

**NON-CATALYTIC SUPERCRITICAL
METHANOL (SCM) AND SUPERHEATED
METHANOL VAPOUR (SMV) FOR FATTY ACID
METHYL ESTERS (FAME) SYNTHESIS FROM
JATROPHA AND SEA MANGO OILS**

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UNIVERSITI SAINS MALAYSIA

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**NON-CATALYTIC SUPERCRITICAL METHANOL (SCM) AND
SUPERHEATED METHANOL VAPOUR (SMV) FOR FATTY ACID
METHYL ESTERS (FAME) SYNTHESIS FROM JATROPHA AND SEA
MANGO OILS**

by

ANG GAIK TIN

**Thesis submitted in fulfilment of the requirements
for the degree of
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LIST OF ABBREVIATION

ANOVA	Analysis of variance
ASTM	American Society of Testing and Materials
CCD	Central Composite Design
CFD	Computational fluid dynamics
DOE	Design of Experiment
DG	Diglycerides
EIA	United States Energy Information Administration
EPA	United States Environment Protection Agency
EN	European Standards
EU	European Union
FAAE	Fatty acid alkyl esters
FAEE	Fatty acid ethyl esters
FAME	Fatty acid methyl esters
FFA	Free fatty acids
FID	Flame ionization detector
GC	Gas Chromatograph
GC/MS	Gas chromatography mass spectrometry
LPG	Liquefied petroleum gas
Gly	Glycerol
IS	Internal standard
MeOH	Methanol
MG	Monoglycerides
MR	Molar ratio
OFAT	One factor at a time
PFAD	Palm fatty acid distillate
ROH	Alcohol
RMSE	Root mean square error
RSM	Response Surface Methodology
SCDMC	Supercritical dimethyl carbonate
SCE	Supercritical ethanol
SCF	Supercritical fluid

SCM	Supercritical methanol
SCMA	Supercritical methyl acetate
SMV	Superheated methanol vapour
TG	Triglycerides

LIST OF SYMBOLS

A	Reaction time code (min)
A_i	Pre-exponential Factor, $i = 1,2,3,4,5,6, 7$ and 8
Ar	Area of methyl esters in chromatogram
B	Reaction temperature code ($^{\circ}\text{C}$)
C	Molar ratio of methanol to oil code (mol/mol)
C	Concentration
Ea_i	Activation Energy, $i = 1,2,3,4,5,6,7$ and 8 (J/mol)
F_j	Flow rate (mL/min)
F-value	Ratio of model mean square to residuals mean square
G_j	Rate of generation (mol/s)/(mol/min)
k_i	Reaction rate constants, $i = 1,2,3,4,5, 6,7$ and 8 ($\text{dm}^3/\text{mol s}$)/ ($\text{dm}^3/\text{mol min}$)
n	Number of experiment
P_c	Critical pressure
r	Rate of formation of species
R	Gas constant (J/mol.K)
R^2	Correlation coefficient
T	Reaction temperature (K)
T_c	Critical temperature
t	Reaction time (secs)/(min)
V	Volume (dm^3)
x_{exp}	Experimental data
x_{sim}	Simulation data
Σ	Summation
α	CCD rotatable value
ρ	Density

**TINDAKBALAS LAMPAUGENTING METANOL (SCM) DAN
LAMPAUPANAS WAP METANOL (SMV) TANPA MANGKIN UNTUK
SINTESIS ASID LEMAK METIL ESTER (FAME) DARI MINYAK
JATROPHA DAN LAUT MANGGA**

ABSTRAK

Projek penyelidikan ini dijalankan untuk menyiasat potensi tindakbalas transesterifikasi daripada minyak jatropha dan minyak laut mangga dalam satu langkah tanpa menggunakan mangkin untuk pengeluaran biodiesel atau asid lemak metil ester (FAME). Pada permulaannya, tindakbalas lampaugenting metanol (SCM) tanpa mangkin telah dijalankan dengan menggunakan minyak laut mangga sebagai sumber trigliserida (TG). Analisis statistik kaedah rekabentuk eksperimen (DOE) telah digunakan untuk menyelidik pengaruh masa tindakbalas, suhu tindakbalas dan nisbah molar metanol berbanding minyak dalam lingkungan 10 – 50 min, 320 – 400 °C dan 20 – 60 mol/mol masing-masing. Keadaan optimum telah didapati pada 380 °C, 40 min dan 45:1 mol/mol nisbah methanol berbanding minyak dengan menghasilkan biodiesel yang berkandungan 78 % w/w. Selepas itu, pembangunan matematik model berdasarkan mekanisme tindakbalas SCM telah dijalankan. Model pertama yang menggabungkan kedua-dua tindakbalas ulang alik transesterifikasi dan esterifikasi telah disahkan dengan menggunakan penyelesaian persamaan pembezaan biasa (ODE45). Tenaga pengaktifan yang tertinggi pada 40 kJ/mol dan pemalar kadar tindakbalas yang terendah $2.50 \times 10^{-5} \text{ dm}^3/\text{mol s}$ telah mengesahkan bahawa tindakbalas pertama TG untuk menghasilkan diglyserida (DG) merupakan langkah yang mengehendkan kadar keseluruhan tindakbalas SCM. Selain itu, teknologi baru iaitu tindakbalas lampaupanas wap methanol (SMV) tanpa mangkin

telah dibangun untuk transesterifikasi dan esterifikasi sumber minyak. Dalam perkembangan awal, minyak *jatropha curcas* telah digunakan sebagai sumber TG dalam tindakbalas SMV. Pengaruh masa tindakbalas, suhu tindakbalas, kadar aliran metanol dan jisim minyak pada permulaan tindakbalas terhadap kandungan FAME dan kadar pengeluaran FAME telah diselidik dalam lingkungan 0 – 240 min, 260 – 300 °C, 1 – 3 mL/min dan 40.0 – 70.0 g, masing-masing. Keputusan yang diperolehi menunjukkan bahawa penghasilan biodiesel tertinggi iaitu 71.54 % w/w dicapai pada suhu tindakbalas pada 290 °C, kadar aliran metanol pada 2 mL/min bagi jisim minyak permulaan pada 40.0 g dengan 88.81 % w/w FAME kandungan, menunjukkan teknologi SMV berpotensi tinggi dalam menghasilkan FAME. Di samping itu, keputusan telah menunjukkan bahawa kadar pengeluaran FAME yang tinggi boleh diperolehi apabila jisim minyak permulaan ditambahkan. Oleh itu, jisim minyak permulaan telah ditetapkan pada jumlah isipadu yang lebih tinggi iaitu 100 mL dan sistem eksperimen telah diubahsuai dengan menggantikan preheater kepada relau pijar yang bersuhu tinggi dan memperkenalkan halangan ke dalam ruang tindakbalas. Minyak laut mangga telah digunakan sebagai sumber TG selepas pengubahsuaian telah dijalankan. Daripada keputusan, halangan yang merujuk kepada silinder cap dengan dua plat berlubang telah berjaya meningkatkan pengeluaran FAME (g). Kesan kadar aliran metanol dan suhu tindakbalas antara julat 1 – 4 mL/min dan 260 – 290 °C, masing-masing terhadap hasil FAME, pengeluaran FAME (g) dan kadar pengeluaran FAME (g/min) telah dikaji dengan isipadu minyak yang tetap iaitu 100 mL. Hasil kajian telah menunjukkan bahawa kadar aliran metanol lebih tinggi dan suhu tindakbalas dapat meningkatkan pengeluaran FAME. Selepas itu, matematik model sistem SMV yang menggabungkan kedua-dua tindakbalas ulang alik transesterifikasi dan esterifikasi

telah dibangun dan disahkan dengan menggunakan penyelesaian ODE45. Tenaga pengaktifan tertinggi pada 50 kJ/mol dan pemalar kadar tindakbalas yang rendah pada $1.62 \times 10^{-4} \text{ dm}^3/\text{mol min}$ menyokongkan bahawa tindakbalas TG menghasilkan DG merupakan langkah yang mengehadkan kadar tindakbalas dalam sistem SMV. Kesimpulannya, tindak balas SMV telah menunjukkan potensi yang besar dalam pengeluaran biodiesel dengan menggunakan bahan mentah yang berkandungan FFA yang tinggi .

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ABSTRACT

This research project was carried out to investigate the potential of one-step non-catalytic transesterification reaction of *jatropha curcas* and sea mango oils for biodiesel or fatty acid methyl esters (FAME) production. Initially, non-catalytic supercritical methanol (SCM) was carried out by utilizing sea mango oil as triglycerides (TG) feedstock. Statistical analysis method of design of experiment (DOE) was employed to investigate the effect of reaction time, reaction temperature and molar ratio of methanol to oil in the range of 10 – 50 min, 320 – 400 °C and 20 – 60 mol/mol, respectively. The optimum conditions were found to be 380 °C, 40 min and 45:1 mol/mol of methanol to oil, resulting in 78 % w/w biodiesel content. Subsequently, development of mathematical model based on SCM reaction mechanism was conducted. This maiden model of FAME production incorporating both reversible transesterification and esterification was verified using an ordinary differential equation (ODE45) solver. The highest activation energy of 40 kJ/mol and the lowest reaction rate constant of $2.50 \times 10^{-5} \text{ dm}^3/\text{mol s}$ confirmed that the first stepwise reaction of TG to produce diglycerides (DG) was the rate-limiting step in SCM system. Apart from that, new technology which is non-catalytic superheated methanol vapour (SMV) was developed for transesterification and esterification of oil feedstock. In the initial development, *jatropha curcas* oil was utilized as TG feedstock in the SMV system. The effects of reaction time, reaction temperature,

methanol flow rate and initial oil mass on the FAME production rate and FAME content were studied at the range of 0 – 240 min, 260 – 300 °C, 1 – 3 mL/min and 40.0 – 70.0 g, respectively. Results obtained showed that the highest biodiesel yield at 71.54 % w/w was achieved at reaction temperature of 290 °C, methanol flow rate at 2 mL/min for the initial oil mass at 40.0 g with 88.81 % w/w FAME content, implying the huge potential of SMV technology in producing FAME. In addition, it was observed that higher FAME production rate can be obtained when the initial oil mass is increased. Therefore, initial oil mass was fixed at higher volume which was 100 mL and experimental system was modified by replacing the preheater to a high temperature crucible furnace and introducing obstacle into the reaction chamber. Sea mango oil was utilized after modification had been carried out. From the results, obstacle which refers to cylinder cap with two perforated plates had successfully increased the FAME production (g). The effects of methanol flow rate and reaction temperature between the range of 1 – 4 mL/min and 260 – 290 °C, respectively on FAME yield (%), FAME production (g) and FAME production rate (g/min) was studied accordingly at a constant oil volume of 100 mL. Results showed that higher methanol flow rate and reaction temperature can increase the FAME yield and production. Subsequently, mathematical modelling of semi-batch SMV system, incorporating both reversible transesterification and esterification was developed and verified by using ODE45 solver. The highest activation energy of 50 kJ/mol and the low reaction rate constant of $1.62 \times 10^{-4} \text{ dm}^3/\text{mol min}$ corroborated that the reaction of TG to become DG as the rate limiting step in SMV system. As a conclusion, SMV reaction is showing its great potential in biodiesel production by using feedstock with high content of FFA.