

CONTENTS

	Page
CONTENTS	vi
LIST OF TABLES	x
LIST OF ILLUSTRATIONS	xiii
LIST OF ABBREVIATIONS AND SYMBOLS	xvi
CHAPTER	
1 INTRODUCTION	1
1.1 Background and Rationale	1
1.2 Literature Review	2
1.3 Objectives of this Present Work	6
1.4 Expected Result	7
1.5 Scopes	7
2 THEORIES	8
2.1 History of Biodiesel	8
2.2 Esterification	9
2.3 Transesterification	9
2.4 Saponification	10
2.5 Rate Law of Reversible Reaction	10
2.6 Kinetics of Esterification	12
2.7 Kinetics of Transesterification	13
2.8 Activation Energy	14
2.9 Raw Materials	15
2.9.1 Oils and Fats	15
2.9.2 Alcohol	16

CONTENTS (Cont')

	Page
2.10 Effect of Parameter in Biodiesel Procedure	18
2.10.1 Catalyst	18
2.10.2 Molar Ratio of Methanol to Oil	18
2.10.3 Mixing Intensity	19
2.10.4 Reaction Temperature	19
2.10.5 Moisture and FFA Content	19
2.11 Specifications and Properties of Biodiesel	19
2.12 Method of High Free Fatty Acid Oils and Fats	21
2.13 Runge-Kutta Method for Solving Ordinary Differential Equation (O.D.E)	22
3 RESEARCH METHODOLOGY	24
3.1 Materials	25
3.2 Apparatus	25
3.3 Two-Stage Process	26
3.3.1 The Experiment of Two-Stage Process	26
3.3.2 Reaction Conditions	27
3.3.3 Sampling	27
3.3.4 Monitoring Analysis	27
3.4 Kinetics of Two-Stage Process	28
3.5 Two-Stage Process Modeling	28
4 RESULTS AND DISCUSSION	32
4.1 Pre-Experiment for Two-Stage Process of Biodiesel Production from MCPO	32
4.1.1 The Amount of Methanol (MeOH)	32
4.1.2 The Speed of Stirrer	33

CONTENTS (Cont')

	Page
4.1.3 The Amount of Catalyst	34
4.1.3.1 The Amount of H ₂ SO ₄	34
4.1.3.2 The Amount of NaOH	35
4.1.4 Water and H ₂ SO ₄ Separation	36
4.1.5 Purification Methods	37
4.1.6 Reaction Time	38
4.2 Two-Stage Process of Biodiesel Production from MCPO	39
4.2.1 Esterification	39
4.2.2 Transesterification	40
4.2.3 Effect of Methanol Ratio on Two-Stage Process	41
4.2.4 Effect of Temperature on Two-Stage Process	42
4.2.5 The Properties of Methyl Ester from MCPO	44
4.3 Kinetics of Two-Stage Process	45
4.3.1 Rate Coefficients and Reaction Rates of Two-Stage Process	45
4.3.2 Activation Energies (E _a) of Two-Stage Process	47
4.4 Two-Stage Process Modeling	49
5 CONCLUSIONS	58
5.1 Two-Stage Process	58
5.2 Two-Stage Process Modeling	59
5.3 Recommendations	59
REFERENCES	60
APPENDIX A CALCULATION OF THE MOLECULAR WEIGHT OF MCPO	66
APPENDIX B KARL FISCHER ANALYSIS	69

CONTENTS (Cont')

	Page
APPENDIX C COMPARISON OF ANALYTICAL INSTRUMENT	71
APPENDIX D RAW DATA FOR THE TWO-STAGE PROCESS	74
APPENDIX E ANALYTICAL DATA FOR THE TWO-STAGE PROCESS	81
APPENDIX F % DATA ERROR MEAN AND STANDARD DEVIATION IN CATEGORIES OF THE TWO-STAGE PROCESS FROM MATLAB7 CURVE FITTING TOOL	95
VITAE	99

LIST OF TABLES

TABLE		Page
2.1	Fatty acid structure	16
2.2	The percentage of common fatty acids in oils and fats	17
2.3	The requirement of commercial biodiesel qualities and quantities in Thailand	20
2.4	The requirement of biodiesel qualities and quantities for agricultural engines in Thailand	21
3.1	Pre-experiment conditions for the two-stage process production	29
4.1	Comparison between properties of methyl ester from MCPO and some requirements of biodiesel qualities and quantities in Thailand	44
4.2	Rate coefficients and reaction orders for esterification reaction	46
4.3	Rate coefficients for transesterification reaction	46
4.4	Activation energies (cal/mol) of the two-stage process at different molar ratios of methanol to oil	49
A.1	The concentration of compounds in MCPO from analysis using standard methods	68
D.1	FFA conversion in MCPO by using a 1:1 molar ratio of methanol to oil at a temperature of 55 degree Celsius	75
D.2	FFA conversion in MCPO by using a 1:1 molar ratio of methanol to oil at a temperature of 60 degree Celsius	75
D.3	FFA conversion in MCPO by using a 1:1 molar ratio of methanol to oil at a temperature of 65 degree Celsius	75
D.4	FFA conversion in MCPO by using a 2.5:1 molar ratio of methanol to oil at a temperature of 55 degree Celsius	76
D.5	FFA conversion in MCPO by using a 2.5:1 molar ratio of methanol to oil at a temperature of 60 degree Celsius	76

LIST OF TABLES

TABLE		Page
D.6	FFA conversion in MCPO by using a 2.5:1 molar ratio of methanol to oil at a temperature of 65 degree Celsius	76
D.7	FFA conversion in MCPO by using a 3.5:1 molar ratio of methanol to oil at a temperature of 55 degree Celsius	77
D.8	FFA conversion in MCPO by using a 3.5:1 molar ratio of methanol to oil at a temperature of 60 degree Celsius	77
D.9	FFA conversion in MCPO by using a 3.5:1 molar ratio of methanol to oil at a temperature of 65 degree Celsius	77
D.10	ME conversion in MCPO by using a 2.5:1 molar ratio of methanol to oil at a temperature of 55 degree Celsius	78
D.11	ME conversion in MCPO by using a 2.5:1 molar ratio of methanol to oil at a temperature of 60 degree Celsius	78
D.12	ME conversion in MCPO by using a 2.5:1 molar ratio of methanol to oil at a temperature of 65 degree Celsius	78
D.13	ME conversion in MCPO by using a 5:1 molar ratio of methanol to oil at a temperature of 55 degree Celsius	79
D.14	ME conversion in MCPO by using a 5:1 molar ratio of methanol to oil at a temperature of 60 degree Celsius	79
D.15	ME conversion in MCPO by using a 5:1 molar ratio of methanol to oil at a temperature of 65 degree Celsius	79
D.16	ME conversion in MCPO by using a 7.5:1 molar ratio of methanol to oil at a temperature of 55 degree Celsius	80
D.17	ME conversion in MCPO by using a 7.5:1 molar ratio of methanol to oil at a temperature of 60 degree Celsius	80

LIST OF TABLES

TABLE		Page
D.18	ME conversion in MCPO by using a 7.5:1 molar ratio of methanol to oil at a temperature of 65 degree Celsius	80
F.1	Rate coefficients and reaction orders of esterification from MATLAB7	96
F.2	Rate coefficients of transesterification from MATLAB7	96
F.3	Comparison between the % data error mean and the standard deviation in categories of the two-stage process between raw data and MATLAB7	98

LIST OF ILLUSTRATIONS

FIGURE		Page
3.1	Diagram of research methodology	24
3.2	Equipment used in this study	26
3.3	Two-stage process	30
3.4	Diagram of the two-stage process modeling	31
4.1	Effect of stirring speed on FFA conversion in MCPO by using a 20:1 molar ratio of methanol to FFA, at a temperature of 60 degree Celsius, catalyzed by 10 %wt H ₂ SO ₄ of FFA	33
4.2	Effect of the amount of H ₂ SO ₄ on FFA conversion in MCPO by using a 10:1 molar ratio of methanol to FFA, at temperature of 60 degree Celsius, and a speed of stirrer of 300 rpm	35
4.3	Effect of the amount of NaOH on ME conversion in MCPO by using a 6:1 molar ratio of methanol to TG, at temperature of 60 degree Celsius, and a speed of stirrer of 300 rpm	36
4.4	Standing time for water and H ₂ SO ₄ separation of first stage process	36
4.5	Effect of purification method on FFA conversion in MCPO under a 10:1 molar ratio of methanol to FFA, at temperature of 60 degree Celsius, a speed of stirrer of 300 rpm, and catalyzed by 5 %wt H ₂ SO ₄ of FFA	37
4.6	Variations of the reaction mixture composition during esterification of MCPO by using a 10 %wt H ₂ SO ₄ of FFA and a 10:1 molar ratio of methanol to FFA at 60 degree Celsius	49
4.7	Variations of the reaction mixture composition during transesterification of MCPO by using a 0.6 %wt NaOH of TG and a 6:1 molar ratio of methanol to TG at 60 degree Celsius	40

LIST OF ILLUSTRATIONS (Cont')

FIGURE		Page
4.8	Effect of molar ratio of methanol to oil on FFA concentration in MCPO using 10 %wt H ₂ SO ₄ of FFA and a stirring rate of 300 rpm at 55 (A), 60 (B), 65 (C) degree Celsius, respectively	42
4.9	Effect of molar ratio of methanol to oil on FFA in MCPO using 0.6 %wt NaOH of TG and a stirring rate of 300 rpm at 55 (A), 60 (B), 65 (C) degree Celsius, respectively	43
4.10	The temperature dependency of reaction rate coefficients of esterification at a 10:1 molar ratio of methanol to FFA	47
4.11	The temperature dependency of the reaction rate coefficients of transesterification at a 6:1 molar ratio of methanol to TG	48
4.12	The procedure used in the two-stage process part	51
4.13	Inputting initial concentrations of substances (FFA, ME, and WT) in %wt	51
4.14	Unit conversions for concentration in the esterification reaction (%wt to mol/L)	52
4.15	Conditions for reducing FFA concentration in MCPO	52
4.16	The table and curves of the component concentrations (FFA, ME, and WT) in mol/L	53
4.17	Unit conversions for concentration in the esterification reaction (mol/L to %wt)	53
4.18	The table and curves of FFA, ME, and WT concentrations the optimal condition in mol/L	54
4.19	Unit conversions for concentration in the esterification reaction (mol/L to %wt) of the optimal condition	54
4.20	Inputting initial concentrations of TG, DG, MG, and GL in %wt	55

LIST OF ILLUSTRATIONS (Cont')

FIGURE		Page
4.21	Unit conversions for concentrations in the transesterification reaction (%wt to mol/L)	55
4.22	Conditions for producing ME from MCPO	56
4.23	The table and curves of TG, DG, MG, ME, and GL concentrations in mol/L	56
4.24	Unit conversions for concentratiois in the transesterification reaction (mol/L to %wt)	57
C.1	Comparison of FFA determination between TLC/FID and Titration	72
C.2	Comparison of ME determination between TLC/FID and GC/FID	72
C.3	Comparison of GL determination between Titration and GC/FID	73
E.1	Remained methanol content in the first stage solution	82
E.2	Ester content of first-stage process at different times	83
E.3	Free fatty acid value of MCPO	84
E.4	MG, DG and TG content in MCPO	85
E.5	The % ester content of biodiesel produce from MCPO	86
E.6	Density of biodiesel prepared from MCPO	87
E.7	Flash point and viscosity of biodiesel from MCPO	88
E.8	Sulphur content of biodiesel made from MCPO	89
E.9	Sulphur ash content of biodiesel made from MCPO	90
E.10.1	Water and sediment in biodiesel obtained from MCPO	91
E.10.2	Water and sediment in biodiesel obtained from MCPO	92
E.11	Acid number of biodiesel made from MCPO	93
E.12	Free GL, MG, DG, TG, and total GL in biodiesel produced from MCPO	94

LIST OF ABBREVIATIONS AND SYMBOLS

A	Pre-exponential factor or frequency factor
A	The initial reactant
ACE	The acid-catalyzed esterification
AL	Alcohol
ASTM	American standard test method
[AL]	The molar concentration of alcohol
[A]	The molar concentration of alcohol
[A]	The molar concentration of reagent A
a	Order of free fatty acid in reaction sequence
a	Order of reagent A
a	The coefficient of reagent A
[a, b]	Interval
B	The initial reactant
BCM	The base-catalyzed methanolysis
[B]	The molar concentration of reagent B
b	Order of alcohol in reaction sequence
b	Order of reagent B
b	The coefficient of reagent B
C	The product
$C_{12}H_{24}O_2$	Lauric
$C_{14}H_{28}O_2$	Myristic
$C_{16}H_{32}O_2$	Palmitic
$C_{18}H_{30}O_2$	Linolenic
$C_{18}H_{32}O_2$	Linoleic
$C_{18}H_{34}O_2$	Oleic
$C_{18}H_{36}O_2$	Stearic

LIST OF ABBREVIATIONS AND SYMBOLS (Cont')

$C_{20}H_{40}O_2$	Arachidic
$C_{22}H_{42}O_2$	Erucic
$C_{22}H_{44}O_2$	Behenic
$C_{24}H_{48}O_2$	Lignoceric
CPOME	Mixed crude palm oil methyl Ester
[C]	The molar concentration of product C
c	Order of ester in reaction sequence
c	Order of product C
c	The coefficient of product C
cal	Calorie
cm ³	Cubic millimeter
cSt	Centistokes
D	The product
DG	Diglyceride
[D]	The molar concentration of product D
[DG]	The molar concentration of diglyceride
d	Order of product D
d	Order of water in reaction sequence
d	The coefficient of product D
E	Activation energy, J/mol or cal/mol
E	Ester
E _a	Activation Energies
EN	European test method
[E]	The molar concentration of ester
FAME	Fatty acid methyl ester
FFA	Free fatty acid

LIST OF ABBREVIATIONS AND SYMBOLS (Cont')

[FFA]	The molar concentration of free fatty acid
$f(x,y)$	Function (x,y)
GC/FID	Gas chromatography/ flame ionization detector
GL	Glycerol
[GL]	The molar concentration of glycerol
g	Gram
H_2SO_4	Sulfuric acid
h	Width
I.V.P.	The initial value problem
i	Order
J	Joule
K	Kelvin
KOH	Potassium hydroxide
k_A	The rate coefficient
k_a	The rate coefficient of the forward reaction
k_{-a}	The rate coefficient of the reverse reaction
k_1	The rate coefficient of free fatty acid (forward reaction)
k_2	The rate coefficient of free fatty acid (reverse reaction)
k_3	The rate coefficient of TG (forward reaction)
k_4	The rate coefficient of TG (reverse reaction)
k_5	The rate coefficient of DG (forward reaction)
k_6	The rate coefficient of DG (reverse reaction)
k_7	The rate coefficient of MG (forward reaction)
k_8	The rate coefficient of MG (reverse reaction)
kg/m^3	Kilogram/ cubic metre
k1	The first step of the Runge-Kutta Method calculation

LIST OF ABBREVIATIONS AND SYMBOLS (Cont')

k ₂	The second step of the Runge–Kutta Method calculation
k ₃	The third step of the Runge–Kutta Method calculation
k ₄	The fourth step of the Runge–Kutta Method calculation
L	Liter
ln	Natural logarithm
M	Subinterval
MCPO	Mixed crude palm oil
ME	Methyl ester
ME1	Methyl ester from the first–stage process
MeOH	Methanol
MG	Monoglycerides
[MG]	The concentration of monoglyceride
m	The number of categories
mg/kg	Milligram/ kilogram
mg KOH/g	Milligram potassium hydroxide/ gram
min	Minute
ml.	Milliliter
NaOH	Sodium hydroxide
N _{RE}	Reynolds Number
n	Number of population
n _i	Sizes of categories
O.D.E	Ordinary Differential Equation
ode23	Runge–Kutta Method order 2–3
ode45	Runge–Kutta Method order 4–5
prEN	European test method
R	Alkyl group

LIST OF ABBREVIATIONS AND SYMBOLS (Cont')

R	Gas constant = 8.314 J/mol K or 1.987 cal/mol K
R	Short chain alkyl groups
RK4	The fourth-order Runge-Kutta Method
RPO	Refined palm oil
R^2	The determination coefficient
R'	Alkyl group
R'	Long chain alkyl groups
R''	Alkyl group
R''	Long chain alkyl groups
R''O	Hydrocarbon group
R'''	Long chain alkyl groups
rpm	Revolutions per minute
T	Absolute temperature, K
T	Temperature
TLC/FID	Thin layer chromatography/ flame ionization detector
TG	Triglycerides
TSO	Tobacco seed oil
[TG]	The molar concentration of triglyceride
t	Time
WT	Water
[WT]	The molar concentration of water
xi	Population x
$x_{i,j}$	Data measurements
(x_i, y_i)	The discrete approximations
y_i	Population y
$^{\circ}\text{C}$	Degree Celsius

LIST OF ABBREVIATIONS AND SYMBOLS (Cont')

μ	Mean
μ_i	Mean
σ	The standard deviation
σ_i	Standard deviation
%v	%volume by volume
%v/v	%volume by volume
%vol	%volume by volume
%wt	%weight by weight
%wt/v	%weight by volume
%wt/wt	%weight by weight