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review

Biodiesel Production from Municipal Sewage Sludges

David M. Kargbo*

U.S. EPA Region III, Office of Innovation, Environmental Assessment & Innovation Division, Philadelphia, Pennsylvania 19103

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Biodiesel is a fuel comprised of monoalkyl esters traditionally derived from vegetable oils or animal fats. There is currently an unprecedented increase in interest and demand for biodiesel and other fuels derived from renewable biomass. However, pure vegetable or seed oils are expensive and constitute between 70% and 85% of the overall biodiesel production cost. Municipal sewage sludge is gaining traction in the U.S. and around the world as a lipid feedstock for biodiesel production. It is plentiful and consists of significant concentrations of lipids that can make production of biodiesel from sludge profitable. However, there are challenges to be faced by biodiesel production from waste sludge. Determining how best to collect the different fractions and treat them for maximum lipids extraction is a major challenge. To accelerate biodiesel production, cosolvents and high shear mixing have been proposed. Nevertheless, there is very little information on the cost-effective means of increasing lipid solubility. Alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification and is most often used commercially. However, for lipid feedstocks with greater than 1% free fatty acids (FFAs) such as in sludge, acid catalysis followed by base catalysis is recommended because of soap formation with alkali-catalyzed transesterification and high FFA. To boost biodiesel production, it is suggested that wastewater operators utilize microorganisms that are selected for their oil-producing capabilities. This could increase biodiesel production to the 10 billion gallon mark, which is more than three times the nation's current biodiesel production capacity. The presence of pharmaceutical chemicals in sludge poses a great challenge. This requires a careful selection of treatment technologies and microbes that are selective for these pharmaceutical chemicals. Finally, biodiesel production from sludge could be very profitable in the long run. Currently, the estimated cost of production is $3.11 per gallon of biodiesel. To be competitive, this cost should be reduced to levels that are at or below the current petro diesel costs of $3.00 per gallon.

Introduction

Biodiesel holds significant promise as a potential displacement fuel for petroleum-based diesel fuel. The United States (US) and the world are witnessing an unprecedented increase in interest and demand for biodiesel and other fuels derived from renewable biomass. For example, the production of biodiesel in the US has increased from 75 million gallons in 2005 to 250 million gallons in 2006 and 450 million gallons in 2007,[1] with an expected total capacity of well over 1 billion gallons in the next few years. Nevertheless, this is still a very infant industry compared to petroleum-based diesel. For example, in 2007, the US burned over 60 billion gallons of petroleum-based diesel compared to 450 million gallons of biodiesel. The increasing demand for biodiesel has led to an increasing need for lipid feedstocks such as soybean, canola, rapeseed, sunflower, palm, and coconut oils. Currently, pure vegetable or seed oils are expensive and constitute between 70% and 85% of the overall biodiesel production cost.[2] As a result, the use of alternative nonedible feedstocks such as Jatropha, animal fats, and waste cooking oil is on the rise.

Municipal sewage sludge is gaining traction in the US and around the world as a lipid feedstock for biodiesel production. First, municipal sewage sludge contains significant concentrations of lipids derived from the direct adsorption of lipids onto the sludge. These energy-containing lipids include triglycerides, diglycerides, monoglycerides, phospholipids, and free fatty acids contained in the oils and fats. In addition, microorganisms used in the wastewater treatment process utilize organic and inorganic compounds in the wastewater as a source of energy, carbon, and nutrients. The cell membrane of these microorganisms is a major component of sewage sludge and is composed primarily of phospholipids.[3] It is estimated at 24% to 25% of dry mass of the cell[4,5] and yields about 7% oil from the dried secondary sludge. Other studies[6] have demonstrated that up to 36.8 wt % of the dry sludge is comprised of fatty acids and steroids. With the fatty acids from sludge predominantly in the range of C10 to C18, these are excellent for the production of biodiesel.

Second, sludge is plentiful. In the US alone, approximately 6.2 million dry metric tons of sludge is produced annually by wastewater treatment facilities[7] and is expected to increase in the future due to increasing urbanization and industrialization.

*To whom correspondence should be addressed. E-mail: kargbo.david@epa.gov.

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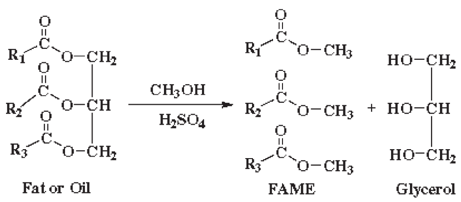
Third, sludge management poses formidable environmental challenges. Land application for agricultural purposes has attracted opposition due to odor and the presence of heavy metals and recently, the potential exposure to emerging pharmaceutical chemicals. Similarly, sludge incineration has resulted in emissions that contain dioxins and heavy metals. Consequently, biodiesel production from sludge as a viable alternative to land disposal will help to solve both energy and environmental problems.

Finally, studies[5] show that integrating lipid extraction processes in 50% of all existing municipal wastewater treatment plants in the US and transesterification of the extracted lipids could produce approximately 1.8 billion gallons of biodiesel, which is roughly 0.5% of the yearly national petroleum diesel demand.

Biodiesel is comprised of fatty acid alkyl esters (FAAEs) produced via base- and/or acid-catalyzed transesterification of lipids using alcohol. Fatty acid methyl ester (FAME) is the term for biodiesel made when methanol is the alcohol used in the transesterification process. Equation 1 is an example of biodiesel production through transesterification of fat or oil in the presence of an acid catalyst producing a mixture of FAMEs and glycerol.



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In the above transesterification process, R1, R2, and R3 are long fatty acid chains with only five of these chains common in most vegetable oils and animal fats. The physical properties of the resulting biodiesel (e.g., octane number, cold flow, and oxidative stability) are usually determined by the relative amounts of the fatty esters. In the above transesterification, approximately one volume of oil or fat yields about one volume of biodiesel.

Challenges

Biodiesel production from sewage sludge poses huge challenges to overcome if commercial opportunities are to be realized. Some of these challenges are not unique to biodiesel production from waste sludge but to the biodiesel industry as a whole. They include challenges from (i) collecting the sludge, (ii) optimum production of biodiesel, (iii) maintaining product quality, (vi) soap formation and product separation, (v) bioreactor design, (vi) pharmaceutical chemicals in sludge; ,(vii) regulatory concerns, and (viii) economics of biodiesel production.

Collecting Sludge. Primary sludge is a combination of floating grease and solids collected at the bottom of the primary clarifier of a wastewater treatment plant after screening and grit removal. Secondary or activated sludge is composed mainly of microbial cells and suspended solids produced during the aerobic biological treatment of wastewater and collected in the secondary clarifier. Biodiesel production from both primary and secondary sludges is currently undergoing intense research. Challenges do exist in determining how best to collect these fractions and treat them for maximum lipids extraction. For example, the yield of FAMEs from primary sludge (maximum yield of 14.5 wt %) is significantly affected by the interactive effects of temperature, acid catalyst concentration, and the methanol-to-sludge mass ratio, while the yield of FAMEs from secondary sludge (maximum yield of 2.5 wt %) is significantly affected by the independent effects of the above three factors. Control over these factors can significantly influence the cost of production.

Production Challenges. The optimum production of biodiesel is faced with huge challenges. First, the lipids containing fatty acids are usually extracted and then transesterified. Recently, an in situ transesterification procedure where the fatty acid containing lipids are simultaneously extracted and transesterified has been being practiced. This reduces the reaction time and the amount of solvent and samples required compared to separate lipid extraction and transesterification processes. This is an ongoing area of intense research. Transesterification reaction times can be shortened by increasing the temperature and the addition of enzymes. For example, the addition of 9−17% lipase enzymes significantly decreased the transesterification reaction of tung oil and hence increased the ester conversion of tung oil.[8]

The optimal conditions were reported to be a 2.2:1 molar ratio of methanol to oil, a reaction time of 18 h, a reaction temperature of 43 °C, and a lipase amount of 14%. Second, reaction completeness (> 98% complete) and fuel deterioration (acid value) continue to be challenging aspects of biodiesel production from traditional feedstocks and should be no different with sludge feedstock. Using higher temperatures to accelerate the reaction requires pressure vessels because the alcohol (methanol) boils at 148 °F (65 °C). The addition of cosolvents and high shear mixing have also been proposed as ways to accelerate the reaction. Third, the careful selection of catalysts is a key component of successful biodiesel production from lipid feedstocks such as sludge. The catalyst acts to deprotonate the alcohol to make it a stronger nucleophile for reaction with the lipids. Current catalysts are slower, require higher temperature and pressure, require longer reaction times, and require high volumes of alcohol. Considerable catalyst research is also being carried out. However, the research is restricted to solid phase, fixed bed catalysts. The correct choice of a catalyst may reduce glycerin cleanup costs. Finally, to minimize production costs, there is a need to minimize excess alcohol requirements. In addition to incorporating a faster reaction with less energy input, a current industry trend is to use reactors that incorporate separations and internally recycle alcohol. This should be useful also when sludge is the feedstock.

Maintaining Product Quality. Modern diesel engines are very sensitive to fuel quality. Consequently, maintaining biodiesel product quality is essential for the growth of the biodiesel industry. To be classified as diesel, the product must meet ASTM D 6751 specifications for the flash point, closed cup, water and sediment, viscosity, sulfated ash, total sulfur, copper strip corrosion, cetane number, cloud point, carbon residue, acid number, free and total glycerin, phosphorus, and vacuum distillation end point. Primary sludge from wastewater treatment facilities is a source of low-quality fats and grease. Given that the yield of primary (low-quality) sludge is higher than that of secondary (higher-quality) sludge, there is a need to improve lipid solubility in the reaction

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mixture during transesterification. This is usually solved by the addition of hexane, which significantly increases the biodiesel production cost. A challenge is to find a more cost-effective means of increasing lipid solubility.

Soap Formation and Product Separation. Base-catalyzed transesterification is much faster than acid-catalyzed transesterification and is most often used commercially.[9] However, a high concentration of free fatty acids (FFA) in the sewage sludge can result in problems such as soap formation and difficulty in product separation (eq 2).

$$\underset{\text{Oleic Acid}}{HO-\overset{\overset{O}{\|}}{C}-(CH_2)_7CH{=}CH(CH_2)_7CH_3} + \underset{\text{Potassium Hydroxide}}{KOH} \rightarrow \underset{\text{Potassium oleate (soap)}}{K^{+}\,{}^{-}O-\overset{\overset{O}{\|}}{C}-(CH_2)_7CH{=}CH(CH_2)_7CH_3} + \underset{\text{Water}}{H_2O} \quad \text{.........2}$$

The soaps formed can gel at ambient temperature, causing the entire product mixture to form a semisolid mass instead of biodiesel. Soaps can also cause problems with glycerol separation and washing. Consequently, biodiesel formation is not suitable for high FFA feeds such as trap grease. For the lipid feedstocks in sewage sludges containing >1% FFA, acid catalysis followed by base catalysis is recommended. Here, FFAs are first converted to methyl esters until FFA < 0.5%, when additional methanol is added followed by the addition of a base catalyst to transesterify the triglycerides to biodiesel. The efficient separation of glycerol is important given that the separated glycerol can be used by industry for manufacturing cosmetics and pharmaceutical formulations.

Water can also be a problem as it hydrolyzes fats to form free fatty acids, which then form soap (eq 3).

$$\underset{\text{Triglyceride}}{\begin{array}{l} CH_2-O-\overset{\overset{O}{\|}}{C}-R_1 \\ | \\ CH-O-\overset{\overset{O}{\|}}{C}-R_2 \\ | \\ CH_2-O-\overset{\overset{O}{\|}}{C}-R_3 \end{array}} + \underset{\text{Water}}{H_2O} \rightarrow \underset{\text{Diglyceride}}{\begin{array}{l} CH_3-OH \\ | \\ CH_3-O-\overset{\overset{O}{\|}}{C}-R_2 \\ | \\ CH_3-O-\overset{\overset{O}{\|}}{C}-R_3 \end{array}} + \underset{\text{Fatty acid}}{HO-\overset{\overset{O}{\|}}{C}-R_1} \quad \text{......3}$$

Bioreactor Design. The bioreactor for wastewater treatment contains microorganisms that use pollutants as the food source to maintain the metabolism of the microorganisms and to generate new microorganisms. A challenge in boosting biodiesel production from sewage sludge is for wastewater operators to utilize microorganisms that are selected for their oil-producing capabilities. This could increase biodiesel production from sewage sludge to the 10 billion gallon mark, which is more than three times the nation's current biodiesel production capacity.

Pharmaceutical Chemicals in Sludge. A review of the applications of lipids in the pharmaceutical field[10] shows that several vegetable oils (almond oil, apricot oil, avocado oil, borage oil, coffee oil, safflower oil, etc.) and fish oil and bird oil have been employed as excipients in cosmetic formulations.

Fatty acids used as lipid regulators are also occurring in wastewaters as emerging contaminants that could end up in sludges.[11] The pharmaceutical industry is concerned about traces of its organic chemicals (that may not be adequately treated) adsorbing on sludge surfaces. There is therefore a need to evaluate the effectiveness of the transesterification process to treat these chemicals and convert them to biodiesel. This may require a careful selection of treatment technologies and microbes that are selective for these chemicals. Conversion of these emerging contaminants to biodiesel will not only help solve an energy problem but will also remove from the environment one of the fastest growing and challenging groups of chemicals.

Regulatory Concerns. Sludge is classified as either Class A or Class B, depending on the type of treatment it has received. Class A sludge has benefited from both pretreatment and treatment at the wastewater facility. While most sludge used for biodiesel production may fall under Class A, its use offsite for biodiesel production may come under scrutiny by regulators and the public. With the added cost of transportation, biodiesel producers may want to establish their operations next to the sludge production facility. Standards for Class B sludge are less stringent, and their use is therefore more regulated. Biodiesel producers may not remove the Class B sludge from its production site.

Economics of Biodiesel Production. Although biodiesel is one of the premier forms of alternative energy, its cost of production has hindered its growth and has made it uncompetitive compared to petro diesel. Analysis by researchers[12] indicates that in biodiesel economics, the feedstock (oil) is about 80% of the production cost.

This makes the availability of cheap and reliable biodiesel feedstock a very important issue in biodiesel production. Currently, the estimated cost of production of biodiesel from dry sludge is $3.11 per gallon of biodiesel[13,14] compared to $3.00 per gallon for petro diesel (as of January 2010). The biodiesel price is broken down to $2.06/gal for centrifuge, drying, and extraction processes and $1.05/gal for other expenses. To be competitive, this cost may need to be reduced to levels that are at or below petroleum diesel costs. One possible solution is for the US Congress to enact a modified biodiesel tax incentive. The 2005 biodiesel tax incentive by Congress sparked a dramatic growth in the biodiesel industry. The credit amounted to $1.00 per gallon blended if the lipid is derived from most major oilseeds grown within the US or animal-based lipids. All other lipid feedstocks receive $0.50 per gallon when blended. This tax incentive should be modified to give equal credit to sludge as biodiesel feedstock. Also, the use of high-frequency ultrasound to significantly reduce production costs of biodiesel has recently been reported.[15]

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Summary

Biodiesel is a fuel comprised of monoalkyl esters of long-chain fatty acids traditionally derived from vegetable oils or animal fats. The US and the world is witnessing an unprecedented increase in interest and demand for biodiesel and other fuels derived from renewable biomass due to rising petroleum fuel costs, increasing concern for the environmental impact of emissions from the combustion of conventional fossil fuels, increasing reliance on foreign oil sources, and decline in domestic oil production. However, pure vegetable or seed oils are expensive and constitute between 70% and 85% of the overall biodiesel production cost. As a result, the use of alternative nonedible crops such as Jatropha, animal fats, and waste cooking oil is on the rise.

Municipal sewage sludge is also gaining traction in the US and around the world as a lipid feedstock for biodiesel production. First, MSS consists of significant concentrations of lipids. Second, it is plentiful. Third, sludge management poses formidable environmental challenges.

There are numerous challenges faced by biodiesel production from waste sludge. First, challenges exists in determining how best to collect the different fractions (primary and/or secondary sludges) and treat them for maximum lipids extraction. Second, in the transesterification process, the critical reaction properties are total glycerol, acid value, and reaction completeness. To accelerate the reaction, cosolvents and high shear mixing have been proposed. There is however very little information on cost-effective means of increasing lipid solubility. Third, alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification and is most often used commercially. However for lipid feedstocks with $>1\%$ FFA, acid catalysis followed by base catalysis is recommended because of soap formation with alkali-catalyzed transesterification and high FFA. Few have attempted to address this challenge by using supercritical methanol, high shear mixing, and the use of cosolvents. A fifth challenge to boost biodiesel production is to utilize microorganisms that are selected for their oil-producing capabilities. This could increase biodiesel production to the 10 billion gallon mark, which is more than three times the nation's current biodiesel production capacity. Developing an easier glycerol cleanup is also a difficult challenge. Finally, the presence of pharmaceutical chemicals in sludge poses a great challenge. This requires a careful selection of treatment technologies and microbes that are selective for these chemicals but can also produce FFAs in the process.

From a regulatory viewpoint, most sludge that will be used for biodiesel production may fall under Class A. Nevertheless, its use offsite for biodiesel production may come under scrutiny by regulators and the public. Biodiesel producers may not remove the Class B sludge from its production site.

Finally, biodiesel production from sludge could be very profitable in the long run. Currently, the estimated cost of production is $3.11 per gallon of biodiesel. To be competitive, this cost may need to be reduced to levels that are at or below petroleum diesel costs.

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