



Glycerol acetals as diesel additives: Kinetic study of the reaction between glycerol and acetaldehyde



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ABSTRACT

Certain acetals can be produced from renewable resources (bioalcohols) and seem to be good candidates for different applications, such as oxygenated diesel additives. This paper addresses the production of acetals (5-hydroxy-2-methyl-1,3 dioxane and 4-hydroxymethyl-2-methyl-1,3 dioxolane) from glycerol and acetaldehyde using Amberlyst 47 acidic ion exchange resin. This ion exchange resin performed well, recording 100% selectivity toward acetal formation at a suitably high initial glycerol concentration. When the initial acetaldehyde concentration was significantly higher than the glycerol concentration, 2,4,6 trimethyl-1,3,5 trioxane was the main reaction product. Unlike other acetalization reactions, the one studied here does not have thermodynamic limitations, and 100% conversion is achieved under different reaction conditions. A kinetic study was performed in a batch stirred tank reactor to study the influence of different process parameters, such as temperature, feed composition and stirring speed. A pseudo-homogeneous kinetic model was developed to describe this reaction kinetics, proving that its rate is just first order on the acetaldehyde concentration under the conditions studied.

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1. Introduction

There has been a significant increase in recent years in the use of isobutylene and bioethanol to produce oxygenated compounds, such as ethyl-tert-butyl ether (ETBE), as petroleum additives. Nowadays, the use of different biofuels in conventional car engines has become one of the technological goals on the path toward sustainable development. Biodiesel is an alternative fuel obtained from vegetable oils or animal fats, and it has several technical advantages over petro-diesel, such as a reduction in exhaust emissions, improved lubricity and biodegradability, higher flash point and reduced toxicity. There are several other properties, such as cetane number, gross heat of combustion and viscosity, which are very similar in both biodiesels and conventional diesels. However, biodiesels have an inferior performance compared to conventional diesels in terms of oxidation stability, nitrogen oxide emissions, energy content and cold weather operability [1].

Biodiesel is obtained from the chemical reaction between methanol (or ethanol) and animal fats or vegetable oils in the presence of a basic or acid catalyst. This reaction is called *transesterification*, and apart from methyl (ethyl) esters (biodiesel), glycerol is formed as a by-product (10 wt.%). Small amounts of this tri-alcohol are currently

being used in pharmaceutical and personal care products (e.g., cosmetic bonding agent for makeup). In order to avoid its incineration, different alternatives are being investigated in the quest for high value added products. Some potential uses include hydrogen gas production, glycerin acetate and acetal formation as potential fuel additives, as composite additive, and its conversion into citric acid, propylene glycol, acrolein, ethanol and epichlorohydrin [2,3].

A possible solution for the disadvantages biodiesels present is the use of suitable additives. Metal-based additives (manganese, iron, copper, barium ...) have so far been the main ones [4], but due to environmental concerns, a number of other additives from renewable sources are being investigated. It is a well-known fact that oxygenated additives reduce HC and CO emissions and provide a high octane and high quality unleaded gasoline. The increase in oxygen content in diesel fuels significantly reduces the emissions of particulate matter. MTBE and ETBE, commonly used as gasoline additives, are not suitable as diesel additives because of their very low cetane numbers (e.g., ETBE cetane number is as low as 2.5). Acetals are more suitable oxygenated additives for diesel fuels [5]. For example 1,1 diethoxy ethane has been proven to reduce exhaust fumes [6], but its low flash point limits its practical use in this area. Heavier acetals derived from glycerol combine positive environmental effects through lower emissions and suitable cetane numbers. As a result, glycerol-derived acetals seem to be good candidates for playing a role in this area [7,8]. However, not all acetals can be used as diesel or biodiesel additives. As previously indicated, some acetals have low flash points, and as a result they are not suitable for use as diesel additives. Glycerol acetals fulfil these diesel specifications, while ethanol acetals require a

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large aldehyde in order to provide acetals with acceptable flash points. Lower molecular weight acetals are being used as surfactants, flavours and disinfectants [3,7] in cosmetics, foodstuffs, pharmaceuticals and fragrances [2,9]. As explained above, large amounts of glycerol are being produced via biodiesel production, and one possible option for producing value added products involves the reaction of glycerol with aldehydes in order to produce acetals. This study considers glycerol and acetaldehyde acetals. Acetaldehyde may also have a renewable origin, as it can be obtained from bioethanol following a dehydrogenation or partial oxidation process [10,11]. Acetals formed from glycerol and acetaldehyde have been investigated for many years. Aksnes et al. [12,13] have published pioneering papers on these cyclic acetals. More recently, other studies have been carried out on the same products, since they are present in different types of wines [14,15] and have a bearing on their flavour.

Acetals can be produced via homogeneous catalytic processes using strong mineral acids as catalysts, such as H_2SO_4 , HF, HCl or *p*-toluenesulphonic acid [6,16,17]. Kaufhold et al. have patented [16] an industrial process for acetal production. Besides a homogeneous strong acid catalyst, this process uses an entrainer with a normal boiling point between 298.15 K and 348.15 K (hexane, pentane). This entrainer must be water insoluble (<3% soluble in water), so the water is continuously removed from the reacting phase, shifting the acetalization reversible reaction in the desired direction. However, these processes lead to corrosion problems, are uneconomical and not eco-friendly [6,7]. The use of a heterogeneous catalyst would overcome most of these problems. Therefore, several solid acid catalysts are currently being tested.

Capeletti et al. [7] have reported the performance of several solid acid catalysts, from commercial, natural and laboratory sources. They conclude that ion exchange resins perform better than other catalysts, allowing equilibrium values to be reached much faster than with other solid alternatives. Some authors have already verified the good behaviour of these catalysts in acetalization reactions [18–21].

This paper's main objective is to study the kinetics of the reaction between glycerol and acetaldehyde, given their potential as renewable resources for producing acetals with possible applications in the biofuel industry. Furthermore, the estimation of these kinetic parameters can be helpful for future studies on the simulation of industrial-scale production.

2. Material and methods

2.1. Materials

Glycerol (99 wt.% for synthesis) and acetaldehyde (99.0 wt.%) from Panreac were used as reagents, with the selected catalyst being Amberlyst 47 supplied by Rohm & Haas. This commercial catalyst was chosen because previous studies of similar processes reported its good activity, stability and suitable mechanical strength [19,22]. 5-hydroxy-2-methyl-1,3 dioxane and 4-hydroxymethyl-2-methyl-1,3 dioxolane standards were not found, so the reaction progress was followed by measuring reactant concentrations. However, glycerol formal (99 wt.%) (a mixture of two of the isomers formed by reacting glycerol with formaldehyde: 1,3-dioxan-5-ol (55 wt.%) and 1,3-dioxolane-4-methanol (45 wt.%) from Acros Organics was used to check and compare the response factor of these acetals with the ones obtained in the reaction studied. As these organic compounds are similar, the order of magnitude of the response factors was also assumed to be similar.

2.2. Analysis

Both the reactants (glycerol—GLY—and acetaldehyde—ACHO—) and the reaction products (mixtures of acetals—Ac— and water—W—) were

analysed by gas chromatography (Agilent 6890 N) using a flame ionization detector (FID) for organic compounds (glycerol, acetaldehyde and acetals) and a thermal conductivity detector (TCD) for water. An Agilent DB-1 60 m × 0.53 mm × 5 μm capillary column was used with Helium as the carrier gas.

2.3. Batch stirred tank reactor (BSTR)

The experiments were carried out in a 1 L glass jacketed stirred reactor (Fig. 1). The reaction temperature was controlled by an external thermostat (Lauda RE 304). This thermostat contains an external thermocouple to be placed inside the reacting mixture and allows controlling the reaction temperature with an accuracy of ±0.02 K. The reactor was also connected to a condenser in order to reflux all the vapours, keeping the reaction volume nearly constant and avoiding emissions by evaporation.

The reactants were loaded into the reactor (total initial volume 0.5 L), and after stabilizing the system to the desired temperature the catalyst was added. Samples were taken at specific time intervals for their analysis by GC. A small piece of glass wool was placed in the output-sampling valve to keep the catalyst amount constant in the reactor. Prior to analysis, the samples were diluted (1.5/10 in volume) in dimethyl sulfoxide (DMS) in order to enhance the analysis results by avoiding peak saturation. DMS was selected because all the compounds are soluble in it, and it does not affect the mixture in the way alcoholic organic solvents do.

Before adding the catalyst sample, and due to its high moisture content, it was first dried at room temperature. Thus, the catalyst

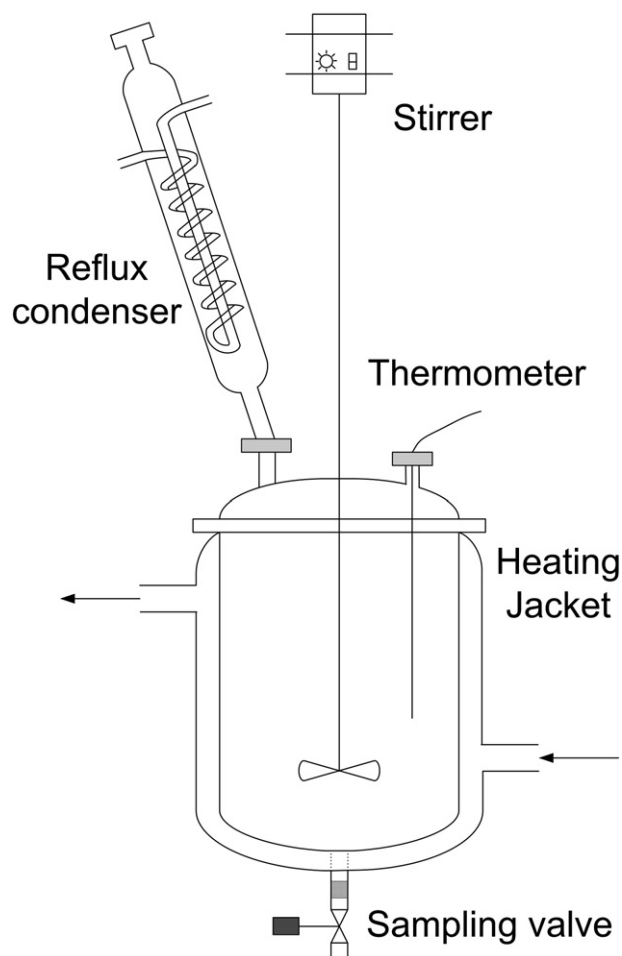


Fig. 1. Schematic drawing of the stirred batch reaction system.

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