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# Emerging Green Technologies for Biodiesel Production

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## Abstract

The current global energy demand is met by burning the non-renewable fossil fuels. As the demand is escalating, resources and reserves are diminishing. In addition, the environment is threatened by the continuous emission of greenhouse gases; mainly CO<sub>2</sub>, which is worrying. Therefore, searching for alternatives is inevitable. Biodiesel received a considerable attention to potentially replace petroleum-based fuels. It can be produced from oil-rich feedstocks through several methods using different technologies, including transesterification. Although alkali catalyzed biodiesel process is commercially viable, several challenges were raised. In this chapter, an overview of the current status of biodiesel production approaches is discussed and the emerging technologies are highlighted. The chapter rewards the attention of using green processes, where the effectiveness of using; microalgae biomass as a green feedstock (compared to conventional crop-based seeds), lipases as green catalysts (compared to conventional chemical catalysts), and green and tunable solvents, such as neoteric solvents and supercritical fluids (compared to conventional volatile organic solvents) are addressed.

**Keywords:** biodiesel, microalgae, lipase, green solvents, microwave

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## 1. Biodiesel

The continuous dwindling fossil fuels supply and increasing atmospheric carbon dioxide emission have put the pressure on finding and developing sustainable alternative fuels. Biodiesel, which is a mixture of fatty acids alkyl esters, is the proposed alternative that can replace to the conventional petroleum diesel. The physical properties of biodiesel are similar to petroleum diesel and can be used without any modifications in the engine [1, 2]. In addition, biodiesel is a renewable, non-toxic and biodegradable fuel that can decrease the

reliance on fossil fuels and reduces harmful gasses emissions [3–8]. Furthermore, biodiesel has lower sulfur and aromatic contents. According to the U.S. Department of Energy statistics and analysis [9], in 2015, the production of biodiesel in the United States alone reached  $1.2 \times 10^9$  gallons. The statistics also indicated that the current biodiesel production in first 6 months of 2016 is about 21% higher than that obtained in 2015, during same duration.

## 2. Feedstocks

### 2.1. Conventional feedstocks

Triglycerides from oil-rich feedstock's, such as soybean, rapeseed, canola, sunflower, and palm, have been commonly used due to their abundant availability [10–16]. The first initiation was by the diesel engine inventor, Rudolf Diesel, who tested the use of peanut oil. However, natural oils are viscose with inappropriate cetane number. Thus, the idea was not accepted and vegetable oils were replaced by petroleum oil [7, 17–19]. The recent concern about limited oil reservoirs and oil explosion increased activities recalled the attention to use oil-rich feedstocks. Oils dilution with solvent, thermal cracking, pyrolysis, micro emulsions and transesterification has been suggested to overcome this viscosity limitation [20, 21]. Among these, transesterification with short chain alcohols, such as methanol and ethanol, in the existence of proper catalyst is the preferred and commonly used approach.

Although vegetable oils are available in large quantities, biodiesel production from these vegetable oils competes with their use as food source, which results in increasing their prices and affect food market. In addition, cultivating oil-rich crops requires lands and freshwater. It was reported that vegetable oil accounts for more than 60% of biodiesel overall production cost [5, 22]. From that prospective, non-edible oils such as those from non-edible plants that are not used in nutrition and can grow in the unfertile lands were suggested. However, freshwater requirement still exist. The use of waste oils and fats have been recommended, where there use is a waste management process [23], but contains large amount of free fatty acids and water which increases the production cost. Furthermore, cannot satisfy the ever-increasing global demands of diesel [24–26].

### 2.2. Green feedstock

Choosing an inexpensive and more sustainable oil feedstock is the critical step to get cost-effective biodiesel. Currently, microalgae, which are micro-organisms, received a promising attention. Due to their high oil content and growth rate, they have been considered as potential feedstock that can replace the conventional diesel [27–31]. Furthermore, cultivation of microalgae cells does not require land development neither freshwater. Several algae strains were found to grow in seawater and wastewater. The oil contents of such feedstocks are usually between 20% and 50% and reach be in some strains to 80% in dry basis. The strain may also change its composition by altering the growth conditions, such as light, nutrients, and temperature. The stressful environment usually results to higher oil productivity.

More interestingly, microalgae cells contain of protein, carbohydrates and lipids, which extend the application domains of produced biomass from food to biofuel. Microalgae cells are also used for CO<sub>2</sub> mitigation. However, to use microalgae biomass for biodiesel production, several steps have to be carried out, which are strain selection, biomass production and harvesting, and oil extraction and conversion.

### 3. Production technologies

Oils derivatization by transesterification is the most common approach used commercially. Typically, transesterification is a reaction between the oil and a short-chain alcohol that results to form an esters mixture and glycerol, as side product. The reaction is commonly take place in the presence of catalyst that can speed up the reaction, where three moles of alcohols are needed to react with 1 mol of the oil. Higher alcohol to oil molar ratios than the stoichiometry, however, is usually employed to produce more biodiesel.

#### 3.1. Conventional catalysts

As mentioned earlier, transesterification reactions are chemically catalyzed, which can be either base or acid catalysts, depending on the oil quality free fatty acids (FFAs) and water contents). Alkali catalysts, such as sodium hydroxide (NaOH) and potassium hydroxide (KOH), are the commonly used, due to their low cost and high achievable yields of more than 98% within a hour at reasonable temperature of 60°C [7, 32]. The reaction starts by preparing the alkoxide solution and charging it to the reactor with oils. The reaction is then heated to the reaction temperature for few hours. Products are then separated by gravity and crude biodiesel is obtained, which needs further washing to recover unreacted oils and alcohols. In addition to neutralization to receive the catalyst used.

Although the process is simple and commercially used, it is not practical with feedstocks containing high free fatty acids (FFAs) and water contents such as those from non-edible and waste oil due to soap formation that lowers the overall production yield and require large amount of catalysts [33, 34]. Pretreatment of oil prior transesterification by acid esterification have been suggested, where sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) is commonly adopted. Although it could be beneficial in enhancing oil quality, the process very slow and requires large amount of alcohols. In addition, acids are corrosive [5, 17, 35].

#### 3.2. Green catalysts

The use of enzymes, which are green catalysts, has been suggested. Among the several available enzymes, lipases (EC 3.1.1.3), which are of hydrolytic enzymes received an increasing attention in biodiesel production. Lipase-catalyzed biodiesel production due to their ability to act on ester bonds, at mild temperatures with less energy needs [35].

Lipases, namely the non-specific one, can convert oils from different sources, including from hose cooking, without any pre-treatment needs with easy product separation and no soap

formation. Among the several studied, lipases from *Candida antartica* [36–44], *Pseudomonas fluorescens* [45, 46], *Pseudomonas cepacia* [47], *Candida rugosa* [48–50] and *Rizhomucor miehei* [51, 52] are commonly used.

Although lipases are superior compared to chemical catalysts, accumulation of glycerol which is a by-product negatively affect the enzyme activity and reaction yield. Glycerol accumulation increases reaction mixture viscosity and forms hydrophilic layer around the enzyme, preventing the reaction substrate to reach enzyme active site [53, 54]. The highest glycerol inhibition effect was found when silica, which has the highest micro-pores structure, was used in the immobilization protocol of the lipase. Continuous removal of produced glycerol from reaction mixture and/or using *tert*-butanol as solvent was proposed [55, 56]. The use of silica gel that can absorb glycerol is also advantageous in such case [57].

The activity of the enzyme was also found to decrease when more than 1.5 molar equivalents of alcohol is used. This is because at certain concentration, alcohols which are hydrophilic become insoluble in oils and tends to strip-off the hydration layer of water from the lipase. Therefore, inhibition and loss in activity [2, 58–60]. Numerous solutions have been proposed to overcome short-chain alcohols inhibition limitation. These include step-wise alcohols addition [38, 61], use of acetates as acceptors [57, 58, 62], lipase pretreatment and activity enhancement [39], use of genetically modified methanol-tolerant lipase and improving the polarity of the reaction medium using organic solvents. The latter is commonly adopted method.

On the other hand, enzymatic biodiesel production is not yet commercialized due to enzymes high costs. Immobilization of the lipase is usually considered to re-use the enzyme in several cycles. Immobilization can also enhance the stability. For example, Novozym®435, which is an immobilized enzyme form of *Candida antartica*, was reused for 12 continuous cycles without any detectable loss in the activity [57] when the non-edible oil from *Jatropha* was transesterified with methanol. Whereas, when *tert*-butanol was used as reaction media Novozym®435 activity was maintained for 200 cycles [63].

## 4. Reaction medium

The solvent-free reaction systems are always the preferable one in enzyme catalyzed processes, however when the reaction is catalyzed by a lipase the use of solvents is essential to prevent the inhibition. By introducing hydrophobic solvents to the reaction, the solubility of reaction substrates increases resulting in reduced inhibition effect of hydrophilic substrates/products. In addition, the viscosity and transport limitations of reaction mixture to enzyme active sites decreases, which results in increased reaction yield [64, 65].

### 4.1. Conventional organic solvents

Numerous organic solvents have been used in biodiesel production, where the hydrophobicity was considered as main factor in selecting the proper solvent [66]. It was found that the

biodiesel production rate increases with the increase in the hydrophobicity of the solvent used, and hydrophilic solvents resulted tend to strip-off the bound water from the enzyme surface is used [39, 67–70]. Generally, the stripping was reported to take place when an organic solvent with Log  $P$  (hydrophobicity)  $<2$  used. *n*-Hexane, which has  $\log P = 3.5$ , has been commonly used, where its effect on enhancing the production yield, compared to solvent-free system, was observed in several studies. These includes the work of Nelson et al. [36], who tested the effect of using *n*-hexane in tallow fats transesterification with methanol at 3:1 methanol to oil molar ratio when catalyzed by *Mucor miehei* lipase. High yield reaching 95%, compared to 19% in solvent free, was obtained.

*tert*-Butanol is another solvent used in lipase catalyzed biodiesel processes. It has been selected as a capable alternative to *n*-hexane that cannot dissolve glycerol and minimize its inhibition effect [1, 13, 71–74]. A high methanol to oil molar ratio of 6:1 could be reached in soybean oils transesterification with Novozym®435, resulting in 60% yield, compared to only 10% in solvent-free system.

## 4.2. Green solvents

Although organic solvents enhance the production yield, an additional downstream unit is required to separate the solvent from the products, resulting in an additional production cost. Moreover, organic solvents are toxic and volatile and their use could pose several environmental issues that should be minimized. Efforts have been made to find alternative non-toxic and environmental benign solvents. In this regard, supercritical  $\text{CO}_2$  and ionic liquids (ILs) have been suggested.

### 4.2.1. Supercritical carbon dioxide

Supercritical fluids are fluids at temperatures and pressures above their critical points. They have been used in several applications. Among the different fluids, supercritical carbon dioxide ( $\text{SC}-\text{CO}_2$ ) and is been the most commonly used. Supercritical  $\text{CO}_2$  is a non-toxic and cheap fluid that appear in abundant with moderate critical parameters [75]. Compared to organic solvents,  $\text{SC}-\text{CO}_2$  has liquid solubilization capacity and gas diffusivity and viscosity, where small changes in the conditions can lead to a significant increase in the properties. These unique physiochemical properties allow it to be used in several applications, including separation and reaction [76–78]. Moreover, easy products separation can be achieved using  $\text{SC}-\text{CO}_2$ .

Although  $\text{SC}-\text{CO}_2$  has been commonly used in esters transesterification in the presence of lipase, its employment in biodiesel production is still new [79]. The compatibility of  $\text{SC}-\text{CO}_2$  with lipases is well recognized, and by using it in biodiesel production, the mass transfer of reaction substrates into enzyme active sites would be enhanced. In spite of the high pressure uses, it was clearly verified that it has minimal effect on enzyme inhibition at pressure less than 200 bars [80, 81]. Comparable yields to organic solvent were achieved when palm kernel and *Jatropha* oils were transesterified in the presence of Novozym®435 in  $\text{SC}-\text{CO}_2$  [75, 82–84].



Higher yield of 80% was obtained when SC—CO<sub>2</sub> was used in microalgae lipids transesterification in the presence of same lipase [42].

Supercritical CO<sub>2</sub> has been also used to extract oils for biodiesel production, such as those oils from vegetable crops [76, 77], microalgae cells [85–90] and fats from animal meat. The use of SC—CO<sub>2</sub> is adopted to minimize the use of toxic solvents and utilize the leftover, after extractions, in other applications such as in food and pharmaceutical industries, unlike *n*-hexane which is toxic and its use is an energy intensive process. Its effectiveness depends on the selected extraction conditions; namely the temperature, pressure and flow rate, where increasing the pressure increases SC—CO<sub>2</sub> density and the extraction yield whereas the temperature has two opposite effect that become equal at crossover pressure. By increasing the extraction temperature, SC—CO<sub>2</sub> density decreases and reduces its capability to solubilize the desired solute, while solute vapor pressure increases resulting in more solutes extraction. Several studies had considered the effectiveness of using SC—CO<sub>2</sub>. For example, similar yields performance of *n*-hexane were reported for oils extraction from *Spirulina platensis* [86], *Spirulina maxima* [87] and *Pavlova* sp. [89] microalgae cells. A higher efficiency was reported in extracting oils from *Chlorococum* sp. and *Nannochloropsis* sp. [90, 91].

As mentioned earlier, SC—CO<sub>2</sub> has many advantages. However, high pressure is needed for pumping and reaching the supercritical state of CO<sub>2</sub>, making the process costly. Depressurization to separate the biodiesel from enriched SC—CO<sub>2</sub> could negatively affect lipase structural confirmation, therefore its stability. To minimize the effect, continuous operation has been also considered. It has been successfully employed for soybean [92], corn oil [93, 94], microalgae and sunflower oils [95]. Taher et al. [55, 56] had stated that the feasibility of using SC—CO<sub>2</sub> for energy production is not evident, but combining oil extraction conversions to biodiesel in SC—CO<sub>2</sub> in one integrated system would be feasible and the additional pumping cost for energy production could be justified and make the overall process more feasible [42, 44, 96]. On the other hand, the presence of water could results to carbonic acid formation that change the reaction pH and denaturant the lipase. CO<sub>2</sub> may also react with the amine groups on the surface of lipase to form carbamates [97].

#### 4.2.2. Ionic liquids

Ionic liquids (ILs) are liquids of low crystallization tendency. They are composed of cations and anions and distinguished from conventional solvents in their non-vapor pressure feature. Thus, known to as "designer solvents." They have developed as green alternative solvents to replace the conventional volatile solvents in several process, including biodiesel production. The first attempt to use them in lipase catalyzed reactions was with [bmim][PF<sub>6</sub>] and [bmim][BF<sub>4</sub>], which were used in several reactions, including transesterification [98]. The selection the proper IL depends on its effect to enhance the enzyme activity reaction substrates/products solubility [99–103].

Typically, by judicious selection of the alkali chain on the cation and anion group, the physicochemical properties of designed IL can be tuned. For example, symmetric and shorter alkyl chains cations in the IL result in a higher melting temperature than those with asymmetric cations [104, 105], and increasing chain branching results in an increased the melting point

[106, 107]. However, it decreases with the increase in anion size. On the other hand, ILs with symmetric and fluorinated anions, have high viscosity, which is not preferable in enzyme catalyzed reactions. Ionic liquids based on cations with aromatic phenyl ring also have high viscosity as well [108].

The miscibility of the reaction substrates with the IL and IL hydrophobicity are main factor affecting the overall reaction yield, where the high solubility of reaction substrates to enhance reaction rate and low solubility of the biodiesel in the IL are the desired features in biodiesel production. The hydrophobicity of the IL depends mainly on the anions used. For example,  $[\text{PF}_6^-]$  and  $[\text{Tf}_2\text{N}^-]$  anions, which are hydrophobic results in making hydrophobic ILs, where those with hydrophilic anions, such as  $[\text{Cl}^-]$ ,  $[\text{Br}^-]$ ,  $[\text{I}^-]$ ,  $[\text{NO}_3^-]$ ,  $[\text{CH}_3\text{COO}^-]$  and  $[\text{CF}_3\text{COO}^-]$  for hydrophilic ILs. The hydrophobicity of ILs can also be affected by the length of the alkyl chain on the cation, in which longer alkyl chain results in a more hydrophobic IL [109–111]. Similar to of organic solvents, hydrophobic ILs are preferable in enzyme catalyzed biodiesel process, wherein hydrophilic ILs may strip-off the essential hydration layer and deactivate the lipase. Moreover, the nucleophilicity of the anion used in the IL combination affect lipase activity and stability, where high nucleophilicity of an IL may affect lipase structure activity interacting with the positively charged sites in lipase [112].

Among the several tested ILs in biodiesel production,  $[\text{PF}_6^-]$  and  $[\text{NTf}_2^-]$  based ILs are commonly used. For example,  $[\text{bmim}][\text{PF}_6]$  and  $[\text{emim}][\text{PF}_6]$  where used in sunflower oil transesterification Novozyme®435. High yield, reaching 98%, was achieved in  $[\text{emim}][\text{PF}_6]$  due to its higher hydrophobicity, however, insignificant products were obtained when  $[\text{BF}_4^-]$ -based ILs were tested [113]. The high yield obtained in  $[\text{emim}][\text{PF}_6]$  compared to  $[\text{bmim}][\text{PF}_6]$  is due to the ability of long-chain cation-based ILs to dissolve reaction substrates, thus the reaction take place in a two-phase system resulting in moderate efficiency.

In addition to ILs uses in lipase catalyzed reaction, they have been employed as green catalyst to overcome the reaction complication and product purification issues in chemical catalyzed reactions. The brønsted acidic ILs  $[\text{PY}(\text{CH}_2)_4\text{SO}_3\text{H}][\text{HSO}_4]$  and  $[\text{CyN}_{1,1}\text{PrSO}_3\text{H}][\text{Tos}]$  was found to be effective in transesterifying cottonseed (92% yield) and coconut (98% yield) oils, respectively, where comparable to that using concentrated sulfuric acid were obtained [114, 115]. Similar yield was also obtained from esterification of long-chain free fatty acids in  $[\text{NMP}][\text{CH}_3\text{SO}_3]$  [116]. In addition, biodiesel yield of 87 and 97% were also achieved using the basic IL  $[\text{bmim}][\text{OH}]$  [117] and  $[\text{hmm}][\text{OH}]$ , respectively [118].

Ionic liquids have been used to extract oils, commonly from microalgae cells as they can be used with wet cells without the need cell walls disruption. In such processes, hydrophilic ILs are used where they have the capability to dissolve algal cell components leaving the oils insoluble and float. The extraction from wet cells of *Chlorella vulgaris* was tested using IL  $[\text{emim}][\text{DEP}]$ , where 40% higher than *n*-hexane-methanol (7:3 v/v) mixture was obtained [119]. The effect of adding a polar solvent with the IL was also evaluated [120]. For example, a mixture of  $[\text{emim}][\text{CH}_3\text{SO}_4]$  and methanol was tested with *Chlorella sp.* cells containing 70% water, and an yield of 75% was achieved at 1:1.2 (w/w) solvents ratio.



The main challenge of employing ILs at industrial scale is in their high costs. Therefore, the recycling step is important. In addition, when long alkyl chain on cation-based ILs is used, the separation step is not easy and continuous recovery of biodiesel from reaction mixture as they produced is vital. Combination ILs with SC–CO<sub>2</sub> (IL-SC–CO<sub>2</sub>) has been recently suggested, where biodiesel can be recovered using SC–CO<sub>2</sub> in an effective manner. Such system was tested for biodiesel production from triolein using Novozym®435 in different ILs and high yields reaching 98% was obtained after 6 h [121].

## 5. Conclusions

Biodiesel production using chemical catalysts and solvents from received the attention to replace conventional diesel fuel. However, the process is not commercialized due to many shortcomings raised. The employment of green catalysts and solvents, either by SC–CO<sub>2</sub> or by ILs has been suggested to several technical restrictions. The use of integrated processes that combine the use of different green catalysts and solvents in a one process to enhance product separation and solvent recover is discussed.

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