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Transesterification in Supercritical Conditions

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1. Introduction

The transesterification or biodiesel production under supercritical conditions (supercritical transesterification) is a catalyst-free chemical reaction between triglycerides, the major component in vegetable oils and/or animal fats, and low molecular weight alcohols, such as methanol and ethanol, at a temperature and pressure over the critical point of the mixture (see Section 1.1). The overall transesterification reaction is shown in Fig. 1.
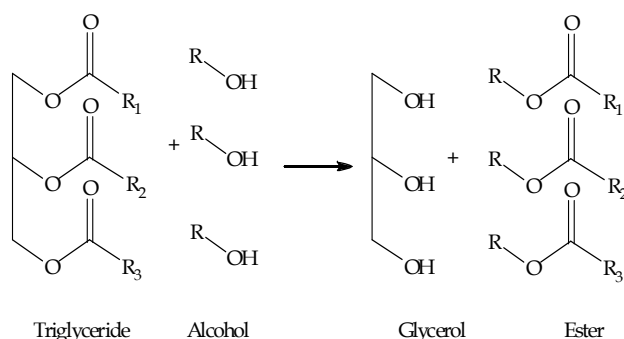

Fig. 1. The overall transesterification reaction (R is a small alkyl group, R_1, R_2 and R_3 are a fatty acid chain)

The reaction mechanism for supercritical transesterification has been proposed to be somewhat alike the acidic-catalyzed reaction as described in Section 1.2.

Since the actual feedstocks are not composed solely of triglycerides, especially the low-grade feedstocks, but are also contaminated with water and free fatty acids, some side reactions also take place under supercritical conditions (see Section 1.3). For example, the esterification of free fatty acids with alcohols increases the fatty acid alkyl ester content in the biodiesel product, while the thermal cracking of unsaturated fatty acids decreases the esters content.

The earlier research on supercritical transesterification mostly employed methanol as the reacting medium and reacting alcohol at the same time due to the fact that it has the lowest critical point and the highest activity (Warabi et al., 2004). Ethanol is also an interesting candidate because it can be industrially produced from renewable sources in many countries nowadays. However, other supercritical mediums, such as methyl acetate (Saka & Isayama, 2009) and dimethyl carbonate (Ilham & Saka, 2009; Tan et al., 2010b), have also

been used to produce biodiesel, but these are not be described in this chapter since the chemical reaction involved is not a transesterification reaction. The reaction parameters and optimal conditions for supercritical transesterification are summarized in Section 1.4.

1.1 The definition of supercritical transesterification

A pure substance ordinarily exists in a solid, liquid or gaseous state, depending on the temperature and pressure. For example, methanol is in a liquid state at ambient temperature (and pressure) and changes to a gaseous state above its boiling point. A gaseous substance can be compressed to a liquid state when a pressure above the boiling point is applied. Until the critical temperature is reached, a gaseous substance cannot be compressed to the liquid state. In the same manner, a compressed liquid substance cannot be heated to a gaseous state at its critical pressure.

Above its inherent critical temperature and pressure, the substance becomes a supercritical fluid, which is a non-condensable dense fluid. In the supercritical state, the density is generally in a range between 20 – 50% of that in the liquid state and the viscosity is close to that in the gaseous state. In other words, the molecules in the supercritical fluid have high kinetic energy like a gas and high density like a liquid. Therefore, the chemical reactivity can be enhanced in this state.

The critical point of any transesterification reaction mixture is mostly calculated by the critical properties of the alcohols and the vegetable oils and/or animal fats. However, the critical properties of vegetable oils and/or animal fats cannot be experimentally measured because they thermally decompose before the critical point is reached. In addition, the molecular structure of vegetable oils and/or animal fats is impossible to know because the exact distribution of the fatty acids chain in triglycerides mixture is unknown.

Therefore to estimate the critical properties of vegetable oils and/or animal fats, their molecular is assumed to be a simple triglyceride (tripalmitin, triolein, etc.) or pseudo-triglycerides (Espinosa et al., 2002), with the proportion of such different simple triglycerides reflecting the actual overall fatty acid composition in the feedstock. The type of simple triglycerides or the pseudo-triglycerides are thus defined by their actual fatty acid profile in the vegetable oils and/or animal fats. For instance, soybean oil has linoleic acid as the major fatty acid, and so it is usually assumed to be trilinolein. Next, the critical properties of the simple triglycerides or the pseudo-triglycerides are estimated by the Fedor and Lydersen group contribution method (Poling et al., 2001), or similar. After the critical properties of each of the triglycerides are estimated, the critical point of the mixture can be estimated by mixing rules, such as the Lorentz-Berthelot-type (Bunyakiat et al., 2006) and the group-contribution with associated mixing rules (Hegel et al., 2008).

For example, the critical temperature and pressure of soybean oil-methanol and palm kernel oil-methanol mixtures are illustrated in Figs. 2 and 3, respectively.

From Figs. 3 and 4, it is clear that the critical point of the reaction mixture depends on the alcohol to oil molar ratio, so the selected alcohol to oil molar ratio will reflect the operating temperature and pressure, as described in Section 2.1. For a high transesterification conversion (triglyceride to alkyl ester) at a constant methanol to oil molar ratio, the operating temperature and pressure have to be approximately 1.5- to 2.0-fold over the critical point of the reaction mixture. For example, the optimal conditions at a methanol to oil molar ratio of 42:1 is 350 °C and 20 MPa, respectively. Therefore, the definition of supercritical conditions is the temperature and pressure above the critical point of the reaction mixture, which is calculated from the critical properties of the vegetable oils and/or animal fats and the alcohols.
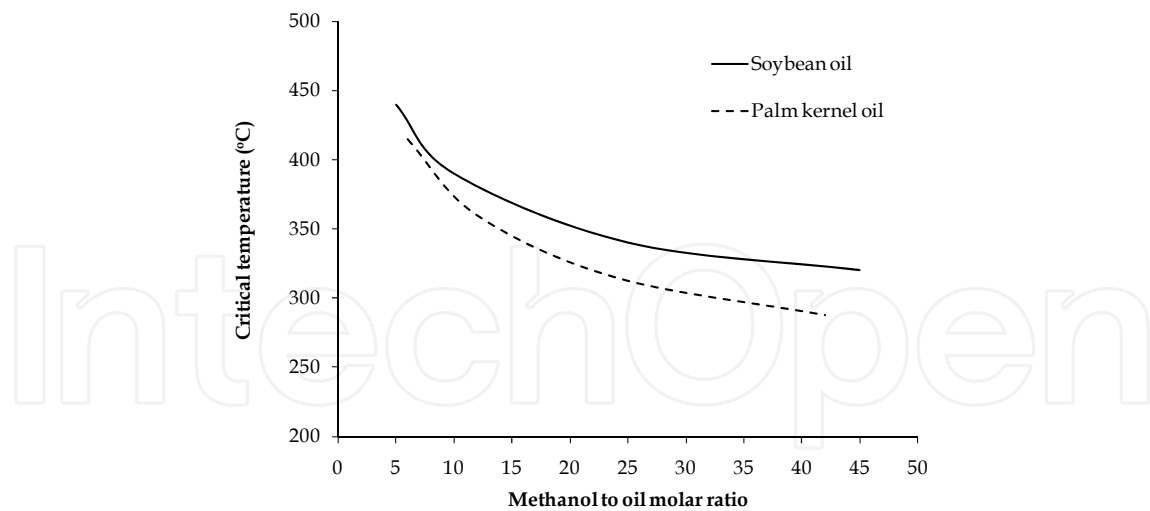
Fig. 2. The estimated critical temperature of soybean oil-methanol (Hegel et al., 2008) and palm kernel oil-methanol (Bunyakiat et al., 2006) mixtures.
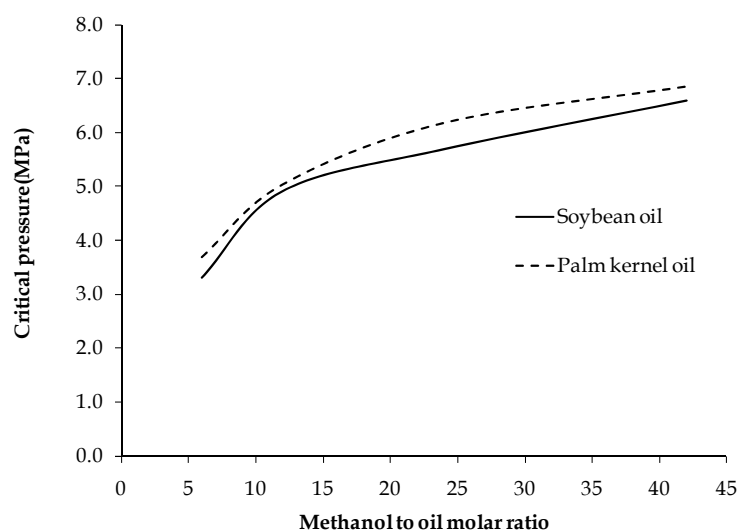

Fig. 3. The estimated critical pressure of soybean oil-methanol (Hegel et al., 2008) and palm kernel oil-methanol (Bunyakiat et al., 2006) mixtures.

1.2 The reaction mechanism of supercritical transesterification

Below the critical point of mixture, transesterification can take place in the presence of acidic or basic catalysts. Thus, the reaction mechanisms of transesterification are divided into acid and base catalyzed paths, as summarized elsewhere (Meher et al., 2006). The reaction mechanism of supercritical transesterification is somewhat similar to the acid catalyzed path in that the hydrogen bond of the alcohol is weakened at high temperatures (Hoffmann & Conradi, 1998). However, whilst the acid-catalyzed transesterification reaction is much slower than the base-catalyzed one at ambient conditions, the supercritical transesterification is much faster and achieves complete conversion of triglycerides to esters rapidly because the chemical kinetics are dramatically accelerated under supercritical conditions.

The reaction mechanism of supercritical transesterification, as shown in Fig. 4, was proposed by the analogues between the hydrolysis of esters in supercritical water (Krammer

& Vogel, 2000) and the transesterification of triglycerides in supercritical methanol (Kusdiana & Saka, 2004b). It is assumed that the alcohol molecule (in this case methanol) directly attacks the carbonyl carbon of the triglyceride because the hydrogen bond energy is lowered; which would allow the alcohol to be a free monomer. In the case of methanol, the transesterification is completed via transfer of a methoxide moiety, whereby fatty acid methyl esters and diglycerides are formed. Consequently, the diglyceride reacts with other methanol molecules in a similar way to form the methyl ester and monoglyceride, the later of which is further converted to methyl ester and glycerol in the last step. The same process is applicable to other primary alkyl alcohols, such as ethanol.
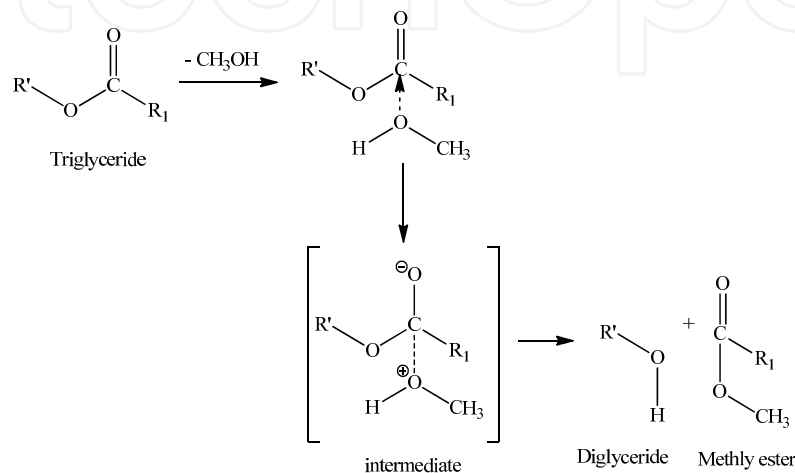

Fig. 4. The proposed reaction mechanism of transesterification in supercritical methanol (R′ is a diglyceride group and R_1 is a fatty acid chain).

1.3 The side reactions in the supercritical conditions

Firstly, the hydrolysis reaction of alkyl esters and triglyceride can take place at over 210 °C (Khuwijitjaru et al., 2004) and over 300 °C (W. King et al., 1999), respectively, in present of water and pressure above 20 MPa. The overall hydrolysis reaction of triglycerides and alkyl esters is shown in Figs. 5 and 6, respectively, with the principal products of the hydrolysis reaction being the respective fatty acids which are subsequently converted to alkyl esters under the supercritical condition by the esterification, as illustrated in Fig. 7.
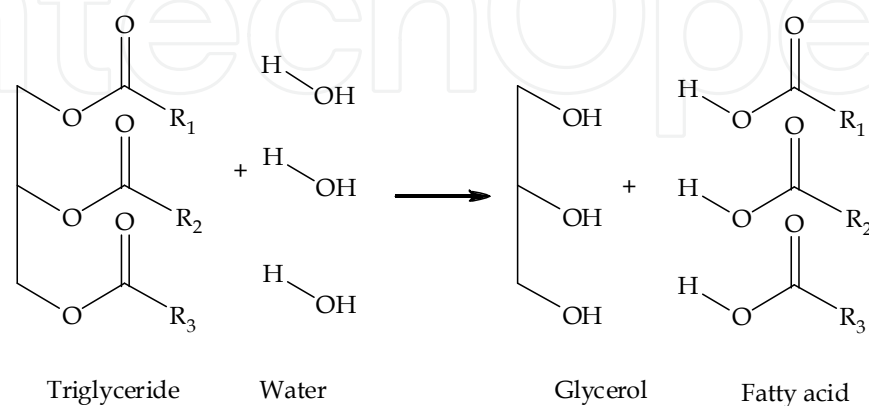

Fig. 5. The overall hydrolysis reaction of triglycerides under supercritical conditions (R is an alkyl group and R_1, R_2 and R_3 are fatty acid chains)
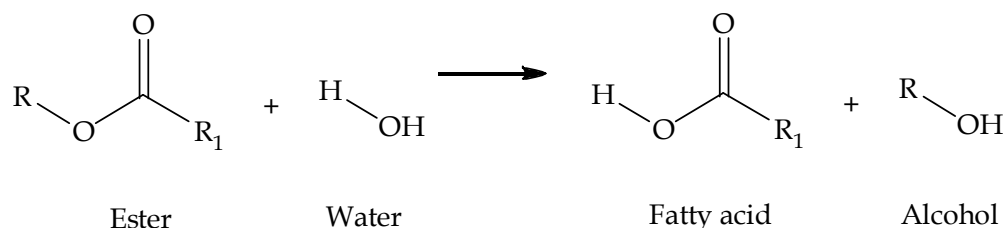
Fig. 6. The hydrolysis reaction of alkyl esters under supercritical conditions (R is an alkyl group and R_1 is a fatty acid chain)
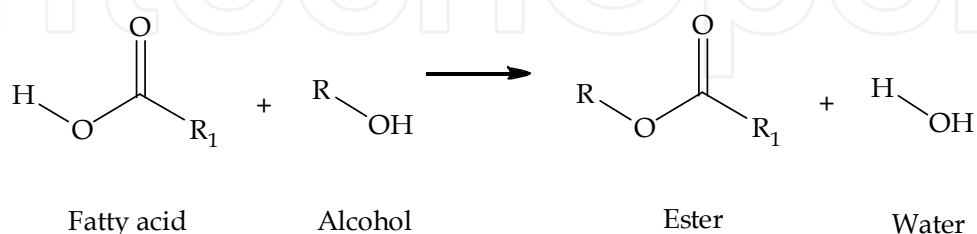

Fig. 7. The esterification reaction under supercritical conditions (R is an alkyl group and R_1 is a fatty acid chain)

In actuality, the hydrolysis reaction or the presence of water and free fatty acids do not affect the final alkyl ester content obtained for supercritical transesterification (Kusdiana & Saka, 2004b), because the alcohols have a much higher reactivity than water at the optimal point of supercritical transesterification. For example, the chemical rate constant for the transesterification of rapeseed oil is approximately 7-fold higher than that for the hydrolysis of soybean oil (Khuwijitjaru et al., 2004; Kusdiana & Saka, 2001).

Secondly, the thermal cracking of unsaturated fatty acids, especially the polyunsaturated fatty acids, occurs at temperatures over 300 °C and reaction times over 15 min (Quesada-Medina & Olivares-Carrillo, 2011). An example of the thermal cracking of a palmitic, oleic and linoleic acid based triglyceride is illustrated in Fig. 8.
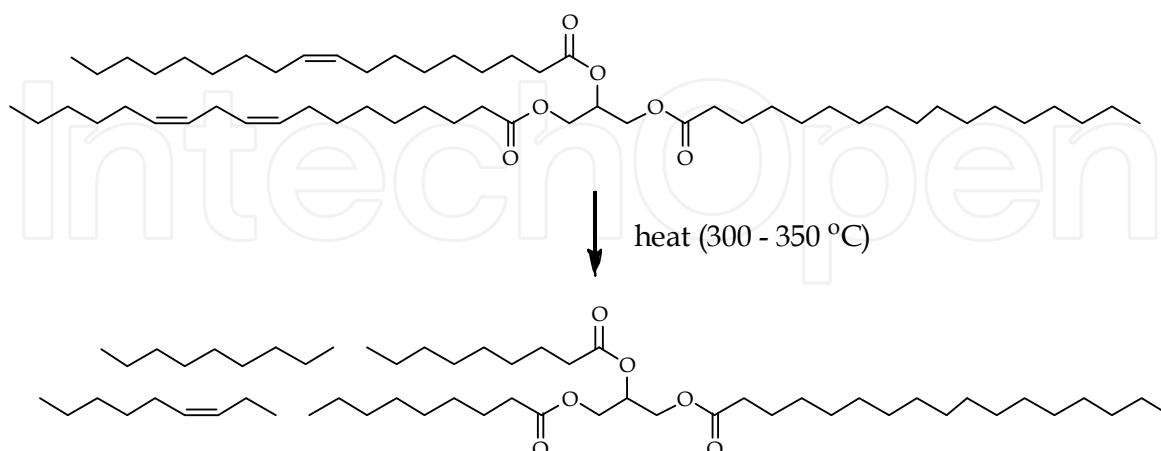

Fig. 8. The thermal cracking reaction of a triglyceride under supercritical conditions at a temperature range of 300 - 350 °C and a reaction time of over 15 min.

The triglyceride product from the thermal cracking reaction can be transesterified afterwards under supercritical conditions to alkyl esters. However, these alkyl esters are not

the fatty acid alkyl esters of the common fatty acids in vegetable oils and/or animal fats. Therefore, the thermal cracking reaction reduces the acceptable primary alkyl ester content, as quantified and defined by the international standard for biodiesel (EN14103), and this is especially the case for the oils with a high polyunsaturated fatty acid content, such as soybean and sunflower oil.

In addition, triglycerides are decomposed to fatty acids and some gaseous products within the temperature range of 350 - 450 °C, as shown in Fig. 9 (Lima et al., 2004; Marulanda et al., 2009). In the same manner, with thermal cracking at 300 - 350 °C, the fatty acids product can be esterified under supercritical conditions, but the alkyl ester content is also decreased. However, the small hydrocarbon molecules of the thermal cracking products could improve some fuel properties of biodiesel, such as viscosity, density and cold flow properties.
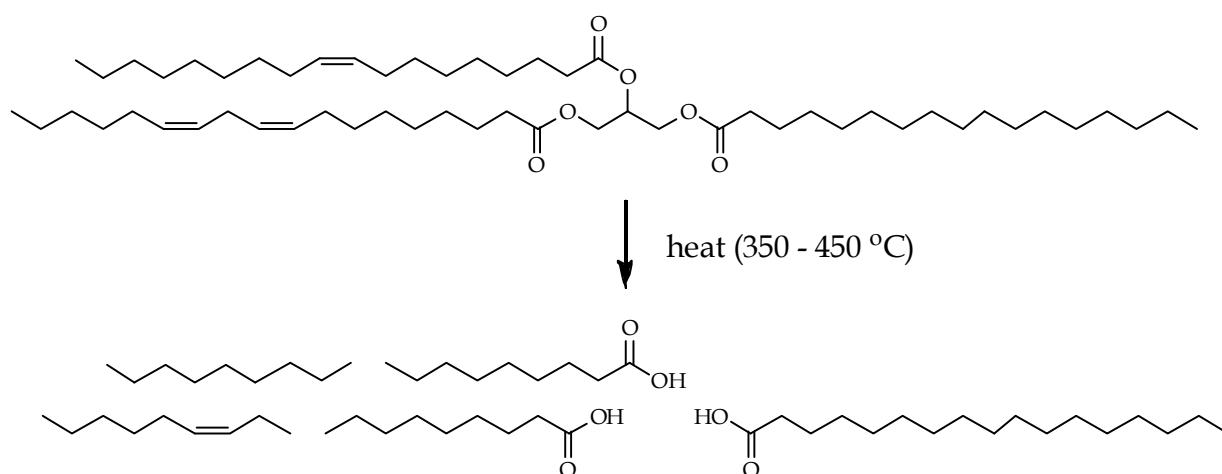

Fig. 9. The thermal cracking reaction of triglycerides under supercritical conditions at temperature range of 350 - 450 °C

1.4 The original reaction parameters and optimal conditions in the early scientific articles

The reaction parameters that were typically investigated in supercritical transesterification reactions are the temperature, pressure, alcohol to oil molar ratio and reaction time in batch and continuous reactors, and are summarized in Table 1.

The extent of the reaction was reported in terms of the % alkyl ester content and the % conversion of triglycerides. The % alkyl esters content refers to the alkyl esters of the common fatty acids in the vegetable or animal oils/fats that can be identified by different analytical techniques, while the % triglycerides conversion implies the remaining triglyceride reactant that is converted to fuels. Note that the % alkyl esters content refers to the specified esters, which must not be less than 96.5%, in the International standard (EN14214) for biodiesel fuel. It should also be noted that a high alkyl esters content infers a high triglyceride conversion, but, in contrast, a high triglyceride conversion does not have to infer a high alkyl esters content because the triglycerides could have been converted by the side reactions to other products.

According to Table 1, the original optimal conditions, defined as yielding the highest extent of reaction as over 90% conversion or over 96% alkyl esters content, were within 300 – 350 °C, 20 – 35 MPa, an alcohol to oil molar ratio of 40:1 – 42:1 and a reaction time of

5 – 30 min, for both methanol and ethanol. These parameters are referred to as the original supercritical transesterification parameters, and have been employed to study the effects of each parameter, the chemical kinetics, the phase behavior and the economical feasibility of the process. Since the original parameters are elevated conditions, innovative techniques are proposed to reduce these original parameters.

2. Process overview

2.1 The effects of reaction parameters on the % conversion in supercritical transesterification

Among the general operating parameters mentioned previously (temperature, pressure, alcohol to oil molar ratio and reaction time), the reaction temperature is the most decisive parameter for indicating the extent of the reaction. This is as a result of the accelerated chemical kinetics and changes to the alcohol's properties. For example, the rate constant of supercritical transesterification is dramatically enhanced some 7-fold as the temperature is increased from 210 to 280 ℃ at 28.0 MPa and a 42:1 methanol to oil molar ratio (He et al., 2007a), whilst the degree of hydrogen bonding also suddenly drops as the temperature is increased from 200 to 300 ℃ at 30.0 MPa (Hoffmann & Conradi, 1998). However, where a maximum alkyl ester content is required, that is for biodiesel production, the higher operating temperatures cause a negative effect on the proportion of alkyl esters obtained in the product due to the thermal cracking reaction. Indeed, the thermal cracking is the chemical limitation of supercritical transesterification, and this is discussed in Section 2.4.2.

Oil type	Alcohol	T (℃)	P (MPa)	Alcohol: oil (mol: mol)	Reaction time (min)	Reactor (size / type) [a]	Extent of reaction[b]	Ref
Coconut & Palm kernel	Methanol	350	19	42:1	7 - 15	251-mL / CT	95% MEC	(Bunyakiat et al., 2006)
Hazelnut kernel & Cottonseed	Methanol	350	NR	41:1	5	100-mL / Batch	95% MEC	(Demirbas, 2002)
Palm and Groundnut	Methanol	400	20	50:1	30	11-mL / Batch	95% Con.	(Rathore & Madras, 2007)
Palm kernel	Methanol	350	20	42:1	30	250-mL / Batch	95% MEC	(Sawangkeaw et al., 2007)
Rapeseed	Methanol	350	45	42:1	4	5-mL / Batch	98% MEC	(Saka & Kusdiana, 2001)
Rapeseed	Methanol	350	20	42:1	30	200-mL / CT	87% MEC	(Minami & Saka, 2006)
Soybean	Methanol	350	20	42:1	30	250-mL / Batch	95% MEC	(Yin et al., 2008a)
Sunflower	Methanol & Ethanol	400	20	40:1	30	8-mL / Batch	97% Con.	(Madras et al., 2004)
Castor	Ethanol	300	20	40:1	NR	42-mL / CT	75% EEC	(Vieitez et al., 2011)
Soybean	Ethanol	350	20	40:1	15	42-mL / CT	80% Con.	(Silva et al., 2007)
Sunflower	Ethanol	280	NR	40:1	5	100-mL / Batch	80% EEC	(Balat, 2008)

[a] CT = Continuous reaction in a tubular vesicle.
[b] Reaction extents are expressed as the % triglyceride conversion (Con.), % methyl esters content (MEC) or the % ethyl esters content (EEC).
NR = not reported

Table 1. The original reaction parameters and optimal conditions of supercritical transesterification for various oil types and alcohols.

The reaction pressure also has a significant effect on the efficiency of the supercritical transesterification reaction below 20.0 MPa, but the effects tend to be negligible above 25.0 MPa (He et al., 2007a; He et al., 2007b), due to the fact that increasing the reaction pressure simultaneously increases both the density of the reaction mixture (Velez et al., 2010) and the degree of hydrogen bonding (Hoffmann & Conradi, 1998) at an otherwise constant temperature and alcohol to oil molar ratio. The transesterification conversion is enhanced with an increased reaction mixture density, due to the resulting increased volumetric concentration of alcohols and the residence time in a tubular reactor, which is commonly used to investigate the effect of pressure. On the other hand, the increasing degree of hydrogen bonding or alcohol cluster size weakens the nucleophilic strength of supercritical alcohols and so the reactivity of supercritical alcohol is reduced with increasing pressure. Thus, the desirable pressure for supercritical transesterification is in the range of 20.0 – 35.0 MPa.

From Table 1, the original alcohol to oil molar ratio for supercritical transesterification is in range of 40:1 – 42:1. The alcohol to oil molar ratio affects the supercritical transesterification efficiency strongly below 24:1, but its effect is then reduced with increasing alcohol to oil molar rations to plateau at over a 50:1 alcohol to oil molar ratio for methanol (He et al., 2007a) or 70:1 for ethanol (Silva et al., 2007) at 330 °C and 20.0 MP. This is likely to be due to the fact that the operating temperature and pressure are much higher than the critical point of the reaction mixture, and are still located in the supercritical region.

As mentioned in Section 1.1, the critical point of the reaction mixture decreases with increasing alcohol to oil molar ratios. Thus, the optimal reaction temperature and pressure at a high alcohol to oil molar ratio is always milder than that at a low molar ratio. Nonetheless, the large amount of alcohol not only increases the required reactor volume but importantly it consumes a large amount of energy to heat the reactant and also to subsequently recover the excess alcohol. The energy for recycling excess alcohol might be minimized by a low temperature separation process, such as the use of a medium-pressure flash drum (Diaz et al., 2009), whereas the additional energy for heating the excess reactant alcohol cannot be avoided. Therefore, the use of assisting techniques, as described in Sections 3.2 – 3.4, have been introduced to decrease the alcohol to oil molar ratio whilst maintaining the transesterification conversion efficiency (and so the fatty acid alkyl ester content).

The effect of the reaction time on the transesterification conversion follows the general rate law. For example, the alkyl ester content increases gradually with reaction time and then remains constant after the optimal point (maximum conversion to alkyl esters) is reached. The optimal reaction time for supercritical transesterification at around 300 – 350 °C varied between 4 to 30 minutes, depending upon the reactor size and type. Since the effect of residence time is directly related to the chemical kinetics of transesterification, the optimal reaction time at low temperatures is longer than that at high temperatures.

2.2 The chemical kinetics and phase behavior in supercritical transesterification
2.2.1 The chemical kinetics of supercritical transesterification

The chemical kinetics of supercritical transesterification is divided into three regions, that of the slow (<280 °C), transition (280 - 330 °C) and fast (>330 °C) regions, and usually follows the first-order rate law with respect to the triglyceride concentration alone (He et al., 2007a; Kusdiana & Saka, 2001; Minami & Saka, 2006). Here, the reaction mechanism is merged into one overall step and the concentrations of all intermediates (mono- and diglycerides) are ignored. However, the first-order kinetic model is only suitable for a high alcohol to oil

molar ratio, due to the insignificant changes in the alcohol concentration, but this increasingly becomes untrue as the alcohol to oil molar ratio decreases.

For the first-order model, the rate constants for each vegetable oil have a different temperature sensitivity, as noticed by the slope of Arrhenius' plot (Sawangkeaw et al., 2010). For example, the rate constants of rapeseed and soybean oil depend more strongly on the temperature than that for sunflower, palm and groundnut oils. The rate constants of saturated triglycerides were found to be faster than unsaturated triglycerides and slow down with increasing levels of double bonds in the triglyceride molecule (Rathore & Madras, 2007; Varma & Madras, 2006). However, saturated fatty acids have a slightly lower reactivity than the unsaturated fatty acids (Warabi et al., 2004).

On the other hand, a second-order kinetic model with respect to both the triglycerides and alcohol concentrations has also been proposed (Diasakou et al., 1998; Song et al., 2008). This divides the transesterification reaction into three steps; the reaction between a triglyceride and an alcohol that generates a diglyceride and an alkyl ester, the diglyceride and alcohol and finally the monoglyceride and alcohol. The concentration of the intermediates is then taken into account and the rate constants are found by mathematical model fitting. Thus, although more complex, the second-order kinetic model is more appropriate than the first-order model for reactions involving alcohol to oil molar ratios below 24:1.

2.2.2 The phase behavior of reactants in supercritical transesterification

The fact that the required optimal operating parameters can become milder with the addition of co-solvents has spurred much interest in the phase behavior of reactants during supercritical transesterification. The phase behavior of soybean oil-methanol with propane as a co-solvent was reported first (Hegel et al., 2007), followed by that for soybean oil-methanol and soybean oil-ethanol with carbon dioxide as the co-solvent (Anitescu et al., 2008). The study of the phase behavior of supercritical transesterification, when performed in a high-pressure view cell, revealed that the liquid - liquid (LL) alcohol - triglycerides mixture transforms to a vapor – liquid - liquid (VLL) phase equilibrium. The VLL equilibrium consists of two immiscible liquid phases (triglycerides and alcohol) and a vapor phase which mainly contains alcohol. Then, the VLL equilibrium changes to a vapor - liquid (VL) phase as a result of the triglycerides dissolving into the supercritical alcohol phase. Finally, the VL equilibrium merges to a one-phase supercritical at nearly the estimated critical point of mixture.

The transition temperature of the VLL to VL equilibriums decreases with increasing methanol to oil molar ratios (Anitescu et al., 2008; Hegel et al., 2007). For example, the reaction mixture of soybean oil and methanol are partially miscible up to temperatures close to 350 °C at a methanol to oil molar ratio of 24:1, while the two liquid phases of soybean oil and methanol become completely miscible at 180 °C and 157 °C with a methanol to oil molar ratio of 40:1 and 65:1, respectively. For a soybean oil-ethanol mixture, it becomes a VL equilibrium at a lower temperature than that for the soybean oil-methanol due to the higher solubility of soybean-oil in ethanol than in methanol (Anitescu et al., 2008).

The transition from a VL system to a one-phase supercritical system was observed near the estimated critical temperature of the mixture, as described in Section 1.1. At a methanol to oil molar ratio of 24:1, the critical temperature of the soybean oil-methanol mixture was 377 °C where the transition temperature was reported to be higher than 350 °C (Anitescu et al., 2008). Moreover, the transition temperature of the two-phase VL to a one-phase supercritical

could be reduced by the addition of gaseous co-solvents, such as carbon dioxide and propane. For instance, the addition of 24% by weight of propane decreased the transition temperature of soybean oil-methanol, at a methanol to oil molar ratio of 65:1, from 315 °C to 243 °C (Hegel et al., 2007). Therefore, the addition of gaseous co-solvents is able to reduce the original severe conditions due to their ability to lower the transition temperature from a VL system to a one-phase supercritical system.

2.3 The advantages and drawbacks of supercritical transesterification

Novel solid heterogeneous catalysts that catalyze the transesterification on acidic or basic surfaces instead of in solution have been proposed to overcome the drawbacks of the conventional homogeneous catalytic method, which in part are the same as the supercritical transesterification. The enzyme catalysts typically also allow for a very high selectivity on the alkyl ester products (Helwani et al., 2009; Lene et al., 2009).

2.3.1 The advantages of supercritical transesterification

The advantages of supercritical transesterification over the conventional homogeneous catalytic method are feedstock flexibility, higher production efficiency and it is more environmentally friendly. The feedstock quality is far less influential under supercritical conditions than with the heterogeneous catalytic method, whilst supercritical transesterification has a similar advantage with respect to the product separation as the novel catalytic methods, but it has a higher production efficiency than both novel catalytic methods. The feedstock flexibility is the most important advantage to consider for biodiesel production methods because the resultant biodiesel price strongly depends on the feedstock price (Kulkarni & Dalai, 2006; Lam et al., 2010). The free fatty acids and moisture in low-grade feedstocks and hydrated ethanol pose a negative effect on the basic homogeneous and heterogeneous catalytic methods. Whereas, free fatty acid levels and moisture contents in the feedstock do not significantly affect supercritical transesterification with methanol or ethanol. Therefore, supercritical transesterification is more suitable for use with the low-grade and/or the hydrated ethanol feedstocks (Demirbas, 2009; Gui et al., 2009; Kusdiana & Saka, 2004b; Vieitez et al., 2011). For example, the in-situ transesterification of wet algal biomass in supercritical ethanol gave a 100% alkyl ester yield (Levine et al., 2010).

Supercritical transesterification has a better production efficiency than the conventional catalytic method because it requires a smaller number of processing steps. For instance, the feedstock pretreatment to remove moisture and free fatty acids, and the post-production product treatment steps, such as neutralization, washing and drying, are not necessary. In addition, the rate of reaction under supercritical conditions is significantly faster than the conventional catalytic method, so that the supercritical transesterification requires a smaller reactor size for a given production output.

With respect to environmental aspects, supercritical transesterification does not require any catalysts or chemicals, whilst the waste from the pretreatment and post-treatment steps are also reduced, since those steps are not necessary, leading to the generation of insignificant waste levels. However, the distillation process to recover the excess alcohol requires a large amount of energy which reduces the environmentally friendly advantage of the process (Kiwjaroun et al., 2009). Thus to maintain an environmentally friendly advantage, low-energy separation methods, such as medium pressure flash drum, must be applied to recover the excess alcohol (Diaz et al., 2009).

2.3.2 The drawbacks of supercritical transesterification

The original parameters to achieve a high transesterification conversion were a high temperature (330 – 350 °C), high pressure (19 – 35 MPa) and high alcohol to oil molar ratio (1:40 – 1:42). Indeed, the high temperature and pressure requires both an expensive reactor and a sophisticate energy and safety management policy. As a result of the high alcohol to oil molar ratio a large energy consumption in the reactants pre-heating and recycling steps is required. Moreover, the high amount of alcohol in the biodiesel product retards the biodiesel-glycerol phase separation. Therefore, the use of those original parameters results in high capital costs, especially for the reactor and pump, being somewhat higher than the novel catalytic methods.

To increase the technical and economical feasibility of supercritical transesterification, further studies are required to reduce the energy consumption and operating parameters of this process. For example, the integration of a heating and cooling system can improve (reduce) the energy demand. The experimental techniques that have demonstrated the ability to lower the original parameters for supercritical transesterification are illustrated in sections 3.2 – 3.4.

2.4 The economical feasibilities and chemical limitations of supercritical transesterification

The economical feasibilities of supercritical transesterification, compared with the conventional homogeneous catalytic methods, have been studied by computer simulation (van Kasteren & Nisworo, 2007). These studies usually employed the original parameters for transesterification in supercritical methanol (350 °C, 20.0 MPa and 1:42 methanol to oil molar ratio) and the general parameters for the conventional catalytic methods, such as a reaction at 60 °C, 0.1 MPa and a methanol to oil molar ratio of 9:1. With respect to chemical limitations, supercritical transesterification is limited by the operating temperature due to the thermal cracking of the unsaturated fatty acids.

2.4.1 The economical feasibilities of supercritical transesterification

Supercritical transesterification with the original reacting parameters is economically competitive compared to the conventional catalytic method especially when low-grade feedstocks are employed (van Kasteren & Nisworo, 2007). As expected, the supercritical transesterification has a larger capital cost, due to the required reacting and pumping systems, than the conventional catalytic method, but has no additional capital and operating costs on feedstock pre-treatment, product post-treatment and waste management.

For a better economic feasibility, research into ways to reduce the high operating conditions and lower energy consumption are warranted. For example, supercritical transesterification is not economically feasible when the heating and cooling integration is not employed (Marchetti & Errazu, 2008), while it is a feasible method when heat integration and the presence of catalysts are applied (D'Ippolito et al., 2006; Glišic et al., 2009; van Kasteren & Nisworo, 2007). The addition of calcium oxide as a solid catalyst and the reduction of the alcohol to oil molar ratio significantly decreased the total energy demand and improved the economic feasibility as well (Glišic & Skala, 2009). Furthermore, the addition of propane as co-solvent also enhanced the economic feasibility of supercritical transesterification with methanol (van Kasteren & Nisworo, 2007). However, additional feasibility studies on other assisting techniques that lower the original parameters (see Sections 3.2 - 3.4) are still required.

2.4.2 The chemical limitation of supercritical transesterification

To fulfill the international standard of biodiesel (EN14214), which requires over 96.5% esters content, thermal cracking of polyunsaturated fatty acids is a serious obstacle. At over 300 $^\circ$C and a reaction time of over 15 min, the methyl linoleate content in biodiesel decreases by approximately 10% compared with the level in the feedstock (Quesada-Medina & Olivares-Carrillo, 2011). Whereas, the % recovery of biodiesel samples which are prepared from various vegetable oils remains constant after exposure with supercritical methanol at 270 $^\circ$C over 40 min (Imahara et al., 2008). Therefore, the 96.5% alkyl esters content requirement for biodiesel cannot be achieved when an operating temperature of over 300 $^\circ$C and a reaction time of over 15 min are employed.

To prevent this thermal degradation, the suggested temperature for supercritical transesterification is below 300 $^\circ$C, and preferably 270 $^\circ$C. However, the required reaction time to nearly complete transesterification conversion at a 42:1 alcohol to oil molar ratio is then significantly longer at more than 90 min (Minami & Saka, 2006). This prolonged reaction time might cause a decline in the production efficiency obtained by supercritical transesterification, but it could be shortened by the use of assisting methods, as discussed in Sections 3.2 – 3.4.

On the other hand, the gradual heating technique in a tubular reactor has been demonstrated to avoid the thermal cracking of unsaturated fatty acids and shorten the reaction time at the same time (He et al., 2007b). For instance, when the reaction mixture is heated in a tubular reactor gradually from 100 $^\circ$C at the inlet to 320 $^\circ$C at the outlet, the biodiesel product obtained after 25 min of reaction time has an over 96% methyl ester content (He et al., 2007b).

3. Process improvements

The process improvements to the supercritical transesterification can be divided into three routes; the addition of the co-solvents, the use of catalysts and process modifications. The general goal, to reduce the original parameters altogether, is the most challenging aspect for supercritical transesterification. The reduced parameters are 270 – 300 °C, 15 – 20 MPa and an alcohol to oil molar ratio of 24:1 – 35:1.

3.1 The chronological development of supercritical transesterification

In 1998, non-catalytic transesterification of soybean oil at the near-critical point of methanol (230 $^\circ$C, 6.2 MPa and a 27:1 methanol to oil molar ratio) was invented as an alternative method to produce biodiesel, but this method obtained only an 85% methyl ester content after over 10 hours (Diasakou et al., 1998). In 2001, the pioneering transesterification of rapeseed oil in supercritical methanol at 350 $^\circ$C, 45 MPa and a 42:1 methanol to oil molar ratio, attaining a high methyl ester content (98%) after only 4 min was reported (Kusdiana & Saka, 2001; Saka & Kusdiana, 2001). Transesterification in supercritical methanol has evolved continuously since 2001.

In 2002, the transesterification of cottonseed, hazelnut kernel, poppy seed, safflower and sunflower derived oils in supercritical methanol were evaluated, with a nearly complete transesterification reaction being found for all of the vegetable oils (Demirbas, 2002). Meanwhile, the effect of water and free fatty acids (Kusdiana & Saka, 2004b), the catalytic effect of a metal reactor for supercritical transesterification with methanol (Dasari et al.,

2003; Kusdiana & Saka, 2004a) and the reactivity of supercritical alcohols were all reported (Warabi et al., 2004). In 2004, the first supercritical transesterification of sunflower oil with ethanol and supercritical carbon dioxide in the presence of a lipase enzyme were investigated in a batch reactor (Madras et al., 2004). However, during 2001 – 2005, the maximum alkyl ester contents were generally observed at nearly the same reaction conditions as that reported earlier by the Japanese pioneers (Kusdiana & Saka, 2001; Saka & Kusdiana, 2001).

In 2005, carbon dioxide and propane were introduced as co-solvents to obtain milder operating parameters for the supercritical transesterification with methanol (Cao et al., 2005; Han et al., 2005). Then, the two-step supercritical process (Minami & Saka, 2006) was demonstrated to reduce those operating parameters. In the following years, various catalysts were employed to assist the supercritical transesterification to achieve the maximum alkyl esters content but at milder operating conditions (Demirbas, 2007; Wang et al., 2008; Wang et al., 2007; Wang & Yang, 2007; Yin et al., 2008b). The continuous production of biodiesel in supercritical methanol was reported in 2006 (Bunyakiat et al., 2006) (Minami & Saka, 2006) and 2007 (He et al., 2007b). Therefore, the research focus on the reduction of the elevated operating conditions and continuous process has been ongoing since 2005.

In 2007, the gradual heating technique was introduced to limit or prevent thermal cracking of the unsaturated fatty acids and so prevent the reduction in the final methyl esters content obtained (He et al., 2007b). At the same time, the effect of using co-solvents to reduce the viscosity of vegetable oils was successfully investigated (Sawangkeaw et al., 2007). Supercritical transesterification in ethanol was studied in a continuous reactor in 2008 (Vieitez et al., 2008). In 2009, carbon dioxide was applied to supercritical transesterification with ethanol to reduce the operating conditions (Bertoldi et al., 2009). From 2007 to 2010, numerous additional studies, such as vapor-liquid equilibria of binary systems (Anitescu et al., 2008; Fang et al., 2008; Shimoyama et al., 2008; Shimoyama et al., 2009; Tang et al., 2006), phase behavior of the reaction mixture (Glišic & Skala, 2010; Hegel et al., 2008; Hegel et al., 2007), thermal stability of unsaturated fatty acids in supercritical methanol (Imahara et al., 2008) and process simulation and economic analysis (Busto et al., 2006; D'Ippolito et al., 2006; Deshpande et al., 2010; Diaz et al., 2009; van Kasteren & Nisworo, 2007) were reported, leading to a better understanding of the supercritical transesterification process.

3.2 The addition of co-solvents

The co-solvents that have been used in supercritical transesterification are liquid co-solvents, such as hexane and tetrahydrofuran (THF), and gaseous co-solvents, such as propane, carbon dioxide (CO_2) and nitrogen (N_2). Both types of co-solvents have different purposes and advantages that will be presented accordingly.

The liquid co-solvents are added into the supercritical transesterification reaction to reduce the viscosity of the vegetable oils, which might otherwise pose some pumping problems in a continuous process (Sawangkeaw et al., 2007). Since hexane is the conventional solvent for vegetable oil extraction, it could be possible to combine the supercritical transesterification after the extraction process using hexane for both. Additionally, THF improves the solubility of alcohols in the triglyceride and so forms a single phase mixture, allowing a single high-pressure pump to be employed to feed the reaction mixture into the reactor. A small amount of liquid co-solvent, up to ~20% (v/v) of hexane in vegetable oil, neither affects the

transesterification conversion nor lowers the original operating parameters. Whereas, an excess amount of hexane shows a negative effect on the final obtained alkyl esters content due to dilution and obstruction of the reactants (Tan et al., 2010a).

The addition of gaseous co-solvents to the supercritical transesterification reaction aims to reduce the original operating parameters. Due to the fact that the critical properties of gaseous co-solvents are much lower than alcohol and triglycerides, the addition of a small amount of gaseous co-solvents dramatically decreases the critical point of the reaction mixture allowing the use of milder operating parameters. For example, 0.10 mole of CO_2 or 0.05 mole of propane per mole of methanol lowers the reaction temperature and methanol to oil molar ratio to 280 °C and 1:24, respectively (Cao et al., 2005; Han et al., 2005). Furthermore, it was reported that the addition of N_2 improved the oxidation stability and reduced the total glycerol content in the biodiesel product (Imahara et al., 2009). Gaseous co-solvents have the advantage of easier separation from the product than the liquid co-solvents. For instance, they can be separated from the biodiesel product by expansion without using additional energy at the end of the transesterification process, unlike the liquid co-solvents that typically need to be recovered by distillation.

3.3 The use of catalysts

The homogeneous acidic and basic catalysts, such as H_3PO_4, NaOH and KOH, have been applied to supercritical transesterification to obtain milder operating conditions (Wang et al., 2008; Wang et al., 2007; Yin et al., 2008b). However, despite the milder operating conditions and faster rate of reaction obtained compared to the catalyst-free process, the addition of homogeneous catalysts is not an interesting idea because the problem of subsequent catalyst separation and waste management still remain, the same situation as with the conventional homogeneous catalytic process. The use of solid heterogeneous catalysts might enhance the technical and economical feasibility of using supercritical transesterification as a result of the ease of separation of the catalysts. However, the acidic and basic heterogeneous catalysts have different characteristics and advantages, as will be discussed below.

The acidic heterogeneous catalysts, such as WO_3/ZrO_2, zirconia-alumina, sulfated tin oxide and $Mg–Al–CO_3$ hydrotalcites, have been evaluated in the supercritical transesterification process (Helwani et al., 2009). However, despite the presence of the catalysts, the chemical kinetics of the acidic heterogeneous catalysts at atmospheric pressure were slower than the catalyst-free process. For example, the transesterification of soybean oil in supercritical methanol at 250 °C and a 40:1 methanol to oil molar ratio in the presence of WO_3/ZrO_2 as catalyst still takes 20 hours to attain a 90% conversion level (Furuta et al., 2004). However, the acidic catalysts are less sensitive to moisture and free fatty acid content than the basic catalysts and so they could be appropriate for low-grade feedstocks.

Alternatively, basic heterogeneous catalysts, such as CaO (Demirbas, 2007) MgO (Demirbas, 2008) and nano-MgO (Wang & Yang, 2007), have been applied to supercritical transesterification to reduce the original operating conditions. These catalysts have the ability to catalyze the transesterification reaction at the boiling point of alcohols and are stable at supercritical conditions. As expected, the rate of reaction at the supercritical conditions is faster than that at lower temperatures. For example, the CaO catalyst takes over 180 min to reach over 95% conversion at 65 °C (Liu et al., 2008), but only 10 min to reach complete conversion at 250 °C (Demirbas, 2007). Unfortunately, the basic catalysts can

be poisoned by the presence of water and free fatty acids. Therefore, further studies on using low-grade feedstocks with basic heterogeneous catalysts are still required.

3.4 The process modifications

The two-step process is based on firstly a hydrolysis reaction in subcritical water to obtain fatty acid products and then secondly the transesterification and esterification reactions in supercritical alcohol to form the alkyl esters product. The two-step process reduces the optimal operating parameters successfully since the hydrolysis and esterification reactions reach complete conversion at a lower temperature than the transesterification reaction does (Minami & Saka, 2006). Nonetheless, the two-step process is more complicated than the single-step process. For example, the process has high-pressure reactors that connect in series with a high-pressure water-glycerol-fatty acid phase separator. Furthermore, the glycerol-water stream, which is contaminated by trace amounts of fatty acids, requires more separation units. Although a distillation tower is the simplest separation unit for handling the glycerol-water stream, it consumes a large amount of energy to operate.

The high-temperature process involves increasing the operating temperature to 400 to 450 °C (Marulanda et al., 2009; Marulanda et al., 2010), so that the operating pressure, methanol to oil molar ratio and reaction time for complete conversion are reduced to 10.0 MPa, 6:1 and 4 min, respectively. As expected, the unsaturated fatty acids are partially consumed by thermal degradation but the oxidation resistance or storage stability of the product might be enhanced. Under these conditions it was reported that triglyceride and glycerol convert to oxygenate liquid fuel with a conversion of up to 99.5%. The glycerol dehydration both increases the fuel yield by up to 10% and reduces the amount of glycerol by-products (Aimaretti et al., 2009). By using the high-temperature process, the simultaneous conversion of triglyceride, free fatty acids and glycerol to liquid fuel is an alternative option that will increase the feasibility and profitability of supercritical transesterification.

4. Process prospective

In this section, the process prospective is split into two on the basis of the operating temperature since the temperature is the key parameter and chemical limitation for supercritical transesterification. The low-temperature approach aims to produce biodiesel that fulfills the 96.5% alkyl esters content requirement for biodiesel, while the high-temperature approach proposes an alternative method to synthesize the biofuel from a triglyceride-base biomass in supercritical conditions.

4.1 The low-temperature approach

The term "Low-temperature approach" defines supercritical transesterification within a temperature range of 270 – 300 °C so as to avoid the thermal degradation of unsaturated fatty acids and to maximize the alkyl esters content in the product. Without the assistance of any co-solvent, catalyst or other process modification techniques, the low-temperature approach employs a high pressure, a high alcohol to oil molar ratio and a long reaction time to achieve the >96.5% alkyl esters content required for biodiesel composition by the international standard. However, with the assisting techniques, as mentioned in Sections 3.2 – 3.4, the optimal conditions of low-temperature approach generally involve 20 – 30 MPa, an

alcohol to oil molar ratio of 24:1 and a reaction time over 30 min. The biodiesel product, which typically exceeds the 96.5% alkyl esters content of the international standard for biodiesel (EN14214), can be used as biodiesel.

For future research involving the low-temperature approach, the use of low-grade feedstocks and/or heterogeneous catalysts are very interesting topics. Alternatively, studies on scale up continuous reactors which are more suitable for an industrial scale are required. These have been successfully evaluated in lab-scale tubular reactors (Bunyakiat et al., 2006; He et al., 2007b; Minami & Saka, 2006), but an evaluation on a scaled-up reactor is presently lacking. An optimal reaction time to achieve over 96.5% alkyl esters content is the most important finding for the low-temperature approach studies because it corresponds with reactor sizing and reflects on the economical feasibility.

4.2 The high-temperature approach

The high-temperature approach uses supercritical transesterification at temperatures over 400 ºC, as described in Section 3.4. Even though the mono-alkyl esters content in the product from the high-temperature process is always lower than the biodiesel specification value of 96.5%, it can be proposed as an alternative biofuel that would require further studies on engine testing and fuel properties itself. Improved fuel properties, such as the viscosity and density of the biofuel product, from the high-temperature approach have been proposed (Marulanda et al., 2009). Furthermore, the operating temperature and pressure used in the high-temperature approach are close to those for catalytic hydrocracking in conventional petroleum refining, so it has a high possibility that it can be realized in an industrial scale.

Since the high-temperature approach, as recently initiated, has evaluated the triglycerides found in soybean oil (Anitescu et al., 2008) and chicken fat (Marulanda et al., 2009; Marulanda et al., 2010) only, then additional research into other triglycerides are needed. In addition, studies on the economical feasibility and environmental impact are also required. Indeed, the complete fuel properties need examining along with engine testing for the biofuel product for the high-temperature approach (Basha et al., 2009). On the other hand, the fine studies on the reactions pathways and/or chemical kinetics are also attractive works to better understand the high-temperature approach.

5. Conclusion

Supercritical transesterification is a promising method for a more environmentally friendly biodiesel production as a result of its feedstock flexibility, production efficiency and environmentally friendly benefits. For extended details, the review articles on supercritical transesterification with methanol (de Boer & Bahri, 2011; Sawangkeaw et al., 2010), or ethanol (Balat, 2008; Pinnarat & Savage, 2008) and other supercritical technologies (Lee & Saka, 2010; Tan & Lee, 2011) are also available elsewhere.

Even though the knowledgebase of this process has been growing the past decade, more work is still required for an adequate understanding of the process. In spite of its advantage of feedstock flexibility, there has so far been very little research on the use of low-grade feedstocks in supercritical transformation. Furthermore, prospective studies for both the low-temperature and high-temperature approaches, as mentioned previously, are required to realize supercritical transesterification at an industrial scale.

6. Acknowledgments

7. References

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Biodiesel - Feedstocks and Processing Technologies

Edited by Dr. Margarita Stoytcheva

The book "Biodiesel: Feedstocks and Processing Technologies" is intended to provide a professional look on the recent achievements and emerging trends in biodiesel production. It includes 22 chapters, organized in two sections. The first book section: "Feedstocks for Biodiesel Production" covers issues associated with the utilization of cost effective non-edible raw materials and wastes, and the development of biomass feedstock with physical and chemical properties that facilitate it processing to biodiesel. These include Brassicaceae spp., cooking oils, animal fat wastes, oleaginous fungi, and algae. The second book section: "Biodiesel Production Methods" is devoted to the advanced techniques for biodiesel synthesis: supercritical transesterification, microwaves, radio frequency and ultrasound techniques, reactive distillation, and optimized transesterification processes making use of solid catalysts and immobilized enzymes. The adequate and up-to-date information provided in this book should be of interest for research scientist, students, and technologists, involved in biodiesel production.

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