

# Rh Catalyzed Hydroformylation of High Molecular Weight Olefins in CO<sub>2</sub> Expanded Liquid Polymers

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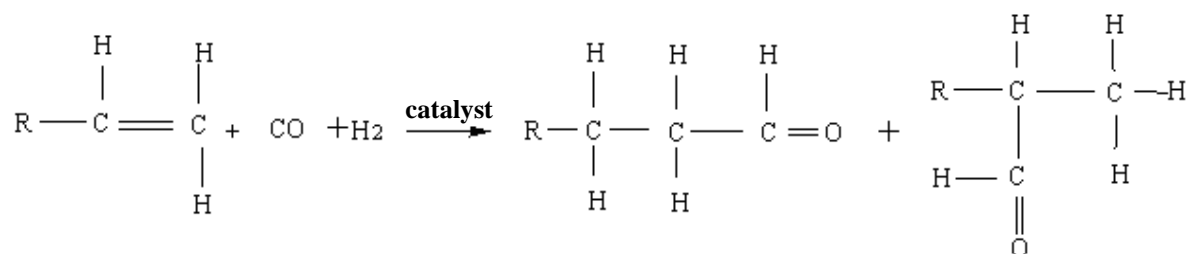
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Hydroformylation of 1-octene was studied in PEG/scCO<sub>2</sub> biphasic solvent using Rh(CO)<sub>2</sub>(acac) as catalyst precursor and triphenylphosphine as ligand. The effect of reaction temperature and total pressure of syngas on the performances of the catalytic system were studied. In all hydroformylation reactions, the products were n-nonanal and 2-methyl nonanal, except in a blank reaction carried out in the absence of CO<sub>2</sub> where also octane was detected in the products.

The conversion of 1-octene increased with the temperatures and the total pressures of syngas. Furthermore, it was found that scCO<sub>2</sub> significantly enhances the olefin conversion.

## INTRODUCTION

The hydroformylation of olefins is a well-known commercial process involving the reaction of an olefin, CO, and H<sub>2</sub> in the presence of a catalyst to produce aldehydes or alcohols.<sup>1</sup>



Generally, both cobalt and rhodium complexes are used as homogeneous catalysts in industrial processes. Even if Rh based homogeneous catalysts would be preferred in industrial applications there are some limits in their utilization for hydroformylation of high molecular weight olefins because it is difficult to recover the product without catalyst deactivation or losses. To overcome these problems, development of new synthetic strategies under mild conditions has received much attention. For example, different studies were based on the immobilization of the homogeneous catalysts on various inorganic and organic supports to eliminate the catalyst recovery steps,<sup>2,3</sup> the utilization of phase transfer catalysis, emulsions, or supported aqueous phase catalysis (SAPC) in biphasic systems to improve catalyst/substrate contacts,<sup>4</sup> the adoption of novel temperature or pressure-tuneable solvent media which make possible to carry out the reaction in a homogeneous system and to recover the catalyst by pressure or temperature induced phase separation.<sup>5</sup>

Recently biphasic PEG/scCO<sub>2</sub> systems have been proposed as environmentally benign reaction media for different chemical reactions. PEG has been tested extensively and it was found to be inexpensive, thermally stable, toxicologically innocuous, and environmentally benign for chemical reactions and phase-transfer catalysis.<sup>6-9</sup> High molecular weight PEGs are waxy solids and become expanded low viscosity liquids under CO<sub>2</sub> pressure. These molten PEGs are capable of dissolving organic compounds including metal catalysts.

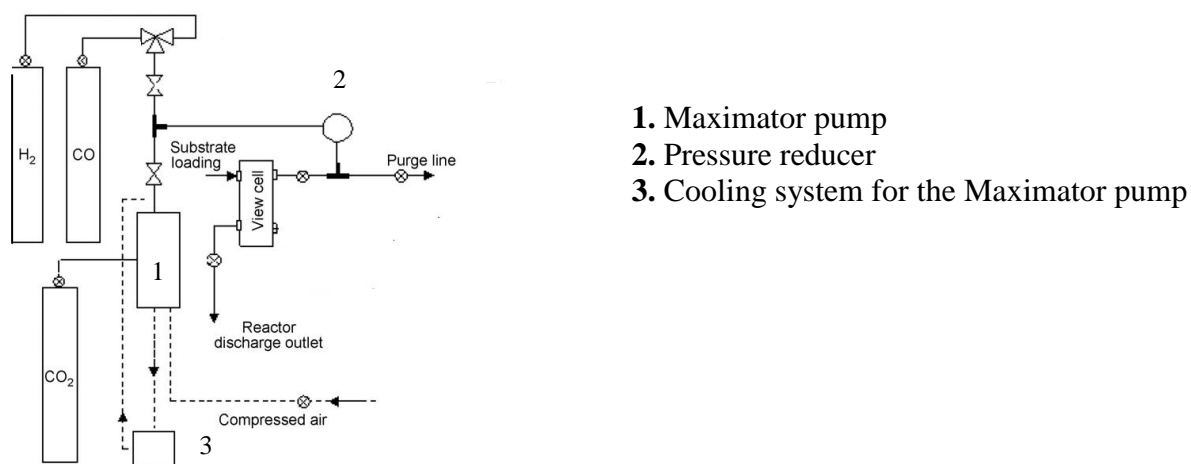
Therefore, the efficient combination of carbon dioxide and poly(ethylene glycol) could offer a medium to carry out the reaction in the polymer phase recovering the product by scCO<sub>2</sub> extraction leaving the catalyst entrapped in the PEG-rich phase.

In this work the PEG/scCO<sub>2</sub> biphasic solvent is tested in the hydroformylation of 1-octene using Rh(CO)<sub>2</sub>(acac) as catalyst precursor and triphenylphosphine as ligand. Preliminary results were obtained performing hydroformylation reactions at different temperatures and total pressure of syngas.

## MATERIALS AND METHODS

The 1-octene (>98%) was obtained from Aldrich and used as received. Carbon monoxide, hydrogen and carbon dioxide (respectively 99.90, 99.999 and 99.998% purity) were purchased from Rivoira and were used without further treatment. Ethyl acetate and heptane from Fluka, were used respectively as diluent and internal standard for the analysis of the reaction mixture. The catalyst precursor rhodium(I) dicarbonylacetylacetonate [Rh(CO)<sub>2</sub>(acac)] and the ligand triphenylphosphine [PPh<sub>3</sub>] were obtained from Aldrich.

Hydroformylation experiments were carried out with a 50 cm<sup>3</sup> high-pressure stainless steel windowed reactor with a magnetic stirrer, a high-pressure liquid pump, and a backpressure regulator (see Figure 2).



**Figure 2.** Experimental apparatus for hydroformylation reactions

In a typical run, the reactor was charged with Rh(CO)<sub>2</sub>(acac), PEG600 and ligand triphenylphosphine. After batch wise purging with CO<sub>2</sub> at atmospheric pressure, CO and H<sub>2</sub> were delivered, at room temperature, through a pressure reducer, controlling the loaded

amount by monitoring the partial pressure of each component. The reactor was heated at 40°C overnight to solubilise the catalyst in the polymer. Then it was cooled at room temperature, depressurized and 1-octene was introduced. The reaction mixture was heated at fixed temperature and liquid CO<sub>2</sub> was charged by an air driven Maximator pump while the stirring was commenced and the reaction was continued for 4 hours. After the reaction, the reactor was cooled in an ice-water bath to room temperature and depressurized with a backpressure regulator. The reaction mixture was dissolved with ethyl acetate. Then, the organic products were analyzed by a Perkin Elmer Clarus 500 gas chromatograph (GC) equipped with a SGE BPX5 1.0 capillary column (fused silica, length 30 m, internal diameter 0.53 mm) using a flame ionization detector (FID) and helium 5.5 as carrier gas. Calibration was done for 1-octene, octane and nonanal against the internal standard using solutions of known concentration prepared gravimetrically. Branched aldehydes were assumed to have the same response factor than the linear isomer.

## RESULTS

In this study we started to investigate the effect of process conditions on the hydroformylation of 1-octene in PEG/scCO<sub>2</sub> biphasic solvent.

The primary goal was to evaluate if the performances of the catalyst could be affected by changes in the operating temperature (see Entry 1-3, Table 2).

**Table 1** Range of conditions investigated for hydroformylation reactions.

	Symbol (unit)	Value
Reactor temperature	T (°C)	60-100
Reactor pressure	P <sub>TOT</sub> (MPa)	14-21
Amount of syngas	P <sub>CO</sub> =P <sub>H<sub>2</sub></sub> (MPa)	1-2 (at T=20°C)
Substrate concentration	[1-octene] (M)	0.4
Ligand/catalyst	L/C (mol/mol)	30
Volume of PEG600	V (mL)	5
Reaction time	t (h)	4
Reactor volume	V (mL)	50

We performed hydroformylation reactions at three different temperatures i.e. 60, 80 and 100°C and, at the highest investigated temperature, also in the absence of CO<sub>2</sub>. For all reactions carried out in the presence of carbon dioxide the only detected products were nonanal and isononanal with molar ratio L/B that decreased with the temperature. When the reaction was performed without CO<sub>2</sub> at 100°C (Entry 4, Table 2) we observed a marked decrease of olefin conversion accompanied by octane formation with yield of 3 %. It was then confirmed that PEG expansion by CO<sub>2</sub> improves the performances of the process.

To understand the influence of the total pressure of syngas on the hydroformylation reaction it was performed a reaction with P<sub>H<sub>2</sub></sub>=P<sub>CO</sub>=1 MPa (Entry 5, Table 2). We have found a significant abatement of the olefin conversion and a slight increase of the molar ratio of linear to branched aldehyde.

**Table 2** Effect of reaction temperature, total pressure of syngas and presence of CO<sub>2</sub> on the hydroformylation of 1-octene in PEG/scCO<sub>2</sub> biphasic systems.

Entry	P <sub>CO</sub> /MPa	P <sub>H<sub>2</sub></sub> /MPa	P <sub>TOT</sub> /MPa (T=60°C)	P <sub>TOT</sub> /MPa (T=100°C)	T/°C	X/% <sup>a</sup>	L/B <sup>b</sup>
1	2	2	14	14	60	47	3.1
2	2	2	14	15	80	78	3.0
3	2	2	14	16	100	98	2.7
4	2	2	4	4	100	49	3.3
5	1	1	14	21	100	50	3.5

Reaction conditions are the same as in Table 1.

<sup>a</sup> Conversion of 1-octene

<sup>b</sup> Molar ratio of linear to branched aldehydes.

## CONCLUSION

The use of PEG/scCO<sub>2</sub> biphasic system as reaction medium for the Rh catalyzed hydroformylation of 1-octene was investigated in the present work, at temperatures comprised between 60 and 100°C. At the highest investigated temperature the effect of syngas pressure and of CO<sub>2</sub> as expander agent of the polymer phase were also studied. Collected results indicate that the olefin conversion increases with T and that the presence of CO<sub>2</sub> improves the performances of the catalytic system.

Further research is going on to study the possibility of recovering products by extraction with scCO<sub>2</sub> without leaching of the catalytic system.

## ACKNOWLEDGEMENTS

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