

Advances in Catalytic Technologies for Biodiesel Fuel Synthesis

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1. Introduction

The greenhouse effect and its consequences are a growing concern for humanity. Ways to reduce greenhouse gas emissions are being sought, both through appropriate technological solutions and through cross-border agreements that oblige and encourage countries to reduce their greenhouse gas emissions. A significant proportion of greenhouse gases are emitted by the transport sector. In some EU countries, this amount is the highest compared with other industrial and agricultural sectors.

Another problem facing humanity is the depletion of fossil energy resources, the associated rise in the price of mineral resources, and the energy crises affecting continents. Therefore, there is a growing call for the use of alternative energy sources, the use of which not only reduces energy dependence on oil resources, but also reduces greenhouse gas emissions. To address these issues, biofuels produced from renewable energy sources have been introduced in the transport sector. The development of the production and use of biofuels is promoted by the national laws and regulations of individual countries; in EU countries, the production and use of biofuels is promoted by approved directives and regulations, which specify the target amounts of biofuels usage.

As an alternative to mineral diesel, biodiesel is produced from vegetable oil using a transesterification process with methanol. The process is well researched and implemented in the industry. Biodiesel is produced and used in relatively large quantities, usually blended with up to 10% mineral diesel. The synthesis of biodiesel requires the use of catalysts that accelerate the transesterification process. This synthesis is usually carried out using potassium or sodium hydroxide as catalysts. It should be noted that in EU countries, biodiesel accounts for a larger share of biofuels used in transport than bioethanol. Various oil feedstocks are used for biodiesel production, depending on climatic conditions and the ability to grow certain oilseeds. In EU countries, most biodiesel is produced from rapeseed, which is also used to produce edible oil. With the expansion of biodiesel production, an increasing share of agricultural land has been devoted to the cultivation of biodiesel feedstocks. This has led to public dissatisfaction with the use of edible raw materials for technical purposes, increasing competition for edible oil and biodiesel for raw materials, and rising edible oil prices. Therefore, the use of other feedstocks for biodiesel production, including non-edible oils or fatty wastes, has been explored. However, the use of new types of feedstocks requires appropriate new technological solutions, especially if low-quality feedstocks or waste are used, and the possibilities for using conventional methods and alkaline catalysts are limited.

Another problem with the development of biodiesel production is that, in using food-grade feedstocks for biodiesel synthesis, the cost of its production by conventional methods is still too high for biodiesel to compete in the market with mineral diesel. Therefore, ways are being sought to reduce the cost price of biodiesel production, both by using cheaper feedstocks and by using fewer energy- and material-intensive processes with higher biodiesel yields.

From an environmental point of view, biodiesel synthesis technology needs to be improved, as the synthesis uses synthetic methanol produced from natural gas, application of alkaline catalysts results in soap formation, the final product must be purified



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from soaps—and glycerol. With the introduction of more environmentally friendly technologies, opportunities are being sought to replace chemical catalysts with enzymatic catalysts—lipases or heterogeneous catalysts of natural origin. Possibilities for preventing the formation of glycerol during transesterification, by converting it to other components that may be included in the fuel, are also being investigated.

Conventional biodiesel synthesis uses two main processes. In the first stage, the oil is extracted from the oilseeds, in the second stage it is transesterified with methanol. The simplification of biodiesel production can involve a so-called simultaneous oil extraction and transesterification process, which eliminates the oil pressing or extraction stage and thus reduces energy consumption. This is one way to reduce the cost of biodiesel; however, so far, it is only in the research stage.

It is well known that the use of conventional biodiesel in a diesel engine reduces the concentration of harmful components in the exhaust gas. However, the production and use of biodiesel from new feedstocks and the application of new technologies require comparative studies of new fuels to assess the concentration of harmful components in engine emissions. It is equally important to assess the environmental properties of new fuels, such as biodegradation in the natural environment, and to perform a life cycle analysis. Articles published in the Special Issue “Advances in Catalytic Technologies for Biodiesel Fuel Synthesis” address all of these issues.

2. A Short Review of the Contributions in This Issue

Possibilities to reduce the cost price of biodiesel production by avoiding the oil extraction stage are examined by Makareviciene et al. [1]. A review of the research related to the simultaneous oil extraction and transesterification process is presented, and the obtained results are summarized. The authors emphasize the need to explore new opportunities for biodiesel to be competitive in the market. The article analyses the raw materials used in the in situ process and the impact of their quality and preparation methods on the transesterification efficiency. Optimal process conditions using chemical catalysts and different alcohols are presented. Possibilities for increasing the efficiency of the process by using additional solvents are indicated. Considerable attention is paid to the analysis of the possibilities of using biocatalysts. It is stated that the use of enzymes as a catalyst requires a lower process temperature, but it is not possible to use a large excess of alcohol because of enzymes inactivation. Although enzymatic catalysis is more environmentally friendly, the authors nevertheless note that greater interest is still associated with the use of chemical catalysis in in situ biodiesel synthesis, where, like conventional transesterification, four independent variables—catalyst, alcohol content, temperature, and duration—and their interactions have influence on biodiesel yield. The use of solvents has been found to increase process efficiency, but their removal requires additional energy costs; therefore, some authors suggest using mineral diesel instead of organic solvents, resulting in a mixture of mineral diesel and biodiesel that can be used as fuel in a diesel engine.

Experimental studies of enzymatic in situ process using mineral diesel as additional solvent are presented by Santaraite et al. [2]. Spoiled rapeseed with an oil acidity of more than 2% was used for the study. Application of non-food-grade seeds solves the problems of competition with the food sector, and such raw material is cheap. The amount of mineral diesel was such that the reaction product contained 10% biodiesel in a mixture with mineral diesel. A more efficient catalyst was selected by evaluating the activity of 11 lipases. The article discusses the yields of fatty acid methyl esters and the dependence of the content of monoglycerides, diglycerides, and triglycerides in biodiesel on the amount of catalyst, the process temperature, and the process duration. The optimal reaction conditions under which the resulting fuel meets the requirements for diesel fuel have been determined.

In order to increase the consumption of biofuels in the transport sector, researchers are also exploring the use of fuel blends. The direct use of oil in blends instead of biodiesel reduces the material and energy costs associated with oil transesterification. Aguado-Deblas et al. [3] studied the physical, chemical, and environmental properties of two-component

and three-component mixtures. Diethyl carbonate and soybean or sunflower oil presented in the two-component blends in various ratios, and mineral diesel was added to the three-component blends. Diethyl carbonate was chosen because of its biological origin. Its additive has been found to improve the physical and chemical properties of the fuel, such as density and viscosity, and the multi-component fuel has higher oxygen content and cetane number compared with mineral diesel; an improved ignition quality of blends was observed. Adding a mixture of oil and diethyl carbonate to mineral diesel reduced engine smoke by up to 92–95%. In addition, the two-component blend of oil and diethyl carbonate is 100% renewable. The authors point out that such a mixture can be used directly in diesel engines. Blending fuel components is one of the simplest ways to produce fuel from renewable sources, and the direct use of oil to produce such blends reduces the cost of biofuels compared with conventional biodiesel.

Wu et al. [4] proposes that the use of biofuels can be increased by production of biodiesel blends with ethanol. The resulting fuel is produced exclusively from biomass resources. It was found that ethanol incorporation into palm biodiesel can address some of the shortcomings of biodiesel. The authors state that ethanol helps to increase peak cylinder pressure and heat release rate. The addition of ethanol to fuels has a significant effect on the CO content of combustion products. The addition of 15% ethanol in the mixture was found to cause a 71% smoke reduction. However, it has been observed that increasing the ethanol concentration in the fuel increases HC and NO_x emissions.

Given that, in the production of biodiesel, the purification of the reaction product from soaps and glycerol consumes a large amount of water and generates almost 10 times more wastewater than the resulting biodiesel, Bačić et al. [5] proposes the application of an integrated biodiesel production process for transesterification of edible sunflower oil, catalysed by commercial lipase, with simultaneous extraction of glycerol from the reaction mixture. Choline chloride and glycerol and choline chloride and ethylene glycol mixtures can be used as glycerol extraction agents. Using the response surface methodology, the optimal conditions for the enzymatic transesterification of edible sunflower oil with methanol were determined. The obtained results are important for further research into the possibilities of using waste oil for biodiesel synthesis applying a biotechnological method.

Recently, there has been a growing interest in the use of non-food raw materials for biodiesel production. The ability of various microorganisms to synthesize oil and their suitability for biodiesel synthesis has been investigated. A lot of work is related to the possibilities of using microalgae. Yeast also accumulates oil in its own cells. Komzolova and Morgunov [6] analysed the possibilities of using yeast *Torulaspora globosa* VKPM Y-953 for biodiesel synthesis. The researchers found that increasing the concentration of zinc in the culture medium resulted in higher oil yield and decreased protein content in yeast cells. The presence of zinc in the culture medium also affects the fatty acid composition of the oil. The authors of the article found that biodiesel produced from *Torulaspora globosa* VKPM Y-953 oil meets the requirements of the standards for biodiesel; therefore, *Torulaspora globosa* VKPM Y-953 may be one of the potential raw materials for biodiesel production in the future.

3. Conclusions

Biodiesel, produced from vegetable oils or fats through a catalytic process of alcohol transesterification, is one of the alternative fuels used in the transport sector to replace mineral diesel. Recently, the development of biodiesel production and use has been facing challenges. One challenge is public dissatisfaction with the use of food-grade raw materials for biodiesel synthesis, and the other is the high production cost; therefore, biodiesel cannot compete in the market with mineral diesel. These problems can be solved by using new non-food feedstocks for biodiesel synthesis, using fewer energy- and material-intensive syntheses and product purification methods. The application of enzymatic catalysis using lipases is environmentally promising. The cost price of biofuels can be further reduced by producing blends of oil or biodiesel with ethanol or other suitable components. The use of

new types of raw materials and innovative processes requires not only the assessment of the physical and chemical properties of the resulting fuels and their compliance with the standards, but also the analysis of performance with a strong focus on the identification of harmful components in engine exhaust gases.

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