# Enhanced hydroformylation of 1-octene in n-butane expanded solvents with Co-based Complexes

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# Enhanced hydroformylation of 1-Octene in *n*-butane expanded solvents with Co-based Complexes

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## Abstract

The use of *n*-butane expanded liquids (BXLs) as reaction media to enhance Co-catalyzed hydroformylation of 1-octene has been successfully demonstrated. Both 1-octene as well as typical hydroformylation mixtures are volumetrically expanded by *n*-butane at typical hydroformylation conditions (~ 50% expansion at 1.8 MPa of *n*-butane and 180 °C). By replacing up to 20% of the traditional solvent (toluene) in the reaction mixture with compressed *n*-butane, the TOF for Co-catalyzed 1-octene hydroformylation with triphenylphosphine ligand was enhanced by approximately 20% in the BXL system. The higher TOF in BXLs is attributed to the improved syngas availability in the pressure-tunable BXL phase compared to the traditional liquid phase. The main impediment to TOF enhancement is catalyst precipitation beyond a certain level of *n*-butane dissolution in the liquid phase. Hence, catalyst complexes that show improved solubility in the BXL phase are desirable to better harness the potential benefits offered by gas-expanded liquids.

Keywords: *Hydroformylation, gas-expanded solvent, 1-octene, cobalt complex*

## Introduction

Hydroformylation, also known as oxo synthesis or oxo process, is one of the largest industrial homogeneous catalytic processes with applications in the manufacture of fine chemicals, pharmaceuticals and specialty chemicals. Hydroformylation involves the addition of a formyl group (CHO) to a carbon-carbon double bond. The most commonly used hydroformylation catalysts are either unmodified or modified rhodium and cobalt complexes. Rhodium-based catalysts are widely used in the lower olefin ($C<5$) hydroformylations. However, they are not well suited for higher olefin hydroformylation because the Rh complexes are unstable at typical temperatures required for product separation/distillation. Hence, the less expensive cobalt-based catalysts are used for industrial higher olefin hydroformylation, even though harsh reaction temperatures (~180°C) and pressures (~20 MPa) are needed to activate and maintain the catalyst complex.[1-4]

Gas-expanded liquids (GXLs) are generated by dissolving compressible gases such as $CO_2$ and light olefins in an organic solvent. The liquid phase volumetrically expands upon dissolution of the compressed gas.[5, 6] Compared to traditional organic solvent, GXLs provide both process and environmental advantages while allowing operation at much lower pressures than supercritical fluids.[7-9] Previously, several groups including ours have clearly demonstrated that for phosphine modified rhodium catalyzed 1-octene hydroformylation reaction, turnover frequency (TOF) and regioselectivity (*n/i*) are significantly enhanced as well as pressure tunable in $CO_2$-based media.[10-13] In the case of carbon dioxide-expanded liquids (CXLs), the observed beneficial effects on hydroformylation activity and selectivity are attributed to the favorable tunability of

$H_2$/CO ratio in the CXL phase.[14]

Besides $CO_2$, the use of other gases as expansion media to create GXLs has also been reported.[15, 16] In comparison to $CO_2$ ($T_c$ = 31.0 °C; $P_c$ = 7.38 MPa), propane ($T_c$ = 96.6 °C; $P_c$ = 4.25 MPa) and *n*-butane ($T_c$ = 152.0 °C; $P_c$ = 3.70 MPa) possess higher critical temperatures but lower critical pressures. Consequently, propane and *n*-butane can expand organic solvents at higher temperatures and lower pressures compared to $CO_2$. Recently, we demonstrated that the solubilities of $H_2$ and CO in either propane-expanded or propylene-expanded phase are greater than those in the neat organic solvents, by as high as 78% at 70 °C and 1.5 MPa.[17] For rhodium/triphenylphosphine catalyzed propylene hydroformylation performed in the 70-100 °C range and pressures up to 2.0 MPa, the *n/i* aldehyde ratio is increased by up to 45% in propane-expanded liquids (PXLs). This is attributed to the increased $H_2$/CO ratio in the GXL phase. Like propane, reaction media expanded by *n*-butane, whose critical temperature is close to typical reaction temperatures (160-180°C) for Co-based hydroformylation, has the potential to enhance activity and selectivity at milder pressures.

In this manuscript, we experimentally quantify the volumetric expansion of typical hydroformylation mixtures by *n*-butane, including the solubility of the Co catalyst complexes in such BXLs. The activity and selectivity of Co-catalyzed hydroformylation of 1-octene were compared in neat solvent media and BXLs. The experimental results reveal that the TOF was enhanced more than 20% in BXL media with a 20% reduction in organic solvent usage. The increased TOF in BXLs is attributed to the improved syngas availability in the BXL phase compared to neat solvent.

## Experimental

### *Materials*

The purchased materials are listed in Table 1. All organic compounds were used as is unless otherwise noted.

### *Apparatus and methods*

*Volumetric Expansion and Catalyst Solubility Experiments:*

The experimental setup for investigating catalyst solubilities and solvent expansion with *n*-butane is illustrated in **Error! Reference source not found.**. It consists of a ~80 cm$^3$ Jerguson® Series 20™ liquid level gage (Clark-Reliance Corp.), thermocouples (Omega Engineering, Inc., type T, ±1.0 °C), pressure transducer (Omega Engineering Model PX835-2KSI, 0-13.79 MPa ±0.5%) and an oven (from a Applied Separations Model 7700 Speed® SFE unit, <240 °C). A Mitutoyo Digimatic® height gage with Titan® cathetometer is used to measure the expanded liquid volume (each mm division corresponds to a volume of 0.54 cm$^3$). The liquid level gage is located in the oven, and the gage will henceforth be referred to as the 'view cell'.

In a typical run, the system was evacuated with a vacuum pump, and the resulting vacuum was used to pull a known amount of organic liquid into the view cell through a port located in the bottom of the cell. The liquid consists of either pure solvent or a mixture of solvents and reactants at various compositions representative of typical hydroformylation reaction mixtures. Enough liquid was introduced into the system such that the meniscus in the view cell was visible using the cathetometer, looking through a round window located in the oven door. The mixture was then brought to the desired temperature, and the level recorded. Known amounts of *n*-butane were gradually introduced using a syringe pump. The gas was bubbled through a 2-micron frit immersed in the liquid, at the end of a vertical 1/16" stainless steel tube introduced into the view cell through a side port at the top of the cell. The expansion of the organic liquid by *n*-butane was recorded in terms of the relative increase in the liquid volume from the initial state (*n*-butane-free, equilibrated pressure, $P_0$) to the final state (*n*-butane expanded, equilibrated pressure, $P$) at the same temperature. The volumetric expansion ratio was calculated using Equation 1.

$$\frac{V}{V_0} = \frac{V(T,P)}{V(T,P_0)} \tag{1}$$

The volumetric expansion data are also predicted by Peng-Robinson equation of state (PR-EoS) with van der Waals' mixing rules embedded in the Aspen Plus® software.[18, 19] This simulation method has been previously demonstrated to satisfactorily predict the volumetric expansion as well as VLE data for $CO_2$- and propane-expanded solvent systems.[10, 17, 20] The equation and parameters used in the VLE simulations are shown in the Supplementary Materials (Section S1 & Table S1).

The cloud point pressure at which the dissolved Co catalyst complex precipitates was also measured during the expansion study. Operating pressures below the cloud point are used for performing homogeneous hydroformylation in BXLs, whereas pressures above the cloud point may be exploited for catalyst precipitation post-reaction.

### *Hydroformylation experiments:*

The hydroformylation reaction was performed in a 50 $cm^3$ high-pressure autoclave reactor in a semi-batch mode. The equipment description and procedures are described elsewhere.[14] In a typical run, a known amount of liquid solution containing substrate, dissolved catalyst and organic solvent are first introduced into the reactor. The reactor head space was flushed with nitrogen at ambient conditions to remove air. The reactor was then heated to the desired temperature with stirring. Following this step, *n*-butane was pumped into the reactor to attain the desired operating pressure for performing homogeneous catalysis in BXLs, as determined from the volumetric expansion study. The system was allowed to sit for approximately 30 minutes to equilibrate. Stirring was then temporarily halted and premixed syngas stored in the external gas reservoir was then introduced into the reactor to a predetermined syngas partial pressure. The stirrer was then set to 1000 rpm to start the reaction. For investigating the effects of different $H_2/CO$ ratios, the reactor was pressurized initially with CO and $H_2$ to achieve the desired initial $H_2/CO$ ratio while feeding syngas with a molar $H_2/CO$ ratio of 2 from the external reservoir. During the experiments, the temperature and pressure in the syngas reservoir as well as the reactor were monitored and recorded by LabView® data acquisition system. At the end of the reaction period, the autoclave was placed in an ice-bath to quench the reaction and contents carefully transferred into another container for immediate chromatographic analysis. Figure 2 (corresponding to Table 3, Entry #3,) shows typical pressure and temperature profiles during the batch experiments.

The TOF was calculated from the linear portion of the syngas consumption profile corresponding to low (<20%) 1-octene conversion. The syngas consumed from the reactor gas phase due to reaction is continuously replenished from an external reservoir to maintain a constant reactor pressure. Thus, the moles of syngas consumed in the reaction is estimated from the measured pressure drop in the external reservoir at a constant temperature. Further, if the desired product is nonanol, each mole of 1-octene should react with two moles of hydrogen and one mole of carbon monoxide.

$$\mathrm{TOF}\ (\mathrm{h}^{-1}) = \frac{\text{Moles of syngas consumed at low } (< 20\%) \text{ octene conversion}}{(\text{moles of Co})(\text{batch time})} \quad (2)$$

$S_{nonanol}$, $S_{aldehyde}$ and $S_{octane}$ are defined as the number of moles of nonanol, aldehyde and octane formed respectively, relative to the total number of moles of reaction products formed at the end of the batch run. The *regio*-selectivity (*n/i*) was estimated as the molar ratio of the linear to branched alcohols in the product. The carbon and hydrogen balances are estimated by calculating the moles of syngas consumed (from the observed pressure drop in the syngas reservoir) and comparing the value with the moles of hydrogen and carbon added in the products. Sample calculations are shown in the Supplementary Materials (Section S2 & Table S2). The combined deficit for molar carbon and hydrogen balances is less than 5% in all the runs reported here (Table S3).

## Results and discussion.

### *Volumetric Expansion and Catalyst Solubility studies:*

The purpose of conducting *n*-butane-expansion and catalyst solubility studies was to determine the operating conditions for performing homogeneous hydroformylation. **Error! Reference source not found.** shows the volumetric expansions of 1-octene by *n*-butane measured at pressures ranging from 0 to 2.4 MPa at 170 °C and 180 °C. As seen from Figure 3, the liquid phase containing only 1-octene was increased exponentially upon *n*-butane pressurization (by up to two-fold at 2.2 MPa, 170 °C and 2.4 MPa at 180 °C). As expected, the volumetric expansion is greater and more sensitive to pressure at the lower temperature (170 °C) as compared to the higher temperatures (180 °C). The experimental data are predicted reasonably well by simulations performed using Aspen

Plus® software employing the Peng–Robinson equation of state (PR-EOS).

**Error! Reference source not found.** shows the expansion of model hydroformylation reaction mixtures representing different conversion levels (0%, 30%, 70%) by *n*-butane at 180 °C. Knowledge of the volume expansion of typical reaction mixtures by *n*-butane as well as catalyst solubility in the expanded phase guide the choice of operating conditions (*P*, *T*, and composition) for the reaction studies. These include the extent of volumetric expansion at various *n*-butane pressures and the range of pressures where 1-octene hydroformylation in BXLs can be performed homogeneously. As seen in Figure 4, all the tested hydroformylation solvents demonstrate good miscibility with *n*-butane at mild pressures. Nearly 50% expansion was noticed as butane partial pressure is increased to 1.8 MPa. The measured expansion ratios were almost identical for the various reaction mixtures with an initial volume of 20 mL. However, catalyst precipitation was observed in *n*-butane expanded solvents around 1.3 MPa. The presence of polar nonanol slightly increases the cloud point pressure suggesting improved catalyst solubility in such mixtures. The observation of catalyst precipitation demonstrates the potential of exploiting *n*-butane as an antisolvent for catalyst recovery post reaction.

Volumetric expansion studies were also performed at different starting volumes (15, 20 and 25 ml) at 180°C with and without 6.0 MPa syngas ($H_2$/CO ratio = 2) in the gas phase (**Error! Reference source not found.**). The observed expansion behavior was almost identical for the different starting volumes. Further, the presence of 6.0 MPa syngas did not have a significant effect on the overall expansion (which is dominated by *n*-butane dissolution) even though the syngas solubility should increase at higher *n*-butane pressure based on such observation with other gas-expanded liquids.[14,17,21,22] The simulation results also confirm that the $V/V_0$ values are 1.01 and 1.02 for $H_2$/1-octene and CO/1-octene systems, respectively, at 6.0MPa and 180°C.[20] This is to be expected as CO ($T_c$ = -138.7°C) and $H_2$ ($T_c$ = −239.95°C) are far removed from their critical temperatures at the expansion conditions.[6]

*Reaction in neat organic solvents.*

The benchmark reaction for Co-catalyzed hydroformylation of 1-octene was carried out at 180°C in a batch reactor with a syngas partial pressure of 6.0 MPa. As inferred from Table 2, more than 85% nonanol yield (*n/i* ~2) with negligible aldehyde formation is obtained in neat organic solvent, which matches well with the literature.[23]

The influence of operating conditions was first investigated in neat organic solvent to determine suitable conditions for testing the reaction in BXLs. Activity data on Co/TPP at various temperatures, pressures, $H_2$/CO ratios and catalyst concentrations are summarized in

Table 3. The reaction temperature was varied at syngas pressures of 6.0 MPa (Entries# 1-3), the syngas pressure was varied at 180 °C using identical cobalt concentration (Entries# 4-6), the $H_2$/CO ratio was varied from 1:1 to 3:1 at syngas pressures of 6.0 MPa (Entries# 7-8) and the catalyst concentration was varied from 250 ppm to 2000 ppm at 6.0 MPa syngas and 180 °C (Entries# 9-11). As inferred from Table 3, the reaction rate (TOF) as well as nonanol yield are reduced at lower temperatures with increased selectivity towards aldehydes, hydrogenation and isomerization products. In general, both the TOF as well as the yield of the desired nonanol (> 85%) are favored at the higher temperatures.

An increase in the syngas pressure resulted in higher TOFs and *n/i* ratios (Table 3, Entries #3-6). However, at the highest syngas pressure (8 MPa), side reactions including 1-octene hydrogenation and isomerization also occur decreasing the nonanol selectivity. At identical syngas pressures, while a $H_2$/CO ratio of 2 is optimum for maximizing the reaction rate, alcohol yield and *n/i* ratio, a higher ($H_2$/CO ratio of 3) favors the formation of the hydrogenation product (Table 3, Entries 7-8).

Figure 6 compares the syngas conversion as a function of time at different catalyst concentrations. It is shown that increasing catalyst concentration clearly increases the syngas consumption rate while enhancing the linear alcohol yield (Table 3, Entries# 9-11). However, the TOF (defined in eq. #2) decreases at higher catalyst concentrations with diminishing effect beyond 1000 ppm.

The mechanisms for phosphine modified Co-catalyzed hydroformylation have been well studied.[24-27] Figure 7 is a schematic for the well accepted catalytic mechanism for Co-catalyzed hydroformylation reactions. The active species is a 16-electron hydride complex, $[HCo(CO)_2L]$ (L=CO or phosphine), in equilibrium with the 18-electron tricarbonyl $[HCo(CO)_3L]$ complex. Co-ordination of alkene and insertion into the Co–H bond generates a cobalt–alkyl complex which is followed by CO-insertion to give an acyl species. Hydrogenation of the acyl liberates the aldehyde and regenerates the active hydride species. The alcohol is then formed by the hydrogenation of aldehyde. It has been reported that for Co-catalyzed hydroformylation, sufficiently high CO partial pressures are required to stabilize the carbonyl complexes and that the rate-limiting step is the hydrogenation of the acyl intermediate.[27-29] On the other hand, lower CO partial pressures shift the equilibrium toward the active species $HCo(CO)_2L$, implying the requirement of an optimum CO concentration in the reaction phase. In other words, an optimum $H_2/CO$ ratio in the reaction phase is required to maximize the reaction rate. As discussed earlier, progressively higher $H_2/CO$ ratios favor the hydrogenation product adversely affecting the linear alcohol selectivity. A $H_2/CO$ ratio of 2 is typically used industrially. Given that $H_2/CO$ may be easily tuned in gas-expanded liquids with syngas of a fixed composition,[14, 17] we chose to investigate *n*-butane expanded reaction media for optimizing Co-catalyzed hydroformylation.

### *Reaction in n-butane expanded solvents*

For the 1-octene hydroformylation runs in *n*-butane-expanded media, volumetric expansion ratios from 1.0 to 1.2 were investigated to maintain homogeneous reaction conditions. The syngas partial pressure was fixed at 6.0 MPa, while system pressure was increased with *n*-butane addition to create BXLs. To eliminate the dilution effect caused by *n*-butane dissolution, the amount of pure organic solvent was reduced (guided by the volumetric expansion data) to maintain an identical initial liquid volume in all the runs. In this way, the initial catalyst and reactant concentrations are kept nearly constant in the various runs.

As seen in Table 4, at homogeneous reaction conditions (*n*-butane partial pressure < 1.2 MPa), the TOFs were up to 22% greater in the BXL phase compared to neat toluene (Table 3, entry 3). However, *n*-butane addition has less of an effect on the *n*/*i* ratio. The enhanced TOF in the BXL phase is attributed to increased syngas solubility in that phase. As expected, catalyst precipitation occurs when *n*-butane partial pressure was increased beyond 1.3 MPa (Figure 4), causing a significant reduction in the TOF and nonanol yield (Table 4, Entry #4).

To further clarify the effect of *n*-butane addition, the reactions were run with different solvents and gases to replace the butane in the liquid and vapor phases while maintaining identical initial concentrations of the substrate (1-octene) and catalyst in the liquid phases. The comparison experiments were designed as follows: (1) an expanded toluene mixture ($V/V_0$=1.2) is subjected to a total pressure of 7.1 MPa, with the partial pressures of syngas and *n*-butane being 6.0 and 1.1 MPa, respectively; (2) an expanded 1-octanol mixture ($V/V_0$=1.2) at otherwise identical conditions as run 1; (3) replacing *n*-butane with *n*-hexane (with polarity similar to *n*-butane) in the liquid phase maintaining the same initial volume as in other runs but under a total pressure of 6.0 MPa syngas alone; (4) toluene alone as solvent (as in run 1) but using pure syngas (7.1 MPa) in the vapor phase; (5) toluene alone as solvent (as in run 1) but replacing n-butane in the vapor phase with $N_2$ by using a mixture of syngas (6.0 MPa) and $N_2$ (1.1 MPa).

As shown in Figure 8, the TOF in *n*-butane-expanded toluene (run 1) is 30% greater than that in *n*-hexane at (Run 3) with similar *n/i* ratios observed in both runs. Compared to reaction in the toluene-BXL system, higher TOF and *n/i* are observed in 1-octanol-BXL system indicating beneficial effects of the polar product. Higher syngas partial pressures (7.1 MPa, Run 4) with neat solvent (toluene) are needed to match the TOF and *n/i* observed with toluene-BXL system that uses lower syngas partial pressure (6.0 MPa, Run 1), indicating enhanced syngas availability in the BXL phase. However, when a syngas partial pressure of 6.0 MPa and a $N_2$ partial pressure of 1.1 MPa were used with toluene as solvent (Run 5), a decrease in the TOF is observed. These results provide clear evidence that the beneficial effects of BXLs on the observed TOF and *n/i* ratio during Co-catalyzed 1-octene hydroformylation are due to *n*-butane dissolution in the liquid phase.

**Error! Reference source not found.** summarizes results of Co-catalyzed 1-octene hydroformylation performed in *n*-butane expanded octanol. As inferred from Table 5, TOFs are generally enhanced at increased butane partial pressures at constant initial volumes (i.e., constant initial 1-octene and catalyst concentrations) as long as homogenous reaction conditions without catalyst precipitation are maintained. At a *n*-butane partial pressure of 1.3 MPa (Table 5, Entry #4), the TOF is 25% higher than in neat octanol (Table 5, entry 1). At higher partial pressure of 1.5 MPa (Table 5, Entry #5), the TOF markedly decreases, attributed to catalyst precipitation induced by increased dissolution of *n*-butane. However, the cloud point pressure that induces catalyst precipitation is greater (1.5 MPa) in 1-octanol-BXL (1.5 MPa) than in toluene-BXL system (1.3 MPa). In other words, the polar octanol as an effective co-solvent favoring enhanced catalyst solubility.

These results clearly show that the addition of *n*-butane has a beneficial effect on the TOF for Co-catalyzed 1-octene hydroformylation. However, the strong anti-solvent effect of *n*-butane results in catalyst precipitation and limits its application to relatively low *n*-butane partial pressures. The potential benefits of BXLs may be maximized by designing catalysts that show improved solubility in the reaction mixture. In this context, promising candidates include Co complexes containing fluorophosphines that have been reported to exhibit high solubility in *sc*$CO_2$ as well as enhanced performance for 1-octene hydroformylation.[30, 31]

## Conclusion

The application of *n*-butane expanded liquids (BXLs) as reaction media for Co-catalyzed 1-octene hydroformylation was successfully demonstrated. Volumetric expansion studies show that *n*-butane can significantly expand the volume of 1-octene and typical hydroformylation mixtures, by up to 50% at 1.8 MPa and 180 °C. For Co-catalyzed 1-octene hydroformylation at 180°C, enhanced TOFs (~ 20%) are observed in BXLs compared to neat solvent at relatively mild pressures. However, increased *n*-butane dissolution in toluene at higher pressures (1.3 MPa) induces catalyst precipitation, decreasing TOFs and nonanol yield. These first results clearly point out the need for designing Co complexes with improved solubility in BXL media and thereby better exploit these promising reaction media in industrial hydroformylation.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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## List of Tables

Table 1: Materials used in this Work

| Material | Purity | Company |
|---|---|---|
| 1-Octene | 98% | Sigma-Aldrich, In |
| Toluene | anhydrous, 99.8% | Sigma-Aldrich, In |
| Decane | anhydrous, ≥99% | Sigma-Aldrich, In |
| 1-Octanol | 99% | Sigma-Aldrich, In |
| Triphenylphosphine (TPP) | 99% | Sigma-Aldrich, In |
| Cobalt(III) acetylacetonate | 99.99% | Sigma-Aldrich, In |
| Hydrogen | 99.99% | Matheson Tri-Gas Co. |
| Syngas | 49.5% $H_2$ with balance being CO | Matheson Tri-Gas Co. |
| *n*-butane | 99.9% | Matheson Tri-Gas Co. |
| Nitrogen | 99.9% | Matheson Tri-Gas Co. |

Table 2: Benchmark reaction for Co-catalyzed hydroformylation of 1-octene

| | X, % | *n/i* | $S_{nonanol}$ % | $S_{octane}$ % |
|---|---|---|---|---|
| Benchmark | 88.7 | 1.9 | 86.1 | 13.9 |
| Literature | 90.3 | 2.2 | 86.5 | 13.5 |

T = 180°C, P = 6.0 MPa, $H_2$/CO = 2:1; [Co] = 1000 ppm, 1-octene/toluene = 3/2 (V/V), Catalyst: cobalt acetylacetonate; P/Co (molar) = 10; Ligands: triphenylphosphine; t = 8 h; X refers to 1-octene conversion; *n/i* refers to nonanol isomers.

Table 3. Co-catalyzed hydroformylation of 1-octene in neat organic solvent

| No. | T, °C | P, MPa | $H_2$/CO | [Co], ppm | X, % | *n/i* | TOF, $h^{-1}$ | $S_{nonanol}$, % | $S_{nonanal}$, % | $S_{octane}$, % | $S_{inter-octene}$, % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 160 | 6.0 | 2:1 | 1000 | 93.2 | 3.26 | 17.2 | 11.2 | 19.8 | 30.1 | 38.9 |
| 2 | 170 | 6.0 | 2:1 | 1000 | 91.9 | 2.08 | 76.3 | 80.4 | 1.9 | 15.0 | 2.6 |
| 3 | 180 | 6.0 | 2:1 | 1000 | 89.0 | 1.85 | 95.0 | 86.3 | Trace | 12.9 | 0.8 |
| 4 | 180 | 3.0 | 2:1 | 1000 | 64.6 | 1.52 | 51.6 | 80.3 | trace | 16.8 | 2.3 |
| 5 | 180 | 5.0 | 2:1 | 1000 | 82.0 | 1.77 | 77.7 | 83.1 | trace | 14.4 | 3.5 |
| 6 | 180 | 8.0 | 2:1 | 1000 | 93.6 | 2.03 | 135.2 | 81.4 | trace | 15.6 | 3.0 |
| 7 | 180 | 6.0 | 1:1 | 1000 | 90.2 | 1.72 | 81.7 | 32.3 | 24.0 | 26.3 | 17.4 |
| 8 | 180 | 6.0 | 3:1 | 1000 | 92.1 | 1.98 | 129.2 | 80.5 | trace | 19.5 | trace |
| 9 | 180 | 6.0 | 2:1 | 250 | 76.5 | 1.52 | 111.4 | 75.9 | 4.1 | 16.4 | 3.6 |
| 10 | 180 | 6.0 | 2:1 | 500 | 87.7 | 1.69 | 83.6 | 86.3 | trace | 13.7 | trace |
| 11 | 180 | 6.0 | 2:1 | 2000 | 91.2 | 1.87 | 74.6 | 86.4 | trace | 13.6 | trace |

Catalyst: cobalt acetylacetonate; Ligand: triphenylphosphine; t = 4 h; volumetric 1-octene/toluene/decane (internal standard) = 12/7/1; P/Co (molar) = 10; ($H_2$/CO) refers to intial molar ratio in the reactor (molar $H_2$/CO in external reservoir = 2 in all cases); X refers to 1-octene conversion; *n/i* refers to nonanol isomers.

Table 4: Co-catalyzed hydroformylation of 1-octene in BXL-toluene

| No. | $P_{n\text{-butane}}$, MPa | $V/V_0$ | X, % | *n/i* | TOF, $h^{-1}$ | $S_{nonanol}$, % | $S_{nonanal}$, % | $S_{octane}$, % | $S_{inter\text{-}octene}$, % |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.4 | 1.05 | 90.2 | 1.93 | 101.2 | 85.8 | Trace | 13.3 | 0.9 |
| 2 | 0.7 | 1.10 | 91.2 | 1.88 | 104.5 | 86.5 | Trace | 12.3 | 1.2 |
| 3 | 1.1 | 1.20 | 91.8 | 1.85 | 116.3 | 87.1 | Trace | 11.8 | 1.1 |
| 4 | 1.3 | 1.40 | 84.2 | 2.03 | 41.6 | 60.2 | 4.5 | 22.8 | 12.5 |

T = 180°C, $P_{syngas}$ = 6.0 MPa, Initial $H_2/CO$ in reactor and $H_2/CO$ in external reservoir (molar) = 2:1; Catalyst: cobalt acetylacetonate; Ligand: triphenylphosphine; t = 4 h; P/Co (molar) = 10; Initial liquid phase volume: 20 mL; X refers to 1-octene conversion; *n/i* refers to nonanol isomers.

Table 5: Co-catalyzed hydroformylation of 1-octene in BXL-octanol

| No. | $P_{n\text{-butane}}$, MPa | $V/V_0$ | X, % | *n/i* | TOF, $h^{-1}$ | $S_{nonanol}$, % | $S_{nonanal}$, % | $S_{octane}$, % | $S_{inter\text{-}octene}$, % |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0 | 1.00 | 99.5 | 2.06 | 111.6 | 85.2 | 0.5 | 12.9 | 1.4 |
| 2 | 0.7 | 1.10 | 99.3 | 2.08 | 127.2 | 86.4 | 0.5 | 12.3 | 0.8 |
| 3 | 1.1 | 1.20 | 98.8 | 2.14 | 134.7 | 85.3 | Trace | 13.3 | 1.4 |
| 4 | 1.3 | 1.30 | 99.2 | 2.13 | 141.6 | 84.3 | Trace | 14.5 | 1.2 |
| 5 | 1.5 | 1.40 | 98.4 | 2.20 | 67.5 | 68.6 | 3.0 | 18.3 | 10.1 |

T = 180°C, $P_{syngas}$ = 6.0 MPa, Initial $H_2/CO$ in reactor and $H_2/CO$ in external reservoir (molar) = 2:1; Catalyst: cobalt acetylacetonate; Ligand: triphenylphosphine; t = 4h; P/Co (molar) = 10; Initial liquid phase volume: 20 mL; X refers to 1-octene conversion; *n/i* refers to nonanol isomers.

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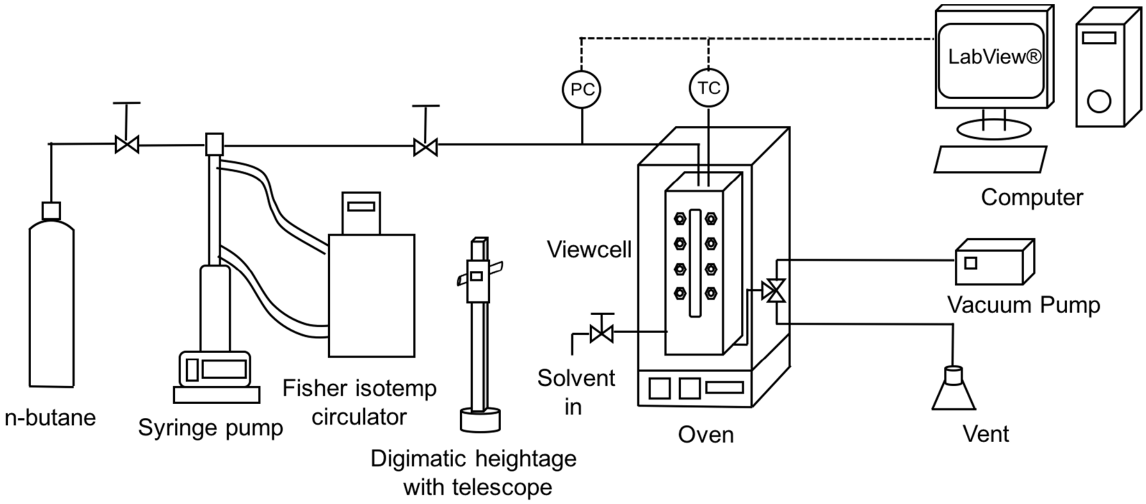

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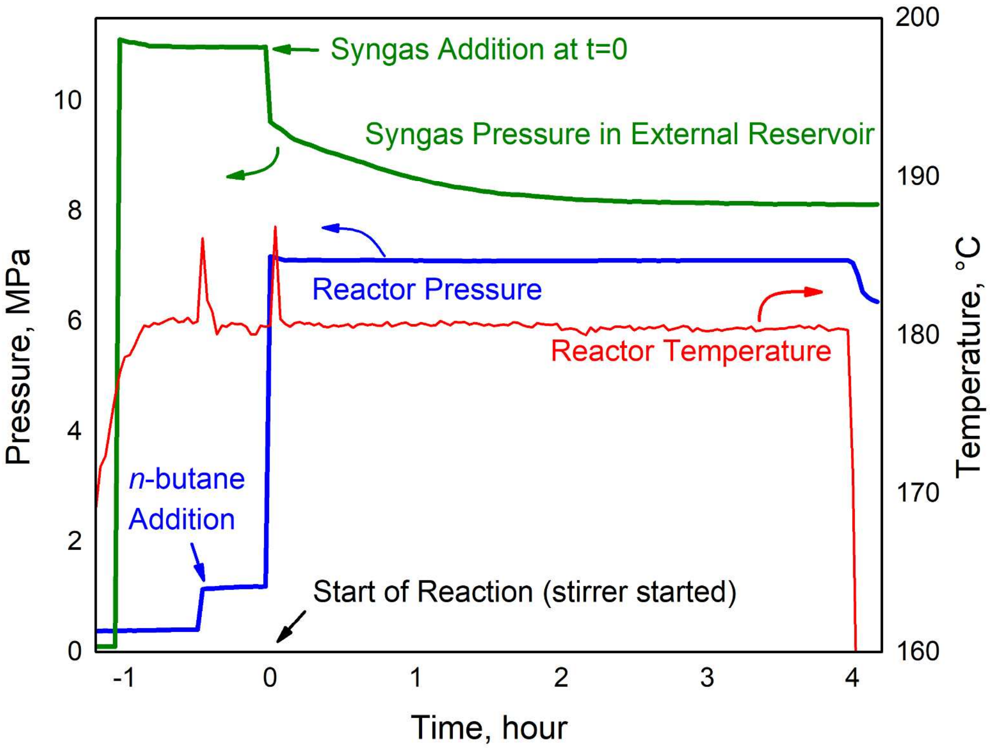

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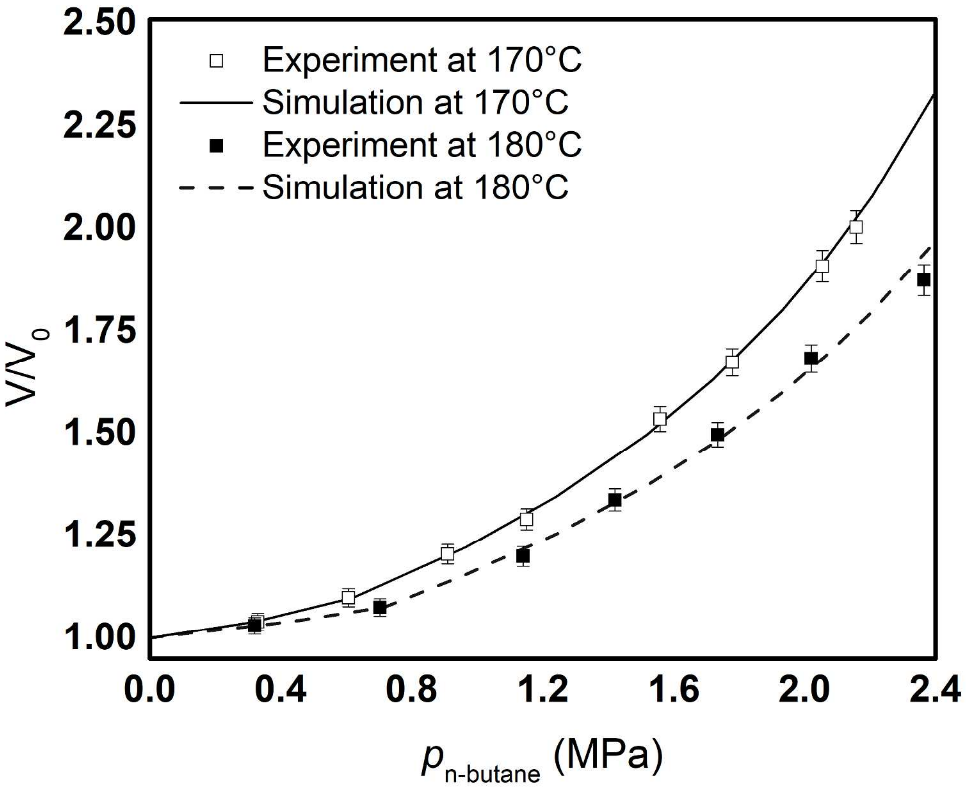

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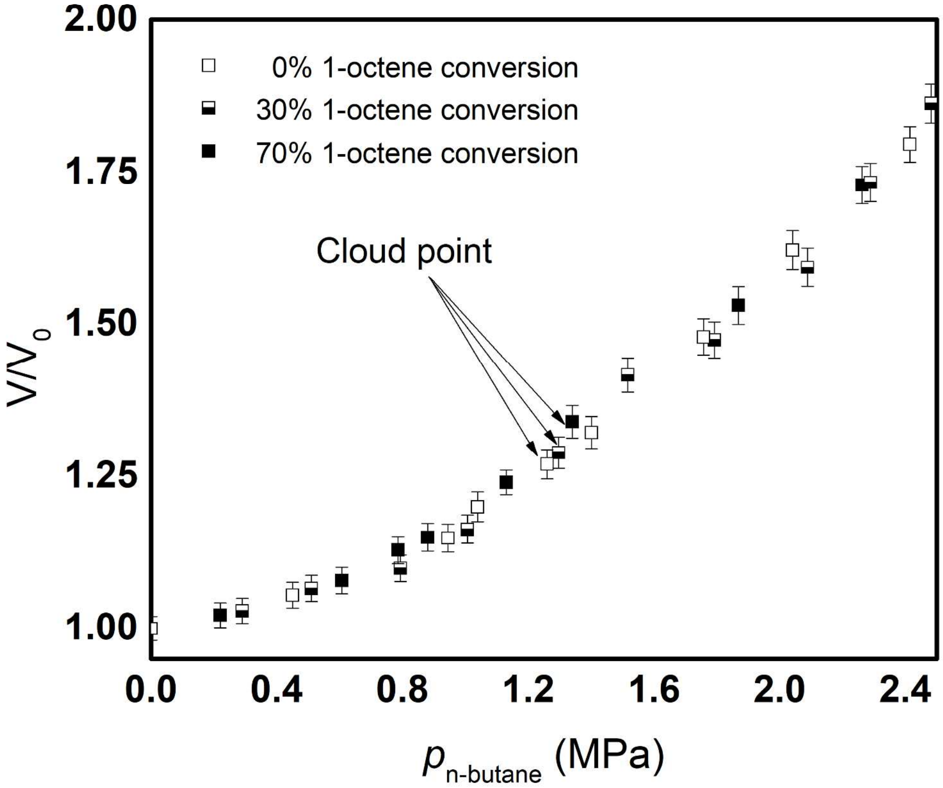

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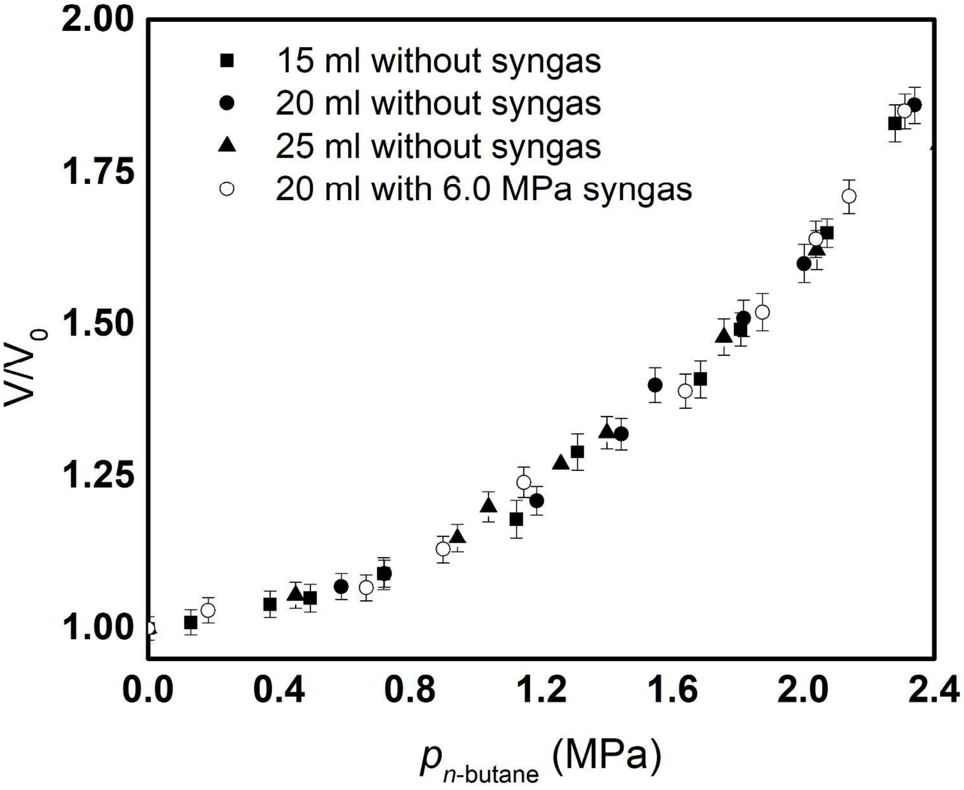

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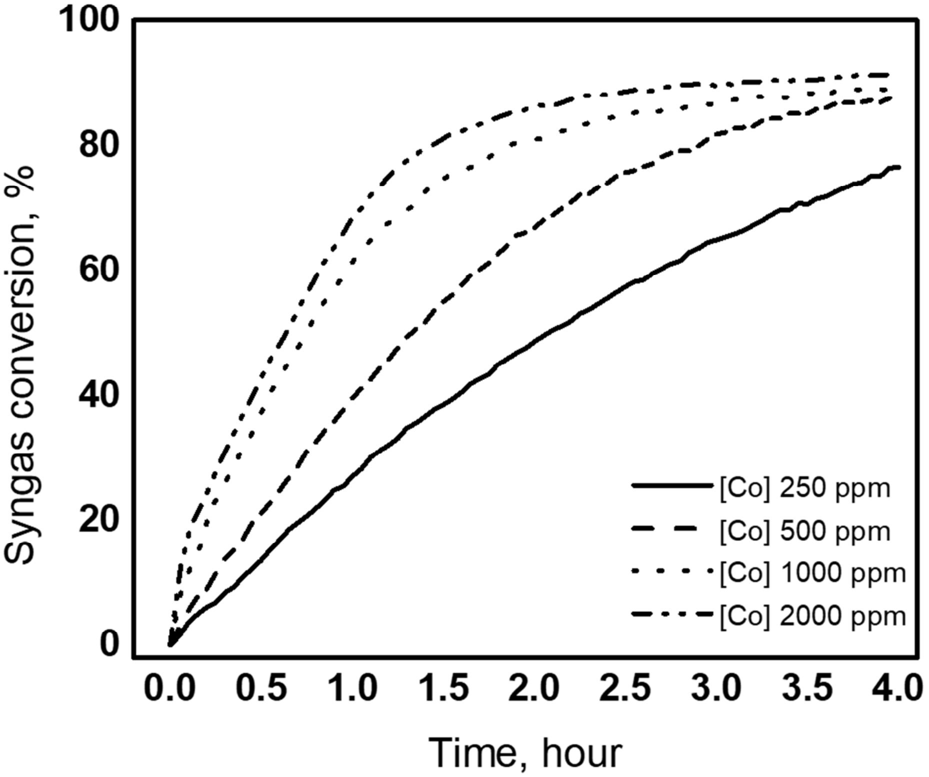

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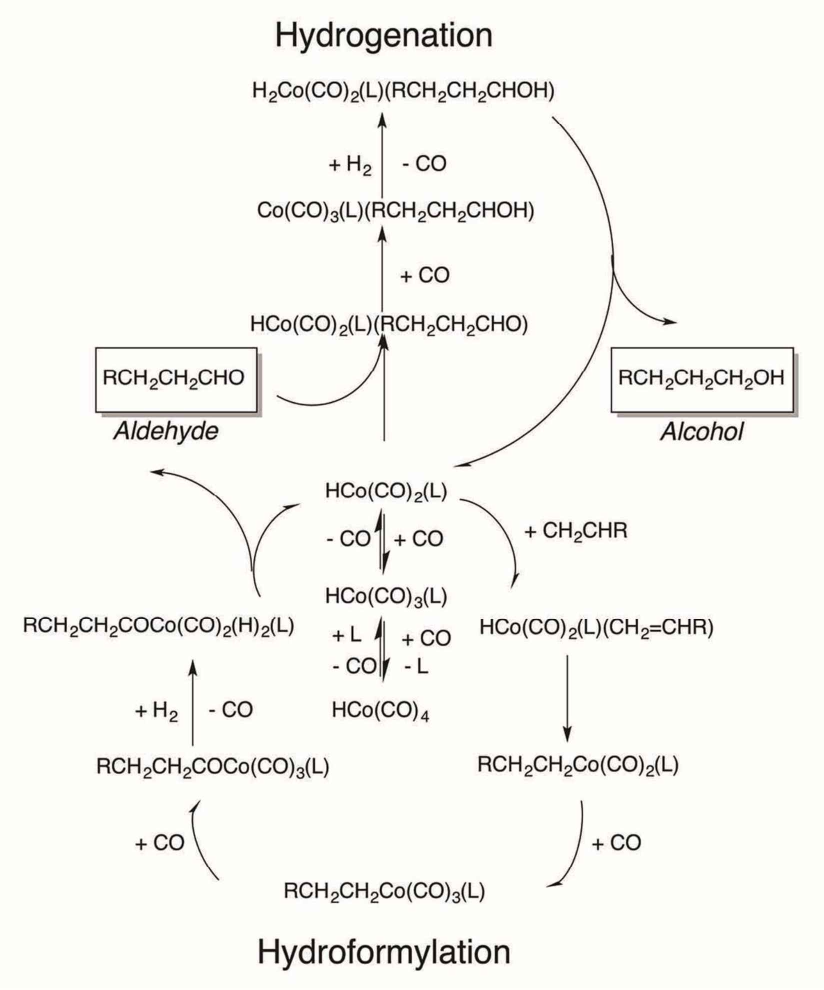

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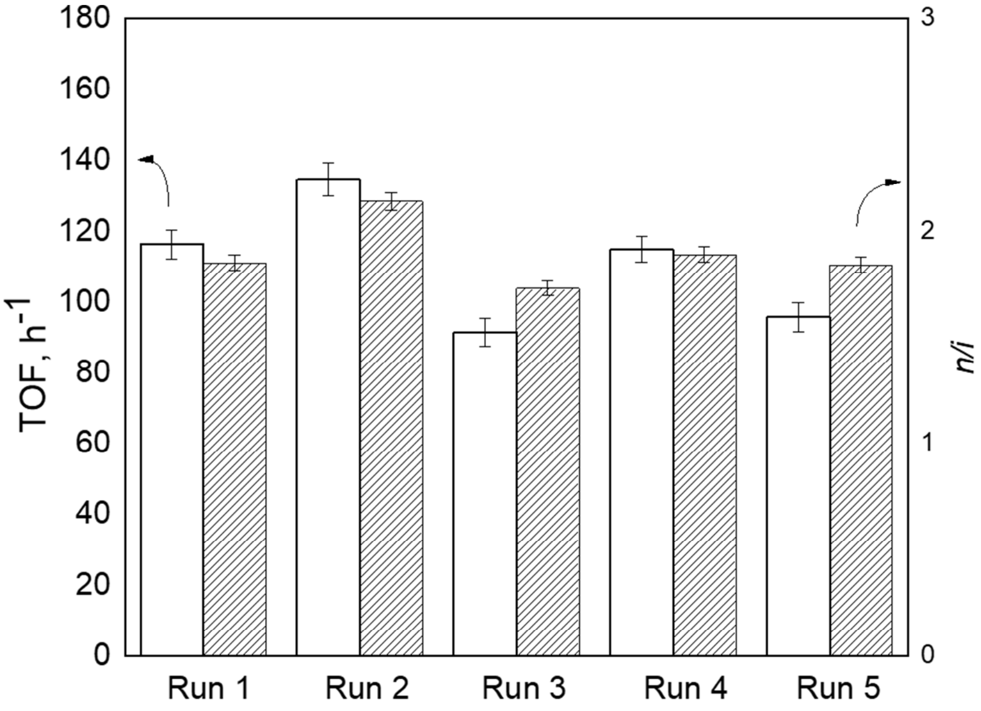

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## Graphical Abstract