

Supplementary Information: Auto-tandem catalytic reductive hydroformylation with continuous multiphase catalyst recycling

Phase behavior simulation

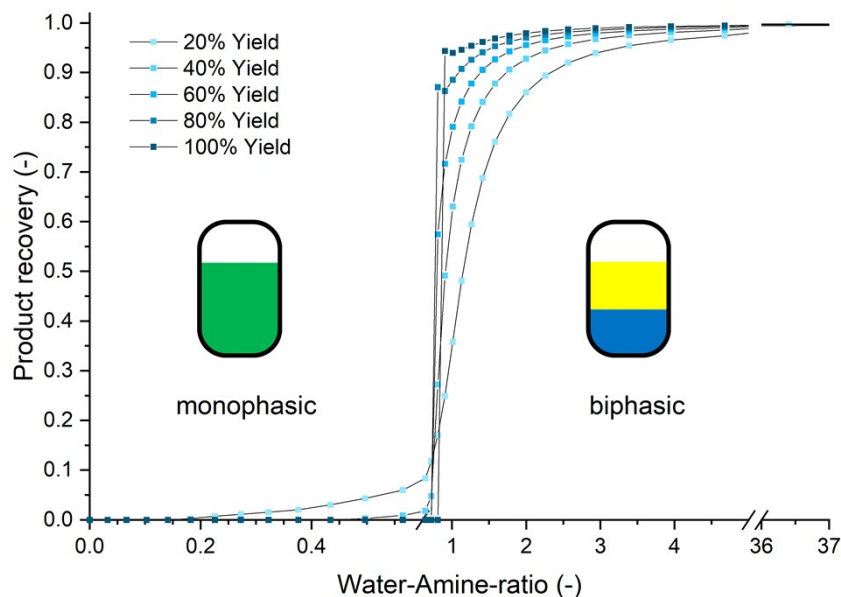


Figure 1 - Water-Amine-Ratio phase behavior simulation using Aspen Plus. Modeled with UNIFAC, $T = 25^{\circ}\text{C}$, 18 ml Aqueous phase at given ratios, 12 ml organic phase (1-octene (Substrate) with respective conversion to n-nonanol / Heptane), $\text{Product recovery} = n_{\text{alcohol, second phase}} / n_{\text{alcohol, total}}$

The phase behavior simulation with Aspen Plus shows a switch of phase behavior approximately at equal water and amine mass fractions. When using a catalyst phase with higher water fractions (high Water-Amine-ratio), a second, organic phase forms. This phase predominantly contains non-polar reaction components (1-octene, n-heptane, n-nonanol), so the reaction products can be separated by simple decantation.

The amount of alcohol separated from the catalyst phase (product recovery) increases with higher water content of the catalyst phase as well as with increasing alcohol concentrations (high yields). The latter may be due to a small solubility of alcohols in the water/amine mixture used as catalyst phase.

FT-cut composition

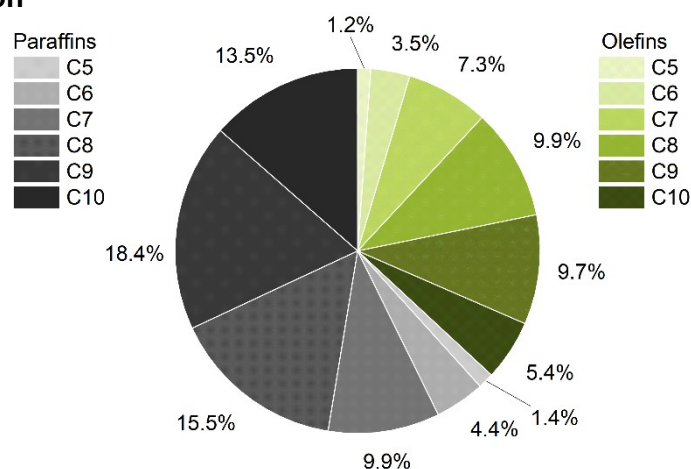


Figure 2 - Composition of C5-C10 FT cut containing olefins

Time Profile Experiment

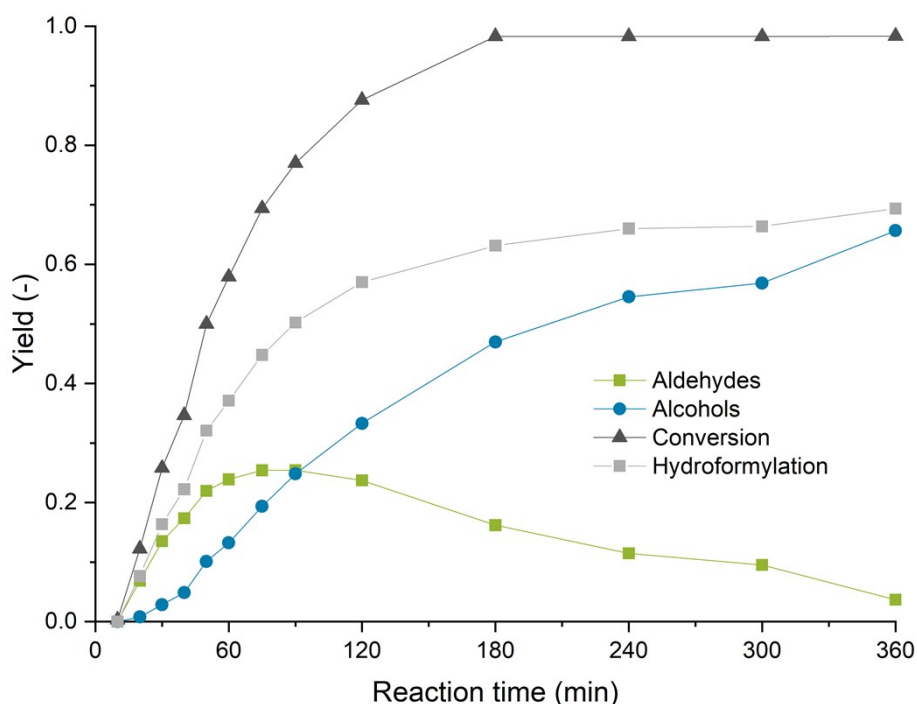
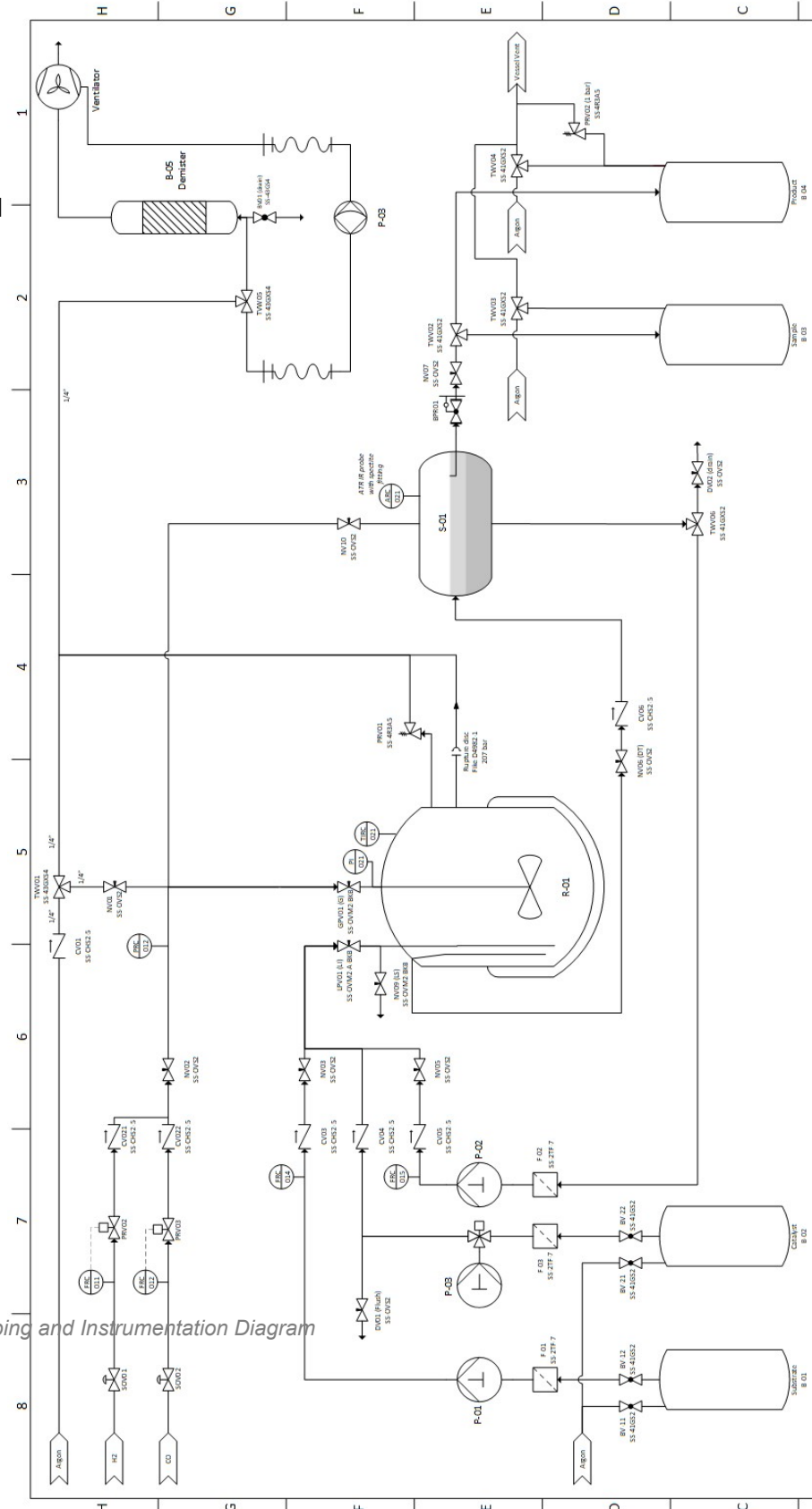


Figure 3 - Yield-Time experiment. Conditions: $c_{cat} = 0.5 \text{ mol\% (substrate)}$, $Rh:Amine = 1:400$, $T = 80^\circ\text{C}$, $p = 75 \text{ bar}$, $CO/H_2 = 1:2$, $\phi_{org} = 0.4$, $V_{liq} = 120 \text{ mL}$, $Water:Amine = 1.5$, $n = 2000 \text{ min}^{-1}$, catalyst = $Rh(acac)(CO)_2$, $Amine = DMAE$, $Y_{hyfo} = Y_{aldehydes} + Y_{alcohols}$

To investigate the selectivity of the reaction, a time profile experiment was conducted. In the beginning of the reaction, predominantly aldehydes and olefin isomers are formed. (Figure 5) The rate of hydroformylation decreases at higher conversion; probably because of a lower available substrate concentration. Alcohols are formed already in the first 30 minutes of the experiment. After 90 minutes, only minor amounts of additional aldehydes are formed, hence the formation of alcohols leads to a decreasing aldehyde concentration. This experiment demonstrates that two separate reactions occur independently; the formed aldehydes represent intermediates and react further to alcohols and show a decreasing concentration after 90 minutes.

Under the applied conditions, full conversion was reached after 180 minutes. Since α -olefins can be formed by back-isomerization and internal olefins can undergo hydroformylation as well, hydroformylation still takes place after full conversion is reached. After 360 minutes, almost all previously formed aldehydes have been converted to alcohols. The lower yields after 90 minutes compared to batch experiments is caused by a lower pressure of 75 bar and increased liquid volume in the reactor; 120 mL were used instead of 30 mL to reduce disturbances by the withdrawal of samples.

Miniplant PID and



Instrumentation			
ELEMENT	QTY	PART-NO.	DESCRIPTION
P-01	1	WA Dose Lite HP	Piston Pump substrate
P-02	1	WA Dose Lite HP	Piston Pump catalyst cycle
P-03	1	Laybold TriVac D88	Vacuum Pump
P-04	1	Cetoni Nemesis 2800	Syringe Pump Catalyst feed

Vessels and reactors		
ELEMENT	QTY	DESCRIPTION
B-01	1	Substrate vessel
B-02	1	Catalyst vessel
B-03	1	Sample vessel
B-04	1	Product vessel
B-05	1	316L-50DF-150 Decanter vessel
R-01	1	Parr Instruments 4560 Hydroformylation reactor
S-01	1	Phase separator (Decanter)

Updated by: Puschel

REV.	1
Drawing number	REDIFUEL_PID_VERSIONS
created	Puschel
size	A3
updated by	Puschel
REDIFUEL reductive hydroformylation pilot plant PID	
All piping in 1/8" 316/316L tubing unless otherwise noted	