



Short communication

# Biodiesel synthesis: A study of the triglyceride methanolysis reaction with alkaline catalysts


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## ABSTRACT

The rates of soybean oil methanolysis under NaOCH<sub>3</sub>, KOCH<sub>3</sub>, NaOH and KOH catalysis were determined at 30.0, 40.0, 50.0 and 60.0 °C using a refractometric method for online monitoring of this reaction. The influences of the metallic cations and anions on the catalysis were studied. Potassium promotes faster reactions than sodium. For the reactions catalyzed by hydroxides, the rate constants are less sensitive to temperature than those catalyzed by methoxides. The proposed reaction mechanism was based on the formation of ionic pairs at the interface of the methanol and oil phases and in the methanol phase.

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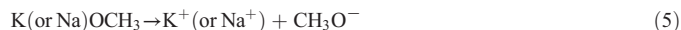
## 1. Introduction

Biodiesel is a renewable alternative fuel to petroleum diesel, and it consists of a mixture of fatty acid alkyl esters (FAAEs) primarily produced through the triglyceride (TG) transesterification reaction with methanol (methanolysis) [1,2]. Methanolysis proceeds via three reversible and consecutive reactions (Eqs. (1–3)). Diglycerides (DGs) and monoglycerides (MGs) are intermediate species in this mechanism, and glycerol (GL) is a byproduct. The global process is described by Eq. (4).



Alkaline catalysts are most often used for these reactions owing to their relatively low cost and capability of promoting high conversion in few minutes under moderate conditions [1,2]. The most studied alkaline catalysts for the methanolysis reaction are NaOH, NaOCH<sub>3</sub>, KOH and KOCH<sub>3</sub> [3].

As suggested in the literature [2,4], methoxide ions are responsible for the catalysis process and are formed from the dissociation of the corresponding alkaline methoxide in a methanol solution (Eq. (5)) or from a reaction between alkaline hydroxide and methanol (Eq. (6)). Methoxide ions act as nucleophilic agents and react with the glyceride carbonyl carbon, which forms a tetrahedral intermediate. In this intermediate, a glycerate ion is removed from the original ester molecule, and a methyl ester is formed, which is a biodiesel molecule.



When these catalysts are used, the reactants must not contain water or free fatty acids because water decreases the reaction yield due to ester hydrolysis, and fatty acids deactivate the catalysts due to the production of soap [5–7]. Soap formation is not expected when alkaline methoxides are used as catalysts without water or free fatty acids in the reaction mixture. However, alkaline hydroxides might produce soap through an ester saponification reaction, even without water and free fatty acids [4,8].

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Although several previous studies have evaluated the efficiency of alkaline catalysts (particularly, NaOH, NaOCH<sub>3</sub>, KOH and KOCH<sub>3</sub>) for biodiesel synthesis, a systematic and comparative report on the activities of these catalysts is not available. In most of the previous studies that compared the activities of these catalysts, the experiments used the same catalyst weights (therefore, different molar quantities) and initial raw material weights [5,9–12]. This approach brings misinterpretations because often some catalysts are judged more efficient than others as a result of their chemical nature, when in fact this greater efficiency stems from the fact that they are being employed in larger quantities (molar). Hence, it is not possible to obtain fundamental information on the influence of the chemical species involved in the process, which may impair the elucidation of a mechanism for this reaction. Therefore, although these studies are relevant from an economic point of view, for allowing estimate the cost/benefit that the catalyst offer to the industry, they do not allow to estimate the relative activity of catalysts.

Vincent and co-workers [4] compared the catalytic activity of NaOH and KOH in the methanolysis of sunflower oil employing the same molar ratio catalyst/triglycerides. These authors observed that the time required for conversion with KOH (5 min) was three times lower than with NaOH (15 min). However, Arzamendi and co-workers [13] have investigated the methanolysis of the same oil with LiOH, NaOH, KOH, RbOH and CsOH. These authors observed that, with the exception of LiOH (where there was an induction period for the reaction), all hydroxides had the same performance. Although the reaction conditions employed by both groups of authors are not identical, the information presented in the literature as to the performance of NaOH and KOH are being contradictory.

An apparent consensus related to alkaline catalysts is that maximum conversion is achieved after 1 h at 60 °C and with a methanol:oil molar ratio of 6:1 [14]. However, some reports have suggested that maximum conversion is observed at shorter times, such as 20 min under similar conditions or 5 min for a 90% conversion of triglycerides to methyl esters [4,11,15–17]. For the methods typically adopted to monitor biodiesel synthesis, especially chromatographic methods, this rapid conversion renders most of the analytical methods kinetically inadequate because they are not applicable to consecutive determinations in short time intervals. Consequently, the time interval in which most of the reaction occurs cannot be reliably monitored. Nevertheless, a considerable amount of work is reported in the literature regarding kinetic investigations based on these analytical methods [15,18–22].

In a previous study in our laboratory, we constructed an experimental device to measure the refractive index, which facilitated online monitoring of biodiesel synthesis catalyzed by KOCH<sub>3</sub> [1]. This system is suitable for kinetic studies of alkaline transesterification because the data are acquired in relatively short time intervals (approximately 5 s) and because additional chemical treatment of the sample is not required.

Until the moment, no kinetic study of the methanolysis reaction occurred in biodiesel synthesis was conducted to compare the efficiency of alkaline catalysts NaOH, NaOCH<sub>3</sub>, KOH and KOCH<sub>3</sub> in the same molar ratio to the triglyceride with a method which does not affect the chemical equilibrium. The goal of the current study is to compare the role of these catalysts in this reaction and to investigate the influence exerted by the catalysts (hydroxide or methoxide) and the associated metal cations (Na<sup>+</sup> and K<sup>+</sup>) on the reaction mechanism.

## 2. Material and methods

### 2.1. Materials

Commercial soybean oil was used in this study. The methanol (99.8%, Synth, Brazil), NaOH (99.8%, Synth, Brazil), KOH (85%, VETEC, Brazil) and NaOCH<sub>3</sub> (30% solution in methanol, VETEC, Brazil) reactants were used as received.

### 2.2. Biodiesel synthesis and monitoring method

The biodiesel synthesis experiments were performed in triplicate using soybean oil (150.0 g), methanol (30.0 g) and the catalyst (0.0157 mol). The reaction conditions included mechanical agitation at 400 rpm and temperatures of 30.0, 40.0, 50.0 and 60.0 °C, which were controlled using a thermostatic bath.

The experimental system and the method used in this study to monitor the soybean oil methanolysis reaction were identical to those previously introduced by Tubino and co-workers [1]. The refractive index was measured at short time intervals until the end of the reaction when it became constant or when random sharp variations were observed. These random deviations are likely associated with glycerol, which was present in excess at the end of the reaction and which could not be efficiently separated by the system owing to its high quantity.

### 2.3. Selection of experimental data associated with methanolysis

Under the reaction conditions used, the refractive index in the early stages of monitoring varies because of the mixing of the methanol phase and the triglyceride phase. Due to the transformation of the triglycerides into mono alkyl esters, methanolysis has an additional influence on the refractive index value of the mixture [1]. For kinetic purposes, only the experimental data obtained after the maximum dispersion of the reactants were considered because the main reaction significantly contributes to the change of the refraction index only after this stage. This situation can be clearly observed by comparing the variation of the refractive index versus time curves (Fig. 1). The first curve was obtained without a catalyst (the refractive index varies only because of the mixing of the reagents), and the second curve was obtained after the addition of KOH (the refractive index varies after the mixing of the reagents due to the occurrence of the reaction).

## 3. Results and discussion

### 3.1. Monitoring biodiesel synthesis and kinetics

The acquired data were used to plot variations in the refractive index  $\Delta n_D^{20}$  as a function of time,  $t$  (Fig. 2). The  $t < 0$  region represents emulsification of the catalyst solution in methanol and oil, and the  $t > 0$  region corresponds to glyceride transformation into methyl esters.

Not all of the curves can be superposed in the  $t < 0$  region (Fig. 2), which suggests that emulsion formation occurred as a function of time with weak reproducibility. It is difficult to fully control all of the variables associated with transport. However, the  $\Delta n_D^{20}$  versus reaction time curves (in the  $t > 0$  region) are strongly reproducible, which is particularly important for kinetic investigations into methyl ester formation from glycerides.

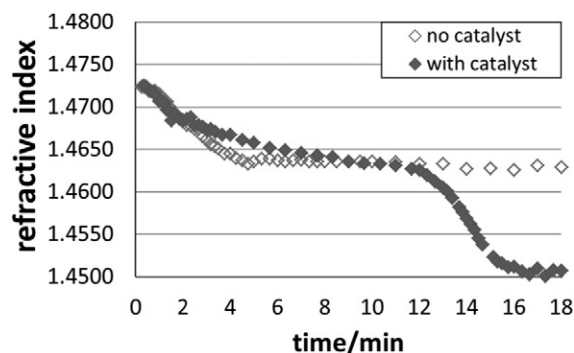


Fig. 1. Transesterification reaction – variation of the refractive index as function of time for the reactive mixture without catalyst and with catalyst (KOH).

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