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Supercritical Fluid Technology in Biodiesel Production: A Review

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Abstract

The finite nature of fossil fuels necessitates consideration of alternative fuels from renewable sources. The term biofuel refers to liquid, gas and solid fuels predominantly produced from biomass. Biofuels include bioethanol, biomethanol, biodiesel and biohydrogen. Biodiesel, defined as the monoalkyl esters of vegetable oils or animal fats, is an attractive alternative fuel because it is environmentally friendly and can be synthesized from edible and non-edible oils. Various methods have been reported for the production of biodiesel from vegetable oil and fats such as Transesterification, non-catalytic Supercritical fluid technology, micro emulsion, pyrolysis etc. In this article, the potential of supercritical fluids (SCF) as a sustainable route for biodiesel production is discussed and compared with conventional catalytic reactions. Although, the advantages of catalyst free SCF process are apparent; there are concerns regarding the huge energy required to conduct supercritical reaction at elevated temperature and pressure. Hence, there are challenges facing SCF process which need to be addressed before it could be a sustainable technology in the future.

Keywords: Supercritical fluid, Biodiesel, Biofuel, Non-catalytic, Alcohol.

1. Introduction

During the past 25 years, worldwide petroleum consumption has steadily increased, resulting in higher standards of living, increased transportation and trucking, and increased use of plastics and other petrochemicals [1]. In 1985, total worldwide petroleum consumption was 2807 million tons, but in 2008, the figure reached 3928 million tons [2], with an average annual growth rate of almost 1.5%. However, the petroleum is a finite source for fuel that is rapidly becoming scarcer and more expensive. At the end of 2008, according to BP's annual Statistical Review of World Energy, the world proven oil reserves were estimated at 1.7×10^{11} tons with a reserve-to-production (R/P) ratio of 42 years. In addition, petroleum-based products are one of the main causes of anthropogenic carbon dioxide (CO2) emissions to the atmosphere. Today, the transportation sector worldwide is almost entirely dependent on petroleum-derived fuels. One-fifth of global CO2 emissions are created by the transport sector, which accounts for some 60% of global oil consumption [3]. Around the world, there were about 806 million cars and light trucks on the road in 2007. These numbers are projected to increase to 1.3 billion by 2030 and to over 2 billion vehicles by 2050 [4]. This growth will affect the stability of ecosystems and global climate as well as global oil reserves [5]. There are active research programs to reduce reliance on fossil fuels by the use of alternative and sustainable fuel sources, and thus to increase the time over which fossil fuels will still be available. As an alternative to petroleum-based transportation fuels, bio-fuels can help to reinforce energy security and reduce the emissions of both greenhouse gases (GHGs) and urban air pollutants.

The term bio-fuel is referred to as liquid or gaseous fuels for the transport sector that are predominantly produced from biomass. A variety of fuels can be produced from biomass resources including liquid fuels, such as bioethanol, methanol, biodiesel, Fischer–Tropsch diesel, and gaseous fuels, such as hydrogen and methane .Biodiesel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats. Biodiesel production is a very modern and technological area for researchers due to the relevance that it is winning everyday because of the increase in the petroleum price and the environmental advantages. Biodiesel is defined as fatty acid alkyl ester and is derived from triglycerides via transesterification reaction with alcohol such as methanol and ethanol. In this reversible reaction, 1 mole of triglycerides will react with 3moles of alcohol to produce one mole of glycerol and three moles of fatty acids. If methanol is used as the source of alcohol, methyl esters of fatty acids will be formed. On the other hand, if ethanol is used, ethyl esters of fatty acids will be produced. Both of these fatty acids are commonly known as biodiesel. Generally, the sources of triglycerides are obtained from oil-bearing crops such as rapeseed, soybean and palm. Transesterification reaction can proceed with or without the presence of catalyst. However, without any catalysts the reaction proceeds in an extremely slow rate due to the two phase nature of oil and alcohol. Thus, catalysts are normally added to increase the reaction rate and enhance the yield of biodiesel. Transesterification reaction can be catalyzed by both homogeneous and heterogeneous catalysts. In addition, the catalysts can be either acidic or alkaline such as sulfuric acid, hydrochloric acid, sodium hydroxide and potassium hydroxide which are all homogeneous catalysts. In fact, most of the conventional commercial plants producing biodiesel from vegetable oils have been using these homogenous catalysts. On the other hand, heterogeneous catalysts are being extensively developed for transesterification reaction as well. The main advantage of heterogeneous catalyst is the simplified separation process of biodiesel from catalyst which is relatively easier compared to homogeneous reaction as the catalyst and products are in different physical phase.

Recently, there is a new trend in transesterification reaction with the advancement of supercritical fluids (SCF) reaction to produce biodiesel which do not require the presence of any catalysts. In this non-catalytic process, only reactants are added in the reaction mixture and heated to supercritical alcohol conditions to produce biodiesel which makes the process relatively simple and cost-effective. Although SCF reaction seems to be a promising technology which could solve existing problems of catalytic reactions, there has been a lot of debate on the efficiency of SCF reaction in terms of energy utilization and safety issue due to the high pres- sure and temperature employed in this technology. Hence, there are challenges and issues that need to be addressed before SCF technology can play a major role in biodiesel production. Consequently, this study aims to review recent trend and progress of transesterification reaction involving catalytic and non-catalytic SCF technologies and subsequently highlights the challenges of SCF process in order to be the main reaction route to produce a sustainable source of biodiesel in the future. Finally, some constructive recommendations to overcome the obstacles facing SCF technology will be proposed as well.

2. Transesterification

Transesterification reaction or also known as alcoholysis is the main reaction that occurs during biodiesel production between triglycerides and alcohol to produce fatty acid alkyl esters and glycerol. Fig.1 shows the overall transesterification reaction between the two main reactants. The objective of transesterification reaction is to reduce the viscosity of vegetable oils to a value similar to conventional diesel. Neat vegetable oils could not be used directly in the diesel engine due to its high viscosity and low volatility. Besides, it will also cause some carbon deposit and injector coking in the diesel engine. Generally, transesterification is an equilibrium reaction between triglycerides (TG) and alcohol (ROH) which consists of three consecutive and reversible reactions where diglycerides (DG) and monoglycerides (MG) are formed as intermediates. In this reaction, one of the alkoxy groups in the triglycerides is replaced by another alkoxy group in the alcohol to form a new ester compound which is the fatty acid alkyl ester (RCOOR). Finally, after all the three alkoxy groups available in triglycerides have been replaced, three mol of fatty acid alkyl ester and one mole of glycerol molecule will be formed. As these reactions are reversible, a larger amount of alcohol than stoichiometry requirement is usually employed to shift the reaction equilibrium to produce more alkyl ester.

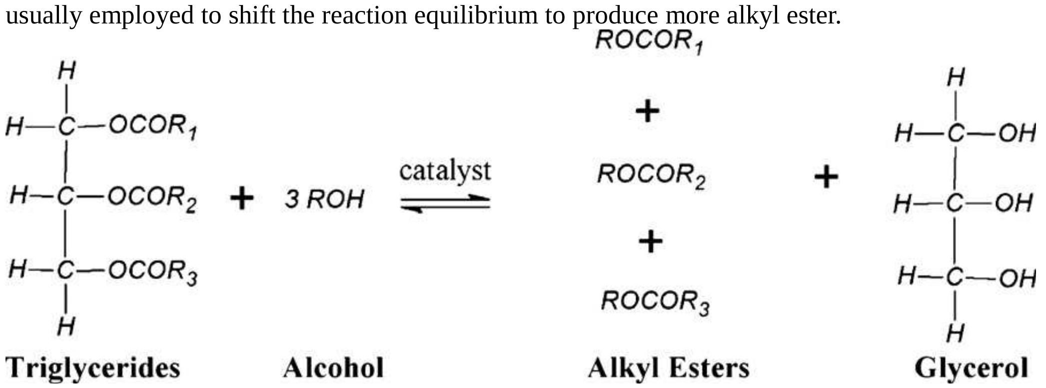

Fig.1. General Transesterification reaction between triglycerides and alcohol

2.1 Catalytic Reactions

Generally, alcohol and vegetable oil are not miscible to form a single phase of solution. Hence, the poor contacts are between these two reactants causes Transesterification reaction proceeds relatively slow. Consequently, vigorous mixing and stirring are carried out in order to promote and enhance solubility between these reactants and subsequently improve the reaction rates. Apart from that, temperature plays a crucial role in determining the reaction rate of the Transesterification reaction. For instance, at ambient temperature, the reaction requires upto 8h for completion. On the other hand, if the reaction was conducted at 60^0C, a mere 90 min of reaction time will be needed. Hence, introduction of catalysts at elevated temperature will improve the reaction rates and biodiesel yield as it is able to solve the problems of two-phase nature between oil and alcohol. Homogeneous base catalysts such as sodium hydroxide and potassium hydroxide are commonly and widely used in commercial biodiesel plant throughout the world. These soluble catalysts are inexpensive and effectively enhanced biodiesel production by producing intermediate of methoxide which will react with oil to produce biodiesel and glycerol. However, if the vegetable oil contains a high proportion of free fatty acids (FFA) or water, side formation of soap from FFA and base catalysts will occur which affect the yield of biodiesel substantially. Hence, homogeneous acid catalysts including sulfuric acid, phosphoric acid and hydrochloric acid are more suitable to be employed as no side reaction will occur in oils/fats which contain high percentage of FFA and water. Homogeneous acidic and alkaline catalysts processes have been proven to be able to produce a significantly high yield of biodiesel from triglycerides and alcohol in a short reaction time. However, these homogeneous reactions have several weaknesses and drawbacks which make them unattractive in terms of economic consideration. For instance, homogeneous phase of catalyst and products makes separation and purification steps complex and energy-consuming. Moreover, the alkaline and acidic waste water generated from the separation required additional cost for disposal. Apart from that, the recovery of glycerol is difficult due to the solubility of excessive methanol and catalyst. Besides, alkaline- catalyzed reaction is not recommended if high FFA and water content are present in vegetable oils or other triglycerides sources such as tallow, non-edible oils and waste cooking oil.

Recently, there has been growing interest in heterogeneous catalytic transesterification reaction due to its advantages com- pared to homogeneous reactions. For instance, problems facing homogeneous catalytic reaction such as tedious separation and purification of biodiesel will not arise as the catalyst and products are in different phase. Furthermore, heterogeneous catalysts can be recovered and reused easily which reduces the cost of catalyst significantly. Besides, it is not affected by the presence of high content of FFA in oils/fats. However, compared to homogeneous reaction, heterogeneous process proceeds at a relatively slower reaction rate due to the three-phase system of oil, alcohol and solid catalyst. In addition, solid catalysts are sensitive to the presence of water in reaction mixture which leads to leaching phenomenon of active compounds in catalysts. Consequently, catalyst efficiency is adversely affected and resulted in lower biodiesel yield. On the other hand, enzymes such as lipase are also extensively employed as well in transesterification reaction to enhance the reaction rate. Immobilized enzymes on a support material were found to be able to produce high purity of biodiesel and allow easy separation of glycerol. Furthermore, immobilized enzymes can be used repeatedly to increase the cost effectiveness of this catalytic process. However, enzymatic reaction suffers from long reaction time and inhibition effect of glycerol on enzymatic activities which makes the process becomes uneconomical.

2.2 Non catalytic Supercritical fluid (SCF) technology

A fluid heated to above the critical temperature and compressed to above the critical pressure is known as a supercritical fluid. A supercritical fluid is any substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist. The transesterification of triglycerides by supercritical methanol (SCM), ethanol, propanol and butanol has proved to be the most promising process. Table 1 shows the critical temperatures and critical pressures of the various alcohols. A non-catalytic biodiesel production route with supercritical methanol has been developed that allows a simple process and high yield because of simultaneous transesterification of triglycerides and methyl esterification of fatty acids. Because of having similar properties to petrodiesel, biodiesel, a transesterified product of vegetable oil, is considered as the most promising one for a Diesel fuel substitute. A reaction mechanism of vegetable oil in SCM was proposed based on the mechanism developed by Krammer and Vogel [6] for the hydrolysis of esters in sub/supercritical water. The basic idea of supercritical treatment is based on the effect of the relationship between pressure and temperature upon the thermo physical properties of the solvent, such as dielectric constant, viscosity, specific weight and polarity.

Homogeneous and heterogeneous catalytic reactions have been shown to have several limitations which include sensitivity to high water and FFA content, complicated separation and purification of biodiesel, enormous amount of reaction time and exorbitant cost of catalysts which make the process uneconomical. Collectively, these weaknesses arise due to utilization of catalysts in transesterification reaction. However, without the presence of catalysts, the reaction rate is too slow for it to produce considerable yield of biodiesel. Hence, researchers around the world have been developing numerous alternative technologies which can solve the problems facing catalytic reaction by using non-catalytic processes. One of them is by applying supercritical alcohol (SCA) technology, which has been getting a lot of attention lately [7, 8]. This novel technology utilizes SCA conditions to allow the usually immiscible oil and alcohol to form a single phase of solution. This would solve the problems of limited contact area between these two reactants which causes the reaction to occur at a slow rate for methanol critical temperature and pressure are 239^{0}C and 8.1MPa,respectively while for ethanol; it is 243^{0}C and6.3MPa,respectively. Moreover, without the presence of catalyst in the process the cost of production can be reduced substantially. In SCA reaction, triglycerides and alcohol are heated until the critical temperature and pressure of alcohol is reached and allows transesterification reaction to occur.

Table1:
Critical Temperatures and Critical Pressures of Various alcohols:

Alcohol	Critical temperature (K)	Critical pressure (MPa)
Methanol	512.2	8.1
Ethanol	516.2	6.4
1-Propanol	537.2	5.1
1-Butanol	560.2	4.9

During supercritical conditions of alcohol, the solubility parameter of alcohol is reduced substantially to a value near to triglycerides which leads to formation of a homogeneous phase between these two reactants. Hence, transesterification reaction can proceed without the presence of catalyst and the reaction rate for SCA was found to be superior to catalytic reactions as well[9]. In addition, downstream processes to separate biodiesel from glycerol were found to be simple with the absence of catalyst and the glycerol obtained was found to be of high purity. Furthermore, SCA process has a high tolerance towards impurities such as FFA and water in oils/fats and no side reaction of saponification was reported [10]. Instead, in this non-catalytic reaction, transesterification of triglycerides and esterification of FFA occur simultaneously in reaction mixture which leads to higher biodiesel yield. Furthermore, the presence of water will not adversely affect the reaction rate but was found to cause hydrolysis of triglycerides to FFA which subsequently can be esterifies to produce fatty acid alkyl esters. Hence, SCA reaction allows the employment of inexpensive feedstock such as waste oils/fats which commonly contained high proportion of these impurities.

Recently, there is an emergence of a new SCF technology which employs methyl acetate as supercritical medium rather than alcohol [11, 12]. The application of alcohol in conventional transesterification reaction produces glycerol as side product which leads to oversupply and devaluation in the market value biodiesel shows inferior performance at low temperature due to high viscosity and cloud point which limits its commercial application at cold climate countries. Therefore, biodiesel additive is commonly added into biodiesel to enhance its performance during cold season.

On the other hand, in Supercritical Methyl Acetate (SCMA) reaction, Fatty Acid Methyl Esters and triacetin, instead of glycerol are produced. Triacetin, a valuable fuel additive is formed simultaneously which leads to simplified downstream processes compared to conventional catalytic reactions while the mixture of FAME and Triacetin, a can be utilized as biodiesel, rather than FAME only .In this the mass ratio of FAME to triacetin was found to be approximately 4:1 in weight percent basis. Consequently, the total theoretical weight of biodiesel (FAME and triacetin) was found to be 125%, instead of 100% (FAME only). Hence, SCMA reaction is a promising technology for biodiesel production which not only can improve the quality of biodiesel but also minimizes the cost of producing biodiesel additives. Apart from that, in this glycerol-free process, separation and purification processes are simpler and less energy-intensive since both products could be utilized as biodiesel mixture.

3. Challenges and Limitations of SCF Technology

Although SCF technologies have enormous advantages compared to conventional catalytic reactions as discussed previously, there are several challenges and weaknesses that need to be addressed before SCF could play a major role in biodiesel production.

3.1. Energy consumption

One of the weaknesses of SCF technology is the apparent high energy required to reach the supercritical conditions of the solvent. The high temperature and pressure needed in the process, depending on the type of solvents employed, consume a huge amount of energy which is unsustainable in the longterm.For instance, in SCM reaction, the temperature and pressure must be above 239^0C and 8.1 MPa, respectively in order to achieve supercritical methanol state which makes SCF technologies an energy intensive process. Comparatively, it is widely reported that conventional catalytic reactions only require average reaction temperature < 150^0C and atmospheric pressure for optimum biodiesel production [13]. In addition, there are also concerns that the energy utilized in the process is more than the energy provided by biofuel obtained from SCF technology .In other words; more energy is required to yield products (biofuel) which have less energy content. Introducing, Integrated heating and Cooling system could improve SCF process in terms of energy consumption. Consequently, it is claimed that SCF technology is unsustainable in terms of energy consumption and subsequently not suitable for biodiesel production.

3.2 Cost

Apart from energy consumption, one of the major obstacles in commercialization efforts of SCF technology is the huge cost involved in the process. For instance, the elevated temperature and pressure needed in supercritical conditions required huge amount of energy which involved expensive expenditure in high pressure pumps and furnaces. Furthermore, employment of SCF technology to produce biodiesel requires high amount of solvent to push the reversible reaction to produce more biodiesel. Consequently, the high cost of reactant as well as additional processes to recover unreacted solvent increases the total expenditure in SCF reaction. In addition, due to the nature of SCF reaction conditions, the material of construction for most reactors in SCF technology is usually fabricated with additional strength and durability in order to sustain the extreme conditions. On top of that, the cost to fabricate a unique and huge reactor for commercialization purposes will be enormous. Hence, the costs involved in operation and maintenance of SCF process is relatively higher compared to conventional catalytic reactions.Therefore, employing Two-stage reaction is advantageous and recommended. Consequently, there has been limited commercialization projects of supercritical based biodiesel production due to the huge amount of costs involved in materials, operation and maintenance [14].

4. Conclusion

The advantages of SCF technology in biodiesel production compared to conventional catalytic reactions are enormous and vital in solving issue of energy security in the future. The supercritical fluid technology as sustainable route for biodiesel production has potential compared to catalytic process. However, there are several challenges which need to be addressed before SCF technology could play a major role as the main route for renewable and sustainable biodiesel production. Hence, several recommendations such as employing two-stage reaction or introducing integrated heating and cooling system are discussed in this article which could improve SCF process in terms of energy consumption as well as costs of material and equipment.

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