



E47329

นายเรือใหญ่ ส่วนแก้ว

กรมการช่างศิลปกรรม



E47329

การศึกษาพารามิเตอร์ของการผลิตไบโอดีเซลในเมทานอลภาวะเหนือวิกฤต
ในเครื่องปฏิกรณ์แบบท่อ

นายเรืองวิทย์ สว่างแก้ว



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต

สาขาวิชาเคมีเทคนิค ภาควิชาเคมีเทคนิค

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2553

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

PARAMETRIC STUDY OF BIODIESEL PRODUCTION IN SUPERCRITICAL METHANOL
IN A TUBULAR REACTOR

Mr. Ruengwit Sawangkeaw

A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy Program in Chemical Technology

Department of Chemical Technology

Faculty of Science

Chulalongkorn University

Academic year 2010

Copyright of Chulalongkorn University

Thesis Title	PARAMETRIC STUDY OF BIODIESEL PRODUCTION IN SUPERCritical METHANOL IN A TUBULAR REACTOR
By	Mr. Ruengwit Sawangkeaw
Field of Study	Chemical Technology
Thesis Advisor	Associate Professor Somkiat Ngamprasertsith, Doctorat de l'INP
Thesis Co-Advisors	Associate Professor Kunchana Bunyakiat Professor Jean-Stéphane CONDORET, Doctorat de l'INP

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of
the Requirements for the Doctoral Degree

..... Dean of the Faculty of Science
(Professor Supot Hannongbua, Dr. rer. nat.)

THESIS COMMITTEE

EE



..... Chairman

(Associate Professor Tharapong Vitidsant, Doctorat de l'INPT)

..... Thesis Advisor
(Associate Professor Somkiat Ngamprasertsith, Doctorat de l'INPT)

..... Thesis Co-Advisor
(Associate Professor Kunchana Bunyakiat)

..... Thesis Co-Advisor
(Professor Jean-Stéphane CONDORET, Doctorat de l'INPT)

Chawalit Ngamcharussrivichai Examiner
(Assistant Professor Chawalit Ngamcharussrivichai, Ph.D.)

..... K. Poochinda Examiner
(Kunakorn Poochinda, Ph.D.)

..... External Examiner
(Suchada Butnark, Ph.D.)

เรื่องวิทย สว่างแก้ว : การศึกษาพารามิเตอร์ของการผลิตไบโอดีเซลในเมทานอลภาวะเหนือวิกฤตในเครื่องปฏิกรณ์แบบท่อ. (PARAMETRIC STUDY OF BIODIESEL PRODUCTION IN SUPERCRITICAL METHANOL IN A TUBULAR REACTOR)

อ. ที่ปรึกษาวิทยานิพนธ์หลัก : รศ. ดร. สมเกียรติ งามประเสริฐสุทธี, อ. ที่ปรึกษา

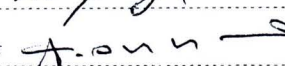
วิทยานิพนธ์ร่วม : รศ. กัญจนา บุญเกียรติ, Prof. Jean-Stéphane CONDORET, Doctorat de l'INPT, 3 หน้า.

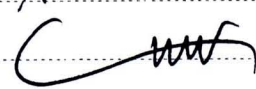
E47329

การผลิตไบโอดีเซลในเมทานอลภาวะเหนือวิกฤตมีข้อได้เปรียบกว่ากระบวนการแบบดั้งเดิมซึ่งใช้ตัวเร่งปฏิกิริยาเอกพันธ์ ได้แก่ มีประสิทธิภาพสูงและใช้วัตถุดิบได้หลากหลายกว่า อย่างไรก็ตามพบว่าร้อยละเมทิลเอสเทอร์สูงสุดในเครื่องปฏิกรณ์แบบต่อเนื่องในเมทานอลภาวะเหนือวิกฤตต่ำกว่าในเครื่องปฏิกรณ์แบบแบตช์เล็กน้อย จุดประสงค์แรกของงานวิจัยนี้คือศึกษาผลของตัวทำละลายร่วมที่ใช้ลดความหนืดในเครื่องปฏิกรณ์แบบต่อเนื่องระดับขยายขนาด โดยศึกษาผลของตัวทำละลายร่วมด้วยการออกแบบการทดลองแบบ 2^3 แฟกทอเรียล พบว่าตัวทำละลายร่วมไม่มีผลอย่างมีนัยสำคัญต่อร้อยละเมทิลเอสเทอร์ จุดประสงค์ที่สองคือการพัฒนาการวิธีประมาณเวลาในการเกิดปฏิกิริยาของการผลิตไบโอดีเซลในเมทานอลภาวะเหนือวิกฤตอย่างต่อเนื่อง โดยใช้แบบจำลองทางเทอร์โมไดนามิกส์ (PR-MHV2-UNIQUAC) ซึ่งมีการปรับพารามิเตอร์อันตรกิริยาร่วมกับจลนพลศาสตร์ของการผลิตไบโอดีเซลในเมทานอลภาวะเหนือวิกฤตจากน้ำมันปาล์มและคุณมวลสารพื้นฐานในเครื่องปฏิกรณ์แบบท่อ พบว่าแบบจำลองที่สร้างขึ้นสามารถทำนายค่าที่ได้จากผลการทดลองได้ดีที่อุณหภูมิต่ำกว่า 320°C เนื่องจากไม่มีผลของการแตกตัวทางความร้อนของกรดไขมันไม่อิ่มตัวและแสดงให้เห็นถึงผลของการเปลี่ยนแปลงแฟกเตอร์สภาพอัดได้ของของผสมที่ทำให้อัตราการเกิดปฏิกิริยาช้าลงในเครื่องปฏิกรณ์แบบท่อ นอกจากนี้วิธีประมาณเวลาในการเกิดปฏิกิริยาที่พัฒนาขึ้นโดยสันนิษฐานว่าแฟกเตอร์สภาพอัดได้ไม่คงที่นั้นแสดงให้เห็นว่าร้อยละเมทิลเอสเทอร์ที่ได้จากเครื่องปฏิกรณ์แบบต่อเนื่องมีค่าต่ำลงเล็กน้อยเท่านั้น ซึ่งเกิดจากการแตกตัวทางความร้อนที่อุณหภูมิ 350°C และเวลาในการเกิดปฏิกิริยามากกว่า 30 นาที

ภาควิชา เคมีเทคนิคลายมือชื่อนิสิต..... 

สาขาวิชา เคมีเทคนิคลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก..... 

ปีการศึกษา 2553ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม..... 

ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม..... 

4873890023 : MAJOR CHEMICAL TECHNOLOGY

KEYWORDS : VEGETABLE OIL / BIODIESEL / TRANSESTERIFICATION /
SUPERCRITICAL METHANOL / CONTINUOUS PRODUCTION

RUENGWIT SAWANGKEAW : PARAMETRIC STUDY OF BIODIESEL
PRODUCTION IN SUPERCRITICAL METHANOL IN A TUBULAR REACTOR.

ADVISOR : ASSOC.PROF.SOMKIAT NGAMPRASERTSITH, DOCTORAT DE
L'INPT., CO-ADVISOR : ASSOC.PROF.KUNCHANA BUNYAKIAT, PROF. JEAN-
STÉPHANE CONDORET, DOCTORAT DE L'INPT, 3 pp.

E47329

Biodiesel production in supercritical methanol (SCM) has several advantages over that employing homogeneous catalysts; i.e. better production efficiency and feedstock flexibility. However, the maximum methyl esters (ME) content, which was found in our continuous SCM reactor, was slightly lower than the batch SCM reactor. The first objective was to investigate effects of co-solvents used for viscosity reduction in scale-up continuous reactor, on ME content. The investigation was successfully done by 2^3 factorial design and found that the amount of co-solvents had no significant effect on ME content. The second objective was to develop residence time estimation method for continuous production of biodiesel in SCM. A compressible flow model, derived from general mole balance in a tubular reactor, transesterification kinetic of palm oil in SCM, and thermodynamic model (PR-MHV2-UNIQUAC) with adjusted binary interaction parameters was employed. The model was adequate to predict final conversion at below 320 °C, when thermal degradation reaction of unsaturated fatty acids (UFA) did not interfere. It was illustrated that development of compressibility factor slowed down the rate of transesterification reaction in SCM in a tubular reactor. Finally, the residence time estimation method based on compressibility changes was successfully attempted and demonstrated that ME content in continuous tubular reactor was only slightly reduced by thermal degradation of UFA at 350 °C and residence time longer than 30 min

Department : Chemical Technology..... Student's Signature

Field of Study : Chemical Technology..... Advisor's Signature

Academic Year : 2010..... Co-Advisor's Signature

Co-Advisor's Signature

Ruengwit Sawangkeaw
Somkiat Ngamprasertsith
Kunchana Bunyakiat
[Signature]

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude my supervisors, Associate Professor Somkiat Ngamprasertsith, Ph.D., Associate Professor Kunchana Bunyakiat and Professor Jean-Stéphane CONDORET, Ph.D. who reviewed this thesis during its preparation and offered many helpful suggestions, supervision and much encouragement throughout pass five years of my research. I also would like to acknowledge Associate Professor Tharapong Vitidsant, Ph.D., Assistant Professor Chawalit Ngamcharussrivichai, Ph.D. Mr. Kunakorn Poochinda, Ph.D. and Miss Suchada Butnark, Ph.D. for their participation on the dissertation chairman and members of thesis committee, respectively.

I wish to express my thankfulness to all people in the associated institution and companies for their kind assistance and collaboration: Madam Séverine CAMY, Ph.D. and Monsieur Pablo E. HEGEL, Ph.D. for encouragements and helpful suggestion during this research at Institut National Polytechnique de Toulouse, Laboratoire de Génie Chimique in France.

Sincerest appreciation also extends to Chulalongkorn University Dutsadi Phiphat Scholarship, the Center for Petroleum, Petrochemicals and Advanced Materials for financial support of this research and Chumporn Palm Oil Industry Co. Ltd. for supplying the palm kernel oil samples.

Many thanks are due to technicians, researchers, colleagues, fellow students and friends at the Department of Chemical Technology for their helps, supports, encouragement and friendships.

Finally, I wish to acknowledge the support, encouragement and love of my friends and family throughout my Ph.D. program.

CONTENTS

	Page
ABSTRACT (IN THAI).....	iv
ABSTRACT (IN ENGLISH)	v
ACKNOWLEDGEMENTS	vi
CONTENTS	vii
LIST OF TABLES	x
LIST OF FIGURES.....	xii
CHAPTER I: INTRODUCTION	1
1.1. Background	1
1.2. Objectives.....	2
1.3. Scope of dissertation	3
CHAPTER II: THEORY AND LITERATURE REVIEWS.....	4
2.1. Biodiesel.....	4
2.2. Biodiesel production with conventional method.....	4
2.3. Biodiesel production with heterogeneous catalysts and lipase	7
2.4. Biodiesel production with supercritical methanol (SCM).....	8
2.4.1. Chronological development of biodiesel production with SCM.....	10
2.4.2. Effect of operating parameters on biodiesel production with SCM.....	11
2.4.2.1. Temperature	11
2.4.2.2. Pressure	15
2.4.2.3. Methanol to oil molar ratio	15
2.4.2.4. Reaction time	16
2.4.2.4.1. Batch reactor.....	17
2.4.2.4.2. Continuous reactor (residence time).....	17
2.4.2.5. Mixing intensity and dispersion in tubular reactor	19
2.4.3. Chemical kinetics of biodiesel production with SCM.....	22
2.4.4. Phase behavior and binary vapor-liquid equilibrium (VLE) of biodiesel production with SCM	25

2.4.5. Innovative technologies for milder operating parameters in biodiesel production with SCM	29
2.4.5.1. Addition of co-solvents.....	29
2.4.5.2. The addition of catalysts to the SCM reaction.....	33
2.4.5.3. Modification of the SCM reaction	34
2.5. Literature reviews.....	36
CHAPTER III: EQUIPMENTS AND EXPERIMENTAL PROCEDURES	47
3.1. Effect of cc-solvents.....	47
3.1.1. Equipments.....	47
3.1.2. Materials.....	47
3.1.3. Experimental procedure	47
3.1.3.1. The 250-mL reactor	47
3.1.3.2. The 5.5-mL reactor	48
3.1.4. Analysis of methyl esters	48
3.2. Effect of additional parameters and scale-up reactor optimization	49
3.2.1. Equipments.....	49
3.2.1.1. The scale-up reactor	49
3.2.1.2. The 250-mL and 5.5-mL reactors	50
3.2.2. Materials.....	50
3.2.3. Experimental procedure	50
3.2.3.1. The scale-up reactor.....	50
3.2.3.2. The 250-mL and 5.5-mL reactor.....	50
3.2.3.3. The 5.5-mL reactor to investigate the effect of delay quenching time	50
3.2.4. Analysis of methyl esters	51
3.3. Residence time estimation method.....	51
3.3.1. Equipments.....	51
3.3.2. Materials.....	52
3.3.3. Experimental procedure	52
3.3.4. Analysis of methyl esters	52

CHAPTER IV: EFFECT OF CO-SOLVENTS..... 53

4.1. Reaction among vegetable oil, methanol and co-solvents..... 53

4.2. Effect of co-solvents on ME content in a 250-mL reactor 55

CHAPTER V: EFFECT OF ADDITIONAL PARAMETERS AND
SCALE-UP REACTOR OPTIMIZATION 58

5.1. Effect of reaction time on ME content in 250-mL batch reactor 58

5.2. Effect of temperature gradient between reactor wall and bulk fluid 58

5.3. Effect of contaminants in crude palm kernel oil 60

5.4. Effect of co-solvents on ME content in biodiesel production in a 5.5-mL reactor 61

5.5. Effect of delayed quenching time..... 64

5.5.1. Effect of delayed quenching time in a 5.5-mL batch reactor..... 64

5.5.2. Effect of delay quenching time in scale-up reactor..... 64

5.6. Effect of pressure and process optimization..... 66

CHAPTER VI: RESIDENCE TIME ESTIMATION METHOD 70

6.1. Description of the compressible flow model as a tool to estimate the residence time..... 70

6.1.1. Thermodynamic model 70

6.1.2. Compressible flow model 71

6.2. Fitting of the thermodynamic model and binary interaction parameters 73

6.3. ME content prediction by the compressible flow model..... 77

6.4. Residence time estimation procedure..... 83

CHAPTER VII: CONCLUSIONS AND RECOMMENDATION 84

7.1. Conclusions 84

7.2. Recommendation..... 85

REFERENCES 87

APPENDICES 96

APPENDIX A THE STATISTICAL ANALYSIS OF THE REGRESSION MODEL FOR
SCALE-UP REACTOR..... 97

APPENDIX B THE EXAMPLES OF PROGRAMING CODE FOR MATLAB ® SOFTWARE
WITH SIMULIS TOOLBOX..... 101

BIOGRAPHY 105

LIST OF TABLES

	Page
Table 2.1 Advantages and disadvantages of heterogeneous and lipase catalysts.....	7
Table 2.2 Operating parameters for a high conversion efficiency of lipid to biodiesel with SCM.....	13
Table 2.3 Molar ratio and mole fraction at the inlet and outlet of the tubular reactor, calculated by assuming 100% conversion at the outlet.	18
Table 2.4 Optimal condition, reactor design, Reynolds and axial Péclet number of the continuous biodiesel production with SCM in a tubular reactor.....	21
Table 2.5 Reactions rate constant (k) as linear function of temperature, pre-exponential factor (k_0) and activation energy (E_a)	24
Table 2.6 Studies on the VLE of biodiesel production with SCM summary.	27
Table 2.7 Binary interaction parameters of the VdW mixing rule which correspond with the thermodynamic model in Table 2.6.....	28
Table 2.8 Demonstrated techniques for reducing the operating parameters of biodiesel production with SCM.	30
Table 2.9 New operating parameters of biodiesel production with SCM by the techniques outlined in Table 2.8.....	31
Table 4.1 Experimental data from employed THF process in 250-mL reactor for 10 min with crude PKO as reactant	55
Table 4.2 Experimental data from employed hexane process in 250-mL reactor for 10 min with crude PKO as reactant	56
Table 4.3 Analysis of variance from employed THF process in 250-mL reactor for 10 min with crude PKO as reactant	56
Table 4.4 Analysis of variance from employed hexane process in 250-mL reactor for 10 min with crude PKO as reactant	57
Table 5.1 Experimental data from 5.5-mL reactor for 10 min with crude PKO as reactant, temperature controlled by fluidized sand bath	60
Table 5.2 Experimental data from employed THF process in 5.5-mL reactor for 10 min with refined PKO as reactant.....	61

Table 5.3 Experimental data from employed hexane process in a 5.5-mL reactor for 10 min
with refined PKO as reactant..... 62

Table 5.4 Analysis of variance from employed THF process in a 5.5-mL reactor for 10 min
with refined PKO as reactant..... 62

Table 5.5 Analysis of variance from employed hexane process in 5.5-mL reactor for 10 min
with refined PKO as reactant..... 63

Table 5.6 The ME content in products from scale-up reactor with different cooling systems 65

Table 5.7 The experimental conditions and results from CCD to reinvestigate the effect of
pressure, temperature and methanol to oil molar ratio in scale-up reactor 66

Table 5.8 Analysis of variance of results in Table 5.7 67

Table 6.1 Calculated binary interaction coefficients for UNIQUAC model..... 73

Table 6.2 Methanol mole fraction in liquid (*x*) and vapor (*y*) phase of
triolein + methanol VLE..... 74

Table 6.3 The methanol mole fraction in liquid (*x*) and vapor (*y*) phase of
methyl oleate + methanol VLE. 75

Table 6.4 The methanol mole fraction in liquid (*x*) and vapor (*y*) phase of
glycerol + methanol VLE..... 76

Table 6.5 The observed and calculated ME content from various reacting conditions..... 78

Table A1. The statistical values of the regression model for scale-up reactor from
Design Expert ® 6.0 software 97

Table A2. The estimated coefficients and its standard error in the regression model
for scale-up reactor at ±95% confident interval from Design Expert ® 6.0 software.... 98

Table A3. The residual analysis of actual and predicted value for the regression model
for scale-up reactor 99

LIST OF FIGURES

	Page
Figure 2.1. Common reactions for biodiesel production processes.....	5
Figure 2.2. Conventional biodiesel production scheme from waste cooking oils with acid pretreatment followed by alkaline catalytic process or two-step acidic-basic transesterification.....	6
Figure 2.3. Biodiesel production with SCM scheme.....	8
Figure 3.1 Schematic diagram of scale-up tubular reactor for biodiesel production with SCM....	49
Figure 3.2 Schematic diagram of lab-scale tubular reactor.....	51
Figure 4.1 GC-MS chromatogram of mixed methyl esters standard.....	53
Figure 4.2 GC-MS chromatogram of biodiesel from employed THF process in 250-mL reactor for 10 min with crude PKO as reactant.	53
Figure 4.3 GC-MS chromatogram of THF phase in 250-mL reactor for 10 min with crude PKO as reactant.	54
Figure 4.4 GC-MS chromatogram of hexane phase in 250-mL reactor for 10 min with crude PKO as reactant.	54
Figure 5.1 Changes in ME content with time of co-solvent free process from transesterification of crude PKO in 250-mL reactor at 350 °C and the methanol to oil molar ratio of 42:1.	58
Figure 5.2 Comparison of GC chromatogram of biodiesel product from crude PKO at various temperatures, indicating some noises observed as in c) and d)	59
Figure 5.3 The ME content versus the delayed quenching time in 5.5-mL tube reactor	64
Figure 5.4 The scale-up reactor after replaced cooling bath with heat exchanger	65
Figure 5.5 The plot of experimented and calculated value by Equation 5.3	68
Figure 5.6 The response surface of ME content versus temperature and pressure at methanol to oil of 35:1	68
Figure 6.1 Experimental (Exp) and calculated (Cal) P-x-y diagram of triolein + methanol VLE.....	75
Figure 6.2 Experimental (Exp) and calculated (Cal) P-x-y diagram of methyl oleate + methanol VLE.....	76

Figure 6.3 Experimental (Exp) and calculated (Cal) P-x-y diagram of glycerol + methanol VLE..	77
Figure 6.5 The plot of experimented and calculated ME content by Eq. 6.6 (♦) or Eq.6.7 (○)....	78
Figure 6.6 The relationship between %relative error of calculated value from Eq. 6.6 and reaction temperature.....	79
Figure 6.7 The relationship between %relative error of calculated value from Eq. 6.6 and methanol to oil molar ratio.....	79
Figure 6.8 The relationship between %relative error of calculated value from Eq. 6.6 and pressure	80
Figure 6.9 The changes in the compressibility of the reaction mixture along the length of the tubular reactor in run no. 1 (◇), 2 (+), 3 (□), 4 (×), 5 (○), 17 (●) and 22 (▲).	81
Figure 6.10 The changes in the molar volume of the reaction mixture along the length of the tubular reactor in run no. 1 (◇), 2 (+), 3 (□), 4 (×), 5 (○), 17 (●) and 22 (▲).....	82
Figure A1. The normal plot of the residuals.....	100
Figure A2. The relationship between residuals and run number.....	100
Figure A3. The relationship between residuals and predicted values	100