

# CONTINUOUS HOMOGENEOUS HYDROFORMYLATION WITH NANOFILTRATION FOR RETENTION OF SOLUBLE POLYMER SUPPORTED RHODIUM CATALYST COMPLEXES

Jing Fang<sup>\*1,2</sup>, Ranjan Jana<sup>2,3</sup>, Kirk Snavely<sup>1,2</sup>,  
Jon Tunge<sup>2,3</sup>, Bala Subramaniam<sup>1,2</sup>

<sup>1</sup>Department of Chemical and Petroleum Engineering, <sup>2</sup>Center for Environmentally Beneficial Catalysis

<sup>3</sup>Department of Chemistry, University of Kansas, Lawrence, KS 66045

## Summary

Continuous 1-octene hydroformylation with steady 1-octene conversion (50%), aldehyde selectivity (~98%) and *n/i* ratio (3.5) was demonstrated in a stirred, polyimide membrane-based nanofiltration reactor at 50°C and 3 MPa syngas. By complexing Rh with specially designed soluble polymer-bound bulky bidentate phosphorus ligands, the Rh was effectively retained in the reactor, reducing its leakage to only a few tens of ppb in the effluent. These low leakage levels enhance the practical feasibility of this concept and also obviate the need for elaborate, solvent/energy-intensive catalyst separation steps post reaction. This concept opens up new avenues for performing benign catalysis with homogenous catalyst complexes at high productivity and selectivity.

## Keywords

Hydroformylation, polymer bound phosphorus ligands, membrane filtration, CO<sub>2</sub>-expanded liquids

## Introduction

Conventional cobalt-based higher olefin hydroformylation processes require harsh conditions (140-200°C and up to 300 bars).<sup>1,2</sup> Further, the recovery of cobalt-based catalyst complex is tedious and involves much acids contributing to waste and toxicity. To operate at milder conditions (<100 bar and <100°C), Rh-based complexes may be used but near-quantitative Rh recovery with minimal use of solvents is needed for economic viability. This is a challenge since the Rh complex decomposes during product distillation. For homogeneous 1-octene hydroformylation on Rh/triphenylphosphine complexes, we have previously shown that CO<sub>2</sub>-expanded liquids (CXLs) provide enhanced rate and linear aldehyde selectivity at mild conditions (~40 bar and 60°C).<sup>3,4</sup> Comparative economic analyses based on plant scale simulations of the CXL process and a conventional process revealed that the Rh recovery must be 99.8%/pass for the CXL process to be economically viable. This translates to 560 ppbw Rh addition as makeup.<sup>5</sup> In this contribution, we show how nanofiltration membranes coupled with soluble polymer-supported bulky catalyst complexes may be used to form Rh complexes that could be effectively retained in the reaction mixture (Figure 1). This obviates the need for elaborate, solvent-intensive, post-reaction catalyst separation steps.

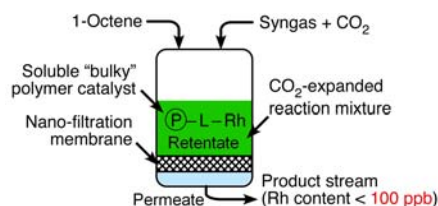


Figure 1. The schematic of reaction coupled with membrane filtration

## Experimental

Figure 2 shows the schematic of the membrane filtration setup. The reactor is made of 316 stainless steel with a volume of 270 mL and rated to operate up to 50°C and 70 bars. The STARMEM<sup>®</sup> nano/ultra-filtration membrane is made of highly cross-linked asymmetric polyimide. The molecular weight cut-off (MWCO) of the membrane ranges from 200 to 400 Daltons, based on 90% retention of the solute. The reactor is equipped with a magnetic driven impeller. A thermocouple, interfaced with LabView<sup>®</sup> data acquisition, measures the solution temperature. The solvent or the substrate is pumped into the cell by a Primeline<sup>™</sup> HPLC pump.

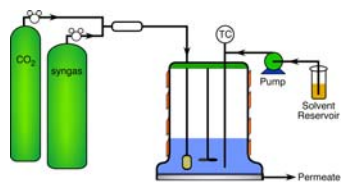


Figure 2. Membrane filtration setup configuration

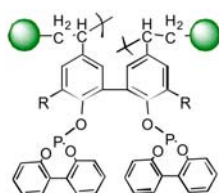


Figure 3. Polymer bound bidentate phosphorus ligand

The homogeneous catalytic systems tested for filtration consist of the catalyst precursor  $\text{Rh}(\text{acac})(\text{CO})_2$  and bulky polystyrene based polymer bound bidentate phosphorus ligand (PBB10) dissolved in solvent and/or substrate. The ligand has an average molecular weight around 10,000 Daltons. Figure 3 provides the structure of this phosphorus ligand. The shaded circles represent the polymer backbone.<sup>6,7</sup> Inductively coupled plasma optical emission spectroscopy (ICP-OES) was employed to quantify the rhodium and phosphorus concentrations in the starting catalyst solution, the retentate and the permeate.

## Results

To test for Rh retention, a continuous filtration run with a toluene solution of the PBB10-based rhodium complex was performed using constant  $\text{N}_2$  pressure to force the solution through the membrane. As shown in Figure 4, the permeate flux during the entire 7.5 h run remained constant.

The Rh and P concentrations in the effluent were high initially and decreased with time, suggesting the removal of either unbound Rh and P from the initial mixture and/or those bound to polymers that are lower than the molecular weight cutoff of the membrane. The Rh and P concentrations lined out at ppb levels ( $\sim 50$  ppb) after several hours showing retention of Rh in the reactor. The amounts of Rh and P lost during the line out period are 2.1 wt% and 1.9 wt%, respectively.

A continuous run for 1-octene hydroformylation catalyzed by PBB10 modified rhodium complex was carried out at  $50^\circ\text{C}$  and under syngas pressure of 3.0 MPa. The solution was kept stirred at a speed of 1000 rpm. As shown in Figure 5(a), after an 8-hour start-up period, the conversion, regioselectivity ( $n/i$  ratio) and selectivity towards aldehydes reach stable values (50%, 3.5 and 98% respectively) for the following 14 hours. As shown in Figure 5(b), the flux remains constant throughout the run, demonstrating that the membrane remains permeable without fouling. Further, the Rh content in the permeate

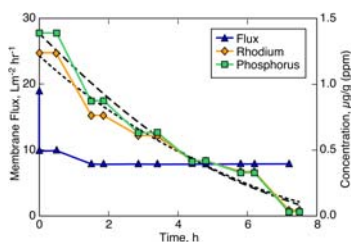


Figure 4. Membrane flux, rhodium and phosphorous concentrations in permeate for continuous filtration without reaction: [Rh] and [P] in initial catalyst solution are 121 and 144 ppm, P/Rh molar ratio = 4;  $T = 21^\circ\text{C}$ ;  $P = 1.0$  MPa ( $\text{N}_2$ )

decreases from 140 ppb and reaches a steady value of 20 ppb during the 22-hour run while the P content decreases from 6.7 to 1.5 ppm. The Rh leakage clearly exceeds the economic viability criterion.

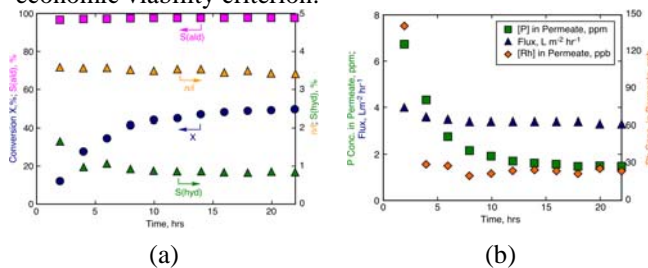


Figure 5. Experimental results for continuous 1-octene hydroformylation with in situ membrane filtration [Rh] and [P] in initial catalyst solution are 241.6 and 400.4 ppm, P/Rh molar ratio = 5.6,  $T = 50^\circ\text{C}$ ,  $P = 30$  bars (syngas)

These results along with a model of the membrane reactor will be presented and discussed.

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