



Glycerol-free biodiesel production through transesterification: a review



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ABSTRACT

Waste oils are becoming increasingly more important as feedstock for the production of fuels and chemicals. However, the high level of impurities in waste oils limits their use in transesterification reactions where methanol is used as acyl acceptor. A second consequence of increased biodiesel production is the oversupply of glycerol into the market that has caused a sharp decrease in glycerol prices. Novel production routes are thus necessary to limit glycerol formation while also allowing the use of crude or contaminated oil as feedstock. The aim of this work is to review the state of glycerol-free biodiesel synthesis routes with emphasis on routes using methyl acetate or dimethyl carbonate (DMC) as acyl acceptors. Dimethyl carbonate is favoured as acyl acceptor when using biocatalysts for synthesis, while methyl acetate is favoured as acyl acceptor in supercritical-assisted transesterification. Both dimethyl carbonate and methyl acetate as acyl acceptors are able to tolerate impurities such as free fatty acids, but methyl acetate has a higher tolerance for water in the feedstock than dimethyl carbonate. The performance of both acyl acceptors in the presence of used motor oils and industrial greases need to be investigated to assess the suitability for industrial application.

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1. Introduction

Depleting fossil fuel reserves and an increasing awareness of the impact of energy production on society and the environment has catalyzed the search for cleaner energy resources. Biodiesel and bioethanol is set to remain the primary replacement fuels for fossil-based diesel and petroleum respectively. Biodiesel is defined as a mixture of fatty acid methyl esters derived from renewable lipid-rich feedstock such as vegetable oils, animal fats and algae [1]. The most significant advantages of using biodiesel as replacement for or in blends with fossil-based diesel is reduced greenhouse gas emissions due to recycling of carbon dioxide, better lubricating properties with lower sulphur content due to the presence of free fatty acids and monoglycerides and lower environmental impact due to the biodegradability of biodiesel [2,3].

Transesterification is the production of esters from the reversible reaction between a fatty acid (oil or fat) and an alcohol (usually methanol or ethanol) using a strong alkaline catalysts (sodium or potassium hydroxide) [1]. Base-catalyzed transesterification is the preferred method for biodiesel production, because of the high conversions obtained with a short reaction time at a relatively low cost [4]. The alcohol and catalyst forms an alkoxide and water before it is added to the oil. The addition of this extra water can be prevented by using an alkoxide such as sodium methoxide or potassium methoxide instead of an alcohol and an alkaline catalyst. A number of excellent reviews on different aspects of biodiesel production through transesterification have been published [1,3,5–9]. Both homogenous and heterogeneous base and acid catalysts are used in transesterification [12]. Homogeneous catalysts have a higher reported reaction rate and activity, but heterogeneous catalysts make downstream catalyst and product recovery easier [5].

Methanol is preferred as alcohol reagent for industrial biodiesel processes, because it is relatively inexpensive and glycerol separation through settling is easily achieved, even if emulsions were formed [10,11]. The reversible nature of the transesterification reaction requires an excess of methanol (usually in a molar ratio of 6:1 methanol to oil) to enable complete conversion of fatty acids. Glycerol, a by-product from chemically catalyzed transesterification of fatty acids, is immiscible in fatty acid methyl esters (FAME) and is removed from the biodiesel layer through settling and decantation after completion of the reaction. The residual methanol and catalyst are dispersed between the biodiesel and glycerol liquid layers upon settling of the reaction mixture. Water washing of the biodiesel layer to remove residual catalyst, methanol, traces of glycerine and unreacted tri-, di- and mono-glycerides is still the most popular biodiesel purification method. Water volumes as high as three times the volume of biodiesel are used and this wash water needs to be cleaned to environmental specifications before it can be released from the plant.

Government incentives to stimulate worldwide biodiesel production ultimately led to an over-supply of glycerol and the collapse of glycerol market prices. This greatly influenced the revenue from biodiesel production plants [12] because of the lower income due to glycerine sales. This initiated research into the use of crude and purified glycerol as feedstock for bio-chemicals production [13–18]. Reported conversions were however relatively low, and the expensive biocatalyst necessary to convert crude glycerol to high value products pushed research into the direction of trying to eliminate the formation of glycerol during the reaction. Developments on glycerol-free biodiesel processes are still at research level, but a number of interesting ideas have been proposed. The aim is to develop a process that still produces fatty acid alkyl ester as biodiesel, but also produces value added by-product to lower the overall biodiesel production cost.

Two acyl acceptors that have been proposed in literature to replace methanol are methyl acetate and dimethyl carbonate. Supercritical methods with and without the presence of a bio-enzyme catalyst for the reactions have been investigated. Stoichiometric reaction schemes to produce biodiesel from triglycerides using methyl acetate and dimethyl carbonate as acyl acceptors are summarised in Fig. 1.

Dimethyl carbonate is an environmentally friendly replacement for phosgene in the production of polycarbonate, iso-cyanate and various other methylation reactions [19]. Dialkyl carbonates have been considered as oxygenates for the replacement of methyl *tert*-butyl ether (MTBE) because of its relatively low environmental impact and high oxygen content [20].

Su and co-workers [21] were the first to report on the transesterification of vegetable oil using dimethyl carbonate as acyl acceptor. Dimethyl carbonate is traditionally produced through the reaction of phosgene with methanol over a catalyst [19]. Chemicals that are more hazardous are slowly being replaced by shorter chain dialkyl carbonates as solvents and reagents in the chemical production industry. One of the main by-products of the reaction between triglycerides and dimethyl carbonate is fatty acid glycerol carbonate monoester that can decompose to glycerol carbonate as by-product. Leino and co-workers [20] suggested a possible route for the production of dimethyl carbonate from methanol and carbon dioxide (CO₂). Methanol and CO₂ can both be manufactured from renewable carbon sources. Production of biodiesel with dimethyl carbonate as reagent that was produced via the capturing of CO₂ thus increases biodiesel's attractiveness as a cleaner fuel [22]. Transesterification of triglycerides with methyl carbonate instead of methanol results in the formation of cyclic glycerol carbonate esters of fatty acids [22].

Fatty acid glycerol carbonate monoesters has a detrimental effect on the flow properties of biodiesel and limits the blending of biodiesel to a ratio of approximately 20:80, but exhibit properties comparable to that of biodiesel [23]. Fatty acid glycerol carbonate monoesters quickly decompose further to form glycerol carbonate and citramalic acid as by-products [24,25] when triglycerides react with dimethyl carbonate in the supercritical state. Glycerol carbonate was shown to be biodegradable, has a low toxicity and flammability and can be used as a bio-chemical precursor for the production of polycarbonates, polyurethanes, glycidol-based polymers and surfactants [26]. Citramalic acid is a chiral building block used for the synthesis of metal (ii) citramalates for application in material production as well as the production of chemical intermediates for synthesis of pharmaceutical products [27,28].

Fabbri and co-workers [22] attempted to produce an alternative biodiesel containing both FAME and fatty acid glycerol carbonate monoesters. A mixture of sodium methoxide in methanol (30% w/w) and dimethyl carbonate was used to transmethylyate soybean oil to a mixture of FAME containing glycerol carbonate and glycerol dicarbonate as by-products. The high molecular mass of fatty acid glycerol carbonate influenced the final diesel viscosity and cold filter plugging point (CFPP) negatively. Dawodu and co-workers [29] conducted similar experiments and found that high FAME conversions could only be obtained in the presence of a methoxide catalyst and at elevated temperatures and pressures.

Kurle et al. [23] used dimethyl carbonate and triazabicyclodecene (TBD) to replace methanol and sodium methoxide respectively. The catalyst (TBD) could be recovered through filtration and the excess DMC was recovered through distillation or water washing. An Aspen simulation of the process showed that at least six water-washing stages are necessary to lower the DMC content in the diesel to below 10%. The addition of another reagent (DMC) in all cases increased the overall cost of production through either increased reagent cost or through increased separation costs. The additional costs could be recovered though by the high value of the glycerol carbonate and glycerol dicarbonate by-products formed. Glycerol carbonate and glycerol dicarbonate needs to be separated from the FAME and fatty acid glycerol carbonate monoesters mixture using a solvent such a methyl *tert*-butyl ether [22], which is not environmentally friendly or of biomass origin.

The use of methyl acetate as acyl acceptor for biodiesel production in the presence of a biocatalyst is not as well studied as the use of dimethyl carbonate. The biggest advantage of using methyl acetate over dimethyl carbonate is that methyl acetate leads to the formation of 1,2,3-triacetoxypropane (commonly referred to as triacetin) as by-product

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