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Review

Opportunities for simultaneous oil extraction and transesterification during biodiesel fuel production from microalgae: A review

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ABSTRACT

The biodiesel industry has undergone stable growth over the past decade. The biodiesel production process is relatively complex and rather expensive relative to the production of mineral diesel, and thus to retain production shares and expand the industry, there is a growing demand for changes related to the search for new raw materials and advanced technologies. Microalgae have attracted considerable attention as a potential biodiesel raw material. This article presents an overview of possible applications of one new form of technology, the so-called in situ technology for simultaneous oil extraction and transesterification. The article also describes ways of applying this technological tool for biodiesel production from microalgae oil.

Contents

1. Introduction

As transport is considered to be one of the main atmospheric pollution sources, this sector will undergo significant changes related to the

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replacement of fossil fuels by biofuels. Directive 2009/28/EC of the European Parliament and Council of April 23, 2009 was adopted to promote the use of biofuels and other renewable fuels for transport purposes, and it established a mandatory target to increase the share of biofuels used in the transportation sector by 10% of all fuel consumption by 2020.

Biodiesel is recognized as an attractive liquid fuel that presents several benefits. First, biodiesel is more environmentally friendly as its use releases fewer emissions into the environment relative to the use of mineral diesel. When evaluating environmental air pollution related to biofuels, concentrations of hydrocarbons, carbon monoxide, solid particles and of other compounds such as formaldehydes and polycyclic aromatic compounds are found in motor engine oxides. Concentrations of CO and CH in engine emissions significantly decline when biodiesel is added to conventional diesel [1]. Relative to pure mineral diesel, biodiesel and biodiesel mixed with mineral diesel degrade faster in the environment [2,3].

Biodiesel can be produced from oils of different types of oil plants [4], animal fats [5,6] and waste materials as well as from algae [7]. Currently the interest in the application of microalgae for food and technical purposes is growing. The use of algae for biofuel production is advantageous because microalgae rapidly grow and accumulate oil, and growing algae utilize carbon dioxide. Compared to other raw materials, algae are marked by high oil output per unit of surface-area: it is possible to obtain up to several times higher amount of oil comparing with oil plants grown on a territory of the same size.

Biodiesel production technologies have been widely recognized for >50 years [8]. The process referred to as transesterification when oil (triglyceride) is chemically reacted with methanol or other alcohol and then subjected to a catalyst, forming fatty acid methyl esters or higher order alcohol esters. Methanol, ethanol, propanol and other higher alcohols may be used in transesterification; however, methanol and ethanol are used most frequently. Methanol is recognized for its low price and physical and chemical properties [9,10]. Ethanol is preferable to methanol in that it is produced from biomass and thus is renewable and is less toxic to the environment. The by-product of this reaction is glycerol. Different factors affect oil transesterification: free fatty acid content, water content, alcohol-to-oil molar ratios, types and concentrations of catalysts, reaction temperatures, stirring speeds, and relative densities [11,12,13].

Biodiesel production that also involves raw material derivation and preparation (which is not the case for waste materials) is a rather long and relatively expensive process. Oil extraction and transesterification are energy-intensive processes. Oil is typically extracted from raw materials through pressing or extraction subjected to different solvents. This process requires thermal and electric energy inputs. Considerable hexane losses are incurred during oil extraction by hexane. During oil production from soybeans, the manufacturer incurs 3800 l of hexane losses after using 3000 tons of raw materials per day [14].

To reduce biodiesel production costs, innovative, modern technologies must be used during biodiesel production. One technological approach may involve simultaneous oil extraction and transesterification – a so-called “in situ” process that facilitates direct fatty acid ester formation without involving intermediate oil extraction during biodiesel production. This approach eliminates the oil extraction process, thus reducing equipment needs.

This paper presents a broad analysis of ways of applying the above-described approach with various raw materials, of the effectiveness of this approach in the midst of changing different process conditions, and of raw material preparation methods and additional measures needed to improve the efficiency and quality of final products.

2. Advantages of “in situ” processes

As noted above, energy and technological process resources, raw materials and time may be saved if more innovative technologies were used in biodiesel production. For conventional biodiesel production technologies, different materials are used during oil extraction and fatty acid ester production stages for both extraction and transesterification reactions. For example, oil from oil plants is extracted by hexane, whereas transesterification is performed by methanol, etc. Therefore, conventional biodiesel production methods require the use of a considerable amount of organic solvents and access to powerful machinery equipped with heating and stirring capacities [15]. Methanol may perform dual functions in cases of “in situ” technologies: serving as a chemical solvent for oil extraction and as a reactant, thus reducing chemical solvent inputs [16,17]. Applications of “in situ” technology enable one to eliminate certain stages (from raw material extraction to biofuels production (Fig. 1)), thus reducing equipment installation and maintenance and energy consumption costs [18].

When comparing conventional biodiesel production technologies with in situ technologies, it may be stated that simultaneous transesterification leads to the generation of higher fatty acid esters yields [19,20]. Based on research data provided by Vicente et al. [21], in cases of in situ technology use after 8 h of reaction at 65 °C in the presence of BF_3, H_2SO_4 and HCl as acid catalysts, >99% of fatty acid methyl esters in all three cases are produced, whereas when applying conventional technology esters, the ratio falls within a range of 91.4–98%. Such higher biodiesel yields may be attributable to glyceride, free fatty acid and phospholipid participation in cases of in situ transesterification [17].

3. Factors affecting the efficiency of in situ transesterification

In situ technologies may be applied to virtually any oil raw material of vegetable, waste or algae origin. However, attention should be paid to material consistency levels (wet, dry, etc.), raw material particle sizes, oil compositions (content of free fatty acids, etc.) and to proper transesterification conditions (reactant and catalyst contents, reaction times, temperatures, etc.).

Most previous studies involving simultaneous transesterification via alkaline or acid catalysts have involved the use of dry raw materials [22,23,24]. Number of methods is employed for microalgae drying. Sun drying, spray drying, drum drying, and freeze drying are commonly used for algae bio mass preparation. Sun drying is an oldest and cheapest drying method utilized solar radiation source. The disadvantages of this method are long drying time, large drying area, possibilities to loss of microalgae biomass. In addition, sun dried biomass can be exposed by bacterial and microbial contamination. Application of spray drying method is comparative expensive and might cause deterioration of algae cells [25]. Currently the freeze drying method is used by many researchers. Freeze dried microalgae cells are disrupted, the fine powder obtained can be subjected directly for oil extraction and transesterification [26]. Freeze drying method has been used in algae lipid from different microalgae species [27–30]. However, research results show that application of freeze drying is time consuming method and requires high investment. Comparison of different drying methods is presented in the Table 1 [31].

According to some scientists, attention should be paid to selection of raw material drying methods as such approaches affect oil contents and compositions. Widjaja et al. [32] showed that the best results are obtained by drying microalgae biomass at low temperatures under vacuum conditions; at a temperature of 60 °C, lipid content in raw materials begins to decline slightly, whereas when drying temperatures increase to 80 °C, lipid content significantly decreases. This overall decline in lipid content in raw materials may be attributable to the oxidation of fatty acids at high temperatures. Mono- and poly-unsaturated fatty acids tend to oxidize faster; saturated fatty acids are less reactive [33].

When discussing uses of microalgae for biodiesel production, it should be stressed that algae biomass drying requires considerable energy inputs. According to Xu et al. [34] data, thermal treatments of