



Coupling hydrogen separation with butanone hydrogenation in an electrochemical hydrogen pump with sulfonated poly (phthalazinone ether sulfone ketone) membrane



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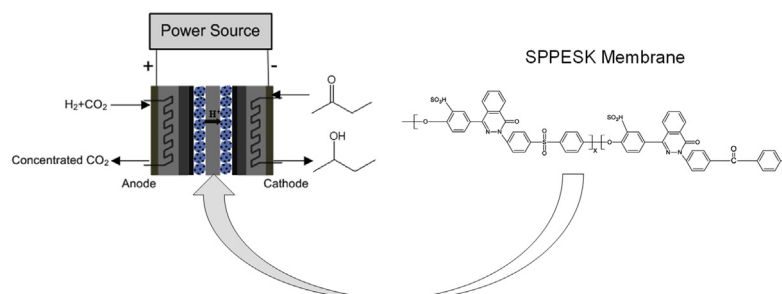
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HIGHLIGHTS

- Hydrogen separation and butanone hydrogenation are coupled in an EHP with high rate.
- Hydrogenation is more stable with SPPEK due to lower swelling and CO₂ permeation.
- Energy efficiency of the H₂/CO₂ EHP separator is superior to pure H₂ or H₂O.

GRAPHICAL ABSTRACT



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ABSTRACT

This work reports the novel work of coupling H₂/CO₂ separation with biomass-derived butanone hydrogenation in non-fluorinated sulfonated poly (phthalazinone ether sulfone ketone) (SPPEK) electrochemical hydrogen pump (EHP) reactor. Due to higher resistance to swelling, SPPEK-based EHP reactor exhibits more excellent reaction rate in elevated temperature (60 °C) and higher butanone concentration (2 M) as 270, 260 nmol cm⁻² s⁻¹, respectively, higher than 240, 200 nmol cm⁻² s⁻¹ of Nafion-based EHP reactors. Also, the SPPEK-based EHP reactor remains 90% of initial hydrogenation rate after 4 batches, better than that of Nafion-based EHP reactors, which is only 62%. The energy efficiency of EHP separator reaches 40% under H₂/CO₂ mixture feed mode, and electricity of about 0.3 kWh is consumed per Nm³ H₂ product, being superior to energy consumption compared with alternative processes like PSA and electrolysis of water. In addition, SPPEK-based EHP exhibits better hydrogenation stability due to lower CO₂ permeation than Nafion. With increasing CO₂ content in H₂ feed, hydrogenation rate almost keeps constant at around 210 nmol cm⁻² s⁻¹ in SPPEK-based EHP reactor while decreases fast to

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50 nmol cm⁻² s⁻¹ in Nafion/PTFE-based EHP reactor. These results show integration of gas separation with hydrogenation reactor is feasible in SPPEsk-based EHP reactor.

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1. Introduction

Biomass is an abundant and environmentally friendly energy source that has the potential to replace diminishing fossil fuels and produce fuels and chemical products [1,2]. In the conversion of cellulosic biomass into stable hydrocarbon fuels, hydrogenation of carbonyl groups in ketones, aldehydes and acids is considered to be an important step [3]. Hydrodeoxygenation of biomass-derived carbohydrates is also required to obtain desirable properties, such as high energy density and stability for combustion of liquid transportation fuels [4].

Conventionally, heterogeneous catalytic hydrogenation of ketones is implemented in three-phase reactors, e.g. batch autoclave slurry reactor with high pressure (~55 bar) and temperature (~433 K) [5] due to low solubility of hydrogen in the liquid reactants, which makes the dissociation of hydrogen on catalyst surface to be rate limiting step in the overall reaction. By contrast, electrocatalytic hydrogenation has the advantage of delivering in-situ atomic hydrogen to catalyst surface in a moderate, safe and efficient way without high pressure and turbulent mixing. A series of biomass-derived oxygenates have been hydrogenated in different types of electrocatalytic hydrogenation reactors, such as static single or two-chamber cells, and circulating single cell [6–8]. However, these processes always need a liquid supporting electrolyte, which is difficult to be separated from the products.

In order to address the issues of product separation and environmental pollution caused by liquid electrolytes, electrochemical hydrogen pump (EHP), with proton exchange membrane (PEM) as solid electrolyte, is proposed as an attractive electrocatalytic hydrogenation reactor. As shown in Fig. 1, with power supply, hydrogen at the anode is electrochemically oxidized to produce protons, which transport across the PEM and are reduced to dissociated hydrogen atoms on the cathode catalyst surface and then get involved in hydrogenation with the adsorbed liquid reactant species. A variety of unsaturated organic compounds

containing C=C [9–13], C=O [14–17] and S–S [18] bonds have been successfully hydrogenated in EHP reactors. For instance, Benziger [15] and Huber [16] selected acetone as the model compound of biomass derivatives, and investigated its hydrogenation with different catalysts and operating parameters [14,15]. We reported the great effects of hydrophobicity of diffusion layer on hydrogenation of different volatile reactants, i.e., butanone and maleic acid in aqueous solutions [19].

One of the unique features of EHP is the ability to separate hydrogen from H₂/CO₂ [20,21], H₂/N₂ [22,23], H₂/CH₄ [24] mixtures, which are major sources of hydrogen and widely derived from reformed gas, ammonia and methanol purges and various refinery tail gases. Compared with the state-of-the-art pressure-controlled hydrogen production technologies, such as pressure swing adsorption (PSA), gas absorption and membrane separation [25], the EHP separator operates under atmospheric pressure with low operating costs, and can give high hydrogen purity (greater than 99%). Hydrogen can also be produced from water electrolysis in EHP reactors, but it consumes too much electricity and is not economically competitive to the currently commercialized hydrogen production technologies. Since current methods of biomass conversion mostly require large quantities of pure hydrogen gas [26], the cost of hydrogen can be comparable to or much higher than that of biomass itself [15]. Consequently, it is urgent to develop an inexpensive method to produce hydrogen for biomass derivatives hydrogenation.

We herein report the coupling of hydrogen separation with biomass derivatives hydrogenation in an EHP reactor to make hydrogenation more convenient and efficient. In our previous work, Nafion/PTFE catalyst coated membrane (CCM) was used in EHP reactors to perform hydrogenation of butanone [19]. Although the hydrogenation rate was higher than that of the high-pressure catalytic hydrogenation, we observed damage of catalyst layer at high butanone concentration and long reaction time due to the high swelling ratio of Nafion in butanone and the product 2-

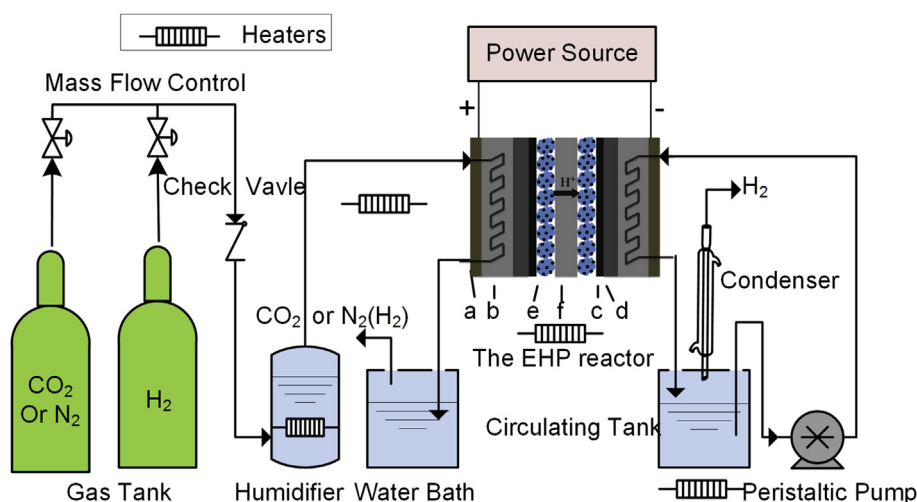


Fig. 1. Setup of the EHP separator & reactor for butanone hydrogenation with H₂/CO₂ (N₂) as anode feedstock. Temperature control is employed at the humidifier, anode inlet, EHP reactor and cathode circulating tank. a) Current collecting plate; b) Serpentine flow channel in graphite blocks; c) Microporous layer of GDL; d) Macroporous layer of GDL; e) Catalyst layer; f) Proton exchange membrane.

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