INDUSTRIAL PROCESSES

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Introduction

Biodiesel is a fuel that is made up of monoalkyl esters of long-chain fatty acids present in vegetable oils and animal fats. It may also be used as a blendstock where it is mixed with petroleum fuel before use. It has the advantages of being environmentally friendly, producing safe emissions, having increased lubricity, and having a low sulfur content (ADM). It can be produced using renewable resources and is energy efficient. It is most useful as a fuel for diesel engines. It is nontoxic and biodegradable, and has the potential to reduce global warming (Conley, 2006).

This paper throws light on the production process involved in the manufacture of biodiesel, the important factors affecting its production and use, and the current industrial concerns regarding the large scale use of biodiesels.

1. Major processing steps from raw material to finished product

1.1 Raw materials used

The raw materials commonly used for the production of biodiesels are short chain alcohols, vegetable oils and animal fats. Among vegetable oils, rapeseed, soybean, palm, sunflower, safflower, peanut, linseed, canola, flax, avocado, olive, coconut oils and oil obtained from microalgae are used. Non-edible oils such as castor, cotton, tung, jatropha and jojoba oils are also used due to their lesser cost. Among short chain alcohols, methanol is used most frequently and ethanol is used less often. Among animal fats, acidic grease from pork, poultry, cattle and fish are used (Romano and Sorichetti, 2010).

1.2 Transesterification of oils or fats

The first step in the biodiesel production process is the transesterification of vegetable oils or animal fats. This reaction breaks down esters found in the raw material to give a mixture of esters of the fatty acids present in the raw material. When this mixture of fatty acid methyl esters (FAME) is purified, biodiesel is obtained. The reaction can be basic, acidic or enzymatic based on the catalyst used. The catalysts used most often for this reaction are sodium and potassium hydroxides (Romano and Sorichetti, 2010). A general transesterification reaction is presented in the equation below:

$$RCOOR' + R''OH \Leftrightarrow R'OH + RCOOR''$$

where RCOOR' is an ester,

R"OH is an alcohol

R'OH is glycerol

RCOOR" is a mixture of esters.

1.2.1 Heating of oil

This step is performed in order to speed up the transesterification reaction. The oil is usually heated at a temperature of 120 to 140 ºF and electric sources are used for this purpose. In order to ensure that the heating of oil is an even process, it should be continuously stirred (WMRC).

2. Mixing of alcohol and catalyst

Before the addition of the oil to the reaction, the alcohol and catalyst need to be thoroughly mixed. The alcohol needs to be free of all water content. The ratio of alcohol to oil should be 3:1 where 1 mol of oil is allowed to react with 3 mol of alcohol to give 3 mol of the final product. This mixture of alcohol and catalyst is known as an alkoxide, which is used in the transesterification reaction (Romano and Sorichetti, 2010).

3. Chemical reaction

The alkoxide is mixed with oil at certain standard conditions of time and temperature. The mixing of oil and alcohol requires a very high temperature of about 50 to 60 ºC and constant stirring to ensure uniform mixing of the substances. This process leads to the formation of emulsions which need to be removed in the later stages (Romano and Sorichetti, 2010).

3. Separation of the reaction products

The mixture of fatty acids is separated from glycerin by decantation and on account of their different densities, they form two phases. The lower phase comprises of excess alcohol and the catalyst while the upper phase comprises of a mixture of monoglycerides, diglycerides and triglycerides. This separation may be achieved either by gravitational effects or centrifugation; the former is quite slow whereas the latter is expensive. Once the formation of the two phases is complete, the layers are physically separated (Romano and Sorichetti, 2010).

4. Purification of the reaction products

The mixture of fatty acid methyl esters (FAME) obtained from the transesterification process often contain impurities such as minute quantities of alcohol and catalyst and these need to be removed by subsequent purification steps. Water-soluble contaminants such as methanol, glycerin and catalyst are removed by successive washing with water. In the first step of washing, acidified water is used in order to neutralize the ester mixture. This is followed by two additional steps of washing with plain water. After the washing steps, the mixture is dried to remove any traces of water and further purified (Romano and Sorichetti, 2010).

In some cases, an air bubble wash may also be used after the water washes. Air is bubbled through the mixture for approximately 8 hours such that only the surface of the mixture is agitated. After this process, the contaminants that have collected at the surface are drained out (WMRC).

The ester mixture may be purified by the use of ion exchange resins or silicates. In large scale production plants, glycerin and methanol are also purified for reuse in the transesterification reaction or for other purposes (Romano and Sorichetti, 2010).

2. Important factors for biodiesel production

2.1 Effect of raw material used

The most commonly used raw material for the production of biodiesel is edible vegetable oils due to its widespread availability. The predominant raw material differs with the country – rapeseed oil is used in Canada, soybean oil is used in US, sunflower oil is used in Europe, and palm oil is used in Southeast Asia. Non-edible plant oils that are attractive options are leaves and stems of plants, biomass obtained from waste and non-edible oils from plants. Animal fats is the most sought after option for raw material as it is a cost effective substrate. The methyl esters produced from animal fats are noncorrosive, clean, renewable, and have a low FFA content (Ahmia et al., 2014).

The new option for raw material that has gained popularity in the recent years is microalgae. Algal biomass obtained from these photosynthetic microorganisms have a high oil content, high viscosity and low volatility. Hence, the transesterification of this substrate helps in reducing the overall viscosity of the reaction mixture and increasing its fluidity (Ahmia et al., 2014).

2.2 Effect of concentration of catalyst

Sodium hydroxide is the most common catalyst used for transesterification reaction. Studies have shown that an increase in the concentration of sodium hydroxide results in a decrease in the yield of the final product. An increase in the catalyst:oil ratio of 0.5 to 1.5% results in a significant decrease in the amount of biodiesel produced. This is because an excess of sodium hydroxide in the reaction mixture results in the formation of soap which facilitates the dissolution of methyl ester in the layer of glycerol. This interferes with the purification steps resulting in a lower yield of biodiesel (Attanatho et al., 2004).

2.3 Effect of temperature

High reaction temperatures are usually recommended for transesterification reaction because at high temperature, the rate of the reaction increases and the time taken for the reaction to take place decreases. However, if the temperature of the reaction is increased beyond the recommended range, it leads to a decrease in the yield of biodiesel as very high temperatures encourage the process of saponification of triglycerides and faster vaporization of methanol. Hence, it is strongly recommended that the temperature of the reaction lie below the boiling point of the alcohol used to prevent its vaporization. Based on the type of raw material used, the temperature of the reaction should be between 50 to 60 ºC (Gashaw and Teshita, 2014).

Studies have been performed to explore the effects of performing the reaction at room temperature. Results show that at room temperature, within a time of 60 minutes, the conversion rate is only 78% as compared to using a higher temperature for the reaction. Hence, although the reaction can be successfully carried out at room temperature, it will take a longer time to reach completion. However, if butanol is the alcohol used in the reaction, the rate of the reaction is very slow at room temperature and a high reaction temperature is a must (Gashaw and Teshita, 2014).

2.4 Effect of time

The best product yield is obtained when the transesterification reaction is carried out for less than 90 minutes. As transesterification is a reversible reaction, if the reaction time is increased, soap formation occurs and there is a loss of methyl esters. This results in a loss of biodiesel yield (Onoja and Ochala, 2013).

2.5 Effect of methanol to oil molar ratio

This is one of the most important factors affecting product yield. As per research standards, a reaction of 3 moles of alcohol and 1 mole of triglyceride yield 1 mole of glycerol and 3 moles of fatty acid methyl esters. However, several industries use a ratio of 5.6 to 7.8:1 for better results. This is because an excess of alcohol in the reaction mixture shifts the reaction equilibrium towards product formation, increasing the yield of the final product (Mahgoub et al., 2015).

2.6 Effect of intensity of mixing

Transesterification is generally a slow process as oil and alcohol do not mix with each other completely. Hence, the reaction takes place only in the interphase of these two liquids. In order to ensure maximal contact between the two reactants, intense and continuous mixing is essential. In general, mechanical mixing at an agitation speed of 400 rpm is ideal to achieve the best results (Jagadale and Jugulkar, 2012).

2.7 Effect of free fatty acids (FFA) and moisture content

The FFA and moisture content of the raw material are key determinants in biodiesel yield. If the raw material has a high FFA content, it will result in increased soap formation resulting in a decreased yield of final product. Increased water content in the raw material will increase the rate of hydrolysis which will reduce the amount of methyl esters formed in the reaction. Hence, ideally, the water content in the raw material should be 0.5% to obtain good biodiesel yield (Gashaw et al., 2015).

2.8 Effect of type of alcohol used

Studies show that the most widely recommended alcohol for the production of biodiesel is methanol, followed by ethanol and lastly, butanol. Methanol is preferred over ethanol because when ethanol undergoes ethanolysis, stable emulsions are formed, whereas upon methanolysis, the emulsions break down easily and do not interfere with the reaction. The presence of a large, non-polar group in ethanol makes its emulsions highly stable and this makes the purification of the biodiesel more difficult. Also, use of methanol gives a higher yield of biodiesel as compared to ethanol (Hossain et al., 2010).

2.9 Effect of product costs

Biodiesel is an attractive fuel alternative as it is made from renewable resources and is sustainable. However, the total cost of production of the biodiesel is largely dependent on the raw material used, the method of production of biodiesel, and source of transport, as opposed to the price of crude petrol. The cost of vegetable oils and methyl esters produced from them is quite high and turns out to be at least 4 times more expensive than diesel fuels. The cost of raw material alone accounts for about 60 to 75% of the total cost of biodiesel production. The variations in the cost of feedstock has its effect on the cost of biodiesel too. However, biodiesel is still under consideration due to the recent increases in the cost of petroleum and the uncertainty of its availability in the future (Koh and Ghazi, 2011).

Options for low-cost oils include jatropha, karanji, pongamia, waste cooking oils and animal fats. However, these materials tend to have a lot of FFA content which have an effect on the yield of biodiesel. These substances need to be pretreated before proceeding with the reaction, and this further adds to the cost of production. Glycerol recovery also increases the cost and it help if the biodiesel production plant has its own system for recovering glycerol at the end of the reaction. Further, the use of glycerol for other purposes makes it economically feasible and decreases the overall production costs (Koh and Ghazi, 2011).

2.10 Environmental considerations

Biodiesel is an environment-friendly substitute of other fuels and hence, is a topic of much discussion worldwide. It does not add any extra carbon dioxide to the atmosphere as the gas released during its consumption is reused in the growth of its raw materials. It also releases a comparatively lesser amount of carbon monoxide, hydrocarbons and particulate matter into the environment. Its sulfur emissions are virtually nil and the emission of the cancer-causing polycyclic aromatic hydrocarbons is decreased by about 80% with the use of biodiesels. However, they release more nitric oxide and its derivatives as compared to other fuels (Koh and Ghazi, 2011).

2.11 Legislation and regulations

The production and consumption of biodiesels depends to a large extent on legislation and regulations in different countries. The United States Environmental Protection Agency issues new rules annually regarding the production and use of cellulosic biofuels, advanced biofuels, total renewable fuel and biomass-based diesel based on the Renewable Fuel Standard volume requirements. It is also involved in the determination of the use of fuels in vehicles. The state of California has passed a policy regarding Low Carbon Fuel Standard (LCFS) to reduce emissions of greenhouse gases from vehicles. All these and other government policies play a role in the production of amount and types of biodiesels (US Energy Information Administration, 2012).

3. Current industrial concerns regarding biodiesel production

There are a number of concerns facing the industry today with regards to production of biodiesels. Some of these are listed below:

3.1 Impact on food supplies

The selection of raw materials used for biodiesel production involves selecting food crops and lands which will have an effect on the food crop grown in that region for the purpose of generating food products. This is especially a concern in developing countries where some food products are scarce and need to be imported from other countries. If farmers see a better economic gain in growing crops for biodiesels than for their food value, large numbers of them might shift to producing raw materials for biodiesels, bringing down the amount of food crops grown. This issue has already affected the growth of crops such as corn, sugar and soybeans (RIRDC, 2007).

3.2 Improvement in feedstock yield

As the demand for raw materials for biodiesel production is on the rise, it is necessary to meet the demand by increasing production of raw materials. Processes such as breeding programs, plant genomics, and engineering of desirable traits need to be considered to improve the quality of the end product (King, 2010).

3.3 Impact on water supplies

Crops grown for the purpose of producing biofuels require large amounts of water for their growth. This becomes a problem in areas where water supply is not optimum. Also, spillage of materials involved in biodiesel production such as ethanol can contaminate rivers, affecting water used for irrigation purposes and aquatic life in the region (Ottinger, 2007).

3.4 Impact on forests

Growing large numbers of crops for biodiesel production requires large amounts of lands and it might require cutting down trees for this purpose. This practice would have drastic impacts on greenhouse effect, land erosion, biodiversity, and decrease in wood supplies for construction. A review of the situation in Brazil revealed that 148 million acres of forest area would need to be cleared in order to provide land for growing crops for biodiesel production (Ottinger, 2007).

3.5 Impacts of monoculture cultivation

Growing just one crop continuously on the same piece of land for the purpose of biodiesel production can have largely detrimental effects on the quality and productivity of the land. It also affects the quality of soil and environment in that region. A solution for this problem would be regular crop rotation to conserve soil fertility and land productivity (Ottinger, 2007).

3.6 Product specifications

Industries that produce biodiesel on a large scale need to keep up with the market specifications of biodiesels in terms of quality and cost. Petroleum suppliers and engine manufacturers have high demands regarding the purity levels of the biodiesels. A number of agencies have set guidelines for the product specifications and these need to be strictly observed in order to remain in the competition (Anderson et al., 2003).

3.7 Processing concerns

In order to improve efficiency of biodiesel production, it is important to optimize the processing of the product. This may be done by introducing different densification techniques such as briquetting and pelletizing, cutting down costs of transport, and developing reliable preservation techniques to enable modifications in the pre-conversion stage (King, 2010).

3.8 Difficulty in obtaining funds

Due to increasing prices in the current market scenario, venture capitalists and angel investors have become skeptical about investing in these kinds of ventures and it is also very difficult to get bank loans for funding pilot projects. In general, ventures in the field of biotechnology requires a very large amount of capital and the returns are slow and sometimes, doubtful. Also, first-timers in the field of biodiesel production rarely know tricks to reduce costs and which category of consumers to target (King, 2010).

Conclusion

In conclusion, biodiesel is a very attractive fuel alternative in that it is made from renewable resources and is sustainable, and also it is quite safe for the environment. The only drawback is its cost and the effects its production has on the use of agricultural resources. However, a number of studies are being conducted to invent cheaper ways of producing biodiesels, so that they can be adopted in the relevant industries more widely.

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