# CHAPTER II

# THEORY AND LITERATURE REVIEWS

## 2.1. Biodiesel

Before 2000, biodiesel was widely referred to an alternative diesel fuel which was made from renewable biological sources such as vegetable or animal oils/fats [21]. In actuality, the use of vegetable or animal oils/fats as alternative fuels can be achieved in several ways; a heat fuel, a blending with diesel fuel, and as micro-emulsion mixture. However, vegetable or animal oils/fats have the major composition as triglyceride which may cause some combustion problems, e.g. coking and carbon deposits on the injectors and increasing the lubricant viscosity due to its high molecular weight and high viscosity. Thus, chemical modification processes such as thermal cracking, soap pyrolysis and transesterification were introduced to reduce the molecular weight of vegetable or animal oils/fats before using them as alternative fuel [22]. Among the chemical modification processes, the transesterification of triglyceride is the most promising process to produce alternative fuels from vegetable or animal oils/fats. For instance, the process produces the oxygenate fuels that burn cleaner than conventional diesel and do not generate the aromatic compounds. The term "biodiesel" is now specifically referred to the mixture alkyl esters of long chain fatty acids practically derived from the transesterification reaction between glycerides feedstock and low molecular weight alcohols such as methanol or ethanol, for use in compression ignition engine [22-25].

## 2.2. Biodiesel production with conventional method

Typical reactions that take place during biodiesel production are shown in Figure 2.1. Transesterification reaction, which is a major path to produce biodiesel, occurs between triglyceride vegetable or animal oils/fats with alcohols to form esters (biodiesel) and glycerol. The overall transesterification is simplified in Figure 2.1(a). In the presence of water, triglyceride can be partially hydrolyzed to fatty acids and diglyceride under suitable conditions (catalyzed or supercritical condition), as shown in Figure 2.1(b). Those fatty acids, including the free fatty acids (FFA) present in the feedstock, also convert to the desired product (biodiesel) through esterification reaction in present of acid catalysts or supercritical condition, as shown in Figure 2.1(c), or undesired product (fatty acid salt or soap), as shown in Figure 2.1(d).
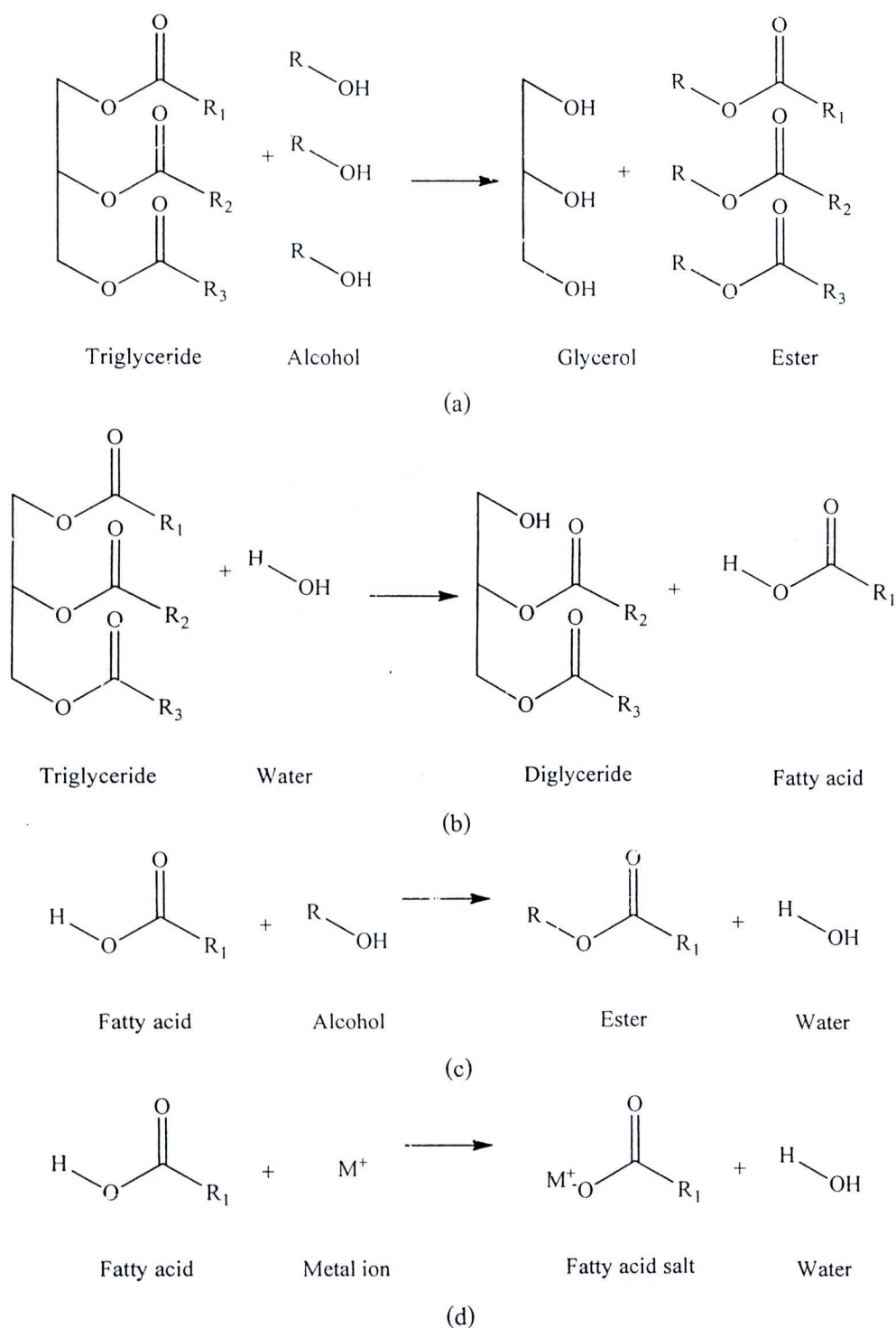
**Figure 2.1.** Common reactions for biodiesel production processes: (a) transesterification, (b) hydrolysis, (c) esterification and (d) saponification.

Conventional biodiesel production uses inexpensive feedstocks such as waste cooking oils, and employs homogeneous catalysts, such as NaOH and $H_2SO_4$ (Figure 2.2). Note that the

first set of reactor, separator and methanol recovery units is not needed when pretreated or refined triglyceride is used as feedstock.
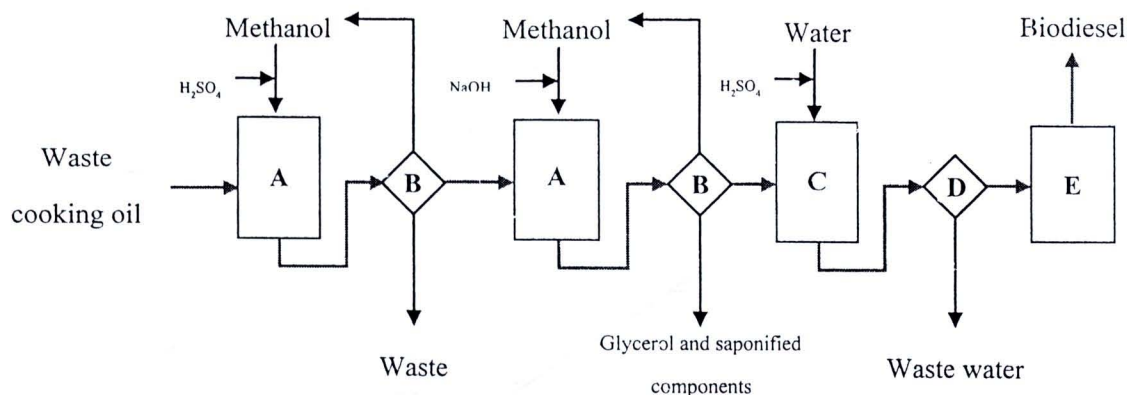


**Figure 2.2.** Conventional biodiesel production scheme from waste cooking oils with acid pretreatment followed by alkaline catalytic process or two-step acidic-basic transesterification: (A) Reactor (60 – 65 °C, 0.1 MPa and 6:1 – 9:1 methanol to oil molar ratio) , (B) Product separation and methanol recovery unit, (C) Water washing unit, (D) Separation unit and (E) Biodiesel drying unit.

The conventional process has some disadvantages, especially from environmental, production efficiency and feedstock flexibility points of view [21-23]. Firstly, the conventional process produces large volume of waste water and some saponified components that need to be treated before discharging to the environment or recycling to the process. Chemicals that are used as a catalyst and neutralizers are difficult to recover. Secondly, as the conventional production process for pretreated or refined triglyceride consists of four separate steps, namely, reacting, separating, washing and drying, the overall production time takes over four hours. The washing step that removes the saponified components in the crude biodiesel is the longest of these steps, since the saponified components interfere with and retard phase separation. Thirdly, the conventional process requires refined and expensive vegetable oils as feedstocks, i.e. lower than 0.06% (v/v) moisture and 0.50% (w/w) free fatty acids [21]. As a consequence, this increases the price of the biodiesel and reduces its sustainability, since the requirement of such virgin oils, rather than waste cooking oils, is indirect conflict with human or animal food grade feedstocks.

A two-step acidic-basic transesterification process is an alternative for inexpensive feedstocks, including spent waste and crude vegetable oils, it is more complicated, more time consuming and generates more waste that requires subsequent treatment than the single step transesterification [26, 27]. For instance, the acidic pretreatment step does not only generate additional wastes, but also requires more basic catalyst to neutralize the pretreated product.

### 2.3. Biodiesel production with heterogeneous catalysts and lipase

Novel catalytic processes, such as heterogeneous and lipase catalysts, have been developed to disentangle the drawbacks of homogeneous catalysts, but they still have some hurdles themselves. [28-38]. The advantages and disadvantages of heterogeneous and lipase catalysts are summarized in Table 2.1.

**Table 2.1** Advantages and disadvantages of heterogeneous and lipase catalysts.

| Catalysts | Advantage | Disadvantage |
|---|---|---|
| Heterogeneous acid catalysts | - Less sensitive to FFA and water in feedstocks<br>- Catalyze esterification and transesterification reaction simultaneously | - Complicated catalyst synthesis procedures may lead to higher cost<br>- Reaction normally take place at high temperature and high methanol to oil molar ratio<br>- Leaching of catalyst active sites may result in catalyst deactivate and product contamination |
| Heterogeneous basic catalysts | - Relatively faster rate of reaction than acid catalysts<br>- Reaction can occur at mild conditions<br>- High possibility to reuse and regenerate | - Poisoning of catalyst when exposed to air and moisture<br>- Soap will form at the FFA content > 2%wt<br>- Leaching of catalyst active sites may result in catalyst deactivation and product contamination |

**Table 2.1 (Cont'd)** Advantages and disadvantages of heterogeneous and lipase catalysts.

| Catalysts | Advantage | Disadvantage |
|---|---|---|
| Enzyme | - Insensitive to FFA and water in feedstocks<br>- Transesterification can take place at temperature lower than conventional catalysts, e.g. NaOH or KOH<br>- Product purification is very simple | - Very slow rate of reaction<br>- Relatively higher cost than other catalysts<br>- Sensitive to alcohol, typically methanol that can denature and deactivate enzyme |

## 2.4. Biodiesel production with supercritical methanol (SCM)

Biodiesel production with SCM has been introduced to overcome catalytic problems. A simple schematic for biodiesel production with SCM is shown in Figure 2.3.
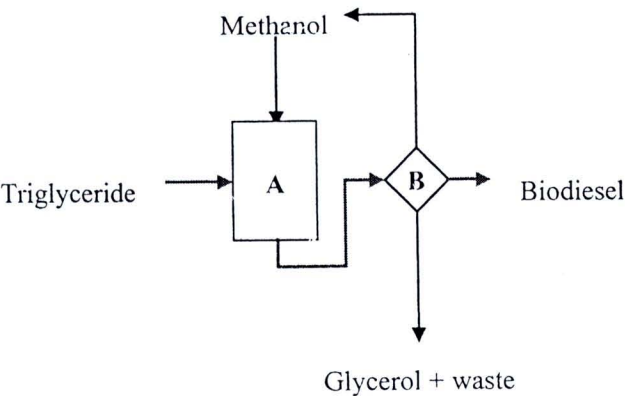


**Figure 2.3.** Biodiesel production with SCM scheme: (A) Reactor (300 – 350 $^\circ$C, 19 – 45 MPa and 40:1 – 42:1 methanol to oil molar ratio) and (B) Product separation and methanol recovery unit.

With regard to environmentally friendly aspects, transesterification, for the case of transfer of the fatty acid components from glycerol to methanol to form fatty acid methyl esters (FAME), biodiesel in SCM does not require any catalysts or auxiliary chemicals and does not generate significant wastes [6, 7, 39, 40]. With regard to the FAME production efficiency, biodiesel production by SCM requires a minimum number of processing steps because the feedstock pretreatment to remove moisture and free fatty acids, as well as some of the product post treatment steps, such as neutralization, washing and drying, are not necessary. As a consequence, biodiesel production with SCM has a low overall production time. In addition, the rate of reaction at supercritical conditions is fast, so that the biodiesel production with SCM

requires a small reactor size for a given production output. With regard to feedstock flexibility, as the moisture and FFA contents in the feedstock do not significantly affect biodiesel production by SCM [41, 42] it is suitable for use with waste cooking oils or other low-grade feedstocks.

Biodiesel production with SCM offers an optimistic alternative to the catalytic method since it does not have inherent disadvantages such as saponified products or catalyst deactivation. Biodiesel production process with SCM has advantages over other processes in its low use of auxiliary chemicals, and chemicals associated with waste water treatment and feedstock pre-treatment. Even though the energy requirement could be a major operating cost, this is much easier to deal with than chemicals. The overall process is simple since many discrete operations such as catalyst preparation, product neutralization and purification are not required. Although biodiesel price depends greatly on feedstock price [2], feedstock flexibility becomes a remarkably strong advantage of the biodiesel production with SCM.

Biodiesel production with SCM still has several challenges in its research and development. The key operating parameters are pressure, temperature and methanol to oil molar ratio. To achieve the highest oil and methanol to FAME conversion rates and yields, high pressures (19 to 45 MPa), high temperatures (320 to 350 $^\circ$C) and high methanol to oil ratios (40:1 to 42:1) have been reported in early studies [6, 7, 39]. In fact, the high pressure and temperature reaction conditions require not only an expensive reactor but also a sophisticated energy and safety management policy. Furthermore, the high methanol to oil ratio needs a significant energy input to recover the excess methanol for recycle. Using the parameters mentioned earlier on a commercial scale results in the capital costs being somewhat higher than the conventional process.

Therefore, current research is focused upon reducing the high operating pressure, temperature and methanol to oil molar ratio required for biodiesel production with SCM. To date the operating pressure, temperature and methanol to oil molar ratio that employ in early studies have been reduced successfully by several techniques, such as the addition of co-solvents or catalysts and by using a modified supercritical process (see section 2.4.5.) On the one hand, the goal to reduce operating pressure, temperature and methanol to oil molar ratio altogether is certainly the most challenging aspect of biodiesel production with SCM, while on the other hand, parameters, such as pressure, methanol to oil molar ratio and residence time, can be simultaneously reduced by increasing the operating temperature.

## 2.4.1. Chronological development of biodiesel production with SCM

In 1998, non-catalytic transesterification of soybean oil at near-critical point of methanol (230 °C, 6.2 MPa and 27:1 methanol to oil molar ratio) was invented to provide an alternative biodiesel production method, but this method obtained only 85 % by weight of methyl esters in product at over 10 hours [43]. Until 2001, Japanese pioneers promoted the transesterification of rapeseed oil with SCM at 350 °C, 45 MPa and 42:1 methanol to oil molar ratio, this process was given a high degree of attention due to the methyl esters (ME) content (98%) was observed at only 4 min [6, 39]. Then, the biodiesel production with SCM has been evolved continuously since 2001.

In 2002, the transesterification of cottonseed, hazelnut kernel, poppy seed, safflower and sunflower oil in SCM was investigated and nearly complete reaction was reported [7]. At the same time, continuous production of biodiesel from palm kernel and coconut oil with SCM in lab-scale tubular reactor was developed in our laboratory [44] and then the scale-up reactor was constructed in 2005 [20]. Meanwhile, the effect of water and free fatty acids in vegetable oils feedstock [41] and the catalytic effect of metal reactor in biodiesel production with SCM [45] and the reactivity of triglyceride with supercritical alcohols were also reported [46]. However, during the year of 2001 – 2005, the maximum ME content was generally observed at the same condition as reported earlier by the Japanese pioneers [6, 39].

In 2005, carbon dioxide and propane were introduced as co-solvents to obtain milder operating parameters of biodiesel production with SCM [8, 47]. Then, the two-step supercritical process [10] was also demonstrated to reduce those operating parameters. In the following years, various catalysts were employed to assist the SCM process to achieve the maximum ME content at milder operating conditions [48-52]. Furthermore, the first article on continuous production of biodiesel with SCM was published by our research group [9], then by the Japanese [10] and Chinese [11] researchers, respectively. Therefore, the research focus on reduction of the elevated operating conditions and continuous process has been ongoing since 2005.

In 2007, the gradual heating technique was introduced to prevent thermal degradation that cause low ME content [11]. At the same time, the effect of co-solvents employed to reduce viscosity of vegetable oils was investigated successfully in our laboratory [53]. From 2007 to 2009, numerous additional studies such as vapor-liquid equilibria of binary systems [16-19, 54, 55], phase behavior of reaction mixture [15, 56, 57], thermal stability of unsaturated fatty acids in

SCM [58] and process and economic analysis [12, 13, 59, 60] were reported to the better understanding of biodiesel production with SCM.

## 2.4.2. Effect of operating parameters on biodiesel production with SCM

Operating parameters, as employed by previous researchers, to obtain high yield of FAME production with SCM are summarized in Table 2.2. The extent of reaction is reported either as methyl esters (ME) content or as triglyceride conversion. It should be noted that the ME content refers to methyl esters of common FFA in vegetable or animal oils/fats that can be identified by different analytical techniques, while the triglyceride conversion implies the remaining triglyceride reactant. The discussion for each parameter is presented accordingly.

### 2.4.2.1. Temperature

All the reported studies to date have shown that the reaction temperature is the most critical parameter for determining the extent of reaction, especially across the critical temperature of methanol (239.6 $^\circ$C). The ME content level rises two- to three-fold as the temperature increases from 200 to 350 $^\circ$C at a constant pressure and methanol to oil molar ratio. The temperature has a strong influence on the conversion rate. For instance, the rate constant increases approximately seven-fold as the temperature is increased from 210 to 280 $^\circ$C at a pressure of 28.0 MPa and a methanol to oil molar ratio of 42:1. Likewise, the apparent activation energy increases from 11.2 kJ/mol at 210 to 230 $^\circ$C (subcritical region) to 56.0 kJ/mol at 240 to 280 $^\circ$C (supercritical region) at 28.0 MPa and 42:1 methanol to oil molar ratio [61].

Although, high temperature clearly enhances the rate of reaction, an excessively high temperature can lead to a negative effect on the ME content. Thermal degradation of unsaturated fatty acids (UFA) was reported in some studies within the temperature range of 320 to 350 $^\circ$C. For example, Sawangkeaw et al. [53] found thermal degradation of UFA in a 250-mL batch reactor due to the temperature gradient between the reactor wall and the bulk fluid. However, the ME content was only slightly reduced because the feedstock used (palm kernel oil) was low in UFA. In contrast, when using soybean oil, which contains over 80% UFA as a feedstock, thermal degradation of the UFA significantly reduces the ME content obtained [11].

Thermal degradation of UFA is a prominent concern in the selection of the triglyceride source against those sources with a high level of UFA. Appropriate temperature for biodiesel production with SCM in an isothermal system is lower than 300 $^\circ$C, and is preferably less than 270 $^\circ$C so that the maximum ME content in the biodiesel can be obtained [58]

Gradual heating of the reaction mixture has been shown to be effective in avoiding UFA thermal degradation [11]. By gradual heating (100 to 320 $^\circ$C) the reaction mixture, the ME content obtained improved to 96%, compared to 77% obtained from uniform heating at 310 $^\circ$C.

Some studies have reported that the thermal degradation of UFA at 350 $^\circ$C significantly decreases the ME content but slightly increases the cloud point [58] and decreases the viscosity [62] of the obtained biodiesel. For instance, the FAMEs obtained from rapeseed and linseed oil decompose by approximately 20 and 50 % by weight, respectively, at 350 $^\circ$C after 40 min of contact time, while the cloud point increases by only 1 or 2 $^\circ$C.

The thermal degradation of UFA esters, triglyceride and glycerol at 400 to 450 $^\circ$C in SCM has been reported to generate several low-molecular weight compounds that could improve the cold flow properties as well as the viscosity of the biodiesel produced [63-65]. However, biodiesel production with SCM at temperature higher than 350 $^\circ$C is considered as a modification of supercritical process to lower other operating parameters and additional details are described in Section 2.4.5.

**Table 2.2** Operating parameters for a high conversion efficiency of lipid to biodiesel with SCM.

| Researchers | T (°C) | P (MPa) | MeOH to Oil molar ratio | Reaction time (min) | Oil type | Reactor type | Heating and cooling rate (°C/sec) | ME content/ Conversion (%) |
|---|---|---|---|---|---|---|---|---|
| Saka and Kusdiana [6] | 350 | 45 | 42:1 | 4 | Rapeseed | 5-mL BRsh | 30 and -100 | >95% ME content |
| Demirbas [7] | 350 | N/R | 41:1 | 5 | Hazelnut kernel and Cottonseed | 100-mL BR | 0.33 and N/R | 95% ME content |
| Madras et al. [66] | 400 | 20 | 40:1 | 30 | Sunflower | 8-mL BR | N/R | 97% Conversion |
| Rathore and Mardras [67] | 400 | 20 | 50:1 | 30 | Palm and Groundnut | 11-mL BR | N/R | 95% Conversion |
| Yin et al. [68] | 350 | 20 | 42:1 | 30 | Soybean | 250-mL BRs | 0.33 and N/R | 95% ME content |
| He et al. [61] | 280 | 25 | 42:1 | 30 | Soybean | 200-mL BRs | N/R | 90% ME content |
| Sawangkeaw et al. [53] | 350 | 20 | 42:1 | 30 | Palm kernel | 250-mL BRs | N/R | 95% ME content |
| Cao et al. [47] | 320 | N/R | 33:1 | 10 | Soybean | 250-mL BRs | 0.33 and N/R | 95% ME content |
| Bunyakiat et al. [9] | 350 | 19 | 42:1 | 7 to 15 | Coconut and Palm kernel | 251-mL TR | N/R | 95% ME content |

*N/R: Not Reported; BR: Batch Reactor; BRsh: Batch Reactor with shaking, BRs: Batch Reactor with stirrer, TR: Tubular Reactor, MFR: Mixed Flow Reactor*

**Table 2.2 (cont'd)** Operating parameters for a high conversion efficiency of lipid to biodiesel with SCM.

| Researchers | T (°C) | P (MPa) | MeOH to Oil molar ratio | Reaction time (min) | Oil type | Reactor type | Heating and cooling rate (°C/sec) | ME content/ Conversion (%) |
|---|---|---|---|---|---|---|---|---|
| He et al. [11] | 310 100 to 320 | 32 | 40:1 | 25 | Soybean | MFR and 75-mL TR in series | N/R | 77% ME content (Uniform heating) 96% ME content (Gradual heating) |
| Minami and Saka [10] | 350 | 20 | 42:1 | 30 | Rapeseed | 200-mL TR | N/R | 87% ME content |
| Anitescu et al. [54] | 350 to 400 | 10.0 to 25.0 | 3:1 to 6:1 | 1 to 2.5 | Soybean | 7-mL TR | N/R | ~98% Conversion |
| Marulanda et al. [63] | 400 | 30 | 9:1 | 6 | Chicken fat | 2-mL TR | N/R | 80% ME content 99% Conversion |

*N/R: Not Reported; BR: Batch Reactor; BRsh: Batch Reactor with shaking, BRs: Batch Reactor with stirrer, TR: Tubular Reactor, MFR: Mixed Flow Reactor*

### 2.4.2.2. Pressure

Data on the effect of pressure on biodiesel production with SCM are limited since these reactions have principally been conducted in batch reactors. The pressure in a batch reactor cannot be controlled independently from density since it varies with the presence of both the reactants and products. In practice, the reaction pressure can be adjusted by altering the initial amounts of oil and methanol, calculated by the use of appropriate Equations of State and mixing rules for triglyceride and methanol [14], but the final pressure will deviate from its calculated value due to composition change during the reaction.

The effect of pressure on the extent of reaction can, however, be investigated with a tubular flow reactor in which the system pressure is controlled by a backpressure regulator. A wide range of operating pressures from 10 to 35 MPa has been investigated with respect to the maximum conversion efficiency to FAME. Below 20 MPa, the reaction pressure affects the ME content significantly within the temperature range of 270 to 350 $^{\circ}$C, but the effect decreases above this pressure [11, 61] For example, at a temperature of 280 $^{\circ}$C, a residence time of 30 min and a methanol to oil molar ratio of 42:1, the MEs content increases significantly from 55 % to 85 % as the pressure increases from 7.5 to 20 MPa, yet only slightly increases to 91 % at 35 MPa. The reaction pressure does not significantly affect the conversion efficiency at 400 $^{\circ}$C, but rather slightly changes the composition of product [63]. At an operating pressure between 10 and 30 MPa at 400 $^{\circ}$C, a methanol to oil molar ratio of 3:1 to 9:1 and a residence time of 3 to 10 min, complete conversion (>99 %) while approximately 80 % ME content was found [54, 63].

### 2.4.2.3. Methanol to oil molar ratio

The transesterification reaction requires a stoichiometric methanol to oil molar ratio of 3:1, while the operating ratio varies from 3:1 to 42:1. From Table 2.2, a ME content of the FAME produced at 270 to 350 $^{\circ}$C was up to 95 % for a batch reactor and up to 85 % for a continuous flow reactor when a methanol to oil molar ratio of over 40:1 was employed. A high molar ratio of methanol increases the contact area and reduces the transition temperature (see Section 2.4.3.) [6].

Nevertheless, further increasing the methanol ratio above 50:1 yields no further benefits [11]. When a methanol to oil molar ratio of 6:1 to 9:1 at 400 to 450 °C is used, complete conversion can be achieved. Excess methanol is also consumed for other thermal reactions such as etherification of glycerol [63].

The relatively high methanol to oil molar ratio requires an enormous energy expense for recycling the excess methanol, as well as requiring a large volume of methanol within the recycle loop. In fact, energy plays an important role in the operating cost as well as the environmental load of biodiesel production with SCM. An LCA study revealed that biodiesel production by a single stage SCM transesterification consumes more energy in recycling the excess methanol than for feedstock pumping and reactor heating and also generates a significant environmental load [69]. Techniques to reduce the consumed energy for methanol recycle are urgently needed to develop practical green biodiesel production processes.

Diaz et al. introduced a medium pressure flash drum and heat pump to recover the excess methanol in biodiesel production by SCM at the methanol to oil molar ratio of 24:1 or 40:1 in their model-based cost minimization studies. The use of a heat pump significantly reduces the energy consumption and operating cost, rendering the operating costs at the methanol to oil molar ratio of 24:1 and a 40:1 to be only slightly different [59].

### 2.4.2.4. Reaction time

In general, the effect of the reaction time in a batch reactor can be studied and obtained simply by first heating the reactor to initiate the reaction, holding at this temperature for various times to allow the reaction to go to completion and then quenching the reactor to terminate the reaction. In contrast, the reaction time in a continuous reactor is estimated by the reactor volume over the volumetric flow rate and is influenced by a non-ideal flow behavior. The residence time is treated not as a single-value variable but rather is treated as an average value as shown in Table 2.2. The effect of reaction time will be discussed separately in the following section.

### 2.4.2.4.1. Batch reactor

The effect of reaction time on conversion efficiency in biodiesel production with SCM follows the general rate law. For instance, the ME content increases gradually with reaction time and then levels off when the maximum ME content or optimal point is achieved. The optimal reaction time varied between 4 to 30 min

The reactor heating and cooling rates need to be maximized for the best precision of reaction time measurement in batch reactor studies. For example, the accurate optimal reaction time obtained by Saka and Kusdiana [39], was by using the fastest heating rate (30 °C/s) and cooling rate (100 °C/s). For slow heating rate (0.33 °C/s), the optimal reaction time is lower than the actual value as the reaction can occur before the temperature set point is reached. On the other hand, during cooling, the reaction continues until the ambient temperature is reached. Saka and Kusdiana [6] used a molten tin bath as the heating medium whereas in other works, electrical heating was used. The difference in the heating source may affect the results.

The optimal reaction time, as assigned by the rate law, is a function of the temperature and concentration. Therefore, the optimal reaction time cannot significantly increase with the reactor volume in an isochoric system. However, the optimal reaction time in a larger batch reactor was observed to be higher than that of Saka and Kusdiana [6], probably because of some unconsidered effects, such as the degree of mixing intensity, as discussed in Section 2.4.2.5.

### 2.4.2.4.2. Continuous reactor (residence time)

Studies on the residence time in tubular reactors [40, 41] have employed the Equation (2.1):

$$\tau = \frac{V}{F_M \dfrac{\rho_M}{\rho_M'} + F_O \dfrac{\rho_O}{\rho_O'}} \tag{2.1}$$

Where $\tau$ is the residence time, $V$ is the reactor volume, $F$ is the volumetric flow rate at ambient conditions and $\dfrac{\rho}{\rho'}$ is the density ratio between the ambient and supercritical condition. The subscripts M and O refer to

methanol and vegetable oil, respectively. The density of SCM can be found from the literature [70], while the density of vegetable oil is assumed to be constant from ambient to system conditions.

The volumetric flow rate of a compressible fluid mixture depends on the mixture density, which is a function of pressure, temperature and composition. Therefore, changing the mole fraction as the reaction progresses and decreasing the pressure probably influences the volumetric flow rate in the isothermal system. It is clear that the mole fraction at the inlet and the outlet deviate largely with a declining methanol to oil molar ratio, as show in Table 2.3.

**Table 2.3** Molar ratio and mole fraction at the inlet and outlet of the tubular reactor, calculated by assuming 100% conversion at the outlet.

| | Molar ratio at inlet | | | | Molar ratio at outlet | | | |
|---|---|---|---|---|---|---|---|---|
| **MeOH:Oil** | **Methanol** | **Oil** | **FAMEs** | **Glycerol** | **Methanol** | **Oil** | **FAMEs** | **Glycerol** |
| High | 42 | 1 | 0 | 0 | 39 | 0 | 3 | 1 |
| Medium* | 24 | 1 | 0 | 0 | 21 | 0 | 3 | 1 |
| Low* | 6 | 1 | 0 | 0 | 3 | 0 | 3 | 1 |
| | Mole fraction at inlet | | | | Mole fraction at outlet | | | |
| **MeOH:Oil** | **Methanol** | **Oil** | **FAMEs** | **Glycerol** | **Methanol** | **Oil** | **FAMEs** | **Glycerol** |
| High | 0.98 | 0.02 | 0.00 | 0.00 | 0.91 | 0.00 | 0.07 | 0.02 |
| Medium* | 0.96 | 0.04 | 0.00 | 0.00 | 0.84 | 0.00 | 0.12 | 0.04 |
| Low* | 0.86 | 0.14 | 0.00 | 0.00 | 0.43 | 0.00 | 0.43 | 0.14 |

* *A small amount (0.1 mole per mole of methanol) of $CO_2$ was added as co-solvent but the $CO_2$ mole fraction is ignored for simplicity.*

The global fluid density, as represented by the summation of the methanol and oil densities, is not appropriate at supercritical conditions. However, Equation (2.1) could be an acceptable approximation for a methanol to oil molar ratio of 42:1 to avoid the otherwise complicated calculation, because the fluid properties deviate slightly from those of pure methanol. The residence time estimation method has to be modified for varying volumetric flow rates

because it becomes important as the methanol to oil molar ratio is reduced as discussed in Section 2.4.4.

Equation (2.1) has been found to be adequate to estimate the residence time at high methanol to oil molar ratios (40:1 to 42:1) [9, 10]. The residence time significantly effects the conversion to FAMEs at temperatures higher than 280 $^{\circ}$C as the rate constant increases sharply beyond this temperature. For tubular reactor studies, Bunyakiat et al. [9] showed that the residence time impacts the conversion efficiency largely at temperatures higher than 300 $^{\circ}$C, a finding which agrees with the work of Minami and Saka [10] who studied conditions at ~20 MPa and a 42:1 methanol to oil molar ratio. As for mixed flow and tubular reactors in series, He et al. [11] reported that the conversion increased strongly with a residence time above 280 $^{\circ}$C, at 32 MPa and a 40:1 methanol to oil molar ratio. However, they did not present the detailed calculation of the residence time. The effect of residence time is related directly to the chemical kinetics of transesterification as illustrated in Section 2.4.2.

### 2.4.2.5. Mixing intensity and dispersion in tubular reactor

The effect of the mixing intensity has not been investigated directly according to the information summarized in Table 2.2. A high mixing intensity will enhance the rate of heat and mass transfer in the reactor and this will reflects upon the reaction time required for the maximum conversion.

With respect to batch reactors, the highest conversions can be achieved in a short time by shaking the reactor as the reaction progresses. For instance, the highest ME content of >95 % at ~ 4 min was found with shaking [6], while in similar studies but using a slightly different feedstock and elevated temperatures revealed high ME content but at ~30 min [66, 67], while in stirred batch reactors (250 mL) with a somewhat poor mixing behavior, the highest ME content was found after 30 min reaction time [53, 68]. In contrast, using a large reactor without shaking, Demirbas reported a high conversion to FAME of 95 % in ~ 5 to 11 min [7]. This seemingly conflicting result should be investigated further by varying the mixing intensity in a batch reactor equipped with a stirring mechanism.

For a tubular flow reactor, the reaction mixture is largely mixed by the fluid shear force that depends on flow patterns. which can be identified by the Reynolds number. At a high methanol to oil molar ratio, the Reynolds number calculation might be simplified by using the properties of SCM only, and is estimated by Equation (2.2).

$$\text{Re} = \frac{D(v\rho)}{\mu} \tag{2.2}$$

where D, $(v\rho)$ and $\mu$ are the tube inside diameter, total mass flux and dynamic viscosity, respectively.

Busto et al. [12] introduced an axial Péclet number, calculated by Equation (2.3), to describe the performance of the tubular reactor for biodiesel production with the SCM:

$$\text{Pe} = \frac{vL}{D_M} \tag{2.3}$$

where $v$, L and $D_M$ are the fluid velocity, reactor length and molecular diffusivity, respectively. For estimation of the fluid velocity, the density of fluid was assumed to be pure methanol. They assumed that the molecular diffusivity of SCM was $5 \times 10^{-7}$ $m^2$/s. The Reynolds and Péclet number are calculated, base on the obtained from literatures, and are summarized in Table 2.4.

Some assumptions were made in calculating the results shown in Table 2.4. The mass flow rate was evaluated by the residence time and the methanol to oil molar ratio used was that at optimal conditions, except for the work of Bunyakiat et al. [9], where the data was available in our research group. The density of methanol, rapeseed and soybean oil at ambient conditions were assumed to be 792, 920 and 905 $kg/m^3$ respectively. Finally, He et al. [11] employed a gradual heating technique and, therefore, the density and dynamic viscosity of methanol were estimated from the average temperature between the inlet and outlet of the reactor.

**Table 2.4** Optimal condition, reactor design, Reynolds and axial Péclet number of the continuous biodiesel production with SCM in a tubular reactor.

| Parameters | Bunyakiat et al. [9] | Minami and Saka [10] | He et al. [11] |
|---|---|---|---|
| Temperature ($^{o}$C) | 350 | 350 | 340 |
| Pressure (MPa) | 19 | 20 | 32 |
| Methanol to oil molar ratio | 42:1 | 42:1 | 40:1 |
| Reactor inside diameter (m) | $7.75 \times 10^{-3}$ | $1.20 \times 10^{-3**}$ | $4.00 \times 10^{-3}$ |
| Reactor length (m) | 5.50 | $80.00^{**}$ | 6.00 |
| Mass flow rate (kg/s) | $7.97 \times 10^{-5}$ | $1.43 \times 10^{-5}$ | $2.42 \times 10^{-5}$ |
| Cross sectional area ($m^2$)$^*$ | $4.71 \times 10^{-5}$ | $1.13 \times 10^{-6}$ | $1.26 \times 10^{-5}$ |
| Total mass flux (kg/m$^2$ s)$^*$ | 1.69 | 12.69 | 1.93 |
| Fluid dynamic viscosity (kg/m s)$^*$ | $3.09 \times 10^{-5}$ | $3.22 \times 10^{-5}$ | $2.48 \times 10^{-5}$ |
| Fluid density (kg/m$^3$)$^*$ | 188.80 | 197.53 | 541.19 |
| Fluid average velocity (m/s)$^*$ | $8.96 \times 10^{-3}$ | $6.42 \times 10^{-2}$ | $3.56 \times 10^{-3}$ |
| Reynolds number$^*$ | 424 | 473 | 310 |
| Péclet number$^*$ | $9.85 \times 10^4$ | $1.03 \times 10^7$ | $4.27 \times 10^4$ |

*As calculated by the authors* **Values from personal communication*

The performance of the FAME production with SCM in the tubular reactors can be interpreted via the Reynolds and Péclet numbers (Table 2.4), where the calculation of all reactors shows similar results. The Reynolds number indicates the effect of the mixing intensity, and the Péclet number indicates the effect of dispersion. All reactors are in a laminar regime at optimal conditions, so that, the maximum conversion is found at higher residence time than the reaction time in a batch reactor due to somewhat poor mixing intensity. All reactors have a Péclet number of over 1,000 and so their behavior are somewhat close to that of an ideal plug flow reactor and the effect of dispersion or back-mixing is diminished [12].

The performance of tubular reactors can be improved by increasing the mixing intensity; however, enhancing either the mass flux or the reactor diameter to maximize the Reynolds number is not an attractive idea. Both terms cannot be

increased simultaneously for the synergistic effect because the mass flux is inversely related to internal diameter at a fixed mass flow rate.

A better mixing intensity in the tubular reactor for biodiesel production with SCM can be achieved by other operations. The reduction of the fluid viscosity by adding some co-solvents, such as $CO_2$ or propane, can increase the Reynolds number. On the other hand, the addition of inert packing materials or static mixers into the tubular reactor can also enhance the mixing intensity. However, for tubular reactors with a small diameter, a static mixer is more interesting than packing material to avoid reactor channeling and plugging. In conclusion, further study into the effect of mixing intensity will be required to improve the efficiency of the supercritical process.

### 2.4.3. Chemical kinetics of biodiesel production with SCM

Transesterification rate equations were first proposed by Diasakou et al. [43] in 1998 and simplified by Kusdiana and Saka [39] in 2001. Since excess methanol is used, the methanol concentration is assumed to be constant during the reaction. Therefore, the simplified equation is pseudo-first order with respect to triglyceride concentration alone. The reaction rate constants for rapeseed oil transesterification at temperatures from 200 $^{\circ}$C to 487 $^{\circ}$C increase sharply at 280 $^{\circ}$C [39]. Hegel et al. [56] found similar result using soybean oil and explained that the sharp increase was due to a phase transition from two-phase to single-phase. The evaluation of soybean oil transesterification over the temperature range of 210 $^{\circ}$C to 280 $^{\circ}$C shows that the rate constants increase sharply at the critical temperature of methanol (239 $^{\circ}$C) [61]. On the other hand, rate constants of several vegetable oils  fall onto one straight line from subcritical to critical and supercritical temperatures of methanol (200 to 400 $^{\circ}$C) [66, 67, 71]. To extract more information, an overlay of Arrhenius' plot of various vegetable oils is shown in Figure 2.4 and the rate constants ($k$), pre-exponential factor ($k_0$) and activation energy ($E_a$) are summarized in Table 2.5.
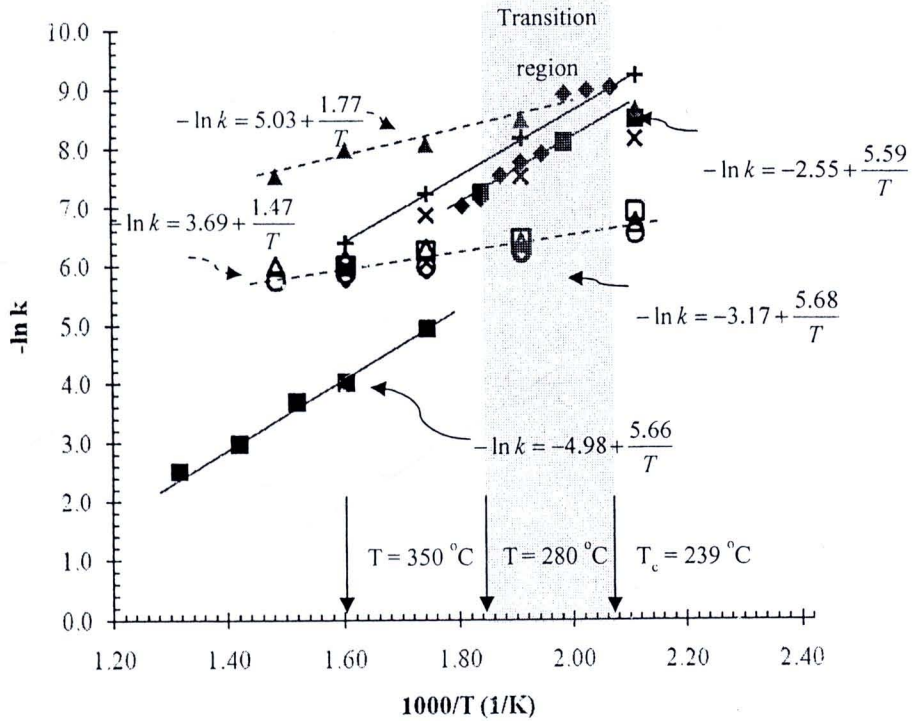
**Figure 2.4.** Overlay Arrhenius plot of (■) Rapeseed [39], (♦) Soybean oil [61], (▲) Sunflower [66], (□) Palm, (△) Groundnut, (O) *P. pinnata* and (◊) *J. curcas* [67] and (×) Castor and (+) Linseed oil [71] transesterification in the SCM reaction.

According to Figure 2.4, the slopes of the lines for each vegetable oil with SCM have different temperature sensitivities. For example, the rate constants of rapeseed, soybean, castor and linseed oils depend more strongly on the temperature than that for sunflower, palm, groundnut, *P. pinnata* and *J. curcas* oils.

He et al. [61] studies the effect of pressure on the conversion in the transition region (239 to 280 °C) and modifies the Arrhenius Equation by including the pressure term as shown in Equation (2.4):

$$k = k_0 \exp\left(-\frac{E^{\neq} + P\Delta V^{\neq}}{RT}\right) \tag{2.4}$$

where $k$, $k_0$, $E^{\neq}$, $\Delta V^{\neq}$, $P$, $R$ and $T$ are the rate constant, pre-exponential factor, activation energy, reaction activation volume, pressure, universal gas constant and temperature, respectively. The numerator in the parentheses ($E^{\neq} + P\Delta V^{\neq}$) implies the apparent activation energy of the reaction. From their experimental results [61], the product of activation volume and pressure ($P\Delta V^{\neq}$) contributes to approximately 10% of

the apparent activation energy at pressures above 20 MPa. The modified Arrhenius Equation provides a better estimate of the transesterification rate constant with SCM.

**Table 2.5** Reactions rate constant (k) as linear function of temperature, pre-exponential factor ($k_0$) and activation energy ($E_a$)

| Researchers | Oil type | Investigated conditions | | | $\ln k = \ln k_0 - \dfrac{E_a}{RT}$ | | $E_a$ |
| | | T (°C) | P (MPa) | MeOH to oil molar ratio | $k_0$ (s$^{-1}$) | $\dfrac{E_a}{R}$ (K) | (kJ/mol) |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Kusdiana and Saka [39] | Rapeseed | 200 to 270 | 7 to 12 | 42:1 | 0.30 | 4.63 | 38.48 |
| | | 300 to 487 | 19 to 105 | | 6.87E-3 | 5.66 | 47.09 |
| He et al. [61] | Soybean | 210 to 230 | 28 | 42:1 | 514.96 | 1.35 | 11.22 |
| | | 240 to 280 | | | 5.85E-3 | 6.72 | 55.91 |
| Mardas et al. [66] | Sunflower | 200 to 400 | 20 | 40:1 | 0.39 | 1.77 | 14.74 |
| Rathone et al. [67] | Palm | 200 to 400 | 20 | 40:1 – | 2.60 | 1.80 | 14.94 |
| | Groundnut | | | 50:1 | 1.30 | 1.27 | 10.54 |
| | P. Pinnata | | | | 0.82 | 1.14 | 9.45 |
| | J. Curcas | | | | 1.68 | 1.37 | 11.37 |
| Verma et al. [71] | Castor | 200 to 350 | 20 | 40:1 | 0.54 | 4.21 | 35.00 |
| | Linseed | | | | 7.80E-2 | 5.59 | 46.50 |

Song et al. [72] studied the chemical kinetics of transesterification of refined, bleached and deodorized (RBD) palm oil with SCM. The rate constant was found by an integral method or numerical fitting of the experimental data to the kinetic model. However, they found that the second order rate Equation, with respect to both the concentration of oil and methanol, fit the data almost as well as the first order rate Equation. The rate constants that were predicted from the subcritical to the supercritical region were somewhat different from earlier works [39, 61]. However, the apparent activation energy of the transesterification reaction was nearly the same as that of Diasakou et al. [43] and also obeyed the second order model. Their kinetic model had a coefficient of determination of $R^2 = 0.9578$ and was able to predict the observed

conversion well. This model seems to be more suitable than the pseudo-first order model at a low methanol to oil molar ratio because the concentration of methanol is included in the model.

### 2.4.4. Phase behavior and binary vapor-liquid equilibrium (VLE) of biodiesel production with SCM

The phase behavior in biodiesel production with SCM has gained much interest due to the unusual behavior of the rate constant that increases with increasing pressure and the fact that the required optimal operating parameters can become milder with the addition of co-solvents.

Early works on the transesterification with SCM were based on the supercritical conditions of methanol, under which a single-phase mixture was assumed. However, more recent works on phase behavior, performed in a high-pressure view cell reveal that complete reaction can be obtained in either a single-phase supercritical or a two-phase VL region [56, 57]. For instance, the reaction between soybean oil and methanol at 300 °C and 9.6 MPa is observed as a two-phase VL, resulting in biodiesel with a ME content of 99% [56], while a single-phase supercritical mixture is observed beyond 350 °C and 10.0 MPa, with 99% triglyceride conversion [54].

Transition temperature of VLL to VL equilibria decrease with increasing methanol to oil molar ratios [54, 56]. For example, Anitescu et al. reported [54] that reaction mixtures are partially miscible up to temperature close to 350 °C at a methanol to oil molar ratio of 24:1, while Hegel et al. [48] observed that the two liquid phases become completely miscible at 180 °C and 157 °C with a methanol to oil molar ratio of 40:1 and 65:1, respectively.

Transition from a two-phase VL system to a one-phase supercritical system is found to occur near the critical temperature (T$_c$) of the mixture, as calculated from the methanol to oil molar ratio and co-solvents [54]. For instance, the critical temperature of the mixture predicted by Group Contribution with Association (GCA) EOS was 377 °C at a methanol to oil molar ratio of 24:1 [56] where the transition temperature observed is higher than 350 °C [54]. Marulanda et al. [65] also reported that a critical point of

triglyceride + methanol mixture has $T_c$ of 300 and 400 $^\circ$C at molar ratio of 42:1 and 6:1, respectively which corresponds with the optimal conditions for high conversion.

The addition of propane reduces the transition temperature of the two-phase VL to a one-phase supercritical. For example, the transition temperature at a methanol to oil molar ratio of 65:1 can be reduced from 315 $^\circ$C (predicted $T_c$ of 327 $^\circ$C) to 243 $^\circ$C (predicted $T_c$ of 247 $^\circ$C) when 24% by weight of propane is added to the reaction [56].

In actuality, the vapor-liquid equilibrium (VLE) of biodiesel production with SCM is complicated because the system is not only a multi-component one, but also is under supercritical conditions [73]. A biodiesel system can consist of 5 to 8 types of FAMEs, reaction intermediates such as mono- and diglycerides, and a combination of FFAs in the triglyceride feedstock.

Binary systems have been investigated in some fundamental studies on the phase behavior in SCM, of major components and methanol and correlated with particular thermodynamic models summarized in Table 2.6, with the binary interaction parameters for the van der Waals (VdW) mixing rule being given in Table 2.7.

The binary VLE of triolein + methanol [19] and sunflower oil + methanol [14] were investigated at temperatures below the critical point of methanol so as to avoid the effects of interference due to composition changes as the transesterification reaction progressed. Since the exact molecular structure of sunflower oil is unknown, the critical properties of triolein are assumed, as estimated by Gani et al. [74, 75]. The Peng–Robinson (PR EOS) and the VdW mixing rule models have been tested on the sunflower oil + methanol system and give approximately 1 to 2 % relative deviation at temperatures below 220 $^\circ$C. Therefore, it can be deduced that the PR EOS and VdW mixing rules can be used to predict the triolein + methanol system within the temperature range of 60 to 220 $^\circ$C, due to the agreement between these two reports [14, 19].

**Table 2.6** Studies on the VLE of biodiesel production with SCM summary.

| Researchers | Binary system | Measurement range | | Proposed thermodynamic model |
|---|---|---|---|---|
| | | T ($^\circ$C) | P (MPa) | |
| Tang et al. [19] | Triolein + MeOH | 60 – 190 | 6.00 – 10.00 | PR EOS and VdW mixing rule |
| Glišic et al. [14] | Sunflower oil + MeOH | 200 – 230 | 2.90 – 5.60 | RK-ASPEN EOS and VdW mixing rule |
| Shimoyama et al. [18] | Methyl myristate + MeOH Methyl laureate + MeOH | 220 – 270 | 2.16 – 8.49 | PRASOG model |
| Fang et al. [55] | FAMEs C18 mixture + MeOH | 250 – 300 | 2.45 – 11.45 | PR EOS and VdW mixing rule |
| Shimoyama et al. [16] | Methyl myristate + MeOH Methyl laureate + MeOH | 220 – 270 | 2.16 – 8.49 | SRK, WS mixing rule and COSMO-SAC theory |
| Shimoyama et al. [17] | Glycerol + MeOH | 220 – 300 | 2.27 – 8.78 | PR-SV EOS and VdW mixing rule |
| Hegel et al. [56, 57] | Methyl oleate + Glycerol + MeOH + Propane | 270 – 315 | 7.00 – 21.1 | GCA EOS model |
| Glišic et al. [15] | Sunflower oil + MeOH | 150 – 210 | 1.1 – 4.5 | RK-ASPEN EOS and VdW mixing rule |

Flash calculations, using the Redlich-Kwong-ASPEN (RK-ASPEN) EOS and VdW mixing rules with optimized binary interactions [14], of the triolein + methanol system have been used for methanol to oil molar ratios of 42:1 to clarify the role of phase behavior on the rate constants. From the calculations, one can infer that a high rate of reaction takes place only in the vapor phase at low density, whereas in the liquid phase a low reaction rate mainly occurs. Thus, it can be concluded that biodiesel production with SCM at a methanol to oil molar ratio of 42:1 is a low-density vapor phase reaction.

**Table 2.7** Binary interaction parameters of the VdW mixing rule which correspond with the thermodynamic model in Table 2.6.

| Researchers | EOS | Binary system | Binary interaction parameter | |
| --- | --- | --- | --- | --- |
| | | | $k_{ij}$ | $l_{ij}$ |
| Tang et al. [19] | PR | Triolein + MeOH | 0.0289 | -0.0109 |
| Glišic et al. [14] | RK-ASPEN | Sunflower oil + MeOH | $\dfrac{-2.0000T(K)}{1000} + 0.6799$ | $\dfrac{1.7589T(K)}{1000} - 1.2175$ |
| Fang et al. [55] | PR | Methyl C18 esters mixture + MeOH | $\dfrac{-261.7100}{T(K)} + 0.6069$ | 0.1450 |
| Shimoyama et al. [18] | PR-SV | Glycerol + MeOH | $\dfrac{176.7000}{T(K)} - 0.3977$ | -0.0990 |

The binary VLE of methyl laurate ($C_{12}$) + methanol and methyl myristate ($C_{14}$) + methanol is found to correlate with the mole fraction of each phase using the Peng–Robinson Stryjek–Vera (PR-SV) EOS and ASOG mixing rule (PRASOG model) [18]. The FAMEs C18 mixture + methanol [55] system have also been studied in a similar apparatus with the classical PR EOS and VdW mixing rules to model the system. The C18-methyl ester mixture + methanol system obeys the PR EOS and VdW mixing rule as equally well as did the triolein + methanol system, although the temperature range between the two systems was different.

The phase behavior of soybean oil + methanol + propane has been investigated and modeled by Group Contribution with Association (GCA) EOS [56, 57]. Unlike the previous works, which were aimed to fit the model to the composition of each phase, this work calculated the phase envelope of the final reaction mixture (methyl oleate + methanol + glycerol + propane) to study the role of phase behavior on conversion. The results show that the reaction mixture possibly becomes a single phase at lower temperatures by adding propane as co-solvent.

Studies on the VLE of biodiesel production with SCM shows that the initial (triglyceride + methanol) and final (FAMEs + glycerol + methanol) reacting systems follow different thermodynamic models, and this is probably because of the changing polarity of the mixing fluids and that the polarity of the mixed fluids affects the

predictive ability of the model. For instance, the COSMO-SAC model is more predictive than the UNIFAC model for the FAMEs + methanol system [16]. Therefore, it should be noted that no single thermodynamic model is available that can correlate the VLE of both the initial and the final states of the reaction system.

The VLE of sunflower oil + methanol was observed in high-pressure view cell and simulated composition profile during the reaction took place by ASPEN PLUS® software ® at 210 °C, 4.5 MPa and 42:1 methanol to oil molar ratio [15]. The mixture at the beginning of reaction is the equilibria of two liquids (methanol rich phase and oil phase) and one vapor phase (pure methanol). After 10 hours the reaction was complete and obtained single phase mixture of 52.3, 42.4 and 5.3 % by weight of methanol, FAMEs and glycerol, respectively. The composition profile in each phase during the reaction took place was predicted well by thermodynamic model which proposed in their previous work [14].

## 2.4.5. Innovative technologies for milder operating parameters in biodiesel production with SCM

Elevated operating temperature, pressure and methanol to oil molar ratio are the primary obstacles for commercial scale biodiesel production with SCM, as mentioned in the introduction. The demonstrated techniques for lowering those operating parameters and the new parameters are summarized in Tables 2.8 and 2.9, respectively. The demonstrated techniques can be divided into three groups: (i) the addition of co-solvents, (ii) the addition of catalysts and (iii) the modification of the SCM reaction.

### 2.4.5.1. Addition of co-solvents

The addition of co-solvents can decrease the optimal operating parameters i.e. temperature, pressure and methanol to oil molar ratio because the co-solvents assist the VLL methanol-oil mixture transition to VL and become a single phase. Carbon dioxide is a good solvent for small and moderate sized organic molecules, while propane is an excellent solvent for vegetable oils. Small amounts of co-solvents, for example, 0.10 mole of $CO_2$ or 0.05 mole of propane per mole of methanol are typically used [8, 47] resulting in high conversion at relatively low

operating parameters because the co-solvents increase the homogeneity of the system and do not affect the reaction mechanism.

**Table 2.8** Demonstrated techniques for reducing the operating parameters of biodiesel production with SCM.

| Researchers | Demonstrated technique | Lowered operating parameter |
| --- | --- | --- |
| Cao et al. [47] | Using propane as a co-solvent | T, P, M and t |
| Han et al. [8] | Using $CO_2$ as a co-solvent | T, P, M and t |
| Anitescu et al. [54] | Using $CO_2$ as a co-solvent | P, M and t |
| Wang et al. [48] | Using 0.5% (w/v) NaOH as a catalyst | T, P, M and t |
| Yin et al. [51] | Using 0.1% (w/v) KOH as a catalyst | T, P, MeOH and t |
| Wang et al. [50] | Using 0.2% (w/v) $H_3PO_4$ as a catalyst | T, P and t |
| Demirbas [49] | Using 3% (w/v) CaO as a catalyst | T, P and t |
| Wang and Yang [52] | Using 3% (w/v) Nano-MgO as a catalyst | T, P, M and t |
| Minami and Saka [10] | Using two-step technology | T, P, MeOH and t |
| D'Ippolito et al. [13] | Using separated two tubular reactors | T, P and M |
| Marulanda et al. [64, 65] | Using high operating temperature | P, M and t |

*T: temperature; P: pressure; M: methanol to oil molar ratio; t: reaction time*

Anitescu et al. [54] suggested that biodiesel production with SCM should be carried out within the temperature range of 350 to 400 $^\circ$C, a pressure range of 10.0 to 30.0 MPa and a residence time of 2 to 3 minwith $CO_2$ as co-solvent. Under these conditions, they report that the decomposition (or dehydration) of glycerol takes place and the transesterification reaction is shifted forward. The authors claim that the inert co-solvent (e.g., $CO_2$) used to enhance the oil-alcohol miscibility may also act as diluents to slow down the FAME thermal decomposition. Since the addition of $CO_2$ increases the oil-methanol miscibility, the methanol to oil molar ratio can be reduced to 6:1 while maintaining nearly complete conversion. Additionally, they state that an enormous excess of methanol is not necessary within the temperature

range of 350 – 400 °C as the reaction occurs instantly at the inlet and then forms a homogeneous phase and reacts to completion shortly afterwards.

**Table 2.9** New operating parameters of biodiesel production with SCM by the techniques outlined in Table 2.8.

| Researchers | T (°C) | P (MPa) | MeOH to Oil molar ratio | Reaction time (min) | Oil type | Reactor type | ME content/ Conversion (%) |
|---|---|---|---|---|---|---|---|
| Cao et al. [47] | 280 | 12.8 | 24:1 | 10 | Soybean | 250-mL BRs | 98% ME content |
| Han et al. [8] | 280 | 14.3 | 24.1 | 10 | Soybean | 250-mL BRs | 98% ME content |
| Anitescu et al. [54] | 400 | 20.0 | 6:1 | 1.6 | Soybean | 7-mL TR | ~98% Conversion |
| Wang et al. [48] | 250 | 6.0 | 24:1 | 10 | Rapeseed | 200-mL BRs | 97% ME content |
| Yin et al. [51] | 160 | 10.0 | 24:1 | 10 | Soybean | 250-mL BRs | 98% ME content |
| Wang et al. [50] | 310 | 13.0 | 40:1 | 12 | Soybean | TR | 96% ME content |
| Demirbas [49] | 252 | N/R | 41:1 | 6 | Sunflower | 100-mL BR | 98% ME content |
| Wang and Yang [52] | 250 | 24.0 | 36:1 | 10 | Soybean | 200-mL BRs | 96% ME content |
| Minami and Saka [10] | 280 | 20.0 | 24:1 | 30 | Rapeseed | 200-mL TR | 95% ME content |
| D'Ippolito et al. [13] | 290 | 14.0 | 10:1 | N/R | N/R | TR | ~99% Conversion |
| Marulanda et al. [64, 65] | 400 | 10.0 | 6:1 to 9:1 | 4 | Soybean | TR | ~99% Conversion |

*N/R: Not Reported; BR: Batch Reactor; BRsh: Batch Reactor with shaking, BRs: Batch Reactor with stirrer, TR: Tubular Reactor, MFR: Mixed Flow Reactor*
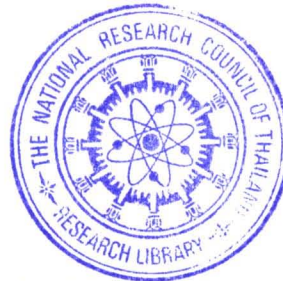
Imahara et al. [76] hypothesized that the addition of $CO_2$ improves the conversion in a batch reactor because the system pressure is enhanced, since the pressure of the $CO_2$ containing system is higher than the base system, which consisted of methanol and vegetable oil in the isothermal reactor. The hypothesis was tested under mild conditions of 270 $^\circ$C and 10.8 MPa for a slow reaction to clarify the effect of adding $CO_2$ on the conversion. However, it was found that the addition of $CO_2$ did not increase the ME content significantly in either batch or continuous reactors in a quasi-constant pressure. Moreover, an excess amount of $CO_2$ reduces the ME content due to the dilution and obstruction of the reactants.

Other co-solvents, such as $N_2$, hexane and THF, are presently being investigated for their effect on biodiesel production with SCM, but to date, the co-solvents evaluated do not significantly increase the conversion, specifically at high methanol to oil molar ratios where, for example, Imahara et al. [76] reported no benefit for a methanol to oil molar ratio of 42:1, but could not draw a conclusion for lower methanol to oil molar ratios. However, Anitescu et al. [54] observed a two-phase mixture of methanol and soybean oil at 400 $^\circ$C and 20.0 MPa with a 6:1 methanol to oil molar ratio, which merged into a single phase with almost 100% conversion by the addition of 4% mole of $CO_2$ in methanol. In conclusion, additional studies on the effect of co-solvents at low methanol to oil molar ratios are necessary to clarify the role of co-solvents in biodiesel production with SCM.

In terms of product purification and co-solvent recycling, gaseous co-solvents, such as $CO_2$ and propane, are more attractive than liquid co-solvents. Only a small amount of gaseous co-solvents (0.1 mole per mole of methanol) are required for milder operating parameters, and these can be easily separated from the final product by expansion. While liquid co-solvents and methanol can be simultaneously recovered by distillation, as their boiling points are close to that of methanol (65 $^\circ$C, 66 $^\circ$C and 69 $^\circ$C for methanol, THF and $n$-hexane respectively), this requires an additional energy input. On the one hand, hexane is immiscible in methanol, thus phase separation is necessary for hexane recycling. On the other hand, THF is completely miscible in methanol and improves the solubility of methanol in vegetable oils and forms a single phase mixture of vegetable oil/methanol/THF at

ambient temperature and pressure [77, 78]. Such phase behavior is beneficial as the methanol/THF mixture can be recycled directly, with only a small amount of methanol addition being required to replace that lost in each cycle. In conclusion, the addition of liquid co-solvents requires additional separation steps, while the addition of gaseous co-solvents requires only a few additional separation steps that offset its strong point in biodiesel production with SCM.

### 2.4.5.2. The addition of catalysts to the SCM reaction

By adding the appropriate catalysts, it has been shown that both the optimal temperature and reaction time become lower, but the methanol to oil molar ratio could not be reduced. For example, the addition of nano-MgO increases the rate constant some 11.2 fold from $4.20 \times 10^{-4}$ s$^{-1}$ to $4.72 \times 10^{-3}$ s$^{-1}$ at a temperature of 250 $^{\circ}$C, and transesterification with nano-MgO catalysts reach the point of maximum conversion faster than that in the absence of the catalyst at low temperatures [52].

Wang et al. [48] studied the reaction of crude rapeseed oil in the SCM reaction with NaOH as a catalyst and reported that soap formation does not take place at supercritical conditions and that the rate of reaction is faster than that in the catalyst free condition. The crude rapeseed oil employed in their work had a 1% (w/w) moisture content and an unknown FFA content. In fact, the reaction between NaOH and the FFA occurs rapidly due to the strong opposite charges of both species. Thus, it can be deduced that the reaction between the SCM and the FFAs is possibly faster than that between the strong base and weak acid reaction, and as a result, the soap formation did not occur in the SCM reaction. When 0.1% (w/v) KOH was added [51], the reaction of refined soybean oil went to completion under milder conditions, as expected. On the other hand, in the investigation into the reaction of acidic and refined soybean oil with SCM, with and without the addition of $H_3PO_4$ as the catalyst, the acidic soybean oil provides a higher ME content than the refined oil, as the FFAs probably act as catalyst [50]. The addition of $H_3PO_4$ accelerates the reaction markedly because it is a stronger acid than the FFAs. Therefore, the presence of a weak acid in the feedstock, or the addition of $H_3PO_4$, improves the ME content in the SCM reaction under these conditions.

In general, the addition of homogeneous catalysts to the SCM reaction is not an attractive idea, despite the faster resultant rate of reaction than the catalyst free process, because of the problems of subsequent product purification and waste management that are seen in the conventional process.

Heterogeneous catalysts, such as nano-MgO and CaO, have been applied for biodiesel production with SCM [49, 52], where maximum conversion is achieved at relatively low temperatures and pressures compared with catalyst-free conditions. The addition of heterogeneous catalysts to the SCM reaction is an attractive idea to lower the operating parameters, since the subsequent catalyst separation is easier and can be recycled, unlike the homogeneous catalysts. In conclusion, further studies on heterogeneous catalysts in the SCM reaction, such as the effect of water and FFAs, and the durability and reusability of catalysts, would be very interesting.

### 2.4.5.3. Modification of the SCM reaction

The first modification of the SCM reaction, namely the two-step or the Saka-Dadan process was presented by Minami and Saka. [10] In the first step, vegetable oils are hydrolyzed in subcritical water at 280 $^\circ$C and 20.0 MPa to obtain fatty acid products. Then, glycerol and water are removed from the fatty acid products in a high-pressure phase separator. In the second step, the fatty acids are esterified in SCM at 280 $^\circ$C and 20.0 MPa to biodiesel.

The two-step process reduces the harsh optimal operating parameters successfully due to several points. First, the hydrolysis reaction does not need to go to completion because all the glycerides (mono-, di- and tri-glycerides) are converted to FAMEs in the next step. Second, mono- and di-glycerides have a higher reactivity than the triglyceride and so, these undergo almost complete reaction. Third, the esterification and transesterification reactions in the SCM reaction are driven forward as a result of the removal of the by-products (both water and glycerol). Fourth, the fatty acids have a somewhat better solubility in the SCM because they are relatively smaller molecules with a higher polarity than the triglyceride. Finally, Minami and Saka reported that the rate of the esterification reaction is enhanced since fatty acids act as acidic catalysts [10].

However, against the above is that the two-step process is more complicated than the single-step process, especially from the point of view of the process design, where it requires both more design and operating skills. The process has high-pressure reactors that connect in series with a high-pressure water-glycerol-FFA phase separator. Furthermore, the sweet water (aqueous solution of glycerol) stream, which is contaminated by trace amounts of FFAs, requires more separation units to manage. For instance, the distillation tower is the simplest separation unit for handling the sweet water, but consumes a large amount of energy to operate, being somewhat the same as in the case of methanol recycling.

The second modification of the SCM reaction, the dual-reactor process, was introduced by D'Ippolito et al. [13], who suggested the technique of employing two reactors with intermediate glycerol removal to lower the operating parameters. This technique has been studied in biodiesel production by homogeneous, heterogeneous and enzyme catalytic systems [79-81] . Computer simulation shows that by using this technique, the methanol to oil molar ratio and pressure can be reduced from 42:1 to 10:1 and from 14.0 to 10.0 MPa, respectively, but the temperature cannot be significantly reduced without loss of transesterification efficiency. These authors suggest that approximately 75% of the conversion can be achieved in the first reactor and that the reaction proceeds to completion in the next reactor. Although the dual-reactor process can significantly improve the economical feasibility of biodiesel production with SCM in computer simulations, it should be noted that the optimal operating parameters from simulation results were low and, this means that some experimental verification is still required.

The third modification of the SCM reaction was the increasing of operating temperature to 400 to 450 °C by Marulanda et al [64, 65]. The operating pressure, methanol to oil molar ratio and reaction time for complete conversion were reduced to values of 10.0 MPa, 6:1 and 4 min, respectively. Since the critical point of mixture depend on the methanol to oil molar ratio as mention in Section 2.4.4, the reaction mixture at 6:1 methanol to oil molar ratio can perform in single phase at 400 °C effectively.

According to the reactions of vegetable oil with SCM above 400 °C, the UFA is partially consumed by thermal degradation then the oxidation resistance or storage stability of the biodiesel is enhanced. Marulanda et al. [64, 65] reported that thermal degradation at 400 °C simultaneously converts UFA esters, triglyceride and glycerol to oxygenated liquid fuel with triglyceride conversion up to 99.5 % and without gaseous product loss. In addition, glycerol dehydration not only increases the fuel yield by up to 10 %, but also reduces the amount of glycerol by-products [82]. Given that the price of glycerol decreased in price by 1/10th of its value from 2004 to 2006 [83], the reduction in glycerol yield will have no detrimental consequence. Rather, the simultaneous conversion of glycerol to liquid fuel is an alternative option will increase the profitability of biodiesel production with SCM. Furthermore, the transesterification with SCM at 400 to 450 °C reduces the required reaction time by significantly enhancing the chemical kinetics of the transesterification and other side-reactions. The reactions of vegetable oil with SCM at 400 to 450 °C illustrate several advantages for biodiesel production with SCM, such as improvement of fuel properties, conversion of glycerol to liquid fuel and acceleration of the reaction kinetics.

Triglycerides conversion to biodiesel with SCM at 400 to 450 °C might ultimately lead to a biodiesel product that fails to meet the designated International standard (EN14214) as its ME content is less than 96.5 %. However, such a biodiesel product might be considered as an alternative biofuel that would require further studies on engine testing and fuel properties itself [63].

## 2.5. Literature reviews

Diasakou and coworkers studied on the thermal non-catalytic transesterification of soybean oil with methanol [43]. Experiments were carried out at temperature of 220 and 235°C, initial pressure of 5.5 and 6.2 MPa and methanol to oil molar ratio of 6:1 to 27:1 in a Parr reactor model 4560. After the reaction was finished, the samples withdrawn from the reactor were rapidly cooled and stored about 24 hours, a spontaneous phase separation occurred. The lower, heavy glycerol phase was glass clear, and the top, ester phase, were obtained. The ester phase was washed four times with water at 30 °C to
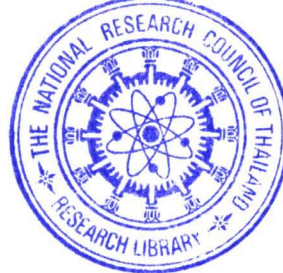
remove the possible traces of alcohol and glycerol and then analyzed. The samples were analyzed by thin layer chromatograph fitted with a flame ionization detector (TLC/FID). A reaction mechanism was proposed as a first order irreversible reaction and a corresponding kinetic model had fitted with the experimental data. The rate constants of the kinetic model were determined. It is observed that ME content has surpassed 85 wt% after 10 h reaction time at 235°C and 67 wt% after 8 h at 220°C.

Saka and Kusdiana investigated transesterification reaction of rapeseed oil with SCM [6]. The experiment was carried out in a 5-mL batch reactor made of Inconel-625 at temperature of 350 and 400 °C, pressure of 45 to 65 MPa, and with methanol to oil molar ratio of 42:1. The reactor was charged with a given amount of rapeseed oil (2.00 g) and methanol (3.36 g). Then, the reactor was shaken and quickly immersed into the molten tin bath at 350 or 400 °C, and kept for a set time (10 to 240 seconds). When the set time was achieved, the reactor was quenched in a water bath to stop the reaction. The content in the reactor was then allowed to settle for phase separation. The upper and lower portions were analyzed by HPLC. The lower portion was glycerol by comparing with standard glycerol chromatogram, and the upper portion was methyl ester. From the result, the optimal conditions found were temperature of 350 °C, pressure of 19.0 MPa and 240 seconds, with 98 % ME content in product.

Kusdiana and Saka studied the kinetic of transesterification reaction of rapeseed oil in subcritical and supercritical methanol within temperature range of 200 to 500 °C, pressure range of 10.0 to 65.0 MPa and methanol to oil molar ratio range of 3.5:1 to 42:1 [39]. The equipments and experimental procedure were employed from their previous work [6]. The results indicated that the rate of reaction increased dramatically in the supercritical region. It was evident that at subcritical temperature below 239 °C, the reaction rates were slow but much higher at supercritical state, with the rate constant increased by a factor of about 85 at the temperature of 350 °C. The reaction temperature of 350 °C was considered as the best condition, with the methanol to oil molar ratio being 42:1 and pressure of 45.0 MPa.

Demirbas investigated the transesterification of six vegetable oils (cottonseed, hazelnut kernel, poppy seed, rapeseed, safflower seed and sunflower seed) with SCM [7]. The study was carried out in a 100-mL reactor made of 316-stainless steel at reaction temperature in range of 177 to 350 °C and methanol to oil molar ratio in range of 1:1 to 41:1. In typical run, the reactor was charged with given amount of vegetable oil (20 to 30 g) and methanol (30 to 50 g). After each run, the gas was vented, and the content was poured into a collecting vessel, then the ME content was analyzed by GC. The optimal conditions were temperature of 350 °C, mole of methanol in vegetable oil of 41:1 and 200 seconds of reaction time, with product of over 95 % ME content.

Kusdiana and Saka investigated the effect of water and free fatty acid on the yield of methyl esters in transesterification of triglycerides and esterification of fatty acids as treated by SCM comparing with homogeneous catalytic process [41]. The reactor and experimental employed procedure the same as in their previous study [6]. For transesterification reaction, the presence of water (less than 5 %wt) and free fatty acid (less than 30 %wt) did not have a significant effect on the ME content, as complete conversions were achieved regardless of the content of water or free fatty acid. For acidic and basic catalyzed reaction, the ME content dramatically decreases with increasing water and free fatty acid content. For esterification reaction, the amount of water had a negative effect on the ME content which was catalyzed by both acidic and basic catalyst.

Warabi and coworkers investigated the reactivity of esterification and transesterification reaction with various alcohols ($C_1$ to $C_8$) with fatty acids ($C_{16}$ to $C_{18}$) and rapeseed oil, respectively [46]. The reactor and experimental procedure employed were the same as in their previous study [6]. The reaction temperature was set at 300 °C in all experiments while the pressure varied due to vapor pressure each alcohol was unequal. The results showed that transesterification of rapeseed oil were slower than esterification of fatty acids for any type of alcohols. According to types of alcohol and reactivity, methanol was the most reactive, while 1-octanol was the less reactive, that was in correspondence with their critical point. Furthermore, saturated fatty acids such as palmitic and stearic acids had slightly lower reactivity than that of the unsaturated fatty acids such as oleic, linoleic and linolenic acid.

Madras and coworkers studied the transesterification of rapeseed oil and cottonseed oil in SCM and supercritical ethanol (SCE) [66]. The effects of temperature (200 to 400 $^\circ$C) and methanol to oil molar ratio (40:1 to 42:1) were studied in a 8-mL batch reactor. The amount of methanol and vegetable oil were adjusted by trial and error to maintain the pressure of 20.0 MPa at desired temperature. This study indicated that the conversion in SCM was slightly lower than that in SCE, which was contrasting with Warabi and coworkers finding [46]. An explanation for higher conversions in SCE may be attributed to the solubility of the oil in the SCE system. The optimal conditions were 400 $^\circ$C, 20 MPa and alcohol to oil molar ratio of 40:1 at 30 min for both alcohols. Moreover, this study investigated the enzyme-catalyzed biodiesel production in supercritical carbon dioxide ($SCO_2$), but only 30% conversions were obtained at optimal conditions.

Cao and coworkers prepared biodiesel from soybean oil with SCM and propane as co-solvent [47]. A 250-mL cylindrical reactor made of stainless steel, equipped with a magnetic stirrer and internal cooling was used. The reaction vessel was charged with a given amount of soybean oil (50 to 70 g) and methanol (60 to 80 g) with different molar ratios, and a known amount of propane was then added to the reactor as co-solvent. The addition of propane at the propane to methanol molar ratio of 0.02:1 to 0.1:1 in the reaction system significantly decreased the severity of the conditions required for the supercritical reaction. The optimal conditions found from this study were the temperature of 280 $^\circ$C, the pressure of 13 MPa, methanol to vegetable oil molar ratio of 24:1 and propane to methanol molar ratio of 0.04:1.

Han and coworker investigated effect of carbon dioxide as co-solvent in biodiesel production from soybean oil in SCM [8]. The study was conducted in a 250-mL stainless steel reactor. The given amount of soybean oil, methanol and carbon dioxide were charged altogether in the reactor. The addition of carbon dioxide significantly reduced the optimal conditions of production biodiesel with SCM. The optimal amount of carbon dioxide was 0.1 per mole of methanol. At the temperature of 280 $^\circ$C, the pressure of 13 MPa and methanol to vegetable oil molar ratio of 24:1, nearly complete conversions were obtained. The results from this work were similar with the addition of

propane as co-solvent [47]; carbon dioxide is non-flammable, it is more appropriate than propane.

Bunyakiat and coworkers invented the continuous production of biodiesel by the transesterification reaction of coconut oil (CCO) and palm kernel oil (PKO) in supercritical methanol without using any catalyst [9, 44]. The oil and methanol were pumped in two different lines by HPLC pumps, preheated separately while flowing in the coil preheaters. After preheating, the two lines were mixed at the reactor inlet. Both the preheat lines and the reactor were immersed in an electrically heated salt bath. Experiments were studied at 270, 300 and 350 °C at a pressure of 10.0 and 19.0 MPa with various methanol to oil molar ratios from 6:1 to 42:1. It was found that the best condition to produce biodiesel from CCO and PKO was; reaction temperature 350 °C; methanol to vegetable oil molar ratio 24 and residence time 400 seconds. The ME content was 90 % and 85 % for CCO and PKO, respectively. The produced methyl ester fuel properties met the specification of the ASTM biodiesel standards.

He and coworkers developed the continuous system for transesterification of vegetable oil with SCM in a tubular reactor [11]. Increasing the methanol to vegetable oil molar ratio, reaction pressure and reaction temperature enhanced the ME content in the product effectively. However, thermal degradation of unsaturated fatty acid (UFAs) methyl esters occurred when the reaction temperature was over 300 °C, leading to loss of material. The optimal reaction condition under isothermal process was 310 °C, 35 MPa, 40:1 methanol to vegetable oil molar ratio at 25 minof residence time; whereas, the maximum ME content was only 77%. Consequently, they proposed a gradual heating to solve the thermal degradation of UFAs, then ME content could be increased to 96 %.

Minami and Saka studied kinetics of triglyceride hydrolysis in subcritical water and fatty acid methyl esterification in SCM for biodiesel production in a two-step process in a continuous tubular reactor [10]. The objectives of this paper were two folds; to obtain the high-quality biodiesel fuel and to reduce the temperature and pressure at optimal condition. In the two-step method, backward reaction of glycerol with methyl esters can be suppressed because glycerol is removed prior to methyl esterification. The high-quality biodiesel fuel can be produced, which has low total glycerol content comparing with the one-step method [6]. The hydrolysis of triglyceride in subcritical

water and methyl esterification in supercritical methanol can allow more moderate reaction conditions (270 °C, 7 to 20 MPa and 1:1 v/v water to oil or methanol to oil ratio). Furthermore, initial fatty acid in vegetable oil was found to act as acid catalyst, and simple mathematical models were proposed in which regression curves could fit well with experimental results. The optimal condition of this process was 270 °C and 24:1 methanol to vegetable oil molar ratio, that was milder than the one-step process [ ].

He and coworkers investigated transesterification kinetic of soybean oil with supercritical methanol at temperature range of 200 to 280 °C and pressure range of 8.7 to 36 MPa in 200-mL batch reactor [61]. The apparent activation energies were found different with the subcritical and supercritical temperature of methanol, which were 11.2 and 56.0 kJ/mole, respectively. The reaction pressure considerably influenced the ME content in the pressure range from ambient pressure up to 25.0 MPa (280 °C, 42:1). At pressure below 15.5 MPa, the pressure had a considerable impact on the ME content, for instance, the ME content increased from 56.1 % at 8.7 MPa to 81.7 % at 15.5 MPa. However, the influence of pressure on ME content was small within the at pressure range of 15.5 to 25.0 MPa and it was negligible above 25.0 MPa. The effect of pressure on the rate of reaction could be interpreted with the transition-state theory that was described by the reaction activation volume ($\Delta V^{\neq}$) in Equation (2.4). At pressure of 28 MPa, the product between the reaction activation volume and pressure accounts for 10.3% of the apparent activation energy.

Varma and Madras investigated the kinetics of biodiesel production with SCM and SCE from 200 to 350 °C at 200 bar [71]. The kinetics of the reaction was assumed to be the first order, and the activation energies were determined. The rate constants for the transesterification in SCM were influenced by the composition of the vegetable oils. For example, the rate constants decreased with amount of saturated and mono-unsaturated fatty acid in vegetable oils. This clearly shows that the transesterification reaction rate in SCM was the highest for the triglycerides of saturated fatty acid followed by triglycerides of unsaturated acids. The activation energies determined from the slope of the regressed line of Arrhenius plot are 35, 55, 46.5, and 70 kJ/mole for castor oil methyl ester, castor oil ethyl ester, linseed oil methyl ester, and linseed oil ethyl ester, respectively.

Kasteren and coworkers described a process model to estimate the cost of industrial scale biodiesel production from waste cooking oil with SCM [60]. A continuous production of biodiesel from waste cooking oil model has been studied for three plant capacities (125,000, 80,000 and 8,000 tones biodiesel/year) by ASPEN Plus® simulation software ®. It was found that biodiesel with SCM can be scaled up yielding high purity of methyl esters (99.8%) product and almost pure glycerol (96.4%) attained as by-product. The economic assessment of the biodiesel plant shows that biodiesel can be sold at US$ 0.17/L for the largest capacity, US$ 0.24/L for the medium capacity and US$ 0.52/L for the smallest capacity. The sensitive key factors for the economic feasibility of the plant were ranked as raw material price, plant capacity, glycerol price and capital cost. Overall conclusion was that the process can technically and economically compete with existing alkali and acid catalyzed processes, especially for using waste cooking oil as feedstock.

Busto and coworkers studied the influence of the axial dispersion on the performance of tubular reactors during the transesterification vegetable oil in supercritical methanol [13]. The miscibility of the FAME + MeOH + TG system was measured at various methanol to oil molar ratios, 40 °C and 0.1 MPa. Furthermore, the Pressure-Temperature curve was determined in a 32-mL autoclave vessel at various methanol molar to ratios at temperature range of 40 to 300 °C and pressure range of 0.1 to 20 MPa. The miscibility of the FAME + MeOH +TG system, Pressure-Temperature diagram and kinetic data from the other literatures [39] were used to predict the conversion by computer simulation. The axial dispersion was described by Péclet Number, $Pe = Lu/D_M$; $L$ is length of the reactor; $u$ is the space velocity; and $D_M$ is molecular diffusivity. The lower $Pe$ number decreased global conversion by performs the back-mixing phenomena, while it increased with temperature and methanol to oil molar ratio. In conclusion, the $Pe$ number should be in the range of 100 to 1000 to diminish the effects of back-mixing phenomena in tubular reactors and residence time should also be equal or lower than an hour, while axial lengths cannot be lower than 2 meters.

Imahara and coworkers investigated thermal stability of biodiesel as prepared by SCM process [58]. Due to conditions in high temperature and high pressure, biodiesel prepared may possibly be thermally degraded. Thermal stability of pure FAME and actual biodiesels from various feedstocks was studied, and discussed the effect of thermal degradation on fuel properties, mainly cold flow properties. It was found that polyunsaturated methyl esters such as methyl linoleate and methyl linolenate were partly decomposed and isomerized from *cis*-type to *trans*-type at the temperature higher than 300 $^{\circ}$C. These behaviors were also observed for actual biodiesel fuels prepared from linseed and safflower oils, which consist of high polyunsaturated fatty acids. However, their temperatures of cloud point and pour point are not significantly changed above 300$^{\circ}$C after exposure to SCM.

Demirbas investigated biodiesel production in supercritical methanol with calcium oxide [49]. The experiments were performed in a 100-mL reaction vessel equipped with a magnetic stirrer. The calcium oxide (60 to 120 mesh) was soaked in methanol with vigorous stirring in another small reactor before adding into reaction vessel. The catalytic transesterification ability of CaO was quite weak under ambient temperature. For instance, the ME content was observed only to be 5 % in 3 hours at temperature of 62 $^{\circ}$C, while the addition of CaO at higher temperature evidently increased the rate of reaction. The transesterification reaction was essentially completed (over 99%) at 253 $^{\circ}$C within 6 min with 3 wt% CaO and 41:1 methanol to oil molar ratio that approximately 2.5-fold faster that non-catalytic process.

D'Ippolito and coworkers proposed a process design in order to minimize the heat consumption and pumping power in biodiesel production with SCM. The two reactors with intermediate glycerol removal are used coupling with a heat recovery by heat exchangers and adiabatic flash drums were proposed. A computer simulation was built with experimental and literatures data. The operation mode and the process conditions were determined on the basis of the minimization of the energy consumption (heat duty, cooling services, pumping power) and the fulfillment of product quality constraints (maximum amount of bound glycerin and methanol in biodiesel). The results indicate that carrying out the transesterification reaction in two reactors enables the use of a low methanol to oil molar ratio of 10:1 – 15:1. The preferred operation mode

designed first reaction stage in the perfectly mixed state and the second reaction stage in plug flow mode. The process design under these conditions not only can reduce the total pressure of the system but also recover the sensible heat of the product outlet stream which can be used to completely vaporize the unreacted methanol in final product.

Glišic and coworkers discovered vapor-liquid equilibria (VLE) of triglycerides + methanol mixtures at different temperatures between 200 and 230 °C, and a range of pressures between 1.0 and 5.6 MPa in a 2000-mL batch reactor [14]. The vapor and liquid phase samples were taken from the bottom and top of the reactor, respectively, then methanol was evaporated and subsequently the triglycerides content present in both the liquid and vapor phase was determined gravimetrically using a high precision analytical balance. The experimental data were correlated using the Peng-Robinson, Soave-RK and RK-ASPEN equations of state and different mixing rules. The best results were obtained with the RK-ASPEN EOS and the VdW mixing rule, which was then used to calculate the distribution of the phases at designed pressures and temperatures use for biodiesel production with SCM.

Shimoyama and coworkers introduced activity coefficient models since they are usually predictive without needing to optimize the entire binary interaction parameters to available VLE data [16]. The authors reported that the COSMO-Segment Activity Coefficient (COSMO-SAC) model was suitable for use with a high-pressure system, including both polar and non-polar components. The COSMO-SAC model was compared with the Universal Functional Activity Coefficient (UNIFAC) model using SRK EOS and Wong-Sandler (WS) mixing rules [84]. The COSMO-SAC model gave a better estimation for the methyl myristate + methanol and methyl laurate + methanol systems than PRASOG model [18]. Unfortunately, the authors did not predict the C18-methyl ester mixture + methanol VLE using COSMO-SAC model [16].

Shimoyama and coworkers also studied the VLE of the glycerol + methanol system using the PRASOG model to correlate the data, comparing with the PR-SV EOS and VdW mixing rules [17]. Interestingly, the PRASOG model without interaction parameters predicted the vapor phase composition more precisely than the VdW mixing rules with adjusted binary interaction parameters. However, the calculated results derived from the PR-SV EOS and VdW mixing rules with two adjustable parameters have a

lower average relative deviation in both the liquid and vapor phases than those derived from the PRASOG model.

Glišic and Skala analyzed the energy consumption in biodiesel production with SCM by ASPEN Plus® simulation software [85]. This study analyzed the existing and recently published data related to design of larger scale plant for biodiesel production with SCM and illustrated the problem of insufficiency of the previously in the literature published. The continuous process flow sheets for biodiesel production (10,000 ton/year) with SCM and homogenous catalytic conventional was constructed by using the thermodynamic model which proposed in their previous work [14]. This study indicated that sensitivity of energy balance calculation depended strongly on thermodynamic models for representing a real complex mixture. Although the biodiesel production with SCM consumes large energy in reaction step, but a small amount of energy could be used for biodiesel and glycerol purification. In conclusion, the total energy consumption was 2326kW for conventional process and 2407kW for SCM process.

Kiwjaroun and coworkers employed the Life Cycle Assessment (LCA) as a tool to study the environmental impact of biodiesel production by homogeneous catalytic and SCM process from refined and crude palm oil [69]. The energy consumption for 10,000 ton/year capacity plant of each process was calculated in HYSIS ® process simulator with the NRTL and UNIQUAC as thermodynamic model. It was found that the supercritical process always generated a higher impact on the environment for both crude palm oil and refined palm oil due to it required large amounts of methanol during the reaction and consequently the energy consumption in methanol recirculation in the recycle loop. For instance, the SCM process at 42:1 methanol to oil molar ratio had 18,140 kg/h of methanol in recycle loop, compared to only 1,400 kg/h in the conventional process. Therefore, the energy consumption for methanol recycling has to be reduced by additional technique such as replacing the dilation column with medium pressure flash drum [59] or innovative technologies as mention in Section 2.4.5. to make the SCM process feasible from the environmental point of view.

Wang and Yang employed nano-MgO as a catalyst for biodiesel production by soybean oil with SCM [52]. The experiments were carried out in a 200-mL batch reactor (diameter 50 mm, height 128 mm) with a magnetic stirrer. It was observed that the transesterification reaction was essentially completed at 230 $^{\circ}$C within 10 min with 3 wt% nano-MgO and the methanol to oil molar ratio of 36:1. Such high reaction rate with nano-MgO was mainly owing to the lower activation energy of 75.94 kJ/mol. However, the activity of nano-MgO was slightly lower than the 60 to 120 mesh CaO as reported by Demirbar [49].

Demirbas used waste cooking oil as a feedstock to produce biodiesel with SCM comparing with homogeneous catalytic process [42]. The presence of free fatty acids (FFA) and water always produced negative effects in homogeneous catalytic process, whereas FFA react with methanol to perform biodiesel in SCM process. The effect of temperature and methanol to oil molar ratio were investigated in a batch reactor as described in his previous work [7]. In conclusion, the 98 % ME content was obtained from waste cooking oil at 300 $^{\circ}$C and 40:1 methanol to oil molar ratio within 20 min of reaction time while approximately 85% ME content was observed at 60 $^{\circ}$C with 6%wt of KOH and 24:1 methanol to oil molar ratio and 2 h reaction time.