

# State of the art of biodiesel production under supercritical conditions



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## ABSTRACT

This paper reviews the current status of biodiesel production mainly under supercritical conditions. Various methods such as homogeneous acid- and alkali-catalyzed transesterification, heterogeneous acid and alkali-catalyzed transesterification, enzyme-catalyzed transesterification, and supercritical reactions have been employed so far to synthesize biodiesel. Herein, we review the reaction mechanisms and experimental results for these approaches. Recently, supercritical biodiesel production has undergone a vigorous development as the technology offers several advantages over other methods, including the fact that it does not require a catalyst, short residence time, high reaction rate, no pretreatment requirement, and applicability to a wide variety of feedstock. This technology was first designed for biodiesel production using methanol and ethanol. Biodiesel production without glycerol as a byproduct is attractive and has been achieved using supercritical methyl acetate and dimethyl carbonate (DMC). Most recently, biodiesel production in supercritical *tert*-butyl methyl ether (MTBE) has been developed also. In this review, supercritical biodiesel production will be discussed in detail. Empirical rate expressions are derived for biodiesel production in supercritical methanol, ethanol, methyl acetate, DMC, and MTBE in this study for the first time. These rate equations are critical to predicting biodiesel yields and to comparing the reaction behaviors in different solvents. Lastly challenges for improving energy recovery in supercritical biodiesel production and recommendations for future work are provided.

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## 1. Introduction

Research on renewable energy has attracted a tremendous attention because of the challenges due to global climate change and environmental pollution problems associated with fossil fuel combustion. One of the most notable forms of renewable energy is biodiesel, which can be derived from the biomass including vegetable oil, animal fats, and microalgae. Biodiesel exhibits favorable biodegradability [1] and has lower particulate matter and CO emissions [2, 3, 4, 5], lower sulfur contents [6], and higher cetane numbers [7] than conventional diesel fuel.

In 1893, Rudolph Diesel operated his engines using vegetable oil (peanut oil) because petroleum was not available at that time. The direct application of vegetable oil was however problematic due to its high viscosity. Techniques are available to reduce the viscosity of vegetable oil, including dilution [8], microemulsion [9], pyrolysis [10], and transesterification [11]. In the dilution method, a vegetable oil is mixed with or diluted by a diesel fuel. It was reported in 1980 that Caterpillar Brazil Co. used a 10 vol% mixture of vegetable oil in diesel fuel to maintain total power without any adjustment to the engine [12]. A blend of 20% (vol) vegetable oil and 80% (vol) diesel fuel was also successfully used [12]. Another approach to reducing the viscosity of is microemulsion, in which butanol, hexanol, and octanol are usually used as solvents [13]. Pyrolysis of vegetable oil has also been employed at elevated temperatures in the presence of a catalyst for viscosity reduction. Schwab et al. [8] found that even though the viscosity of the pyrolyzed soybean oil (10.2 mm<sup>2</sup>/s at 37.8 °C) was higher than that of the ASTM specification range for diesel fuel, it was still acceptable for use in engines.

All methods just discussed are associated with problems due to carbon deposition and contamination. Transesterification is known to be the best technique for production of biodiesel due to its physical and chemical similarity with conventional diesel fuel. The process produces little or no deposits. Various transesterification processes are summarized in Fig. 1, each having its own advantages and disadvantages. Among them, supercritical biodiesel production is a promising route as it offers unique advantages over other methods, including the fact that it does not require a catalyst and has a shorter reaction time. Supercritical biodiesel production can be applied to a wide variety of feedstock. No feedstock pretreatment is necessary, and separation and purification of products are relatively easy. As shown in Fig. 1, supercritical biodiesel production can use a variety of solvents ranging from methanol, ethanol, methyl acetate, dimethyl carbonate (DMC), or *tert*-butyl methyl ether (MTBE).

This review aims to provide a review on the latest advances in supercritical biodiesel production and a better understanding of the chemical processes by examining at a detailed level the mechanisms of triglycerides reactions with methanol, ethanol, methyl acetate, DMC, and MTBE. Empirical rate expressions are derived for reactions in these solvents for the first time. These rate equations are critical to predicting the product yield and to unraveling the reaction behaviors. Factors affecting supercritical biodiesel production are discussed in detail, including temperature, residence time, pressure, and oil-to-reactant molar ratio. Finally, the challenge for improving energy recovery and recommendations for future work are presented.

## 2. Biodiesel production processes

Biodiesel is mainly produced by reacting triglycerides with short-chain alcohols such as methanol and ethanol in a transesterification process (Fig. 1). These methods, along with their advantages and drawbacks, are discussed in what follows.

### 2.1. Homogeneous catalysts

Two types of homogeneous catalysts for biodiesel production are homogeneous acid catalysts and homogeneous alkali catalysts.

#### 2.1.1. Homogeneous acid-catalyzed transesterification

So far, hydrochloric acid (HCl) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) have been the most commonly used catalysts for acid-catalyzed transesterification. Compared with an alkali-catalyzed process, the acid catalyst holds the advantages that it can catalyze esterification and transesterification simultaneously [14], that it is not sensitive to the presence of free fatty acid (FFAs) in the feedstock, and that it can be applied to low-cost lipid feedstock such as waste cooking oil [15]. Zhang et al. [16] reported that acid catalysis performed better when the amount of FFAs in the feedstock was greater than 1 wt%.

Fig. 2 shows the mechanism of homogeneous acid-catalyzed transesterification for biodiesel production using methanol. This mechanism involves the protonation of the carbonyl group, nucleophilic attack of methanol to produce a tetrahedral intermediate, followed by proton migration and intermediate breakdown. This sequence is repeated two more times to generate biodiesel and glycerol.

Even though the acid catalyst is insensitive to the presence of FFAs, it requires more severe reaction conditions than alkali-

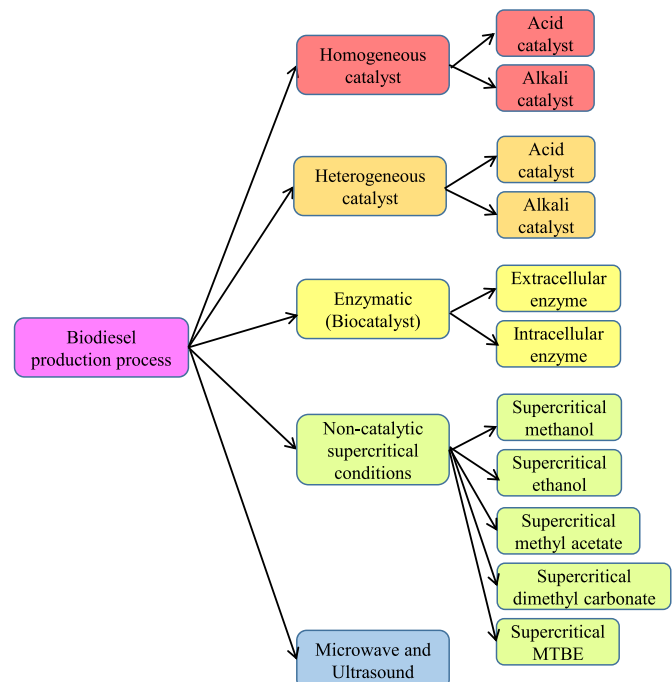


Fig. 1. Several methods to produce biodiesel.

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