



Biodiesel synthesis with alkaline catalysts: A new refractometric monitoring and kinetic study



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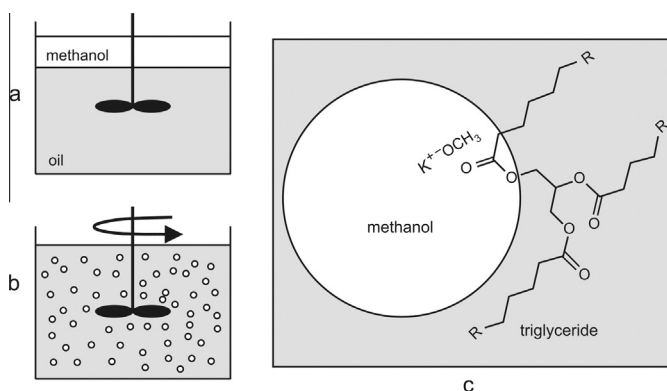
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HIGHLIGHTS

- The online monitoring method proposed is relatively simple and inexpensive.
- Two steps were identified in the alkaline methanolysis of triglycerides.
- The mixing step consumed most of the time of the overall reaction.
- The kinetics of methanolysis are best described by a zero-order model.
- The catalysis of methanolysis with KOCH₃ should be described as heterogeneous.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, an experimental system was designed to allow the online monitoring of a chemical reaction in continuous flow leading to biodiesel synthesis using a portable digital refractometer. The proposed method was applied to the monitoring of the methanolysis of soybean oil using KOCH₃ as the catalyst at temperatures from 30 to 60 °C, allowing data acquisition in a relatively simple, reliable and cheap fashion. It was also possible to identify, discriminate and monitor the mixing (emulsification) and the reaction steps, with the former being the rate determinant. The methanolysis reaction is better represented by a zero-order kinetic scheme than by a pseudo-first-order scheme; the activation energy was determined to be (31.3 ± 1.8) kJ mol⁻¹. This behavior suggests that methanolysis with alkaline catalysts, usually considered as a homogeneous process, should in fact be assumed to be heterogeneous. Therefore, the rate of mixing controls the reaction kinetics and is a key factor in decreasing the transesterification time.

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1. Introduction

The instability of the petroleum market, the limited availability of crude oil and particularly the environmental impact related to the use of fossil fuels have been encouraging the use of alternate

fuels. Biodiesel is an alternative fuel to petroleum diesel, and much attention has been given to the processes related to the synthesis and application of the biodiesel worldwide [1]. From a chemical composition point of view, biodiesel is a mixture of fatty acid alkyl esters obtained from renewable raw materials such as vegetable oils and animal fats. Transesterification is the most employed process for obtaining biodiesel, in which the triglycerides react with

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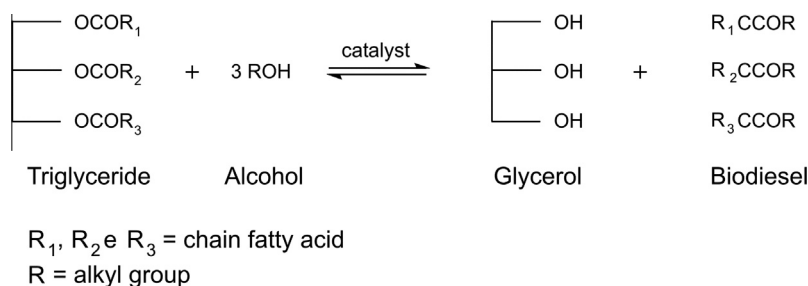


Fig. 1. General chemical equation of a triglyceride transesterification.

low molecular weight alcohols (the alcoholysis reaction), such as methanol and ethanol (Fig. 1).

Biodiesel is commonly produced by the transesterification of triglycerides with methanol (the methanolysis reaction) and alkaline compounds such as NaOH, NaOCH₃, KOH and KOCH₃, the most employed and studied catalysts. The global transesterification process can be described by consecutive and reversible steps in which diglycerides and monoglycerides are intermediates and glycerol is a byproduct (Fig. 2). Because each step is reversible, the alcohol is added in excess in relation to the initial amount of triglycerides to achieve the maximum generation of product (biodiesel and glycerol). Although the reaction proceeds via the simple mixing of the reactants, the use of catalysts is always necessary to rapidly achieve maximum conversion.

The kinetic equations are expressed as follows:

$$\frac{d[\text{TG}]}{dt'} = -k_1[\text{TG}]^j[\text{ROH}]^k + k_{-1}[\text{DG}]^l[\text{BD}]^m$$

$$\begin{aligned} \frac{d[\text{DG}]}{dt'} = & k_1[\text{TG}]^j[\text{ROH}]^k + k_{-2}[\text{MG}]^n[\text{BD}]^o - k_{-1}[\text{DG}]^l[\text{BD}]^m \\ & - k_2[\text{DG}]^p[\text{ROH}]^q \end{aligned}$$

$$\begin{aligned} \frac{d[\text{MG}]}{dt'} = & k_2[\text{DG}]^p[\text{ROH}]^q + k_{-3}[\text{GL}]^r[\text{BD}]^s - k_{-2}[\text{MG}]^n[\text{BD}]^o \\ & - k_3[\text{MG}]^t[\text{ROH}]^u \end{aligned}$$

$$\begin{aligned} \frac{d[\text{BD}]}{dt'} = & k_1[\text{TG}]^j[\text{ROH}]^k + k_2[\text{DG}]^p[\text{ROH}]^q + k_3[\text{MG}]^t[\text{ROH}]^u \\ & - k_{-1}[\text{DG}]^l[\text{BD}]^m + k_{-2}[\text{MG}]^n[\text{BD}]^o - k_{-3}[\text{GL}]^r[\text{BD}]^s \end{aligned}$$

$$\frac{d[\text{GL}]}{dt'} = k_3[\text{MG}]^t[\text{ROH}]^u + k_{-3}[\text{GL}]^r[\text{BD}]^s$$

where $j, k, l, m, n, o, p, q, r$ and s are the orders with respect to each reactant.

Several authors have adopted this set of equations for the kinetic study of the alcoholysis of vegetable oils. The concentrations

are determined by any analytical method, and the set of differential equations is analytically (or numerically) solved, assuming values for the indexes $j, k, l, m, n, o, p, q, r$ and s [2–6]. Richard and coworkers have also explicitly included the catalyst in the reaction rate equation, assuming a third-order reaction law [7].

In some reports, the kinetic scheme is simplified with respect to the reversible/consecutive reaction scheme shown in Fig. 2, assuming either irreversible/non-consecutive schemes [8], pseudo-first-order reaction schemes [9,10] or pseudo-second-order steps [10]. Models considering only the first (irreversible) step (triglyceride → diglyceride) [10] or the global reaction (triglyceride → biodiesel) [11–13] can also be found. A change in the reaction rate law along the course of the reaction (assuming pseudo-first-order kinetics at the initial stage and first- or zero-order kinetics at the final stage) has also been discussed [8]. A treatment of the global reaction as a zero-order kinetic process, to the best of our knowledge, has not been presented until now, although zero-order kinetics has been attributed to last reaction step while the initial steps have been treated with different orders, especially for the very beginning of the reaction [8,12]. This analysis suggests that the kinetics of biodiesel synthesis is an open question.

Despite the previous work available in the literature [5,11,13,14], a new study of the kinetic behavior of alkaline methanolysis can increase the understanding of the parameters that control the global process rate and identify the most relevant factors that should lead to the optimization of the biodiesel synthesis.

An apparent consensus related to the alkaline catalysts is that the maximum conversion is achieved after 1 h at 60 °C and a methanol:oil molar ratio of 6:1 [15]. However, some reports suggest that maximum conversion is observed at shorter times, such as 20 min at similar conditions [16,17] or 5 min for a 90% conversion of triglycerides to methyl esters [16–19].

The fast conversion observed for the methanolysis reaction makes most of the analytical methods usually adopted for monitoring the biodiesel synthesis, especially chromatographic methods, inadequate for a kinetic investigation. These analytical methods are not applicable for consecutive determinations in such small time intervals due to analytical limitations, such as the

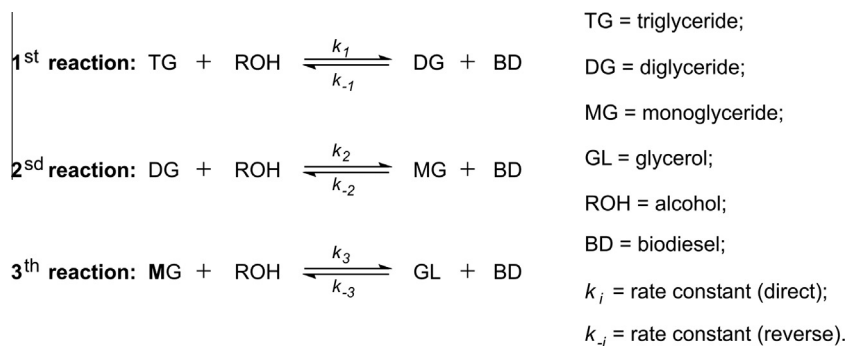


Fig. 2. Representative scheme for the sequential steps of the transesterification of a triglyceride.

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