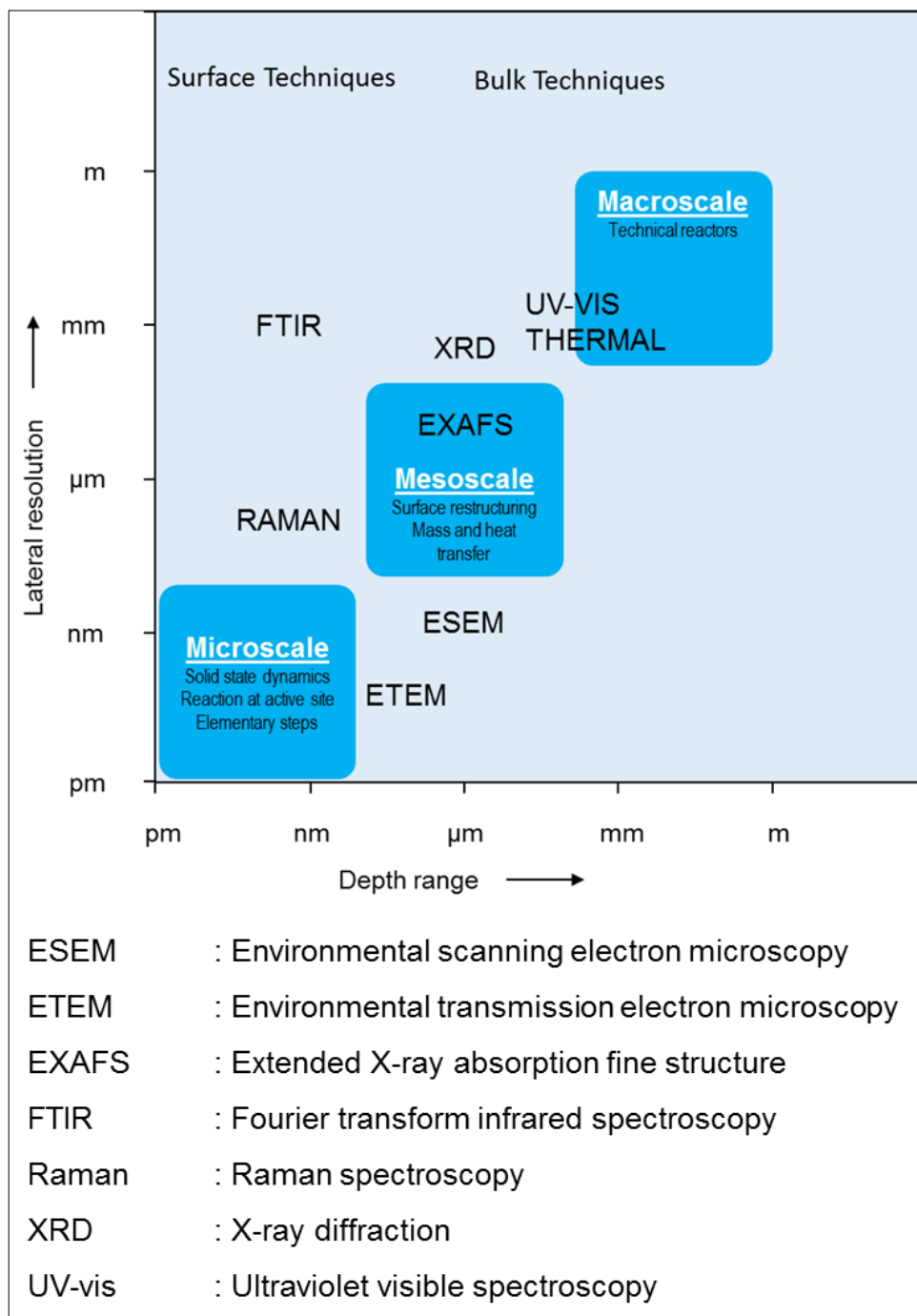


Figure 2.13: General characteristics of a few in situ characterization techniques (Bravo-Suárez et al., 2013).

Characterization of synthesized catalysts is an indispensable phase of catalytic research. This is to analyse morphology, rate of adsorption/ desorption, intermediate reactions and other physicochemical characteristics (Bravo-Suárez et al., 2013). Figure 2.13 shows a few general characteristics of in situ characterization techniques classified according to depth of range and lateral resolution (Bravo-Suárez et al., 2013). In general heterogeneous catalysts constitute solid porous particles. According to the size of pores they are classified as Macro pores (pores > 50 nm), Mesopores ($2 < \text{pores} < 50$ nm) and Micro pores (pores < 2 nm) (Leofanti et al., 1997). Apart from classical spectroscopic methods, a large number of in situ surface and bulk characterization techniques are used (Bell et al., 2008; Deutschmann, et al., 2009; Leofanti et al., 1998).

2.9 Synthesis of calcium based heterogeneous catalysts from renewable sources

Use of renewable or waste shells in synthesis of heterogeneous catalyst has been increased phenomenally. Noteworthy advantages of these renewable sources and catalysts (Chouhan & Sarma, 2011) are listed below:

- i. Rich source of calcium
- ii. Higher basicity
- iii. Low cost of raw material
- iv. Less synthesis costs
- v. Lower solubility
- vi. Modest catalytic activity
- vii. Aids in sustainable development
- viii. Add value to reusable applications
- ix. Waste utilization helps in environment friendly disposal

Table 2.7 reviews on biodiesel production from various feedstocks utilizing calcium based catalysts via transesterification process. While Table 2.8 summarizes use of renewable wastes for calcium catalysts synthesis and their catalytic applications in biodiesel production. Kawashima et al. (2009) investigated the transesterification of rapeseed oil using activated CaO with methanol, and reported a 90% biodiesel yield (Kawashima et al., 2009). Islam et al., (2013) synthesized calcium carbonate nanoparticles with a 20 ± 5 nm diameter from cockle shells (Islam et al., 2013), while Margaretha et al., (2012) reported a surface area (S_{BET}) of 17 m²/g and pore volume of 0.04 cc/g CaO synthesised from *Pomacea* shells that was utilized in biodiesel production from palm oil (Margaretha et al., 2012). Buasri et al. (2013a) derived CaO from mussel shells S_{BET} of 89.91m²/g, cockle shells S_{BET} of 59.87m²/g and scallop shells S_{BET} of 74.96 m²/g for biodiesel synthesis from palm oil (Buasri et al., 2013b). Tan et al. (2015b) utilized CaO that was synthesized from waste chicken-eggshell with a S_{BET} of 54.6 m²/g and from calcinated ostrich-eggshell with a S_{BET} of 71.0 m²/g for the transesterification of waste cooking oil (Tan et al., 2015b).

Hwa et al. (2014) investigated the transesterification reaction catalysed CaO S_{BET} of 9.2 ± 0.80 m²/g that had a crystalline size of 66.3 ± 3.20 nm and obtained a 90% biodiesel yield from *Jatropha* oil (Hwa et al., 2014). Taufiq-Yap et al. (2011) S_{BET} : 9.5 m²/g reported a 85% biodiesel production from *Jatropha* oil (Taufiq-Yap et al., 2011), while Choudhury et al. (2014a) reported a 89.36% biodiesel yield with a CaO catalyst of S_{BET} : 7.114 m²/g using an ultrasound effect with crude *Jatropha* oil (Choudhury et al., 2014b).

Table 2.7: Summary of primary parameters impact on biodiesel production via heterogeneous catalyzed transesterification.

Feedstock	Catalyst (wt. %)		Methanol (mol:mol)	Time (min)	Temperature (°C)	Agitation (rpm)	Yield (%)
Chinese tallow oil	CaO	1.5	12	90	70		99.8
Jatropha oil	H ₂ SO ₄ , CaO	2	8	150	65	700	90
Jatropha/ Karanja oils	ZnO-CaO	5	12	60/90	65		98.2/95.8
Karanja oil	H ₂ SO ₄ , CaO	2.5	8	150	65		95
Microalgae	CaO	9	150	60	65	300	84.11
Mustard oil	CaO	3	9	360	65		93.3
Nahor oil	H ₂ SO ₄ , Li/CaO	5	10	240	65		94
Palm oil	CaO	3	8	360	60	700	93
Palm oil	Ca(OH) ₂	5	5	50	-	*	96
Palm oil	CaO	15	18	4	-	*	96.7
Palm oil	CaO-SiO ₂	9	15	480	65		80.2

Table 2.7 continued

Palm oil	CaO	8	9	60	60	#	92.7
Palm oil	CaO	1	9	120	65	900	98
Rapeseed oil	CaO	2.5	9	180	65		89.1
Rapeseed oil	KF/CaO	3	9	180	70		97.5
Soybean oil	KBr/CaO	2	6	120	65		98.5
Soybean oil	KI/CaO	1 ^{&}	10	240	50	400	79.5
Soybean oil	CaO	12	24	480	60		94.1
Soybean oil	CaO	3	9	180	65		95
Waste cooking oil	H ₂ SO ₄ , Ba/CaO	1	6	180	65	900	> 98
Waste cooking oil	CaO	5	6	120	65		> 86
Waste frying oil	CaO	2	6.03	420	60		87.28
Waste frying oil	CaO	-	6.03	360	60		> 89
Waste frying oil	CaO	8	18	180	65		95.84

[&](mol/g), ^{*}Microwave irradiation, [#]Ultrasonic power (120 W)

Source: (Roschat et al., 2016)

Table 2.8: Summary of Calcium based catalysts synthesized from renewable wastes for biodiesel production.

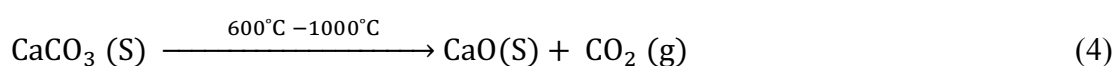
Waste shell	Calcination		Surface area (m ² /g)	Pore Volume (cm ³ /g)	Pore diameter (°A)	Feedstock	Catalyst (wt. %)	Biodiesel yield (%)	Reference
Mussel shell	1000 °C	4 h	89.91	0.13	34.55	Palm	10	95.90	A
Cockle shell	1000 °C	4 h	59.87	0.087	25.53	Palm	10	94.13	A
Scallop shell	1000 °C	4 h	74.96	0.097	30.55	Palm	10	95.44	A
Duck eggshell	900 °C	4 h	128.5	0.1	34.08	Palm	20	92	B
Chicken eggshell	900 °C	4 h	136.1	0.12	34.12	Palm	20	94	A
Chicken-eggshell	1000 °C	4 h	54.6	0.0148	5.44	Waste cooking oil	1.5	94	C
Ostrich-eggshell	1000 °C	4 h	71	0.0218	6.13	Waste cooking oil	1.5	96	C
<i>Pomacea</i> Shells	900 °C	2 h	17	0.04	32	Palm oil	4	95.61	D
Sea Snail	900 °C	3.5 h	24	0.0582	810 nm	Waste frying oil	2	87.28	E
River snail shell	800 °C	3 h	3.495	0.01.872	21.425	Palm oil	5	98.5	F

^A(Buasri et al., 2013b); ^B(Buasri et al., 2013a); ^C(Tan et al., 2015b); ^D(Margaretha et al., 2012); ^E(Birla et al., 2012); ^F(Roschat et al., 2016)

These studies show that CaO can be a promising catalyst for biodiesel production since catalysts with lower particle sizes and a higher surface area contributes to enhancing the transesterification reaction rate. Very scant work, however, has been devoted to the synthesis of CaO as a nano-catalyst that focuses on reducing the particle size and increasing the surface area for biodiesel production (Goyal et al., 2013; Kumar et al., 2007; Mansourpoor, 2012; Noshadi et al., 2012; Pradhan et al., 2012; Vicente et al., 1998; Yee et al., 2011) especially from the largely available sustainable waste resources such as seashells.

2.9.1 Methods of catalyst synthesis from shells

In order to produce calcium based catalysts from renewable sources a large number of synthesis methods are testified. The waste shells predominantly contain CaCO₃ components hence a temperature of 600°C-1000°C has be utilized for calcium based catalyst synthesis (Shan et al., 2016), Eq. (4). Various calcium catalyst synthesis methods are described in the following sub-sections.



2.9.1.1 Calcination (Direct use)

Margaretha et al. (2012) synthesised CaO from *Pomacea* sp. shells calcination at 900°C for 2 h, that was utilized in biodiesel production from palm oil (Margaretha et al., 2012). Buasri et al. (2013) derived CaO by calcination of mussel shells, cockle shells and scallop shells at 600-900°C for 4h for biodiesel synthesis from palm oil (Buasri et al., 2013b). Tan et al. (2015) utilized CaO that was synthesized from calcination of waste chicken-eggshell and

ostrich-eggshell at 1000°C for 2 h for the transesterification of waste cooking oil (Tan et al., 2015b).

2.9.1.2 Co-solvent

The reagents such as diethyl ether (DEE), tetrahydrofuran (THF) and acetone are being employed as co-solvents to improve the kinetics of reactions as well as significant improvement in FAME (Leung et al., 2010). Roschat et al. (2016) synthesized CaO catalyst from River snail shells by calcining at 800°C for 3 h. The catalyst was utilized to produce palm biodiesel together with 10% v/v of THF and methanol. As a result biodiesel yield of $98.5\% \pm 1.5$ was reported (Roschat et al., 2016). Further, according to Leung et al. (2010) review, adoption of co-solvent methods advances alcohol solubility in triglycerides besides, easy recovery of co-solvent and excess alcohol in one step.

2.9.1.3 Hydration-dehydration

Morphology of metal oxide catalyst can be enhanced by hydration – dehydration technique. This catalyst synthesis process comprises hydration (water treatment) at low or trivial temperature subsequently hydration at relatively high temperature. The dehydration phase decomposes the metal oxide and transforms into an active catalyst. Yoosuk et al. (2011) modified catalytic activity of dolomite with hydration–dehydration method, as a result an active heterogeneous catalyst was obtained for palm biodiesel production (Yoosuk et al., 2011). Yoosuk et al. (2010) synthesizes an active CaO having higher surface area, less crystallinity, and superior basic sites from calcite while, the catalytic activity of CaO was investigated in transesterification of palm oil to biodiesel (Yoosuk et al., 2010b).

2.9.1.4 Thermal hydration-dehydration

Thermal hydration-dehydration is an effective catalyst synthesis protocol for improving surface morphology of a metal oxide catalyst (Shan et al., 2016). Asikin-Mijan et al. (2015) developed an active CaO catalyst using waste clamshell (*Meretrix meretrix*) by employing a hydration–dehydration procedure. The clamshell were calcined at 900°C followed by 12h refluxing at 60°C then re-calcination for 3 h at 600°C. As a result of extended hydration process, both basicity and surface area of synthesized catalyst were considerably improved (Asikin-Mijan et al., 2015).

2.9.1.5 Dissolution-precipitation

Jindapon et al. (2016) developed a mixed base heterogeneous catalyst, which comprises compounds of Calcium, Zinc and Aluminium (ZSA). ZSA was synthesized following dissolution-precipitation protocol utilizing waste seashells with co-existence of alumina and zinc nitrate. Calcination of ZSA at 500°C resulted in active nano-crystalline structured catalyst with high basicity. The catalytic activity was measured through transesterification of palm oil to biodiesel. An optimal yield of 98% was reported at optimal reaction conditions besides, the catalyst was stable for five recycle uses (Jindapon et al., 2016).

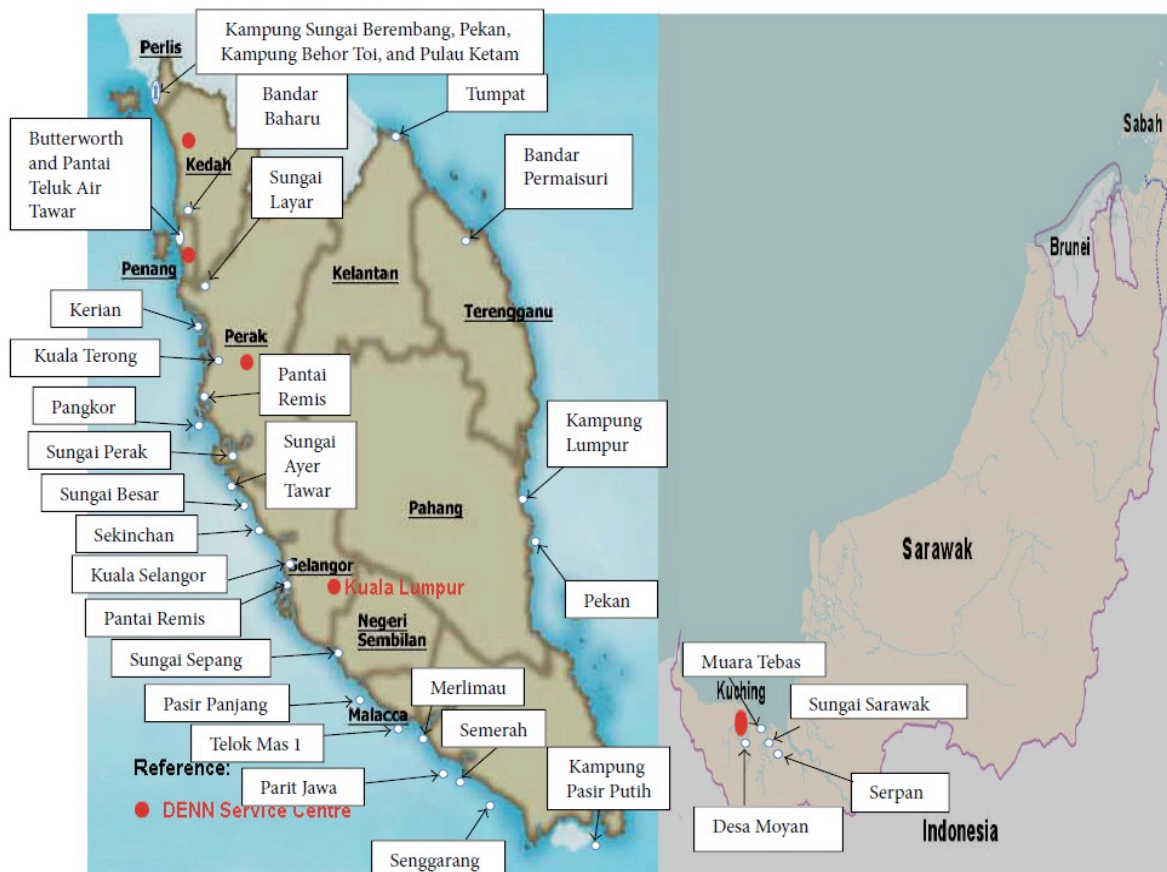


Figure 2.14: Seashell potential zones of Malaysian coastal areas (Hossen et al., 2015; Rahim et al., 2012).

2.9.2 *Polymesoda erosa*: A potential raw material source for catalyst synthesis

Malaysia is a rich source for aquatic seashells due to extensive coastal regions across the country. Figure 2.14, shows the Malaysian geographical coastal regions map which is potential for diversified sea foods and aquatic shells. *Polymesoda erosa* (*P. erosa*) has been widely reported throughout the Indo-Pacific geographic region as a prominent fishery source in many tropical and sub-tropical islands. *P. erosa* seashell has large rounded, thick-shelled bivalve reaching about 110 mm length. Exterior has sculpture of distinct concentric growth lines, often developed as ridges with strong and wide hinge and in white or with thick olive-

brown periostracum color whereas interior color is white. Scientifically *P. erosa* belongs to 23375 Corbiculidae families and locally it is called as Lokan (Bachok et al., 2003). From the works of Hossen et. al. (2015) and Rahim et. al. (2012), it was obvious that *P. erosa* shells are abundantly available in the coastal regions of east and west Malaysia (Hossen et al., 2015; Rahim et al., 2012). However, to the best of literature survey, no research has reported on synthesis of CaO nano-catalyst from *P. erosa* seashells.

2.10 Jatropha as a biodiesel feedstock

Jatropha curcas Linnaeus (JCL), an euphorbia family member, is a fast growing plant in marginal and non-agriculture fields and is fully adaptable to tropical and subtropical climates (Koh & Mohd, 2011) and, moreover, the oil content of the *Jatropha* seed is about 20%-60% (Achten et al., 2008; Gübitz et al., 1999; Koh & Mohd, 2011). JCL presence in native and exotic range of geographic regions across the globe shown in Figure 2.15 (Orwa et al., 2009; Silitonga et al., 2013). JCL, has attained the researcher's attention as one of the best suited non-edible vegetable oil feedstock for biodiesel fuel production via transesterification due to its agro-medical tangible interests as well as not affecting the human food cycle (Meher et al., 2013).

The physicochemical properties of a biodiesel depends on FAC of corresponding feedstock. On the contrary, vegetable oil feedstocks FAC varies according to seeds breed, meteorological conditions and type of agricultural land utilized. The FAC of JB from Thailand (Borhanipour et al., 2014; Winayanuwattikun et al., 2008) and China (Yang et al., 2012) were tabulated from literature to correlate their FAC variations with respect to the geographical regions (see Table 2.9). The dissimilarities in FAC in these feedstocks would

reflects in discrete fractions of SAFs, MUFAs, PUFAs, DU and LCSF of the biodiesels at large and physicochemical properties of biodiesel produced.



Figure 2.15: *Jatropha curcas* plantations across the globe (Orwa et al., 2009; Silitonga et al., 2013).

Table 2.9: Fatty acid composition (wt %) of Jatropha biodiesels from Thailand and China.

Fatty acid (Cnc:nb)	Thailand*		China ^{\$}	
Lauric acid (C12:0)	0.05	0.14	0	0
Myristic acid (C14:0)	0.02	0.17	0	0
Palmitic acid (C16:0)	14.58	14.82	13.90	13.80
Palmitoleic acid (C16:1)	0.77	0.81	0	0.70
Stearic acid (C18:0)	11.7	4.15	7.80	7.10
Oleic acid (C18:1)	69.28	40.98	55.90	46.10
Linoleic acid (C18:2)	3.31	38.61	19.60	32.30
Linolenic acid (C18:3)	0.04	0.27	1.40	0
Arachidic acid (C20:0)	0.19	0.06	1.20	0
Eicosenoic acid (C20:1)	0.07	0	0	0
Behenic acid (C22:0)	0	0	0	0
Erucic acid (C22:1)	0	0	0.20	0

*(Borhanipour et al., 2014; Winayanuwattikun et al., 2008) ^{\$}(Yang et al., 2012)

2.11 Feedstock fatty acid composition influence on physicochemical properties of biodiesel

The influence of biodiesel fatty acid composition on their physicochemical properties reviewed in the following sections.

2.11.1 Cetane number

Cetane number (CN) is a primary ignition and combustion quality indicator of a fuel being used in diesel engines. The higher the CN, the shorter the ignition delay (ID) time i.e. time lag between fuel injection and ignition initialization in a combustion chamber. The higher CN ensures good fuel combustion quality, better cold start and engine performance as well as low white smoke formation and emissions (Ramos et al., 2009). Although CN of diesel fuels and octane number (ON) for gasoline are theoretically similar, in general fuels having higher CN likely to have low OS and vice versa. Biodiesel fuels standards ASTM D6751 and EN14214 have specifies a minimum CN of 47 and 51 according to described CN testing protocols D613 and EN ISO 3104/ 3105 respectively, while ASTM D975 standard states a minimum CN limit of 40 for petro diesels (Gerhard Knothe, 2005). The cetane scale is standardized with two reference hydrocarbons. A low quality standard 2,2,4,4,6,8,8,-heptamethylnonane ($C_{16}H_{34}$ or HMN), a highly branched hydrocarbon with low ignition characteristics, assigned to a minimum level CN of 15. A high quality standard, hexadecane ($C_{16}H_{34}$), which is a long straight chain compound with good ignition quality was earmarked at high level CN of 100 on the cetane scale (Knothe, 2005).

The biodiesel fuel CN correlates with feedstock FAP used for production. The CN increases with higher the SFA molecules, increasing fatty acid chain length and straightness

(Knothe et al., 2003). On the other hand, higher degree of unsaturated fatty acid contents results in lower CNs (Ramos et al., 2009). Although factors like diesel engine technology, fuel injection pressures generally contributes exhaust emissions variations, reportedly NO_x emissions rises with enriched fatty acid DU and lessen LCSF. Hence, despite the fact that biodiesel fuels reports higher CN compared to petro diesels, diesel engines fueled with biodiesels emits marginally higher NO_x exhaust fractions (Knothe, 2005; Knothe et al., 2003).

2.11.2 Oxidation stability

The biodiesel oxidation stability (OS) is one of the important property affecting quality of fuel together other major properties includes viscosity, density and water content. According to biodiesel standard EN 14214, a minimum of 6 h, OS is defined at 110 °C. The contents of biodiesel's such as about 10% higher oxygen as well as rich polyunsaturated methyl ester are the major cause for a poor degree of OS and affects their wide spread of use (Borhanipour et al., 2014; Ramos et al., 2009). This due to the loss of natural antioxidants' present in the feedstock oils during their transesterification (Chuah et al., 2015). Similar observations were noted by Shahabuddin et al. (2012) and Rashid et al. (2014) recommended antioxidant treatment to avoid auto oxidation and to meet a minimum standard of 6 h OS limit for most of the biodiesel's (Rashid et al., 2014; Shahabuddin et al., 2012). Also, the factors like fuel exposure to high temperature gradients, light, air; presence of metal traces and PUFA's equally contributes to OS variations as a result of increased oxidation rates (Chuah et al., 2015).

2.11.3 Calorific value

Calorific value (CV) one of the primary fuel characteristics to estimate its suitability for a given application. CV is the amount of energy measured while full combustion of a fuel sample per unit weight. European biodiesel standard EN 14214 specified a minimum CV of 35 MJ/kg (Table 1). Though, high oxygen contents of biodiesel improves fuels combustion efficiency and reduces fuel oxidation potency, in general this causes biodiesels CV lower than that of petro diesel (45.82 MJ/kg) (Silitonga et al., 2013). The fuel elements such as carbon, oxygen, hydrogen and sulfur are of primary interest for combustion process in diesel engines. Hence, these elemental composition, location and nature of bonds corresponding to fuel molecules determines CV of a fuel (Rao, 2011).

2.11.4 Iodine value

Iodine value (IV) is a measure of fatty acids unsaturation level in feedstock oil and identical for the respective biodiesels (Knothe, 2006; Rao, 2011; Ramos et al., 2009). IV is expressed in amount of iodine (I_2) in centigrams reacts with per 100 g of biodiesel sample. I_2 , upon adding, reacts with PUFA structures containing double bonds, ($C_n:2$), within the oil samples (Borhanipour et al., 2014). The net IV is limited by total fatty acids DU as a result IV affects polymerization of glycerides and fuels oxidation stability leading to particle depositing in diesel engine's fuel injectors (Lin & Lin, 2012; Ong et al., 2013). Higher DU emerged in JB_{EM} fragments thus higher IV. On the other hand higher SFAs contributes in lowering IV (Ramos et al., 2009). EN 14214 biodiesel standard specifies IV as max. 120g I_2 /100g (Table 6), however vegetable oil feedstocks for biodiesel production such as sunflower, soybean, grape seed oil are exempted (Ramos et al., 2009).

2.11.5 Acid value

Acid value (AV) defined as amount of potassium hydroxide (KOH) in milligrams required to neutralize fatty acids contents present in one gram of the fuel sample. According to ASTM D6751, EN 14214 standards, following ASTM D664 or EN 14104 test methods, acid value of biodiesel fuel limited to max. 0.5 mg KOH/g respectively (Silitonga et al., 2013). Mainly three forms of acid components emerges in biodiesel samples namely residual mineral acids, residual FFAs and organic acids during biodiesel production, hydrolysis or as byproducts of oxidation processes (Barabás & Todorut, 2011). The AV is related to fatty acids or FFA in the biodiesel or in their feedstocks (Fernando, Karra, Hernandez, & Jha, 2007). Higher amount of AV leads to higher AV (Fernando et al., 2007; Silitonga et al., 2013). AV indicates lubricant degradation of a fuel being used in the engines and the higher AVs corrosive to the engine parts thereby lowers engine efficiency besides sludge and gum formation (Atabani et al., 2013; Borhanipour et al., 2014; Chattopadhyay & Sen, 2013). The physical storage biodiesel conditions such as temperature affects the fuel's AV due to increasing oxidative reactions over high temperatures, results in increase of AV (Shahabuddin et al., 2012). The higher degree of unsaturated fatty acids of biodiesels contributes higher acid values. According to Deng et al., (2011) the unsaturated fatty acids (palmitoleic, oleic, linoleic, Linolenic acids) are susceptible to increased oxidation and more unstable over storage causes increase in biodiesel AV (Deng et al., 2011).

2.11.6 Water content

Water content (WC) in biodiesel is an important fuel quality parameter (Atadashi et al., 2012). WC adsorb and exists in fuels as free water, soluble water and or emulsified water forms. The amount of WCs adsorption on to the fuel primarily reliant on FAC and

temperature. The Biodiesel's FAC consists hygroscopic prone compounds led to adsorb increased levels of soluble water during their storage than petro diesels (Atadashi et al., 2012). Further, biodiesels can absorb moisture either during production or transportation process (Fregolente et al., 2012). Biodiesel standards ASTM D6751 and EN 14214 specified a maximum of 500 mg/kg water content (Barabás & Todorut, 2011). Even, due to more hydrophilic nature, stored biodiesel fuels are susceptible intensified water adsorption, water and sediment accumulates at the lower layers of storage tanks in the forms of free water specifically fluctuations over poor fuel storage practices such as temperature and relative humidity (Barabás & Todorut, 2011; Fregolente et al., 2012; Barua, 2011). Ideally, 30–40°C of temperature and vacuum of 0.05 bar are practiced on commercial scale production systems for biodiesel dewatering (Atadashi et al., 2012).

The configuration and degree of olefinic unsaturation (mono, di and triolefins) present in biodiesel feedstocks determines their oxidative and thermal reactivity (Arisoy, 2008). The olefinic fatty acid decomposition produces primary oxidative derivatives such as hydroperoxides by following a peroxide chain mechanism, which degenerates biodiesel fuel properties like heating value, cetane number and flashpoint (Arisoy, 2008; Lin & Lin, 2012). Free WC and sediments present in biodiesel fuel tanks causes of microbial growth leading to sludge and slime formation and rusts ferrous based metals tank by enhances oxidation rates over storage periods due to peroxidation chain mechanism (Atadashi et al., 2012; Barabás & Todorut, 2011; Fregolente et al., 2012; Lin & Lin, 2012; Barua, 2011). As a result, the sedimentations hampers free flow of fuel through diesel engine's fuel filters and fuel lines and reduces their life expectancy, thereby damages the metallic engine parts and also fuel injection system by corrosion (Lin & Lin, 2012; Barua, 2011). According to Fregolente et al.

(2015) by employing hydrophilic hydrogel adsorbents free water and soluble water contents from the samples could be reduced to minimum (Fregolente et al., 2015).

2.11.7 Kinematic viscosity

Kinematic viscosity (KV) is a major decisive and important flow features of an engine fuel, especially KV can be contemplated as one of the primary restriction in their wide spread of usage (Borhanipour et al., 2014). KV measures internal fluid's resistance to shearing flows under gravity at 40 °C. KV of a fuel influences basic process such as fuel injection, lubrication, blending, atomization, volatility and combustion. Low KV indicates fuels poor lubrication in the dynamic engine parts, results in increased moving mechanical parts wear resulting in leakage thereby raises of engine power losses and durability issues (Atadashi et al., 2010; Borhanipour et al., 2014; Rao, 2011). Higher KV levels corresponds to insufficient amount of fuel supply, indigent fuel injection and soot deposition on engine components like injectors, piston rings, valves (inlet and outlet) (Xue et al., 2011). Moreover, high KV can induces highest temperature and pressure in the engine's combustion chamber as a consequence of early fuel injection at high line pressure transmission causing fuel combustion nearer to its top dead center (Canakci & Sanli, 2008).

Higher KV results in inferior fuel atomization quality and contributes in combustion degradation. In addition, improper biodiesel blending in virtue of high KV, makes up insufficient air - fuel mixing which leads to poor combustion, losses in engine power and higher exhaust emissions (Canakci & Sanli, 2008; Rao, 2011; Xue et al., 2011). Higher KV values can also influences low temperature fuel flow working, ignition delays and cold engine startup problems (Borhanipour et al., 2014; Ong et al., 2013; Rao, 2011). Biodiesel standards ASTM D6751, EN 141214 specifies KV testing methods and limits as ASTM D445 (1.9-6.0

mm²/s) and EN ISO 3104/ 3105 (3.5-5.0 mm²/s) respectively at a temperature of 40°C (Table 6). KV of pure biodiesel's is higher than petro diesels (2.91 mm²/s). Fuels' KV is highly correlated with its FAC. Higher SFA factor and long carbon chain structures contributes in increased KV levels; on the contrary, increase of fatty acid unsaturation levels (increasing number of double bonds) results in lower KV(Ong et al., 2013; Silitonga et al., 2013).

2.11.8 Density

The density (DE) of a substance is a measure of its mass per unit volume. The biodiesel fuel's density is major concern on their use. According to EN 14214 standard specified biodiesel density for their use in diesel engines is 800-900 kg/m³ (Table 6). In diesel engines the fuel injection and air-fuel mixing systems operates at 300-350 K temperature over pressures of 15-50 MPa. The rate of fuel injection and volume are directly relays on the fuel's density. Higher density values indicates compactness of particles in the fuel which results in injecting relatively more fuel mass into the diesel engine's combustion chamber. According to the density properties of pure fatty acids as presented in Table 6, the density value decreases with molecule chain length and increases with fatty acid DU therefore SFA were reported higher density values than USFAs (Barabás & Todorut, 2011).

2.11.9 Cloud point

Poor low temperature fluid flow characteristics of biodiesel fuels can be one of the major limitations for use (Knothe, 2005). Cloud point (CP) is a temperature where a liquid fatty components tends to grows into crystals in the biodiesel begins cloudy structure formation. As the amount of SFAs raises the CP increases whereby inflates solidification of SFAs and thickens the biofuel grows. This is due to the fact that SFA compounds (C_n: 0) have

demonstrated higher melting points than USFA which rapidly grows into crystalline agglomerate structures as operating temperatures decrease. The agglomerated fuel fragments clog fuel injectors and filters in the diesel engines causing major low temperature operational troubles. ASTM D6751 and EN 14214 biodiesel standards, discussed fuel specifications pertaining to low temperature properties. ASTM D2500 test methods are recommended for measuring of CP but limit is not specified, yet a test report required.

2.11.10 Pour point

Pour point (PP) is an important operating feature of biodiesel especially at low temperatures (Demirbas, 2009; Saxena et al., 2013). The PP of a liquid fuel is defined as a minimum temperature at which fuel's fatty acid contents first turn into semi solid fragments. Further these fragments grow into solid waxes and agglomerate affects fuel filters and flow lines by clogging (Knothe, 2005). Hence PP is the lowest operating temperature of a liquid fuel sufficient to flow without losing its basic physical properties (Demirbas, 2009). Therefore liquid fuels having higher PP are recommended to be kept warm for use at low temperature geographical regions (Barua, 2011). The biodiesel fuel measures notably higher PP than that of petroleum based diesel fuel and significantly varies with FAP of feedstock (Bhuiya et al., 2016; Knothe, 2008). The important fatty acid structural characteristics of biodiesel that include length of carbon chain, nature of branching, double bonds orientation and DU greatly influence the freezing point of fatty acids hence the PP results vary (Knothe, 2003; 2005; 2008; Barua, 2011; Silitonga et al., 2013). Presence of higher quantities of SFA contents in feedstocks yields biodiesels with relatively higher PP values (Knothe, 2005; 2008; Barua, 2011; Silitonga et al., 2013).

2.11.11 Flash point

Flash point (FP) is a critical fuel criterion refers to safety specifications during storage, transportation and handling (Borhanipour et al., 2014; Silitonga et al., 2013; Yoon et al., 2008). FP of a liquid fuel defined as a minimum temperature at which a required amount of combustible vapour of air-fuel mixture, which contributes for auto-ignition on heating up of the fuel by a spark or flame. The volatility and FP values of a fuel are inversely correlated and yet, FP illustrates contrast in flammability, volatile characteristics of various fuels (Bhuiya et al., 2016; Demirbas, 2009; Shahabuddin et al., 2012). The diesel engines combustion chambers were not equipped with an additional ignition mechanism, therefore fuels with lesser ignition temperature were highly recommended for using in diesel engines however fuels having FP more than 66°C regarded as safe for use. ASTM D6751, EN 14214 biodiesel standards describes minimum specifications of FP as min. 130°C and min. 101°C according to test methods ASTM D 93 and EN ISO 3679 respectively (Table 21), while ASTM D975 standard indicates FP of 60°C-80°C limits for petro diesel (Bhuiya et al., 2016). Though FP temperatures of biodiesels and corresponding vegetable feedstocks measures marginally lower, long carbon chains and increasing number of double bonds in the fatty acid structures significantly impacts on increase of gross FP (Samavi et al., 2016). The higher contents of USFAs specially Oleic acid (C18:1) and Linoleic acid (C18:2) presence affects in increasing the biodiesels' FP values (Demirbas, 2009; Mofijur et al., 2012).

2.11.12 Cold filter plugging point

Cold filter plugging point (CFPP) refers fuel performance parameter at low temperature operating conditions. Biodiesel's cold flow properties are one of the primary constraints in its prevailing utilization (Sajjadi et al., 2016). Distillate fuel oils (diesel fuel or fuel oils)

develops wax settling problems at low operating temperatures (-10°C, -15°C) due to fuel fractions that prone to gel and or crystallize formation and starts plugging of fuel filters, injectors and fuel lines. The ASTM and European biodiesel standards doesn't specified any limits for CFPP but standard testing methods based on ASTM D6371, and UNE-EN 14214 were discussed to quantify low temperature fuel flow properties. However, each country have specified cold flow property testing protocols and limits based on regional climatic conditions such as temperature for different seasons of a year. Among the fatty acids components, the SFA contents have greater impact on low temperature fuel properties whereas USFAs shows insignificant effect. Especially the SFAs Palmitic acid (C16:0) and Stearic acid (C18:0) quickly precipitates' upon low temperatures.

2.12 Mathematical modeling based optimization

Response surface methodology (RSM) is a mathematical modelling technique applied to analyse influence of input parameters direct and interactions impact on the response functions and to optimize Eq. (5).

$$Y = \beta_0 + \sum_{i=1}^3 \beta_i k_i + \sum_{i=1}^3 \beta_{ii} k_i^2 + \sum \sum_{i < j=1}^3 \beta_{ij} k_i k_j \quad (5)$$

Where 'Y': Objective function;

k_i and k_j : Decision variables in the uncoded form and

$\beta_0, \beta_i, \beta_{ii}$ and β_{ij} : Coefficients of intercept, linear, quadratic and interactions.

The real-time research problems with multiple objective functions require multi response simultaneous optimization approach. Apart from many techniques constrained optimization, contour plot overlying for each response and desirability approaches are mostly

utilized. Amongst, the desirability approach is significant due to its ease of use and built-in accessibility through statistical based analysis software (Khoobakht et al., 2016; Sivaramakrishnan & Ravikumar, 2013). Desirability value of a response may ranges between '0' (undesirable) and '1' (most desirable). However, each response function may be set to optimize through minimize, maximize or a specific goal by which its desirability is obtained. The overall desirability of multiple response functions is obtained by their relative importance ranking over other responses (Sivaramakrishnan & Ravikumar, 2013).

Many state-of-the-art works have been performed on optimizing the primary transesterification process parameters such as manipulating the catalyst ratio, methanol ratio reaction time and their potential interactions to achieve optimal biodiesel yield using RSM as a statistical and optimization tool (Choudhury et al., 2014b; Choudhury et al., 2013; Goyal et al., 2013; Kumar et al., 2007; Mansourpoor, 2012; Noshadi et al., 2012; Pradhan et al., 2012; Vicente et al., 1998; Yee et al., 2011). Kumar et. al. (2007) have reported the use of RSM based central composite rotatable design (CCRD) to curtail FFA percentage from *Jatropha* using H_2SO_4 and KOH as catalysts (Kumar et al., 2007). Meanwhile, central composite design (CCD) based RSM was utilized for optimizing biodiesel yields from *Jatropha* oil using catalysts such as sulfated zirconia-alumina (Yee et al., 2011), H_2SO_4 and NaOH (Goyal et al., 2013). In addition a RSM Box-Behnken design was utilized for studying the effect of ultrasound in biodiesel synthesis from *Jatropha* (Choudhury et al., 2014b; Choudhury et al., 2013; Choudhury et al., 2014c) and soyabean (Choudhury et al., 2014a) oils.

The significant reaction parameters influence the JB production through the transesterification reaction that includes catalyst loading, methanol to oil ratio, reaction time,

heating temperature, and the stirring rpm among others were ascertained (ANR et al., 2016; Goyal et al., 2012; Okullo et al., 2010; Pradhan et al., 2012; Rashid et al., 2008). Many researchers have explored optimal parametric sufficiency as well as each reaction parameter over their minimum and maximum levels. The intrinsic impact of a parameter and their potential interactions to achieve the optimal FAME yield was investigated using the RSM as an optimization and statistical analysis tool (Choudhury et al., 2014b; Choudhury et al., 2013; Choudhury et al., 2014c; Dhingra et al., 2013a, 2014; Goyal et al., 2013; Kumar et al., 2007; Mansourpoor, 2012; Rajendra et al., 2009; Yee et al., 2011). The RSM was widely adopted based on three designs of CCD; CCRD (Kumar et al., 2007; Okullo et al., 2010; Rajendra et al., 2009) and Box-Behnken design (Choudhury et al., 2014b; Choudhury et al., 2013; Choudhury et al., 2014c) for obtaining optimal FAME. Many state-of-the-art studies have reported that the choice of reaction parameters directly contributes to the biodiesel conversion process as well as their interactions influence on the FAME yield at large. A combination choice of two (Kumar et al., 2007; Vicente et al., 1998), three (ANR et al., 2016; Choudhury et al., 2014b; Choudhury et al., 2013; Choudhury et al., 2014c; Kumar et al., 2007; Mansourpoor, 2012; Okullo et al., 2010; Rashid et al., 2008), four (Goyal et al., 2013; Goyal et al., 2012; Noshadi et al., 2012; Pradhan et al., 2012; Rajendra et al., 2009), and five (Dhingra et al., 2013a, 2014) reaction parameters were manipulated and studied by using RSM for a maximum FAME yield from various feedstocks.

The RSM based FAME optimization was noted in scholarly reports such as Vicente et al. (1998) who testified over two factors such as temperature (20°C-75°C), catalyst concentration (0.2-1.8 wt%) using sunflower oil in the presence of various homogeneous and heterogeneous catalysts (Vicente et al., 1998). A higher FAME conversion was reported over temperature (20°C-50°C) and catalyst concentration of 1.3 wt %. ANR et al. (2016) analyzed

the impact of three parameters including reaction time, catalyst ratio, and methanol to the *Jatropha* pretreated oil over FAME yield by utilizing the RSM model based on two-block-CCD (ANR et al., 2016). An optimal yield of 98.54% was at time 133.1 min, catalyst 0.02:1 (w/w), and methanol to the pretreated oil 5.15:1 mol/mol. Goyal et al. (2012) reported the impact of four reaction parameters including the methanol-oil ratio, reaction time, NaOH - catalyst concentration and temperature over transesterification of *Jatropha curcas* oil (Goyal et al., 2012). A CCD based four factor-five level was utilized to analyze the parametric impact on the FAME yield. An optimal FAME field of 98.3% was reported at 11:1 molar ratio, 1%w/w catalyst, 54°C temperature and 110 min time. Apart from this, Noshadi et al. (2012) synthesized biodiesel by the transesterification of waste cooking oil using heteropolyacid as catalyst in a reactive distillation column (Noshadi et al., 2012).

A CCD based RSM was followed to optimize the FAME yield considering four process parameters methanol-to-oil ratio, reboiler duty, feed temperature and feed flow. Rajendra et al. (2009) utilized the artificial neural networks (ANN) and genetic algorithm (GA) by developing a MATLAB program to reduce FFA in different vegetable oil feed stocks during the pretreatment of biodiesel production (Rajendra et al., 2009). Parameters such as vegetable oil acid value, catalyst concentration, methanol/oil ratio and time were considered for modeling. Subsequently, the RSM based CCRD was used to test ANN data set. Dhingra et al. investigated on Karanja (Dhingra et al., 2014) and *Jatropha* (Dhingra et al., 2013a) biodiesels production optimization by considering five reaction parameters using the RSM standalone and coupled with GA (Dhingra et al., 2014). Analysis of variance (ANOVA) R^2 of 84.55%, 84.27% and yields 94.2093%, 93.5% were noted respectively.

Among the reaction parameters considered for the optimal FAME yield investigations methanol to oil ratio, the catalyst concentration and reaction temperature were well studied over various feedstocks. From the literature, it is evident that other two primary reaction parameters stirring speed (Dhingra et al., 2013a, 2014; Okullo et al., 2010; Pradhan et al., 2012) and reaction time (ANR et al., 2016; Dhingra et al., 2013a, 2014; Goyal et al., 2013; Goyal et al., 2012) were less studied together with their impact on the transesterification reaction process. To the best of the literature survey a very scant work was accounted yet on the study of all the five transesterification reaction parameters that include catalyst loading, methanol to oil ratio, heating temperature, stirring speed and reaction time; which need to be under taken.

Apart from conventional analytical methods statistical based mathematical modelling techniques such as RSM were widely utilized for analysing the engine performance and emission analysis (Dhingra et al., 2013b; Khoobbakht et al., 2016; Kumar et al., 2007; Sivaramakrishnan & Ravikumar, 2013). RSM together with desirability approach facilitates to predict the input decision variables over a precise range within the optimal experimental rotations and also to analyse their factorial interactions on the response functions. Further, these approaches can be utilized for real-life problems comprising multiple objectives which need to be optimized simultaneously (Khoobbakht et al., 2016; Sivaramakrishnan & Ravikumar, 2013).

2.13 Diesel engine performance and exhaust emissions

A large number of studies were devoted to report on critical investigations on biodiesel fueled diesel engine performance and exhaust emission characteristics. A few scientific investigations analyzed the relevance of biofuel properties as well as their direct impact on

diesel engine performance, thermal efficiency and emissions (Chattopadhyay & Sen, 2013; Ong et al., 2014; Rao, 2011; Rizwanul et al., 2014; Shojaeefard et al., 2012; Sivaramakrishnan & Ravikumar, 2013).

Sivaramakrishnan & Ravikumar (2013) investigated on compression ratio influence on single cylinder, 4 stroke Kirloskar TV 1, DI engine performance include brake thermal efficiency (BTE) and brake specific fuel consumption (BSFC) and exhaust emissions (NO_x, HC, and CO) using Karanja biodiesel blended- PD fuel over B10-B50 (Sivaramakrishnan & Ravikumar, 2013). Optimal parameters include compression ratio of 17.9, B10 and engine power of 3.81 kW were obtained following RSM and desirability approach. From the test results of all fuel blends, while increasing of compression ratio contributes in increase of BTE, BSFC and NO_x on the other hand CO and HC emissions reduces. Chattopadhyay et al., (2013) studied Kirloskar diesel engine performance using cottonseed oil biodiesel blends B10 and B20 and they have reported that the BTE, BSFC and exhaust gas temperature (EGT) as well as reduction of exhaust emissions include CO, CO₂, smoke opacity and HC except NO_x as compared to PD (Chattopadhyay & Sen, 2013).

Shojaeefard et al. (2012) performed experiments on a 4-cylinder 4-stroke direct injection compression agricultural engine fueled with B30 castor biodiesel blends (Shojaeefard et al., 2012). The engine performance and exhaust emissions were predicted following ANN based methodology. The study reports on decline of engine power and increase in BSFC due to poor calorific value and higher density of castor biodiesel. Further, except NO_x, all other exhaust emissions were reduced to lower levels.

Ong et al. (2014) reported experimental evaluation of a CI diesel engine performance and exhaust emission results using biodiesel blends prepared from three feedstocks include

Jatropha, Calophyllum inophyllum and Ceiba pentandra. They have analyzed physicochemical properties of B10, B20, B30 and B50 biofuel blends. B10 blends of all biodiesels have resulted in high engine performance and shown a significant decrease in smoke opacity, CO₂ and CO and slight rise in NO_x exhaust emissions, and the variations are attributed to the biofuel properties. Rao (2011) investigated on JB properties influence on Kirloskar-AV1, DI-CI engine performance and emissions over various injection timing. Though higher engine performance and lower HC, CO, smoke density were noted, increase in combustion timing contributed in higher NO_x emissions due to high density of JB fuel as well as presence of unsaturated fatty acids, C18:1 and C18:2.

Rizwanul et al. (2014) analyzed physicochemical characteristics of Malaysian Alexandrian laurel biodiesel blends and investigated their influence on performance and emission characteristics utilizing B10 and B20 blend fuels. Experiments were conducted on a 4 cylinder IDI engine under varying engine speeds and constant load conditions. They have reported a decrease in brake power and increase in BSFC which are attributed to lower calorific value and higher viscosity of the biofuels. Further to note, apart from NO_x, lesser exhaust emissions were recorded. The reasons for 2.12% - 8.32% of higher NO_x were correlated with poor atomization due to high viscosity leading to delayed combustion. Additionally, higher oxygen contents of the blends reduces smoke opacity by 7.78% - 13.28% compared to PD. Apart from conventional analytical methods statistical based mathematical modelling techniques such as RSM and desirability approach were widely utilized for analysing the engine performance and emission analysis as well as to predict the input decision variables over a precise range within the optimal experimental rotations (Dhingra et al., 2013b; Khoobbakht et al., 2016; Kumar et al., 2007; Sivaramakrishnan & Ravikumar, 2013).

2.13.1 Advantages and disadvantages of diesel engines.

The numerous advantages of diesel engines comprises, the robustness of engine design enable it to bears higher levels of combustion pressures, hence they offer an extended engine life span besides, exhibits 15% higher efficiency in transforming fuel into mechanical energy. The diesel engines are suitable for fueling with alternative fuels such as biodiesels and vegetable/ waste cooking oils based fuels. Due to less flammability of diesel fuel, which causes diesel engine invulnerable to vapour lock causing lesser fire risks. Diesel engines provides sustained fuel efficiency at higher engine loads and produce high torque levels even at lower engine speeds. Also, it releases less heat in exhaust and cooling channels. The diesel engines can be operated with greater reliability, in spite of spark plugs, high tension leads and coils, therefore these engines are well suited for damp working conditions such as marine applications. Since the diesel engines releases lesser amount of CO₂ and CO emissions per unit utilization of they are suitable for underground applications (“Rapid racer,” 2016; Tan et al., 2015a).

The leading disadvantages of diesel engines lesser band range of engine rpm, rough and noisy in operation. They demonstrations lesser engine power to weight ratio, because of raised engine components strength to bear high pressures besides to run at low speeds. These engines needs high initial capital and also involves regular maintenance costs. (“Rapid racer,” 2016; Tan et al., 2015a).

2.14 Summary of literature review and research gap

The literature review indicates that biodiesel is a potential biofuel source to meet the phenomenally growing liquid fuel needs of the world. Furthermore, significant enhancement

in the biodiesel production across the globe would not only alleviates dependency on fossil fuels but also contributes in lowering greenhouse gas emissions at large. Feedstocks are the primary resource constraints for the biodiesel production. Therefore research and development of sustainable non-edible vegetable oil feedstocks would enable the biodiesel industries in continues production and supply of biodiesel. A very limited research has been devoted in exploring the impact of FAC on biodiesel physicochemical properties. This analysis would provide a fundamental knowledge in developing the sustainable non-edible feedstock resources.

These studies signifies that CaO can be a promising catalyst for biodiesel production. In the same way heterogeneous catalysts with lower particle sizes and a higher surface area contributes to enhancing the transesterification reaction rate. Further to note a very scant work, however, has been devoted to the synthesis of CaO as a nano catalyst that focuses on reducing the particle size and increasing the surface area for biodiesel production especially from the largely available sustainable waste resources such as seashells. It has been found that, a very insignificant research has been carried out in heterogeneous catalyst reusability, stability and leaching analysis. A very less works have been carried out on mathematical modelling of biodiesel blends fueled diesel engine performance and exhaust gas characteristics. These approaches would result in prediction of engine performance and exhaust gas emissions as well as optimization of the engine operating parameters.

CHAPTER 3

METHODOLOGY

3.1 Materials

Polymesoda erosa seashells were collected from a local village Muara Tebas, Sarawak, Malaysia. Laboratory grade chemicals that included methanol (MeOH) >99% pure), H₂SO₄ 95-97%, KOH, double distilled deionized water and calcium oxide (UNI-CHEM chemical reagents, CAS No.: 1305-78-8, M.W.56.08) were used as a reference catalyst. To get CJO originated from east Malaysian region, the *Jatropha* seeds were purchased from a local *Jatropha* agriculture farm sited in Asajaya, Sarawak, Malaysia. Then, CJO was extracted from their seeds using a hand operated nut and seed oil expeller at a mechanical engineering workshop, UNIMAS. Similarly the CJO originated from west Malaysian region was obtained from the energy laboratory stocks.

3.2 Synthesis of nano CaO catalyst

The nano CaO catalyst was prepared using calcination–hydration–dehydration of the *P. erosa* shells to obtain a fine powder following a technique reported by Niju et al. (Niju et al., 2014, 2016). Approximately 500 gm of *P. erosa* seashells were cleaned to remove the edible portion and any other impurities, rinsed thoroughly using distilled water, and then dried in a hot air oven at 105°C for 24h (Yoosuk et al., 2010a). The *P. erosa* shells were finely ground using a blender (Khind blender BL 1512, Malaysia) and then passed through an 80 µm sieve mesh. The micron-sized powder *P. erosa* shells were then calcinated in a chamber furnace (CWF23/13 23 Lt – 1300°C, Carbolite Ltd., U.K.) at 900°C for 2.5h. At 850°C, the calcium

carbonate of *P. erosa* shell powder decomposed to calcium oxide and carbon dioxide as presented in the reaction Eq. (4).

The CaO derived from the *P. erosa* shells was refluxed in water at 60°C for 6hrs and the solid particles were filtered and dried in a hot air oven at 120°C overnight (Yoosuk et al., 2010a). The solid powder was further ground in a Planetary Ball mill (Ritesh) at 200rpm for 3hrs and dehydrated by performing calcination at 600°C for 3hrs to change the hydroxide form to oxide form. Thus, the nano CaO catalyst was synthesized from *P. erosa* shells through the calcination–hydration–dehydration treatment.

3.3 Characterization of nano CaO catalyst

In order to investigate the chemical structure of the synthesized nano CaO catalyst, powder samples of CaO were tested using a Fourier Transform Infrared (FT-IR) Spectrophotometer (Model 100 series, Perkin Elmer) over a 4000 to 280 cm⁻¹ region. The sizes and shapes of the CaO nano-catalyst were obtained by using a Transmission Electron Microscope (TEM) (Hitachi H-7100, Japan). The surface area of nano-CaO, uncalcined *P. erosa* shell and reference-CaO catalyst were studied using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods which were applied to obtain the pore volume and pore diameter (Quantachrome instruments: autosorb iQ-AG-C). The samples of *P. erosa* shells synthesized CaO particle size distribution was studied using particle size distribution analyzer (PSA 1090, 0.04µm-500µm, CILAS, France). Nano-catalyst crystalline properties were investigated using X-ray diffraction (XRD) test from a Shimadzu 6000 X-Ray machine with nickel filtered Cu Kα ($\lambda = 1.542 \text{ \AA}$) radiation. The average crystallite size of the CaO nanoparticles was calculated from line broadening using Scherrer's equation: $D = \frac{0.9\lambda}{\beta \cos \theta}$

where ‘D’ crystalline size (in nm), ‘ λ ’ wavelength of X-ray ($\lambda = 1.542 \text{ \AA}$), ‘ β ’ full width at half maximum (FWHM—in radian) intensity and ‘ θ ’ Bragg diffraction angle ($^\circ$). XRD analysis was carried out over 20-80 $^\circ\text{C}$ at a rate of 2 $^\circ\text{C min}^{-1}$ and a scanning angle of 2θ .

3.4 Biodiesel production

Biodiesel production from CJO was carried out using the synthesized nano CaO catalyst by following standard laboratory procedures. The important transesterification reaction parameters were ascertained and analyzed in contrast with previous studies reported in literature (Deng et al., 2011; Okullo et al., 2010; Yee, 2014). Figure 3.1 describes the major steps involved in biodiesel production that include FFA estimation, acid pretreatment and transesterification using nano CaO catalyst which are comprehensively discussed in the following sections.

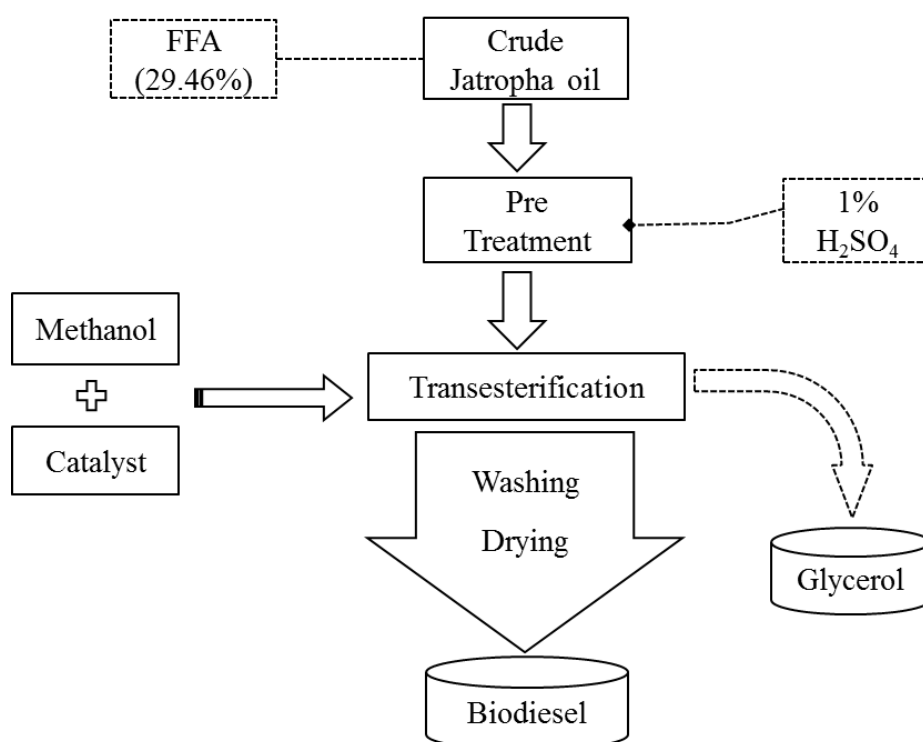


Figure 3.1: Jatropha biodiesel production via two step transesterification.

3.4.1 Acid pretreatment

CJO acid pretreatment was carried out by designing an experimental protocol as reported by (Deng et al., 2011) and (Yee, 2014). The FFA content was estimated in terms of KOH in mg in order to neutralize one gram of fatty acid methyl ester. i.e., 0.1M of KOH was diluted with ethanol, as reported in literature (Azhari, Faiz & Yunus, 2008; Berchmans & Hirata, 2008). Next, 2 ± 0.5 g of CJO together with 50mL solvent consisting of 95% ethanol and diethyl ether in a 1:1 molar ratio were thoroughly mixed in a conical flask using a magnetic stirrer. Titration was carried out by adding a few drops of phenolphthalein to the mixture with the KOH solution when continuously stirred until the color of solution turned pink and lasted for 10 seconds. This was repeated three times for accuracy and the FFA content was measured at 29.47%.

In order to improve the conversion rate for maximum biodiesel yield, the FFA content in CJO was minimized or removed by following a two-step transesterification (Jaliliannosrati et al., 2013). For the first step, acid esterification known as acid pretreatment was performed with H_2SO_4 . Filtered 25 mL of the CJO was heated over 100°C to remove the water content. A mixture of H_2SO_4 and MeOH was prepared by adding the catalyst/ alcohol at a proportional ratio with CJO, by volume, in a three-neck flask fitted with a water cooled condenser setup and heated to 50°C . The CJO sample was added to the mixture, which was continued to heat at 50°C and using a magnetic stirrer at 200rpm. The contents were allowed to settle for 1 hour after the reaction. The oil was washed three times with distilled water and then the oil was separated and heated to remove the water content. Within the CJO, the FFA value was reduced to a minimum value i.e., 1% which is suitable for base catalyzed transesterification (Berchmans & Hirata, 2008).

3.4.2 Transesterification using nano CaO catalyst

The pretreated oil, as obtained in acid pretreatment, which had a minimum FFA value was used together with a highly active nano CaO catalyst for catalyzed transesterification. A mixture of the nano CaO catalyst (0.01-0.03 w/w) was in powder form and methanol, (4-6 mol.) by ratio were prepared and added to the pretreated CJO. The reactants were allowed to react at a stirring speed of 500 rpm and at 60°C for a period of 60 min. to 180 min. The mixture was shaken at 250 rpm for 2 hours using an orbital shaker at room temperature and then allowed to settle for 24 hours. Biodiesel was separated from glycerol, while the methanol-water layer was washed using distilled water. The filtered biodiesel was heated to 100°C while continuously stirred using a magnetic stirrer in order to get moisture free biodiesel.

3.4.3 Design of experiments for maximum JB yield

An experimental model is designed to analyze the transesterification reaction kinetics along with the effects of different reaction parameters, including catalyst concentration, reaction time and methanol ratios were used to optimize the JB yield. A typical RSM three-factor-five-level CCD full factorial two-block model was utilized for the design of experiments and optimization. Using the designed model objective function, JB yield was fitted as a quadratic surface to further optimize dependent factors within a specific sphere for an optimum number of experimental iterations and to analyze linear, quadratic and factorial interactions among different factors (Kumar et al., 2007).

Table 3.1: Factors and levels for transesterification process.

Factor		Level				
		-1.633	-1	0	1	1.633
Catalyst-to-pretreated oil ratio (C)	w/w	0.01	0.014	0.02	0.026	0.03
Reaction time (T)	min.	60	83.3	120	156.7	180
Methanol-to-pretreated oil ratio (M)	mol.	4	4.39	5	5.61	6

The model was built to maximize the dependent factor, and JB yield was the response during transesterification. The catalyst concentration-to-pretreated oil (C), reaction time (T) and methanol-to-pretreated oil (M) were considered as the independent parameters (factors) of the transesterification process to explore their effects on the response. In Table 3.1, the actual levels of the three independent factors together with uncoded and coded values were enlisted. For each combination of levels, with the exception of the center and coded point, a pair of iterations was performed for the remaining points positioned at the factorial and axial levels. Random run order was used for all transesterification iterations to minimize redundancy. For CCD, the distance between the central and axial points is denoted with an ‘ α ’, which acts as a key element in the metamorphosis of the factor levels (Kumar et al., 2007). The present model default ‘ α ’ was 1.633. Metamorphosis of the factors into coded (X) levels to the uncoded levels were obtained from the equations $C = 0.02 + 0.006X$, $T = 120 + 36.7X$ and $M = 5 + 0.61X$.

3.4.4 Model fitting and statistical analysis

The experimental data obtained were analyzed by response surface regression procedure using second-order polynomial as stated in equation Eq. (6)

$$Y = \beta_0 + \sum_{i=1}^3 \beta_i k_i + \sum_{i=1}^3 \beta_{ii} k_i^2 + \sum_{i < j=1}^3 \sum_{j=1}^3 \beta_{ij} k_i k_j \quad (6)$$

Where ‘Y’ is the percentage JB yield; k_i and k_j are the actual independent factors in uncoded form and $\beta_0, \beta_i, \beta_{ii}$ and β_{ij} are intercept, linear, quadratic and interaction constant coefficients respectively. Minitab®16.2.1 software was utilized for response surface regression analysis and ANOVA of the designed model. Confirmatory experiments were performed to validate Eq. (6).

3.5 Transesterification with reference catalyst

The catalytic activity of the synthesized nano CaO catalyst was compared during transesterification of CJO with a commercial CaO catalyst (UNI-CHEM chemical reagents). The commercial CaO was dried in a hot air oven for 2hrs at 100°C before being used as a catalyst. Biodiesel yield optimization experiments were carried out with pretreated CJO so as to obtain optimal reaction parameters using commercial CaO catalyst. At optimal reaction parameters the biodiesel yield conformation experiments were conducted for three successive cycles. The biodiesel yield results were compared with JB yield as obtained using *P. erosa* synthesized nano CaO catalyst.

3.6 Reusability experiments of *P. erosa* synthesized nano CaO and commercial CaO

The catalyst stability and reusability are the major concerns encountered by calcium-based catalysts in the production of biodiesels. This is due to leaching of CaO to other reactant contents during transesterification (Prasertsit et al., 2014; Thitsartarn & Kawi, 2011). Therefore, the reusability of the synthesized nano CaO catalyst was studied by carrying out nine cycles of catalyst reuse reactions, including the fresh cycle. After the first cycle of

transesterification, the mixture was centrifuged at 2000rpm to precipitate the CaO catalyst and this was then washed thrice with n-hexane to remove glyceride residues. This was then dried in an oven overnight and recalcinated at 600°C for 2hrs before reusing. This process was continued for all successive reaction cycles, performed at optimal transesterification parametric conditions i.e., 0.02:1 (w/w) catalyst, 133.1 min. reaction time and 5.15:1 mol. of methanol, to the pretreated oil. Surface morphology of reused catalyst was examined by scanning electron microscopy (SEM, Hitachi TM3030). The biodiesel obtained from each reusability study cycle was tested using an atomic absorption spectrometer (AA-7000, Shimadzu, calcium '422.7nm' hollow cathode lamps as radiation source) and to measure the amount of calcium ions (Ca^{2+}) concentration leached into the biodiesel. The reusability experiments of commercial CaO catalyst were performed using optimal transesterification reaction parameters as obtained from fresh commercial CaO use. After the first use the catalyst was recycled as described above and reused and the JB yield was compared with nano CaO catalyzed JB yield.

3.7 Biodiesel characterization and fuel physicochemical properties analysis

The Jatropha biodiesel produced using CJO from east Malaysian region (Asajaya, Sarawak) is denoted with JB_{EM} or JB in general. The presence of FAME absorption bands in the biodiesel samples was investigated utilizing a Fourier Transform Infrared (FT-IR) spectrophotometer (Model 100 series, Perkin Elmer) over a 4000 to 750 cm^{-1} region. In order to analyze the influence of a feedstock fatty acid composition on biodiesel physicochemical properties, Jatropha biodiesel was produced utilizing CJO originated from west Malaysian region which is referred as JB_{WM} . The FAC of both JB_{EM} and JB_{WM} fuel samples (B100), were measured using a high-end gas chromatograph (GC-2010 Plus, Shimadzu) equipped

with flame ionization detector (FID-2010 Plus) and a ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$) capillary column (following EN 14105 standard method).

3.8 Preparation of Jatropha biodiesel - petro diesel blends and analysis of physicochemical properties

The biofuel blends of Jatropha biodiesel (both JB_{EM} and JB_{WM}) and petro diesel (PD) were prepared in the ratios of their volumes at a temperature of 26°C . The code B100 symbolizes pure JB. The biofuel samples of B5 (5% JB + 95% PD), B10 (10% JB + 90% PD), B15 (15% JB + 85% PD), B20 (20% JB + 80% PD), and B25 (25% JB + 75% PD) were blended. The fuel samples were stirred at 2000 rpm for 30 min using a motor stirrer to obtain homogeneous mixture and kept in vacuum tight sampling bottles. The fuel properties of B100 and JB - PD blend samples that includes acid value, calorific value, cetane number, cloud point, density at 15°C , flash point, kinematic viscosity at 40°C , oxidation stability and pour point were measured. The fuels were characterized using testing apparatus built on ASTM D6751 and EN14214 standards. The fuel testing equipment measuring resolution together with testing standard and uncertainty values were shown in Table 3.2. The fuel characterization protocols were repeated thrice sequentially to ensure precision in measurements and the mean data was reported.

Table 3.2: Jatropha biodiesel and blends fuel properties analysis equipment.

Biodiesel fuel property	Analyser (Make)	Testing standard	Resolution	Uncertainty
Acid value (mg KOH/g)	Automation titratio rondo 20 (Mettler Toledo, Switzerland)	ASTMD664 and EN14111	± 0.001 deviation 0.001%	
Calorific value (MJ/kg)	Bomb calorimeter, 6100 EF Semi auto (Perr, USA)	ASTM D240	± 0.001	± 1.15
Cetane number	Ignition quality tester, 92000-3, IQT TM (Stanhope-Seta, UK)	ASTM D6890	± 0.1	
Cloud point (°C)	Cloud and pour point tester, NTE 450 (Normalab, France)	ASTM D2500	± 0.1	
Cold filter plugging point (°C)	CFPP – Automatic NTL 450 (Normalab, France)	ASTM D6371	± 0.1	

Table 3.2 continued

Density at 15°C (kg/m ³)	Density meter DM40 LiquiPhysics™ (Mettler Toledo, Switzerland)	ASTM D127	±0.1	±0.05
Flash point (°C)	Flash point tester, NPM 440 Pensky- martens (Normalab, France)	ASTM D93	±0.1	±0.26
Iodine value (g I ₂ /100 g)	Automation titratio rondo 20 (Mettler Toledo, Switzerland)	ASTMD664 and EN14111	± 0.1 deviation 0.001%	
Kinematic viscosity at 40 °C (mm ² /s)	Viscometer NVB classic (Normalab, France)	ASTM D445	±0.01	±1.39
Oxidation stability, hr. at 110 °C	873 Rancimat (Metrohm, Switzerland)	EN 14112	±0.01	
Pour point (°C)	Cloud and pour point tester, NTE 450 (Normalab, France)	ASTM D97	±0.1	
Water content (Wt %)	Coulometer, 837 KF (Metrohm, Switzerland)	EN ISO 12937	±0.001%	

3.9 Optimization of biodiesel fuelled diesel engine performance and exhaust emissions

The biodiesel fuelled diesel engine performance and exhaust gas emissions were optimized by developing a mathematical model based on multi-criteria regression analysis combined with desirability approach. The engine operating parameters that include engine operating speed (S), JB-PD fuel blends (B) and Torque (T) were considered for building the mathematical model. The boundary conditions of these parameters were defined by adopting the published experimental data by the engine research group, Department of Mechanical Engineering, University Malaya (UM), Malaysia (Ong et al., 2014). The schematic and specifications of diesel engine testbed and gas analyser were presented in Appendix A.

3.9.1 Mathematical modelling of engine performance and exhaust emissions

A full factorial three-factor- five-level, two-block, CCD based RSM mathematical model was employed to predict the engine performance and exhaust emissions and to analyse the influence of input parameters on the response functions. The engine operating speed (S), JB-PD fuel blends (B) and Torque (T) were selected as primary decision variables. According to the model's design, the objective function, response was set to fit as a quadratic surface and the input decision variables were optimized.

In Table 3.3, the levels of three uncoded decision variables both in actual and coded forms were shown. A second order polynomial regression equation, Eq. (5), was applied to predict the DI-CI engine performance and exhaust emissions experimental results. Analysis of variance (ANOVA) and response surface regression analysis of the designed models were analysed by utilizing Minitab®16.2.1, statistical software.

Table 3.3: Diesel engine operating parameters and constraints for optimization.

Uncoded variable	Symbol	Levels				
		-1.633	-1	0	1	1.633
Engine speed (rpm)	S	1700	1800	1900	2000	2100
Jatropha biodiesel - petro diesel blend (%)	B	B5	B10	B15	B20	B25
Torque (N.m)	T	28	30	32	34	36

In the present research, three engine operating parameters (engine speed, JB-PD blending percentage and torque) were predicted for the optimal responses that include engine performance (BP, BSFC, BTE and EGT) and emissions (NO_x, HC, CO₂, CO and smoke opacity) by employing a desirability approach based response surface optimizer of Minitab®16.2.1 statistical software. The desirability value of a response may ranges between ‘0’ (undesirable) and ‘1’ (most desirable). However, each response function may be set to optimize through minimize, maximize or a specific goal by which its desirability is obtained. The overall desirability of multiple response functions is obtained by their relative importance ranking over other responses. The optimal engine performance and emission results were compared with the experimental results published by UM engine research group.

3.10 Summary of methodology

This chapter detailed methodology for accomplishing all the objectives. In short, a laboratory scale synthesis protocol ‘calcination–hydration–dehydration’ was employed to produce nano CaO from indigenous aquatic seashells *P. erosa*. The synthesized nano CaO was fully characterized using spectrometric techniques including FT-IR, XRD, TEM, BET and AAS. Jatropha biodiesel was produced using crude Jatropha oil in the presence of nano CaO

catalyst and methanol via two-step transesterification. The nano CaO catalyst reusability, stability and leaching were studied over nine reusability cycles. The impact of fatty acid composition on fuel properties of *Jatropha* biodiesel as produced from the feedstocks originated from the east and west Malaysian regions was analyzed according to ASTM D6751 and EN 14214 standard protocols. A mathematical model based on RSM and CCD was followed to predict engine performance and exhaust emission characteristics considering engine speed, JB-PD blending ratios and torque as input parameters at various levels. The parameters were analyzed and optimized employing response surface and desirability approaches.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characteristic analysis of nano CaO catalyst

4.1.1 IR spectra analysis of nano CaO catalyst

The IR spectra of the nano CaO catalyst sample, as shown in Figure 4.1, had a strong broad absorption band at wave numbers $< 600\text{ cm}^{-1}$, which was attributed to the Ca–O group stretching vibrations along with a few weak bands at around 3639 cm^{-1} , 1469 cm^{-1} and 854 cm^{-1} as well. As reported by Mcdevitt & Baun, (1964) and others (Nasrazadani & Eureste, 2008; Zaki et al., 2006) at wave numbers near 400 cm^{-1} and a strong IR absorption band at approximately 290 cm^{-1} with a medium IR band of Ca–O lattice vibrations clearly represents CaO. A medium and sharp absorption bands 1787 cm^{-1} and 1082 cm^{-1} vibrations demonstrating C=O group was noted. However, a weak and medium absorption band occurred at around 3640 cm^{-1} , 1442 cm^{-1} and 669 cm^{-1} - 617 cm^{-1} respectively, due to the asymmetric bending vibration modes of the hydroxyl ‘O–H’ and carbonyl ‘C=O’ groups. According to Margaretha et al. (2012), this mainly happened due to atmospheric moisture and CO_2 absorption onto the calcinated catalyst surface and which lead to the eventual formation of Ca(OH)_2 and CaCO_3 (Margaretha et al., 2012).

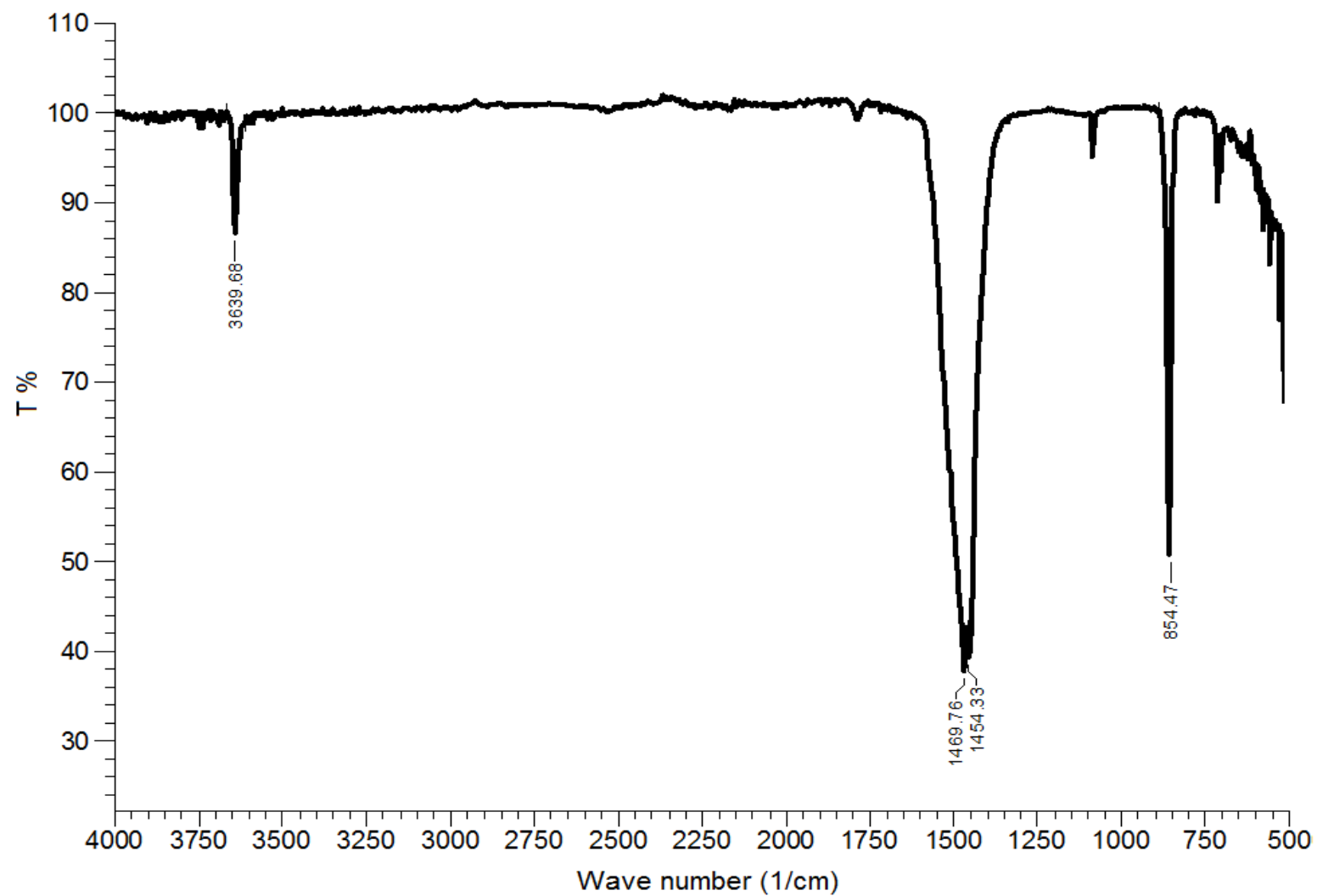


Figure 4.1: IR spectrum of CaO catalyst as synthesized from *P. erosa* shells.

4.1.2 TEM analysis of nano CaO catalyst

TEM analysis was carried out to determine the morphology, size and crystalline nature of the synthesized nano CaO catalyst. TEM images of the CaO nanoparticles showed rod (a) and spherical (b) shape as shown in Figure 4.2. The average sizes of the CaO nanoparticle from TEM images were 66.2nm and 548.7nm for those that were spherical or rod-shaped, respectively. This agrees with results of previous studies (Mirghiasi et al., 2014). From the TEM image, it was found that the CaO nanoparticles agglomerated, likely due to their high specific surface area and strong tendency to form aggregates.

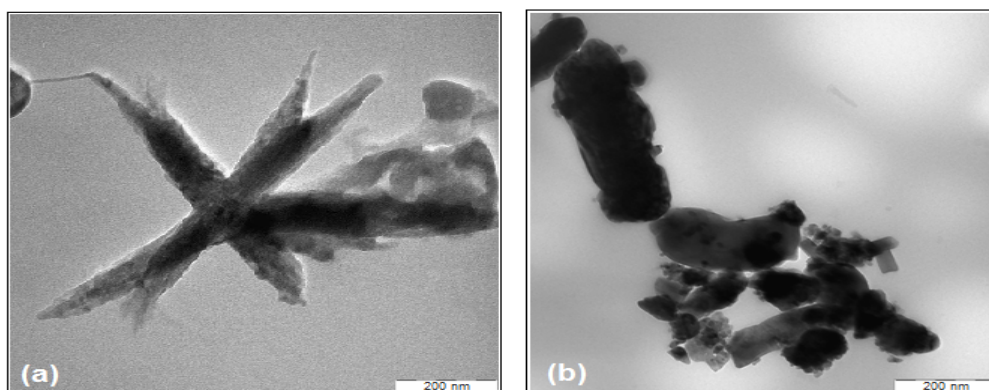


Figure 4.2: TEM images of nano CaO catalyst (a) Rod shape (b) Spherical shape.

4.1.3 BET and BJH analysis of nano CaO catalyst

The BET and BJH results of the newly synthesized nano CaO, unclacined *P. erosa* and reference CaO catalysts had surface areas of 90.61 m²/g, 4.8 m²/g and 36.6 m²/g, average pore diameters of 34.351 nm, 9.154 nm and 13.86 nm and pore volumes of 0.778cc/g, 0.011 cc/g and 0.126 cc/g, respectively. The reported average pore diameter of catalyst materials are between 2 nm – 50 nm, which represents mesopores and illustrates their suitability as a catalyst, adsorption, energy storage and also indicates the presence of active sites at the nano-

CaO catalyst external surface (Ren, Ma, & Bruce, 2012). The newly synthesized nano CaO catalyst from *P. erosa* seashells reported in this research has a higher surface area.

4.1.4 Particle size analysis of nano CaO catalyst

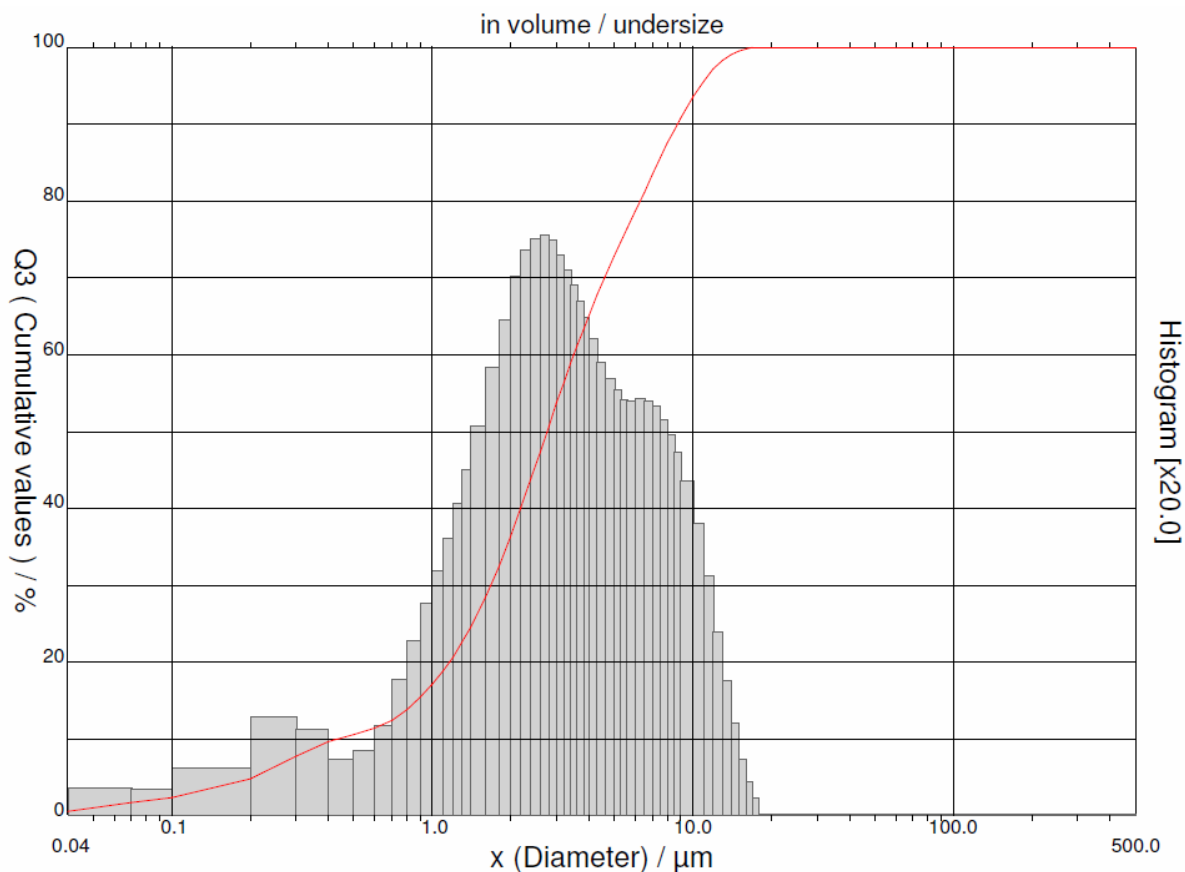


Figure 4.3: Particle size distribution of nano CaO catalyst synthesized from *P. erosa* shells.

The *P. erosa* seashells synthesized CaO particles demonstrated bimodal particle sizes as shown in Figure 4.3. The particle sizes are in the range of 0.44μm-6.55μm with a mean particle size of 3.62μm. The difference in mean and median particle sizes of nano CaO catalyst synthesized from *P. erosa* shells is very less. Therefore the ‘calcination-hydration-dehydration’ synthesis protocol caused a mix of micro and nano catalyst particles together

with a few large agglomerates. The results are comparable and consistent with the literature reports of Tan et al. (2015b).

4.1.5 XRD analysis of nano CaO catalyst

The XRD pattern of the CaO nanoparticles are depicted in Figure 4.4, which reveals a sharp diffraction pattern of CaO and miller indices values (h, k, l) at plane (0,1,2), (1,0,0), (1,0,4), (2,0,0), (2,0,0), (2,2,0), (3,1,1) and (2,2,2) corresponding to 2θ values 23.16° , 29.54° , 36.1° , 39.56° , 43.3° , 48.64° , 57.62° and 60.84° respectively. These patterns are consistent with a standard card of a calcite CaO powder sample (JCPDS file No. 00-037-1497). The crystalline sizes of the CaO nanoparticles were calculated and found to be 66.3nm and a similar result was reported in literature by other researchers (Mirghiasi et al., 2014; Taufiq-Yap et al., 2015).

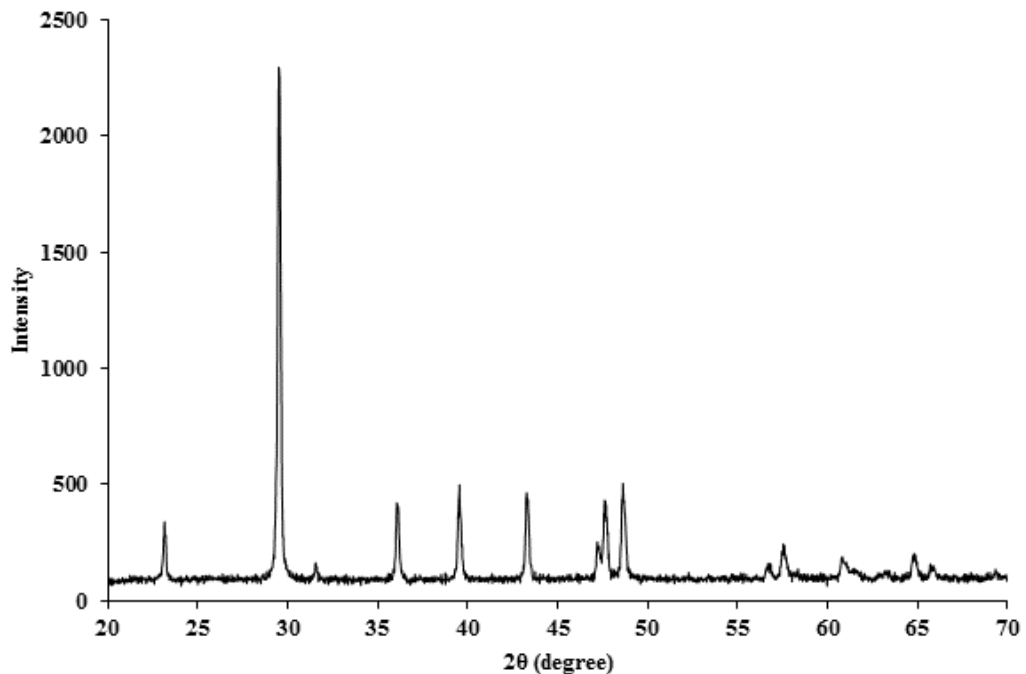


Figure 4.4: XRD pattern of nano CaO catalyst as prepared from *P. erosa* shells.

In this study, nano CaO catalyst was synthesized from *P. erosa* seashells and had a relatively high surface area and a small particle size and hence we state it as a ‘highly active’ nano CaO catalyst. This could improve catalyst diffusion drawbacks and led to better flow channels, rapid interactions between the reactants and subsequently refines the catalytic activity of nano CaO to improve transesterification reaction kinetics (Buasri et al., 2013b; Teo et al., 2015; Thiele, 1939).

4.2 Jatropha biodiesel production and yield analysis

4.2.1 CJO Acid pretreatment

Biodiesel synthesis is highly influenced by the FFA value of CJO. The oil sample has a high FFA content, leading to lower biodiesel yields, especially during transesterification reactions when catalyzed by solid catalysts (Deng et al., 2010; Deng et al., 2011; Jaliliannosrati et al., 2013). Experimental results of sulphuric acid pretreatment to CJO are graphically summarized in Figure 4.5. Different proportions of the acid catalysts ranging from 1% - 6% to CJO ratio by volume for various acid concentrations were reported. It was evident that at 1% of H₂SO₄ the results showed that the FFA value of CJO was reduced to 1%, which is fairly adequate for the next step of transesterification i.e., nano CaO catalyzed transesterification process (Jaliliannosrati et al., 2013).

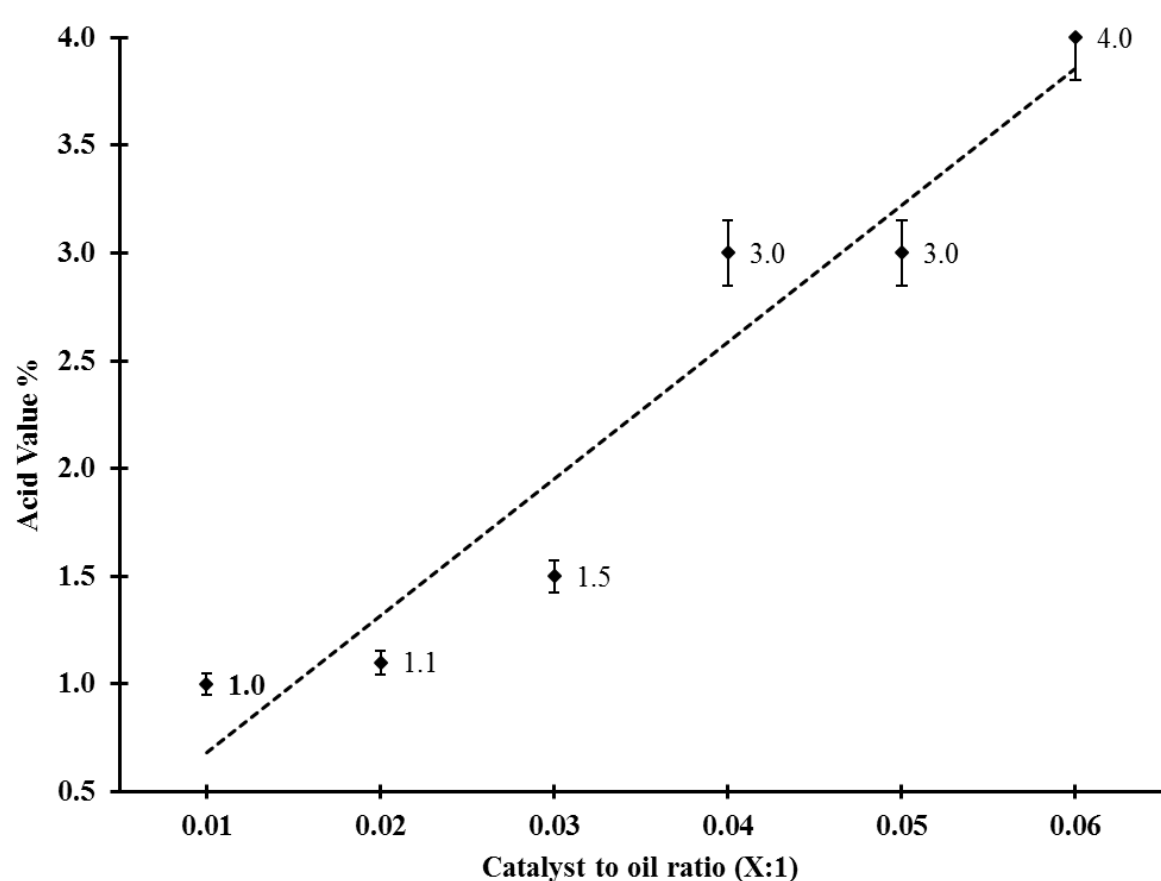


Figure 4.5: Reduction of free fatty acid percentage from crude Jatropha oil using H_2SO_4 catalyst.

Results of various proportions of alcohol to ester yields and reaction time to ester yields were presented to identify the optimum condition for the highest ester yield as shown in Figure 4.6, and eventually the ester yield increased proportionally with increased methanol percentages up to a certain level. However, at 60% of methanol to oil ratio (by volume) the highest ester yield of 98.4% was reported as optimal. From reported observations, during acid pretreatment, ester yields continuously decrease with increasing reaction time and hence, it was observed that the optimum reaction time for acid pretreatment was 1 hour only. Furthermore, an increase in reaction time did not contribute to any higher percentage of conversion due to the possible reversible process of esterification (Deng et al., 2010).

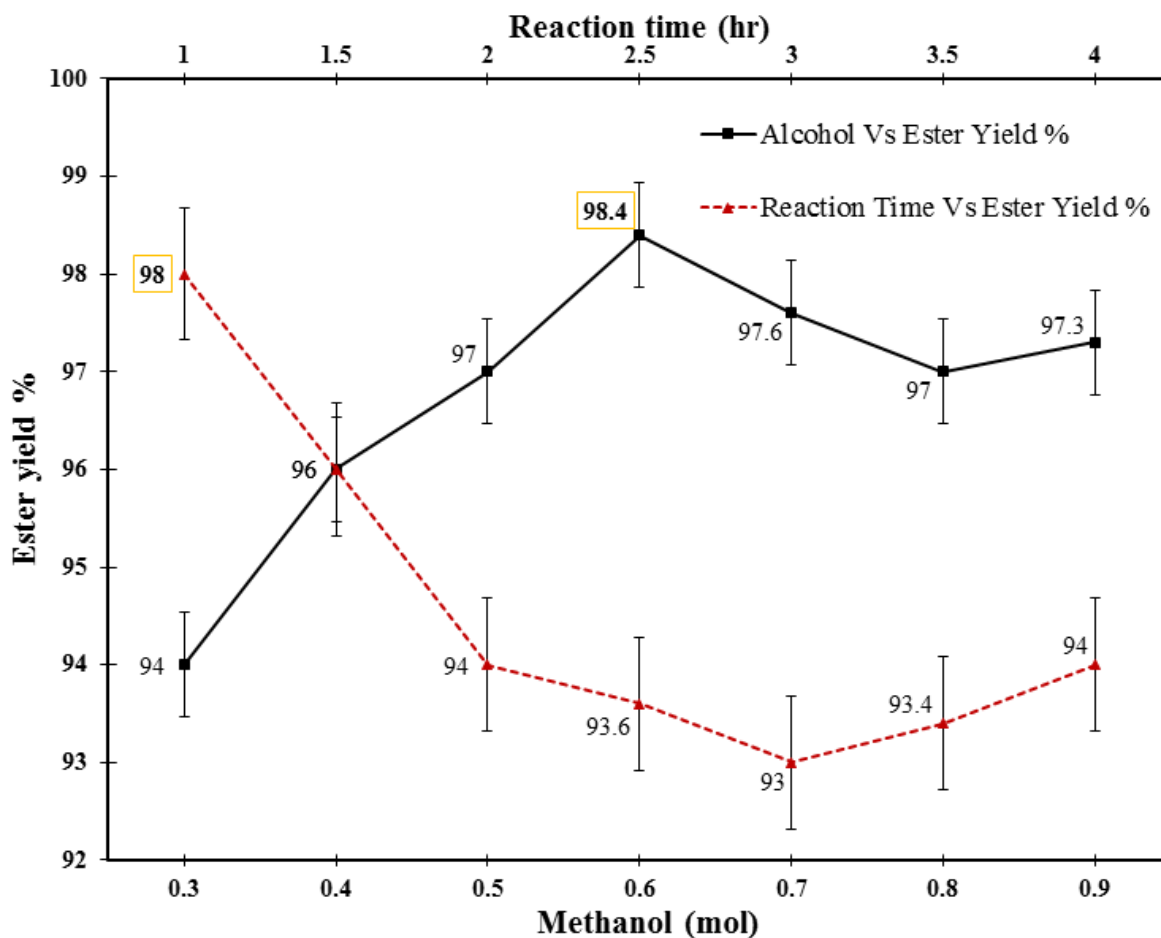


Figure 4.6: Effect of Methanol to oil ratio (mol) and Reaction time (hr) on ester yield.

4.2.2 CCD analysis for transesterification and prediction of JB yield

The summary of the two block, three factor – five level, full factorial CCD results matrix are presented in Table 4.1. The JB yield percentage obtained from the experimental results as well as the regression model predictions as a response to the coded and uncoded sets are shown in Table 4.1. A total of 20 random experimental iterations were conducted to analyze the effects of uncontrolled factors. A standard order, as marked in Table 15, was followed for all iterations in which six iterations corresponding to the axial points in combination with factors at either its minimum (-1.633) or maximum (1.633) level while the others were at zero. Six iterations were conducted to determine the experimental error, at the central point,

as well as the adequacy of the data sets and the remaining eight iterations were performed at factorial levels. The comparative results of the experimental yield and predicted percentage of JB yield are graphically shown in Figure 4.7. It can be noted that the predicted JB yield and experimental results were very closely adjoining; indeed, this indicates the reliability of the model investigated and since there is an intimate interaction among the selected three independent input parameters and the dependent response parameter on the JB yield.

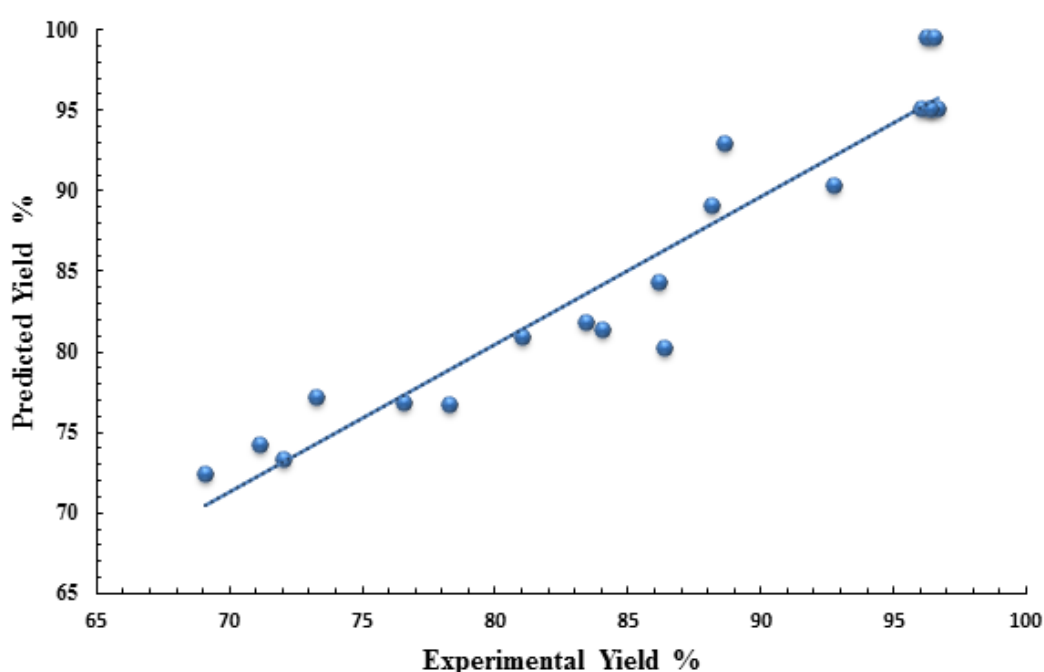


Figure 4.7: Comparative graph between experimental and predicted yield percentage of Jatropha biodiesel.

Table 4.1: CCD matrix for prediction of Jatropha biodiesel yield.

Run	Standard	Point	Block	Levels of experimental Factor values: Actual (Coded)			Yield	Prediction
Order	Order			Catalyst	Time	Methanol	(%JB)	
				C: (w/w)	T: (Min)	M: (Mol.)		
1	20	Center	2	0.02 (0)	120.00 (0)	5.00 (0)	96.3	99.42
2	13	Axial	2	0.01 (-1.633)	120.00 (0)	5.00 (0)	81.1	80.85
3	14	Axial	2	0.03 (1.633)	120.00 (0)	5.00 (0)	83.5	81.76
4	19	Center	2	0.02 (0)	120.00 (0)	5.00 (0)	96.6	99.42
5	18	Axial	2	0.02 (0)	120.00 (0)	6.00 (1.633)	88.2	89.04
6	17	Axial	2	0.02 (0)	120.00 (0)	4.00 (-1.633)	84.1	81.28
7	15	Axial	2	0.02 (0)	60.00 (-1.633)	5.00 (0)	86.4	80.20
8	16	Axial	2	0.02 (0)	180.00 (1.633)	5.00 (0)	88.7	92.92
9	5	Fact	1	0.01 (-1)	83.26 (-1)	5.61 (1)	72.1	73.21
10	8	Fact	1	0.03 (1)	156.74 (1)	5.61 (1)	92.8	90.26
11	10	Center	1	0.02 (0)	120.00 (0)	5.00 (0)	96.4	95.08

Table 4.1 continued

12	1	Fact	1	0.01 (-1)	83.26 (-1)	4.39(-1)	73.3	77.16
13	11	Center	1	0.02 (0)	120.00 (0)	5.00 (0)	96.1	95.08
14	6	Fact	1	0.03 (1)	83.26 (-1)	5.61 (1)	71.2	74.17
15	3	Fact	1	0.01 (-1)	156.74 (1)	4.39(-1)	78.3	76.65
16	2	Fact	1	0.03 (1)	83.26 (-1)	4.39(-1)	69.1	72.32
17	7	Fact	1	0.01 (-1)	156.74 (1)	5.61 (1)	86.2	84.31
18	4	Fact	1	0.03 (1)	156.74 (1)	4.39 (-1)	76.6	76.81
19	12	Center	1	0.02 (0)	120.00 (0)	5.00 (0)	96.7	95.08
20	9	Center	1	0.02 (0)	120.00 (0)	5.00 (0)	96.4	95.08

4.2.3 Regression model analysis for optimal JB yield

The summary of the multiple regression coefficients of the model obtained from the statistical software Minitab®16.2.1, are shown in Table 4.2. The significance of each coefficient that was determined, is presented by the P value (probability). Regression coefficients β_1, β_2 and β_3 represent linear factors 'C' 'T' and 'M'; β_{11}, β_{22} and β_{33} represent quadratic coefficients C^2, T^2 and M^2 whereas β_{12}, β_{13} and β_{23} represents factorial interaction coefficients 'CT', 'CM' and 'TM' of factors 'C' 'T' and 'M', respectively, and these were significant. The JB yield percentage of prediction along with the determined coefficients are presented in Eq. 7. The impact of the regression coefficients on the response rely on the sign antecedent to the coefficient.

The negative sign contributed to the combative impact and the coadjuvancy impact was by a positive sign. Based on Eq.7, all three linear factors 'C' 'T' and 'M' and the interactions 'CT', 'CM' and 'TM' contributed to a significant combative impact on the JB yield, whereas the quadratic intercepts C^2, T^2 and M^2 have reciprocal impact on the JB yield percentage. Further, it is noted from the summary of Table 4.2., that among the three linear terms, β_1 denotes the catalyst concentration that had the highest impact on the JB yield since ' β_1 ' reported the highest P-value of 0.803. Meanwhile, ' β_{12} ' ' β_{13} ' representing the interactions 'CT: (catalyst concentration) x (reaction time)' and 'CM: (catalyst concentration) x (methanol ratio)' had P-values of 0.395 and 0.327, respectively, which showed similar impacts on the JB yield.

Table 4.2: Estimated regression coefficients for biodiesel yield.

Coefficient	Value	SE	T	P
Constant				
β_0	97.2511	1.6201	60.03	0
Block	-2.173	0.9035	-2.405	0.04
Linear				
β_1 (C)	0.4555	1.7704	0.257	0.803
β_2 (T)	6.3633	1.7704	3.594	0.006
β_3 (M)	3.8819	1.7704	2.193	0.056
Quadratic				
β_{11} (C ²)	-18.1155	2.905	-6.236	0
β_{22} (T ²)	-12.8655	2.905	-4.429	0.002
β_{33} (M ²)	-14.2655	2.905	-4.911	0.001
Interaction				
β_{12} (CT)	3.3334	3.7324	0.893	0.395
β_{13} (CM)	3.8667	3.7324	1.036	0.327
β_{23} (TM)	7.7334	3.7324	2.072	0.068

Meanwhile, the interaction ‘TM: (reaction time) x (methanol ratio)’ (P-value: 0.068) had a much smaller effect compared to the other interactions. Critically, from both signs of the regression coefficients and their respective P-values, the linear terms ‘C’, ‘T’, and ‘M’ and the corresponding interaction terms ‘CT’ and ‘CM’ were significant. Further, the P-values for all the three quadratic terms were between 0 – 0.002, which conformed that quadratic interactions had no impact on the JB yield. The regression model equation was

found to provide a very accurate description of the experimental data, indicating that it was successful in capturing the correlation between the factors to the yield of JB.

$$\text{JB Yield} = +97.2511 + 0.4555 C + 6.3633 T + 3.8819 M - 18.1155 C^2 - 12.8655 T^2 - 14.2655 M^2 + 3.3334 CT + 3.8667CM + 7.7334TM \quad (7)$$

4.2.4 ANOVA for biodiesel Yield

Sufficiency of the regression model was verified through analysis of variance (ANOVA) as shown in Table 4.3. The regression model had a strong effect at the 95% confidence level and conformed to the tests conducted. The transesterification experimental factors considered in this study had an impact of 91.92% (R^2) as a total variation and 82.94% of adj R^2 . This indicates a high correlation and close performance predictions of the model. Moreover, the P-value for the associated model was 0.001, which further indicates its direct implication, precision and fitness.

In addition the P-value for lack-of-fit marked 'null', shows sufficiency to the overall model, with a P-value of 0.016 for the linear factors that include catalyst concentration (C), reaction time (T) and methanol ratio (M); a P-value of 0.177 for factorial interactions (CT, CM and TM) which emphasizes their direct impact on the JB yield. Further, square or quadratic terms (C^2 , T^2 and M^2) impact is null on the JB yield since the corresponding P-value was zero.

Table 4.3: ANOVA for Jatropha biodiesel yield.

Source	DF	Sum of Squares	Adj Sum of Squares	Adj Mean of squares	F-Value	P-Value
Blocks	1	90.65	90.66	90.658	5.78	0.04
Regression	9	1513.91	1513.91	168.212	10.73	0.001
Linear	3	278.84	278.84	92.946	5.93	0.016
Square	3	1138.47	1138.47	379.49	24.21	0
Interaction	3	96.6	96.6	32.2	2.05	0.177
Residual Error	9	141.05	141.05	15.672		
Lack-of-Fit	5	140.82	140.82	28.165	500.71	0
Pure Error	4	0.22	0.22	0.056		
Total	19	1745.61				
$R^2 = 91.92\%$		Adj. $R^2 = 82.94\%$				

4.2.5 Impact analysis of transesterification parameter - interaction

Distinctive impacts of catalyst concentration (C), reaction time (T) and methanol to pretreated oil ratio (M) on the response JB yield are depicted graphically in contour and surface plots in Figure 4.8 (a-c). The results shown in Figure 4.8(a) indicates that there is a precise impact of C and T factors on the response parameter JB yield. The response with regards to increased reaction time from 60 min, starting from a catalyst concentration of 0.001 w/w, proportionately increased to mean values of 120 min and 0.02 w/w, and beyond this the response become saturated. It was also noted that at 98% and above the JB yield was possible with an appropriate combination of these two parameters.

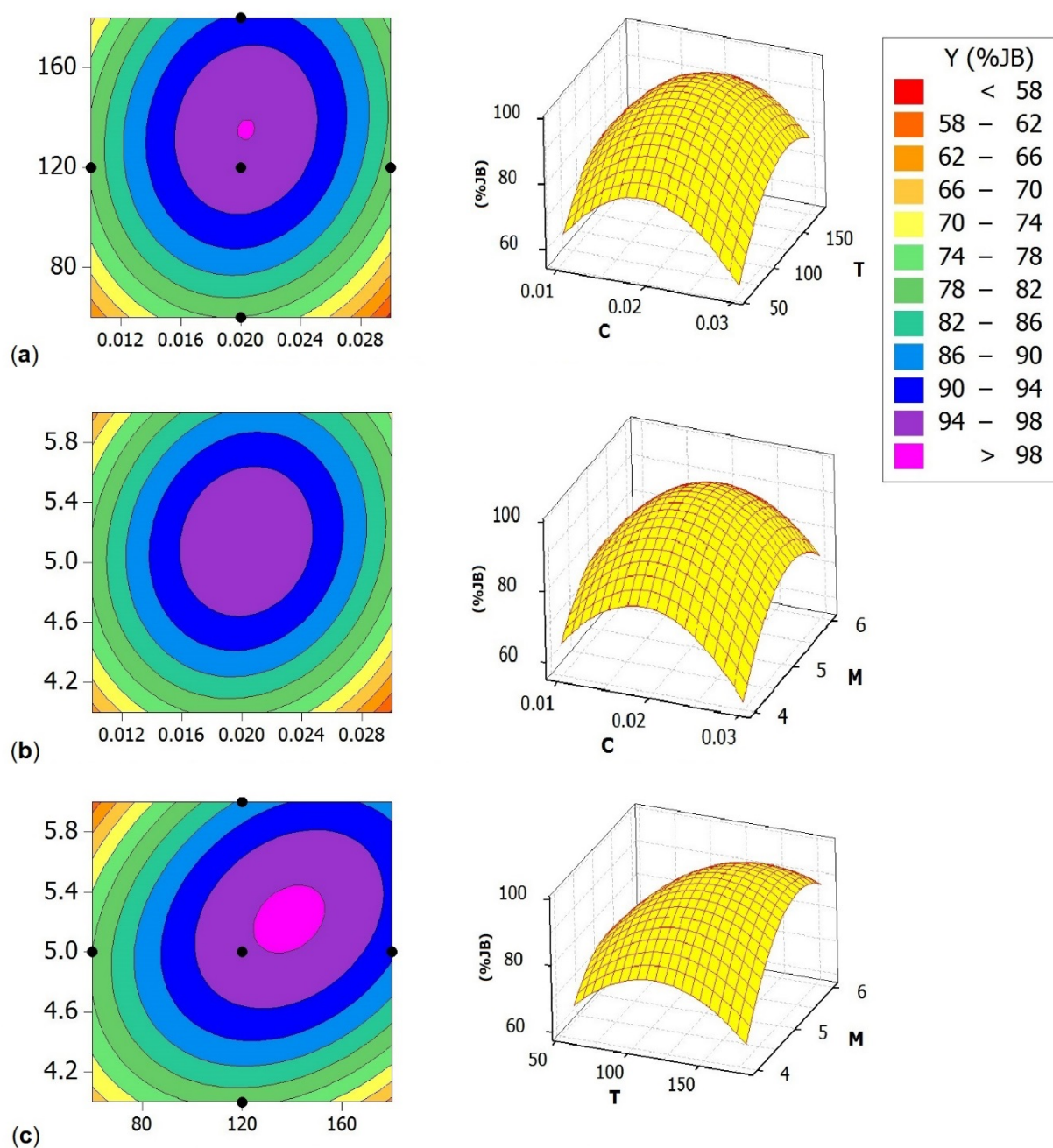


Figure 4.8: Contour and surface plots of (a) catalyst concentration and reaction time interactions impact on JB yield % (b) methanol to pretreated oil ratio and catalyst concentration interactions impact on JB yield % (c) methanol to pretreated oil ratio and reaction time interactions impact on JB yield %.

Figure 4.8(b) demonstrates the impact of methanol to pretreated oil ratio and catalyst concentration interactions on the response, JB yield. From the contour plot, the response region depicts only a range of 94% - 98% and hence, it is evident that there is a moderate impact of these interactions on the response. As per the results presented in Figure 4.8(c) the response region at and above 98% is significant, which indicates that methanol to pretreated oil ratio and reaction time interactions have a relatively high impact on the response of JB yield. In summary, by appropriate selections of the input parameter range at their mean values (C: 0.02, $120 < T < 180$ min and $5 < M < 5.4$) the response parameter of JB yield can be maximized.

4.3 Optimization of transesterification parameters for maximum JB Yield

The transesterification parameters catalyst concentration (C), reaction time (T) and methanol to pretreated oil ratio (M) were analyzed from the contour plots, as reported in Figure 4.8(a-c), and are summarized for the optimal parameters to obtain the maximum JB yield. Using the simulated environment of Minitab, the transesterification parameters were estimated as (C: 0.020 w/w; T: 133.1 min and M: 5.15 mol.) for the maximum JB yield, which was found to be 98.54%. These estimations were considered for experimental validation through transesterification and had maximum performance.

4.4 Biodiesel yield analysis using commercial CaO catalyst

Transesterification of the pretreated CJO and the oven dried commercial CaO catalyst along with methanol were carried out. The experiments were conducted following standard protocol to obtain the optimal biodiesel yield. The highest biodiesel yield of 94.7% was noted at transesterification reaction parameters that include commercial CaO catalyst concentration

of 0.03 w/w, reaction time of 145 min and methanol to pretreated oil ratio of 6 mol. Biodiesel yield conformation experiments were conducted at optimal reaction parameters for three successive cycles using fresh commercial CaO catalyst in each cycle. A biodiesel yield of 94.7% $\pm$ 0.3% was obtained as optimal. The biodiesel yield obtained using *P. erosa* synthesized nano CaO catalyst has resulted 3.84% higher yield as compared to commercial CaO catalyst.

Table 4.4: Comparison of biodiesel yield and transesterification reaction parameters using *P. erosa* synthesized nano CaO and commercial CaO catalysts.

Biodiesel yield/ Reaction parameter	<i>P. erosa</i> nano CaO catalyst	Commercial CaO catalyst
Biodiesel yield	98.54 %	94.7%
Catalyst concentration	0.020 w/w	0.030 w/w
Reaction time	133.1 min	145 min
Methanol to oil ratio	5.15 mol	6 mol

In Table 4.4, variation in optimal reaction parameters of transesterification using *P. erosa* synthesized nano CaO and commercial CaO are tabulated. It can be observed that apart from biodiesel yield all three reaction parameters of *P. erosa* synthesized nano CaO catalyzed transesterification were comparatively better than commercial CaO catalyzed reaction. This can be correlated with the increased catalytic activity of *P. erosa* synthesized nano CaO catalyst over commercial CaO.

4.5 Reusability analysis of nano CaO catalyst

Transesterification of pretreated CJO using both newly synthesized nano CaO and commercial CaO together with catalyst reuse tests were conducted at obtained optimal

conditions. Results of JB yield using from both newly synthesized nano CaO and commercial CaO were shown Figure 4.10. Based on the SEM micrographs in Figure 4.9(a-i), there were changes on the catalyst surface structure of CaO during nine successive catalyst reuse cycles; and resulting variations in JB yield were noted. The CaO particles continued to sustain with spherical morphology during the first three cycles of transesterification and hence the JB yield average variant was 0.4%. However, due to agglomeration of other particles with the catalyst and leaching of CaO to the other reactants of the transesterification, this led to a gradual decrease in the availability of active catalyst for the reaction.

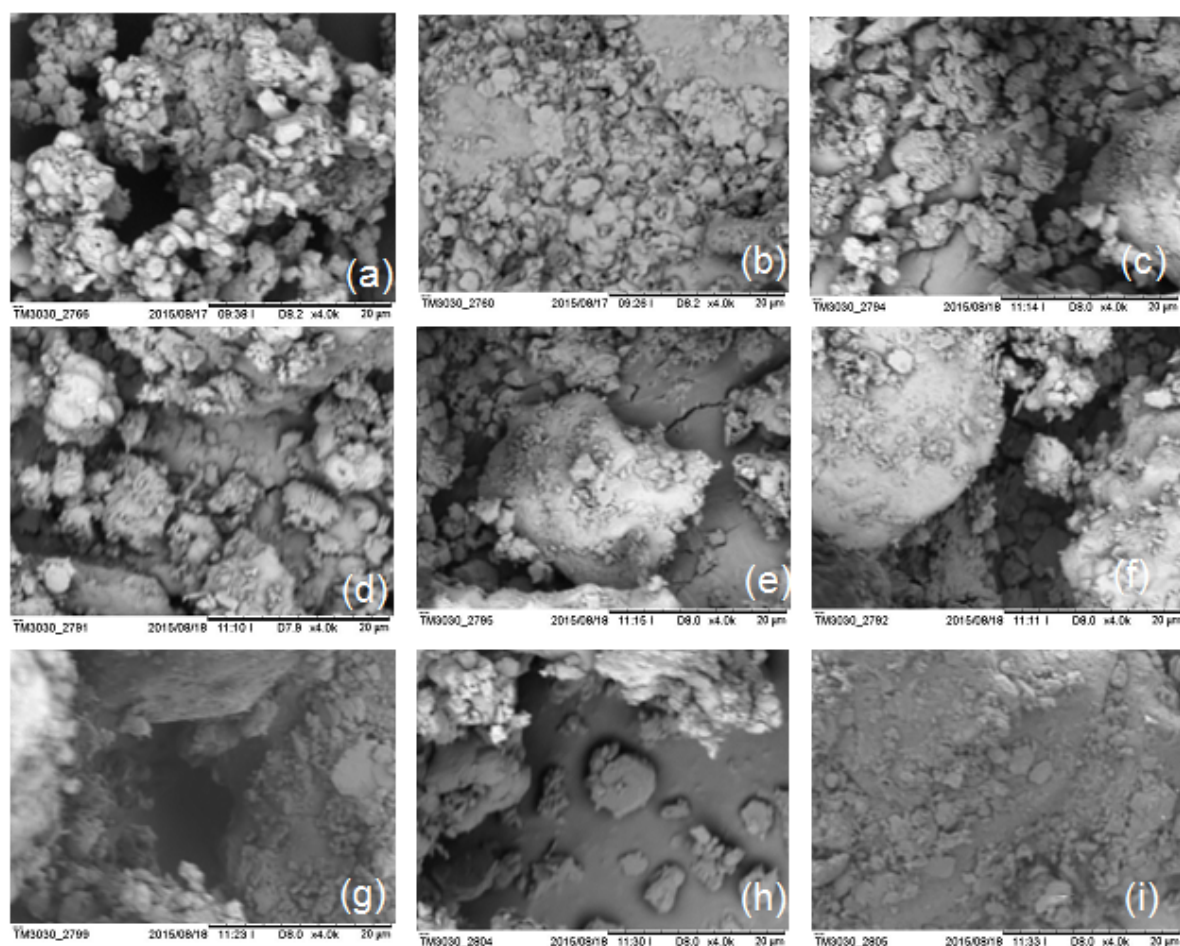


Figure 4.9(a – i): SEM micrographs of nano CaO catalyst showing changes on the catalyst surface structure in nine catalyst reuse cycles.

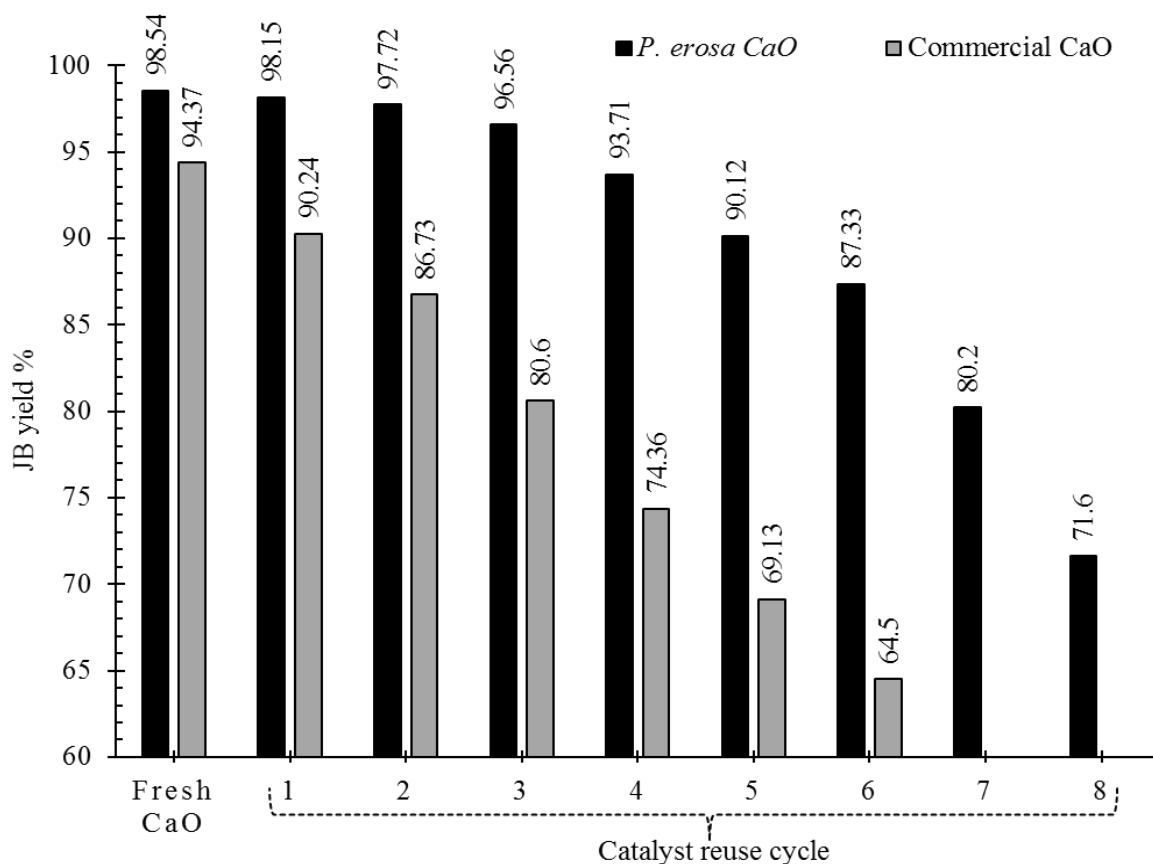


Figure 4.10: JB yield% using nano CaO and commercial CaO catalyst reusability cycle analysis at optimal transesterification reaction conditions.

It was observed that for the newly synthesized nano CaO catalyst, this was stable until the sixth cycle with an average 95.8% JB yield. Figure 4.10 it can be seen that during reuse of commercial CaO lower JB percentages as compared to nano CaO catalyst. This can be attributed to loss of active sites to carry out catalytic reaction transesterifying the triglycerides of CJO. When comparing CaO catalyst reusability studies in literature Tan et al. (2015b) reported a 75% biodiesel yield after five recycle test runs. Meanwhile Taufiq-Yap et al. (2011) conducted six reusability runs with 4wt.% CaO catalyst at 338 K temperature with a

6hr reaction time and a 15:1 methanol ratio for transesterification of *Jatropha curcas* oil and reported a 85% and 50% biodiesel yield in the first and sixth cycle, respectively.

Table 4.5: Leaching results of *P. erosa* synthesized nano CaO catalyst in reuse cycle.

<i>P. erosa</i> nano CaO catalyst reuse cycle	Leaching of Ca ²⁺ metal ion (ppm)
Fresh catalyst	1.21ppm±0.23
First cycle	2.92ppm±0.89
Third cycle	4.12ppm±0.31
Fifth cycle	3.62ppm±0.43
Sixth cycle	4.78ppm±0.18
Seventh cycle	6.16ppm ±1.17

The calcium ion (Ca²⁺) concentration in JB produced from all the successive reuse cycles was tested using atomic absorption spectroscopy. The results are tabulated in Table 4.8. The test report revealed minimal active Ca²⁺ loss in the JB produced when using fresh *P. erosa* nano CaO at 1.21ppm±0.23, which changed to 2.92ppm±0.89, 4.12ppm±0.31, 3.62ppm±0.43, 4.78ppm±0.18 and 6.16±1.17 for the first, third, fifth, sixth and seventh cycle, respectively. However the metal ion (Ca²⁺) leaching was in a range of 1.21ppm – 4.78ppm up to sixth cycle, which implies the suitability of JB produced that complies with transport vehicle fuel standards EN 14214. However, the seventh reuse cycle, there was a remarkable drop in the active calcium element content, subsequently resulting in reduced biodiesel yield and increased Ca²⁺ leaching. Hence, the reusability study shows that the *P. erosa* nano CaO catalyst was stable for six transesterification reaction cycles. A comparison of JB yield of

this research (98.54%, using fresh nano CaO catalyst) is relatively improved than results (96%, using fresh Ostrich CaO catalyst) reported by Tan et al. (2015b).

4.6 IR spectrum analysis of Jatropha biodiesel

The Figure 4.11 depicts the IR spectrum of Jatropha biodiesel. The functional group of O-H showed strong absorption bands at 2852 cm^{-1} and 2924 cm^{-1} and a medium absorption bands at 3009 cm^{-1} . These absorption peaks of O-H confirmed that the sample was a FAME or biodiesel. Moreover, the JB fuel showed absorption spectrum peaks between 1000 cm^{-1} – 1300 cm^{-1} due to the presence of the C-O group. The absorption peaks 1361 cm^{-1} , 1436 cm^{-1} and 1458 cm^{-1} –OH bending vibrations, –C–O–H in-plane bending vibrations, –CH₃ out-of-plane bending vibrations, –CH₂– wagging and twisting vibrations. The strong absorption band 1741 cm^{-1} indicates presence of C=O, esters. The weak absorption bands 615 cm^{-1} C-H bend shows presence of alkynes; 846 cm^{-1} , 877 cm^{-1} signifies C-H bend and 1168 cm^{-1} denotes C-C(O)-C stretch esters on the other hand the strong absorption peak 723 cm^{-1} indicates CH₂ bend representing alkanes.

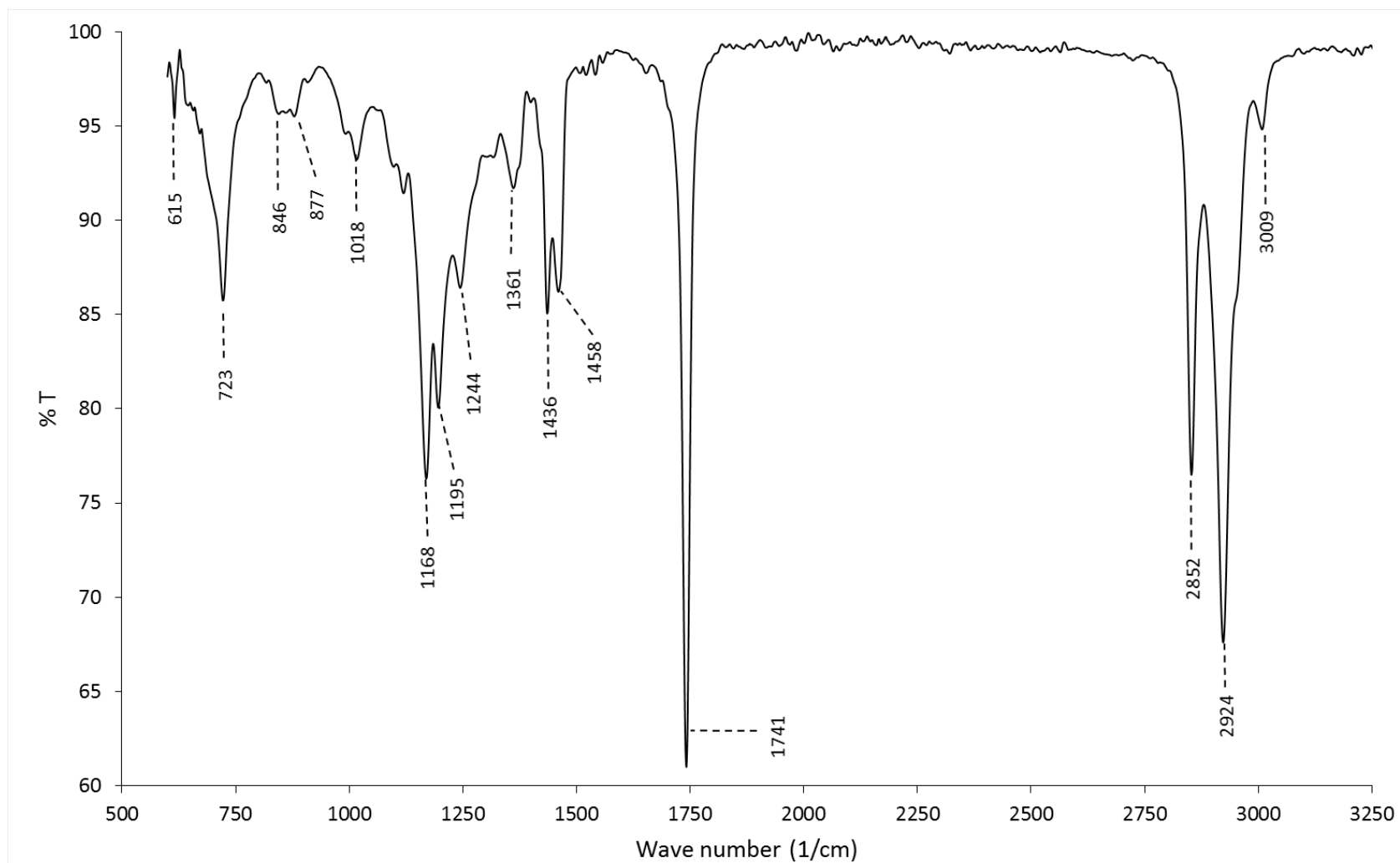


Figure 4.11: Infrared spectra of Jatropha biodiesel.

4.7 Analysis of Jatropha biodiesel feedstock fatty acid profile

The fatty acid composition has a significant role in determining biodiesel fuel characteristics. Table 4.6 summarizes FAC mass fractions of Jatropha biodiesel obtained from east and west Malaysian geographical regions (JB_{EM} and JB_{WM}). The USFAs, Oleic acid (C18:1) and Linoleic acid (C18:2) contributes dominant FAC in both JB_{EM} and JB_{WM} samples yet, JB_{EM} contains 1.48% higher C18:2 mass fraction, which is a PUFA having melting point of -5°C. Among FAC, a share of USFAs 80.27 wt % and 78.63 wt % reported in JB_{EM} and JB_{WM} respectively. The SFAs Palmitic acid (C16:0), Stearic acid (C18:0) present in JB_{EM} and JB_{WM} samples. Although, additionally, JB_{EM} contains 0.42% of Lauric acid (C12:0), Myristic acid (C14:0) and Arachidic acid (C20:0) existents, it can be seen that JB_{EM} is relatively more unsaturated. The observed FAC variations of the JB oil samples indicates likely diverse agro geographic and cultivation conditional effects of the JCL seed (Fernandes et al., 2015).

$$DU = (MUFA C_n:1, wt. \%) + 2(PUFA C_n:2, wt. \%) + 3(PUFA C_n:3, wt. \%) \quad (8)$$

$$LCSF(1) = (0.1 \times C_{16:0}) + (0.5 \times C_{18:0}) + (1 \times C_{20:0}) + (1.5 \times C_{22:0}) + (2 \times C_{24:0}) \quad (9)$$

$$LCSF(2) = \frac{\sum(MP_n \times C_n \text{ wt. \%})}{100} \quad (10)$$

Table 4.6: Fatty acid composition (wt %) and categorization of Jatropha biodiesels from East and West Malaysian geographic regions.

Fatty acid (Cnc:nb)	Fatty acid composition (wt %)	
	JB _{EM}	JB _{WM}
Lauric acid (C12:0)	0.12	0
Myristic acid (C14:0)	0.10	0
Palmitic acid (C16:0)	13.20	14.35
Palmitoleic acid (C16:1)	0.71	1.52
Stearic acid (C18:0)	6.11	7.02
Oleic acid (C18:1)	43.86	43.15
Linoleic acid (C18:2)	35.40	33.92
Linolenic acid (C18:3)	0.30	0.04
Arachidic acid (C20:0)	0.20	0
Eicosenoic acid (C20:1)	0	0
Behenic acid (C22:0)	0	0
Erucic acid (C22:1)	0	0
Saturated fatty acids (SFAs)	19.73	21.37
Mono unsaturated fatty acids (MUFAs)	44.57	44.67
Poly unsaturated fatty acids (PUFAs)	35.70	33.96
Degree of unsaturation (DU)	116.27	112.63
Long chain saturated factor, LCSF (1)	4.58	4.95
Long chain saturated factor, LCSF (2)	12.71	13.85

⁽¹⁾ Based on fatty acids composition wt % of C18:0 - C24:0

⁽²⁾ Based on melting point, MP_n (°C) of fatty acids, C14:0 – C24:0

The biodiesel fuel properties can be characterized by their fatty acid parameters like degree of unsaturation (DU) and Long chain saturated factor (LCSF). DU was calculated according to Ramos et al. (2009) and Chuah et al. (2015) using Eq. (8) in which MUFAs and PUFAs mass fractions are considered (Chuah et al., 2015; Ramos et al., 2009). Long chain saturated factor (LCSF) based on SFAs composition was defined. The Long chain saturated factor LCSF (1) was calculated by using empirical Eq. (9) considering mass fractions (wt %) of SFAs (C16:0 – C24:0) (Sajjadi et al., 2016). Long chain saturated factor, LCSF (2) was obtained from a composition model based Eq. (10) taking into account of SFAs (C16:0 – C24:0) melting point (MP_n) and their mass fraction (C_n wt %) (Chuah et al., 2015; Sajjadi et al., 2016). The SFA, MUFA, PUFA, DU, LCSF (1) and LCSF (2) values are tabulated in Table 4.6. Various characteristics of pure fatty acids (C12:0 – C20:0) including molecular weight (Mw), MP_n , density at 15°C, kinematic viscosity, cetane number, calorific value and flash point values from the literature were presented in Table 1.6. It can be seen that the properties such as MP_n , KV, CN and CV of pure fatty acids inflates with carbon chain length and reduces with their DU specifically noted that these properties of USFA were lesser than SFA. On the other hand density value decreases with molecule chain length and increases with fatty acid DU therefore SFA were reported higher density values than USFAs.

Table 4.7: Physicochemical fuel properties of Jatropha biodiesels from East and West Malaysian regions and Petro diesel.

Fuel property	JB _{EM}	JB _{WM}	Petro diesel
Acid value (mg KOH/g)	0.38	0.29	0.15
Calorific value (MJ/kg)	36.48	38.64	45.82
Cetane number	53	56.5	49.7
Density at 15°C (kg/m ³)	876.4	884.5	839
Iodine value (g I ₂ /100 g)	88.8	86.5	-
Kinematic viscosity at 40°C (mm ² /s)	4.02	4.47	2.91
Oxidation stability (h)	9.65	9.74	23.7
Water content (Wt %)	0.04	0.032	0.0038
Cloud point (°C)	3.7	4.1	2
Cold filter plugging point (°C)	1.2	-0.94	-8
Flash point (°C)	167	163	71.5
Pour point (°C)	1.6	2.2	1
Diglyceride (Wt %)	0.034	0.036	-
Free glycerine (Wt %)	0	0.01	-
Monoglyceride (Wt %)	0.321	0.323	-
Total ester (Wt %)	99.12	98.95	-
Triglyceride (Wt %)	0	0	-
Carbon (Wt %)	76.531	76.535	86.166
Hydrogen (Wt %)	12.283	12.136	13.504
Oxygen (Wt %)	11.185	11.328	-

Table 4.8: Physicochemical fuel properties of Jatropha biodiesel - petro diesel blends.

Fuel property	JB _{EM} 10	JB _{EM} 20	JB _{EM} 30	JB _{EM} 50	JB _{WM} 10	JB _{WM} 20	JB _{WM} 30	JB _{WM} 50
Cetane number	50.99	51.09	51.65	52.85	51.40	51.84	52.76	54.70
Oxidation stability (h)	20.81	15.74	11.71	10.08	20.80	15.71	11.66	10.06
Iodine value (g I ₂ /100 g)	9	18.3	27.8	47.4	8.7	17.8	26.6	45.9
Calorific value (MJ/kg)	44.88	43.53	42.75	40.32	45.09	43.94	43.39	41.36
Acid value (mg KOH/g)	0.17	0.18	0.19	0.23	0.16	0.17	0.18	0.21
Water content (Wt %)	0.007	0.011	0.016	0.028	0.006	0.01	0.013	0.024
Kinematic viscosity at 40 °C (mm ² /s)	3.45	3.53	3.89	3.97	3.54	3.67	4.10	4.25
Density at 15 °C (kg/m ³)	841.5	848.5	856.2	869.0	842.3	850.2	858.7	873.2
Cold filter plugging point (°C)	-7.79	-7.02	-5.87	-3.88	-8.02	-7.58	-6.65	-5.19
Flash point (°C)	83.2	83.5	85.9	96.9	82.8	82.9	85.0	95.4
Cloud point (°C)	3.1	4.2	4.3	5.0	3.3	4.5	4.6	5.4
Pour point (°C)	1.0	1.2	1.3	1.4	1.1	1.3	1.5	2.0

4.8 Analysis of physicochemical properties of Jatropha biodiesel and blends

The physicochemical fuel properties test results of pure Jatropha biodiesel (B100) produced using feedstocks originated from East and West Malaysian regions (JB_{EM} and JB_{WM}), their biodiesel blends (B10, B20, B30 and B50) and petro diesel were given in Tables 4.7 and 4.8 respectively. The influence of Jatropha biodiesel fatty acid composition on their physicochemical fuel properties were analyzed in the following sections. The phenomenal variations in fuel properties of JB and their blends in comparison with petro diesel values were graphically presented (see Figures 4.12-4.23).

4.8.1 Cetane number of JB-PD biodiesel blends

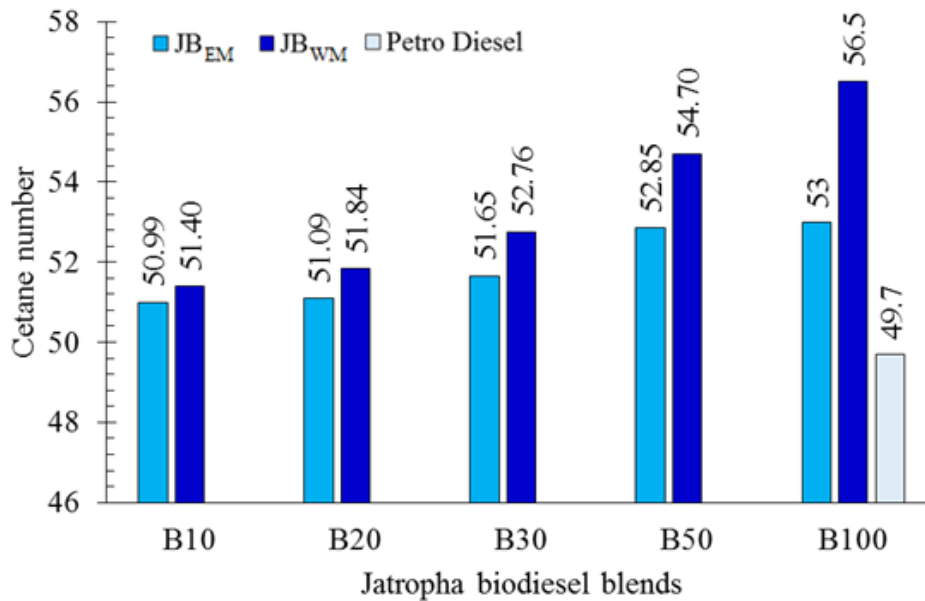


Figure 4.12: Cetane number results of JB-PD biodiesel blends.

From Table 4.7, Higher CN were resulted for JB_{WM} (56.5) than JB_{EM} (53), as JB_{WM} samples enriched with SFAs include Palmitic acid (C16:0) and Stearic acid (C18:0) compared to JB_{EM} (Knothe et al., 2003) and similar observations were reported (Ramos et al., 2009). The

MUFAs fragments ($C_n:1$) contributes to greater CN values yet, the MUFA for both JB_{WM} (44.57), JB_{EM} (44.67) nearly equal hence there is no considerable impact accounted (Table 4.6). Further, presence of Linoleic acid (C18:2) and Linoleic acid (C18:3) contents in JB_{EM} (44.67) lead to higher DU and resulted in lowering its CN (Ramos et al., 2009). The CN test results of blends of JB – petro diesel were shown in Table 4.8. The higher CN values can be noted with increasing amount of JB fuel percentages and are close to the values of petro diesel (see Figure 4.12). This is due to the fact that upon blending with petro diesel, the quantities of SFA contents in biodiesel decreases which results in low CN values.

4.8.2 Oxidation stability of JB-PD biodiesel blends

The fuel samples, JB_{EM} and JB_{WM}, were tested for OS following EN 14112 standard method using Rancimat apparatus (Switzerland) at 110 °C, results are shown in Table 4.7. The JB_{EM} (9.65 h), OS is higher than that of JB_{WM} (9.74 h). Although the OS difference is not significantly higher, which can be correlated with distinct FAP percentages in biodiesel samples. The OS decreases by increment of fatty acid DU, which makes them more susceptible to oxidation due to presence of higher oxygen and USFA contents. USFA that include Palmitoleic (C16:1), Oleic (C18:1) and Linoleic (C18:2) contributed higher DU of JB_{EM} (116.27 wt %) than JB_{WM} (112.63 wt %), see Table 4.6. Borhanipour et al. (2014) had reported similar observations and concluded on biodiesel fuels OS improvement either by antioxidant treatment or blending with petro diesel. Table 1.6 shows the OS test values of JB and petro diesel blends. The changing trends of OS over blending can be seen from Figure 4.13. The petro diesel indicated a higher OS of 23.7 h. Among the JB blends, OS values decreases by the increase of biodiesel percentage. This results can be correlated with decrease of USFA contents besides percentage of oxygen amount in the biofuel blends. Further,

blending of biofuels with petro diesels ensures their higher suitability for storage and transit conditions.

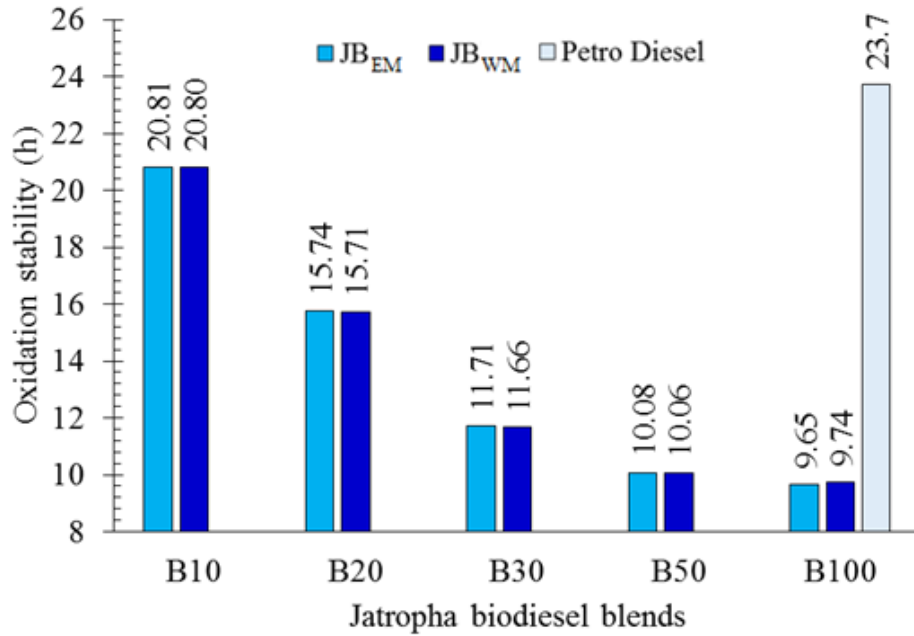


Figure 4.13: Oxidation stability results of JB-PD biodiesel blends.

4.8.3 Calorific value of JB-PD biodiesel blends

Table 4.7 presents CV of JB_{EM} (36.48 MJ/kg) and JB_{WM} (38.64 MJ/kg). The samples tested according to ASTM D240 standard methods they comply with EN 14214 standards. CV of a fuel increases with fatty acid molecule chain length (Knothe, 2005). The values of LCSF based on both FAC and melting points of fatty acids, as shown from Table 4.6, indicates effect of long chain fatty acids on CV of JB_{EM} and JB_{WM}.

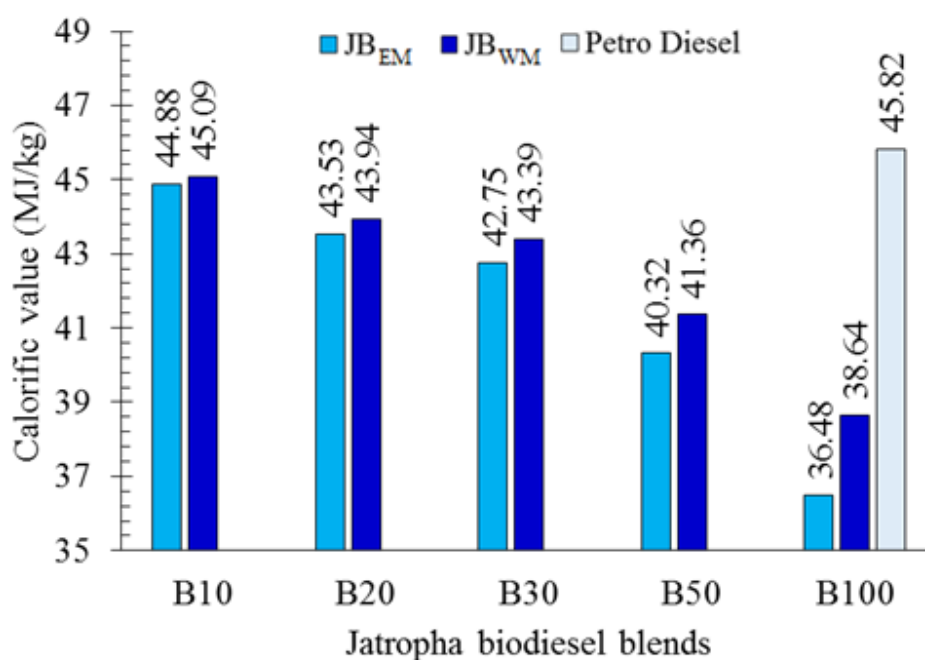


Figure 4.14: Calorific value results of JB-PD biodiesel blends.

The petro diesel fuel consists a very less or null fractions of oxygen and large ranges of hydrocarbon mixtures however, the biofuels comprises over 10% of oxygen from their elemental composition which ensures their complete combustion (Borhanipour et al., 2014). Among the primary elements carbon and hydrogen principally contributes for thermal energy. The higher aggregate values of oxygen fractions proportionately effects in lowering hydrogen and carbon elemental percentages which yields in lesser energy contents in the fuels (Rao, 2011). The difference in resulted CV of biofuels is not significant due to marginal differences in their elemental composition. On the other hand the CV of petro diesel noted higher value (45.82 MJ/kg) which can be attributed to existence of higher percentage of carbon element as comparative to biofuels (Table 4.7). As seen in the comparative graph, Figure 4.14, the CV of JB – petro diesel blends phenomenally increased with reducing proportions of biofuel contents. This is due to the fact that petro diesels encompasses higher

CV than B100 samples and hence blending contributes in improving of CV of corresponding JB blends.

4.8.4 Iodine value of JB-PD biodiesel blends

The IV test results for JB_{EM} and JB_{WM} 88.8g I₂/100g and 86.5g I₂/100g respectively were in accordance with EN 14214 limits (see Table 1.5). Deviation in IV is a significant indication which is due to PUFA, Linoleic acid (C18:2) contents 1.48 wt. % higher in JB_{EM} samples (Table 4.6), these results are found to be in agreement with reported literature (Borhanipour et al., 2014).

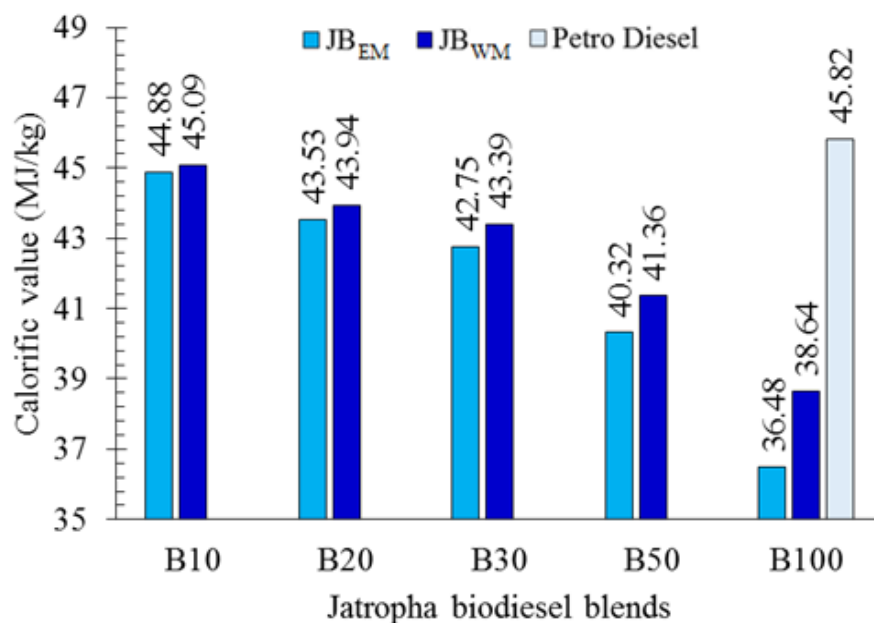


Figure 4.15: Iodine value results of JB-PD biodiesel blends.

Further to note, marginally higher SFA esters, Palmitic (C16:0) and Stearic (C18:0) acid contents of JB_{WM} samples causes lowering its IV. The petro diesel samples does not contain any fractions of iodine. According to the IV test results of JB and petro diesel blends tabulated in Table 1.6 and comparative graph shown in Figure 4.15, IV decreases

significantly through blending. The IV of blends noted to be minimum for decreased proportions of JB. As a result of reduced IV, the biofuels oxidation stability increases and hence minimizes the particle deposition in the fuel injectors while used in the diesel engines(Lin & Lin, 2012; Ong et al., 2013).

4.8.5 Acid value of JB-PD biodiesel blends

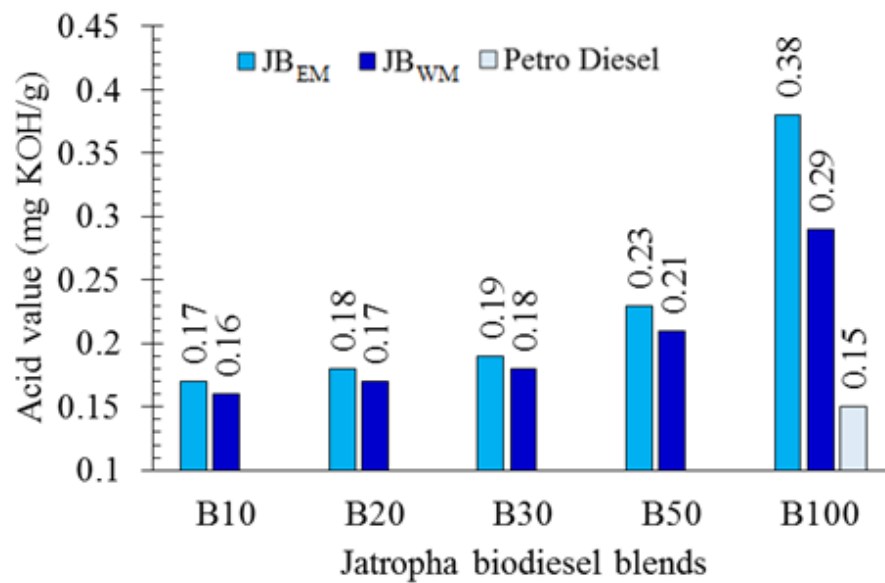


Figure 4.16: Acid value results of JB-PD biodiesel blends.

AV of JB_{EM}, JB_{WM} fuels measured according to ASTM standard, D664 test methods (Table 3.2). The AV results JB_{EM} (0.38 mg KOH/g); JB_{WM} (0.29 mg KOH/g) shown in Table 4.7 were meeting the ASTM and European standards for use (Table 1.6). The AV results of JB-petro diesel blends presented in Table 4.8 and Figure 4.16. The least AV is shown for petro diesel. These results illustrates that the AV decreases with reducing percentage of JB in making of a blend. Though, the biofuel AV variances persistent through blends and close to that of petro diesel. The possible reason for AV variation was USFAs. The total of USFAs

for JB_{EM} is higher than JB_{WM} samples. In addition the higher DU of JB_{EM} (116.27 wt %) indicates its greater oxidative susceptible nature due to unstable double bonded hydrocarbon chains and hence increase of AV over storage compared to JB_{WM} .

4.8.6 Water content of JB-PD biodiesel blends

The WC test results of JB fuel and blends are shown in Tables 4.7 and 4.8. Among the biofuel samples, JB_{EM} has higher WC (0.04 wt %) than JB_{WM} samples (0.032 wt %). Similar trends were observed with JB blends (Figure 4.17). The WC difference correlates with degree of unsaturated olefinic fatty acids present in the fuels. The olefinic unsaturation contents (C18:1, 2, 3) noted to be higher in JB_{EM} , 79.56 wt %, than JB_{WM} samples (77.11 wt %). In addition, oxidative decomposition of unsaturated olefinic fatty acids over storage periods and biodiesel production process also considerably affects WC levels (Atadashi et al., 2012).

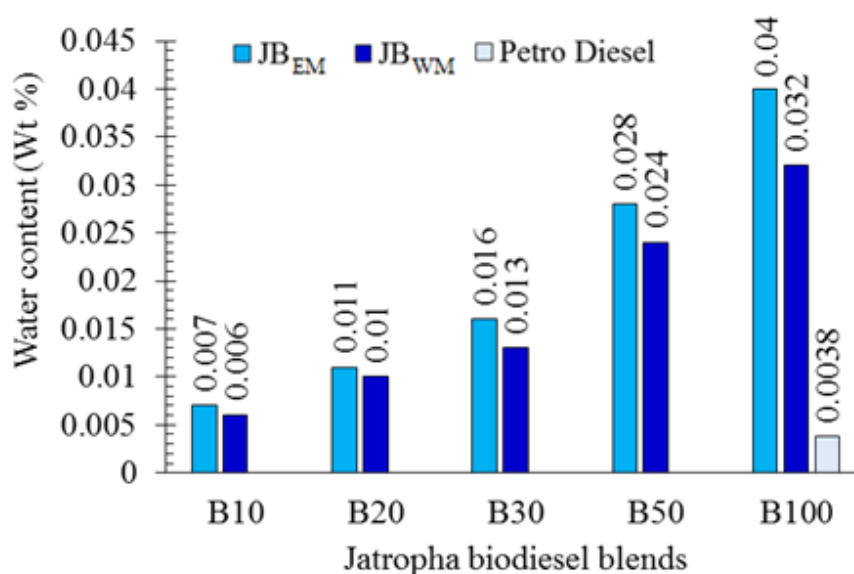


Figure 4.17: Water content results of JB-PD biodiesel.

4.8.7 Kinematic viscosity of JB-PD biodiesel blends

The KV of biodiesel's JB_{EM} (4.02 mm²/s) and JB_{WM} (4.47 mm²/s) are within the allowable limits as per ASTM and European standards (Table 4.7). The difference in KV of biofuels can be due to the FAC disparities and unsaturation levels. Higher SFAs and LCSF fractions increases KV. For JB_{EM} samples both SFAs and LCSF proportions are comparatively less than JB_{WM} which is due to higher fatty acid amounts of Palmitic acid (C16:0) and Stearic acid (C18:0). Besides, JB_{EM} consists more degree of unsaturation due to higher PUFAs, as a result, the KV of JB_{EM} resulted less (Ong et al., 2013; Silitonga et al., 2013).

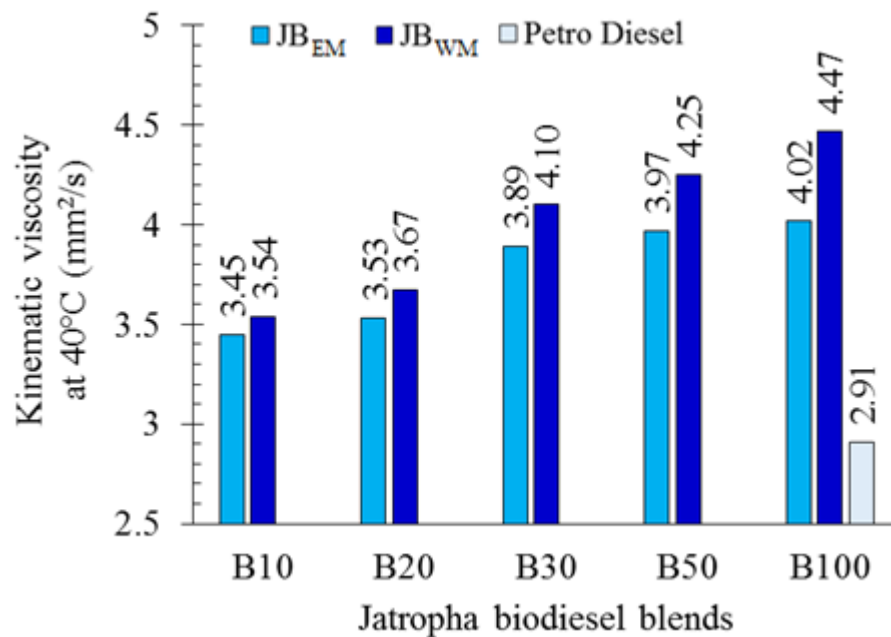


Figure 4.18: Kinematic viscosity (at 40°C) results of JB-PD biodiesel blends.

Oxidation stability of a fuel can influence KV since oxidation promotes FFA formation, isomerization of C=C, saturation levels and production of fatty acids having higher molecular weight (Silitonga et al., 2013). Since JB_{EM} (9.65 h) shows lesser oxidation stability than JB_{WM} (9.74 h) it can be correlated with their KV difference and JB_{WM} samples

referred to show higher KV. The KV test values of pure JB, petro diesels and their blends were shown in Figure 4.18 and Table 4.8. Among all the KV of B100 samples were noted to be higher than petro diesels and blends. However, blending of JB fuels with petro diesels resulted in reducing the blends. The difference in FAC consequence of JB fuels continued to effect the KV of their blends thus, the blends of JB_{WM} fuel lead to higher KV values compared to JB_{EM} samples.

4.8.8 Density of JB-PD biodiesel blends

The density test results of JB_{EM} and JB_{WM} samples are shown in Table 4.7. Higher density of 884.5 kg/m³ was noted for JB_{WM} as compared to JB_{EM} (876.4 kg/m³). The difference in density can be correlated with percentage of SFAs content in the feed stocks. SFAs can contribute in higher density. JB_{WM} contain SFAs of 21.73% whereas 19.73% SFAs noted in JB_{EM} samples (Table 4.6). This is due to the consequence of fuels comprising more SFAs and shorter hydrocarbon chain length are susceptible to be more crystallization, which lead to lowering their volume and increase in density (Borhanipour et al., 2014; Ramírez-Verduzco et al., 2012; Shahabuddin et al., 2012).

Density results of Jatropha biodiesel blended with petro diesel values are shown in Figure 4.19 and Table 4.8. It can be seen that the density values decreases with the increasing quantity of petro diesel. This phenomenon can be correlated with the fuels molecular weight. In comparison, the density levels of biodiesels reported higher values than petroleum based diesels which is directly relays on their FAC as well as purity (Barabás & Todorut, 2011). Since the biodiesel fuels comprises a small fractions of various fatty acids that are having comparable density values, the contrast in densities of corresponding biodiesel fuels is

limited. However, density values of biodiesels are significantly affected by contamination hence the variations in densities indicates presence of contaminants in the fuels.

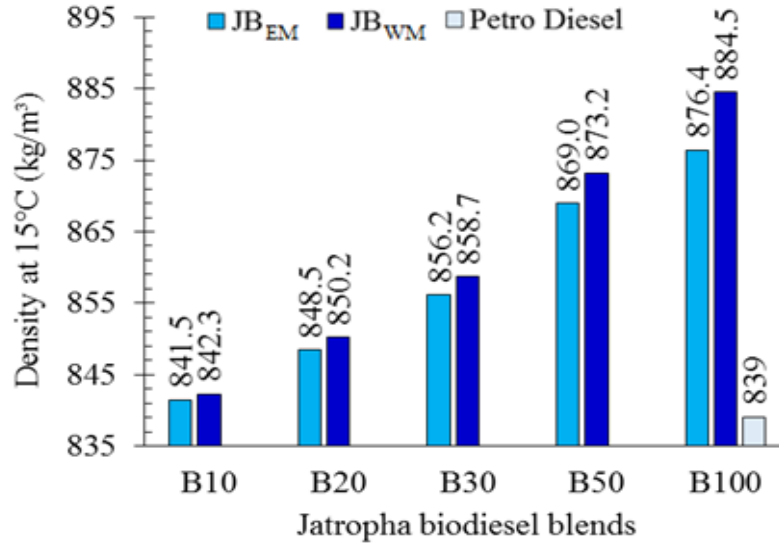


Figure 4.19: Density (at 15°C) results of JB-PD biodiesel blends.

4.8.9 Cloud point of JB-PD biodiesel blends

In Table 4.7 the measured CP values of JB_{EM}, JB_{WM} and petro diesel fuels are shown. The CP of both biodiesels were varied by $\pm 1^\circ\text{C}$. This marginal difference could be referred to differences in fatty acid saturation levels of respective JB. The biodiesel blends with petro diesel demonstrates higher suitability for using at low temperature whether conditions. The CP of biofuel and petro diesel blends were tabulated in Table 4.8. From Figure 4.20, it can be perceived that the CP values of blends reported lower as the quantity of JB% decreases and which are close to that of petro diesel.

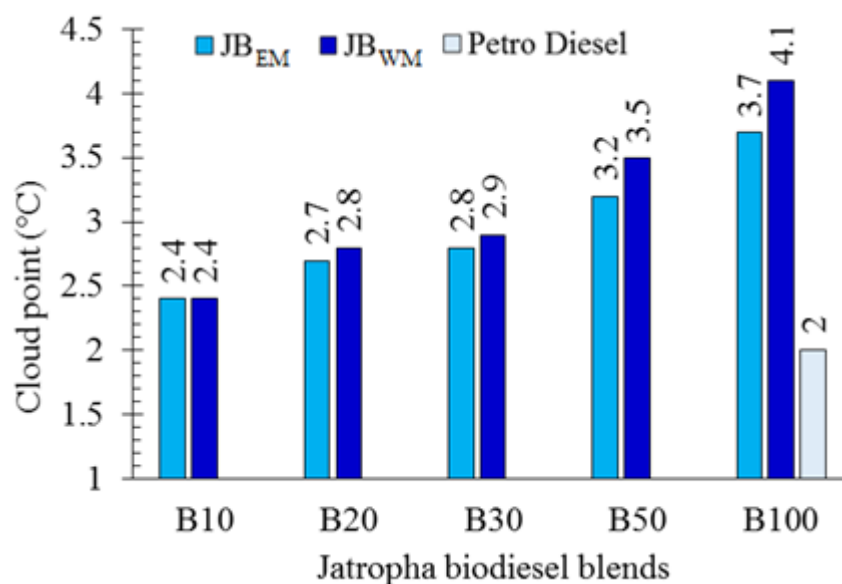


Figure 4.20: Cloud point results of JB-PD biodiesel blends.

4.8.10 Pour point of JB-PD biodiesel blends

The biodiesel standard ASTM D6751 specified limits for PP are -15°C to 16°C. Table 4.7 shows PP values tested according to ASTM D97 standard testing protocols. The biodiesel samples indicates PP results JB_{EM} (1.6°C) and JB_{WM} (2.2°C) are in compliance with ASTM standards. A net PP difference of 0.6°C can be observed, which can be correlated to the fuel's FAP variations. JB_{WM} contains higher SFA mass fractions specifically Palmitic acid (C16:0) and Stearic acid (C18:0) than JB_{EM} samples. Melting points for these SFAs are significantly higher as compared to other fatty acids which freeze faster at lower temperatures.

Increasing levels of DU contribute to lowering the PP of fuels, since the USFAs, that consist of Oleic acid (C18:1), Linoleic acid (C18:2) and Linolenic acid (C18:3) have low or negative melting points which causes lower PP values. Further greater values of LCSF(2), calculated based on melting points of fatty acids, for JB_{WM} reveal the cumulative effect of long chain SFAs and corresponding melting points on the low temperature operating

properties of the liquid biofuel. In Table 4.8 the PP test results of JB blends are presented. From the bar graph shown in Figure 4.21, blending of biofuels with petro diesel slightly lowers their PP, since both the petro diesel and biodiesel fuels utilized have encompasses low and similar PP values.

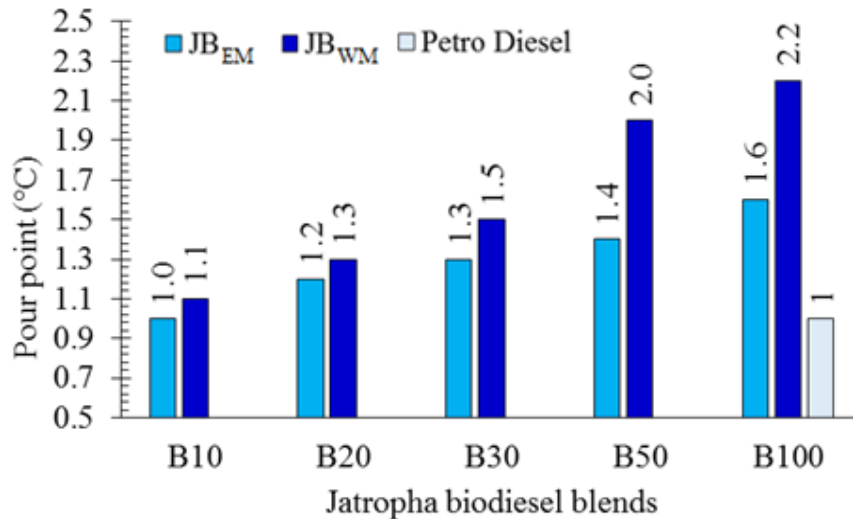


Figure 4.21: Pour point results of JB-PD biodiesel blends.

4.8.11 Flash point of JB-PD biodiesel blends

Table 4.7 shows FP test results of biodiesel fuel samples as JB_{EM} (167°C) and JB_{WM} (163°C) which indicates the biofuels meets all safety limitations of handling, transportation, storage and suitable for use (Borhanipour et al., 2014; Silitonga et al., 2013; Yoon et al., 2008). The experimental FP values of biofuel and petro diesel blends were shown in Table 4.9. The comparative graph of FP results shown in Figure 4.22, indicates that FP values reduces with decreasing amounts of biofuels in the blends. Comparatively FP belongs to both petro diesel and JB blends measured analogues values which are much lesser than FP of B100 fuel samples. This phenomenon can be associated with FAC of the fuels. Specially the petro diesel

fuels comprises a large number of variant hydrocarbon segments on the other hand, in general, the biodiesel fuels made of a very few major fatty acid fractions usually which have equivalent boiling temperatures (Shahabuddin et al., 2012).

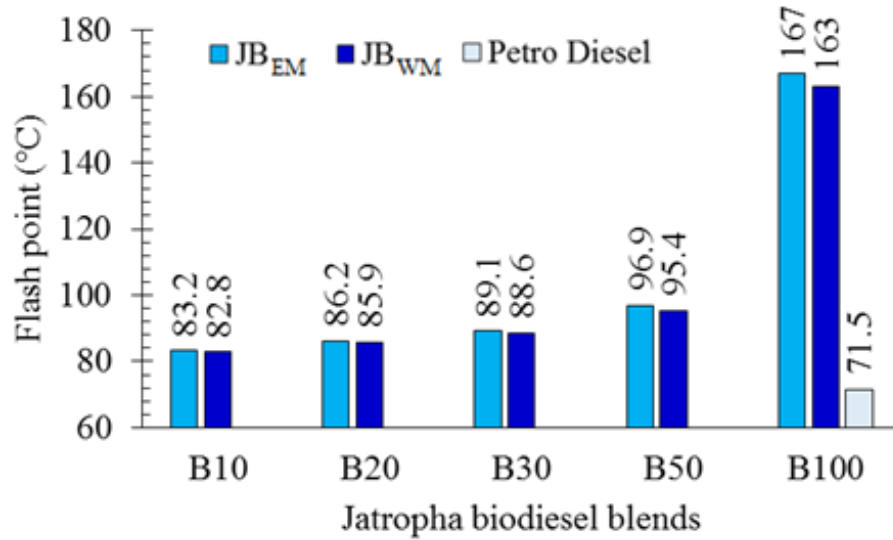


Figure 4.22: Flash point results of JB-PD biodiesel blends.

4.8.12 Cold filter plugging point of JB-PD biodiesel blends

Table 4.7 shows CFPP results of JB_{EM} and JB_{WM} samples, which are tested according to ASTM D6371 standards. JB_{WM} (- 0.94 °C) shown poor CFPP then JB_{EM} (1°C) samples whereas the commercial petro diesel has a minimum value of -8°C. The dissimilarities in CFPP observed can be correlated with SFA and LCSF. The cumulative SFAs were higher in JB_{WM} (21.37 wt %) than JB_{EM} (19.73 wt %) notably JB_{WM} encompasses dominant C16:0 and C18:0 components, which are prone to precipitate first (Ramos et al., 2009). Chuah et al. (2015) have reported similar results (Chuah et al., 2015).

The biodiesels rich in LCSF contributing fatty acids, poorer the low temperature fuel flow properties (Ramos et al., 2009). Further, Ramos et al. (2009) reported that the peanut biodiesel contains high fatty acid fractions of Behenic acid (C22:0) and Lignoceric acid (C24:0) which contributes in high LCSF results in lowest CFPP of 17 °C. However, according to the test results, the JB_{EM} and JB_{WM} fatty acid profiles does not incorporate components of C22:0 and C24:0 (Table 4.6), as a result there is no impact of these fatty acid fractions on the fuels CFPP. The CFPP test results of blends of JB and petro diesel were presented in Table 4.9 and the comparative differences were shown in Figure 4.23. These values indicates that CFPP of JB fuels significantly improved upon blending with petro diesel as well as their fitness for utilizing at low temperatures whether conditions.

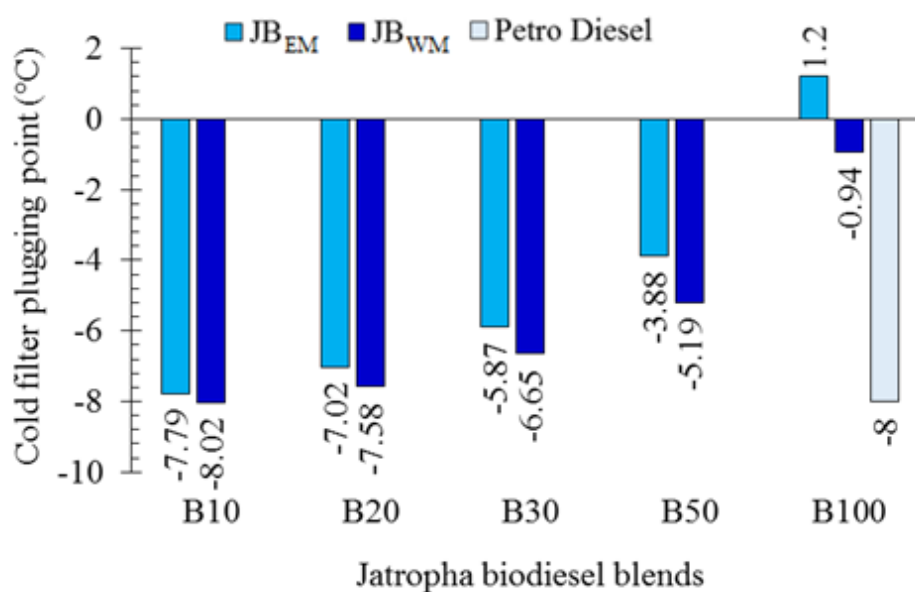


Figure 4.23: Cold filter plugging point results of JB-PD biodiesel blends.

4.9 Jatropha biodiesel - petro diesel blends for performance analysis.

The blends of Jatropha biodiesel and petro diesel (B5, B10, B15, B20 and B25) were prepared and their fuel properties were measured using standard apparatus built on ASTM D6751 and

EN14214 standards. The biofuel properties of JB-PD blends B5-B25 were tabulated in Table 4.19.

Table 4.9: Biofuel properties of Jatropha biodiesel and petro diesel blends B5-B25.

Biofuel property	Blends of Jatropha biodiesel and petro diesel				
	B5	B10	B15	B20	B25
Acid value (mg KOH/g)	0.16	0.17	0.18	0.19	0.21
Calorific value (MJ/kg)	45.34	44.88	44.41	43.53	43.07
Cetane number	50.60	50.93	51.37	51.89	52.42
Cloud point (°C)	2.24	2.43	2.56	2.67	2.78
Density at 15°C (kg/m ³)	839.64	841.50	843.38	848.52	851.61
Flash point (°C)	77.46	81.83	83.77	84.02	86.29
Kinematic viscosity at 40°C (mm ² /s)	3.39	3.45	3.50	3.53	3.64
Oxidation stability (h)	21.52	20.81	17.52	15.74	13.03
Pour point (°C)	1.03	1.06	1.09	1.15	1.24

4.10 Optimization of engine performance parameters

The DI-CI engine performance analysis was carried out in terms of Brake power (BP), Brake specific fuel consumption (BSFC), brake thermal efficiency (BTE), exhaust gas temperature (EGT); which are discussed in the following sections. The predicted engine performance results were tabulated in Table 4.10. The ANOVA and regression results of mathematical model were presented in Table 4.11. The difference between coefficients of determination (R^2) and correlation (R_{adj}^2) for each model is narrow, which indicates presence of significant terms in the respective model. The p-value of a model term conforms its higher impact on

corresponding response (Khoobbakht et al., 2016). Therefore, the model term's having p-value greater than 0.05 were significant. The reference results of engine performance were tabulated in Table A-4 to find the comparative fitness study of the predicted results.

Table 4.10: Predicted results of engine performance.

Run	Block	Point	Coded parameters			Predicted engine performance			
			S	B	T	BP	BSFC	BTE	EGT
			rpm	%	N.m	kW	g/kWh	%	°C
1	2	Center	1900	B15	32	3.645	282.23	30.2	357.21
2	2	Axial	1900	B25	32	3.605	313.38	29.35	375.9
3	2	Axial	2100	B15	32	3.595	295.01	29.13	375.93
4	2	Axial	1900	B15	28	3.44	301.30	28.83	356.64
5	2	Center	1900	B15	32	3.38	282.23	30.2	367.08
6	2	Axial	1900	B5	32	3.47	290.83	29.8	342.78
7	2	Axial	1700	B15	32	3.485	293.74	29.13	356.62
8	2	Axial	1900	B15	36	3.595	275.45	30.34	360.92
9	1	Center	1900	B15	32	3.595	282.23	30.2	354.42
10	1	Cubic	1800	B10	34	3.595	271.57	30.91	357.01
11	1	Cubic	1800	B20	30	3.215	308.95	29.33	360.52
12	1	Center	1900	B15	32	3.255	282.23	30.2	356.18
13	1	Cubic	1800	B20	34	3.66	303.28	28.47	360.64
14	1	Cubic	2000	B20	30	3.508	314.85	29.03	384.65
15	1	Cubic	1800	B10	30	3.48	292.95	28.63	330.01
16	1	Cubic	2000	B20	34	3.595	309.86	28.17	355.24
17	1	Center	1900	B15	32	3.505	284.55	30.2	357.98
18	1	Center	1900	B15	32	3.075	284.55	30.2	358.94
19	1	Cubic	2000	B10	34	3.595	275.96	30.81	360.98
20	1	Cubic	2000	B10	30	3.415	294.02	28.53	351.73

Where S: Engine speed (rpm); B: JB-PD blend (%) and T: Torque (N.m)

Table 4.11: ANOVA and regression results of predicted engine performance.

Interaction	BP		BSFC		BTE%		EGT	
	p-value	coefficient	p-value	coefficient	p-value	coefficient	p-value	coefficient
Constant	0.125	-36.4124	0.098	2397.3300	0.060	-1.7925	0.755	-2924.1400
S	0.051	0.016356	0.603	-1.374180	0.842	0.001209	0.011	2.378520
B	1.000	0.406938	0.000	-15.620800	0.002	0.026878	0.001	-23.194900
T	0.000	1.294840	0.001	-41.266800	0.000	0.045053	0.001	78.121300
S²	0.001	-0.000004	0.009	0.000336	0.000	0.000000	0.005	-0.000234
B²	0.005	-0.001294	0.001	0.211529	0.006	-0.000076	0.403	0.022554
T²	0.000	-0.015977	0.099	0.463777	0.004	-0.000505	0.025	0.430337
S × B	0.665	-0.000014	0.635	0.001750	0.610	-0.000001	0.000	0.016125
S × T	0.723	-0.000028	0.785	0.002500	1.000	0.000000	0.000	-0.054875
B × T	0.000	-0.010688	0.230	0.243567	0.000	-0.000728	0.089	-0.229859
R²	96.28%		92.98%		93.20%		96.32%	
R²(adj)	92.15%		85.18%		85.64%		92.22%	

4.10.1 Brake power

The Figures 4.24(a-c) shows effect of engine speed, JB-PD blending ratio and torque on brake power (BP). Higher BP was observed over medium engine speeds and JB blending percentages compared to lower or upper parametric combinations. As seen from Figures 4.24(b) and 4.24(c), increase in BP was noted while the engine was operated over a torque of 30 N.m.

$$BP = -36.4142 + 0.016S + 0.407B + 1.295T - 0.000004S^2 - 0.001295B^2 - 0.015977T^2 - 0.000014SB - 0.000028ST - 0.010688BT \quad (11)$$

Eq. (11) represents the quadratic regression equation for optimal BP. As seen from Table 4.11, 'BP' model fitness coefficients R^2 (96.28%) and R^2_{adj} (92.15%), specifies a close correlation between the modelled parameters as well as the response. From Table 4.10. A minimum BP of 3.075kW was resulted for a center point (1900 rpm, B15, 32 N.m) and, whereas a maximum BP of 3.66kW at cubic parameters set (1800 rpm, B20, 34 N.m). In general, a due to lower calorific values, biodiesel blended fuels outcomes in lower BP compared to PD. The variation in BP also be attributed to higher density and higher kinematic viscosity of biofuel as well as poor JB-PD blends. Also, as the JB ratio rises in a fuel blend; oxygenation of the fuel raises leading to clean combustion and higher BP over increase in engine torque. On the other hand BP diminishes beyond B15, which is due to the lower fuel combustion quality owing to high viscosity and density besides poor calorific values of a fuel blend. These results were in accordance with the research investigations of Shehata & Razeq, (2011), Ejilah et al., (2010) and Patel et al., (2016). Additionally, poor characteristics of biofuels like atomization and volatility causes in lowering BP (Ong et al., 2014; Patel et al.,

2016). The comparative graph Figure 4.25 shows a close correlation between predicted and reference experimental results.

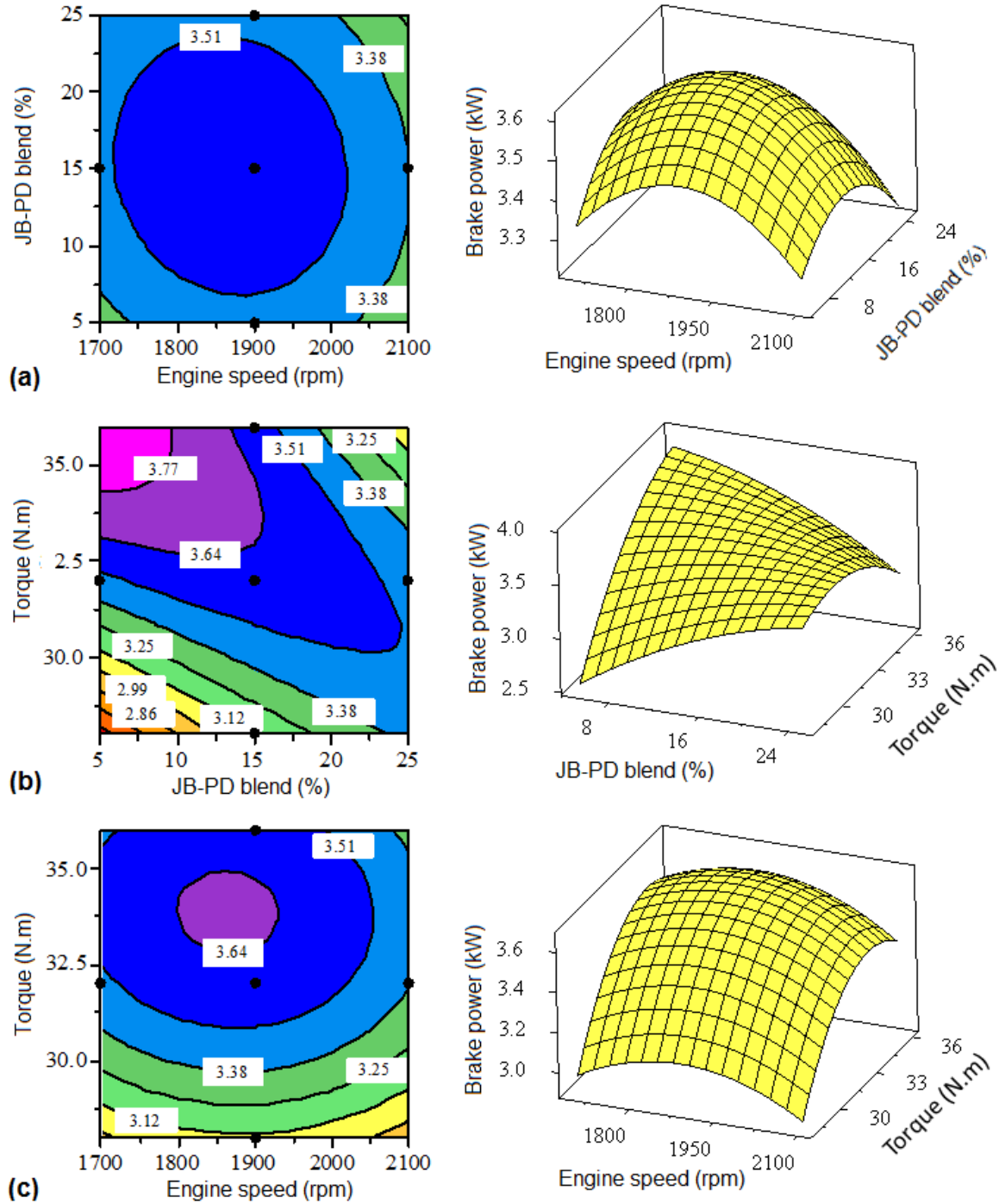


Figure 4.24: Brake power (kW) variations in contrast to the interactions of engine speed, JB-PD blending ratio and torque.

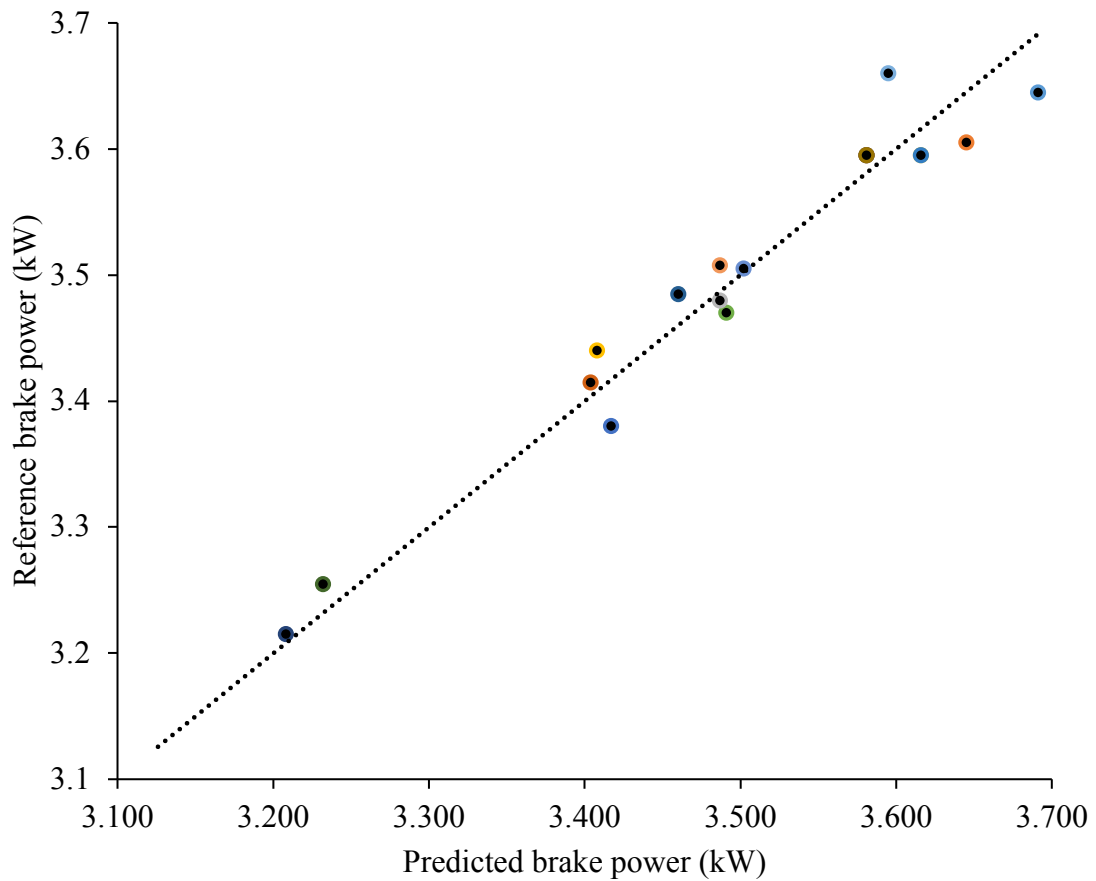


Figure 4.25: Comparative graph showing predicted and reference results of brake power.

4.10.2 Brake specific fuel consumption

Table 4.10 illustrates the predicted results of brake specific fuel consumption (BSFC). A minimum BSFC of 271.57 g/kWh was observed at a cubic parameter set of (1800 rpm, B5, 34 N.m) while a higher BSFC of 314.85 g/kWh was resulted at cubic point (2000 rpm, B20, 30 N.m). As seen from Table 4.11, the fitness of BSFC response surface model was confirmed through its coefficients of goodness R^2 (92.98%) and R^2_{adj} (85.18%). Higher BSFC can be observed over increase of the JB ratio in the fuel blends. This is due to the lowering of fuel's heating value over blending with biodiesels. At higher engine speeds, BSFC increases due to lower combustion and friction heat losses (Ong et al., 2014).

$$BSFC = 2397.33 - 1.374S - 15.621B - 41.267T + 0.000336S^2 + 0.211529B^2 + 0.463777T^2 + 0.00175SB + 0.0025ST + 0.243567BT \quad (12)$$

Among the model terms, both engine speed and JB-PD blends are significant. From Eq. (12), the positive sign of all quadratic and interaction terms indicates their favourable impact though, limited. Figure 4.26(a-c) infers the BSFC response surface and contour plots of the biofuel blends fuelled DI-CI engine. From the surface plots, a BSFC of 275-281.1 N.m was resulted over operating parameters engine speed of 1850 – 1950 rpm, blending ratios of 7.5 – 12.5% and torque 33 – 36.25 N.m. The engine torque and BSFC impacts are in inverse relation. Further, decrease in BSFC was observed with the increasing torque equally on interactions of engine speed and blend ratios. The comparative graph shown in Figure 4.27, indicates a close correlation between predicted and reference experimental results.

The fuel properties such as lower density and kinematic viscosity of fuel blends improves combustion rate and as a result BSFC increases (Mofijur et al., 2013). On the other hand higher density values of a fuel causes higher quantity of fuel injection into the combustion chamber for a given volume and pressure. Besides, lower calorific value of a biofuel results in higher fuel consumption to produce the same power as a fuel with higher calorific value, consequently increases its BSFC (Buyukkaya, 2010). Hence, it can be observed that BSFC of JB-PD blends fuelled engine declines at mid operating parametric values of engine speed and blend ratios. Similar observations were noted in the works of Sivaramakrishnan & Ravikumar (2013) and Ganapathy et al. (2011b).

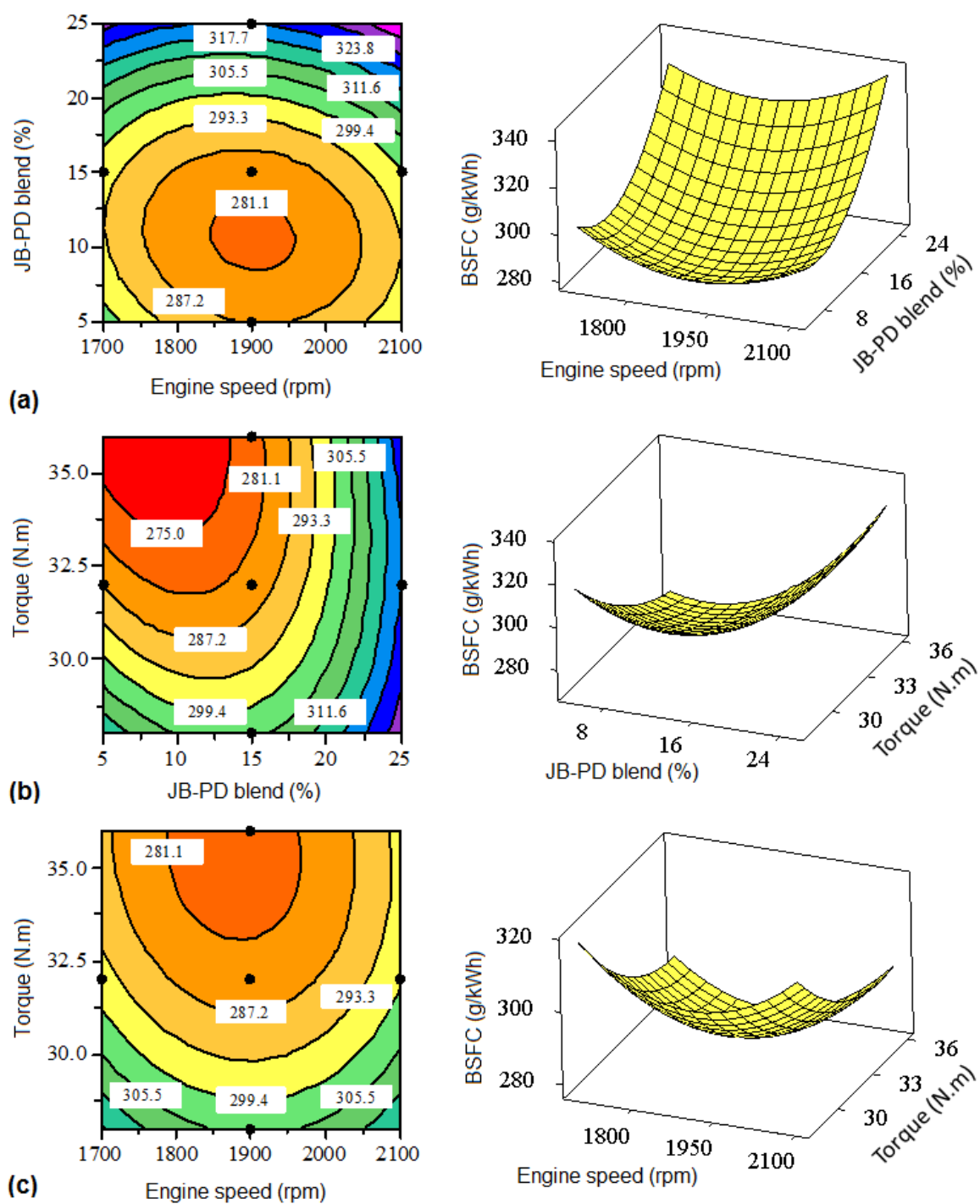


Figure 4.26: Brake specific fuel consumption (g/kWh) variations in contrast to the interactions of engine speed, JB-PD blending ratio and torque.

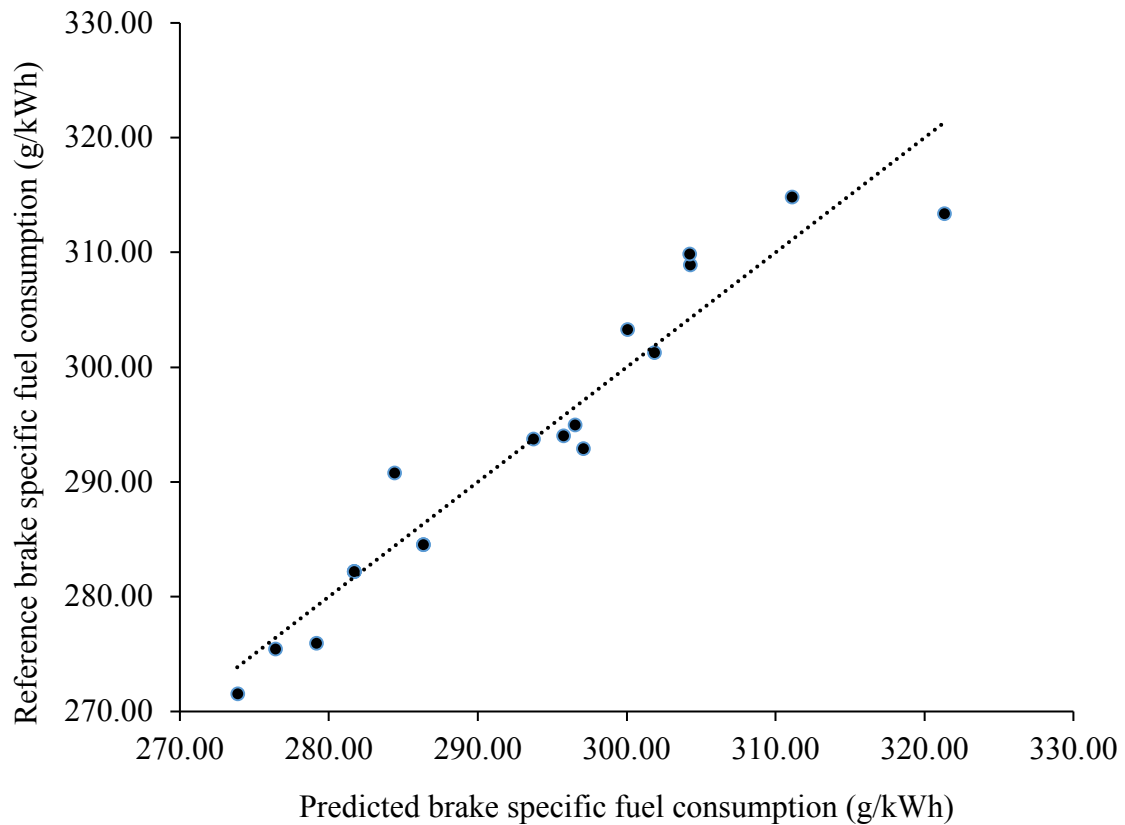


Figure 4.27: Comparative graph showing predicted and reference results of brake specific fuel consumption.

4.10.3 Brake thermal efficiency

Brake thermal efficiency (BTE) determines the engine's efficiency in transforming a fuels' chemical energy into mechanical energy. The variations in BTE with respect to the DI-CI engine operating parameters were shown in Table 4.10. A max. BTE of 30.2% was predicted at a center point of parameters set (1800 rpm, B5, 32 N.m) while a min. BTE of 28.17% was at a cubic point (2000 rpm, B20, 34 N.m). As can be seen from Table 4.11, the BTE coefficients of goodness that include R^2 (93.20%) and R^2_{adj} (85.64%), infers the fitness of BTE response surface model. The BTE significantly increases with the increasing JB ratio in the biofuel blends. This can be correlated with the cetane number of the fuels. Fuel blends having superior cetane number demonstrates good combustion characteristics which would

probably offset the deficiencies of biofuels such as longer ignition delays (Ganapathy et al., 2011b). It can be noted from Eq. (13) that JB blending ratio and engine torque are significant compared to the engine speed. Then again, exception to the interactions of engine speed and torque, both quadratic and interaction terms have shown an insignificant negative impact on resulting BTE%.

$$BTE = -1.793 + 0.001209 S + 0.026878B + 0.045053T - 0.0000003S^2 - 0.000076B^2 - 0.000505T^2 - 0.000001SB + 0.0000001ST - 0.000728BT \quad (13)$$

Figures 4.28(a-c) shows response surface and contour plots of the percentage change in engine's BTE with regard to the variations in operating parameters. From the Figures 4.28(a) and 4.28(b), it can be inferred that higher BTE can be achieved when the engine is operated over medium values such as 1900 rpm, B15 and 32.5 N.m compared to the lower or higher limits of each parameter. This may be due to the formation of improper air fuel mix at higher engine speeds. Similarly Figure 4.28(c) indicates rise in BTE % proportional to increase in engine torque and JB blending ratio. This phenomenon can be attributed to improved rate of combustion with higher torque and higher oxygen content presence in the fuel blends (Buyukkaya, 2010; Ong et al., 2014). The Figure 4.29 interprets a close correlation between predicted and reference experimental results. Henceforth, it can be summarized that the optimal thermal efficiency of an engine be influenced by parameters such as type of fuel, biodiesel blending ratio, engine speed, oxygen content, calorific value and cetane number. Analogous results were noted by other researchers (Ong et al., 2014; Qi et al., 2009; 2010).

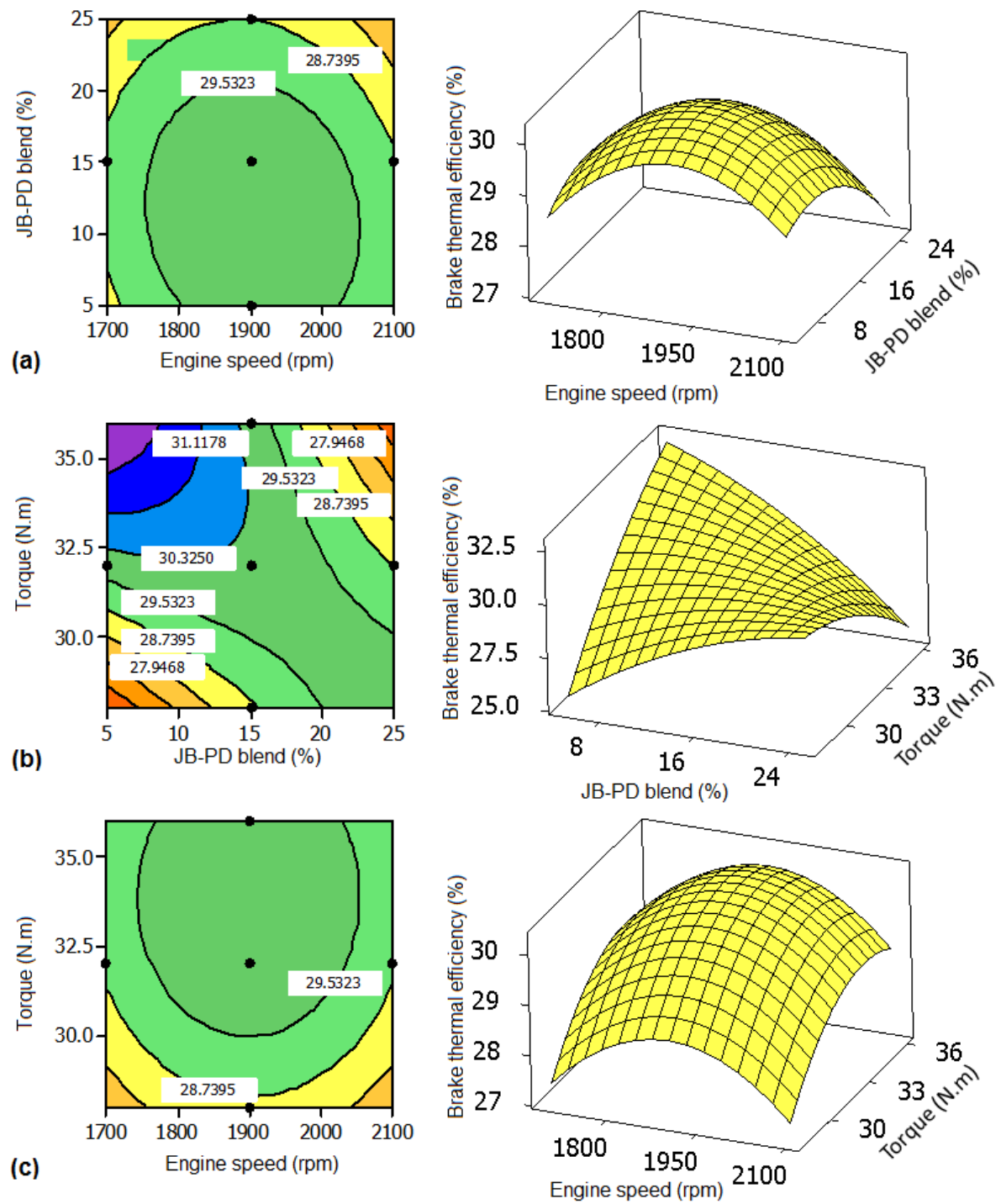


Figure 4.28: Brake thermal efficiency (%) variations in contrast to the interactions of engine speed, JB-PD blending ratio and torque.

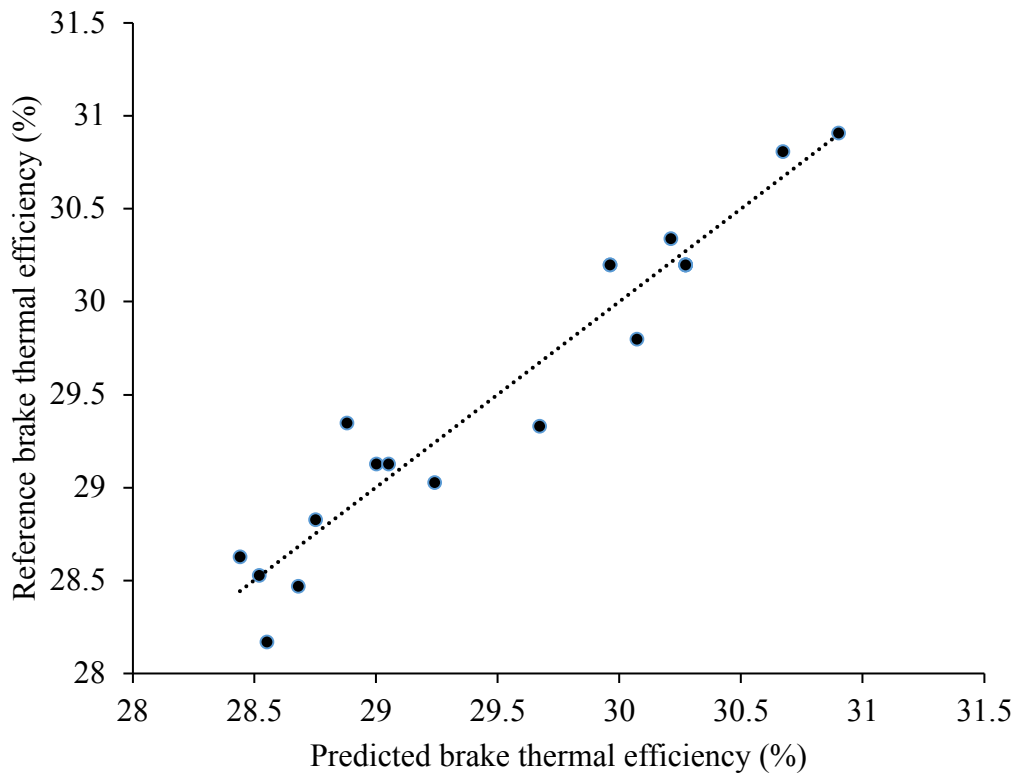


Figure 4.29: Comparative graph showing predicted and reference results of brake thermal efficiency.

4.10.4 Exhaust gas temperature

Exhaust gas temperature (EGT) of an engine specifies, the heat release characteristics of a tested fuel sample over a given combustion conditions. EGT varies with the engine speed, load and variant fuel properties that include oxygen content, calorific value and viscosity (Chattopadhyay & Sen, 2013). The variations in EGT with respect to the interactions of DI-CI engine operating parameters shown in Table 4.10. According to the results obtained, a maximum EGT of 384.65°C was measured at (2000 rpm, B20, 30 N.m) whereas a minimum EGT of 330.01°C was noted at (1800 rpm, B10, 30 N.m). The regression model fitness coefficients of EGT, as shown in Table 4.11, $R^2(96.32\%)$ and $R^2_{adj}(92.22\%)$, indicates close correlation among the modelled terms and EGT.

$$EGT = -2924.14 + 2.379 S - 23.195B + 78.121T - 0.000234S^2 + 0.022554B^2 + 0.430337T^2 + 0.016125SB - 0.054875ST - 0.229859BT \quad (14)$$

The Eq. (14) shows that the EGT model terms are significant in the order of $T > S > B$. In addition, the quadratic terms of blends, torque and a quadratic interaction of engine speed and JB blend ratio have positive impact on EGT. It's known that the quantity of fuel injection will relatively rises with increasing engine speed and conversely get lowers with their higher kinematic viscosity and density values. This phenomenon would affect the quality of fuel combustion and EGT (Kegl, 2011). The response surface interactions of three parameters engine speed, biodiesel blend ratio and torque and their impact on EGT were shown in Figures 4.30(a-c). From the Figure 4.30(a) maximum EGT values could be measured at both lower and higher engine speed and blend ratios. However, the interactions of engine speed and torque at lower and higher limits resulted in minimum EGT, see Figure 4.30(b). The comparative graph Figure 4.31 represents a close correlation between predicted and reference experimental results.

The rate of fuel combustion can be correlated with oxygen content of corresponding fuel. The higher activation energy causes in the combustion chamber through air-fuel intake ratio due to fuel's higher oxygen content which initiate an accelerated chemical reaction. Hence, higher EGT values were noted for the fuel blend B20 over B10 (Nayak & Pattanaik, 2014). In addition, the EGT has a significant impact on concentration of exhaust emissions particles as well as high nitrogen oxide emissions because of lower thermal efficiency (Ong et al., 2014; Sampson & Springer, 1973). The biodiesel demonstrating slow rate of fuel burning and extended ignition delays which in turn effects EGT (Usta, 2005). The biofuels such as B5, B10 and B15 has least EGT compared to other blends. This phenomenon is a

result of lower calorific value of a fuel blend along with reduced combustion phase (Ong et al., 2014).

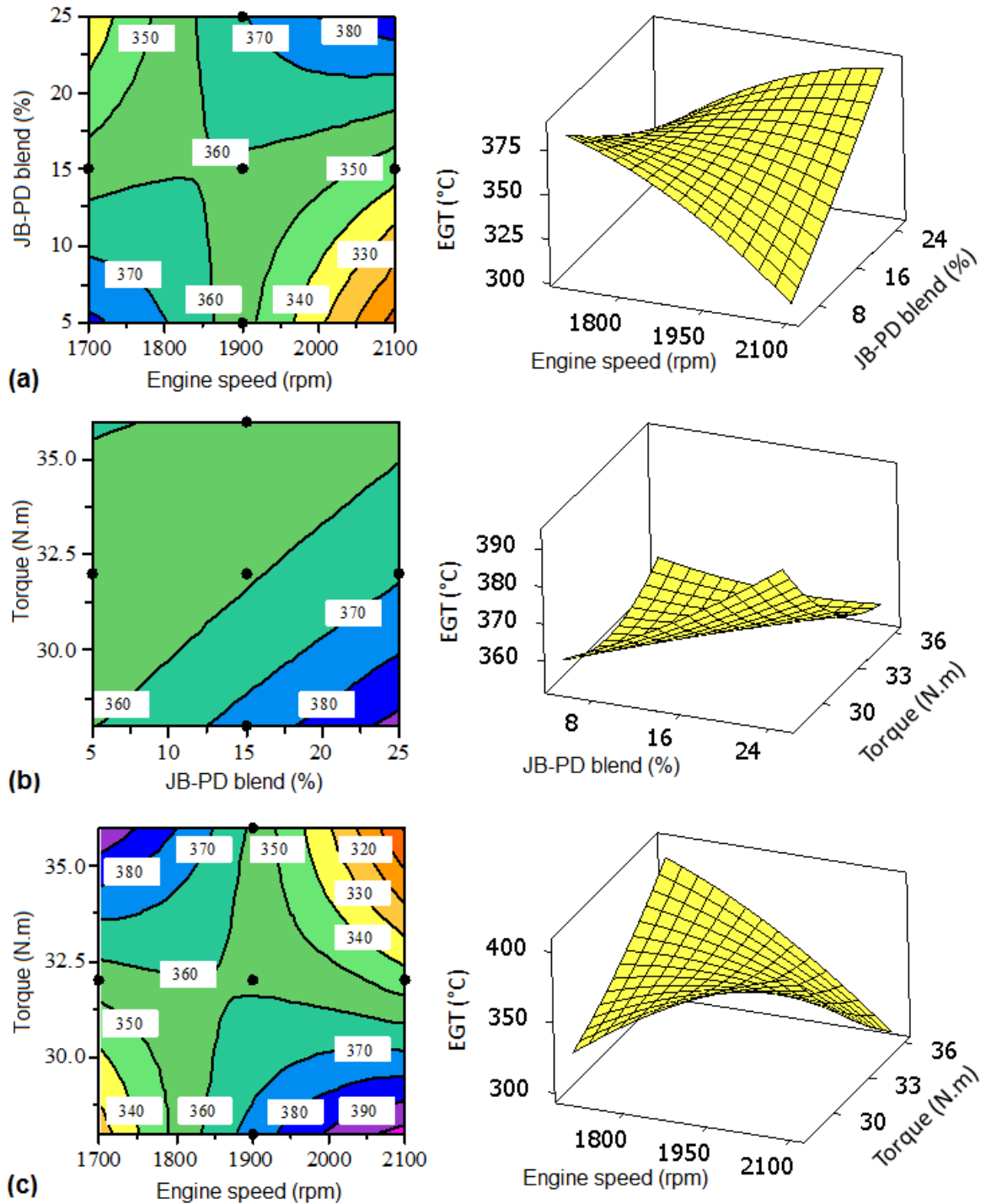


Figure 4.30: Exhaust gas temperature (°C) variations in contrast to the interactions of engine speed, JB-PD blending ratio and torque.

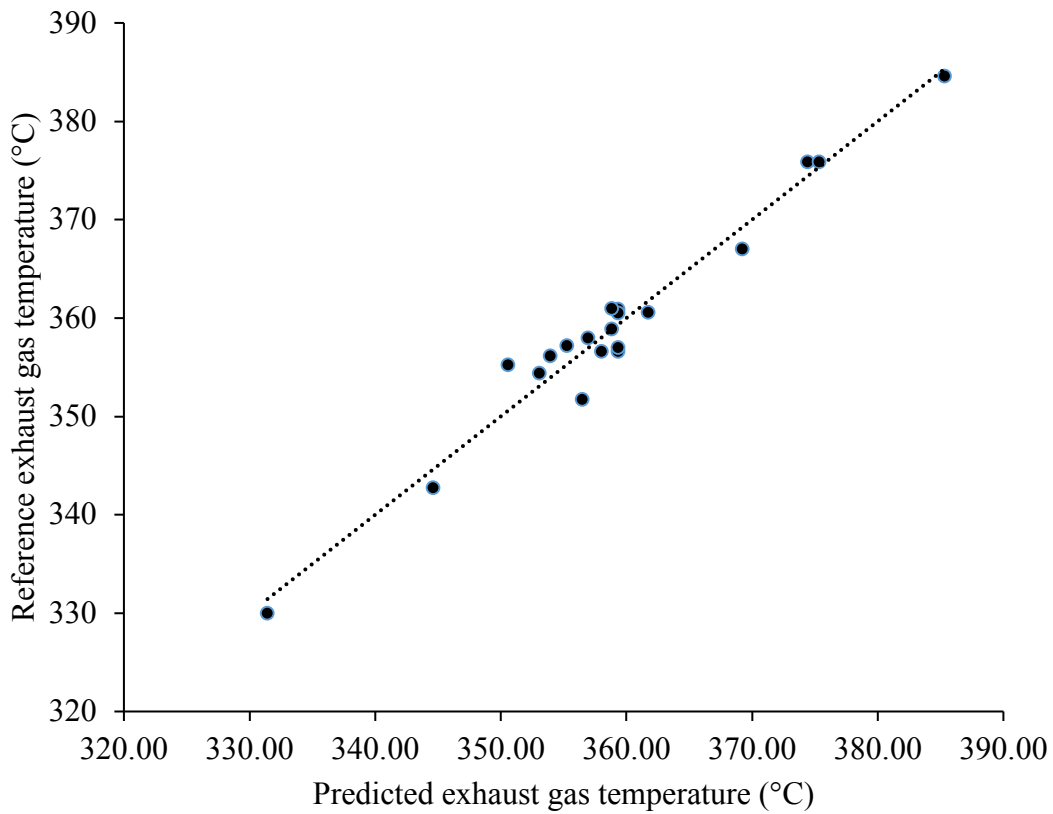


Figure 4.31: Comparative graph showing predicted and reference results of exhaust gas temperature.

4.11 Optimization of exhaust gas emissions

The exhaust gas emissions of DI-CI engine such as NO_x , HC, CO_2 and CO analysed and discussed in the following sections. Table 4.12 presents the predicted results of engine exhaust emissions. ANOVA analytics were tabulated in Table 4.13. The coefficients of determination (R^2) and correlation (R_{adj}^2) for each model found to be narrow, which indicates presence of significant terms in the respective model. Moreover, the impact of model terms on corresponding response can be described through p-value. (Khoobbakht et al., 2016). The model terms having p-value greater than 0.05 are significant. The reference experimental results of exhaust emissions which were utilized to compare and evaluate the predicted results (See Table A-5).

Table 4.12: Predicted results of exhaust gas emissions.

Run	Block	Point	Coded parameters			Predicted exhaust gas emissions				
			S	B	T	Nox	HC	CO ₂	CO	Smoke opacity
			(rpm)	(%)	(N.m)	(ppm vol.)	(ppm vol.)	(%vol.)	(%vol.)	(%HSU)
1	2	Center	1900	B15	32	92	21.4	3.62	0.057	23.9
2	2	Axial	1900	B25	32	94.1	23.7	3.22	0.067	23
3	2	Axial	2100	B15	32	93.9	22.7	3.45	0.070	23.8
4	2	Axial	1900	B15	28	93.9	23.8	3.33	0.079	24.9
5	2	Center	1900	B15	32	93.8	21.4	3.62	0.057	23.9
6	2	Axial	1900	B5	32	93.5	22.1	3.7	0.063	28.5
7	2	Axial	1700	B15	32	93.9	23.4	3.41	0.075	24.8
8	2	Axial	1900	B15	36	91.6	20.7	3.63	0.052	23
9	1	Center	1900	B15	32	90.6	21.4	3.62	0.057	23.9
10	1	Cubic	1800	B10	34	93.2	21.2	3.86	0.058	25.2
11	1	Cubic	1800	B20	30	97	23.6	3.33	0.072	24.4
12	1	Center	1900	B15	32	91.3	21.4	3.62	0.057	23.9
13	1	Cubic	1800	B20	34	94	22.9	3.23	0.070	23.7
14	1	Cubic	2000	B20	30	95.3	24.2	3.35	0.076	23.6
15	1	Cubic	1800	B10	30	95.4	23.1	3.48	0.076	26
16	1	Cubic	2000	B20	34	95.2	23.3	3.27	0.072	23.1
17	1	Center	1900	B15	32	95	21.6	3.6	0.059	23.8
18	1	Center	1900	B15	32	93.1	21.6	3.6	0.059	23.8
19	1	Cubic	2000	B10	34	93.8	21.3	3.81	0.057	24.3
20	1	Cubic	2000	B10	30	93.7	23	3.45	0.073	25.2

Where S: Engine speed (rpm); B: JB-PD blend (%) and T: Torque (N.m)

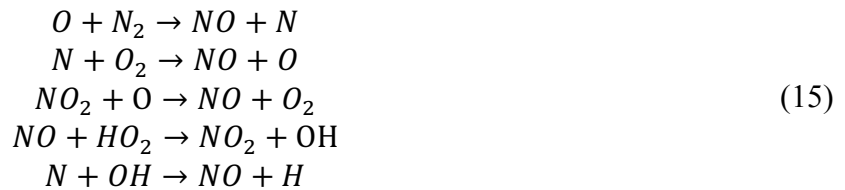
Table 4.13: ANOVA and regression results of predicted exhaust gas emissions.

Interaction	NO _x		HC		CO ₂		CO		Smoke opacity	
	p-value	coefficient	p-value	coefficient	p-value	coefficient	p-value	coefficient	p-value	coefficient
Constant	0.004	393.5780	0.007	267.6330	0.478	-27.9109	0.004	2.4118	0.606	94.3168
S	0.010	-0.240501	0.233	-0.170539	0.746	0.017531	0.109	-0.001553	0.022	-0.044948
B	0.191	-0.354513	0.000	-1.213730	0.000	0.289451	0.003	-0.014061	0.000	-1.209720
T	0.070	-3.778210	0.000	-4.332420	0.005	0.766718	0.000	-0.044910	0.004	-0.682331
S²	0.061	0.000028	0.000	0.000044	0.014	-0.000005	0.000	0.000000	0.258	0.000010
B²	0.000	-0.030757	0.000	0.015807	0.030	-0.001605	0.001	0.000087	0.000	0.018514
T²	0.079	-0.064730	0.001	0.059103	0.048	-0.008907	0.000	0.000596	0.852	0.004147
S × B	0.553	0.000285	0.250	0.000225	0.514	0.000038	0.191	0.000002	0.811	0.000075
S × T	0.008	0.003888	1.000	0.000000	1.000	0.000000	0.987	0.000000	0.962	0.000038
B × T	0.345	0.024436	0.207	0.013196	0.005	-0.010693	0.013	0.000245	0.577	0.009377
R²	91.28%		97.24%		97.88%		96.90%		94.35%	
R²(adj)	81.59%		94.18%		95.51%		93.45%		88.06%	

4.11.1 Nitrogen oxides

The nitrogen oxides (NO_x) exhaust emissions for JB-PD fuel blends at different engine speeds and torque parameters were shown in Table 4.12. The NO_x regression model fitness coefficients R^2 (91.28%) and R^2_{adj} (81.59%), as shown in Table 4.13, indicates good agreement among the modelled terms for optimal NO_x analysis. A minimum NO_x of 90.58 ppm vol. was observed at a center point of (1900 rpm, B15, 32 N.m) whereas a max. NO_x of 97.04 ppm vol. was noted at a cubic parameters set of (1800 rpm, B15, 30 N.m).

The NO_x (NO and NO₂) formation in DI-CI engines is subjected to many interactions in a combustion chamber at dissimilar levels of temperature gradient. The NO_x formation is a result of successive chemical reactions, especially at temperatures above 2100 K, among the atomic oxygen, nitrogen and the hydroxyl radicals (Heywood, 2011; Jachimowski & Wilson, 1980). The formation of various NO_x kinetics can be described through Zeldovich's reaction mechanism series as indicated in Eq. (15) (Heywood, 2011). The low engine speeds and torque would result in higher fuel consumption consequently it stimulates cylinder temperature and emits more NO_x emissions.



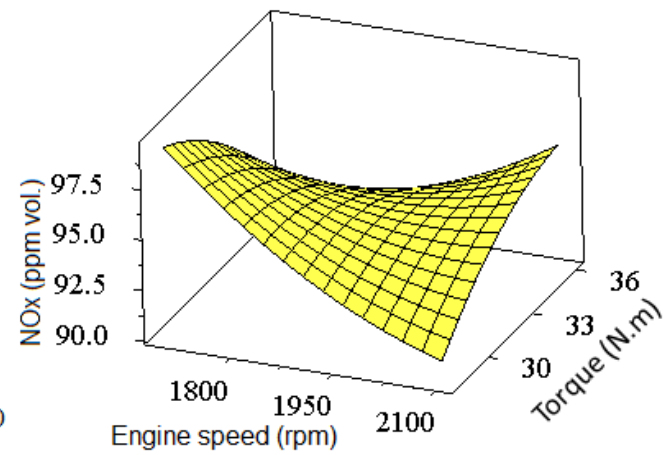
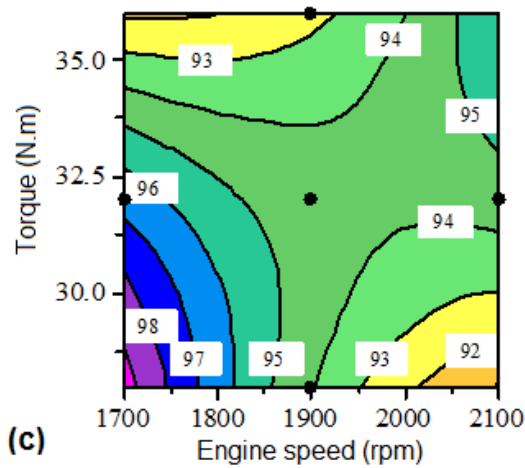
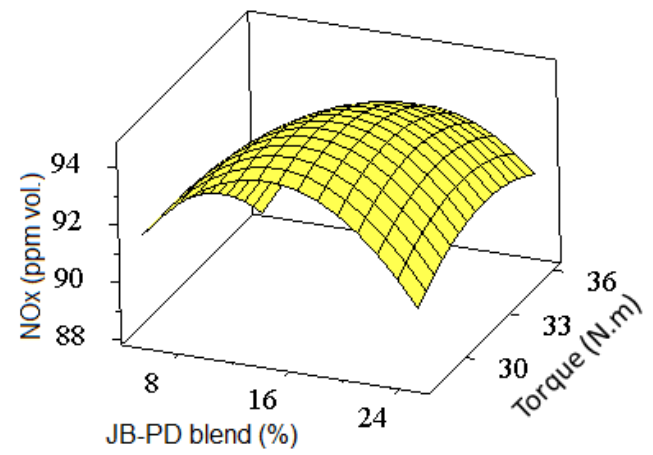
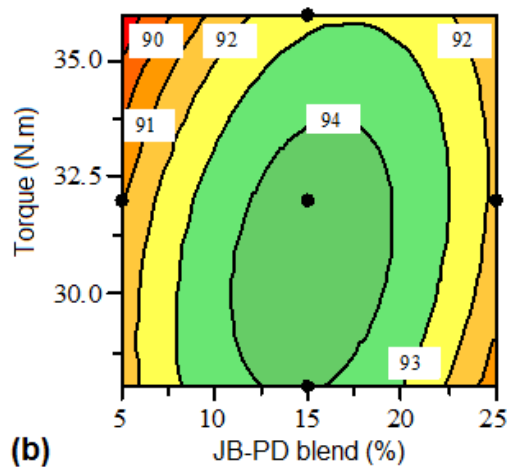
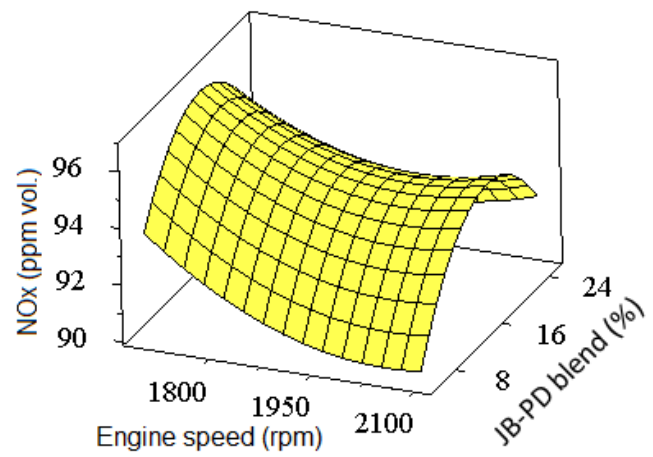
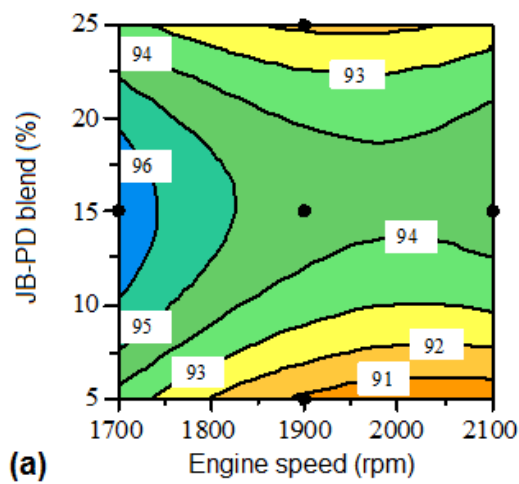


Figure 4.32: NO_x exhaust emission (ppm vol.) variations in contrast to the interactions of engine speed, JB-PD blending ratio and torque.

From the Figures 4.32 (a-c), it can be seen that higher NO_x were noted when the engine is operated lower speeds and torque; while minimum NO_x emissions were measured with lower JB blends. These dissimilarities can be correlated and attributed to the combustion characteristics such as the rate of combustion and time of combustion which in turn regulates the combustion chamber's temperature. The combustion time is primarily affected by ignition delay which is consecutively correlated with fuel's cetane number. The calorific value of biofuel measures lesser than the petro diesel, hence, additional volume of biofuel is to be injected in to the combustion chamber to produce required energy levels through high initial rate of combustion, which in turn escalates NO_x emissions (Rao, 2011).

$$NO_x = 393.578 - 0.241S - 0.355B - 3.778T + 0.00028S^2 - 0.0307568B^2 - 0.06473T^2 + 0.000285SB + 0.003888ST + 0.0244364BT \quad (16)$$

According to the quadratic regression equation for NO_x, Eq. (16), the quadratic terms of engine speed and the interaction terms have highest impact on increasing the NO_x emissions while the JB blending ratio has negative impact on NO_x. As can be seen from the Table 4.9, the cetane number of JB-PD blends increases with percentage of JB ratio. Hence, lesser NO_x emissions were measured from the interactions of biodiesel blends, see Figures 4.32(a) and 4.32(b). The Figure 4.33 interprets a close correlation between predicted and reference experimental results. Enhanced biofuels properties that include kinematic viscosity, density and oxygen contents significantly effects combustion process as compared to petro diesel (Palash et al., 2013). These fuel characteristics contributes in early start of fuel injection, which initiates fuel combustion close to the top dead center as a result NO_x emissions increases. These observations are in agreement with the results reported in

literature asserting rise of NO_x emissions with increasing percentage of biodiesel in the blends (Karavalakis et al., 2016; Sivaramakrishnan & Ravikumar, 2013, 2012).

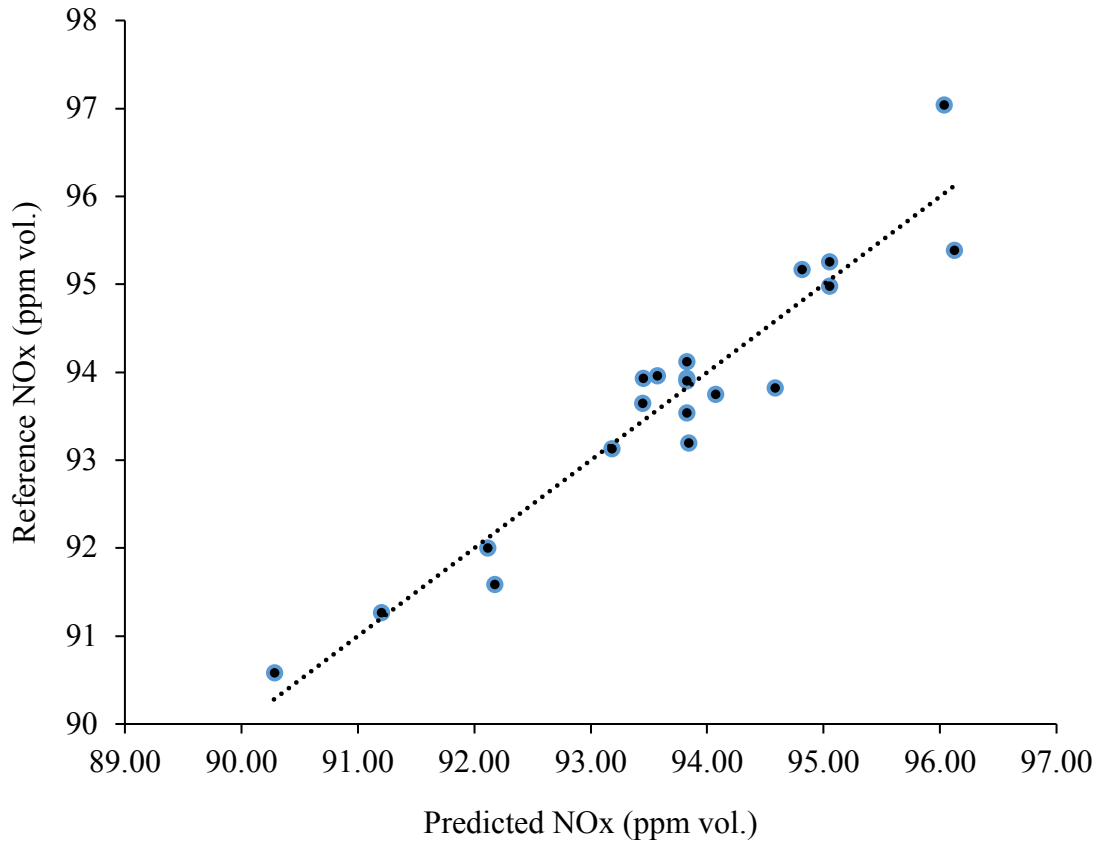


Figure 4.33: Comparative graph showing predicted and reference results of NO_x emissions.

4.11.2 Hydrocarbon

The predicted hydrocarbon (HC) emissions for JB-PD fuel blends were shown in Table 4.12. A minimum HC of 20.74 ppm vol. was noted at an axial point (1900 rpm, B15, 36 N.m) on the other hand a maximum HC of 24.19 ppm vol. was observed for engine operating parameter set of (2000 rpm, B20, 30 N.m). These variations in HC emissions can be attributed to fuel properties of blends' specially viscosity, cetane number and oxygen contents. Also, the fatty acid structural features of a biofuel, for instance, length of carbon chain also

significantly effects the HC emissions. Higher viscosity values' of a fuel restrains its spray quality which results in lesser rate of combustion consequently produce higher HC emissions. Conversely, higher cetane number and oxygen levels of a combusting fuel contributes in clean combustion as well as lowers HC emissions.

$$HC = 267.633 - 0.17054S - 1.2137B - 4.33242T + 0.000438S^2 + 0.01581B^2 + 0.059103T^2 + 0.000225SB - 0.0000001ST + 0.0131963BT \quad (17)$$

According to the Eq. (17), quadratic terms have significant impact on growing emissions of unburnt HC. Additionally, the HC regression model fitness coefficients R^2 (97.24%) and R^2_{adj} (94.18%), reveals a good correlation among the regression modelled terms. The operating parametric interactions of engine speed, biodiesel blend percentage, and torque are shown in Figures 4.34(a) and 4.34(b). It is evident that unburnt HC emissions are minimum at their lower mean values of biodiesel blending ratio, and at mean values of engine speed (Ganapathy et al., 2011b). It is also found that HC emissions rise with increasing engine speed, which is caused due to incomplete fuel combustion as a result of shorter combustion time. Similarly as seen from the Figures 4.34(b) and 4.34(c) higher unburnt HC emissions at lower mean values of engine torque; which can be attributed to the cold start fuel properties (Rao, 2011). The Figure 4.35 infers a close correlation between predicted and reference experimental results. The concentration of unburnt HC emissions can be minimized through preheating and rich mixture of oxygenate fuels with petro diesels (Rao, 2011; Sivaramakrishnan & Ravikumar, 2013).

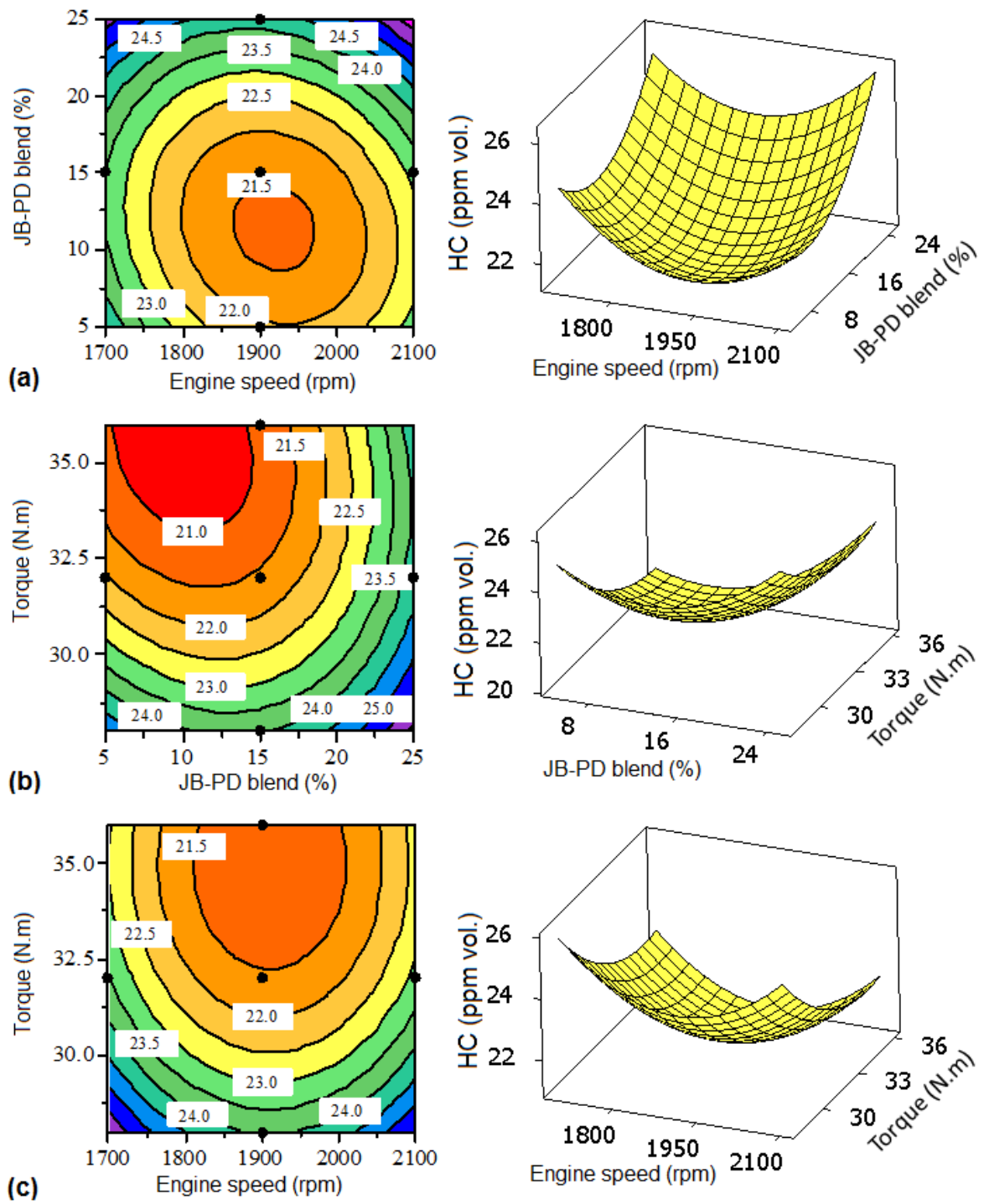


Figure 4.34: Hydrocarbons exhaust emission (ppm vol.) variations in contrast to the interactions of engine speed, JB-PD blending ratio and torque.

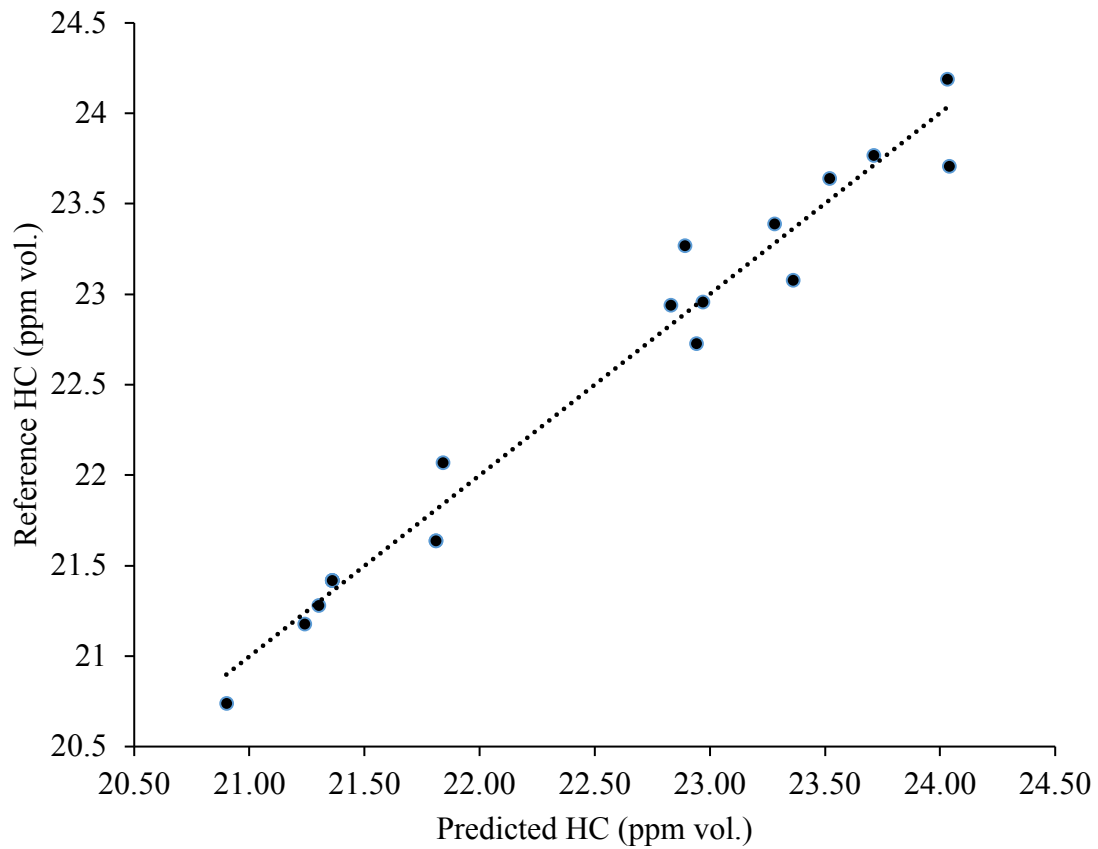


Figure 4.35: Comparative graph showing predicted and reference results of hydrocarbon emissions.

4.11.3 Carbon dioxides

The carbon dioxide (CO₂) emission regression model fitness coefficients R^2 (97.88%) and R^2_{adj} (95.51%) , as illustrated in Tables 4.12 and 4.13, indicates good correlation among the modelled terms for optimal CO₂ emission analysis. A maximum CO₂ of 3.856 %vol. was observed for engine operating parameter set (1800 rpm, B10, 34 N.m) on the other hand a minimum CO₂ of 3.223 %vol. was noted at axial point (1900 rpm, B25, 32 N.m).

$$CO_2 = -27.911 + 0.01753S + 0.2895B + 0.7667T - 0.000474S^2 - 0.00161B^2 - 0.00891T^2 + 0.000375SB + 0.0000001ST - 0.01069BT \quad (18)$$

According to the quadratic regression equation for optimal CO₂ analysis Eq. (18), the variations in engine operating parameters have a positive impact through linear terms compared to the quadratic terms. However the impact of engine speed and torque is very scant over other interactions. Figures 4.36(a) and 4.36(c) illustrates that, lower CO₂ exhaust emissions (3.06 %vol.) were observed for fuel blends over and above B20; this can be attributed to presence of higher oxygen contents besides cetane numbers of a fuel increases linearly with increasing rate of JB ratio's in the biofuel blend. On the other hand, studies by many researchers shown that increasing carbon contents and lower kinematic viscosity of a fuel have contrary impact on the CO₂ exhaust emissions (Karavalakis et al., 2016; Mohammadi et al., 2012; Ong et al., 2014). Figures 4.36(a-c) unveils a trend of higher CO₂ emissions of 3.71 %vol. and 3.97 %vol. over mean engine speeds and higher torque ranges. This is caused due to increasing fuel consumption and enriched combustion at high temperatures. These observations are in agreement with investigation results of Rao, (2011) and Ong et al. (2014). Further, a close correlation between predicted and reference experimental results can be observed from Figure 4.37.

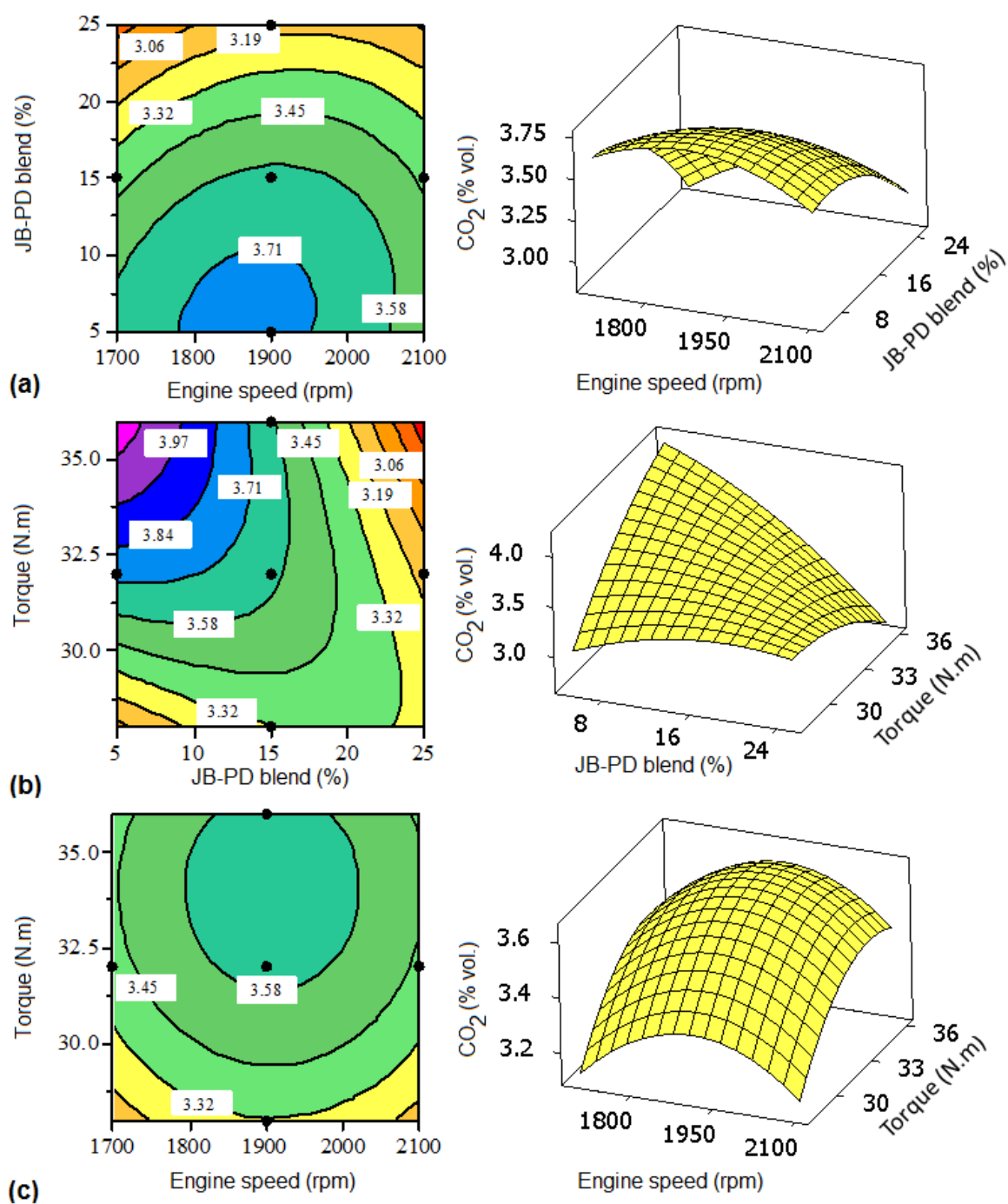


Figure 4.36: Carbon dioxide exhaust emission (%vol.) variations in contrast to interactions of engine speed, JB-PD blending ratio and torque.

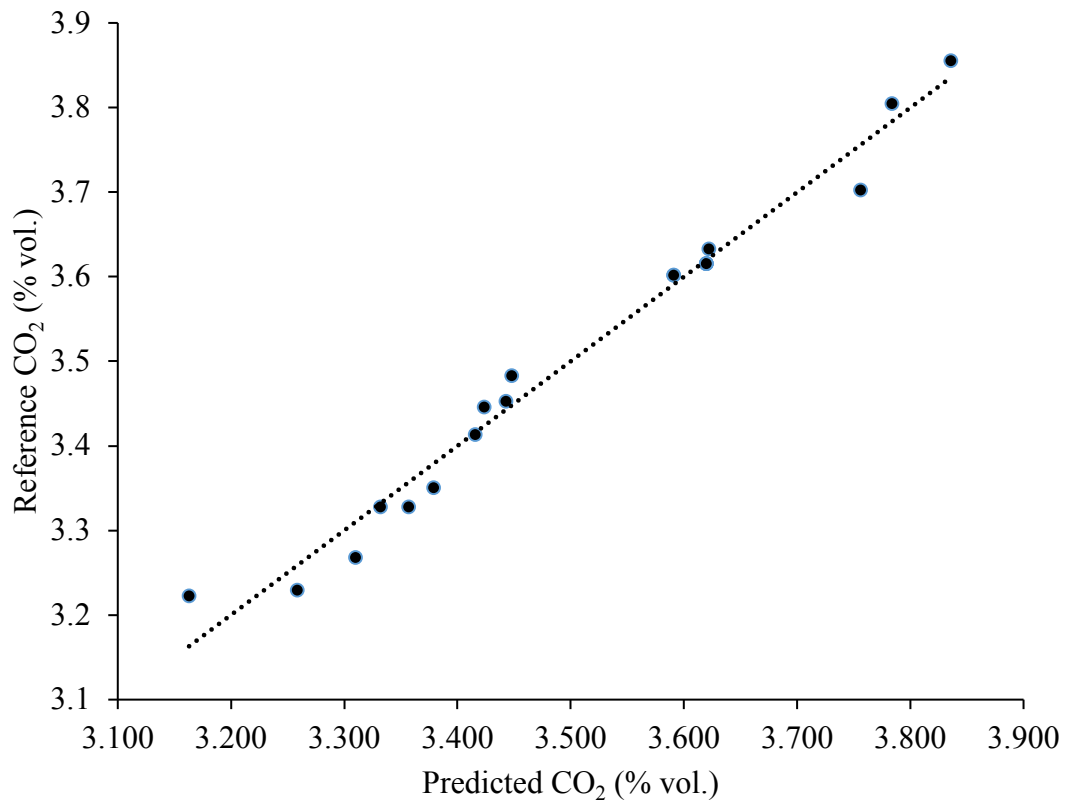


Figure 4.37: Comparative graph showing predicted and reference results of carbon dioxide emissions.

4.11.4 Carbon monoxide

As shown in Table 4.12, the carbon monoxide (CO) emissions measures a maximum CO of 0.079 % vol. and a minimum CO of 0.052 %vol. for operating parameter sets (1900 rpm, B15, 28 N.m) and (1900 rpm, B15, 36 N.m) respectively. The Eq. (19) represents quadratic regression equation for optimal CO analysis. The linear, quadratic and interaction terms of torque parameter are significant compared to other terms. The fitness coefficients of CO regression model $R^2(96.90\%)$ and $R^2_{adj}(93.45\%)$, shown in Table 4.13, signifies close agreement between the modelled terms in analysis of optimal CO emissions.

$$\text{CO} = 2.4118 - 0.00155S - 0.01406B - 0.04491T + 0.0000001S^2 + 0.0000001B^2 + 0.0006T^2 + 0.0000001SB + 0.0000001ST + 0.000245BT \quad (19)$$

The CO emission's variant in contrast with interactions of engine operating parameters speed, torque and JB blending ratio illustrated in Figures 4.38(a-c). It can be observed that minimum 0.055 % vol. of CO emission was noted over 1900 rpm, ~B15% and above 32.5N.m. An increasing tendency of CO exhaust emission at low and high engine speeds and blending ratios can be seen from Figures 4.38(a) and 4.38(c). On the other hand less CO emissions over increasing torque were noted. Reasons for these variations can be attributed to the physicochemical fuel properties besides volumetric consumption of biofuel with varying engine torque. The increased torque could improves combustion cycle efficiency which causes in CO reduction (Behçet et al., 2015; Ganapathy et al., 2011a). The biofuel properties that include high cetane number, low density, low viscosity and presence of higher oxygen contents contributes in improving the rates of fuel combustion, atomization and evaporation which lead to significant reduction in CO emissions (Behçet et al., 2015; Ong et al., 2014). The comparative graph shown in Figure 4.39, indicates a close correlation between predicted and reference experimental results.

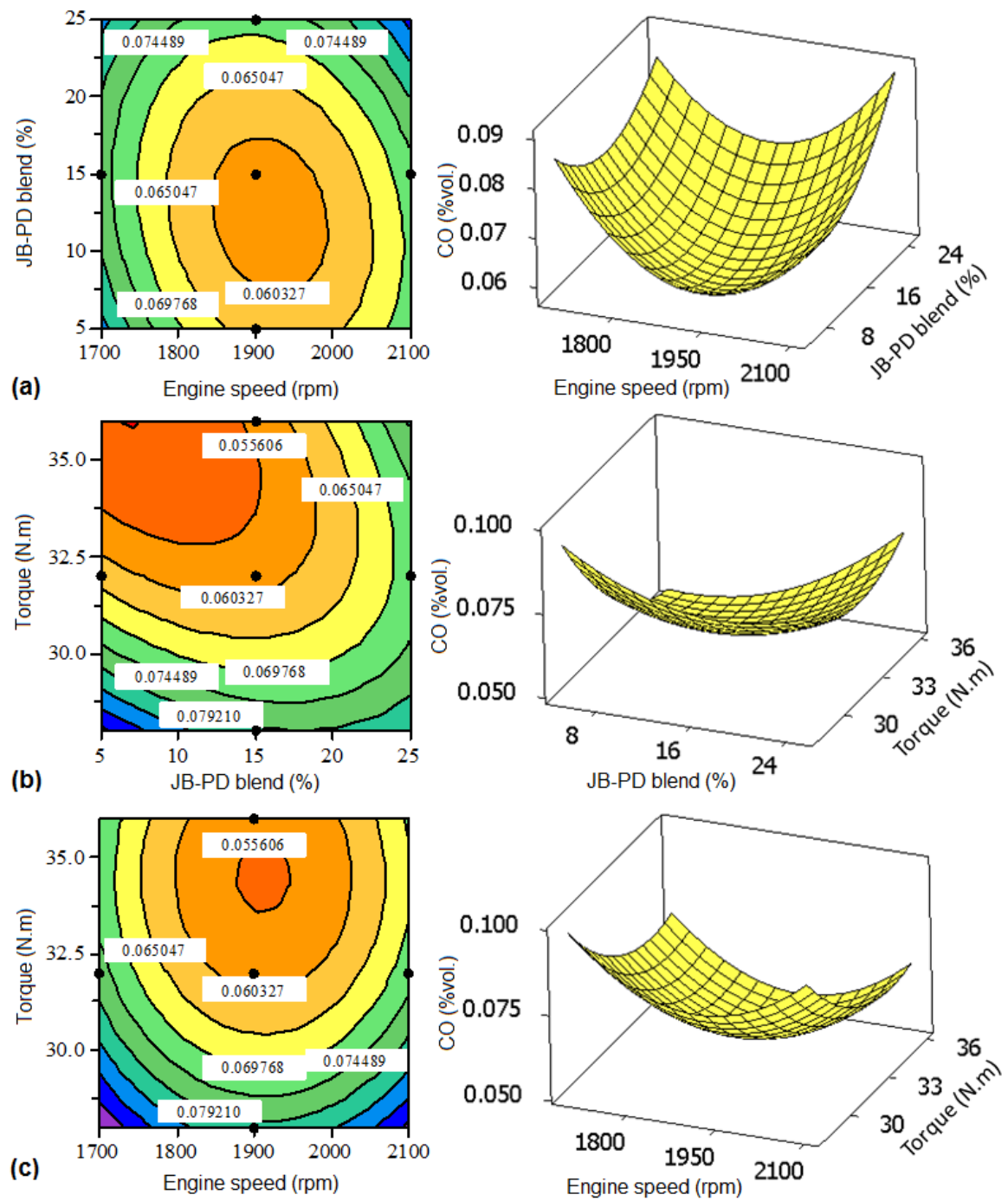


Figure 4.38: Carbon monoxide exhaust emission (%vol.) variations in contrast to the interactions of engine speed, JB-PD blending ratio and torque.

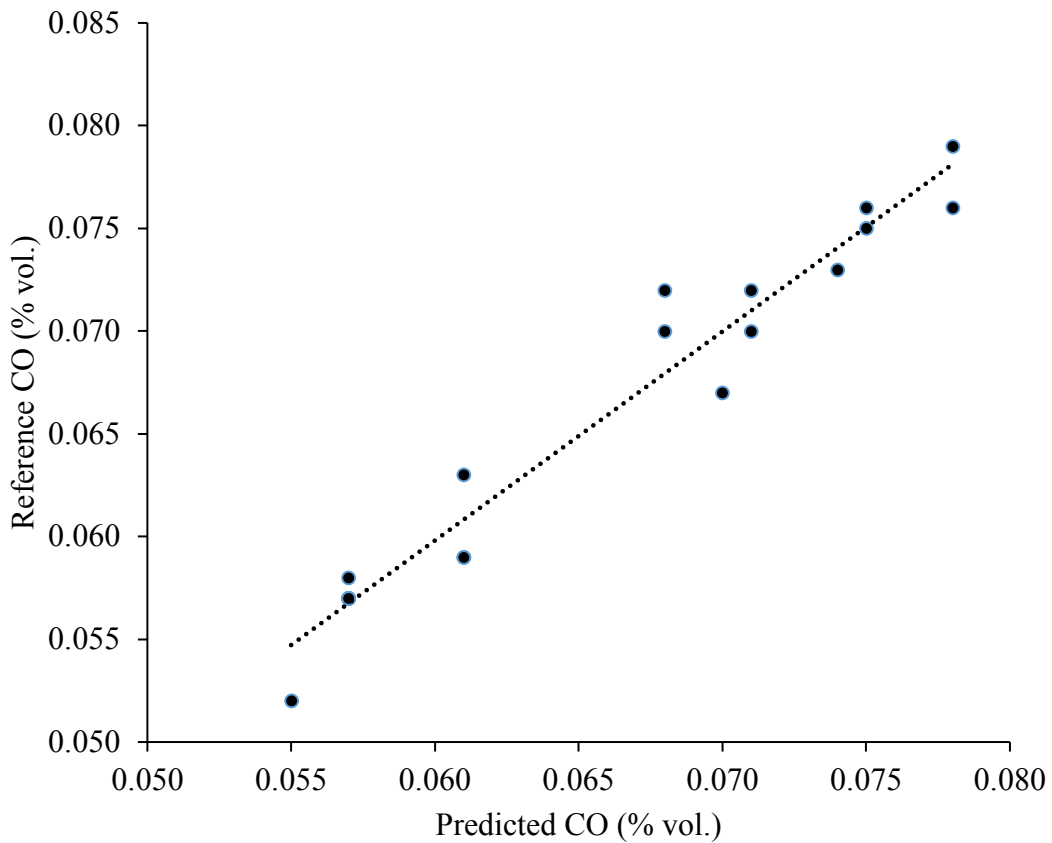


Figure 4.39: Comparative graph showing predicted and reference results of carbon monoxide emissions.

4.11.5 Smoke opacity

The smoke opacity prediction analysis was carried out following a quadratic regression equation as represented in Eq. (20). According to the coefficients, linear terms of JB blend ratio, and torque have higher impact compared to engine speed on smoke opacity variations. However, all the quadratic and interaction terms shows significant favourable effects in improving the smoke opacity. The minimum and maximum smoke opacity of 22.98 %HSU and 25.23 %HSU were measured over (1900 rpm, B25, 32 N.m) and (1700 rpm, B5, 34 N.m) respectively. The regression model goodness coefficients of smoke opacity R^2 (94.35%) and

R_{adj}^2 (88.06%), specifies model's fitness through their close correlation among all the model terms in predicting the smoke opacity.

$$SmOp = 94.3168 - 0.0449S - 1.2097B - 0.6823T + 0.0000001S^2 + 0.018514B^2 + 0.004147T^2 + 0.0000001SB + 0.0000001ST + 0.00938BT \quad (20)$$

Referring to the engine operating parameter interactions illustrated in Figures 4.40(a-c) the smoke opacity diminishes over increase of engine speed and higher percentage of JB in fuel blends. A minimum smoke opacity of 23.4 %HSU was noted over engine speed ~1850rpm, >B15 besides torque >33 N.m values. This can be correlated with increase in biofuel consumption over increasing engine speed (Behçet et al., 2015; Ong et al., 2014). The comparative graph shown in Figure 4.41, indicates a close correlation between predicted and reference experimental results. At lower engine speeds, relatively higher fuel quantity being consumed and out of which few carbon and hydrocarbon fragments may not be fully burnt and hence increases rate of smoke opacity emissions.

The biofuel properties that include higher density, kinematic viscosity contributes in poor air-fuel mixture formation which lead to bad fuel combustion and higher levels of Smoke exhaust emission. Further, it can be observed that higher smoke opacity values were measured when the engine is operated at less torque. A least smoke opacity of 22.8 %HSU was resulted at B20 and torque >35N.m. This phenomenon can be attributed to rich biofuel properties such as higher cetane number, higher oxygen contents which contributes in reducing smoke opacity.

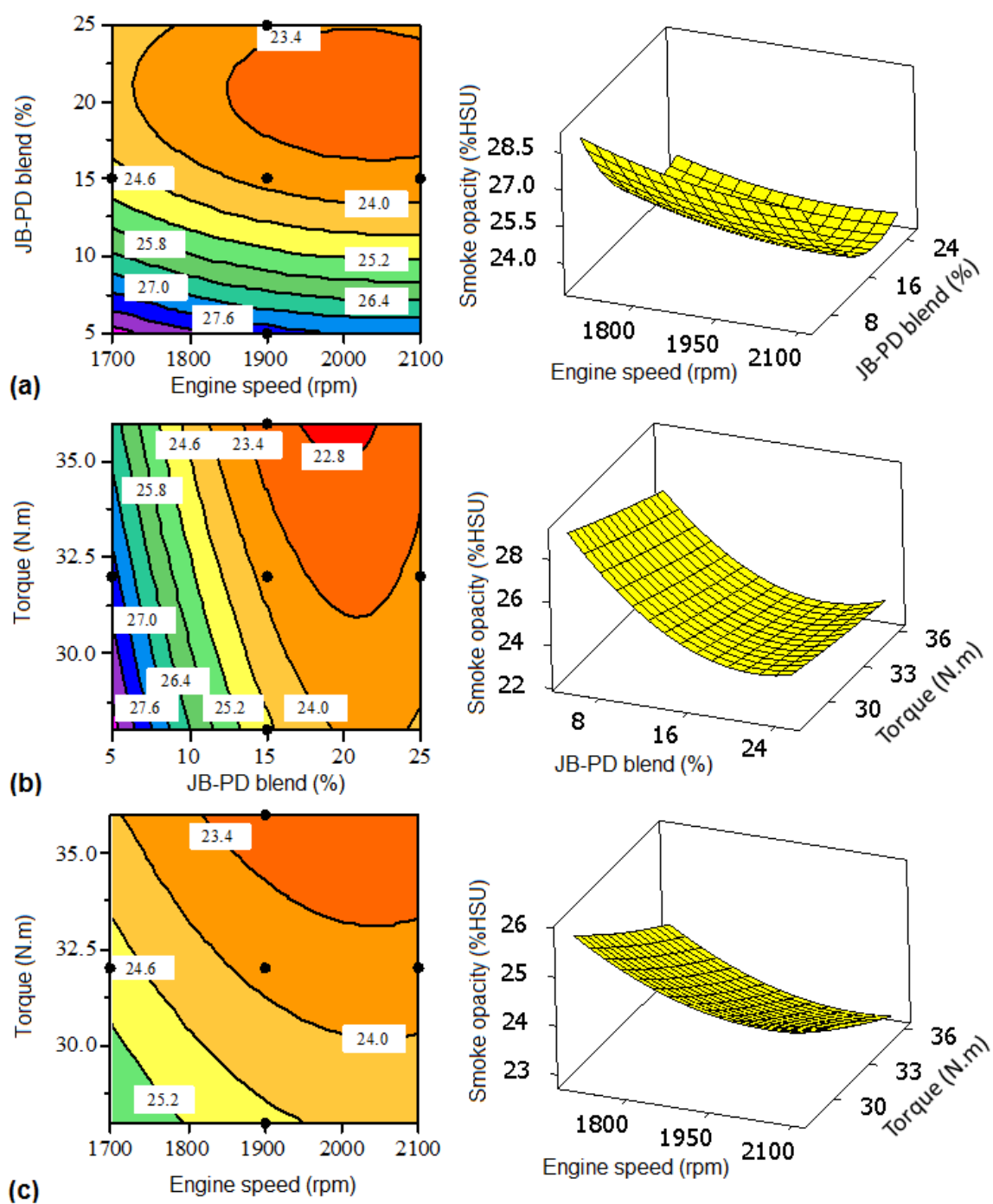


Figure 4.40: Smoke opacity (%HSU) variations in contrast to the interactions of engine speed, JB-PD blending ratio and torque.

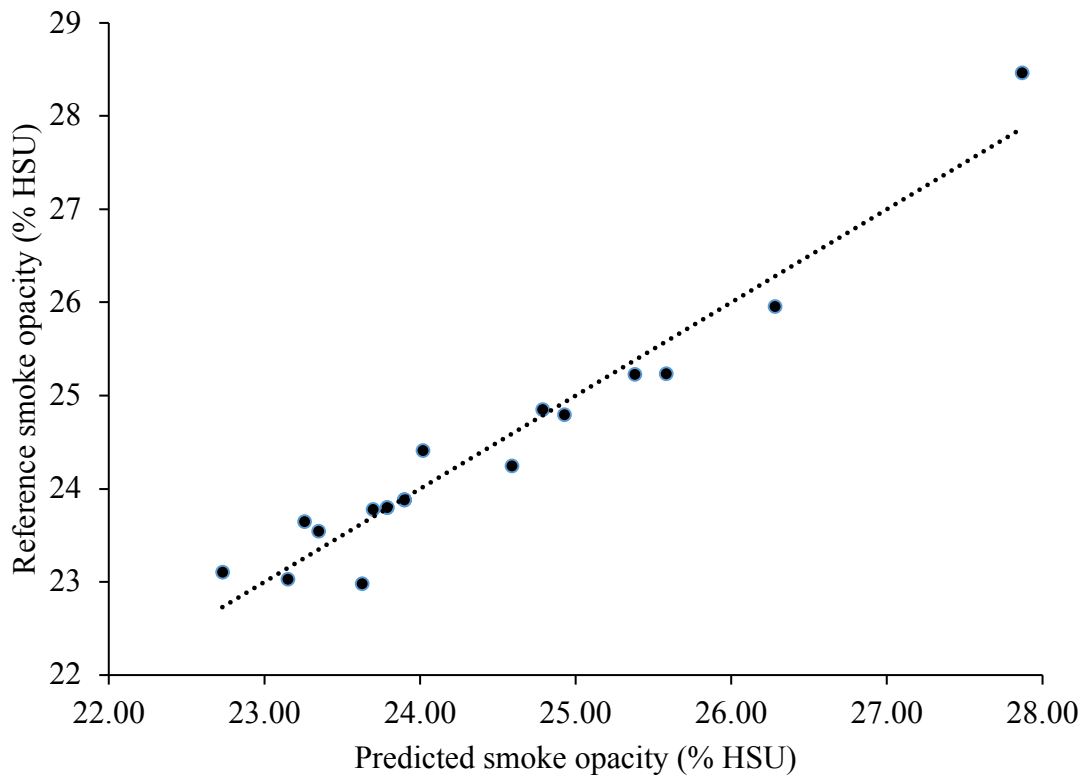


Figure 4.41: Comparative graph showing predicted and reference results of carbon dioxide emissions.

4.12 Optimization of engine performance and exhaust emissions parameters

Response surface optimizer module of Minitab®16.2.1 statistical software was utilized to optimize the engine performance and exhaust gas emission characteristics. The software module is built on desirability approach. The optimal engine operating parameters engine speed, JB-PD blending percentage and torque were predicted according to the optimal level (minimum/ maximum). The predicted optimal operating parameters and corresponding desirability for each response function were illustrated in Table 4.14. It can be seen that the predicted parameters for engine performance and emissions as 1890 rpm $\pm$ 10 rpm of engine speed, 13% (-1.42% to +0.08%) of JB-PD blending ratio and 33 N.m (-2.24 N.m. to +1.69N.m) of engine torque. While, optimal parameters for smoke opacity were 2000 rpm, B18.6% and 35.8 N.m. The overall desirability for multiple objectives was estimated at

0.969, whereas the optimal operating parameters S (1900 rpm), B (13%) and T (33 N.m) were considered so as to optimize the engine performance and emission emissions.

Table 4.14: Optimization of engine performance and exhaust emissions.

DI-CI Engine performance/ emission parameter	Optimal predicted operating parameters			Desirability	Result of DI-CI engine performance/ emissions	
	S (rpm)	B (%)	T (N.m)		Predicted	# Reference
BP (kW)	1880	13.36	32.81	0.985	3.617	3.651
BSFC (g/kWh)	1885	11.58	33.11	0.992	271.8	276.3
BTE (%)	1888	12.54	31.96	0.951	29.4	30.19
EGT(°C)	1885	13.36	33.32	0.969	347.3	358.2
NO _x (ppm vol.)	1882	13.36	30.76	0.938	86.79	94.57
HC (ppm vol.)	1890	11.8	33.87	0.971	20.03	21.47
CO ₂ (%vol.)	1870	13.08	32.4	0.979	3.62	3.67
CO (%vol.)	1900	12.67	34.69	0.973	0.048	0.053
Smoke opacity (%HSU)	2000	18.6	35.8	0.962	24.47	22.55

Where S: Engine speed (rpm); B: JB-PD blend (%) and T: Torque (N.m)

The reference engine performance data was adopted from the published experimental data by the engine research group, Department of Mechanical Engineering, University Malaya (UM), Malaysia (Ong et al., 2014).

As seen from the tabulated results in Table 4.14, the predicted DI-CI engine performance was measured as BP of 3.617 kW, BSFC of 271.8 g/kWh, BTE of 29.4 %, EGT of 347.3°C and exhaust gas emissions were NO_x of 86.79 ppm vol., HC of 20.03 ppm vol., CO₂ of 3.62 %vol., CO of 0.048 %vol. and smoke opacity of 24.47 %HSU. The predicted results were compared with the reference engine performance data was adopted from the published experimental data by the engine research group, Department of Mechanical Engineering, University Malaya (UM), Malaysia (Ong et al., 2014). The predicted and

reference experimental results indicates a close correlation. This research specifies use of B13 biodiesel blends, since the presence of higher oxygen content and other physicochemical characteristics contributes in higher rate of fuel combustion and reduces the exhaust gas emissions.

4.13 Summary of results and discussion

Heterogeneous nano CaO catalyst was successfully synthesized by following ‘calcination–hydration–dehydration’ synthesis protocol using *P. erosa* seashells. The spectrometric techniques including FT-IR, XRD, TEM, BET and AAS confirmed formation of nano CaO particles. The nano CaO catalyzed two step transesterification of crude Jatropha oil yielded 98.54% of Jatropha biodiesel. The study of nano CaO catalyst reusability, stability and leaching over nine reusability cycles confirmed usage of newly synthesized nano CaO catalyst is suitable for six reuse cycles. The FAC of Jatropha feedstock originated from east and west Malaysian regions was analyzed. The physicochemical fuel properties of JB-PD were measured in accordance with ASTM D6751 and EN 14214 standard protocols. The fuel properties are found to be highly commensurate with the biodiesel standard EN 14214. The impact of FAC on fuel properties was studied in detail. The engine performance and exhaust emission characteristics were predicted, analyzed and optimized employing a mathematical model based on response surface and desirability approaches. The predicted engine performance and exhaust emission results were compared with published experimental data by the engine research group, Department of Mechanical Engineering, University Malaya (UM), Malaysia (Ong et al., 2014). The comparison evidently establishes that the predicted engine performance and exhaust emission results are agreed with the reference experimental values.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

- a. According to the present research, nano CaO catalyst was successfully synthesized from *P. erosa* seashells following calcination–hydration–dehydration protocol. The spectrometric analytical results include FT-IR, XRD, TEM and BET have confirmed the formation of newly synthesized CaO particles with a surface area of 90.61 m²/g and diameters of 66±3nm and 584.7nm which are important characteristics for a nano catalyst.
- b. Jatropha biodiesel was produced using newly synthesized using nano CaO catalyst in a two-step transesterification of crude Jatropha oil and which resulted in enhancing the yield of biodiesel. Transesterification reaction kinetics were optimized investigated using a CCD based RSM model, and a 98.54 % JB yield was reported at the optimal parametric conditions 0.02:1 (w/w) catalyst concentration, 133.1 min reaction time and 5.15:1 mol. of methanol to the pretreated oil. In the leaching and reusability study over nine cycles, the catalyst was stable up to the sixth cycle and conforms to an average 95.8% JB yield.
- c. The fuel properties of Jatropha biodiesel as produced from the feedstocks originated from the east (JB_{EM}) and west (JB_{WM}) Malaysian regions were tested according to ASTM D6751 and EN 14214 standard protocols. The FAC of biodiesel can affect physicochemical properties of the JB due to variant degrees of saturated and unsaturated fatty acid levels. The influence of SFA and USFA contents are inversely correlated over biodiesel's fuel properties.

The liquid biofuel properties like CN, CFPP, KV, DE, CP and PP of JB were significantly influenced by the presence of higher FAC corresponding to ($C_n: 0$) which are SFA; on the other hand the fuel properties that include OS, IV, AN, WC, and FP were determined by JB fatty acid structural features such as number of double bonds in the FAC i.e., amounts of USFA and DU. JB_{WM} demonstrated good properties corresponding to low temperature fuel performance (CFPP, CP, FP and PP); clean combustion (CV and CN) and other characteristics that involves OS, AN, IV and WC compared to JB_{EM} samples, on the other hand, relatively lesser CV and DE values were reported for JB_{EM}.

These results confirms the hypothesis, the fatty acid structure varies according to the feedstock origins while the physicochemical properties of the fuels are correlated with the FAC of respective Jatropha biodiesel. Biofuels blending with petro diesels can significantly increases physicochemical properties of the fuels and ensures their suitability for the desired use. Biodiesel fuel characteristics for low temperature operating conditions such as CFPP, PP and CP can be improved by blending with petro diesel. The fuel property test results of JB from both geographic regions were found to be very much in accordance with EN 14214 standards.

- d. The DI-CI engine performance and exhaust emission characteristics are predicted and verified with the published literature. The engine speed, JB-PD blending ratios and torque were considered as input parameters at various levels simultaneously. The DI-CI engine performance was evaluated over varying engine speed (1700 rpm – 2100 rpm), using JB-PD fuel blends of (B5 – B25) and Torque (28 N.m – 36 N.m). The engine speed of 1900 rpm, biodiesel blends of B13% and engine torque of 33 N.m are resulted as optimal parameters. At optimal conditions significant increase in engine

performance was observed through BP, BSFC, BTE and EGT evaluations and comparative analysis utilizing pure PD fuel. The exhaust emission characteristics analysis include NO_x, HC, CO₂, CO and smoke opacity. Although blending of JB with PD reduces exhaust emissions such as HC, CO₂, CO and smoke opacity considerably but the NO_x is noted at higher level compared to pure PD fuel emissions.

5.2 Recommendations

- a. Development of substantial feedstocks besides production of biodiesel fuels following clean and sustainable methods would enable potential to meet renewable fuel demands. Large scale or industrial use of solid heterogeneous catalysts necessarily demands considerable pre-treatment methodologies for biodiesel production.
- b. Malaysia is one of the prime country in palm oil production and exports, developing alternative tropical or semi-arid growing feedstocks for biodiesel such as *Jatropha* would add higher value to national economy. A detailed survey and exposition on suitable marginal lands facilitates in promoting the strategic long-term agriculture estates for growing *Jatropha* plantation across wide spread Malaysian territories.
- c. Design and development of heterogeneous catalyst materials and catalyst synthesis methodologies significantly strengthens the biodiesel production processes. Hence, synthesis of active heterogeneous solid catalysts from renewable wastes such as waste shells, bones etc. is a promising domain for both research and commercial values. Due to presence of large coastal regions and waterways in Malaysia numerous sea shells are being available. A detailed survey on abundantly available renewable wastes provides a basis for strategic planning which adds to sustainable development.

- d. Mechanical feasibility and compatibility of diesel engines is a notable challenge for commercial use of biodiesel's apart from persistent problems such as corrosion of fuel tanks, engine parts. Developing flexible fuel automobile engines that runs on both petro and biofuels would enable the consumers to get adopt with multiple fuels. Additionally, research investigations on anti-corrosive ceramic coatings would improve durability of engine parts corrosive and fuel tanks.

REFERENCES

- Achten, W. M. J., Verchot, L., Franken, Y. J., Mathijs, E., Singh, V. P., Aerts, R., & Muys, B. (2008). *Jatropha* bio-diesel production and use. *Biomass and Bioenergy*, 32(12), 1063–1084.
- Altın, R., Çetinkaya, S., & Yücesu, H. S. (2001). The potential of using vegetable oil fuels as fuel for diesel engines. *Energy Conversion and Management*, 42(5), 529–538.
- Altun, Ş., Yaşar, F., & Öner, C. (2010). The fuel properties of methyl esters produced from canola oil- animal tallow blends by base- catalyzed transesterification. *International Journal of Engineering Research and Development*, 2(2), 2–5.
- ANR, R., Saleh, A. A., Islam, M. S., Hamdan, S., & Maleque, M. A. (2016). Biodiesel Production from Crude *Jatropha* Oil using a Highly Active Heterogeneous Nanocatalyst by Optimizing Transesterification Reaction Parameters. *Energy & Fuels*, 30(1), 334–343.
- Aransiola, E. F., Ojumu, T. V., Oyekola, O. O., Madzimbamuto, T. F., & Ikhu-Omoregbe, D. I. O. (2014). A review of current technology for biodiesel production: State of the art. *Biomass and Bioenergy*, 61, 276–297.
- Arisoy, K. (2008). Oxidative and Thermal Instability of Biodiesel. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 30(16), 1516–1522.
- Asikin-Mijan, N., Lee, H. V., & Taufiq-Yap, Y. H. (2015). Synthesis and catalytic activity of hydration–dehydration treated clamshell derived CaO for biodiesel production. *Chemical Engineering Research and Design*, 102, 368–377.
- Atabani, A. E., Mahlia, T. M. I., Anjum Badruddin, I., Masjuki, H. H., Chong, W. T., & Lee, K. T. (2013). Investigation of physical and chemical properties of potential edible and non-edible

- feedstocks for biodiesel production, a comparative analysis. *Renewable and Sustainable Energy Reviews*, 21, 749–755.
- Atabani, A. E., Silitonga, A. S., Badruddin, I. A., Mahlia, T. M. I., Masjuki, H. H., & Mekhilef, S. (2012). A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renewable and Sustainable Energy Reviews*, 16(4), 2070–2093.
- Atadashi, I. M., Aroua, M. K., Abdul Aziz, A. R., & Sulaiman, N. M. N. (2012). The effects of water on biodiesel production and refining technologies: A review. *Renewable and Sustainable Energy Reviews*, 16(5), 3456–3470.
- Atadashi, I. M., Aroua, M. K., & Aziz, A. A. (2010). High quality biodiesel and its diesel engine application: A review. *Renewable and Sustainable Energy Reviews*, 14(7), 1999–2008.
- Azhari, Faiz, M., & Yunus, R. (2008). Reduction of Free Fatty Acids in Crude *Jatropha curcas* Oil Via. *International Journal of Engineering and Technology*, 5(2), 92–98.
- Bachok, Z., Mfilinge, P. L., & Tsuchiya, M. (2003). The diet of the mud clam *Geloina coxans* (Mollusca, Bivalvia) as indicated by fatty acid markers in a subtropical mangrove forest of Okinawa, Japan. *Journal of Experimental Marine Biology and Ecology*, 292(2), 187–197.
- Balat, M., & Balat, H. (2010). Progress in biodiesel processing. *Applied Energy*, 87(6), 1815–1835.
- Balogh, P., Bai, A., Popp, J., Huzsvai, L., & Jobbágy, P. (2015). Internet-orientated Hungarian car drivers' knowledge and attitudes towards biofuels. *Renewable and Sustainable Energy Reviews*, 48, 17–26.
- Banković-Ilić, I. B., Stamenković, O. S., & Veljković, V. B. (2012). Biodiesel production from non-edible plant oils. *Renewable and Sustainable Energy Reviews*, 16(6), 3621–3647.

- Barabás, I., & Todorut, I.-A. (2011). Biodiesel: quality, emissions and by-products. Montero, G. (Ed.), Biodiesel Quality, Standards and Properties (p. 392). InTech.
- Behçet, R., Oktay, H., Çakmak, A., & Aydın, H. (2015). Comparison of exhaust emissions of biodiesel-diesel fuel blends produced from animal fats. *Renewable and Sustainable Energy Reviews*, 46, 157–165.
- Bell, A. T., Gates, B. C., Ray, D., & Thompson, M. R. (2008). Basic Research Needs: Catalysis for Energy. U.S. DoE. Richland, WA.
- Berchmans, H. J., & Hirata, S. (2008). Biodiesel production from crude *Jatropha curcas* L. seed oil with a high content of free fatty acids. *Bioresource Technology*, 99(6), 1716–1721.
- Bhuiya, M. M. K., Rasul, M. G., Khan, M. M. K., Ashwath, N., Azad, A. K., & Hazrat, M. A. (2014). Second Generation Biodiesel: Potential Alternative to-edible Oil-derived Biodiesel. *Energy Procedia*, 61, 1969–1972.
- Bhuiya, M. M. K., Rasul, M. G., Khan, M. M. K., Ashwath, N., Azad, A. K., & Hazrat, M. A. (2016). Prospects of 2nd generation biodiesel as a sustainable fuel - Part 2: Properties, performance and emission characteristics. *Renewable and Sustainable Energy Reviews*, 55, 1129–1146.
- Birla, A., Singh, B., Upadhyay, S. N., & Sharma, Y. C. (2012). Kinetics studies of synthesis of biodiesel from waste frying oil using a heterogeneous catalyst derived from snail shell. *Bioresource Technology*, 106, 95–100.
- Bodle, R., Donat, L., & Duwe, M. (2016). The Paris Agreement: Analysis, Assessment and Outlook. Dessau-Roßlau: Umweltbundesamt.

- Boey, P. L., Maniam, G. P., & Hamid, S. A. (2009). Biodiesel production via transesterification of palm olein using waste mud crab (*Scylla serrata*) shell as a heterogeneous catalyst. *Bioresource Technology*, 100(24), 6362–6368.
- Borhanipour, M., Karin, P., Tongroon, M., Chollacoop, N., & Hanamura, K. (2014). Comparison Study on Fuel Properties of Biodiesel from *Jatropha*, Palm and Petroleum Based Diesel Fuel. SAE Technical Paper 2014-01-2017.
- Bravo-Suárez, J. J., Chaudhari, R. V., & Subramaniam, B. (2013). Design of Heterogeneous Catalysts for Fuels and Chemicals Processing: An Overview. In *ACS Symposium Series* (Vol. 1132, pp. 3–68).
- Buasri, A., Chaiyut, N., Loryuenyong, V., Wongweang, C., & Khamrisuk, S. (2013a). Application of eggshell wastes as a heterogeneous catalyst for biodiesel production. *Sustainable Energy*, 1(2), 7–13.
- Buasri, A., Chaiyut, N., Loryuenyong, V., Worawanitchaphong, P., & Trongyong, S. (2013b). Calcium oxide derived from waste shells of mussel, cockle, and scallop as the heterogeneous catalyst for biodiesel production. *The Scientific World Journal*, 2013, 1–7.
- Buyukkaya, E. (2010). Effects of biodiesel on a DI diesel engine performance, emission and combustion characteristics. *Fuel*, 89(10), 3099–3105.
- Canakci, M., & Sanli, H. (2008). Biodiesel production from various feedstocks and their effects on the fuel properties. *Journal of Industrial Microbiology and Biotechnology*, 35(5), 431–441.
- Chattopadhyay, S., & Sen, R. (2013). Fuel properties, Engine performance and environmental benefits of biodiesel produced by a green process. *Applied Energy*, 105, 319–326.

- Chauhan, B. S., Kumar, N., & Cho, H. M. (2012). A study on the performance and emission of a diesel engine fueled with *Jatropha* biodiesel oil and its blends. *Energy*, 37(1), 616–622.
- Choudhury, H. A., Chakma, S., & Moholkar, V. S. (2014a). Mechanistic insight into sonochemical biodiesel synthesis using heterogeneous base catalyst. *Ultrasonics Sonochemistry*, 21(1), 169–181.
- Choudhury, H. A., Goswami, P. P., Malani, R. S., & Moholkar, V. S. (2014b). Ultrasonic biodiesel synthesis from crude *Jatropha curcas* oil with heterogeneous base catalyst: Mechanistic insight and statistical optimization. *Ultrasonics Sonochemistry*, 21(3), 1050–1064.
- Choudhury, H. A., Malani, R. S., & Moholkar, V. S. (2013). Acid catalyzed biodiesel synthesis from *Jatropha* oil: Mechanistic aspects of ultrasonic intensification. *Chemical Engineering Journal*, 231, 262–272.
- Choudhury, H. A., Srivastava, P., & Moholkar, V. S. (2014c). Single-step ultrasonic synthesis of biodiesel from crude *Jatropha curcas* oil. *AIChE Journal*, 60(5), 1572–1581.
- Chouhan, A. P. S., & Sarma, A. K. (2011). Modern heterogeneous catalysts for biodiesel production: A comprehensive review. *Renewable and Sustainable Energy Reviews*, 15(9), 4378–4399.
- Chuah, L. F., Yusup, S., Rashid, A., Aziz, A., Bokhari, A., & Zamri, M. (2016). Influence of fatty acids content in non-edible oil for biodiesel properties. *Clean Technology and Environmental Policy*, 18(2), 473–482.
- De Oliveira, F. C., & Coelho, S. T. (2017). History, evolution, and environmental impact of biodiesel in Brazil: A review. *Renewable and Sustainable Energy Reviews*, 75, 168–179.
- DECC. (2012). Bioenergy Strategy - Analytical Annex. London SW1A 2AW.

- Demirbas, A. (2009). Progress and recent trends in biodiesel fuels. *Energy Conversion and Management*, 50(1), 14–34.
- Deng, X., Fang, Z., & Liu, Y. H. (2010). Ultrasonic transesterification of *Jatropha curcas* L. oil to biodiesel by a two-step process. *Energy Conversion and Management*, 51(12), 2802–2807.
- Deng, X., Fang, Z., Liu, Y. H., & Yu, C. L. (2011). Production of biodiesel from *Jatropha* oil catalyzed by nanosized solid basic catalyst. *Energy*, 36(2), 777–784.
- Deutschmann, O., Knözinger, H., Kochloefl, K., & Turek, T. (2009). Heterogeneous Catalysis and Solid Catalysts. In *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA.
- Dhamodaran, G., Krishnan, R., Pochareddy, Y. K., Pyarelal, H. M., Sivasubramanian, H., & Ganeshram, A. K. (2017). A comparative study of combustion, emission, and performance characteristics of rice-bran-, neem-, and cottonseed-oil biodiesels with varying degree of unsaturation. *Fuel*, 187, 296–305.
- Dhingra, S., Bhushan, G., & Dubey, K. K. (2013a). Development of a combined approach for improvement and optimization of karanja biodiesel using response surface methodology and genetic algorithm. *Frontiers in Energy*, 7(4), 495–505.
- Dhingra, S., Bhushan, G., & Dubey, K. K. (2013b). Performance and emission parameters optimization of mahua (*Madhuca indica*) based biodiesel in direct injection diesel engine using response surface methodology. *Journal of Renewable and Sustainable Energy*, 5(6), 63117.
- Dhingra, S., Dubey, K. K., & Bhushan, G. (2014). Enhancement in *Jatropha*-based biodiesel yield by process optimisation using design of experiment approach. *International Journal of Sustainable Energy*, 33(4), 842–853.

- EIA. (2016). International Energy Outlook 2016. International Energy Outlook 2016 (2016th ed., Vol. 0484(2016)). Washington, DC 20585: U.S. Energy Information Administration.
- Ejilah, I. R., Asere, A. A., Polytechnic, F., Programme, M. E., & Technology, L. (2010). The effect of diesel fuel- *Jatropha curcas* oil methyl ester blend on the performance of a variable speed compression ignition engine. *Australian Journal of Agricultural Engineering*, 1(3), 80–85.
- Encinar, J. M., Sánchez, N., Martínez, G., & García, L. (2011). Study of biodiesel production from animal fats with high free fatty acid content. *Bioresource Technology*, 102(23), 10907–10914.
- Erbach, G. (2016). The Paris Agreement: A new framework for global climate action. *European Union*.
- Fernandes, A. M. A. P., El-Khatib, S., Cunha, I. B. S., Porcari, A. M., Eberlin, M. N., Silva, Silva, P. J., Cunha, V. S., Daroda, R. J., & Alberici, R. M. (2015). Chemical Characterization of *Jatropha curcas* L. Seed Oil and Its Biodiesel by Ambient Desorption/Ionization Mass Spectrometry. *Energy & Fuels*, 29(5), 3096–3103.
- Fernando, S., Karra, P., Hernandez, R., & Jha, S. K. (2007). Effect of incompletely converted soybean oil on biodiesel quality. *Energy*, 32(5), 844–851.
- Freedman B, Pryde EH, M. T. (1984). Variables affecting the yield of fatty esters from Transesterification vegetable oils. *Journal of the American Oil Chemists' Society*, 10(61), 1638–1643.
- Fregolente, P. B. L. ., Wolf Maciel, M. R. ., & Oliveira, L. S. (2015). Removal of Water Content From Biodiesel and Diesel Fuel Using Hydrogel Adsorbents. *Brazilian Journal of Chemical Engineering*, 32(4), 895–901.

- Fregolente, P. B. L., Fregolente, L. V., & Maciel, M. R. W. (2012). Water Content in Biodiesel, Diesel, and Biodiesel–Diesel Blends. *Journal of Chemical & Engineering Data*, 1(1), 1–5.
- Fries, P., & Cook, K. (2011). *Biofuels Vital Graphics - Powering a Green Economy*. (A. Solgaard & I. Rucevska, Eds.). Grenoble, France: Division of Technology, Industry and Economics (DTIE), UNEP.
- Ganapathy, T., Gakkhar, R. P., & Murugesan, K. (2011a). Influence of injection timing on performance, combustion and emission characteristics of *Jatropha* biodiesel engine. *Applied Energy*, 88(12), 4376–4386.
- Ganapathy, T., Gakkhar, R. P., & Murugesan, K. (2011b). Optimization of performance parameters of diesel engine with *Jatropha* biodiesel using response surface methodology. *International Journal of Sustainable Energy*, 30(sup1), S76–S90.
- Gautier, C. (2008). *Oil, Water, and Climate: An Introduction*. Cambridge University Press.
- Götz, K., Singer, A., Schröder, O., Pabst, C., Munack, A., Bünger, J., & Krahel, J. (2014). Exhaust Gas Emissions from Heavy-Duty Engines and Passenger Cars with Different After-Treatment Systems Running on Hydrotreated Vegetable Oil (HVO). In SAE Technical Paper 2014-01-2827 (p. 10).
- Goyal, P., Sharma, M. P., & Jain, S. (2012). Optimization of Esterification and Transesterification of High FFA *Jatropha curcas* Oil Using Response Surface Methodology. *Journal of Petroleum Science Research*, 1, 36–43.
- Goyal, P., Sharma, M. P., & Jain, S. (2013). Optimization of transesterification of *Jatropha curcas* oil to biodiesel using response surface methodology and its adulteration with kerosene. *Journal of Materials and Environmental Science*, 4(2), 277–284.

- Gübitz, G. M., Mittelbach, M., & Trabi, M. (1999). Exploitation of the tropical oil seed plant *Jatropha curcas* L. Bioresource Technology, 67(1), 73–82.
- Hanim, A. (2016). All systems go for B10 biodiesel; shoring up CPO prices, reducing stock seen. The Star Online. Kuala Lumpur, Malaysia.
- Hassan, M. H., & Kalam, A. (2013). An overview of biofuel as a renewable energy source : development and challenges. Procedia Engineering, 56, 39–53.
- Heywood, J. (2011). Internal Combustion Engine Fundamentals (1st ed.). Tata Mcgraw Hill Education.
- Hook, M., & Tang, X. (2013). Depletion of fossil fuels and anthropogenic climate change-A review. Energy Policy, 52, 797–809.
- Hossen, M. F., Hamdan, S., & Rahman, M. R. (2015). Review on the Risk Assessment of Heavy Metals in Malaysian Clams. The Scientific World Journal, 2015, 1–7.
- Hubbert, M. K. (1956). Nuclear Energy and the Fossil Fuels. Spring Meeting of the Southern District. Division of Production.
- Hwa, S., Rashid, U., & Taufiq-yap, Y. H. (2014). Biodiesel production from crude *Jatropha curcas* oil using calcium based mixed oxide catalysts. Fuel, 136, 244–252.
- Islam, K. N., Bakar, M. Z. B. A., Ali, M. E., Hussein, M. Z. Bin, Noordin, M. M., Loqman, M. Y., Miah. G., Hashim, U. (2013). A novel method for the synthesis of calcium carbonate (aragonite) nanoparticles from cockle shells. Powder Technology, 235, 70–75.
- Jachimowski, C. J., & Wilson, C. H. (1980). Chemical kinetic models for combustion of hydrocarbons and formation of nitric oxide (No. NASA TP-1794). Washington DC.

- Jaliliannosrati, H., Amin, N. A. S., Talebian-Kiakalaieh, A., & Noshadi, I. (2013). Microwave assisted biodiesel production from *Jatropha curcas* L. seed by two-step in situ process: Optimization using response surface methodology. *Bioresource Technology*, 136, 565–573.
- Janaun, J., & Ellis, N. (2010). Perspectives on biodiesel as a sustainable fuel. *Renewable and Sustainable Energy Reviews*, 14(4), 1312–1320.
- Jena, P. C., Raheman, H., Prasanna Kumar, G. V., & Machavaram, R. (2010). Biodiesel production from mixture of mahua and simarouba oils with high free fatty acids. *Biomass and Bioenergy*, 34(8), 1108–1116.
- Jindapon, W., Jaiyen, S., & Ngamcharussrivichai, C. (2016). Seashell-derived mixed compounds of Ca, Zn and Al as active and stable catalysts for the transesterification of palm oil with methanol to biodiesel. *Energy Conversion and Management*, 122, 535–543.
- Joshi, G., Rawat, D. S., Lamba, B. Y., Bisht, K. K., Kumar, P., Kumar, N., & Kumar, S. (2015). Transesterification of *Jatropha* and *Karanja* oils by using waste egg shell derived calcium based mixed metal oxides. *Energy Conversion and Management*, 96, 258–267.
- Karavalakis, G., Johnson, K. C., Hajbabaei, M., & Durbin, T. D. (2016). Application of low-level biodiesel blends on heavy-duty (diesel) engines: Feedstock implications on NO_x and particulate emissions. *Fuel*, 181(2016), 259–268.
- Kawashima, A., Matsubara, K., & Honda, K. (2008). Development of heterogeneous base catalysts for biodiesel production. *Bioresource Technology*, 99(9), 3439–3443.
- Kawashima, A., Matsubara, K., & Honda, K. (2009). Acceleration of catalytic activity of calcium oxide for biodiesel production. *Bioresource Technology*, 100(2), 696–700.

- Kegl, B. (2011). Influence of biodiesel on engine combustion and emission characteristics. *Applied Energy*, 88(5), 1803–1812.
- Kessler, J., & Sperling, D. (2016). Tracking U.S. biofuel innovation through patents. *Energy Policy*, 98, 97–107.
- Khoobakht, G., Najafi, G., Karimi, M., & Akram, A. (2016). Optimization of operating factors and blended levels of diesel, biodiesel and ethanol fuels to minimize exhaust emissions of diesel engine using response surface methodology. *Applied Thermal Engineering*, 99, 1006–1017.
- Knothe, G. (2005). Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel Processing Technology*, 86, 1059–1070.
- Knothe, G. (2006). Analyzing Biodiesel: Standards and other Methods. *Journal of the American Oil Chemists' Society*, 83(10), 823–833.
- Knothe, G. (2008). “Designer” biodiesel: Optimizing fatty ester composition to improve fuel properties. *Energy and Fuels*, 22(2), 1358–1364.
- Knothe, G. (2010). Biodiesel and renewable diesel: A comparison. *Progress in Energy and Combustion Science*, 36(3), 364–373.
- Knothe, G., Matheaus, A. C., & Ryan, T. W. (2003). Cetane numbers of branched and straight-chain fatty esters determined in an ignition quality tester. *Fuel*, 82, 971–975.
- Koh, M. Y., & Mohd, G. T. I. (2011). A review of biodiesel production from *Jatropha curcas* L. oil. *Renewable and Sustainable Energy Reviews*, 15(5), 2240–2251.
- Kouzu, M., Kasuno, T., Tajika, M., Yamanaka, S., & Hidaka, J. (2008). Active phase of calcium oxide used as solid base catalyst for transesterification of soybean oil with refluxing methanol. *Applied Catalysis A: General*, 334(1–2), 357–365.

- Krishna Reddy, A. V., Shiva Shankar, M., & Apparao, K. (2010). Experimental determination of brake thermal efficiency and brake specific fuel consumption of diesel engine fuelled with biodiesel. *International Journal of Engineering and Technology*, 2(5), 305–309.
- Kumar Tiwari, A., Kumar, A., & Raheman, H. (2007). Biodiesel production from *Jatropha* oil (*Jatropha curcas*) with high free fatty acids: An optimized process. *Biomass and Bioenergy*, 31(8), 569–575.
- Lam, M. K., Lee, K. T., & Mohamed, A. R. (2010). Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: a review. *Biotechnology Advances*, 28(4), 500–18.
- Lam, M. K., Lee, K. T., & Mohamed, A. R. (2009). Life cycle assessment for the production of biodiesel: A case study in Malaysia for palm oil versus *Jatropha* oil. *Biofuels, Bioproducts and Biorefining*, 3(6), 601–612.
- Lee, A. F., Bennett, J. A., Manayil, J. C., & Wilson, K. (2014). Heterogeneous catalysis for sustainable biodiesel production via esterification and transesterification. *Chemical Society Reviews*, 43(22), 7887–7916.
- Lee, H. V., Juan, J. C., Binti Abdullah, N. F., Nizah Mf, R., & Taufiq-Yap, Y. H. (2014). Heterogeneous base catalysts for edible palm and non-edible *Jatropha*-based biodiesel production. *Chemistry Central Journal*, 8(1), 30.
- Leofanti, G., Padovan, M., Tozzola, G., & Venturelli, B. (1998). Surface area and pore texture of catalysts. *Catalysis Today*, 41(1–3), 207–219.
- Leofanti, G., Tozzola, G., Padovan, M., Petrini, G., Bordiga, S., & Zecchina, A. (1997). Catalyst characterization : characterization techniques. *Catalysis Today*, 34(3–4), 307–327.

- Leung, D. Y. C., & Guo, Y. (2006). Transesterification of neat and used frying oil: Optimization for biodiesel production. *Fuel Processing Technology*, 87(10), 883–890.
- Leung, D. Y. C., Wu, X., & Leung, M. K. H. (2010). A review on biodiesel production using catalyzed transesterification. *Applied Energy*, 87(4), 1083–1095.
- Li-bing, W., Hai-yan, Y. U., Xiao-hui, H. E., & Rui-ying, L. I. U. (2012). Influence of fatty acid composition of woody biodiesel plants on the fuel properties. *Journal of Fuel Chemistry and Technology*, 40(4), 397–404.
- Lin, C. Y., & Lin, Y. W. (2012). Fuel characteristics of biodiesel produced from a high-acid oil from soybean soapstock by supercritical-methanol transesterification. *Energies*, 5(7), 2370–2380.
- Lippke, B., Gustafson, R., Venditti, R., Volk, T., Oneil, E., Johnson, L., Puettmann, M., & Steele, P. (2011). Sustainable biofuel contributions to carbon mitigation and energy independence. *Forests*, 2(4), 861–874.
- Ma, F., & Hanna, M. a. (1999). Biodiesel production: a review. *Bioresource Technology*, 70, 1–15.
- Maniatopoulos, P., Andrews, J., & Shabani, B. (2015). Towards a sustainable strategy for road transportation in Australia: The potential contribution of hydrogen. *Renewable and Sustainable Energy Reviews*, 52, 24–34.
- Mansourpoor, M. (2012). Optimization of Biodiesel Production from Sunflower Oil Using Response Surface Methodology. *Journal of Chemical Engineering & Process Technology*, 3(5), 3–7.
- Margaretha, Y. Y., Prastyo, H. S., Ayucitra, A., & Ismadji, S. (2012). Calcium oxide from *Pomacea* sp. shell as a catalyst for biodiesel production. *International Journal of Energy and Environmental Engineering*, 3(1), 33.

- Mcdevitt, N. T., & Baun, W. L. (1964). Infrared absorption study of metal oxides in the low frequency region ($700\text{--}240\text{ cm}^{-1}$). *Spectrochimica Acta*, 20(1960), 799–808.
- Meher, L. C., Churamani, C. P., Arif, M., Ahmed, Z., & Naik, S. N. (2013). *Jatropha curcas* as a renewable source for bio-fuels - A review. *Renewable and Sustainable Energy Reviews*, 26, 397–407.
- Melo-Espinosa, E. A., Piloto-Rodríguez, R., Goyos-Pérez, L., Sierens, R., & Verhelst, S. (2015). Emulsification of animal fats and vegetable oils for their use as a diesel engine fuel: An overview. *Renewable and Sustainable Energy Reviews*, 47, 623–633.
- Mirghiasi, Z., Bakhtiari, F., Darezereshki, E., & Esmaeilzadeh, E. (2014). Preparation and characterization of CaO nanoparticles from $\text{Ca}(\text{OH})_2$ by direct thermal decomposition method. *Journal of Industrial and Engineering Chemistry*, 20(1), 113–117.
- Mofijur, M., Masjuki, H. H., Kalam, M. A. A., Hazrat, M. A. A., Liaquat, A. M. M., Shahabuddin, M., & Varman, M. (2012). Prospects of biodiesel from *Jatropha* in Malaysia. *Renewable and Sustainable Energy Reviews*, 16(7), 5007–5020.
- Mofijur, M., Masjuki, H. H., Kalam, M. A., & Atabani, A. E. (2013). Evaluation of biodiesel blending, engine performance and emissions characteristics of *Jatropha curcas* methyl ester: Malaysian perspective. *Energy*, 55, 879–887.
- Mohammadi, P., Nikbakht, A. M., Tabatabaei, M., Farhadi, K., Mohebbi, A., & Khatami far, M. (2012). Experimental investigation of performance and emission characteristics of DI diesel engine fueled with polymer waste dissolved in biodiesel-blended diesel fuel. *Energy*, 46(1), 596–605.
- Nasrazadani, S., & Eureste, E. (2008). Application of FTIR for Quantitative Lime Analysis. Denton Texas.

- Nayak, S. K., & Pattanaik, B. P. (2014). Experimental Investigation on Performance and Emission Characteristics of a Diesel Engine Fuelled with Mahua Biodiesel Using Additive. *Energy Procedia*, 54, 569–579.
- Nigam, P. S., & Singh, A. (2011). Production of liquid biofuels from renewable resources. *Progress in Energy and Combustion Science*, 37(1), 52–68.
- Niju, S., Meera S. Begum, K. M., & Anantharaman, N. (2014). Modification of egg shell and its application in biodiesel production. *Journal of Saudi Chemical Society* 18(5), 702–706.
- Niju, S., Meera Sheriffa Begum, K. M., & Anantharaman, N. (2016). Enhancement of biodiesel synthesis over highly active CaO derived from natural white bivalve clam shell. *Arabian Journal of Chemistry*, 9(5), 633–639.
- Noshadi, I., Amin, N. A. S., & Parnas, R. S. (2012). Continuous production of biodiesel from waste cooking oil in a reactive distillation column catalyzed by solid heteropolyacid: Optimization using response surface methodology (RSM). *Fuel*, 94, 156–164.
- Okullo, A., Temu, A. K., Ntalikwa, J. W., & Ogwok, P. (2010). Optimization of Biodiesel Production from *Jatropha* Oil. *International Journal of Engineering Research in Africa*, 3, 62–73.
- Ong, H. C., Masjuki, H. H., Mahlia, T. M. I., Silitonga, A. S., Chong, W. T., & Yusaf, T. (2014). Engine performance and emissions using *Jatropha curcas*, *Ceiba pentandra* and *Calophyllum inophyllum* biodiesel in a CI diesel engine. *Energy*, 69, 427–445.
- Ong, H. C., Silitonga, A. S., Masjuki, H. H., Mahlia, T. M. I., Chong, W. T., & Boosroh, M. H. (2013). Production and comparative fuel properties of biodiesel from non-edible oils: *Jatropha curcas*, *Sterculia foetida* and *Ceiba pentandra*. *Energy Conversion and Management*, 73, 245–255.

- Orwa, C., Mutua, A., Kindt, R., Jamnadass, R., & Anthony, S. (2009). A tree reference and selection guide version 4.0. Agroforestry Database: 4.0.
- Palash, S. M., Kalam, M. A., Masjuki, H. H., Masum, B. M., Rizwanul Fattah, I. M., & Mofijur, M. (2013). Impacts of biodiesel combustion on NO_x emissions and their reduction approaches. *Renewable and Sustainable Energy Reviews*, 23, 473–490.
- Patel, P. D., Lakdawala, A., Chourasia, S., & Patel, R. N. (2016). Bio fuels for compression ignition engine: A review on engine performance, emission and life cycle analysis. *Renewable and Sustainable Energy Reviews*, 65, 24–43.
- Pradhan, S., Madankar, C. S., Mohanty, P., & Naik, S. N. (2012). Optimization of reactive extraction of castor seed to produce biodiesel using response surface methodology. *Fuel*, 97, 848–855.
- Pranab, K. B. (2011). Biodiesel from Seeds of *Jatropha* Found in Assam, India. *International Journal of Energy, Information and Communications*, 2(1), 53–65.
- Prasertsit, K., Phoosakul, P., & Sukmanee, S. (2014). Use of calcium oxide in palm oil methyl ester production. *Songklanakarin Journal of Science and Technology*, 36(2), 195–200.
- Qi, D. H., Chen, H., Geng, L. M., Bian, Y. Z., & Ren, X. C. (2010). Performance and combustion characteristics of biodiesel-diesel-methanol blend fuelled engine. *Applied Energy*, 87(5), 1679–1686.
- Qi, D. H., Geng, L. M., Chen, H., Bian, Y. Z., Liu, J., & Ren, X. C. (2009). Combustion and performance evaluation of a diesel engine fueled with biodiesel produced from soybean crude oil. *Renewable Energy*, 34(12), 2706–2713.
- Qian, J., Shi, H., & Yun, Z. (2010). Preparation of biodiesel from *Jatropha curcas* L. oil produced by two-phase solvent extraction. *Bioresource Technology*, 101(18), 7025–7031.

- Rahim, A. A., Idris, M. H., Kamal, A. H. M., Wong, S. K., & Arshad, A. (2012). Analysis of condition index in *Polymesoda expansa* (Mousson 1849). *Pakistan Journal of Biological Sciences*, 15(13), 629–634.
- Rajendra, M., Jena, P. C., & Raheman, H. (2009). Prediction of optimized pretreatment process parameters for biodiesel production using ANN and GA. *Fuel*, 88(5), 868–875.
- Ramírez-Verduzco, L. F., Rodríguez-Rodríguez, J. E., & Jaramillo-Jacob, A. D. R. (2012). Predicting cetane number, kinematic viscosity, density and higher heating value of biodiesel from its fatty acid methyl ester composition. *Fuel*, 91(1), 102–111.
- Ramos, M. J., Fernández, C. M., Casas, A., Rodríguez, L., & Pérez, Á. (2009). Influence of fatty acid composition of raw materials on biodiesel properties. *Bioresource Technology*, 100(1), 261–268.
- Rao, P.V. (2011). Experimental Investigations on the Influence of Properties of *Jatropha* Biodiesel on Performance, Combustion, and Emission Characteristics of a DI-CI Engine. *World Academy of Science, Engineering and Technology*, 5(3), 629–642.
- Rapid racer. (2016). Car engine - Diesel Engine.
- Rashid, U., Anwar, F., Moser, B. R., & Ashraf, S. (2008). Production of sunflower oil methyl esters by optimized alkali-catalyzed methanolysis. *Biomass and Bioenergy*, 32, 1202–1205.
- Rashid, U., Knothe, G., Yunus, R., & Evangelista, R. L. (2014). Kapok oil methyl esters. *Biomass and Bioenergy*, 66, 419–425.
- Ren, Y., Ma, Z., & Bruce, P. G. (2012). Ordered mesoporous metal oxides: synthesis and applications. *Chemical Society Reviews*, 41(14), 4909.
- REN21. (2016). *Renewables 2016 Global Status Report*. Paris, France.

- Rizwanul Fattah, I. M., Kalam, M. A., Masjuki, H. H., & Wakil, M. A. (2014). Biodiesel production, characterization, engine performance, and emission characteristics of Malaysian Alexandrian laurel oil. *RSC Advances*, 4(34), 17787.
- Roschat, W., Siritanon, T., Kaewpuang, T., Yoosuk, B., & Promarak, V. (2016). Economical and green biodiesel production process using river snail shells-derived heterogeneous catalyst and co-solvent method. *Bioresource Technology*, 209, 343–350.
- Roy, P. K., Datta, S., Nandi, S., & Al Basir, F. (2014). Effect of mass transfer kinetics for maximum production of biodiesel from *Jatropha curcas* oil: A mathematical Approach. *Fuel*, 134, 39–44.
- Sahoo, P. K., & Das, L. M. (2009). Process optimization for biodiesel production from *Jatropha*, *Karanja* and *Polanga* oils. *Fuel*, 88(9), 1588–1594.
- Sajjadi, B., Aziz, A., Raman, A., & Arandiyan, H. (2016). A comprehensive review on properties of edible and non-edible vegetable oil-based biodiesel: Composition, specifications and prediction models. *Renewable and Sustainable Energy Reviews*, 63, 62–92.
- Samavi, M., Ghobadian, B., Ardjmand, M., & Seyfordin, A. (2016). Prediction of biodiesel properties and its characterization using fatty acid profiles. *Korean Journal of Chemical Engineering*, 32(4), 1–8.
- Sampson, R. E., & Springer, G. S. (1973). Effects of exhaust gas temperature and fuel composition on particulate emission from spark ignition engines. *Environmental Science & Technology*, 7(1), 55–60.
- Sánchez, M., Bergamin, F., Peña, E., Martínez, M., & Aracil, J. (2015). A comparative study of the production of esters from *Jatropha* oil using different short-chain alcohols: Optimization and characterization. *Fuel*, 143, 183–188.

- Saraf, S., & Thomas, B. (2007). Influence of Feedstock and Process Chemistry on Biodiesel Quality. *Process Safety and Environmental Protection*, 85(5), 360–364.
- Saxena, P., Jawale, S., & Joshipura, M. H. (2013). A Review on Prediction of Properties of Biodiesel and Blends of Biodiesel. *Procedia Engineering*, 51, 395–402.
- Shahabuddin, M., Kalam, M. A., Masjuki, H. H., Bhuiya, M. M. K., & Mofijur, M. (2012). An experimental investigation into biodiesel stability by means of oxidation and property determination. *Energy*, 44(1), 616–622.
- Shan, R., Zhao, C., Lv, P., Yuan, H., & Yao, J. (2016). Catalytic applications of calcium rich waste materials for biodiesel : Current state and perspectives. *Energy Conversion and Management*, 127, 273–283.
- Shehata, M. S., & Razek, S. M. A. (2011). Experimental investigation of diesel engine performance and emission characteristics using *Jojoba*/diesel blend and sunflower oil. *Fuel*, 90(2), 886–897.
- Shojaeefard, M. H., Etghani, M. M., Akbari, M., Khalkhali, A., & Ghobadian, B. (2012). Artificial neural networks based prediction of performance and exhaust emissions in direct injection engine using castor oil biodiesel-diesel blends. *Journal of Renewable and Sustainable Energy*, 4(6), 63130.
- Silitonga, A. S., Masjuki, H. H., Mahlia, T. M. I., Ong, H. C., Atabani, A. E., & Chong, W. T. (2013). A global comparative review of biodiesel production from *Jatropha curcas* using different homogeneous acid and alkaline catalysts: Study of physical and chemical properties. *Renewable and Sustainable Energy Reviews*, 24, 514–533.
- Sivaramakrishnan, K., & Ravikumar, P. (2012). Investigation on performance and emissions of a biodiesel engine through optimization techniques. *Thermal Science*, 17, 151.

- Sivaramakrishnan, K., & Ravikumar, P. (2013). Optimization of operational parameters on performance and emissions of a diesel engine using biodiesel. *International Journal of Environmental Science and Technology*, 11(4), 949–958.
- Sven, T., Steve, S., & Oliver, S. (2015). *Energy [R]evolution: A sustainable world energy outlook 2015*. Abu Dhabi, UAE: International Renewable Energy Agency.
- Tan, Y. H., Abdullah, M. O., & Nolasco-Hipolito, C. (2015a). The potential of waste cooking oil-based biodiesel using heterogeneous catalyst derived from various calcined eggshells coupled with an emulsification technique: A review on the emission reduction and engine performance. *Renewable and Sustainable Energy Reviews*, 47, 589–603.
- Tan, Y. H., Abdullah, M. O., Nolasco-Hipolito, C., & Taufiq-Yap, Y. H. (2015b). Waste ostrich- and chicken-eggshells as heterogeneous base catalyst for biodiesel production from used cooking oil: Catalyst characterization and biodiesel yield performance. *Applied Energy*, 160, 58–70.
- Taufiq-Yap, Y. H., Lee, H. V., Hussein, M. Z., & Yunus, R. (2011). Calcium-based mixed oxide catalysts for methanolysis of *Jatropha curcas* oil to biodiesel. *Biomass and Bioenergy*, 35(2), 827–834.
- Taufiq-Yap, Y. H., Teo, S. H., Islam, A., & Ng, F. L. (2015). Biodiesel synthesis from photoautotrophic cultivated oleaginous microalgae using sand dollar catalyst. *RSC Advances*, 5, 47140–47152.
- Teo, S. H., Rashid, U., & Taufiq-Yap, Y. H. (2014). Heterogeneous catalysis of transesterification of *Jatropha curcas* oil over calcium-cerium bimetallic oxide catalyst. *RSC Advances*, 4(90), 48836–48847.

- Teo, S. H., Taufiq-Yap, Y. H., Rashid, U., & Islam, A. (2015). Hydrothermal effect on synthesis, characterization and catalytic properties of calcium methoxide for biodiesel production from crude *Jatropha curcas*. *RSC Advances*, 5(6), 4266–4276.
- Thiele, E. W. (1939). Relation between Catalytic Activity and Size of Particle. *Industrial & Engineering Chemistry*, 31(7), 916–920.
- Thitsartarn, W., & Kawi, S. (2011). An active and stable CaO–CeO₂ catalyst for transesterification of oil to biodiesel. *Green Chemistry*, 13(12), 3423.
- UNFCCC. (2016). Marrakech Climate Change Conference - November 2016. United Nations Framework Convention on Climate Change.
- US-EPA. (2010). RFS2: EPA-420-R-10-003. Washington DC.
- Usta, N. (2005). An experimental study on performance and exhaust emissions of a diesel engine fuelled with tobacco seed oil methyl ester. *Energy Conversion and Management*, 46(15–16), 2373–2386.
- Verma, P., Sharma, M. P., & Dwivedi, G. (2016). Impact of alcohol on biodiesel production and properties. *Renewable and Sustainable Energy Reviews*, 56, 319–333.
- Vicente, G., Coteron, a., & Martinez, M., Aracil, J. (1998). Application of the factorial design of experiments and response surface methodology to optimize biodiesel production. *Industrial Crops and Products*, 8(1), 29–35.
- Wahab, A. G. (2016). Malaysia Biofuels Annual 2016 – MY6004. USDA Foreign Agricultural Service, GAIN Report. Kuala Lumpur, Malaysia.

- Wang, R., Hanna, M. A., Zhou, W., Bhadury, P. S., Chen, Q., & Song, B. (2011). Production and selected fuel properties of biodiesel from promising non-edible oils : *Euphorbia lathyris* L ., *Sapium sebiferum* L . and *Jatropha curcas* L . Bioresource Technology, 102, 1194–1199.
- Westphal, G. a, Krahel, J., Munack, A., Rosenkranz, N., Schröder, O., Schaak, J., Pabst, C., Bünge, T., Bünge, J. (2013). Combustion of hydrotreated vegetable oil and jatropha methyl ester in a heavy duty engine: emissions and bacterial mutagenicity. Environmental Science & Technology, 47(11), 6038–46.
- Williams, M. (2012). Biodiesel. Practical Action, United Kingdom (Vol. 1). Rugby, Warwickshire, CV23 9QZ, UK: Practical Action, UK.
- Winayanuwattikun, P., Kaewpiboon, C., Piriyananon, K., Tantong, S., Thakernkarnkit, W., Chulalaksananukul, W., & Yongvanich, T. (2008). Potential plant oil feedstock for lipase-catalyzed biodiesel production in Thailand. Biomass and Bioenergy, 32(12), 1279–1286.
- Xue, J., Grift, T. E., & Hansen, A. C. (2011). Effect of biodiesel on engine performances and emissions. Renewable and Sustainable Energy Reviews, 15(2), 1098–1116.
- Yang, C. Y., Fang, Z., Li, B., & Long, Y. F. (2012). Review and prospects of Jatropha biodiesel industry in China. Renewable and Sustainable Energy Reviews, 16(4), 2178–2190.
- Yee, K. F., Wu, J. C. S., & Lee, K. T. (2011). A green catalyst for biodiesel production from jatropha oil: Optimization study. Biomass and Bioenergy, 35(5), 1739–1746.
- Yee, T. M. (2014). A Study on Biodiesel Production from *Jatropha Curcas* Linnaeus as Green Diesel. Bachelor's Thesis, Universiti Malaysia Sarawak.
- Yoon, S. H., Park, S. H., & Lee, C. S. (2008). Experimental Investigation on the Fuel Properties of Biodiesel and Its Blends at Various Temperatures. Energy & Fuels, 22(1), 652–656.

- Yoosuk, B., Udomsap, P., & Puttasawat, B. (2011). Hydration-dehydration technique for property and activity improvement of calcined natural dolomite in heterogeneous biodiesel production: Structural transformation aspect. *Applied Catalysis A: General*, 395(1–2), 87–94.
- Yoosuk, B., Udomsap, P., Puttasawat, B., & Krasae, P. (2010a). Improving transesterification activity of CaO with hydration technique. *Bioresource Technology*, 101(10), 3784–3786.
- Yoosuk, B., Udomsap, P., Puttasawat, B., & Krasae, P. (2010b). Modification of calcite by hydration-dehydration method for heterogeneous biodiesel production process: The effects of water on properties and activity. *Chemical Engineering Journal*, 162(1), 135–141.
- Yusuf, N. N. A. N., Kamarudin, S. K., & Yaakub, Z. (2011). Overview on the current trends in biodiesel production. *Energy Conversion and Management*, 52(7), 2741–2751.
- Zaki, M. I., Knözinger, H., Tesche, B., & Mekheimer, G. A. H. (2006). Influence of phosphonation and phosphation on surface acid-base and morphological properties of CaO as investigated by *in situ* FTIR spectroscopy and electron microscopy. *Journal of Colloid and Interface Science*, 303(1), 9–17.

APPENDICES

Appendix A: Reference data of engine test bed and exhaust gas analyser

The schematic of engine test bed and gas analysing devises utilized by the UM research team were illustrated as below.

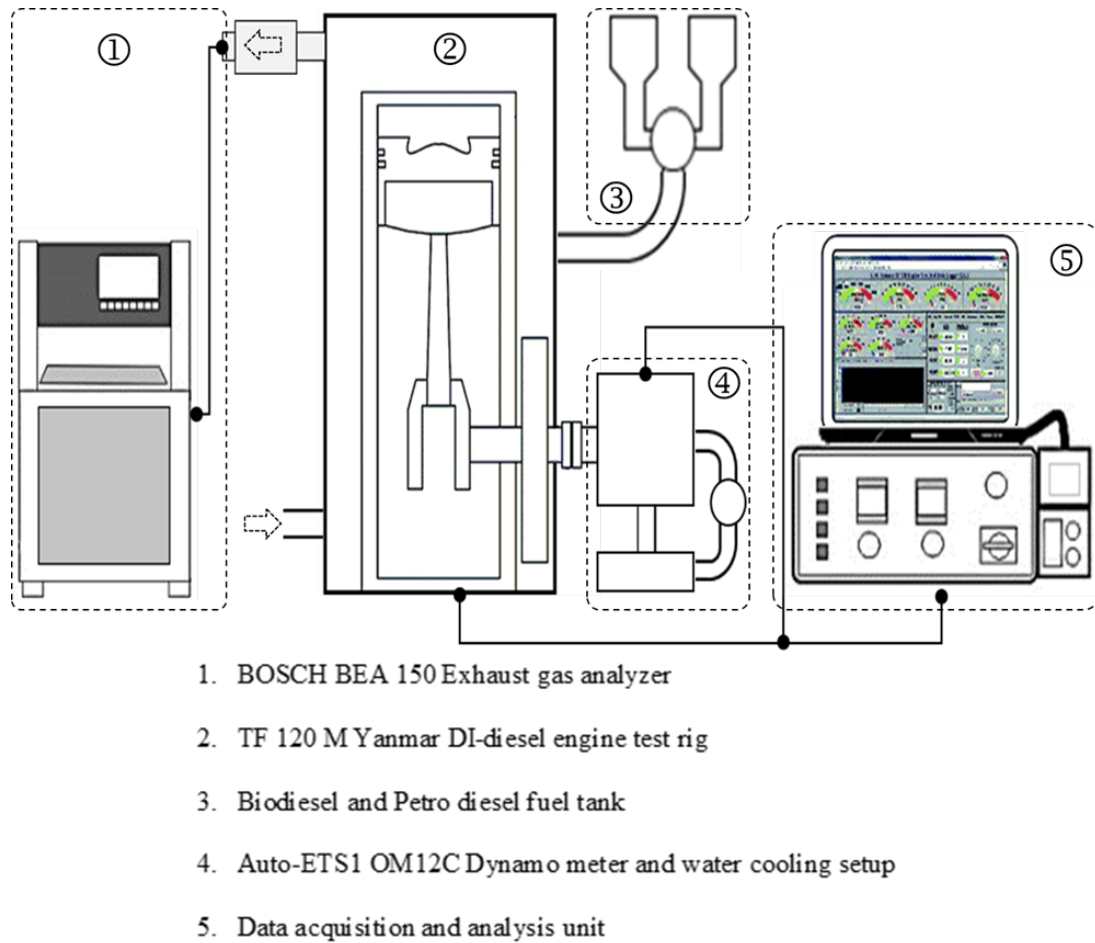


Figure A-1: DI-CI diesel engine and exhaust gas analysis setup (Ong et al., 2014).

Table A-1: Technical specifications of DI-diesel engine[#].

Model	TF 120 M Yanmar
Maximum power	7.7 kW
Maximum engine speed	2400 rpm
Injection timing	17.0 bTDC
Injection system	Direct injection
Injection pressure	200 kg/cm ²
Displacement	0.638 L
Cylinder number	1
Cylinder bore × stroke volume	92 mm × 96 mm
Cooling system	Water cooling
Compression ratio	17.7:1

[#]Adopted from (Ong et al., 2014)

Table A-2: Specifications of dynamometer and control unit setup[#].

Model	Auto-ETS1 OM12C
Accuracy	0.10%
Electricity requirement	220V, 60 Hz, 0.5A
Maximum power	20 kW
Maximum speed	10000 rpm
Maximum torque	80 NM
Operation temperature	0 °C to 70 °C
Operation voltage	230 VAC $\pm$ 10% 50-60 HZ
Output	PC interface with Dyno2000 $\times$ software
Power	VDC $\pm$ 10% @ 50 mA max
Precision	0.005% $\pm$ 1 digit
Screen type	7 Segment 5 LED Character height 10 mm
Speed measurement	Sensor
Water consumption for maximum power	14 L/min
Water pressure	23 lbf/in ²
Weight measurement	Linear (load cell)

[#]Adopted from (Ong et al., 2014)

Table A-3: Measuring specifications of the gas analysing device[#].

Measuring quantity	Range (Resolution)
CO	0.000–10.00% vol. (0.001% vol.)
CO ₂	0.00–18.00% vol. (0.01% vol.)
HC	0–9999 ppm vol. (1 ppm vol.)
NO _x	0–5000 ppm vol. (≤ 1 ppm vol.)
Degree of smoke opacity	0–100% (0.10%)
Oil temperature	–20 to +150 °C (0.16 °C)

[#]Adopted from (Ong et al., 2014)

Table A-4: Reference engine performance data.

Run	Block	Point	Coded parameters			Reference engine performance [#]			
			S	B	T	BP	BSFC	BTE	EGT
			rpm	%	N.m	kW	g/kWh	%	°C
1	2	Center	1900	B15	32	3.691	281.70	30.27	355.28
2	2	Axial	1900	B25	32	3.645	321.30	28.88	374.40
3	2	Axial	2100	B15	32	3.581	296.52	29	375.35
4	2	Axial	1900	B15	28	3.408	301.85	28.75	359.32
5	2	Center	1900	B15	32	3.417	281.70	30.27	369.22
6	2	Axial	1900	B5	32	3.491	284.41	30.07	344.61
7	2	Axial	1700	B15	32	3.460	293.72	29.05	358.02
8	2	Axial	1900	B15	36	3.581	276.40	30.21	359.32
9	1	Center	1900	B15	32	3.581	281.70	30.27	353.10
10	1	Cubic	1800	B10	34	3.581	273.85	30.9	359.32
11	1	Cubic	1800	B20	30	3.208	304.27	29.67	359.32
12	1	Center	1900	B15	32	3.232	281.70	30.27	353.94
13	1	Cubic	1800	B20	34	3.595	300.06	28.68	361.75
14	1	Cubic	2000	B20	30	3.487	311.07	29.24	385.33
15	1	Cubic	1800	B10	30	3.487	297.09	28.44	331.43
16	1	Cubic	2000	B20	34	3.616	304.21	28.55	350.59
17	1	Center	1900	B15	32	3.502	286.34	29.96	356.97
18	1	Center	1900	B15	32	3.126	286.34	29.96	358.81
19	1	Cubic	2000	B10	34	3.616	279.15	30.67	358.81
20	1	Cubic	2000	B10	30	3.404	295.75	28.52	356.48

Where S: Engine speed (rpm); B: JB-PD blend (%) and T: Torque (N.m)

[#] The reference engine performance data was adopted from the published experimental data by the engine research group, Department of Mechanical Engineering, University Malaya (UM), Malaysia (Ong et al., 2014).

Table A-5: Reference exhaust gas emissions data.

Run	Block	Point	Coded parameters			Reference exhaust gas emissions				
			S	B	T	Nox	HC	CO ₂	CO	Smoke opacity
			(rpm)	(%)	(N.m)	(ppm vol.)	(ppm vol.)	(%vol.)	(%vol.)	(%HSU)
1	2	Center	1900	B15	32	92.11	21.36	3.620	0.057	23.90
2	2	Axial	1900	B25	32	93.82	24.04	3.163	0.070	23.63
3	2	Axial	2100	B15	32	93.82	22.94	3.443	0.071	23.70
4	2	Axial	1900	B15	28	93.45	23.71	3.332	0.078	24.79
5	2	Center	1900	B15	32	94.58	21.36	3.620	0.057	23.90
6	2	Axial	1900	B5	32	93.82	21.84	3.756	0.061	27.87
7	2	Axial	1700	B15	32	93.82	23.28	3.416	0.075	24.93
8	2	Axial	1900	B15	36	92.17	20.90	3.622	0.055	23.15
9	1	Center	1900	B15	32	90.28	21.36	3.620	0.057	23.90
10	1	Cubic	1800	B10	34	93.84	21.24	3.836	0.057	25.38
11	1	Cubic	1800	B20	30	96.03	23.52	3.357	0.071	24.02
12	1	Center	1900	B15	32	91.20	21.36	3.620	0.057	23.90
13	1	Cubic	1800	B20	34	93.57	22.83	3.259	0.068	23.26
14	1	Cubic	2000	B20	30	95.05	24.03	3.379	0.075	23.35
15	1	Cubic	1800	B10	30	96.12	23.36	3.448	0.078	26.28
16	1	Cubic	2000	B20	34	94.81	22.89	3.310	0.068	22.73
17	1	Center	1900	B15	32	95.05	21.81	3.591	0.061	23.79
18	1	Center	1900	B15	32	93.18	21.81	3.591	0.061	23.79
19	1	Cubic	2000	B10	34	94.07	21.30	3.784	0.057	24.59
20	1	Cubic	2000	B10	30	93.44	22.97	3.424	0.074	25.58

Where S: Engine speed (rpm); B: JB-PD blend (%) and T: Torque (N.m)

The reference engine performance data was adopted from the published experimental data by the engine research group, Department of Mechanical Engineering, University Malaya (UM), Malaysia (Ong et al., 2014).

Appendix B: Publications

Article B-1: Journal publications

- [1] Reddy, A. N. R., Saleh, A. A., Islam, M. D. S., & Hamdan, S. (2015). Methanolysis of Crude Jatropha Oil using Heterogeneous Catalyst from the seashells and Eggshells as Green Biodiesel. *Asean Journal on Science and Technology for Development*, 32(1), 16–30. <http://ajstd.org/~ajstd/index.php/ajstd/article/view/9/8>
- [2] Reddy, A. N. R., Saleh, A. A., Islam, M. S., Hamdan, S., & Maleque, M. A. (2016). Biodiesel Production from Crude Jatropha Oil using a Highly Active Heterogeneous Nanocatalyst by Optimizing Transesterification Reaction Parameters. *Energy & Fuels*, 30(1), 334–343. <https://doi.org/10.1021/acs.energyfuels.5b01899>
- [3] Reddy, A. N. R., Saleh, A. A., Islam, M. S., & Hamdan, S. (2017). Active Razor Shell CaO Catalyst Synthesis for Jatropha Methyl Ester Production via Optimized Two-Step Transesterification. *Journal of Chemistry*, 2017(1), 20. <https://doi.org/10.1155/2017/1489218>
- [4] Reddy, A. N. R., Saleh, A. A., Islam, S., & Hamdan, S. (2017). Optimization of Transesterification Parameters for Optimal Biodiesel Yield from Crude Jatropha Oil Using a Newly Synthesized Seashell Catalyst. *Journal of Engineering Science and Technology*, 12(10), 10.
- [5] Reddy, A. N. R., Saleh, A. A., Islam, S., Hamdan, S., Rahman, M. R., & Masjuki, H. H., (2018). Experimental evaluation of fatty acid composition influence on Jatropha

biodiesel physicochemical properties. *Journal of Renewable and Sustainable Energy*, 10 (1), 20. <http://aip.scitation.org/doi/full/10.1063/1.5018743>

Article B-2: Conference papers

- [1] Reddy, A. N. R., Saleh, A. A., Islam, M. D. S., & Hamdan, S. (2015). Production of Green Biodiesel from Crude Jatropha Oil using Heterogeneous Catalyst: An Optimized process using Response Surface Methodology (RSM). In *UNIMAS F.Eng Colloquium* (p. 2). Kuching, Sarawak, Malaysia: UNIMAS. (Awarded Best Paper)
- [2] Reddy, A. N. R., Saleh, A. A., Islam, M. D. S., & Hamdan, S. (2015). Biodiesel Synthesis from Crude Jatropha Oil Using an Active Heterogeneous Nano Catalyst: An Optimized Process. In *Fundamental Science Congress* (p. 2). UPM, Sardang, Malaysia.
- [3] Reddy, A. N. R., Ahmed, A., Hamdan, S., KC, D., & Harish, M. (2016). Jatropha Biodiesel Production Evolution using an Active Heterogeneous Nano Catalyst Synthesized from Domestic Waste Chicken Eggshells. In *International conference on Emerging trends in Mechanical Engineering* (pp. 361–365). Hyderabad, India: IFHE.
- [4] Reddy, A., Saleh, A. A., Islam, M. S., & Hamdan, S. (2016). Active Heterogeneous CaO Catalyst Synthesis from *Anadara granosa* (Kerang) Seashells for Jatropha Biodiesel Production. *MATEC Web of Conferences*, 87, 6. <https://doi.org/10.1051/mateconf/20178702008>

Appendix C: Awards

- [1] Awarded Silver medal for research innovation: “Synthesis of a Highly Active and Green Nano–CaO from Seashells” at InTex’2017 on 17-18 May 2017. Presenters: A.N.R. Reddy, A. A. Saleh, S. Hamdan and Dewi H.

- [2] Malaysian Government International Student Award and Malaysian International Scholarship (MIS) - 2015, Ministry of Higher Education, Malaysia. MIS-2015; KPT.B.600-4/1/12 (60).

- [3] Zamalah Siswazah UNIMAS (ZSU) award 2015, Zamalah Graduate Scholarship from Universiti Malaysia Sarawak (UNIMAS), Malaysia.

- [4] Best Presentation Award: “Production of Green Biodiesel from Crude Jatropha Oil using Heterogeneous Catalyst: An Optimized process using Response Surface Methodology (RSM)” in UNIMAS FENG colloquium 2015 on 14 April 2015. Presenters: A.N.R. Reddy, A. A. Saleh, and S. Hamdan

