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Biodiesel production using a membrane reactor

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Abstract

The immiscibility of canola oil in methanol provides a mass-transfer challenge in the early stages of the transesterification of canola oil in the production of fatty acid methyl esters (FAME or biodiesel). To overcome or rather, exploit this situation, a two-phase membrane reactor was developed to produce FAME from canola oil and methanol. The transesterification of canola oil was performed via both acid- or base-catalysis. Runs were performed in the membrane reactor in semi-batch mode at 60, 65 and 70 °C and at different catalyst concentrations and feed flow rates. Increases in temperature, catalyst concentration and feedstock (methanol/oil) flow rate significantly increased the conversion of oil to biodiesel. The novel reactor enabled the separation of reaction products (FAME/glycerol in methanol) from the original canola oil feed. The two-phase membrane reactor was particularly useful in removing unreacted canola oil from the FAME product yielding high purity biodiesel and shifting the reaction equilibrium to the product side.

Keywords: Biodiesel; Methanol; Acid-catalyzed transesterification; Base-catalyzed transesterification; Two-phase membrane reactor

1. Introduction

Biodiesel is a clean-burning diesel fuel produced from vegetable oils, animal fats, or grease. Its chemical structure is that of fatty acid alkyl esters (FAAE). Commercially, biodiesel is produced by transesterification. This reaction consists of transforming triglyceride (TG) into FAAE, in the presence of an alcohol (e.g. methanol, ethanol) and a catalyst (e.g. alkali, acid, enzyme) with glycerol as a major by-product. The reaction scheme is shown in Fig. 1.

In Fig. 1, X represents the alkyl group of the alcohol (e.g. CH_3 for methanol) while R is a carbon chain typically on the order of 11–20 carbon atoms long. The conversion of TG to FAAE comprises three consecutive reversible reactions with diglyceride (DG) and monoglyceride (MG) as intermediate products. Biodiesel is being used increasingly in public transportation in Europe, Japan and North America.

Due to diminishing petroleum reserves and the environmental consequences of exhaust gases from petroleum-derived fuels, such as gasoline and diesel, biodiesel has attracted attention during the past decade as a renewable and environmentally friendly fuel. Because biodiesel is made entirely from vegetable oil or animal fats, it is renewable, environmentally benign (biodegradable), and does not contain any sulphur, aromatic hydrocarbons, metals or crude oil residues.

Like petroleum diesel, biodiesel operates in compression–ignition engines such as those used in farm equipment, and private and commercial vehicles. Essentially no engine modifications are required, and biodiesel maintains the payload capacity and range of diesel. Because biodiesel is oxygenated, it is a better lubricant than diesel fuel, increasing the life of engines, and is combusted more completely. Indeed, many countries are introducing biodiesel blends to replace the lubricating effect of sulfur compounds in low-sulfur diesel fuels (Anastopoulos et al., 2001; Dmytryshyn et al., 2004). The higher flash point of biodiesel makes it a safer fuel to use, handle and store. With its relatively low emission profile, it is an ideal fuel for use

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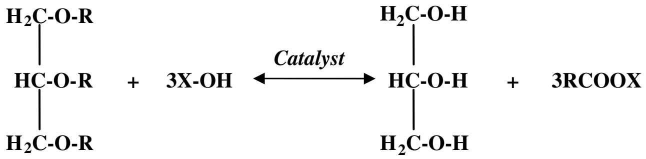

$$\begin{array}{l} H_2C\text{-}O\text{-}R \\ HC\text{-}O\text{-}R \\ H_2C\text{-}O\text{-}R \end{array} + 3X\text{-}OH \xleftrightarrow{Catalyst} \begin{array}{l} H_2C\text{-}O\text{-}H \\ HC\text{-}O\text{-}H \\ H_2C\text{-}O\text{-}H \end{array} + 3RCOOX$$

Fig. 1. Stoichiometric reaction for conversion of triglyceride to fatty acid alkyl esters.

in sensitive environments, such as marine areas, national parks and forests, and heavily polluted cities.

Existing technology to produce biodiesel continues to require government subsidies in order to be profitable. One reason is the high cost of virgin vegetable oil, the source of TG (Coltrain, 2002). In order to reduce production costs and make it competitive with petroleum diesel, low cost feedstock, such as non-edible oils, waste frying oils and animal fats, could be used as raw materials (Zhang et al., 2003a). However, the relatively higher amounts of free fatty acids (FFA) and water in this feedstock results in the production of soap in the presence of alkali catalyst. Thus, additional steps to remove any water and either the FFA or soap from the reaction mixture are required. In fact, commercial base-catalyzed processes often employ an acid-catalyzed pre-esterification reactor to remove excess FFAs.

Alkali-catalyzed transesterification proceeds much faster than that catalyzed by an acid and is the one most used commercially (Freedman et al., 1984). Considerable research has been done on biodiesel made from virgin vegetable oils (e.g. soybean oil, sunflower oil, rapeseed oil) using alkali catalysts. The majority of biodiesel today is produced by alkali-catalyzed (e.g. NaOH, KOH) transesterification with methanol, which results in a relatively short reaction time. However, as mentioned above, the vegetable oil and alcohol must be substantially anhydrous and have a low FFA content because the presence of FFA promotes soap formation. The soap formed partially consumes the catalyst, lowers the yield of esters and renders the downstream separation of the products difficult (Freedman et al., 1984).

Freedman et al. (1985) reported a 98% yield of biodiesel in 1 h using alkali catalysts such as sodium hydroxide or sodium methoxide with alcohols such as methanol, ethanol, and 1-butanol. Freedman et al. (1984) investigated the effect of the molar ratio of the alcohol to oil, type of catalyst (base vs. acid), temperature and degree of refinement of the oil on the yield of biodiesel. For the alkali-catalyzed reaction, the effect of alcohol to oil ratio was found to be the most important variable affecting the yield, while temperature had a significant effect on the initial reaction rate. It also was mentioned in their study that acid catalysts would be more effective when the degree of refinement of oil was low, and for oils that had a high FFA content.

Several studies have been done on the production of biodiesel from waste oils or animal fats (Nye et al., 1983; Watanabe et al., 2001) describing the feasibility of making quality biodiesel from this feedstock while identifying the problems with the FFAs present in the raw materials. Experiments in our laboratory (McBride, 1999; Ripmeester, 1998; Zheng, 2003) showed that greater than 99.5% conversion of waste frying oil to biodiesel could be achieved within a reasonable time period (~3 h at 70 °C) through transesterification with an excess of methanol (methanol:oil molar ratio was >50:1) catalyzed by sulphuric acid. Despite the slower reaction rate, this approach has several advantages over the base-catalyzed method (Canakci and Van Gerpen, 1999; Zhang et al., 2003a,b): it employs a one-step process as opposed to a two-step process; it can handle feedstock with a high FFA content; downstream separation of the biodiesel is straightforward; and a high quality glycerol by-product is produced.

Aside from the slow reaction rate, another drawback of the acid-catalyzed process is the requirement for the reactor to withstand an acidic environment. Nonetheless, our economic assessment carried out on four different continuous processes with different types of oil (virgin vs. waste) and catalysts (acid vs. alkali) showed that although the alkali-catalyzed process using virgin oil had the lowest capital investment cost, the cost of using virgin oil led to a higher total manufacturing cost (Zhang et al., 2003b). When waste frying oil was used in the alkali-catalyzed process, a pre-treatment unit was required to reduce the content of the FFA. Thus, the cost associated with the pre-treatment unit offset the cost savings due to the use of waste frying oil. In contrast, the acid-catalyzed process using waste frying oil did not require a pre-treatment step and had the lowest total manufacturing cost, and the highest profitability. Yet another drawback to the acid-catalyzed process, is that high alcohol to oil ratios are necessary to promote the conversion of oil to FAAE (Freedman et al., 1985). These higher amounts of alcohol increase the reactor size but recycling can mitigate some of the associated increases in cost. Nonetheless, the issue of separating these substantial amounts of alcohol from the FAAE becomes important.

Another issue that plagues biodiesel production is the removal of residual TG and glycerol from the biodiesel product. One approach is to drive the reaction as close to complete conversion of the TG as possible. However, the transesterification of TG is an equilibrium reaction, and there are thus, limits to this approach. Other approaches employ multiple water washing steps of the product stream, which can give rise to a challenging waste treatment problem in the wastewater stream. Karaosmanoglu et al. (1996) studied three different separation methods and found that hot water washing at 50 °C was the best way to separate and purify the biodiesel product. Bam et al. (1995) suggested that glycerine could be added as a solvent to wash impurities. Hayafuji et al. (1999) studied the use of a solid absorbent, such as activated clay, activated carbon, activated carbon fibre, etc. to purify the resultant esters.

Miscibility is an important factor in biodiesel production. The conventional transesterification method results