



Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in: <http://oatao.univ-toulouse.fr/>
Eprints ID: 6130

To link to this article: DOI:10.2202/1542-6580.2758
URL: <http://dx.doi.org/10.2202/1542-6580.2758>

To cite this version: Sawangkeaw, Ruengwit and Witsanee, Satayanon and Kunchana, Bunyakiat and Somkiat, Ngamprasertsith and Camy, Séverine and Condoret, Jean-Stéphane (2011) Continuous Production of Biodiesel with Supercritical Methanol: a Simple Compressible Flow Model for Tubular Reactors. *Walter de Gruyter*, vol. 9 (n°1). pp. A96. ISSN 1542-6580

Any correspondence concerning this service should be sent to the repository administrator: staff-oatao@listes.diff.inp-toulouse.fr

Continuous Production of Biodiesel with Supercritical Methanol: a Simple Compressible Flow Model for Tubular Reactors

Ruengwit Sawangkeaw*

Séverine Camy**

Witsanee Satayanon[†]

Jean-Stéphane Condoret^{††}

Kunchana Bunyakiat[‡]

Somkiat Ngamprasertsith^{‡‡}

*Chulalongkorn University, r_sawangkeaw@yahoo.com

[†]Chulalongkorn University, ja_witsanee@hotmail.com

[‡]Chulalongkorn University, kunchana.b@chula.ac.th

**University of Toulouse, severine.camy@ensiacet.fr

^{††}University of Toulouse, jeanstephane.condoret@ensiacet.fr

^{‡‡}Chulalongkorn University, somkiat.n@chula.ac.th

Continuous Production of Biodiesel with Supercritical Methanol: a Simple Compressible Flow Model for Tubular Reactors*

Ruengwit Sawangkeaw, Witsanee Satayanon, Kunchana Bunyakiat, Séverine Camy, Jean-Stéphane Condoret, and Somkiat Ngamprasertsith

Abstract

From an industrial point of view, the continuous process for biodiesel production with supercritical methanol (SCM) is more appropriate than the batch process. However, lab-scale studies on the continuous process have shown that the maximum conversion always remains slightly lower than that obtained in the batch process. This work proposes a simple compressible flow model to predict the conversion of methanol and oils into methyl esters (ME) along the length of a tubular reactor and further demonstrates the effect of the development of the compressibility factor of the reaction mixture upon the conversion efficiency to ME. The governing equation was derived from a general molar balance in the tubular reactor using transesterification kinetics of refined-bleached-deodorized (RBD) palm oil in SCM coupled with a suitable thermodynamic model with adjusted binary interaction parameters. Vapor-liquid equilibrium data for triolein + methanol, methyl oleate + methanol and glycerol + methanol mixtures were

*Ruengwit Sawangkeaw, Chulalongkorn University. Witsanee Satayanon, Chulalongkorn University. Kunchana Bunyakiat, Chulalongkorn University. Séverine Camy, University of Toulouse, Institut National Polytechnique de Toulouse, France. Jean-Stéphane Condoret, University of Toulouse, Institut National Polytechnique de Toulouse, France. Somkiat Ngamprasertsith, Fuels Research Center, Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok, 10330, Thailand and Center for Petroleum, Petrochemicals and Advanced Materials, Chulalongkorn University, Bangkok, 10330, Thailand. Please send correspondence to Somkiat Ngamprasertsith, somkiat.n@chula.ac.th. We express our sincere appreciation to Chulalongkorn University Dutsadi Phiphat Scholarship, the Center for Petroleum, Petrochemicals and Advanced Materials and the Thai Government Stimulus Package 2 (TKK2555), under the Project for Establishment of Comprehensive Center for Innovative Food, Health Products and Agriculture, for financial support. The authors also wish to express their thankfulness to Dr. Robert Douglas John Butcher (Publication Counseling Unit, Faculty of Science, Chulalongkorn University) for English language editing.

obtained from the literature and then refitted with the thermodynamic model consisting of the Peng-Robinson equation of state and MHV2 mixing rules to find the set of adequate interaction parameters. In order to check the validity of the proposed model, the predicted ME contents were compared with observed values in a lab-scale continuous reactor at various operating temperatures, pressures and methanol to oil molar ratios. The proposed model proved to be adequate for predicting the final conversion to ME for operating temperatures below 320°C, when the thermal degradation reactions of unsaturated fatty acids did not interfere. Our results also illustrate the importance of taking into account the development of the compressibility factor with time and reactor length, since this was shown to be the cause of the lower transesterification reaction rate in the tubular SCM process. The findings in this work could be employed as a knowledgebase to further develop a better model for continuous production of biodiesel with SCM in a tubular reactor.

KEYWORDS: vegetable oil, biodiesel, transesterification, supercritical methanol, fluid phase equilibria, modeling

1. Introduction

Biodiesel production with supercritical methanol (SCM) has several strong advantages over the conventional catalytic process, as summarized elsewhere (Pinnarat and Savage 2008; Juan et al. 2010; Lee and Saka 2010; Sawangkeaw et al. 2010). Although biodiesel production with SCM achieves a maximum conversion at a relatively high temperature and pressure, it does not require any catalyst and does not generate a significant volume of contaminated wastewater or other wastes. Since a high temperature and pressure are employed, a continuous process is more appropriate than a batch process for an industrial approach. Indeed, the continuous process eliminates heating and cooling intervals and allows an easy heat recovery from the hot product effluent through a heat exchanger. In addition, the continuous production of biodiesel with SCM has been shown to be able to be successfully evaluated in lab-scale reactors (Bunyakiat et al. 2006; Minami and Saka 2006; He et al. 2007). However, the maximum conversion obtained in the continuous process was always slightly lower than that of the batch process (Saka and Kusdiana 2001; Sawangkeaw et al. 2007; Song et al. 2008) and this could be investigated with the assisting of an adequate modeling of reactors.

In general, the modeling of supercritical water oxidation and supercritical CO₂ extraction assume that the mixture properties are constant throughout the supercritical medium because they contain only traces of reactant or solute. Thus, such an assumption could be probably still valid for biodiesel production with SCM when the reaction takes place at a methanol to oil molar ratio of over 42:1. Unfortunately, biodiesel production with SCM at a high methanol to oil molar ratio not only requires a massive energy consumption to recycle the methanol, but also employs a large volume of methanol in the recycle loop. Furthermore, in a LCA study (Kiwjaroun et al. 2009), this enormous usage of energy was shown to significantly increase the environmental load, such that it upsets the strong environmental advantage of biodiesel production with SCM. Therefore, for truly green biodiesel production with SCM additional studies are required to decrease the methanol to oil molar ratio as well as to propose a new model without using the assumption of constant fluid properties. The example of assisting techniques to reduce methanol to oil molar ratio such as adding of co-solvents and catalysts were described elsewhere (Yin et al. 2008a; Yin et al. 2008b; Yin et al. 2010). Note that the use of an appropriate thermodynamic model is also crucial to develop such an approach.

In this study, we propose a simple compressible flow model, which takes into account the development of the compressibility factor along the reaction column of the reaction mixture as a second order differential kinetic model, to predict the conversion of the SCM transesterification reaction in continuous

tubular reactor. Note that the effects of compressibility factor changing along the reactor tube are never mentioned in any previous report. A specific adapted thermodynamic model is also proposed from conventional models where specific parameters have been identified from existing high pressure experimental data.

It should be noticed that this model cannot be used in general for all continuous production, but the calculation procedure could be applicable to other continuous reacting processes that involve compressible fluids under high pressure. To apply into the other continuous processes, a compressible flow model has to be modified, i.e. both thermodynamic and chemical kinetics models, in order to be suitable and compatible for the new system. The binary interaction coefficients have to be calculated from either literature or experimental liquid-vapour equilibrium data. For example, the direct carbonation of methanol in supercritical carbon dioxide requires thermodynamic model for CO_2 + methanol + dimethyl carbonate + water and its specific chemical kinetics model. In addition, the binary interaction coefficients for each VLE should be measured in the same experimental apparatus to obtain the best thermodynamic model.

2. Experiment

2.1. Materials

Commercial grade methanol, obtained from I.C.P. Chemicals Co., Ltd., and palm olein oil (with a major fatty acid composition of palmitic 37%, oleic 46% and linoleic 11% acids) from Morakot Industries Co., Ltd., were used with no further purification. The analytical grade methyl heptadecanoate (99.5%) and *n*-heptane (99.5%), which were used in the measurement of the ME content in the biodiesel, were supplied by Fluka and Fisher, respectively.

2.2. Experimental set-up and procedure

The tubular reactor used in this work is presented in Figure 1. A coiled tubular reactor made from stainless steel (SUS316 tubing of 3.18×10^{-3} m-o.d., 7.11×10^{-4} m-thickness and 80 m-length) was employed. A molten salt bath was heated to the desired reacting temperature. The temperature of molten salt bath was controlled by a PID controller (Sigma Model SF48). After temperature stabilization of the bath, palm olein oil and methanol, separately preheated in a molten salt bath in tubular preheaters made from stainless steel (as above except shorter at 6 m in length), were pumped into the reactor by two high-pressure pumps (Thar technology Co. Ltd., model P200 and P50). The methanol to oil molar ratio were adjusted by mass flow rate of palm olein oil and methanol pump, whilst the residence time was calculated from total flow rate of the reactants. K-type

thermocouples (Chromel-Almel) were supplied by a local contributor (VSC advance Co., Ltd). The thermocouples were set at the reactor inlet, outlet and molten salt bath. After the outlet flow was steady, the back-pressure regulator (Swagelok Co. Ltd., model Z85943001) was closed to increase the pressure of the system. The pressure at high-pressure pumps and back-pressure inlet were monitored by three pressure gauges (Swagelok Co. Ltd., model EN 837-1). In addition, 0.5 μm the inline filter (Swagelok Co. Ltd., model SS-2F-0.5) was attached at the back-pressure inlet to prevent the damage from solid particle. The relief valve (Swagelok Co. Ltd., model SS-4R3A) was installed at the heat exchanger outlet. Once the system pressure was constant, which took approximately 3 hours for the system to reach a steady state, the biodiesel products were sampled in triplicate at 15 min intervals and analyzed for the ME content following the EN14214 standard method.

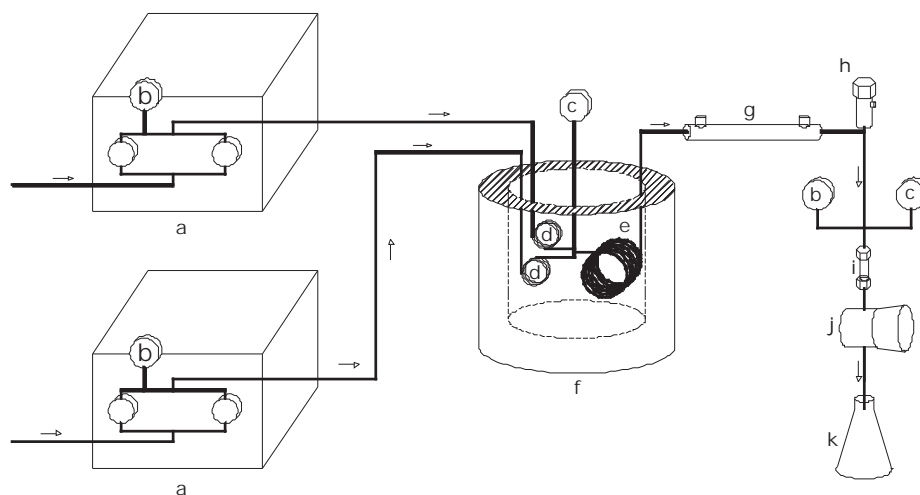


Figure 1. Schematic diagram of lab-scale tubular reactor showing the (a) high pressure pump, (b) pressure gauge, (c) thermocouple, (d) preheater, (e) reactor, (f) molten salt bath, (g) double pipe heat exchanger, (h) relief valve, (i) back-pressure regulator (j), inline filter and (k) sampling flask

3. Description of the model

3.1. Thermodynamic model

A thermodynamic model was used to evaluate the changes in the compressibility factor of the reaction mixture, and was established as being suitable as long as the reaction proceeds in the tubular reactor (Glišić et al. 2009; Glišić and Skala 2009).

However, experimental fluid properties and / or experimental vapor-liquid equilibrium (VLE) data of binary sub-systems are required to find the most suitable thermodynamic model in order to predict such properties and fluid physical state for the reaction system. In actuality, the reaction system is composed of various types of triglyceride, e.g., tripalmitin, triolein, palmito-diolein and palmito-linoleo-olein etc., five to eight types of fatty acid methyl esters (FAMES), and reaction intermediates, such as mono- and diglycerides. To simplify the calculation, we assumed that the reaction system consists of methanol, triolein, methyl oleate and glycerol, with the triolein and methyl oleate representing the palm olein oil and biodiesel (mixture of FAMES), respectively, in accordance with the major fatty acid composition of palm olein oil as mentioned in Section 2.1. Therefore, we employed the existing VLE measurements of triolein + methanol, methyl oleate + methanol and glycerol + methanol binary systems from the literature. This simplification was chosen because of the availability of experimental data in the literature for these binary systems, but not more complex ones.

It is important to note here that the high pressure / high temperature VLE or density experimental data for the triolein / methanol mixture are quite difficult to obtain because of the high reactivity of the mixture under these high operating pressures and temperatures. To find the best model to predict the thermodynamic behavior of the quaternary mixture, we intended to test the classical Peng-Robinson equation of state (PR) (Peng and Robinson 1976) with the mixing rules developed by Huron and Vidal (Huron and Vidal 1979) and modified by Michelsen (Søren and Michael 1990) (MHV2 mixing rules). This approach allows the cubic equation of state PR, suitable for high pressure but poor for mixtures containing polar compounds, to be applied for high-pressure calculations of mixtures involving polar compounds. As the MHV2 mixing rules are based on the calculation of the excess Gibbs energy at zero pressure, this also requires a suitable activity coefficient model, in addition to the equation of state. Here we decided to use the UNIQUAC (Anderson and Prausnitz 1978) activity coefficient model, because the coupling of this model to a cubic EOS via the MHV2 mixing rules has already been shown to be a good model for predicting the high-pressure fluid phase equilibria of mixtures containing polar compounds (Camy et al. 2003), as it is the case here. Moreover, this model is available in Simulis® Thermodynamics (ProSim, France), commercial software for the calculation of fluid phase equilibria and fluid properties.

3.2. Compressible flow model

The general mole balance in a tubular reactor (Foglar 1999) and the transesterification kinetics of refined-bleached-de-odorized (RBD) palm oil in SCM (Song et al. 2008) are illustrated in equation (1) and (2) respectively.

$$\frac{dX_A}{dV} = \frac{-r_A}{F_{A0}} \quad (1)$$

$$-r_A = kC_A^{0.95}C_B^{1.05} \quad (2)$$

where; X is conversion rate, V is reactor volume (m^3), F_{A0} is molar flow rate of triolein at reactor inlet (mole/s), k is rate constant ($\text{mole}/\text{m}^3\cdot\text{s}$), C_A and C_B are triolein and methanol concentration (mole/m^3), respectively.

The chemical kinetics of RBD palm oil was obtained from the literature [7], from investigation in a 4.7-mL batch reactor at 30.0 MPa within the temperature range of 473 – 673 K, a methanol to oil molar ratio range of 3:1 – 80:1, and a reaction time range of 0.5 – 30 min. The rate constant (k) and reaction order were found by an integral method or numerical fitting of the experimental data to the kinetic model, resulting in a high coefficient of determination (R^2) value, at 0.9578, even though it does not include the thermal degradation reaction. The rate constant was defined as a function of temperature as shown in equation (3).

$$k = 4.34 \times 10^5 \times \exp\left(-\frac{1.05 \times 10^5}{RT}\right) \quad (3)$$

where; R is the universal gas constant ($\text{J}/\text{mol K}$) and T is temperature (K)

In a continuous isothermal reactor, the concentration (C) and volumetric flow rate of the mixture corresponding to the inlet conditions can be written as equations (4) and (5) respectively.

$$C = \frac{F}{v_m} \quad (4)$$

$$v_m = v_{m0} \left(\frac{z_m}{z_{m0}} \right) \frac{P_0}{P} \quad (5)$$

where; F is molar flow rate (mole/s), v_m and z_m are volumetric flow rate (m^3/s) and compressibility factor of mixture, respectively. v_{m0} and z_{m0} are volumetric flow rate (m^3/s) and compressibility of mixture at reactor inlet, respectively.

From the experimental observations, values of pressure were found to be only slightly different between the high-pressure pump and the reactor outlet. Therefore, the zero pressure drop assumption was applied and P kept equal to P_0 . Finally, all equations were combined and rearranged to model the conversion change along the tubular reactor, as shown in equation (6).

$$\frac{dX_A}{dL} = \frac{kAF_{A0}}{v_{m0}^2} (1 - X_A)^{0.95} \left(\frac{F_B}{F_{A0}} - 3X_A \right)^{1.05} \left(\frac{z_{m0}}{z_m} \right)^2 \quad (6)$$

where; L is the reactor length (m) and A is the cross-sectional area.

This governing equation was numerically solved for conversion prediction as function of reactor length employing the Runge-Kutta 4th order method using the Matlab® software coupled with the Simulis® Thermodynamic toolbox, to evaluate the compressibility factor and the physical state of the mixture as the reaction proceeds inside the tube. The compressibility factor of the quaternary mixture was estimated by the thermodynamic model described in Section 3.1 with adjusted binary interaction parameters.

Finally, the calculated mole fraction of methyl oleate, which represents the ME content in the biodiesel product, was estimated from the final conversion and compared with the experimental results.

Additionally, assuming a constant compressibility factor leads to equation (6) being reduced to equation (7). The computation was done to estimate the magnitude of the effect of compressibility factor evolution upon ME content and solved by the Runge-Kutta 4th order method using the Matlab® software. The molar volume of the mixture at the inlet of the reactor (v_{m0}) was determined by the PR-MHV2-UNIQUAC thermodynamic model.

$$\frac{dX_A}{dL} = \frac{kAF_{A0}}{v_{m0}^2} (1 - X_A)^{0.95} \left(\frac{F_B}{F_{A0}} - 3X_A \right)^{1.05} \quad (7)$$

4. Results and discussion

4.1. Fitting of the thermodynamic model and binary interaction parameters

The VLE studies of binary systems from the literature (Glišić et al. 2007; Fang et al. 2008; Shimoyama et al. 2009) were fitted by the PR-MHV2-UNIQUAC thermodynamic model, in order to obtain a set of binary interaction parameters for

UNIQUAC as a function of temperature. This fitting was carried out using the least square method with a Simulis® Thermodynamics add-in, inserted in MS-Excel worksheet. The critical properties of triolein, methyl oleate and glycerol were estimated by the Constantinou–Gani group-contribution method (Constantinou and Gani 1994; Constantinou et al. 1995). The obtained interaction coefficients as a function of temperature are given in Table 1.

Table 1. Calculated binary interaction coefficients for the UNIQUAC model.

Binary mixture	Type of data	A_{12} (K)	A_{21} (K)
Triolein + methanol	Isothermal VLE 473 to 503K	$11559.00 - 23.43T$	$-8072.30 + 16.85T$
Methyl oleate + methanol	Isothermal VLE 523 to 573 K	$1698.00 - 3.60T$	$-5713.30 + 12.06T$
Glycerol + methanol	Isothermal VLE 493 to 573 K	$1850.00 - 4.02T$	$-4801.17 + 10.48T$

The VLE experimental data for triolein + methanol, methyl oleate + methanol and glycerol + methanol, and the results from PR-MHV2-UNIQUAC model are shown in Tables 2 – 4 and Figures 2 – 4. The relative error of methanol mole fraction in liquid (x) and vapor (y) phase was calculated from equation (8). Thus, the minus and plus sign illustrated the under and overestimated values respectively.

$$\% \text{Relative Error} = \frac{(\text{Calculated value} - \text{Experimental value})}{\text{Experimental value}} \times 100 \quad (8)$$

Table 2. Methanol mole fraction in the liquid (x) and vapor (y) phase of the triolein + methanol VLE (Glišić et al. 2007).

T (K)	P (MPa)	Experimental result		Calculated result		%Relative Error of x	%Relative Error of y
		x	Y	X	y		
473	3.97	0.9744	0.9997	0.9800	1.0000	0.575	0.030
473	3.67	0.9413	0.9998	0.9543	1.0000	1.383	0.020
473	3.41	0.9087	0.9996	0.9269	1.0000	2.004	0.040
473	2.92	0.8540	0.9996	0.8750	1.0000	2.461	0.040
483	4.53	0.9655	0.9999	0.9800	1.0000	1.502	0.010
483	4.25	0.9557	0.9999	0.9665	1.0000	1.125	0.009
483	3.99	0.9292	1.0000	0.9337	1.0000	0.487	0.000
483	3.11	0.8642	0.9998	0.8166	1.0000	-5.504	0.020
493	4.86	0.9755	0.9997	0.9773	1.0000	0.187	0.029
493	4.80	0.9729	0.9997	0.9756	1.0000	0.276	0.028
493	4.35	0.9569	0.9999	0.9566	1.0000	-0.027	0.008
493	4.04	0.9170	0.9999	0.9287	1.0000	1.271	0.009

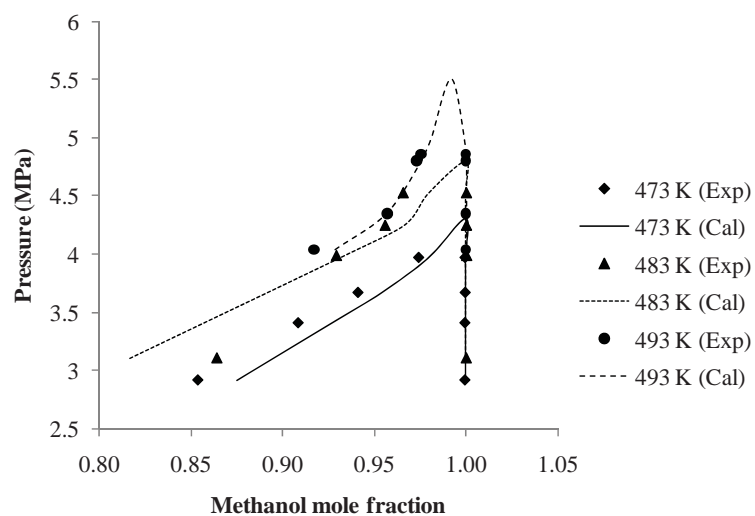


Figure 2. Experimental (Exp) and calculated (Cal) P-x-y diagram of triolein + methanol VLE. The experimental data were measured twice at each point and they have the average deviations of 3.09 % and 0.15 % for liquid and vapor phase measurement, respectively (Glišić et al. 2007).

Table 3. The methanol mole fraction in the liquid (x) and vapor (y) phase of the methyl oleate + methanol VLE (Fang et al. 2008).

T (K)	P (MPa)	Experimental result		Calculated result		%Relative Error of x	%Relative Error of y
		X	y	X	y		
523	2.45	0.4650	1.0000	0.4521	0.9951	-2.780	-0.489
523	5.35	0.7310	0.9999	0.7326	0.9958	0.219	-0.316
523	6.46	0.8140	1.0000	0.8106	0.9954	-0.415	-0.463
523	7.02	0.8630	1.0000	0.8465	0.9949	-1.906	-0.510
523	7.80	0.9160	1.0000	0.8949	0.9937	-2.300	-0.633
548	4.59	0.5750	1.0000	0.5716	0.9930	-0.597	-0.697
548	6.10	0.6930	1.0000	0.6750	0.9936	-2.593	-0.643
548	7.90	0.7900	1.0000	0.7724	0.9935	-2.233	-0.647
548	8.80	0.8380	0.9930	0.8125	0.9933	-3.043	0.029
548	9.48	0.8610	0.9910	0.8394	0.9930	-2.508	0.205
573	6.03	0.6070	1.0000	0.6204	0.9889	2.209	-1.106
573	7.01	0.6990	1.0000	0.6764	0.9901	-3.238	-0.993
573	8.39	0.7510	0.9960	0.7440	0.9916	-0.936	-0.440
573	10.25	0.8330	0.9880	0.8172	0.9942	-1.896	0.623
573	11.45	0.8600	0.9860	0.8532	0.9959	-0.795	1.001

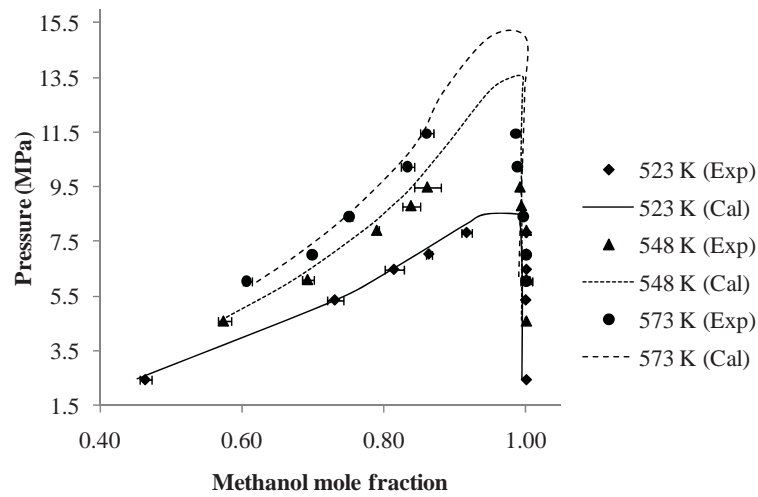


Figure 3. Experimental (Exp) and calculated (Cal) P-x-y diagram of methyl oleate + methanol VLE. The experimental data were measured four times at each point and the average deviations were shown in figure as error bars (Fang et al. 2008).

Table 4. The methanol mole fraction in the liquid (x) and vapor (y) phase of the glycerol + methanol VLE (Shimoyama et al. 2009).

T (K)	P (MPa)	Experimental result		Calculated result		%Relative Error of x	%Relative Error of y
		X	Y	X	y		
493	3.03	0.4780	1.0000	0.4898	0.9924	2.464	-0.757
493	3.41	0.5500	1.0000	0.5577	0.9927	1.392	-0.729
493	3.86	0.6450	1.0000	0.6503	0.9930	0.825	-0.703
493	4.23	0.7010	1.0000	0.7418	0.9932	5.821	-0.676
493	4.67	0.8500	1.0000	0.8523	0.9939	0.276	-0.607
493	5.12	0.9650	1.0000	0.9299	0.9955	-3.642	-0.452
523	4.64	0.4840	1.0000	0.4681	0.9816	-3.287	-1.836
523	5.21	0.5650	1.0000	0.5248	0.9812	-7.119	-1.882
523	6.08	0.6890	1.0000	0.6217	0.9795	-9.766	-2.051
523	6.79	0.8070	1.0000	0.7269	0.9769	-9.925	-2.312
523	7.16	0.8680	1.0000	0.8055	0.9749	-7.197	-2.510
543	5.41	0.4310	1.0000	0.4506	0.9708	4.546	-2.921
543	6.18	0.5090	1.0000	0.5084	0.9698	-0.117	-3.024
543	6.99	0.5920	1.0000	0.5709	0.9674	-3.562	-3.259
543	7.91	0.6970	1.0000	0.6479	0.9623	-7.043	-3.770
543	8.61	0.7800	0.9900	0.7175	0.9546	-8.008	-3.576

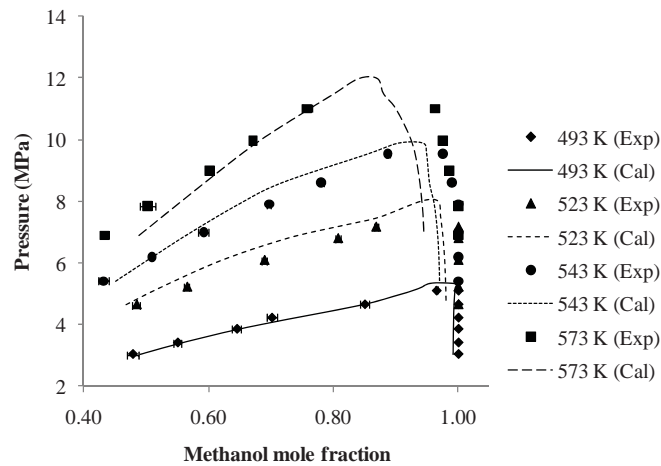


Figure 4. Experimental (Exp) and calculated (Cal) P-x-y diagram of glycerol + methanol VLE. The experimental data were measured four to six times at each point and the average deviations were shown in figure as error bars (Shimoyama et al. 2009).

The PR-MHV2-UNIQUAC model had maximum relative error of 5% for the triolein + methanol and 3% for methyl oleate + methanol, whereas it had maximum relative error of 10% for the glycerol + methanol system that was higher than the relative error of the specific models in the literature due to the different polarity of those mixtures, especially for triolein + methanol and glycerol + methanol. The polarity of the compounds can be ranked by their dielectric constants, being 41.14, 32.60, 3.12 and 3.11 for glycerol, methanol, methyl oleate and triolein, respectively (Perry and Green 1999). Thus, the attractive and repulsive forces within the glycerol + methanol system were somewhat higher than both the triolein + methanol and methyl oleate + methanol systems, and affected the thermodynamic model for VLE prediction. For example, the Peng–Robinson (PR) and the van der Waals (VdW) mixing rule models were tested on the triolein + methanol system and give an approximately 2% relative error (Tang et al. 2006), whereas the Peng–Robinson Stryjek–Vera (PR-SV) Equation of State and ASOG mixing rule (PRASOG model) give an approximately 3% relative error for the glycerol + methanol VLE system (Shimoyama et al. 2009).

4.2. ME content prediction by the compressible flow model

The compressible flow model was tested in various reaction conditions, as shown in Table 5, and the observed values were then plotted against the calculated values (Figure 5). Note that the biodiesel yield, as refer to the ratio between fed palm oil and resultant biodiesel, was observed over 98% in all experiments. Furthermore, the %relative error and residence time for each condition in Table 4 can be calculated by equations (8) and (9), respectively.

$$\tau = \frac{V}{F_0 v} \quad (9)$$

where; τ is residence time (s), F_0 is molar flow rate at the reactor inlet and v is average molar volume of mixture (m^3/mole).

According to Figure 5, the model was good for estimating the %ME content within the temperature range of 553 – 593 K, but overestimated it at 593 – 623 K. Indeed, the %relative error of the calculated values from equation (6) increased with increasing reaction temperatures (Figure 6) which indicated the compressible flow model did not include the negative effects of temperature into the model, especially at high temperature. Whereas, no clear pattern between the %relative error and either the methanol to oil molar ratio (Figure 7) or the operational pressure (Figure 8) was observed that noticed difference between calculated and predicted values were random error. However, the non-zero mean

of %relative error in Figures 7 and 8 was observed due to strong overestimated effect of temperature on %ME content.

Table 5. The observed and calculated %ME content from various reaction conditions.

No.	T (K)	P (MPa)	MeOH: Oil molar ratio	Residence time (min)	ME content (%)			%Relative error	
					Experimented value	Calculated value (6)*	Calculated value (7)**	Calculated value (6)*	Calculated value (7)**
1	551	35	12.0	47.43	35.75±1.2	35.18	41.70	-1.6	16.6
2	553	20	14.4	42.78	37.25±1.0	35.81	41.95	-3.9	12.6
3	553	35	41.4	26.59	27.09±0.5	29.17	31.13	7.7	14.9
4	555	20	38.9	27.29	31.95±1.1	30.82	33.16	-3.5	3.8
5	558	35	21.0	36.90	42.01±1.4	39.65	45.32	-5.6	7.9
6	573	20	27.8	33.41	68.50±2.4	68.60	81.03	0.2	18.3
7	573	35	36.7	34.30	65.67±2.1	69.53	81.56	5.9	24.2
8	573	35	39.6	31.48	69.82±1.6	78.42	87.05	12.3	24.7
9	593	20	23.7	33.93	80.55±2.7	83.88	97.19	4.1	20.7
10	593	20	23.7	37.96	76.38±0.5	82.71	94.20	8.3	23.3
11	593	35	37.3	27.10	57.68±1.4	69.40	80.86	20.3	40.2
12	593	35	22.8	42.24	65.78±3.0	79.20	90.10	20.4	36.9
13	593	35	38.7	25.61	72.42±2.0	76.59	86.60	5.8	19.6
14	623	20	24.8	57.00	73.15±1.4	88.63	98.41	21.2	34.5
15	623	20	16.9	81.04	74.24±1.7	87.76	97.87	18.2	31.8
16	623	20	27.8	26.04	63.26±2.5	84.70	95.69	33.9	51.3
17	623	35	17.1	79.91	69.35±0.5	89.95	99.14	29.7	42.9
18	623	35	35.2	53.53	69.94±2.3	90.07	99.18	28.8	41.8
19	623	35	27.8	26.84	66.41±2.3	86.86	96.72	30.8	45.6
20	623	35	35.9	38.86	69.19±1.3	90.05	99.22	30.2	43.4
21	625	20	17.1	75.63	77.30±0.8	90.42	99.54	17.0	28.8
22	625	35	43.4	35.49	78.00±2.2	87.39	97.01	12.0	24.4

As calculated by * equation (6) or ** equation (7) (see the text).

Within the temperature range of 593 – 623 K, the calculated %ME values were higher than experimented values because the observed %ME was presumed to be reduced by the thermal degradation reaction. Indeed, RBD palm olein oil consists of approximately 46% oleic acid and 11% linoleic acid, respectively. It has been reported that thermal degradation of unsaturated fatty acids occurs at the same temperature range and residence time of 593 – 623 K over 30 min. Note that

the influence of reaction pressure on thermal cracking of unsaturated fatty acids is insignificant above 20 MPa (Marulanda et al. 2010).”

For example, methyl oleate and methyl linoleate decompose by approximately 10% and 20% by weight, respectively, in SCM at 623 K after 30 min contact time (Imahara et al. 2008). Therefore, by extrapolation to this system, 4.6% and 2.2% of methyl oleate and linoleate, respectively, were degradable and so the observed ME content was reduced by 6.8% at 623 K for over 30 min residence time which agree with recently reported results (Quesada-Medina and Olivares-Carrillo 2011).

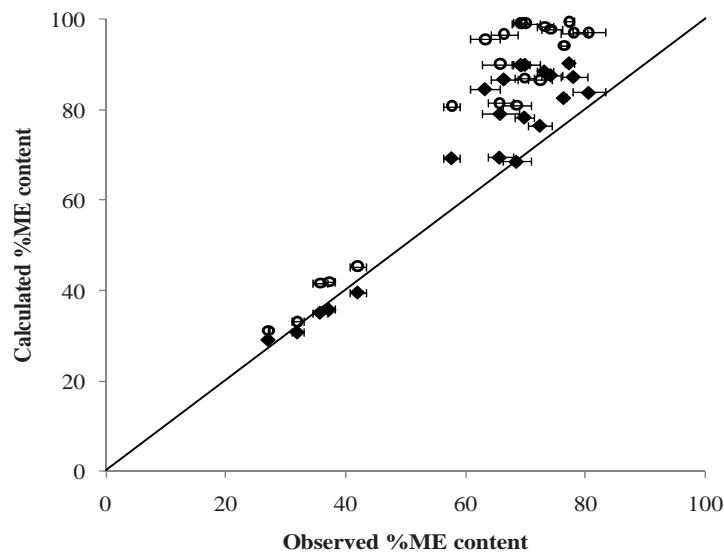


Figure 5. The plot of observed versus the calculated %ME content, as derived by Eq. 6 (♦) or Eq. 7 (○)

According to regression analysis of data in Table 5, the regression model is shown in Eq. 10 with the coefficient of determination (R^2) of 0.9014.

$$\%MEcontent = 72.12 - 5.54A - 0.90B - 3.23C - 22.55A^2 + 28.85A^3 \quad (10)$$

where; A, B and C are temperature, pressure and methanol to oil molar ratio in term of coded unit, respectively.

From Eq. 10, temperature had the highest effect, while pressure and methanol to oil molar ratio had slightly effect on %ME content as similar as mention in the literatures (Sawangkeaw et al. 2010). For the compressible flow model (Eq. 6), the reaction temperature and methanol to oil molar ratio influenced

both chemical kinetics and compressibility factor terms and then reflected to the %ME content. Whereas, the reaction pressure slightly affected the %ME content by regulating only the compressibility factor value.

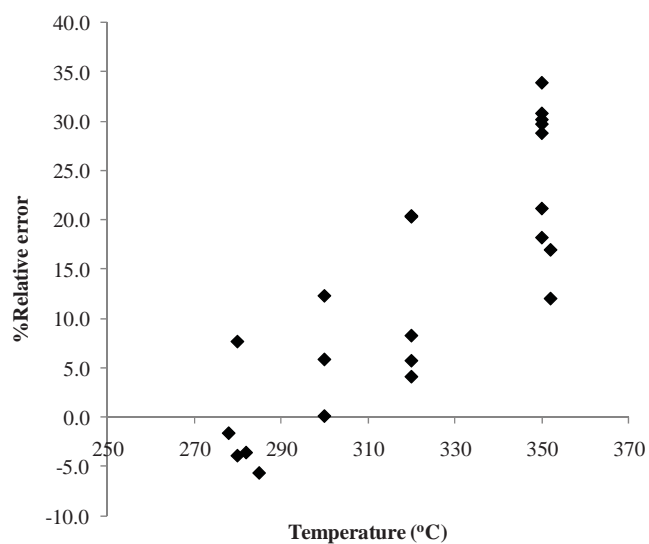


Figure 6. The relationship between the %relative error of the calculated %ME content from Eq. (6) and the reaction temperature.

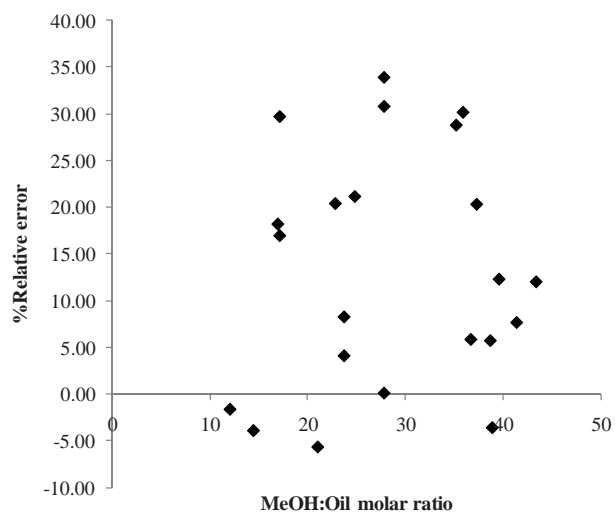


Figure 7. The relationship between the %relative error of the calculated %ME content from Eq. (6) and the methanol to oil molar ratio.

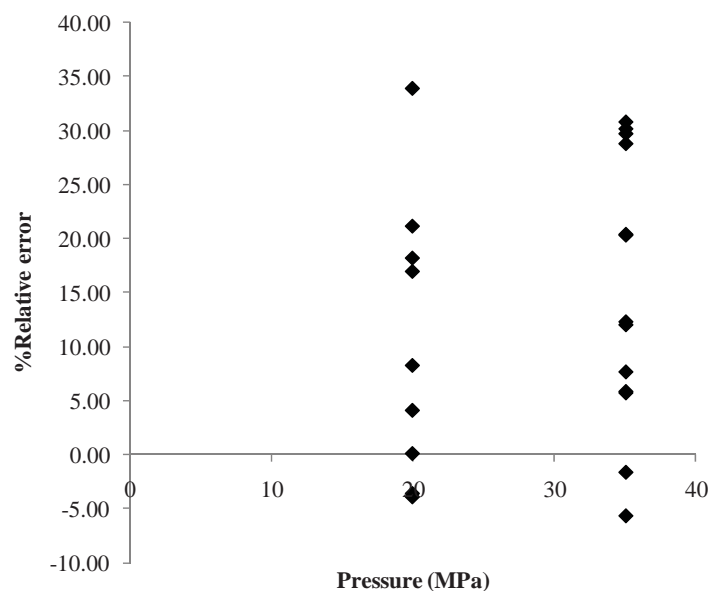


Figure 8. The relationship between the %relative error of the calculated %ME content from Eq. (6) and the pressure.

The fact that variation in the compressibility factor slow down the rate of transesterification slightly, is shown by comparison with calculated values from equation (6) which were approximately 2 – 13% lower than the values derived from equation (7). At a temperature of 553 K, the difference between the calculated values derived from equations (6) and (7) decreased with increasing methanol to oil molar ratios due to the irreversible assumption of kinetic model was more valid at high methanol to oil molar ratio (Song et al. 2008). This can be observed, for instance, by comparison of the difference between the calculated values in either runs 1 and 3 or runs 2 and 4. However, the effect of the changes in the compressibility factor upon the rate of transesterification had the same magnitude, being approximately 10%, at temperatures above 573 K. The effect of the compressibility factor changes that slows down the rate of transesterification could be derived from the fact that by increasing the compressibility factor, the concentration of the reactants decreased.

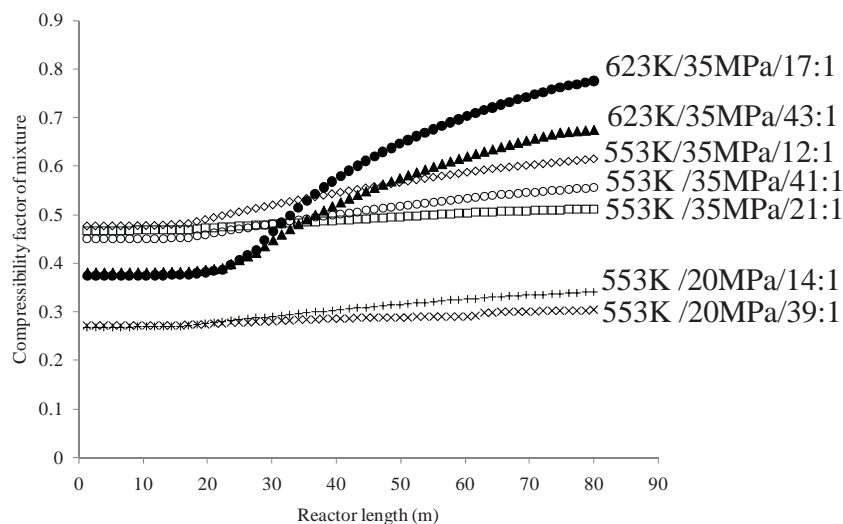


Figure 9. The changes in the compressibility of the reaction mixture along the length of the tubular reactor in run no. 1 (\diamond), 2 (+), 3 (\square), 4 (\times), 5 (\circ), 17 (\bullet) and 22 (\blacktriangle). The abbreviations on the figure are the experimental conditions as the operational temperature (K)/pressure (MPa)/methanol to oil (molar ratio).

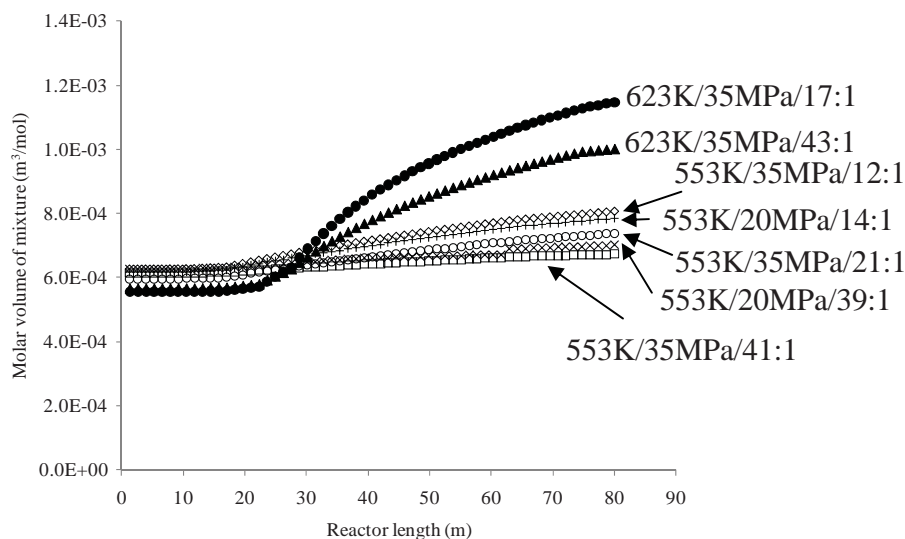


Figure 10. The changes in the molar volume of the reaction mixture along the length of the tubular reactor in Run no. 1 (\diamond), 2 (+), 3 (\square), 4 (\times), 5 (\circ), 17 (\bullet) and 22 (\blacktriangle). The abbreviations on the figure are the experimental conditions as the operational temperature (K)/pressure (MPa)/methanol to oil (molar ratio).

An example of the change in the compressibility factor and the molar volume of the mixture are shown in Figures 9 and 10, respectively. The numerical solution of equation (6) at any reacting conditions was the conversion profile along the reactor length, then the compressibility factor and molar volume at any reactor length could be estimated from known temperature, pressure and composition using PR-MHV2-UNIQUAC model. In other word, the compressibility factor was calculated by $Z=Pv/RT$, with v being the molar volume, obtained from the equation of state. Values from run nos. 1 – 5 were selected to demonstrate the effect of pressure on the changes in the compressibility factor, which, as expected, were higher at 35.0 MPa than at 20.0 MPa. In addition, the values from run nos. 17 and 22 illustrate the effect of temperature on the changes in the compressibility factor and the molar volume of mixture.

For the best model to predict ME content of biodiesel from palm oil in SCM, the VLE data on methyl palmitate + methanol and tripalmitin + methanol has to be integrated into the compressible flow model. Unfortunately, the VLE data on tripalmitin + methanol could not found in literature. However, this compressible flow model could be applicable to biodiesel production in SCM from rapeseed or sunflower oils that have oleic acid as a major fatty acid.

It was clear that the compressibility factor and molar volume at ~623 K rose faster than the values at ~553 K. At a constant temperature and pressure, the changes in the compressibility factor and the molar volume at a low methanol to oil molar ratio was faster than that seen at a high methanol to oil molar ratio. Therefore, the compressibility factor and the molar volume of the mixture were both enhanced with increasing reactor length and they had a steeper slope at high temperatures and lower methanol to oil molar ratios.

The deviation of the predicted %ME values at high temperatures may be due to a number of reasons. Firstly, the real mixture is slightly different from the simulated mixture, as mentioned in Section 3.1. Since the exact chemical formula of vegetable oils does not exist, the deviation from this cause could not be avoided but could probably be minimized by some approaches, such as using a group contribution method to estimate a single pseudo-triglyceride molecule (Espinosa et al. 2002; Hegel et al. 2007; Hegel et al. 2008). Secondly, thermodynamic model predictions at high temperatures have, in general, a higher relative error than at low temperatures. For example, the PR-MHV2-UNIQUAC prediction of glycerol + methanol system had maximum relative error of 10% at 523 K compared to 5% at 493 K. Thirdly, the coefficient of determination of kinetics model at 0.9578 (Song et al. 2008), ~4% of random error was taken into account in our compressible flow model. To use equation (6) at high temperature, the further information on the chemical kinetics of side reactions such as thermal cracking of unsaturated triglycerides were required to modify the equation (6).

5. Conclusion

A simple compressible flow model for biodiesel production in SCM was successfully derived and checked within a temperature range of 553 – 623 K, a pressure range of 20 – 35 MPa and a methanol to oil molar ratio range of 12:1 – 43:1. The PR-MHV2-UNIQUAC thermodynamic model with adjusted binary interaction coefficients was employed to evaluate the changes in the compressibility factor of the reaction mixture during the reaction progress along the reactor length. Although the thermodynamic model fitting of VLE from the literature had a maximum relative error of approximately 10%, the simple compressible flow model was shown to be adequate at temperatures below 593 K. Unfortunately, the prediction was over-estimated at temperatures over 593 K, due to the interference of thermal degradation reaction that was not taken into account in this model. Comparison with computations which does not take into account compressibility changes, demonstrated that the chemical biodiesel production with SCM was lowered by the changing compressibility along the reactor, especially at low methanol to oil molar ratios. It should be noticed that predicted results from this work could not be directly applied to more complex system such a pilot plant reactor yet. For more complicated systems, additional data which are presently lacking need to be taken into account such as the pressure drop, the kinetics of side reactions, the ternary or quaternary phase equilibria data and effect of momentum, heat and mass transfer. For instance, the axial heat transfer in a pilot plant reactor might have an influence on conversion due to the tube diameter being larger than that of a lab-scale reactor.

6. References

- Anderson, T. F. and J. M. Prausnitz (1978). Application of the UNIQUAC Equation to Calculation of Multicomponent Phase Equilibria. 1. Vapor-Liquid Equilibria. *Industrial & Engineering Chemistry Process Design and Development*, 17(4), 552-561.
- Bunyakiat, K., S. Makmee, R. Sawangkeaw and S. Ngamprasertsith (2006). Continuous Production of Biodiesel via Transesterification from Vegetable Oils in Supercritical Methanol. *Energy and Fuels*, 20(2), 812-817.
- Camy, S., J. S. Pic, E. Badens and J. S. Condoret (2003). Fluid phase equilibria of the reacting mixture in the dimethyl carbonate synthesis from supercritical CO₂. *The Journal of Supercritical Fluids*, 25(1), 19-32.
- Constantinou, L. and R. Gani (1994). New group contribution method for estimating properties of pure compounds. *AIChE Journal*, 40(10), 1697-1710.

- Constantinou, L., R. Gani and J. P. O'Connell (1995). Estimation of the acentric factor and the liquid molar volume at 298 K using a new group contribution method. *Fluid Phase Equilibria*, 103, 11-22.
- Espinosa, S., T. Fornari, S. B. Bottini and E. A. Brignole (2002). Phase equilibria in mixtures of fatty oils and derivatives with near critical fluids using the GC-EOS model. *The Journal of Supercritical Fluids*, 23(2), 91-102.
- Fang, T., Y. Shimoyama, T. Abeta, Y. Iwai, M. Sasaki and M. Goto (2008). Phase equilibria for the mixtures of supercritical methanol + C18 methyl esters and supercritical methanol + α -tocopherol. *The Journal of Supercritical Fluids*, 47(2), 140-146.
- Foglor, H. S. (1999). *Elements of chemical reaction engineering*.3, Prentice Hall, New Jersey.
- Glišić, S., I. Lukic and D. Skala (2009). Biodiesel synthesis at high pressure and temperature: Analysis of energy consumption on industrial scale. *Bioresource Technology*, 100(24), 6347-6354.
- Glišić, S., O. Montoya, A. Orlovic and D. Skala (2007). Vapor-liquid equilibria of triglycerides-methanol mixtures and their influence on the biodiesel synthesis under supercritical conditions of methanol. *Journal of the Serbian Chemical Society*, 72(1), 13-27.
- Glišić, S. and D. Skala (2009). The problems in design and detailed analyses of energy consumption for biodiesel synthesis at supercritical conditions. *The Journal of Supercritical Fluids*, 49(2), 293-301.
- He, H., T. Wang and S. Zhu (2007). Continuous production of biodiesel fuel from vegetable oil using supercritical methanol process. *Fuel*, 86, 442-447.
- Hegel, P., A. Andreatta, S. Pereda, S. Bottini and E. A. Brignole (2008). High pressure phase equilibria of supercritical alcohols with triglycerides, fatty esters and cosolvents. *Fluid Phase Equilibria*, 266(1-2), 31-37.
- Hegel, P., G. Mabe, S. Pereda and E. A. Brignole (2007). Phase Transitions in a Biodiesel Reactor Using Supercritical Methanol. *Industrial and Engineering Chemistry Research*, 46(19), 6360-6365.
- Huron, M.-J. and J. Vidal (1979). New mixing rules in simple equations of state for representing vapour-liquid equilibria of strongly non-ideal mixtures. *Fluid Phase Equilibria*, 3(4), 255-271.
- Juan, J. C., D. A. Kartika, T. Y. Wu and T.-Y. Y. Hin (2010). Biodiesel production from jatropha oil by catalytic and non-catalytic approaches: An overview. *Bioresource Technology*, 102(2), 452-460.
- Kiwjaroun, C., C. Tubtimdee and P. Piumsomboon (2009). LCA studies comparing biodiesel synthesized by conventional and supercritical methanol methods. *Journal of Cleaner Production*, 17(2), 143-153.

- Lee, J.-S. and S. Saka (2010). Biodiesel production by heterogeneous catalysts and supercritical technologies. *Bioresource Technology*, 101(19), 7191-7200.
- Marulanda, V. F., G. Animescu and L. L. Tavlarides (2010). Investigations on supercritical transesterification of chicken fat for biodiesel production from low-cost lipid feedstocks. *The Journal of Supercritical Fluids*, 54(1), 53-60.
- Minami, E. and S. Saka (2006). Kinetics of hydrolysis and methyl esterification for biodiesel production in two-step supercritical methanol process. *Fuel*, 85(17-18), 2479-2483.
- Peng, D.-Y. and D. B. Robinson (1976). A New Two-Constant Equation of State. *Industrial & Engineering Chemistry Fundamentals*, 15(1), 59-64.
- Perry, R. H. and D. W. Green (1999). *Perry's Chemical Engineers Handbook*.7, McGraw-Hill, New York.
- Pinnarat, T. and P. E. Savage (2008). Assessment of noncatalytic biodiesel synthesis using supercritical reaction conditions. *Industrial and Engineering Chemistry Research*, 47(18), 6801-6808.
- Saka, S. and D. Kusdiana (2001). Biodiesel fuel from rapeseed oil as prepared in supercritical methanol. *Fuel*, 80(2), 225-231.
- Sawangkeaw, R., K. Bunyakiat and S. Ngamprasertsith (2007). Effect of co-solvents on production of biodiesel via transesterification in supercritical methanol. *Green Chemistry*, 9(6), 679-685.
- Sawangkeaw, R., K. Bunyakiat and S. Ngamprasertsith (2010). A review of laboratory-scale research on lipid conversion to biodiesel with supercritical methanol (2001-2009). *The Journal of Supercritical Fluids*, 55(1), 1-13.
- Shimoyama, Y., T. Abeta, L. Zhao and Y. Iwai (2009). Measurement and calculation of vapor-liquid equilibria for methanol + glycerol and ethanol + glycerol systems at 493-573 K. *Fluid Phase Equilibria*, 284(1), 64-69.
- Song, E.-S., J.-w. Lim, H.-S. Lee and Y.-W. Lee (2008). Transesterification of RBD palm oil using supercritical methanol. *The Journal of Supercritical Fluids*, 44(3), 356-363.
- Søren, D. and L. M. Michael (1990). High-pressure vapor-liquid equilibrium with a UNIFAC-based equation of state. *AIChE Journal*, 36(12), 1829-1836.
- Tang, Z., Z. Du, E. Min, L. Gao, T. Jiang and B. Han (2006). Phase equilibria of methanol-triolein system at elevated temperature and pressure. *Fluid Phase Equilibria*, 239(1), 8-11.
- Yin, J.-Z., Z. Ma, D.-P. Hu, Z.-L. Xiu and T.-H. Wang (2010). Biodiesel Production from Subcritical Methanol Transesterification of Soybean Oil with Sodium Silicate. *Energy & Fuels*, 24(5), 3179-3182.

- Yin, J.-Z., M. Xiao and J.-B. Song (2008a). Biodiesel from soybean oil in supercritical methanol with co-solvent. *Energy Conversion and Management*, 49(5), 908-912.
- Yin, J.-Z., M. Xiao, A.-Q. Wang and Z.-L. Xiu (2008b). Synthesis of biodiesel from soybean oil by coupling catalysis with subcritical methanol. *Energy Conversion and Management*, 49(12), 3512-3516.