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Lactose electroisomerization into lactulose: Effect of the electrode material, active membrane surface area-to-electrode surface area ratio, and interelectrode-membrane distance

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ABSTRACT

The aim of the present work was to study and develop an innovative, clean, and environmentally friendly process for lactulose synthesis by electroactivation of lactose. In this work, the electrode material (type 304 stainless steel, titanium, and copper), dimensionless interelectrode-membrane distance at the cathodic compartment (0.36, 0.68, and 1), and the membrane:electrode surface area ratio (0.23, 0.06, and 0.015) were considered to be the factors that could affect the kinetic conversion of lactose into lactulose. The reactions were conducted under an initial lactose concentration of 0.15 mol/L at 10°C, Froude number (mixing speed) of 2.05×10^{-2}, and electric current intensity of 300 mA for 30 min. The highest lactulose formation yield of 32.50% (0.05 mol/L) was obtained by using a copper electrode, interelectrode-membrane distance of 0.36, and membrane:electrode surface area ratio of 0.23. The 2-parameter Langmuir, Freundlich, and Temkin isotherm models were used for the prediction of the lactose isomerization kinetics as well as the 3-parameter Langmuir-Freundlich isotherm model. It was shown that the lactose isomerization kinetics into lactulose followed the Temkin and Langmuir-Freundlich models with coefficients of determination of 0.99 and 0.90 and a relative error of 1.42 to 1.56% and 4.27 to 4.37%, respectively.
Key words: lactose/lactulose, electrode material, membrane, electrochemical cell, adsorption isotherm

INTRODUCTION

Lactulose is recognized as a prebiotic and it is used in the form of syrup for the treatment of some intestinal disorders. It is slightly sweeter than lactose and can be used as a partial sucrose substitute in some food products (Drakoularakou et al., 2011). Lactulose can also be used as a food supplement in pediatric diets for the development of functional foods and in geriatric medicine for some targeted populations with severe constipation syndrome (Curiale et al., 2013). Lactulose is also widely used as a statement in hepatic encephalopathy. Many processes for the preparation of lactulose by isomerization of lactose are known. Some processes are based on the isomerization of lactose by strong bases, such as $Ca(OH)_2$, NaOH, and KOH. These processes present the drawback that the sugars can be degraded with a decrease in lactulose yield. Moreover, purification steps are necessary to eliminate the degraded products. Isomerization of lactose into lactulose can be enhanced by sodium tetraborate and sodium aluminates. However, these processes are not accepted for final products for food and pharmaceutical applications. The main reason for this is related to the difficulty of aluminum hydroxide and boric acid total elimination (Aider and Halleux, 2007). Lactulose can be also produced following enzymatic treatment of lactose under controlled conditions. This method is based on the enzymatic transgalactosylation from glucose to fructose by using specific enzymes, such as β-galactosidase from *Aspergillus oryzae* or hyperthermostable β-glycosidase from *Pyrococcus furiosus*. The main inconveniences of this method are the high cost of the enzymes used, the low yield of the reaction, and the difficulty of enzyme recovery. Moreover, the enzyme activity decreases after some time of application. Thus, for large-scale industrial applications, this method is not economical (Mayer et al., 2004).

Recently, lactulose was produced following electroactivation of lactose by using a reagentless technology in which no need exists of catalyst addition to the reaction medium. The strong alkaline conditions needed were generated at the lactose solution-electrode (cathode) interface (Aider and Gimenez-Vidal, 2012) and (Aït Aissa and Aïder, 2013a,b, 2014). In the aforementioned studies, the influence of operating factors, such as working temperatures, feed lactose concentration, Froude number (mixing speed), reactor configuration, ion-exchange membrane type, and current densities as

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well as electrical potential on lactose isomerization into lactulose were investigated. Electrode processes are heterogeneous reactions at a metal-solution interface, with kinetics depending on different process variables, such as the electric field potential, electrode material, and reactor geometry (Bamford and Compton, 1986). Moreover, the rate of a surface reaction can significantly differ for a given electrode type in different electrolyte solutions (Timmer et al., 1969) due to the structure of the electrical double layer and the electrode material (Delahay, 1965).

The aim of the present work was to study the effect of electrode material, the ratio of the membrane surface to the electrode surface, and the interelectrode-membrane distance on the yield and kinetics of lactose electroisomerization into lactulose. Sorption isotherm models of Langmuir, Freundlich, Temkin, and Langmuir-Freundlich were used to predict the isomerization kinetics of lactose into lactulose.

MATERIALS AND METHODS

Chemicals

Lactose monohydrate was purchased from Avantor Performance Materials (Center Valley, PA). Standards of lactulose, glucose, galactose, and fructose were purchased from Sigma-Aldrich (St. Louis, MO). Calcium chloride hydrate ($CaCl_2 \cdot 2H_2O$) was purchased from Fisher Scientific, (Mississauga, ON, Canada).

Membranes

The anion (AM-40) and cation (CM-40) exchange membranes used were purchased from the Schekina-Azot (Shchekina, Russian Federation). Before use, membranes (anionic and cationic) were wiped with paper soaked in ethanol and then dipped in a saturated solution of NaCl for 24 h. Thereafter, the membranes were transferred to another solution of NaCl having a concentration equal to the half of the first dip solution for a further 24 h. The same procedure was repeated in a dilute NaCl solution for a further 24 h. Thereafter, the membranes were used in the electroactivation reactor after simple rinsing with distilled water.

Electroactivation Reactor

The electroactivation reactor used in this work has been described in a previous study (Aït Aissa and Aïder, 2013a). The isomerization reaction was conducted in the cathodic compartment, which was filled with lactose solution at an initial concentration of 0.15 mol/L (5%). To ensure the passage of electric current in the lactose solution, 0.05 mol/L of calcium chloride hydrate ($CaCl_2 \cdot 2H_2O$) was added. The central compartment was separated from the cathodic one in which the targeted reaction accrued by a cation-exchange membrane to avoid the migration of the formed hydroxyl ions at the cathode surface to the neighboring compartment. This action permitted us to maintain a high level of alkaline pH, which is fundamental for the isomerization reaction. The active surface area of this membrane was studied as an independent variable and its value was fixed at 0.7, 2.83, and 11.33 cm^2, respectively. The central compartment was separated from the anodic one by an anion-exchange membrane that was impermeable to the positively charged protons to avoid their effect of lowering the pH on the cathodic side. This membrane was used with an active surface area of 2.83 cm^2. The anodic electrode was maintained the same for all the experiments and was made of ruthenium-iridium-coated titanium. In the cathodic compartment, 3 different electrodes were used: dimensionally stable type 304 stainless steel, ruthenium-iridium-coated titanium, and copper. The distance between the cathode and the cation-exchange membrane was varied by means of movable Plexiglas blocks. The central and anodic compartments were filled with a 0.3 mol/L Na_2SO_4 solution.

Sugar HPLC Analyses

Sugars were analyzed by HPLC, which was performed using a Waters Alliance analytical HPLC system (model 715; Waters Corp., Milford, MA) equipped with a refractive index detector (model 140) and using a Sugar-Pack 300 × 6.5 mm column (Waters Corp.). The conditions used were the following: flow rate of 0.5 mL/min, running temperature of 85°C, and an injection volume of 10 μL with HPLC-grade degassed water as the mobile phase. The running time was set at 30 min.

Lactose conversion ($P_{lactose}$), representing the fraction of initial lactose transformed during the reaction, was calculated using Equation 1:

$$P_{lactose}(\%) = \frac{A_{lactose\ initial} - A_{lactose}}{A_{lactose\ initial}} \times 100, \quad [1]$$

where $A_{lactose}$ is the peak area of lactose at time τ and $A_{lactose\ initial}$ is the peak area (given by HPLC) of the standard of lactose samples.

Lactulose yield ($P_{lactulose}$) represented the fraction of initial lactose converted into lactulose divided by the concentration of lactulose standard:

$$P_{lactulose}(\%) = \frac{A_{lactulose}}{A_{lactulose\ initial}} \times 100, \quad [2]$$