Critical technical areas for future improvement in biodiesel technologies

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Abstract
This article analyses critical technical areas that currently limit the success of biodiesel as a fuel. The production process is currently shifting from homogeneous to heterogeneous using solid catalysts for a cleaner process and ease of product separation. The free fatty acid and moisture contents in the raw materials must be sufficiently low to avoid soap formation. The production of biodiesel with full compliance with ASTM D6751-07 or EN 14214:2003 is an uphill task. Current technologies for biodiesel production still do not provide more significant energy surplus. Biodiesel has relatively lower energy content, causing higher fuel consumption. Biodiesel has a drawback in terms of its cold flow properties. A high iodine value can cause degradation and polymerization of biodiesel components. Unconverted monoglyceride, diglyceride and triglyceride impurities will affect the engine performance. The alcohol content in biodiesel can attack rubber seals and gaskets. Biodiesel also can undergo chemical and biological modification to affect its quality in long-term storage. Biodiesel is also associated with high-level NOx emission, a fact that needs special attention.

Keywords: biodiesel, fuel, technical challenges, drawback, improvement

1. Biodiesel as an alternative fuel

Over the past two centuries, 90% of fuel consumed for energy generation and transportation has been contributed by non-renewable fossil fuels [1]. Known crude oil reserves could be depleted in less than 50 years at the present rate of consumption. Therefore, efforts in identifying renewable raw materials for the production of alternatives fuels would ensure that new technologies are available to keep pace with society’s need for new energy sources in the future.

Biodiesel is one of the current favourites to be the next generation fuel. It is made from renewable biological sources such as vegetable oils and animal fats [2]. It is biodegradable, non-toxic and has low emission profile. Chemically, biodiesel is fatty acid methyl esters (FAME) and they are called biodiesel only when used as fuel in diesel engines and heating systems [3, 4]. Biodiesel shows the following general advantages: (1) lower dependence on crude oil, (2) renewable fuel, (3) favorable energy balance, (4) reduction in greenhouse gas emission, (5) lower harmful emission, (6) biodegradable and non-toxic, (7) the use of agricultural surplus, and (8) safer handling (higher flash point than conventional diesel fuel) [3]. Biodiesel is often used as a blend, B20 (20 vol% biodiesel and 80 vol% conventional diesel), rather than as B100 [5].

FAME will be produced by transesterification of oils and fats with methanol in the presence of suitable catalysts. The process yields glycerol as a by-product. The stoichiometry of the reaction requires 3 moles of methanol and 1 mole of triglyceride to give 3 moles of fatty acid methyl ester and 1 mole of glycerol (figure 1). This leads to three consecutive reversible reactions in which monoglycerides and diglycerides are intermediate products. After the reaction, the glycerol is separated by settling or centrifugation and is purified to be used in traditional applications (pharmaceutical, cosmetic and food industries) or in recently developed applications in the fields of animal feed, carbon feedstock in fermentations, polymers, surfactants and lubricants [2]. The methyl ester phase is purified before being used as a diesel fuel. The fatty
acid composition of biodiesel is feedstock dependent, and is affected by factors such as climatic conditions, soil type, and plant health and maturity upon harvest [6].

2. Biodiesel production

2.1. Process selection

The transesterification process for biodiesel production is conventionally achieved using homogeneous acid or base catalysts and is operated in either batch or continuous mode [2]. Sodium hydroxide or sodium methy late is often used as the catalyst and the sodium is recovered after the reaction as sodium glycerate, sodium methyleate and sodium soaps in the glycerol phase. An acidic neutralization step is required to neutralize these salts and this step creates a significant amount of wastewater that requires treatment. Meanwhile, glycerol is obtained as an aqueous solution containing sodium chloride with a final purity of about 80–95% [7]. When sodium hydroxide is used as the catalyst, side reactions forming sodium soaps generally occur [4]. This type of reaction is also observed when sodium methy late is employed and a trace of water is present. The sodium soaps are soluble in the glycerol phase and must be isolated after neutralization by decantation as fatty acids [3].

Much effort has been expended on the search for a solid acid or solid basic catalyst that could be used in a heterogeneously catalyzed process. The use of heterogeneous catalysts does not produce soaps through free fatty acid neutralization and triglyceride saponification [3]. Some solid metal oxides such as those of tin, magnesium and zinc are known catalysts, but they actually act according to a homogeneous mechanism and end up as metal soaps or metal glyc erates [7]. In this new process, the catalyst promotes the transesterification reaction without catalyst loss. However, the reaction needs to be performed at higher temperature and pressure than those in homogeneous processes with an excess of methanol [4]. This will certainly increase the production costs and, therefore, more research work is needed to improve this technology to make it more interesting economically and favorable environmentally.

2.2. Catalysts

The transesterification process is an acid or base catalyzed reaction. Acid catalysts could be in the form of Bronsted acids, preferably sulfonic and sulfuric acids [4]. Despite giving high yields in alkyl esters, the reaction rate is slow, requiring a temperature of above 100 °C for more than 3 h. Basic catalysts are preferred because of the faster process, while the reaction conditions are moderated [8]. Nonetheless, their utilization produces soaps from the neutralization of fatty acids in the oil and triglyceride through saponification. Both soap formations are undesirable side-reactions because they partially consume the catalyst, decrease the biodiesel yield and make the separation and purification steps more difficult [7]. The soap also causes an increase in the viscosity or the formation of gel that interferes in the reaction as well as with the separation of glycerol [4]. The use of heterogeneous solid catalysts could eliminate this problem [7, 9], and the current research focus is centred around this type of catalysis.

2.3. Feed quality

The free fatty acid (FFA) and moisture content are key parameters for determining the viability of the transesterification process [4]. For a complete reaction, an FFA value of lower than 3% is needed and the other materials should be substantially anhydrous [7]. Ideally, it should be kept below 1%. The higher the acidity of the oil, the smaller the conversion efficiency that will result. FFAs react with a basic catalyst to form soap, as a result of which, one part of the catalyst is neutralized and is therefore no longer available for further reaction. Both excess as well as insufficient amounts of catalyst may cause soap formation.

If high FFA value oils are used, they must first be refined by saponification using NaOH solution to form soap to be subsequently separated. Conversely, the first step in the acid catalyzed process can also be used for the esterification of these...
Table 1. Properties of biodiesels from various sources against selected ASTM D6751-07 [12] and EN 14214:2003 standard limits [13]. (Note: Values in bold are outside the standard. N.D.: not determined.)

| Properties                | Standard Method | Limit | Cotton seed oil [14] | Soyabean oil [11] | Rapeseed oil [15] | Palm oil [11] |
|---------------------------|-----------------|-------|-----------------------|-------------------|-------------------|----------------|
| Cetane number             | ASTM D 613 EN ISO 5165 | 47 min 51 min | N.A. | 45 | 61.2 | 62 |
| Flash point (°C)          | EN ISO 3679 | 130.0 min 101 min | 70 | 178 | 180 | 164 |
| Cloud point (°C)          | EN ISO 3617 | Report | N.D. | 1 | -2 | 13 |
| Carbon residue (wt%)      | EN ISO 10370 | 0.05 max 0.3 max | N.D. | 1.74 | 1.1 | N.D. |
| Viscosity (@40°C)         | EN ISO 3617 | 1.9–6.0 3.5–5.0 | 4.0 | 4.5 | 5.7* | 5.7* |

*a* Not complying with EN 14214:2003 standard limit.

FFAs. Next, the transesterification process is completed using alkaline catalysts. The catalysts should also be maintained in an anhydrous state [4]. Prolonged contact with air will diminish the effectiveness of these catalysts through interaction with moisture and carbon dioxide [2]. Unfortunately, the most profitable raw materials for biodiesel such as waste cooking oils and fats or low-value fats usually have a high content of FFA [10]. These are among the challenges facing biodiesel production processes, and proper controls are needed to avoid unnecessary higher production costs and substandard biodiesel.

3. Biodiesel quality

3.1. Compliance with standard

Biodiesel needs to meet strict requirements according to ASTM D6751-07 or EN 14212:2003 to be used as fuel [5] and this could be a very challenging task. In order to produce biodiesel that consistently fulfills the technical regulation, one needs to follow a strict procedure for the raw material, conditions and catalyst, but most importantly, the refining procedure. Most of the literature reports produced biodiesel that are well outside the specifications. Table 1 summarizes the properties of a few biodiesel samples vis-à-vis the ASTM D6751-07 or EN 14214:2003 standard limits. The non-compliances are common in terms of the cetane number that is associated with the ignition delay of the engine [11], flash point and carbon residue which is attributed to partial conversion of triglycerides [2]. A non-compliance with the more stringent viscosity standard limit of EN 14214:2003 is also commonly reported. Thus, more efforts towards better control of the biodiesel production process as well as the efficient refining of the raw biodiesel are very much in demand.

3.2. Energy content

Arguments for an alternative energy source are not complete if the energy level of the alternative fuel is not analyzed. Biodiesel has a low heating value (10% lower than diesel) due to the presence of a substantial amount of oxygen in the fuel. Coupled with higher specific gravity (0.88) as compared to mineral diesel (0.85), the overall impact is approximately 5% lower energy content per unit volume [11]. This results in higher specific fuel consumption values of the biodiesel.

Despite reports on a positive energy balance of about 3:1 for biodiesel [15], a utilizable energy analysis of this fuel leads to an interesting result. This is, to a certain extent, consistent with the controversial report by Pimentel and Patzek [16] which reports that biodiesel production using soybean requires 27% more fossil energy than the biodiesel fuel produced.

Figure 2 shows the energy inputs for various biodiesel production processes. Data by Frondel and Peter [17] have been used as the raw data and by incorporating 16% energy input used for refinement, distribution, delivery, etc of biodiesel [18], new data have been plotted in the figure. Those values are deemed more realistic estimated energy inputs required before the biodiesel can actually meet consumers. Also, the estimated biodiesel energy content commonly reported in the literature is 32.8 MJ l⁻¹ [17]. Taking the highest thermal efficiency of a modern diesel engine as 40% [19, 20], the utilizable energy from biodiesel is only 15.2 MJ l⁻¹. Thus, based on current biodiesel production technologies, the maximum energy surplus that can be offered by this fuel is merely 1.3 MJ l⁻¹. This is far from satisfactory,
bearing in mind that the estimated energy saving for fossil diesel is generally in the realm of two-thirds [17, 21] or about 23.8 MJ l⁻¹ (based on data in [11]). Some processes even consume more energy than the energy that can be offered by the fuel itself to render a deficit energy balance. Thus, despite being rather controversial and arguable, this energy balance shows that biodiesel is currently not a perfect substitute for conventional diesel. Efforts should be dedicated to further improve the production and distribution processes and energy utilization efficiency so that a more significant energy surplus could be materialized.

3.3. Physical and chemical properties

Viscosity is one of the important fuel properties as it controls the characteristics fuel injection in the injector [22]. The viscosity of biodiesel is approximately 1.5 times higher than that of fossil diesel [23]. At low temperature, fuel may thicken and might not flow properly, thereby affecting the performance of fuel lines, pumps and injectors [4]. The effects of viscosity can also be seen in the quality of atomization and combustion of fuel lines, pumps and injectors [4]. The effects of viscosity might not flow properly, thereby affecting the performance of fuel lines, pumps and injectors [4]. The effects of viscosity can also be seen in the quality of atomization and combustion as well as engine wear [6]. B100 biodiesel gels at ~3 °C, and therefore it becomes difficult to use in diesel engines and home heating systems as it may clog filters and cause problems in pumping from the fuel tank to the engine or furnace burner [5].

The lubricity of petroleum diesel (especially those with low sulfur content) increases on the addition of biodiesel [24]. Therefore, blending of conventional diesel and biodiesel could help in obtaining a fuel with acceptable lubricity. The cloud and pour points of biodiesel are higher than those of fossil diesel [5]. Various techniques and empirical models have been investigated for pour and cloud point measurements of pure biodiesel (from different feedstocks) and its blends with diesel fuels. Both the pour point and cloud point of biodiesel and its blends with diesel fuel decrease with biodiesel concentration [6] and with the addition of depressants [25].

A higher iodine value implies higher tendency of the biodiesel to undergo chemical as well as microbial changes that will degrade the fuel. The iodine values of B100 and B50 are 84.4 and 55.7, respectively [5]. The iodine value is decreased, and hence the degree of polymerization decreases, through blending of B100 with fossil diesel fuel. Similarly, the saponification values of B100 and B50 are 183.7 mg KOH g⁻¹ and 94.1 mg KOH g⁻¹, respectively. The saponification value is reduced by half after the blending as fossil diesel does not contain any free fatty acids that can be saponified. The iodine value is slightly higher than half, probably due to the contribution from unsaturated compounds from fossil diesel fuel. As a conclusion, the physical and chemical properties of biodiesel might not permit it to be directly used as a fuel without a proper pre-heating system, blending with conventional fuel or the use of fuel additives.

3.4. Product purity

Ideally, biodiesel needs to be 100% FAME, but practically, low conversion, side reactions and difficulty in product separation result in the presence of impurities in biodiesel. A higher conversion of feedstock oils to esters gives better engine performance [26]. Many impurities in biodiesel such as glycerol, monoglycerides and diglycerides appear unfavorable for optimum engine performance [11]. The monoglycerides cause turbidity (crystals) in the biodiesel. This problem is obvious, especially for transesterification of animal fats such as beef tallow [14]. The impurities raise the cloud and pour points. On the other hand, there is a large proportion of saturated fatty acid esters in the beef tallow esters (almost 50% w/w). This portion makes the cloud point and pour point higher than those of vegetable oil esters [4].

To meet ASTM D 6751-07 or EN 14214:2003, biodiesel should satisfy several specifications. However, to satisfy all the standard characteristics, biodiesel needs to be 99.7% ester [4]. Low-grade biodiesel with low methyl ester conversion affects the quality standard parameters. The use of low-grade biodiesel is a significant issue since the unconverted triglycerides could polymerize and eventually build up in the fuel lines, which could cause significant plugging in fuel filters, power loss and ultimately engine damage [26]. However, obtaining esters in biodiesel is not an easy task as the current technology in the manufacturing and refining of biodiesel are still not so economically favorable [2].

4. Field problems

4.1. Material resistance

In biodiesel production, excess alcohol is used and it is recovered from the product through evaporation [7]. Improper control of this stage results in a residual content of alcohol in biodiesel. A high level of alcohol in biodiesel causes accelerated deterioration of natural rubber seals and gaskets [4]. Therefore, control of the alcohol content is required. B100 may cause rubber seals, some hoses and gaskets from engines older than 1994 to wear faster. Natural or nitrile rubber compounds, polypropylene, polyvinyl and Tygon materials are particularly vulnerable and should be avoided [11]. Teflon, viton and nylon have very little reaction with biodiesel and are among the compatible materials that can be used. Besides, biodiesel also acts as a solvent which can dissolve sediments in diesel fuel tanks and consequently clog fuel filters [27]. This problem often occurs when shifting from conventional diesel to biodiesel using the same fuel system. Polymerization of certain biodiesel components themselves can result in the formation of insoluble deposits. Thus, if biodiesel were to be considered as an alternative fuel, the resistance of some engine parts must first be evaluated and suitable compatible materials must be used. Besides, the possibility of fuel line clogging should first be evaluated when making a shift from conventional diesel to biodiesel.

4.2. Biological stability

Long-term stability of biodiesel is another problem associated with the field application of biodiesel. This fuel tends to deteriorate via hydrolytic and oxidative reactions due to its high degree of unsaturation [4]. This may lead to the formation of insoluble products that cause problems within the fuel system. While biodiesel is generally considered to be insoluble
in water, it actually takes up considerably more water (as much as 1500 ppm) than fossil diesel [26]. In long-term storage, condensed water in the fuel tank can support the growth of bacteria and molds that use biodiesel as the food source. These hydrocarbon-degrading microorganisms will grow as a film or slime that can accumulate as sediment over longer periods of time. The microbial slime can subsequently detach from the wall of the tank and clog fuel filters.

Biodiesel can be stored for long periods of time in closed containers with little head space. Long-term storage in partially filled containers should be avoided as condensation in the container can contribute to the long-term deterioration of the biodiesel [15]. The containers should be away from direct sunlight while the storage temperature should be sufficiently low to avoid oxidative or hydrolytic degradation problems. Biocides are available to treat biodiesel fuel, and with their use at very dilute concentrations, they can inhibit the growth of microbes over a long period of time [27]. In conclusion, several extra precautions should be taken when long-term storage of biodiesel is necessary.

4.3. Engine performance

Several experimental investigations have been carried out by researchers to evaluate the engine performance with different biodiesel blends [11, 28, 29]. Preheating could be needed in some regions to liquefy biodiesel. This will certainly reduce the surplus energy that can be offered by this fuel. With preheating of palm oil methyl esters above room temperature, the brake power output and exhaust emission characteristics improved significantly [29]. Interestingly, most relevant combustion parameters for soy methyl esters such as ignition delay, peak pressure and the rate of pressure rise were close to those observed with fossil diesel combustion at the same engine load, speed, timing and nozzle diameter [28]. It was also found that the ignition delay for the two fuels was comparable in magnitude and the ignition delay of soy biodiesel was found to be more sensitive to nozzle diameter than diesel [11].

4.4. NOx emission

NOx emission by biodiesel engines is a subject of considerable research. As biodiesel generally contains about 10 wt% of oxygen, it can be considered as an oxygenated fuel. The high oxygen content results in the improvement of its burning efficiency and reduction in the particulate matter (PM), CO and other gaseous pollutants [11]. However, it also leads to higher production of NOx (by ∼10%) compared to fossil diesel, particularly under a high-temperature burning environment [30]. The emulsification technique is being investigated to curtail the NOx emission problem from burning biodiesel as it can improve the combustion efficiency of the fuel. However, a surfactant might be needed to reduce the surface tension between dispersed phases to form a continuous phase [31]. Another solution could be from the modification of the engine itself, especially in the aspect of the injection timing during the fuel combustion process [11] or by the use of certain fuel additives [14]. Therefore, the gas emission of conventional diesel engine running on biodiesel should be first evaluated.

5. Conclusions

Despite interesting advantages offered by biodiesel, a few technical problems still remain to limit its successful and practical use. The future success in biodiesel application depends on how well those drawbacks are resolved. The biodiesel production process is currently shifting from homogeneous to heterogeneous using innovative solid catalysts for the sake of high yield, cleaner process and ease of product separation. However, it is not so favorable economically. The free fatty acid and moisture contents in raw materials must be sufficiently controlled to avoid soap formation. The production of biodiesel with full compliance with ASTM D6751-07 or EN 14214:2003 is a very challenging task. Current technologies for biodiesel production processes are still expensive and do not provide more significant energy surplus. Higher fuel consumption is expected with biodiesel due to relatively lower energy content. Biodiesel has a drawback in terms of its cold flow properties in cold environments and auxiliary preheating equipment could be needed. A high iodine value can cause polymerization of biodiesel components, while monoglyceride, diglyceride and triglyceride impurities will also affect the engine performance. The alcohol content in biodiesel can attack some rubbers and polymers causing material failure. Biodiesel also can undergo chemical and biological changes to affect its quality during long storage. Biodiesel is also associated with high-level NOx emission due to its high oxygen content.

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