POLYMER ELECTROLYTE HYDROGEN PUMPING FOR CATALYSIS AND SEPARATIONS

Jay Benziger, James Nehlsen, Ahmed Abdullah
Department of Chemical Engineering
Princeton University
Princeton, NJ 08544

Summary

We demonstrate the use of polymer electrolyte membrane (PEM) hydrogen pump to deliver hydrogen to a hydrogenation reactor or to separate hydrogen from reformate mixtures. PEM hydrogenation reactors supply high hydrogen activity to a supported catalyst by oxidizing water on one side of the membrane and deliver atomic hydrogen to active hydrogenation catalyst. The current density controls the flux of hydrogen to the catalyst surface rather than the hydrogen pressure.
Electrochemical pumping of hydrogen from reformate mixtures of H2, CO2 and H20 using a PEM produces high purity hydrogen (< 100 ppm CO2) at >98% recovery and modest power requirements.

Keywords

Membrane reactors, hydrogen production

Introduction

We report use of Polymer Electrolyte Membrane (PEM) hydrogen pumps in for both catalytic hydrogen and hydrogen purification.

Catalytic hydrogenation reactions aregenerally carried out in three-phase reactors where a solid catalyst is contacted with a liquid phase containing the organic molecule and gaseous hydrogen. Catalytic hydrogenation in the liquid phase is often limited by the solubility of hydrogen in the liquid. High pressure is usually required to have sufficient hydrogen adsorption on the catalyst surface.

An alternative means to deliver hydrogen to the catalyst surface is by electrochemistry. Water may be oxidized to make protons at the anode. The protons move through the electrolyte to the cathode where they are reduced to adsorbed hydrogen atoms. By choosing the cathode as an appropriate catalyst, the adsorbed hydrogen atoms can catalytically hydrogenate olefins, carbonyl compounds, and other unsaturated molecules.

Polymer electrolyte membrane hydrogenation reactors (PEMHR) physically separate the anode and the cathode, inhibiting product diffusion to the counter electrode. The PEMHR also permits one to have distinct phases, aqueous and organic, on either side of the membrane.

The hydrogenation of the organic species competes with hydrogen recombination and desorption. In a PEMHR, some of the hydrogen produced at the cathode ends up as H_2. The selectivity in the PEMHR is the ratio of protons that react with the organic species to the total proton current. Hydrogen gas evolution represents wasted electrical energy. that the PEMHR may be viewed as a conventional heterogeneous catalytic reactor in which the galvanostatically applied current density, rather than the partial pressure of H_2, controls the activity of adsorbed hydrogen on the catalyst surface. Any reaction that can occur in a conventional slurry or gas phase hydrogenation reactor should also occur in a PMR at the same temperature. The PMR effectively decouples the electrochemical reaction of water electrolysis and the catalytic hydrogenation reaction. The electrolysis of water serves only as the hydrogen supply to the catalytic reaction.

Steam reforming of hydrocarbons or coal followed by the water gas shift reaction produces a mixture of H_2, CO_2 and H_20. The most common approaches to purify the hydrogen are by alkaline scrubbing of the gas mixture to remove the CO_2 or pressure swing adsorption. We report an alternative method of electrochemical pumping of hydrogen from reformate mixtures through a polymer electrolyte membrane. This process produces high purity hydrogen (< 100 ppm CO_2) at >98% recovery and modest power requirements. The equipment is essentially a PEM fuel cell run with an applied voltage to pump the hydrogen. Data is presented that shows the efficiency and recovery of this process. The efficiency is limited by mass transport limitations through the porous electrode at high recovery because of the dilution of hydrogen in the CO_2 Process designs and an energy comparison to both alkaline scrubbing and PSA shows the electrochemical pumping is more energy efficient and readily adaptable for many a wide range of process scales.