

JOHANNES RUWWE

Metal alkoxides as catalysts for the biodiesel production

ABSTRACT

Commercial biodiesel production today uses mainly homogeneous alkaline catalysts, which offer performance and cost advantages over other alternatives. Among the alkaline catalysts, metal alkoxides are the most successful, especially in large-scale production units. The major advantages of metal alkoxide catalysts are their selectivity, which allows a good biodiesel yield, and fast and complete conversion to the target product. In addition, the metal alkoxides are available in the form of methanol solutions, which offer handling and safety advantages.

INTRODUCTION

Biodiesel of the FAME (Fatty Acid Methyl Ester) type is commonly produced by transesterification processes where glycerol esters (triglycerides, e.g. vegetable oils, animal fats, and used cooking oils) are converted into methyl esters by reaction with methanol in the presence of a catalyst (1). The large number of catalysts that have been tested and compared include homogeneous alkaline and acid catalysts, enzymes and various heterogeneous catalysts. This topic has already been addressed in various reviews and articles (2, 3). Most studies conclude that alkaline catalysts are the products of choice since they allow high reaction rates and complete conversion under moderate conditions. This closely reflects the industrial biodiesel production scenario, commercial processes running almost exclusively on alkaline catalysts.

ALKALINE CATALYZED TRANSESTERIFICATION

The reaction mechanism of alkaline catalysed transesterification, or alcoholysis, whether in biodiesel production or any other process, is well understood and widely used (4). As steric hindrance is limited in all the molecules involved in the biodiesel process, the reaction mechanism can be classified as S_N2 -AC-B (following A_N+D_N mechanism, also referred to as $B_{AC}2$). This is depicted in Figure 2 (5, 6). In all alkaline catalysed transesterifications that yield methyl

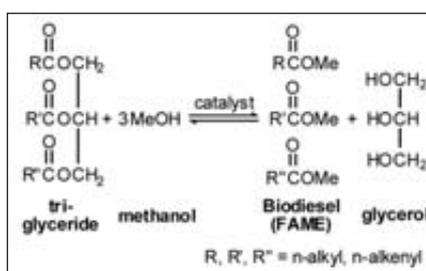


Figure 1. Transesterification of triglycerides: overall reaction scheme

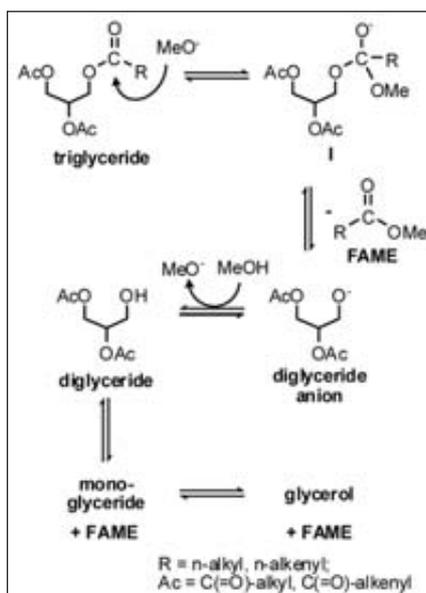


Figure 2. Transesterification reaction mechanism

esters, the only catalytically active species is the methoxide (methylate) anion. This nucleophile attacks one of the carbonyl functional groups of the triglyceride to form the unstable tetrahedral intermediate I. Intermediate I dissociates into a molecule of FAME and a diglyceride anion. Subsequently the diglyceride anion deprotonates methanol to form the corresponding stable diglyceride while the catalytically active methoxide is regenerated.

Once methoxide is regenerated the cycle starts again at another triglyceride or at a di- or mono-glyceride to finally form glycerol and 3 equivalents of FAME.

ALKALINE TRANSESTERIFICATION CATALYSTS

Virtually all industrial biodiesel processes that use alkaline catalysts run on either alkoxides (sodium methoxide, NaOMe, or potassium methoxide, KOMe) or the corresponding hydroxides (NaOH, KOH). Other alkaline catalysts are used only rarely. The reaction mechanism observed in the transesterification process is identical for alkoxides and hydroxides. With alkoxides, the catalyst is used directly in its active form.

Hydroxides do not catalyse the target reaction directly, and must first undergo a pre-forming step in order to form an active catalyst. This occurs with the in situ formation of alkoxides when the hydroxides are dissolved in the appropriate alcohol, which for the biodiesel process is usually methanol. Figure 3 shows this reaction for the examples of NaOH and KOH.

This pre-forming step is an equilibrium reaction and all the species involved coexist, including unreacted hydroxide and liberated water, both of which are unwanted in transesterifications. The concentration of methoxide and all the other compounds depends on the equilibrium constant of the reaction at a given temperature and the starting quantities in the pre-forming step. In biodiesel processes using NaOH and methanol, only these two compounds need be considered; when KOH is used, its ca. 10 percent water content has to be considered as



Figure 3. Reaction of hydroxides with methanol

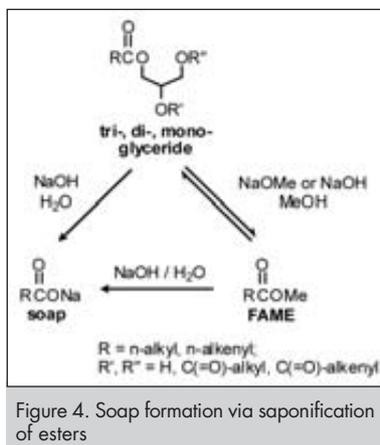


Figure 4. Soap formation via saponification of esters

well. Some investigations of this equilibrium have been published (7), most of them for the sodium hydroxide - methanol case. However, there is little agreement between the findings.

According to *Tarasov et al.* the equilibrium constant for this reaction is small (5.5×10^{-2}), indicating that only slight conversion to the methoxide occurs. *Unmack and Caldin and Long*, on the other hand, suggest a constant that is more than two orders of magnitude higher, in which case the quantity of the methoxide formed would be much higher. A surprising result as regards KOH-methanol mixtures is obtained by *Komers*, who claims that the equilibrium constant strongly depends on the referenced initial composition.

The situation in a biodiesel process is in any case much more complex because methanol is chemically consumed during the process, influencing the equilibrium as well as the amount of glycerol formed. Regardless of the magnitude of the equilibrium constant, the key difference between hydroxides and alkoxides as catalysts is their degree of purity.

Commercial alkoxides are pure products and do not contain water and hydroxides, although methanol solutions of hydroxides are sometimes labelled alkoxide solutions and offered as such on the market.

TRANSESTERIFICATIONS

The lower purity of the hydroxide catalysts affects the performance and selectivity of the transesterification process. The lower concentration of the catalytically active methoxide species may result in somewhat slower conversion rates, and the presence of water and hydroxides leads to the formation of by-products.

Performance considerations

According to *Freedman* (8), similar or even higher conversion rates were observed when 0.5 percent sodium methoxide was used instead of 1 percent sodium hydroxide, especially with low quantities of methanol. The reaction kinetics of alkaline catalysed transesterifications in biodiesel processes have been investigated (9), however, and the reactions were found to be very fast. Hence, the half lives of the reactants in these reactions are very short as compared with batch or residence times; consequently, the conversion rates in biodiesel processes are usually adequate, and are almost independent of the choice of catalyst.

Selectivity considerations

More important in terms of process efficiency is the selectivity advantage of alkoxides over hydroxides. With alkoxides, an unwanted saponification side reaction that occurs in the presence of hydroxides and water can be avoided. Saponification is the reaction of an ester with a hydroxide to form a soap, preferably in the presence of an alcohol-water mixture (10, 5a); under the conditions used in transesterifications this reaction is irreversible. In the biodiesel process, this leads to the formation of soaps, with consumption of either the FAME target product, or the triglyceride raw material. Regardless of which ester is converted into soap, the biodiesel yield will be reduced. These avoidable soaps from saponification are formed in addition to those formed by neutralization of free fatty acids (FFAs). The raw materials used in biodiesel production may contain a certain fraction of FFAs, depending on the refining processes to which the feedstock had been subjected. Neutralization of these FFAs by the alkaline catalyst is unavoidable, and occurs for both alkoxides and hydroxides. However, neutralization with alkoxide liberates methanol,

whereas neutralization with hydroxide liberates water.

Chemically speaking, soaps formed by saponification cannot be distinguished from those formed by neutralization. If the raw material contains virtually no FFAs, no soaps are formed by neutralization. A comparison of biodiesel processes in terms of yield was published by *Aracil et al.* (11). A yield improvement of ca. 12 percent is observed when sodium methoxide is used instead of NaOH as

catalyst; for potassium methoxide, the yield improvement over KOH is reported to be almost 7 percent. The significant reduction in yield observed with hydroxide catalysts was found to be due to saponification.

The unwanted soap by-products usually dissolve in the glycerol phase and are removed together with this process stream; consequently, the purity of the glycerol phase decreases with increase in soap formation.

Soap formation does not necessarily lead to lower biodiesel yield relative to triglyceride; in principle, the soap by-products can be recycled into the biodiesel production process. To do this, they must first be split into the corresponding FFAs. These must be separated from the glycerol phase and converted into biodiesel in an additional esterification process step (distinct from transesterification) using additional equipment. In this case, the reduction in yield is more accurately described as a reduction in capacity.

HANDLING AND SAFETY

Alkaline catalysts in biodiesel processes are used as homogeneous catalysts, i.e. as their methanol solutions, in dissolved form. Alkoxides like sodium methoxide and potassium methoxide are usually commercially available as ready-to-use methanol solutions because they are obtained in that form in industrial production. Sodium methoxide is offered as a 30 percent or 25 percent methanol solution, and potassium methoxide as a 32 percent methanol solution. NaOH and KOH are offered as solids and not premixed in methanol, and must therefore be dissolved by biodiesel producers themselves. Apart from the fact that liquids are preferred to solids in industrial processes on account of easier handling, the dissolution process itself poses a safety risk if not carried out carefully (12). Safety risks arise from the exothermic process of dissolving hydroxides in methanol and from possible difficulties in handling solids, e.g. dust formation or plugged feeder valves.

Koivisto reports significant heats of solution for both NaOH and KOH in methanol (13). Without appropriate cooling, the dissolution process is more than sufficiently exothermic to initiate evaporation of large quantities of methanol, with the formation of potentially explosive mixtures.

As it is almost impossible to protect solids from absorbing atmospheric humidity and/or carbon dioxide, a possible degradation of the hydroxides on storage must also be allowed for. The liquid catalyst solution, on the other hand, is easily protected by nitrogen blanketing and vapour return systems to ensure safety and maintain product quality.

Once in hand, the prepared methanolic hydroxide solution, as well as the ready-to-use methoxide solution, has to be classified as toxic and flammable (due to the methanol content) and corrosive (due to the strongly alkaline material).

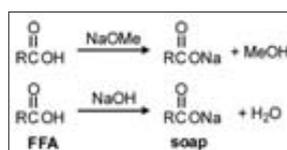


Figure 5. Soap formation via neutralization

CONCLUSIONS

Alkoxides, particularly sodium methoxide and potassium methoxide, in the form of their methanol solutions as well as hydroxides such as NaOH and KOH serve as efficient alkaline transesterification catalysts in the production of quality biodiesel. The use of alkoxides has advantages in terms of biodiesel yield in addition to safety and ease of handling. These advantages make alkoxides the preferred catalyst in commercial biodiesel production, especially in large-scale production plants.

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JOHANNES RUWWE

Evonik Degussa GmbH
Feldmühlestrasse 3
53859 Niederkassel
Germany