



# Application of a sodalite membrane reactor in esterification—Coupling reaction and separation

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## ABSTRACT

A tubular hydroxy sodalite (SOD) membrane was successfully applied in the esterification of acetic acid with ethanol and acetic acid with 1-butanol, to selectively remove water by pervaporation and to overcome the thermodynamic equilibrium limitation of the esterification. The reactions were carried out using equimolar solutions of acetic acid with the appropriate organic alcohol at 363 K using Amberlyst 15 as acid catalyst. The hybrid process drove the esterification reactions almost to completion. The special feature of the SOD-membrane is that it showed absolute selectivity towards water and retained its stability under the reaction conditions. The membrane exhibited a stable water pervaporation performance at pH values above 2.9 for acetic acid–water mixtures.

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## 1. Introduction

Hybrid processes combining reaction and separation are becoming increasingly popular in chemical industry [1–5]. In these, the use of membranes and membrane technology for the selective separation of products from equilibrium limited media to shift equilibria towards higher reaction yields is being progressively recognized [6–16]. Esterification is a classical case of an equilibrium limited reaction [17]. Traditionally the equilibrium limitation is overcome by either using an excess amount of the alcohol or by separating the by-produced water from the reaction through reactive distillation or reactive stripping [18,19]. While the use of excess alcohol may increase the operation costs on the downstream reagent recovery and result in unwanted ether formation [20], reactive distillation is only useful when the products and reactants are not close boiling liquids [19]. In this respect, the use of membrane reactors is attractive as the process efficiency is not limited by the thermodynamic equilibrium conversion while the process costs can be reduced due to the smaller amounts of reactants required and the higher conversions obtained [21–25].

In integrating reaction and membrane separation, typically pervaporation is coupled with the chemical reaction [7,26–33]. In contrast to distillation which is based on the difference in volatilities of the substances, pervaporation solely relies on the solubility and transport rate of each compound. Conventionally membrane reactors are configured as either a batch reactor, where the reaction takes place, followed with an external pervaporation unit built in the recycle to continuously remove water from the reactor [34], or

as an integrated unit where both reaction and separation take place simultaneously [35]. Both configurations have been widely studied in the literature [34]. Next to esterification, other types of equilibrium limited reactions such as etherification and condensation reactions have been investigated [36].

Here we report on the esterification in a membrane reactor of acetic acid with ethanol and with 1-butanol to produce ethyl acetate and butyl acetate, respectively, using Amberlyst 15 as catalyst. A tubular hydroxy sodalite membrane has been used as a highly water selective membrane for water permeation. Hydroxy sodalite (H-SOD) is a zeolite-like material, consisting of sodalite cages only [37]. The material does not contain distinct pores or channels, but consists of an array of cages connected to each other through 4- and 6-rings. The 4-rings are too small to allow permeation of any molecule, but the diameter of the 6-rings is large enough (0.27 nm) to allow only very small molecules such as water (kinetic diameter: 0.265 nm) to pass through [37–39]. Owing to the unique window diameter of the material, absolute separation of water from various organic alcohol streams has been achieved [38]. In using membranes under esterification conditions, it is vital that the membrane preserves its structural integrity. Therefore, a hydroxy sodalite membrane was applied in dehydration of concentrated acetic acid solutions to study its stability under acidic conditions [40].

## 2. Experimental

### 2.1. Membrane preparation

A hydroxy sodalite tubular membrane was made according to a previously reported procedure [41] by means of hydrothermal synthesis on the inner surface of an  $\alpha$ -alumina tubular support

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**Table 1**  
 $\alpha$ -Alumina support properties.

Provider	Inocermic
Number of layers	3
Pore diameter top layer	200 nm
Surface treatments	None
Outer diameter	7 mm
Inner diameter	5 mm
Length permeable section	5 cm

purchased from Inocermic. The support properties are given in Table 1. The synthesis gel was prepared by mixing silicate and aluminate solutions with the final gel molar composition being  $5\text{SiO}_2:\text{Al}_2\text{O}_3:50\text{NaO}_2:1005\text{H}_2\text{O}$ . After the hydrothermal treatment at 413 K for 3.5 h, the tube was thoroughly washed with water and dried under dry air flow overnight. Following, single gas permeation measurements using He and  $\text{N}_2$  were conducted to verify formation of a closed membrane prior to use in the esterification reactions. As water acts as a template during synthesis, the sodalite cages are fully occupied with water. Therefore neither He nor  $\text{N}_2$  should be able to permeate through the cages, unless through membrane defects. At room temperature and under a cross membrane pressure of 0.5 MPa, the membranes were impermeable to nitrogen, and the helium permeance was as low as  $\sim 10^{-10} \text{ mol s}^{-1} \text{ m}^{-2} \text{ Pa}^{-1}$ . This was used as a test of membrane quality before coupling it with the reaction section.

## 2.2. Pervaporation membrane reactor

The experimental set-up used for the reaction-pervaporation experiments is schematically depicted in Fig. 1. The esterification was carried in a 250 ml round bottom flask fitted with a reflux condenser. The flask was inserted in a thermostatic water bath and its temperature was regulated using a thermocouple. 1 mol ethanol or 1-butanol were initially added to the reactor with Amberlyst 15 as catalyst (loading: 100 g/l solution) and heated to the reaction temperature. An equimolar amount of acetic acid was heated separately, and after reaching the reaction temperature it was added to the reactor. Simultaneously, the reaction mixture was started to be continuously pumped through the pervaporation unit at a rate of 50 ml/min. This time was noted as the starting time of the experiment. The conventional esterification reactions were carried out until equilibrium was reached. In membrane facilitated experiments, the time at which the reaction was started parallel to the start up of the membrane system was noted at the starting time of the experiment.

The tubular membrane was initially sealed in a stainless steel membrane module, with the membrane on the inner side of the tube facing the feed ( $A = 15.0 \text{ cm}^2$  effective membrane surface area and a selective layer thickness of about  $1 \mu\text{m}$  [38]); the module was placed in the oven of the pervaporation set-up and was controlled to maintain the same temperature as the reaction medium.

The feed pressure was regulated using a backpressure controller and kept at 0.5 MPa to ensure a liquid phase feed at the exercised temperatures. A two-stage vacuum pump was used to evacuate the permeate side. The pressure at the permeate side was kept at a constant value of 300 Pa and was monitored using a digital vacuum gauge installed between the vacuum pump and the cold traps. The temperature of the feed inside the membrane cell and the permeate temperature were measured using two thermocouples. At steady state conditions, the flux through the membrane was determined by the rate-of-rise method described elsewhere [38].

Samples were withdrawn from both the reactor and the permeate side at regular intervals and immediately quenched for analysis using a GC (HP 6890, column: HP-FFAP) equipped with a thermal conductivity detector (TCD).

## 3. Reactor model

The model reactions which have been used to describe the esterification reactions investigated in this study can be generally expressed as:



where A is acetic acid, B is the alcohol, being either ethanol or butanol, E is the ester and W is the water.

For sole esterification, when an excess of the alcohol is used and if the selectivity of the desired production is 100%, the conversion of the limiting reactant acetic acid, X, can be expressed in the ratio of the acid to ester:

$$\frac{\text{acid}}{\text{ester}} = R_1 = \frac{1 - X}{X} \quad (1)$$

$$X = \frac{1}{R_1 + 1} \quad (2)$$

Hence,

Table 2 gives the reaction mixture composition in the feed at time  $t_1$ . When pervaporation is coupled with esterification, water is removed from the reaction system, and the composition of the reaction changes as given in Table 2. In the pervaporation-aided

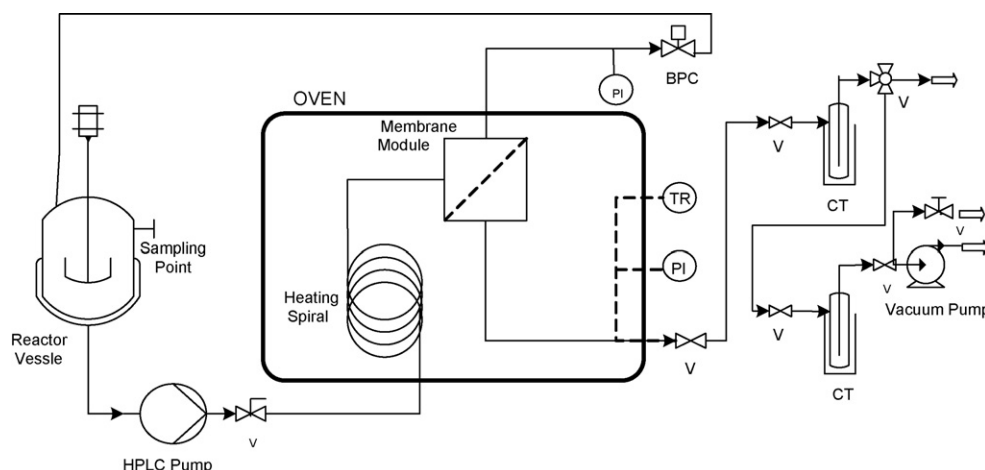


Fig. 1. Schematic drawing of the pervaporation set-up (V, valve; PI, pressure indicator; TR, temperature recorder; BPC, back pressure controller; CT, cold trap).

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