

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Highlights:

- (1) In this work, several methods of biodiesel production were discussed and compared. A conclusion can be drawn that biodiesel production with supercritical methanol is the best one.
- (2) The research status in multi-phase equilibrium of biodiesel production with supercritical methanol was summarized, including related articles, basic data and thermodynamic models.
- (3) Base on summarizing articles and form studies, several important problems concerning phase equilibrium were put forward.

A review of multi-phase equilibrium studies on biodiesel production with supercritical methanol

Jie Xu ^a, Zhao Jiang ^b, Lu Li ^c and Tao Fang ^d,

Biodiesel production with supercritical methanol has several advantages over the conventional process, including being non-catalytic, a high production efficiency and a wide range of potential feed-stocks and required simple post-processing for the product. The high-pressure phase equilibria of the reactants, intermediates and products in supercritical methanol are the basis for these reactions under supercritical conditions. For an improved understanding of the influence of the phase behaviour of multicomponent mixtures on transesterification, studies on phase equilibrium of relative reaction systems and transesterification kinetics are needed. The relationship between the phase behaviour and the reactions should be classified. Due to the sensitivity of the phase behaviour to temperature and pressure and the difficulty of sampling at high temperature and pressure, the study of phase equilibrium involving supercritical methanol is just starting. This paper compares the advantages and disadvantages of several biodiesel production methods and provides a summary of multi-phase equilibrium studies on biodiesel production with supercritical methanol.

1 Introduction

As the use of fossil energy deadlines, the environmental and energy problems have become the restricting factor for sustainable development. Biodiesel is a type of efficient renewable energy resource that can be an alternative for fossil energy. As a result, biodiesel has become a research topic of considerable interest and has gained international attention. Before the 1990s, the biodiesel produced from pure vegetable oil and refined vegetable oil was very expensive, which hindered its development and application. Additionally, biodiesel could not compete economically against conventional diesel. With the development of biodiesel production technologies in recent years, biodiesel produced from waste animal fat and vegetable oil can economically compete economically against conventional diesel¹. Additionally, biodiesel can efficiently reduce the burden of carbon dioxide emissions from transportation and industry and improve the competitiveness of biodiesel. Furthermore, biodiesel emits lower levels of CO, SO_x, NO_x and unburned hydrocarbons than conventional diesel². Currently, a new wave of research on biodiesel production technologies has commenced internationally.

Conventional biodiesel production has several disadvantages, including environment pollution, low productivity and the high purity of feed stocks. In 2001, Saka and Kusdiana³ first produced biodiesel using supercritical methanol. Supercritical methanol is in a special state in which the temperature and pressure are higher than the critical point of methanol (512K, 8.1 MPa). Biodiesel production with supercritical methanol does not require any catalysts or auxiliary chemicals and does not generate significant waste. Furthermore, pretreatment of the feed stocks (for removing moisture and free fatty acids) is not required. The products only require a simple post-treatment process (without neutralisation, washing and drying). Therefore, biodiesel production with supercritical methanol is an environmentally friendly method for producing biodiesel⁴.

To determine the effects of the phase behaviour of a multicomponent mixture on transesterification at high temperature and pressure, several basic problems should be studied, such as the phase equilibria of methanol + triglycerides (reagent system), methanol + diglycerides and methanol + monoglycerides (intermediate product system), methanol + fatty methyl acid esters (product system), transesterification kinetics, and the relationship between phase equilibrium and kinetics. These problems are the most challenging in the research on biodiesel production with supercritical methanol.

2 Several methods for producing biodiesel

2.1 Homogeneous Catalysis

The conventional process for producing biodiesel is shown in Fig. 1⁴. The transesterification process is shown in Fig. 1(a). The transesterification reaction occurs between triglycerides (TG) with alcohols (methanol) to form esters (biodiesel). Under suitable conditions (catalysed or supercritical condition), the triglycerides can be partially hydrolysed to fatty acids and diglycerides (DG), as shown in Fig. 1(b). Also, DGs can be partially hydrolysed to fatty acids and monoglycerides (MG) as shown in Fig.1(c). MGs can be hydrolysed to fatty acids and glycerol as shown in Fig.1 (d). Through the esterification reaction, those fatty acids and the free fatty acids (FFAs) present in the feed-stocks also convert to fatty acid methyl esters (FAMES) as shown in Fig. 1(e). Several undesired by-products (e.g. fatty acid salts) are produced by the reactions between fatty acids and metal ions as shown in Fig. 1(f). This conventional biodiesel production employs a homogeneous catalyst, such as NaOH or H₂SO₄.

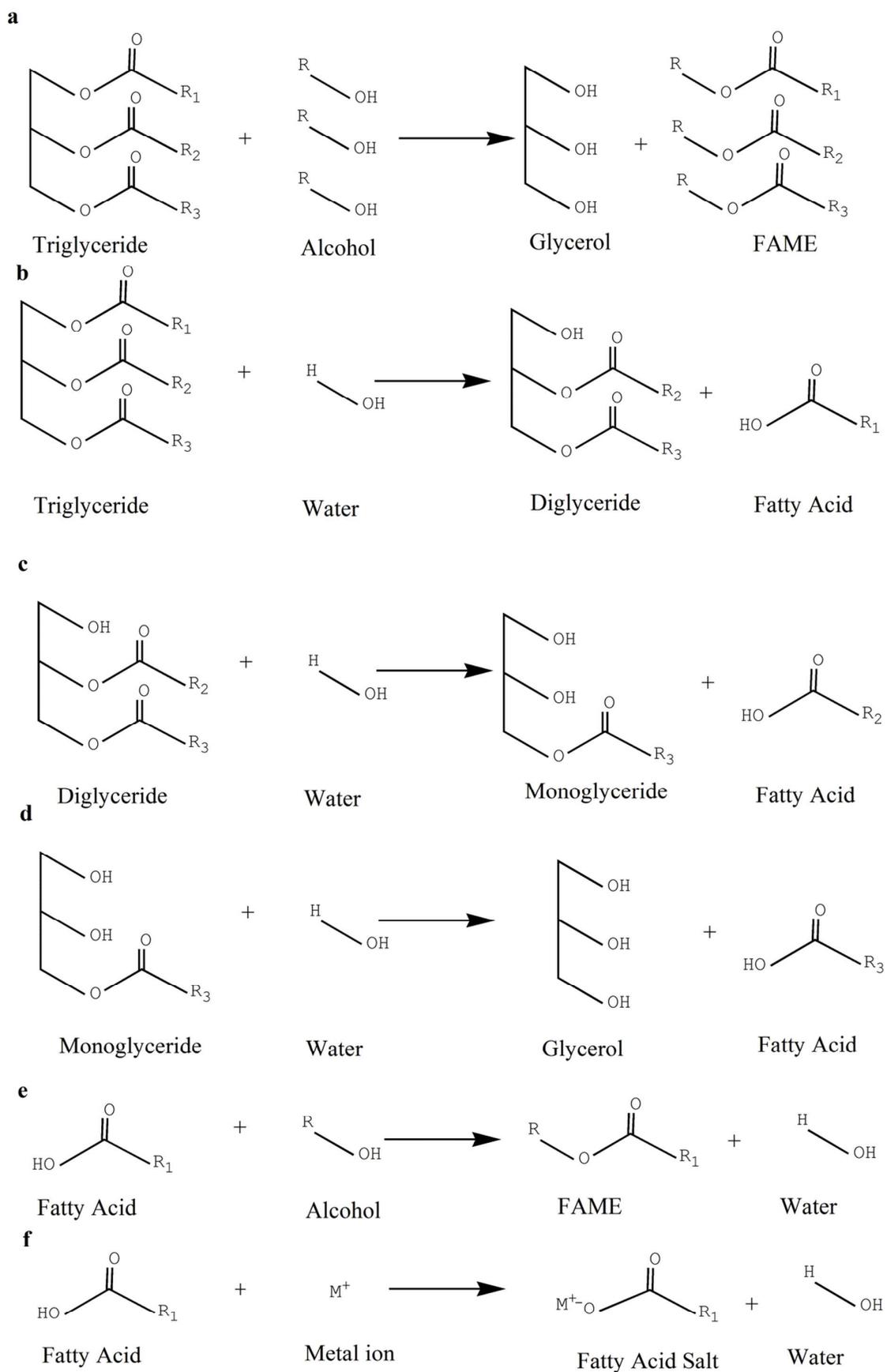


Fig. 1 Conventional process for producing biodiesel

A conventional process for producing biodiesel⁵ involves the following steps: the expelling of raw oil from oil crops with oil cake as by-product; the removal of free fatty acid and other impurities from the raw oil by adding a calculated amount of caustic soda solution while avoiding saponification; a single-step KOH-catalysed transesterification with methanol; the refinement of methyl esters by washing with water; and the use of dry air to eliminate moisture from the fuel. The reactions occurred at 338.15 K with a 6:1 molar ratio of methanol to oil and with 1% of basic catalyst by weight of oil. The nearly 100% methyl ester concentration was obtained at 45 min.

The conventional production of biodiesel has several disadvantages, including environmental pollution, low productivity and high purity feed-stocks. First, the conventional process produces considerable amount of wastewater and several fatty acid salts (saponification products). The wastewater and fatty acid salts should be treated before being discharged to the environment or should be recycled in the process. However, the catalysts and neutralisers used in the process are difficult to recycle and treat. Second, the feed-stocks used in the conventional process require pretreatment and refinement. To remove the saponification components from crude biodiesel, the reaction products must be washed and dried. As a result, the entire production process requires more than 4 hours. Third, the conventional process requires refined and expensive vegetable oil with the moisture content lower than 0.06% (v/v) and a free fatty acids lower than 0.50% (w/w), as the feed-stocks⁶. Consequently, this requirement increases the production cost reduces the competitiveness of biodiesel. Moreover, the use of refined oil as a raw material for producing biodiesel indirectly conflicts with the human need for consuming plant or animal oils.

The two-step transesterification process can utilize inexpensive feed-stocks, including waste oils. Compared with one-step transesterification, the two-step process is significantly more complex, requires additional time and generates added waste and crude products that require extra treatments^{7, 8}.

2.2 Heterogeneous Catalysis and Lipase Catalysis

New catalytic processes, such as heterogeneous catalysis and lipase catalysis, have been developed to address the shortcomings of homogeneous catalysis, but these processes have several disadvantages. Kim et al.⁹ used a Na/NaOH/ γ -Al₂O₃ heterogeneous catalyst for the production of biodiesel from soybean oil. The reactions occurred at 333.15 K with a 6:1 molar ratio of methanol to oil and with 1% of basic catalyst by weight of oil. Using *n*-hexane as the co-solvent with ratio of 5:1 oil to *n*-hexane, the maximum biodiesel production reached 94% at 1 h. Heterogeneous catalysts can be easily separated and recycled to the process, but the feed-stocks should be refined. Generally, heterogeneous catalysts lose their catalytic activity after several reuses^{10, 11}.

Royon et al.¹² studied the enzymatic production of biodiesel via the methanolysis of cottonseed oil using an immobilised *Candida Antarctica* lipase as a catalyst in *t*-butanol. A methanolysis yield of 97% was observed after 24 h at 323.15 K with a reaction mixture containing 32.5% *t*-butanol, 13.5% methanol, 54% oil and 0.017 g enzyme (g oil)⁻¹. With the same mixture, a 95% ester yield was obtained using a one-step fixed bed continuous reactor with a flow rate of 9.6 mL h⁻¹ (g enzyme)⁻¹. Using lipase catalysis can partially solve the problems of refining feed-stocks and product separation. However, because of methanol toxicity, water deactivation and glycerol inhibition, the lipase catalysts lose their catalytic activities after extended use¹³⁻¹⁶. Furthermore, the cost of lipase catalysts is significantly higher than that of conventional catalysts and the lipases' catalytic activities are significantly lower than those of conventional catalysts¹⁷.

2.3 Biodiesel production with supercritical methanol

In recent years, several researchers have attempted to solve aforementioned problems by producing biodiesel with supercritical methanol. In the transesterification reaction with supercritical methanol, no catalysts or auxiliary chemicals are used and no wastes that require special treatment are generated. This process is an environmentally friendly method for producing biodiesel^{3, 18}.

Valle et al.¹⁹ discovered that the non-catalytic transesterification of fodder radish oil with supercritical alcohols can be performed with molar ratios of alcohols to oil in the range of 30:1 to 40:1 and with temperatures of 583-590 K. While the pressures are in the range of 11-14 MPa, high ester contents (more than 96% by weight fraction) can be obtained when the reaction time is greater than 20 min. During product post-treatment, the unreacted alcohol was separated in a vacuum oven at 343 K and 3.3 kPa. Without alcohol, the biodiesel and glycerine become practically immiscible and can be separated by gravimetric precipitation. The biodiesel phase contains several impurities (mainly triglycerides, diglycerides and monoglycerides) and fatty acid methyl esters.

In Tsai's²⁰ work, the transesterification rate increased with temperature but was insensitive to pressure. The presence of CO₂ cannot enhance the reaction rate and increase the yield of FAMES. By using the supercritical process, the presence of FFAs in the raw material provides a positive contribution to the production of FAMES and is regarded as an acid catalyst.

Because the feedstocks do not require complex pretreatment (for removing free fatty acids and moisture) and the products only require a simple post-treatment (without neutralisation, washing and drying), biodiesel production with supercritical methanol is highly efficient and has a relatively short processing time. In addition, the reaction rate under supercritical conditions is very fast. As a consequence, biodiesel production with supercritical methanol requires a smaller reactor than conventional processes. Because the moisture and free fatty acids in the feedstocks do not significantly affect biodiesel production with supercritical methanol, waste oil and low-grade feedstocks can be used in this process.

To decrease the cost of feedstocks, several low-grade feedstocks have been studied to replace the refined oil, such as the by-products from vegetable oil factories, spent oils and microalgae oil²¹. The use of microalgae oil has several advantages. The planting of microalgae does not utilize agricultural land. The acre yield of microalgae is high and can be 8 to 24 times greater than oil crops. Microalgae can adsorb heavy metals, degrade organic matter and purify the environment. In addition, microalgae contain many high value-added components, such as carotene and astaxanthin. All of these advantages can reduce the cost of feedstocks and increase the competitiveness of biodiesel compared with fossil oil²². Using mathematical modelling and engineering computations, Chisti^{23, 24} concluded that biodiesel produced from microalgae oil is the only type of biodiesel that can replace fossil oil. The production of biodiesel with supercritical methanol is suitable for these low-grade feedstocks.

Although biodiesel production with supercritical methanol has many advantages, such as a fast reaction rate, high efficiency and feedstock flexibility, the high temperature and pressure for transesterification are the main obstacles for its application. Therefore, the supercritical process should be optimised to retain its advantages and to reduce the operation and equipment costs. Current research is focused on optimising the operational parameters, including reducing the operating temperature and pressure, obtaining an optimised ratio of methanol to oil or adding cosolvents, such as CO₂ and propane^{25, 26}. A new reaction process that uses hydrolysis and the esterification reaction has been studied to improve the conversion efficiency of the supercritical process²⁷.

2.4 Economic feasibility of biodiesel using supercritical technology

Biodiesel is more significant in today's society and economy because of its remarkable advantages. As a result, energy and economic feasibility analysis are necessary for investigating whether a process is profitable. Because an energy analysis is dependent upon the reaction system and the scale of production, economic analysis is used as an alternative solution²⁸.

Supercritical process is an expensive alternative because of the high operational pressure and temperature requirements. Contrary to conventional processes, the supercritical process can utilize low-grade raw materials, such as waste cooking oil. The cost of waste cooking oil is 110-220 US\$ per tonne²⁹, whereas the cost of refined vegetable oil is 478-650 US\$ per tonne³⁰. Supercritical process has an economic advantage with respect to the raw material.

Biodiesel's selling price is a key variable of this process. The price depends on tax incentives, the price of petroleum oil and the subsidies for transportation. Considering the fossil energy is being used up, the price of petroleum oil is increasing. Different countries have different taxes for their products. In most countries, the use of biodiesel as an environmentally friendly fuel receives tax benefits. Influenced by the increased petroleum oil price and tax incentives, biodiesel's selling price is becoming more competitive.

Alcohol is another important raw material for biodiesel production, and its price is crucial for the economic analysis. Research²⁸ has shown that the internal return rate of biodiesel production suffers a reduction of 82% when the price of alcohol increases from 0.1 to 0.4 US\$/kg. The price of alcohol has a significant influence on the global process.

Glycerol is an important by-product of biodiesel production. The market price for glycerol is extremely variable and depends on purity and availability. Pharmaceutical-grade glycerol (purity above 98%) could be sold at a price of approximately 1.322 US\$/kg³¹, whereas industrial grade glycerol is less expensive because it is produced in large amounts due to the biodiesel industry. As a result, refining glycerol to increase purity is an effective way to enhance economic performance.

In conclusion, biodiesel using supercritical technology has advantages, such as the cost of raw materials and tax incentives, but the expensive costs of operation and equipment still restrict its economic profit.

3 Research status of multi-phase equilibrium studies on biodiesel production with supercritical methanol

The extent of miscibility of the reactants is of extreme importance for all reactions, including the transesterification between methanol and fatty glyceride at high temperature and pressure. To obtain optimised reaction efficiency, the temperature and pressure must be controlled so that the reactants are partially or completely miscible (homogenous) with each other. By studying the multi-phase equilibrium, the relationship between the phase behaviour and the pressure/temperature can be clarified easily. By correlating the experimental data of phase equilibrium with the equation of state (EOS), the operation conditions can be optimized. During transesterification, methanol, diacylglycerols and monoacylglycerols are partially miscible. Additionally, methanol, fatty acid methyl esters and glycerol, are partially miscible. Therefore, research on the multi-compound phase equilibrium has received continuous attention globally.

To elucidate the effects of the phase behaviour of a multicomponent mixture on transesterification, several basic problems should be studied, including the phase equilibria of methanol + triglyceride (reagent system), methanol + diglyceride and methanol + monoglyceride (intermediate product system), methanol + fatty methyl acid esters (product system); transesterification kinetics; and the relationship between phase equilibrium and kinetics. These problems are the most challenging in research on biodiesel production with supercritical methanol.

3.1 Relevant literature

Several researchers have realised that research on the phase equilibria of methanol and reactants (triglyceride), intermediate products (diglyceride and monoglyceride) and products (fatty acid methyl esters and glycerol) in supercritical methanol is the basis for optimising this reaction. Because the supercritical fluids are highly sensitive to temperature and pressure, sampling at high temperature and pressure is difficult. The research on phase equilibrium is just beginning, and there is a lack of basic data. A few reports regarding the phase equilibrium in biodiesel production with supercritical methanol are shown in Table. 1.

Table. 1 Phase equilibrium studies on biodiesel production with supercritical methanol

Researchers	Research systems	Measurement range		Thermodynamic model	
		Temperature (K)	Pressure(MPa)	Equation of State (EOS)	Mixing rule
Tang et al. ³²	Triolein + Methanol	333 - 463	6 - 10	Peng-Robinson	van der Waals
Shimoyama et al. ³³	Methyl myristate + Methanol methyl laurate + Methanol	493 - 543	2.16 - 8.49	Peng-Robinson	ASOG
Shimoyama et al. ³⁴	Glycerol + Methanol	493 - 573	2.27 - 8.78	Peng-Robinson-Stryjek-Vera	van der Waals
Fang et al. ³⁵	Methanol + C18 methyl esters	523 - 573	2.45 - 11.45	Peng-Robinson	van der Waals
Fang et al. ³⁶	Methanol + C18 FAMES + 2,5,7,8-Tetramethyl-2-(5,9,13-trimethyl-tetradecyl)chroman-6-ol	523 - 548	6 - 8	Peng-Robinson	exponent-type mixing rule
Glisic et al. ³⁷	Sunflower oil + Methanol	473 - 503	2.9 - 5.6	Redlich-Kwong-ASPEN	van der Waals
Shimoyama et al. ³⁸	Methyl myristate + Methanol Methyl laurate + Methanol	493 - 543	2.16 - 8.49	Soave-Redlich-Kwong COSMO-Segment Activity Coefficient mode	Wong-Sandler
Hegel et al. ^{39,40}	Methyl oleate + Glycerol + Methanol + Propane	543 - 588	7 - 21.1	Group Contribution with Association model	
Anikeev et al. ⁴¹	MGs, DGs & TGs of fatty acids, FFAs FAMES CO ₂ +methanol	300-700	0-12.9	modified Joback group method	van der Waals
Pinto et al. ^{42,43}	CO ₂ +soybean methyl esters CO ₂ +biodiesel+methanol	303.15-343.15	0-21	Peng-Robinson	Wong-Sandler
Srinophakun et al. ⁴⁴	Methanol + triglycerides Methanol + glycerol + FAME	323.15-823.15	6.95-19.33	GCA-EOS	

3.2 Analysis of literature data

The reported research systems fall into three categories: reactant systems, product systems and byproduct systems. These three types of data are plotted in Fig.2 to Fig.4.

3.2.1 Product systems

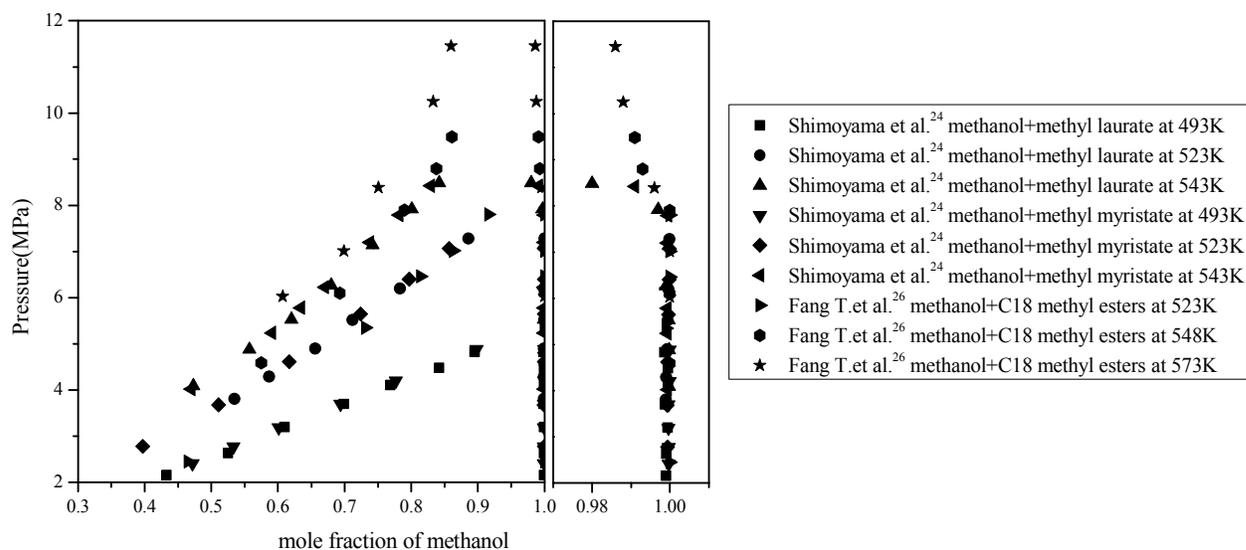


Fig. 2 Experimental data of methanol + methyl laurate/methyl myristate/C18 methyl esters

Fig. 2 is the experimental data of methanol + methyl laurate/methyl myristate/C18 methyl esters. These systems can be treated as the representatives of the product systems. As shown in Fig. 2, the two-phase regions significantly increase with temperature. A notable phenomenon is that the equilibrium pressures of the different systems are similar at the same temperature. When the temperature is 493 K, the equilibrium pressures of the two systems, methanol + methyl laurate ester and methanol + methyl myristate ester, are nearly the same. The same phenomenon appears at 523 K. The peak equilibrium pressures are 4.5 MPa at 493 K and 8 MPa at 523 K for the two systems, respectively. However, the equilibrium pressures increase equably as the temperature increases at the same composition point. Therefore, the molar weight of the FAMEs has little effect on the phase equilibrium of the methanol + FAMEs system. This phenomenon is significant for measuring the equilibrium pressures and compositions of a new system.

3.2.2 Reactant systems

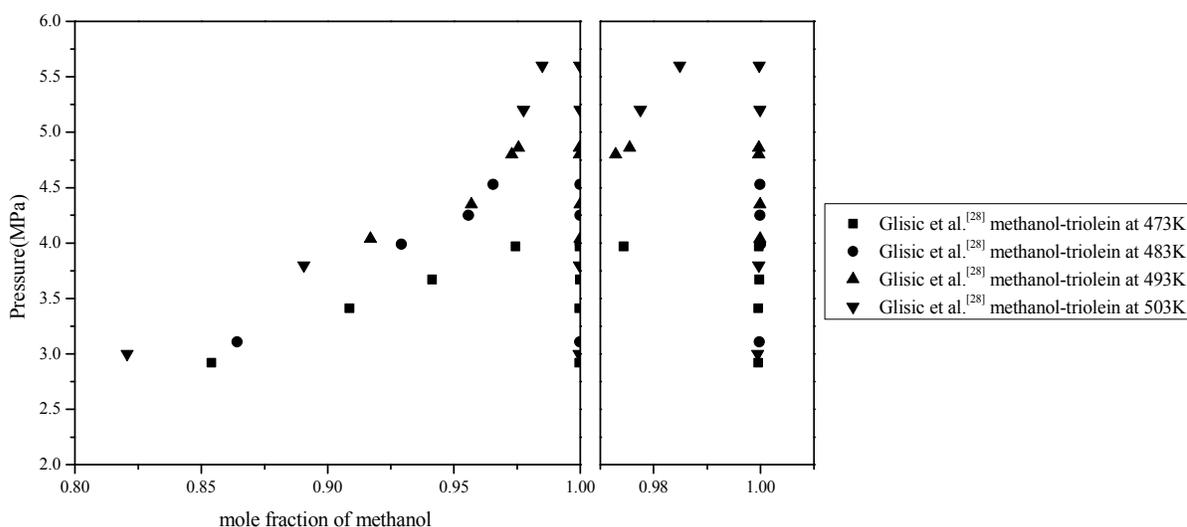


Fig. 3 Experimental data of methanol + triolein

Fig. 3 is the experimental data of methanol + triolein. This system is one of the reported reactant systems. As shown in Fig. 3, the two-phase regions increase with temperature. A few articles discussed the system of methanol + triolein, and no obvious regularity occurs in Glisic's experimental data. Therefore, additional work and experimental data are required for measuring the equilibrium compositions of reactant systems.

3.2.3 By-product systems

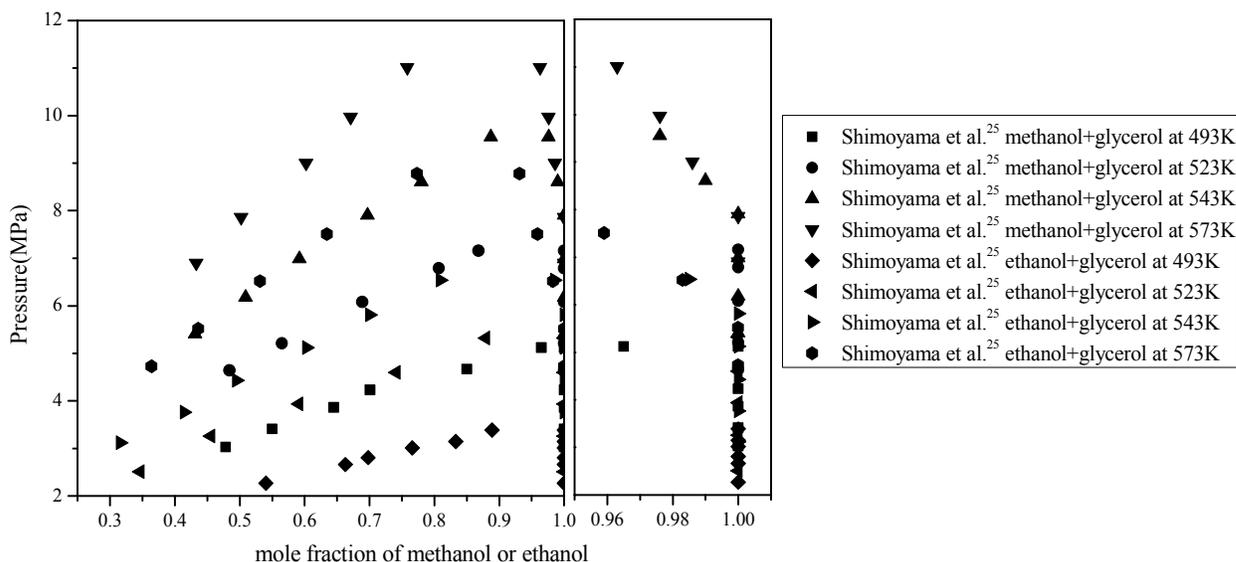


Fig. 4 Experimental data of glycerol + methanol/ethanol

Fig. 4 is the experimental data of glycerol + methanol/ethanol systems. As shown in Fig. 4, the two-phase regions increase with temperature. Contrary to the methanol + FAMES system, the molar weights of the alcohols have a significant effect on the phase equilibrium of the glycerol + alcohols system. The two-phase regions of the glycerol + methanol system are much greater than that of the glycerol + ethanol system at the same temperature. It means that the mutual solubility of ethanol + glycerol is higher than that of methanol + glycerol near and at the critical temperature and pressure of methanol. Additionally, the phenomenon in which the equilibrium pressures equably increase with temperatures at the same composition point appears in two systems. As a result, we can determine whether the equilibrium data are correct when measuring a new system by using this conclusion.

3.3 Thermodynamic models for phase equilibrium

In 2006, Tang³² et al. published the first paper on multi-phase equilibrium study of biodiesel production with supercritical methanol. In this paper, the binary system of triolein + supercritical methanol was studied. To prevent reactions at high temperatures, the phase equilibrium measurement was limited to a low temperature. In a previous report, Glisic³⁷ used sunflower oil as the object of study. In fact, sunflower oil is a mixture of several different fatty glycerides. The system of sunflower oil + methanol is approximately a binary system. In addition, several published works used C18 glyceride and C18 methyl ester as the objects of study. Some studies have also reported on the use of methyl myristate and methyl laurate. However, there are significantly less experimental data for the ternary system and quaternary system than for the binary system.

Many thermodynamic models have been used in the reported works and the equation of state (EOS) is the most employed. Several classical cubic equations of state, such as the Peng-Robinson EOS (PR-EOS), the Redlich-Kwong EOS (RK-EOS)⁴⁶ and their advanced EOSs, have successfully been applied to the experimental data. These EOSs originate from the van der Waals cubic EOS, which attempts to represent PVT behaviour. They are based on the concept of a hard sphere reference term to represent the repulsive interactions and a mean-field term to account for the dispersion and any other long-range forces. The van der Waals mixing rule has been the most used mixing rule for matching the EOSs. According to Fang's early research³⁵, the methanol + C18 esters mixture can be successfully correlated with the PR-EOS and the van der Waals mixing rule. The mixture was a pseudo-binary system, and the interaction parameters could be correlated from experimental data. Except the above thermodynamic models, the group contribution with association (GCA) and the conductor-like screening model (COSMO) have been used to correlate the ternary and quaternary mixtures. The GCA-EOS results from the combination of the statistical theory of associating solutions and the GC-EOS. The residual Helmholtz function is obtained from the sum of three terms representing the contributions of different intermolecular forces: repulsive hard sphere, dispersive mean field and attractive specific interactions. In the COSMO model, a prediction of the activity coefficients in a mixture is performed by using the activity coefficients of the charge segments in a molecular surface. Shimoyama et al.³⁸ have attempted to correlate the experimental data using both the COSMO and UNIFAC models while using a combination of the Soave-Redlich-Kwong (SRK) equation of state with the Wong-Sandler (WS) mixing rules. The correlation results showed that the prediction of the liquid phase using SRK/WS/COSMO-SAC reproduces the experimental data more accurately than calculations using SRK/WS/UNIFAC.

These above results indicate that correlating methanol + ester systems using classical cubic EOS with complex mixing rules provides a good result for describing the vapour phase in over a broad range of temperatures and pressures. Due to the limited prediction capabilities of these approaches, temperature-dependent binary interaction parameters must be obtained from the experimental data. However, the experimental data are poor because of sampling difficulties and the high sensitivity of the phase equilibrium to high temperature and pressure.

With the development of more rigorous explicit association models, the breakthrough in the modelling of polar and highly non-ideal systems overcame the problems of using empirical corrections to cubic EOSs or mixing rules. These association models contain the statistical associating fluid theory (SAFT)⁴⁷, the cubic-plus-association (CPA) EOS^{48, 49}. SAFT was proposed by Chapman et al. and was based on Wertheim's theory. SAFT is a reference for fluids that incorporates both the chain length (molecular shape) and the molecular association. The contributions from the monomeric segments, the formation of chains and the existence of association sites are considered in this model. CPA-EOS is a combination of the SRK-EOS used for the description of the physical interactions with Wertheim's first-order perturbation theory, which can be applied to different types of associating compounds. NguyenHuynh⁵⁰ et al. used the GC-SAFT approach to describe small ester + 1-alkanol systems (from ethanol to butanol). When considering the cross-association interaction between esters and alkanols, reasonable results were obtained. To compare the accuracy of two association models, Grenner⁵¹ et al. described the vapour-liquid equilibria under moderate conditions for several systems including small ester + alcohol mixtures. A lattice model that explicitly accounts for hydrogen bonding, the non-random hydrogen bonding (NRHB) theory, and the PC-SAFT equation were considered. The results revealed that no one of the model is overall superior to the other models.

4 The problems in multi-phase equilibrium studies on biodiesel production with supercritical methanol

At present, several problems exist for multi-phase equilibrium studies on biodiesel production with supercritical methanol. On the one hand, this work is just in the initial stages; on the other hand, the scope and depth of the research are limited. The reliability and accuracy of the predications of these thermodynamic models based on the experimental data cannot be guaranteed. As a result,

these research studies cannot provide sufficient basic data and fundamental information for technology transformation and engineering design. Furthermore, several additional problems exist as follows.

4.1 Phase equilibrium study on methanol + fatty glyceride (reactant system)

To improve the miscibility of the reactants, Cao²⁶ et al. used CO₂ as the cosolvent to reduce the critical point of the mixture. In their work, the transesterification proceeded in a mild conditions and the conversion increased. However, in Imahara's⁵² work, which was conducted at the same reaction pressure, the addition of cosolvent did not increase the yield. Instead, the addition of cosolvent diluted the initial concentration of fatty glyceride and decreased the reaction rate. Therefore, the effect of using CO₂ as the cosolvent is disputed. To resolve this dispute, the phase equilibrium data of methanol + fatty glyceride + CO₂ are required. However, no data are available these two systems. Considering the transesterification of monoglyceride, the intermediate product is the rate-controlling step, and the phase equilibrium of monoglyceride + methanol deserves further study. Additionally, no paper has been reported regarding this binary system.

4.2 Phase equilibrium study on methanol + fatty esters

For all biodiesel produced from fats and vegetable oils, the content of C18 methyl esters is the highest (70 wt. %) followed by C16 methyl esters (20-30 wt. %). Fang^{35,36} first measured and reported the multi-phase equilibrium data of C18 methyl esters (methyl oleate) + methanol and C18 methyl esters + methanol + α -tocopherol. In all of the reported phase equilibrium data, the C16 methyl esters + methanol binary system is not present. However, C16 methyl esters, such as methyl palmitate, are abundant in biodiesel produced from fats and vegetable oils and especially in biodiesel produced from microalgae (as much as 40 wt. %). Thus, measuring and correlating the phase equilibrium data of C16 methyl esters + methanol is important for producing microalgae biodiesel with supercritical methanol.

4.3 Thermodynamic models

Sawangkeaw⁴ determined that no single thermodynamic model is suitable for the whole reaction process because different models are suitable for the reactant system (glycerides + methanol) and product system (FAMEs + methanol) the reaction modifies the polarity of mixtures, and the polarity changes influence the predict ability of the thermodynamic models. However, Tang³² et al. successfully correlated the phase equilibrium of glycerides + methanol (reactants system) using the Peng-Robinson EOS and the van der Waals mixing rule for a temperature range of 333-493K. The thermodynamic model is the same as the one Fang³⁵ used in correlating C18 methyl esters (the main component is methyl oleate) + methanol (products system). The correlation of the phase equilibria is possible for the whole process using a single thermodynamic model for the transesterification between supercritical methanol and glycerides. To validate this hypothesis, the phase equilibria data of the whole reaction process, including the reactant system, intermediate product system and product system, are required.

5 Conclusions

By analysing the advantages and disadvantages of several different method of biodiesel production, it can be concluded that biodiesel production with supercritical methanol has obvious advantages. However, the supercritical fluids are sensitive to pressure and temperature. Additionally, sampling at high temperature and pressure is difficult. As a result, the phase equilibrium study has a delayed start and lacks basic data. In this paper, the research systems, measurement ranges and thermodynamic models in the related literature are summarised. In addition, the experimental data in the literature are classified and plotted, and the thermodynamic models are analysed and compared. Considering the simplicity and accuracy of the calculation, the use of conventional EOS plus one or several correction terms is a relatively feasible simulation method. Based on a summary of the literature, several important problems concerning phase equilibrium were identified.

6 Acknowledgements

The authors would like to acknowledge the following financial supports: National Natural Science Foundation of China (No. 21376186), the Ministry of Education (Doctoral Special Research Foundation No. 20110201110032), China and the Fundamental Research Funds for the Central Universities (New Teacher Research Support Plan No. 08141002 and International Cooperation

Project No. 2011jdhz37 in Xi'an Jiaotong University), Natural Science Basic Research Plan in Shaanxi Province of China (No. 2012JM2010) and the Ministry of Human Resources and Social Security of China (Sci. & Tech. Project for Overseas Scholars, No. 19900001).

Notes and references

^{a, b, c, d} Department of chemical engineering, Xi'an Jiaotong University, Xi'an 710049, China

1. M. Bender, *Bioresource Technology*, 1999, **70**, 81-87.
2. Y.-p. G. Wu, Y.-f. Lin and C.-T. Chang, *Fuel*, 2007, **86**, 2810-2816.
3. S. Saka and D. Kusdiana, *Fuel*, 2001, **80**, 225-231.
4. R. Sawangkeaw, K. Bunyakiat and S. Ngamprasertsith, *The Journal of Supercritical Fluids*, 2010, **55**, 1-13.
5. S. Maiti, P. Bapat, P. Das and P. K. Ghosh, *Fuel*, 2014, **121**, 126-132.
6. F. Ma and M. A. Hanna, *Bioresource Technology*, 1999, **70**, 1-15.
7. S. Zullaikah, C. C. Lai, S. R. Vali and Y. H. Ju, *Bioresour Technol*, 2005, **96**, 1889-1896.
8. R. Potumarthi, C. Subhakar, A. Pavani and A. Jetty, *Bioresource Technology*, 2008, **99**, 1776-1786.
9. H.-J. Kim, B.-S. Kang, M.-J. Kim, Y. M. Park, D.-K. Kim, J.-S. Lee and K.-Y. Lee, *Catalysis Today*, 2004, **93-95**, 315-320.
10. J. M. Marchetti, V. U. Miguel and A. F. Errazu, *Fuel*, 2007, **86**, 906-910.
11. C. Ngamcharussrivichai, W. Wiwatnimit and S. Wangnoi, *Journal of Molecular Catalysis A: Chemical*, 2007, **276**, 24-33.
12. D. Royon, M. Daz, G. Ellenrieder and S. Locatelli, *Bioresource Technology*, 2007, **98**, 648-653.
13. L. Li, W. Du, D. Liu, L. Wang and Z. Li, *Journal of Molecular Catalysis B: Enzymatic*, 2006, **43**, 58-62.
14. W. Du, Y. Xu, D. Liu and J. Zeng, *Journal of Molecular Catalysis B: Enzymatic*, 2004, **30**, 125-129.
15. H. Fukuda, A. Kondo and H. Noda, *J Biosci Bioeng*, 2001, **92**, 405-416.
16. S. V. Ranganathan, S. L. Narasimhan and K. Muthukumar, *Bioresour Technol*, 2008, **99**, 3975-3981.
17. Y. Wang, H. Wu and M. H. Zong, *Bioresource Technology*, 2008, **99**, 7232-7237.
18. D. Kusdiana and S. Saka, *Fuel*, 2001, **80**, 693-698.
19. P. Valle, A. Velez, P. Hegel, G. Mabe and E. A. Brignole, *The Journal of Supercritical Fluids*, 2010, **54**, 61-70.
20. Y. T. Tsai, H. M. Lin and M. J. Lee, *Bioresour Technol*, 2013, **145**, 362-369.
21. T. Pinnarat and P. E. Savage, *Industrial & Engineering Chemistry Research*, 2008, **47**, 6801 - 6808
22. Q. Hu, M. Sommerfeld, E. Jarvis, M. Ghirardi, M. Posewitz, M. Seibert and A. Darzins, *Plant Journal*, 2008, **54**, 621 - 639
23. Y. Chisti, *Biotechnol Adv*, 2007, **25**, 294-306.
24. Y. Chisti, *Trends Biotechnol*, 2008, **26**, 126-131.
25. H. Han, W. Cao and J. Zhang, *Process Biochemistry*, 2005, **40**, 3148 - 3151
26. W. Cao, H. Han and J. Zhang, *Fuel*, 2005, **84**, 347-351.
27. R. B. Levine, T. Pinnarat, Savage and P. E., *Energy Fuels*, 2010, **24**, 5235 - 5243
28. J. M. Marchetti, *Energy Conversion and Management*, 2013, **75**, 658-663.
29. M. M. Gui, K. Lee and S. Bhatia, *Energy*, 2008, **33**, 1646-1653.
30. Y. Zhang, M. Dube, D. McLean and M. Kates, *Bioresource Technology*, 2003, **90**, 229-240.
31. S. Lee, D. Posarac and N. Ellis, *Chemical Engineering Research and Design*, 2011, **89**, 2626-2642.
32. Z. Tang, Z. Du, E. Min, L. Gao, T. Jiang and B. Han, *Fluid Phase Equilibria*, 2006, **239**, 8-11.
33. Y. Shimoyama, Y. Iwai, B. S. Jin, T. Hirayama and Y. Arai, *Fluid Phase Equilibria*, 2007, **257**, 217-222.
34. Y. Shimoyama, T. Abeta, L. Zhao and Y. Iwai, *Fluid Phase Equilibria*, 2009, **284**, 64-69.
35. T. Fang, Y. Shimoyama, T. Abeta, Y. Iwai, M. Sasaki and M. Goto, *The Journal of Supercritical Fluids*, 2008, **47**, 140-146.
36. T. Fang, Y. Shimoyama, Y. Iwai, M. Sasaki and M. Goto, *Journal of Chemical & Engineering Data*, 2010, **55**, 80-84.
37. S. Glisic, O. Montoya, A. Orlovic and D. Skala, *Journal of the Serbian Chemical Society*, 2007, **72**, 13-27.
38. Y. Shimoyama, T. Abeta and Y. Iwai, *The Journal of Supercritical Fluids*, 2008, **46**, 4-9.
39. P. Hegel, G. Mabe, S. Pereda and E. A. Brignole, *Industrial & Engineering Chemistry Research*, 2007, **46**, 6360-6365.

-
- 40.P. Hegel, A. Andreatta, S. Pereda, S. Bottini and E. A. Brignole, *Fluid Phase Equilibria*, 2008, **266**, 31-37.
- 41.V. Anikeev, D. Stepanov and A. Yermakova, *Industrial & Engineering Chemistry Research*, 2012, **51**, 4783-4796.
- 42.L. F. Pinto, P. M. Ndiaye, L. P. Ramos and M. L. Corazza, *The Journal of Supercritical Fluids*, 2011, **59**, 1-7.
- 43.L. F. Pinto, D. I. S. Da Silva, F. Rosa Da Silva, L. P. Ramos, P. M. Ndiaye and M. L. Corazza, *The Journal of Chemical Thermodynamics*, 2012, **44**, 57-65.
- 44.T. Srinophakun and B. Phithakchokchai, *The Journal of Chemical Thermodynamics*, 2011, **43**, 471-478.
- 45.S. B. Glišić and D. U. Skala, *The Journal of Supercritical Fluids*, 2010, **54**, 71-80.
- 46.J. O. Valderrama, *Industrial & engineering chemistry research*, 2003, **42**, 1603-1618.
- 47.E. A. Muller and K. E. Gubbins, *Industrial & Engineering Chemistry Research*, 2001, **40**, 2193–2211
- 48.G. M. Kontogeorgis, M. L. Michelsen, G. K. Folas, S. Derawi, N. von Solms, Stenby and E. H., *Industrial & Engineering Chemistry Research*, 2006, **45**, 4855–4868.
- 49.G. M. Kontogeorgis, M. L. Michelsen, G. K. Folas, S. Derawi, N. von Solms, Stenby and E. H., *Industrial & Engineering Chemistry Research*, 2006, **45**, 4869–4878
- 50.D. NguyenHuynh, A. Falaix, J. P. Passarello, P. Tobaly and J. C. de Hemptinne, *Fluid Phase Equilibria*, 2008, **264**, 184-200.
- 51.A. Grenner, I. Tsivintzelis, I. G. Economou, C. Panayiotou and G. M. Kontogeorgis, *Industrial & Engineering Chemistry Research*, 2008, **47**, 5636–5650
- 52.H. Imahara, J. Xin and S. Saka, *Fuel*, 2009, **88**, 1329-1332.