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Acetalization reaction of ethanol with butyraldehyde coupled with pervaporation. Semi-batch pervaporation studies and resistance of HybSi® membranes to catalyst impacts

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ABSTRACT

Acetals are seen as important bio-based diesel additives. The production of these compounds from an alcohol and an aldehyde suffers from low conversions due to thermodynamic limitations. These limitations can be overcome through the continuous removal of the by-product water. One of the most promising innovative reaction systems is a membrane reactor equipped with a dehydration membrane. Water selective organic/inorganic HybSi® membranes were used for this purpose. As a representative example the production of 1,1 diethoxy butane from ethanol and butyraldehyde was studied. Permeance data were determined from pervaporation dehydration experiments using non-reacting quaternary mixtures at various temperatures. Membrane reactor experiments show that the conversion of the acetalization reaction can be increased from the thermodynamic value of 40% to 70% at 70 °C and a stoichiometric initial composition. The reactor experiments could be predicted using kinetic data of the reaction and a simple empiric membrane performance relation. The chemical stability of the membrane in the presence of aggressive organic solvents, like butyraldehyde, and its mechanical resistance against the solid catalyst particles of Amberlyst 47 were shown to be satisfactory.

1. Introduction

One of the first pervaporation processes studied using a dehydration membrane was the removal of water from ethanol–water mixtures. One of the advantages of doing this separation by using a pervaporation membrane is that complex distillation that is required to break the azeotrope can be avoided. Through the integration of distillation and a membrane step, high separation yields at relatively low capital and operational costs can be achieved [1]. In the recent years several dehydration membranes as well as membrane processes for the production of ethers and esters were developed [2–6].

Acetals are prepared in an equilibrium reaction between an alcohol and an aldehyde with water as a by-product. The thermodynamic limitations in conventional reaction systems result in low conversions for these reactions [7–11]. Sanchez Marcano and Tsotsis [12] were among the first to describe the advantages of a membrane reactor for the applications. The continuous removal of water from the reaction mixture through the application of a pervaporation membrane shifts the reaction to the product side and thus increases the yield [2,3,13–17].

Acetalization reactions are homogeneously catalyzed using strong mineral acids such as H_2SO_4, HF, HCl or p-toluene sulphonic acid [18–20]. The intrinsic disadvantage of these catalysts, corrosive and environmental properties, entails uneconomic processes and it has lead to the development of solid acid catalysts. Capeletti et al. [7] reported the performance of several solid acid catalysts, from commercial, natural and laboratory sources. They concluded that ion exchange resins show better performance than other catalysts reaching equilibrium faster than using other alternatives.

In coupled pervaporation–reaction systems, the reaction and the separation can be carried out in one unit using catalytically active membranes [5,21,22] or in a conventional batch reactor with the membrane separation in a recycle loop [2,3,16,17,23]. The retentate, all the components except water, are then returned to the reactor. A third option would be to combine the reaction and separation in one single unit by using a non-catalytic membrane and an additional catalyst. This option offers more flexibility as the amount of catalyst and the membrane area become decoupled. Also different lifetimes can be accommodated easier as they can be replaced

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independently. In the present article, we propose this decoupled option for the first time for acetalization reactions.

Another important classification concerns the membrane material, with the two main classes being ceramic and polymeric. In esterification processes, where the pervaporation unit is not integrated in the reaction unit, most of the articles report the use of commercial polymeric dehydration membranes [2,3,16,23], whereas in those processes where the reaction and the separation are combined in one single reactor polymeric, ceramic and polymeric/ceramic membranes are applied [5,13,21,22,24].

In this work a hybrid silica membrane (HybSi®, developed at ECN) for dehydration was used. This HybSi® membrane has a very high hydrothermal stability and can be used in the dehydration of various organics [25–29]. This membrane was used in pervaporation testing of binary (ethanol–water) and in the dehydration of multi-component mixtures which contained all reactants and products. These permeation results were used as input into a batch reactor model. Subsequently, the membranes were used in a reactive system containing ethanol, butyraldehyde, 1,1 diethoxy butane, water and Amberlyst 47 as catalyst. The influence of the membrane under different process conditions (temperature, feed concentrations, catalyst loading) on the conversion was determined. A simple batch model was used to check the assumptions that will be used later in a continuous process design study and to assess the feasibility of the membranes in this novel process. The design of a continuous process and the supporting tests will be reported elsewhere.

2. Experimental procedure and equipment used

2.1. Chemicals and catalyst

Ethanol (99.9%, w/w) and butyraldehyde (99%, w/w) from Merck were used as reagents. 1,1 diethoxy butane (97%, w/w) for GC calibration was obtained from Acros Organics. Amberlyst 47 sulphonic ion exchange resin kindly provided by Rohm and Haas was used as catalyst.

2.2. Membrane

In the present study HybSi® inorganic/organic hybrid membranes were used. The hybrid nature of this material lies in the fact that each silicon atom is not only connected to oxygen atoms as in pure silica, but also to an organic fragment. The special feature of HybSi® is that the organic fragments are acting as integral bridging fragments rather than as end standing groups as in methylated silica [25,30].

HybSi® membranes are prepared via a sol–gel process and by coating the sol on top of a tubular porous support. The membranes show a high stability in the dehydration of n-butanol (5 wt% of water) at 150 °C, and were tested for more than 2 years [27,28]; moreover they show a great chemical resistance to acid containing liquid mixtures [26,29]. Apart from the durability and chemical resistance HybSi® membranes present high water selectivity and a high water flux as compared to other available membranes [31]. The separation factors for the separation of water from ethanol are around 220 and water fluxes are around 0.8–1.5 kg m^{-2} h^{-1} [29]. Because of this, HybSi membranes seem to be good candidates to remove the water from an acetal producing reaction mixture without being deteriorated by catalyst particle impacts and the presence of aggressive organic compounds like butyraldehyde.

2.3. Analysis

In case of the binary mixture dehydration tests, both, feed and permeate side mixtures were analyzed through refraction index measurements at 20 °C. The analyses of the quaternary mixture were more complicated. The water content of the feed was measured using Karl Fischer titration method. The contents of the organic components ethanol, butyraldehyde, and 1,1 diethoxy butane were determined by gas chromatography (Shimadzu GC-17A) using a flame ionization detector (FID). A Phenomenex ZB-Wax plus capillary column was used (30 m × 0.25 mm × 0.25 μm) with helium as the carrier gas. In the permeate, the water content was estimated using refraction index. Initial analyses has shown that water and ethanol were by far the main species in the permeate and that small amounts of butyraldehyde and 1,1 diethoxy butane did not affect to the refraction index measurements. The water concentration in the permeate calculated as the difference from 100% of the organics sum was in good agreement with the concentration obtained from refraction index measurements.

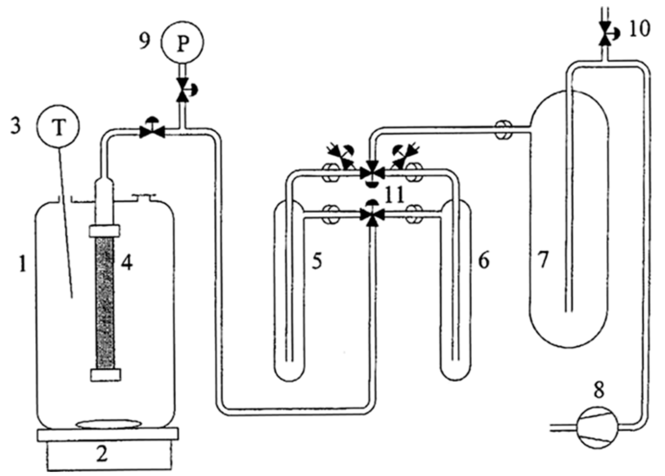

Fig. 1. Simplified schematic drawing of the glass pervaporation unit.

2.4. Reaction–pervaporation system

The experiments were carried out in a semi-batch lab scale glass pervaporation unit. The glass pervaporation equipment is made up of three parts:

- Feed system consisting of a feed vessel of 1.6 L (1), heating/stirring plate (2), stand and membrane (the membrane area used in the experiments was 24.2 cm^2) immersed in the feed mixture (4). There is also an option to use a feed pump to add liquid to the feed.
- Continuous permeate extraction system which consists of large chilled water spiral glass condenser and permeate vessel, chilled water unit, pressure sensor and vacuum pump.
- Permeate sampling system consisting of a connection to a permeate valve and sample vials (11), pressure sensor (9), liquid nitrogen cold trap and vacuum pump.

Samples are collected by condensing the permeate with liquid nitrogen in one of the sample vials. The purpose of the cold trap (7) is to ensure no vapors reach the vacuum pump and/or the atmosphere. The vacuum pressure sensors are connected to a central display unit and the permeate pressure was between 1 and 5 mbar in all the cases. A simplified schematic drawing is shown in Fig. 1.

3. Results and discussion

The reaction under consideration is the acetalization of ethanol (A) and butyraldehyde (B) to produce 1,1 diethoxy butane (C) and