



Determination of the kinetics of biodiesel saponification in alcoholic hydroxide solutions



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HIGHLIGHTS

- Quantitatively investigated kinetics of fatty acid alkyl esters saponification in alcoholic hydroxides.
- FAME saponification occurred 5–7 times more rapidly in ethanol than in methanol.
- Found actual saponification rate constants for the methanol–KOH and ethanol–KOH.
- Found activation energies for the FAME saponification in the alcoholic hydroxides.
- Provided useful data in understanding/modelling base-catalysed transesterification reactions.

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ABSTRACT

The research focused mainly on kinetics of the side reactions occurring during homogeneous base-catalysed transesterification processes, which were not studied previously. The rates of fatty acid methyl esters (FAME) saponification with sodium and potassium hydroxides were investigated in methanol and ethanol (commonly used in biodiesel production) at temperatures of 40, 50 and 60 °C. The effect of water on the rate of FAME saponification in the alcoholic hydroxide solutions was also studied (at 60 °C). The apparent rate constants of FAME saponification were strongly influenced by the types of alcohol, but little affected by variation of the metal hydroxides. The apparent rate constants for FAME saponification using the ethanol hydroxides were 5–7 times higher than for methanol hydroxides. This was due to the lower acidity of ethanol, leading to a higher concentration of hydroxide ions in the ethanol–hydroxide solutions. The rate constant of the FAME saponification increased with temperature. For example, it was 1.31 L mol⁻¹ min⁻¹ at 40 °C, but 3.08 and 5.63 L mol⁻¹ min⁻¹ at 50 and 60 °C in the methanol–NaOH solution. Arrhenius activation energies for the FAME saponification in the alcoholic hydroxides were in the range of 60.3–64.0 kJ mol⁻¹. It was found that the FAME saponification rate in ethanol–hydroxides was 3.5 times higher than that in methanol–hydroxides in the presence of water. This indicates that use of methanol should be preferred over ethanol in alkali-catalysed transesterification, as the amount of soap produced by saponification of triglycerides and alkyl esters will be lower.

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1. Introduction

Transesterification of triglycerides with alcohols with/without catalyst is one method for producing biodiesel, a renewable alternative to diesel. It proceeds via three reversible stepwise reactions [1,2] as follows



Overall reaction:



(TG: triglyceride; DG: diglyceride; MG: monoglyceride; GL: glycerol; ROH: alcohol; AE: alkyl esters).

In alkali-catalysed homogeneous transesterifications, hydroxides and methoxides of sodium and potassium are commonly used. In a hydroxide-catalysed transesterification process, alongside three main transesterification steps (Eqs. (1)–(3)), there can also be saponification of the oil (TG) and the alkyl esters (AE) (Eqs. (6) and (7)) to form soap. This occurs alongside the main reactions due to the existence of the hydroxide-alkoxide equilibrium (Eq.

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(5). This equilibrium shifts towards the formation of hydroxide when the water content is increased. The formation of soap leads to emulsification, which renders the downstream separation of glycerol very difficult. The deleterious effect of water means that in practice transesterification is limited to very dry (<0.5 wt% moisture) vegetable oils.



Saponification of alkyl esters can occur in aqueous hydroxide solutions [3], mixtures of water and soluble organic solvents, such as dimethyl sulphoxide (DMSO) [4], ethanol [5,6] and mixtures of protic solvents, e.g. methanol and dichloromethane [7]. It has been reported that saponification of carboxylic acid esters in hydroxide solutions is a bimolecular reaction, which is first order for ester and hydroxide ions [3,8]. Hydroxide ions attack the carbonyl to form a tetrahedral intermediate, which then decomposes to the products (Fig. 1a). However, recent studies [7,9] found that the reactions did not occur via simple bimolecular collisions, but rather required a molecule of water to form the tetrahedral intermediate. This indicates that a water molecule stabilises the transition-state complex through hydrogen bonding (Fig. 1b). Such hydrogen bonding could also be provided by other protic solvents such as simple alcohols.

The rate of saponification of alkyl esters was strongly dependent on steric and electronic interactions of the esters and metal hydroxides with the solvent [7]. Such interactions determine the rate of saponification in various solvent environments. For instance, the hydroxide anions are highly solvated because of the electronic charge in a predominantly aqueous and protic solvent environment. The solvation of the OH^- anions reduces the rate of direct collisions between the anions and the alkyl ester molecules in the solution [10]. This phenomenon was used to explain the higher rate of saponification of esters in 0.5 M KOH prepared in 80–90% (v/v) DMSO in water than that of 0.5 M KOH prepared in 80–90% (v/v) ethanol in water [4]. 63.5% of the ester was saponified in a 0.5 M KOH solution prepared in 83.5% (v/v) aqueous DMSO, whereas only 9.2% was saponified in a 0.5 M KOH prepared in 83.5% (v/v) aqueous ethanol after 3 min at the same conditions. However, the differences in the rates of saponification of the esters in 0.5 M KOH prepared in 83.5% (v/v) aqueous DMSO and 0.5 M KOH prepared in 83.5% (v/v) aqueous ethanol were not entirely due to the reduction in the desolvation energy of the OH^- in the aqueous DMSO solution. The authors did not take into account the reactions of the KOH with ethanol to form potassium ethoxide (Fig. 2), which reduces the amount of KOH in the solutions and consequently lowering the rate of saponification.

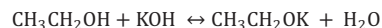


Fig. 2. Ethanol–KOH reaction.

The depletion of metal hydroxide in a saponification mixture containing alcohol where carboxylic acid esters were saponified using 0.1–0.5 M NaOH prepared in approximately 9:1 (v/v) of CH_2Cl_2 /methanol was reported [7]. The presence of sodium methoxide formed by the reaction of NaOH with methanol lead to the transesterification of the original esters to form “methyl ester” [7]. However, the authors explained these results due to “hydroxide ions assisted” bimolecular collisions of methanol and the original esters.

Furthermore, the magnitudes of activation energies for alkyl esters saponification indicate that the differences in the desolvation energies of the OH^- in aqueous/protic and aprotic solvents was not entirely responsible for the higher rates of alkyl esters saponification in dipolar aprotic co-solvents. For instance, the Arrhenius activation energies of 41.40–63.18 kJ mol^{-1} [3,5,6,11] for alkyl esters saponification in aqueous/protic medium were too small to account for the desolvation energy of 423.4 kJ mol^{-1} [9] required for the desolvation of OH^- in the aqueous medium. The values of the activation energies for alkyl esters saponification suggest that the direct collision of desolvated OH^- ions is implausible.

Although extensive research on the kinetics of alkaline hydrolysis of esters has been done, no study has been carried out on the kinetics of fatty acid alkyl esters saponification in alcohol hydroxides. Such investigation is essential to understanding the competitive saponification of biodiesel produced during alkali-catalysed homogeneous transesterification. As methanol and ethanol are commonly used for the biodiesel production, kinetic studies of saponification of fatty acid alkyl esters (biodiesel) in these alcoholic media provide fundamental in choosing alcohol and/or operating conditions to achieve high yield and quality product. In this study, the kinetics of fatty acid methyl esters (FAME) saponification in both methanol–hydroxide and ethanol–hydroxide solutions of NaOH and KOH at a temperature range of 40–60 °C were investigated. These conditions are similar to those used in commercial homogeneously catalysed biodiesel processes. The effect of water on the rate of the FAME saponification in the alcoholic NaOH and KOH solutions was also studied.

2. Materials and methods

2.1. Materials

Refined RSO (Henry Colbeck, UK) used in production of the FAME contained approximately 98.7 wt% triglycerides, 0.03 wt%

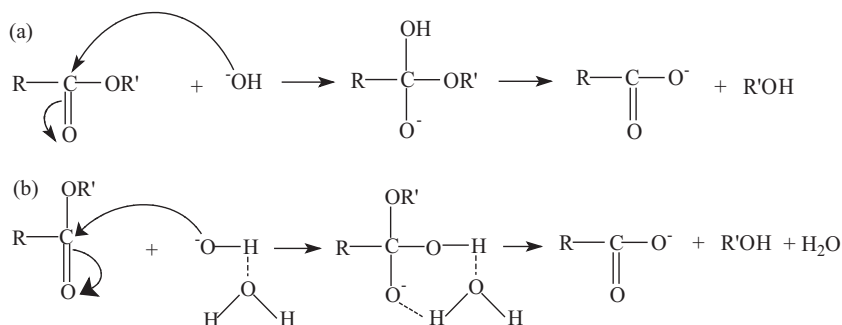


Fig. 1. Saponification of alkyl esters (a) reaction mechanism for alkyl esters saponification; (b) bimolecular collision by solvated hydroxide ions to form H-bond stabilised tetrahedral intermediate.

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