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Supercritical and Superheated Technologies: Future of Biodiesel Production

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Awareness on global warming has led to greater emphasis on renewable energy as the next source of energy. Renewable energy sources such as biofuels, wind energy, hydroelectric power, geothermal and solar powers are the solutions for the world not to be excessively dependent on fossil fuels. These renewable energy sources do not emit excessive harmful gases or particulates to the environmental. Instead, it has the potential to mitigate climate change and solve environmental pollution. Among these renewable energy sources, biofuels particularly biodiesel has been anticipated as the best alternative energy source in transportation sector.

Biodiesel has been receiving high attention from worldwide researchers because biodiesel is a good replacement fuels for fossil fuels. Biodiesel has low carbon emission and thus has minimal impact on environment. In addition, it also has similar chemical structure and energy content with fossil fuels. Therefore, biodiesel can be directly used in existing running vehicles without further modification. Biodiesel can be produced from a variety of feedstock, for instance edible oils, non-edible oils, animal fats and grease, which are renewable, sustainable, biodegradable and environmental friendly.

Biodiesel or fatty acid alkyl esters (FAAE) are commonly produced via trans-esterification reaction between oil (triglycerides) with alcohols. In this reversible reaction, 1 mol of triglycerides will react with 3 mol of alcohol to produce 1 mol of glycerol and 3 mol of FAAE. Fatty acid methyl ester (FAME) is produced when methanol is used as the source of alcohol, while fatty acid ethyl ester (FAEE) is produced when ethanol is used. Trans-esterification reaction can proceeds with or without the presence of catalyst. However, without any catalysts and in mild condition, the reaction proceeds in an extremely slow rate due to immiscibility between oil and alcohol.

Trans-esterification reaction can be catalyzed by both homogeneous and heterogeneous catalysts. Conventional homogeneous catalyst in commercial plant can be either acidic or alkaline such as sulfuric acid, hydrochloric acid, sodium hydroxide and potassium hydroxide. However, separation and purification of biodiesel from catalysts required complicated procedures, due to homogeneous phase of mixture. Other than that, free fatty acid (FFA) available in vegetable oils will react with catalyst to produce unwanted side product such as soap, making the feedstock in homogeneous catalyzed trans-esterification reaction required extra pre-treatment process and increase the production cost.

Subsequently, heterogeneous catalysts, for instance alkaline metal oxide, solid resins, enzyme and zeolites were developed to increase reaction rate and simultaneously simplify separation and purification of product. By using heterogeneous catalyst, FFA will not affect the yield of alkyl esters as there is no soap formation. However, it requires longer reaction time to give substantial amount of yield, implying that heterogeneous catalytic trans-esterification reaction is not efficient for commercial purpose.

In order to eliminate difficulties facing by catalytic trans-esterification reaction, non-catalytic trans-esterification reactions have been proposed, for instance supercritical fluid (SCF) technology and superheated methanol vapor (SMV) technology. Non-catalyzed supercritical trans-esterification reaction had been firstly proposed by Saka et al. [1] to produce biodiesel from triglycerides. In non-catalyzed supercritical technologies, alcohols (methanol, ethanol, isopropanol and isobutanol) will be heated up beyond their critical points to achieve a single fluid phases. Thus, biodiesel can be easily produced in a relatively fast rate without the presence of catalyst in SCF trans-esterification reaction. Separation and purification of biodiesel is relatively easier, simpler and cost effective to catalytic reactions. Table 1 shows the critical temperature and pressure for selected components that are commonly employed in SCF reaction.

At ambient conditions, triglycerides and free fatty acid are relatively non-polar compounds which will not soluble in alcohol. SCF application in trans-esterification reaction is the mixture of alcohol and triglycerides that are heated and pressurized above its critical temperature and critical pressure. Beyond its critical point, alcohol possesses increased mass diffusivity, decreased viscosity and a density that can be manipulated over a large range through relatively small changes in temperature and pressure. For instance, it is clearly shown in Figure 1 [2] that soybean oil and oleic acid are fully miscible with methanol at 300°C and 1650 psia, thus allowing the reaction to proceed even without the presence of catalysts.

Other than that, phase equilibrium between methanol and triglycerides during biodiesel production was studied by Glišić and Skala [3] from subcritical to supercritical region. It was reported that methanol and triglycerides are in equilibrium liquid phase from ambient conditions to subcritical condition. In addition, phase distribution will be affected by reaction mixture, temperature and pressure as shown in Figure 2. At supercritical stage (270°C and 200 bars), there is only a single phase exist during the methanolysis reaction that could produce 95% conversion of triglycerides.

The first advantage of SCF for biodiesel production is its simplicity in product separation as there is no catalyst and unwanted side product formed. Next, various types of oil feedstock can be directly trans-esterified by SCF despite the presence of free fatty acid and water content [4]. The reaction rate in SCF is relatively higher than conventional catalytic trans-esterification which need longer hours

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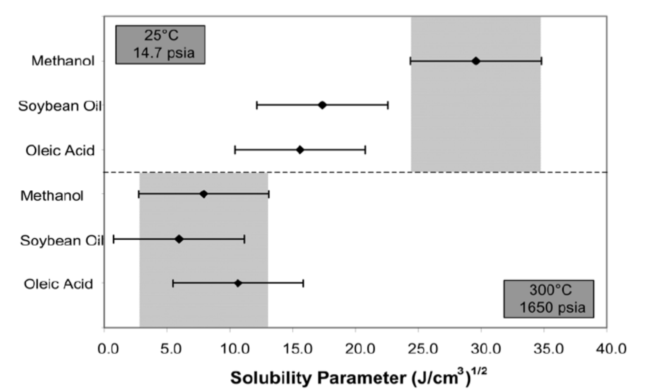

Figure 1: Hansen solubility parameters for methanol, soybean oil and oleic acid at different miscibility range [2].

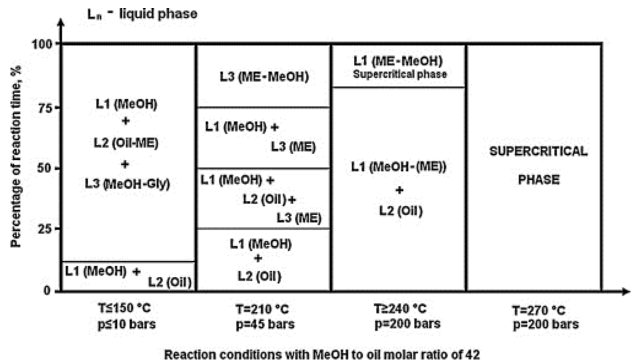

Figure 2: Phase transition during methanolysis of triglycerides at different reaction conditions [3].

of reaction time. However, SCF requires a high energy to reach supercritical stage, making it economically unattractive.

Therefore, a new emerging technology, known as superheated methanol vapor (SMV) was initially proposed by Yamazaki et al. [5]. Superheated methanol refers to methanol vapor that is above the boiling point of methanol (65°C). It possesses a lot of energy to react with triglycerides for biodiesel production. Moreover, superheated methanol could produce high quality light-colored biodiesel or commonly known as "water-white" biodiesel.

In SMV technology, the reaction is also known as reactive distillation process biodiesel and glycerol. Subsequently, the products will be distilled by superheated vapor from the liquid phase into vapor phase. Reaction temperature in SMV technique is relatively high at the range of 220-290°C and atmospheric pressure (0.1 MPa) [5]. As the operating temperature does not exceed the boiling point of all the components, both FAME and glycerol can be easily obtained in the gas sample product. Table 2 shows the boiling point for different triglycerides, methyl esters, methanol and glycerol at different vapor pressure [6].

Although methanol is employed excessively compared with supercritical or conventional technology, methanol could be recycled easily as there is no unwanted soap or by-product. Methanol vapor could be easily separated from biodiesel by using fractional distillation column since both biodiesel and glycerol have higher boiling points than methanol will condense into liquid phase, leaving behind a pure methanol vapor.

One of the main advantages of SMV is simple product separation and purification. In addition, cost of catalyst, pre-treatment on feedstock, post-treatment of product could be avoided. SMV technology also has high tolerance towards feedstock with high water and free fatty content such as *Jatropha curcas* [7] and waste cooking oil [8]. Other than that, economic analysis on SMV technology conducted by Nabetani et al. [8], had shown that SMV required lower production cost than conventional alkaline catalyst. A designed productivity of 6000 kL/yr was used to estimate the production cost needed. The cost required was estimated to be 40.2 yen/L in SMV comparing with 62.5 yen/L in alkaline catalyst method [8]. Thus, it is clearly shown that superheated methanol vapor method could reduce the cost involved in biodiesel production.

As a conclusion, SCF and SMV technologies could be the future in biodiesel production due to simplicity of product separation and purification. The enormous advantages of these processes should be taken into consideration by biodiesel producers throughout the world.

Solvent	Critical temperature (°C)	Critical pressure (MPa)
Methanol	239	8.09
Ethanol	243	6.38
Isopropanol	236	5.37
Isobutanol	275	4.30
Carbon dioxide	31	7.39
Methyl acetate	234	4.69
Dimethyl carbonate	275	4.63

Table 1: Critical properties for several reactants in SCF technology.

	Boiling point		Vapor pressure (Pa)	Reference
	(K)	(°C)		
Methanol	337.9	65	101300	[9]
Glycerol	563	290	101300	[9]
Methyl palmitate	611	338	101300	[10]
Methyl stearate	625	352	101300	[10]
Methyl oleate	622	349	101300	[10]
Methyl linoleate	639	366	101300	[10]
Tripalmitin	690	417	94552	[11]
Triolein	692	419	94552	[11]
Tristearin	586	313	6.66	[6]

Table 2: The boiling point of components.

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