

Biphasic Hydroformylation of Higher Olefins

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Outline

Background

- Hydroformylation
- Biphasic catalysis
- Thermomorphic systems

▪ Thermomorphic Hydroformylation at TDA

- Batch
- Continuous

▪ Process Comparisons

- TDA Thermomorphic vs. BASF Higher Olefin

▪ Relate Work

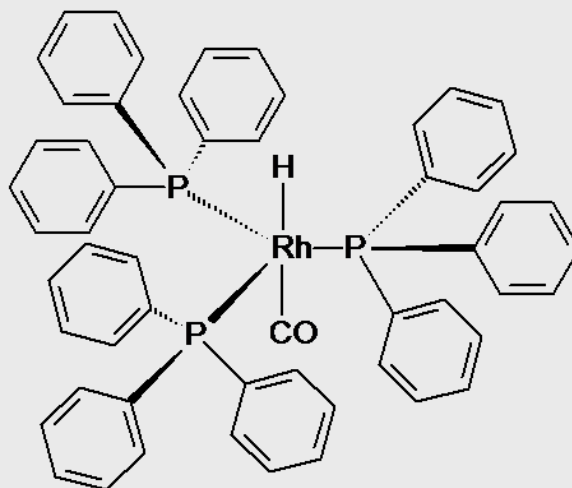
- Asymmetric hydrogenation

▪ Summary

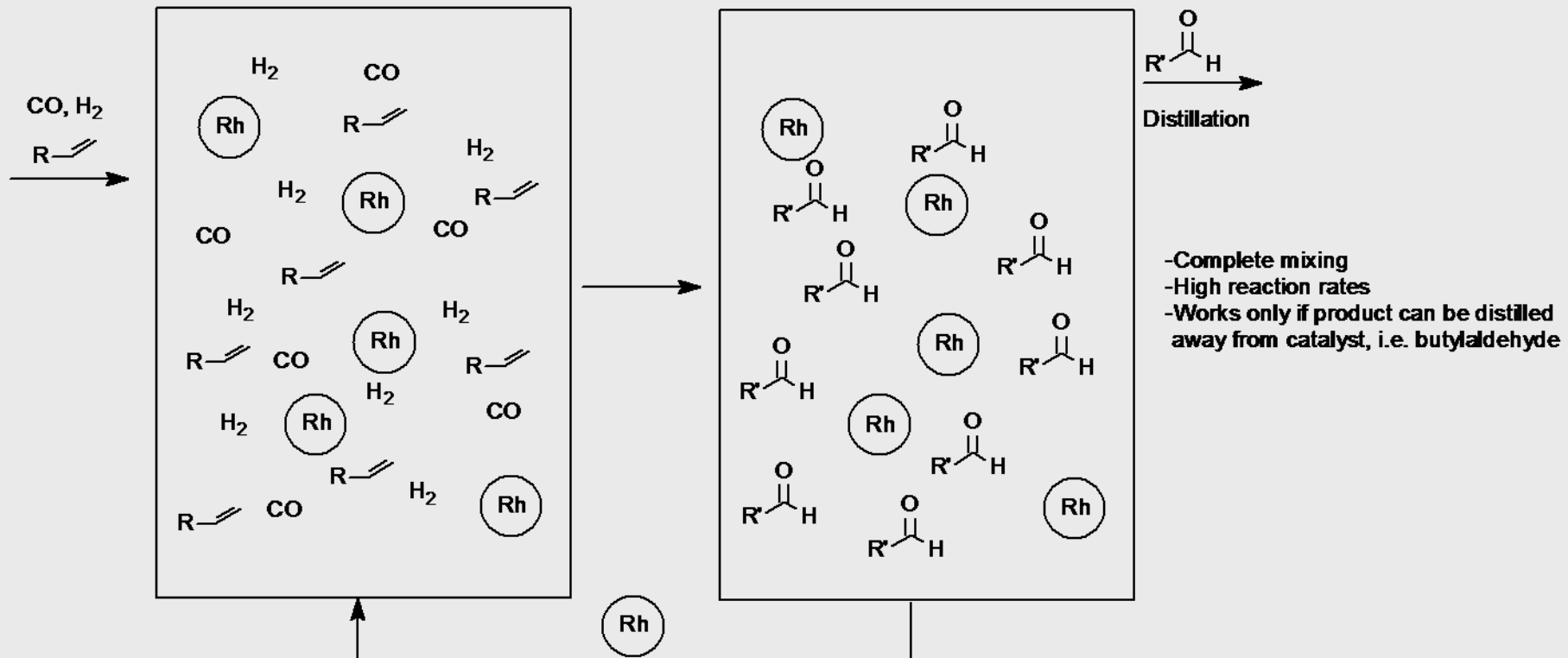
Background

Aldehyde Production

- Rhodium and cobalt catalysts can be used
- Rhodium phosphine catalysts have replaced cobalt catalysts for lower aldehydes (<C₆) because of their higher activity and selectivity
- Because of the high cost of rhodium, catalyst losses have to be very low



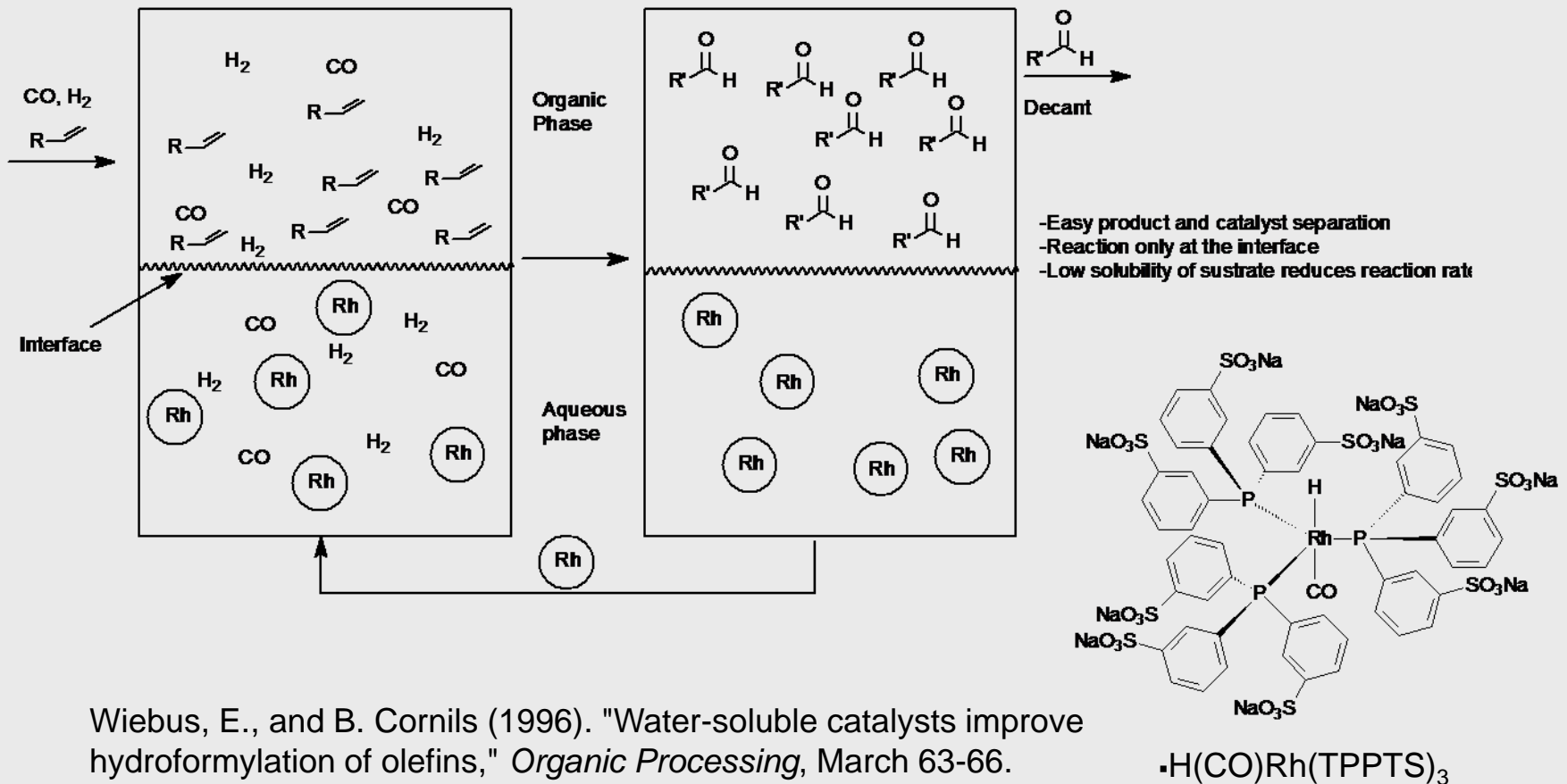
Single-Phase Homogeneous Hydroformylation (lower aldehydes)



Higher Aldehydes

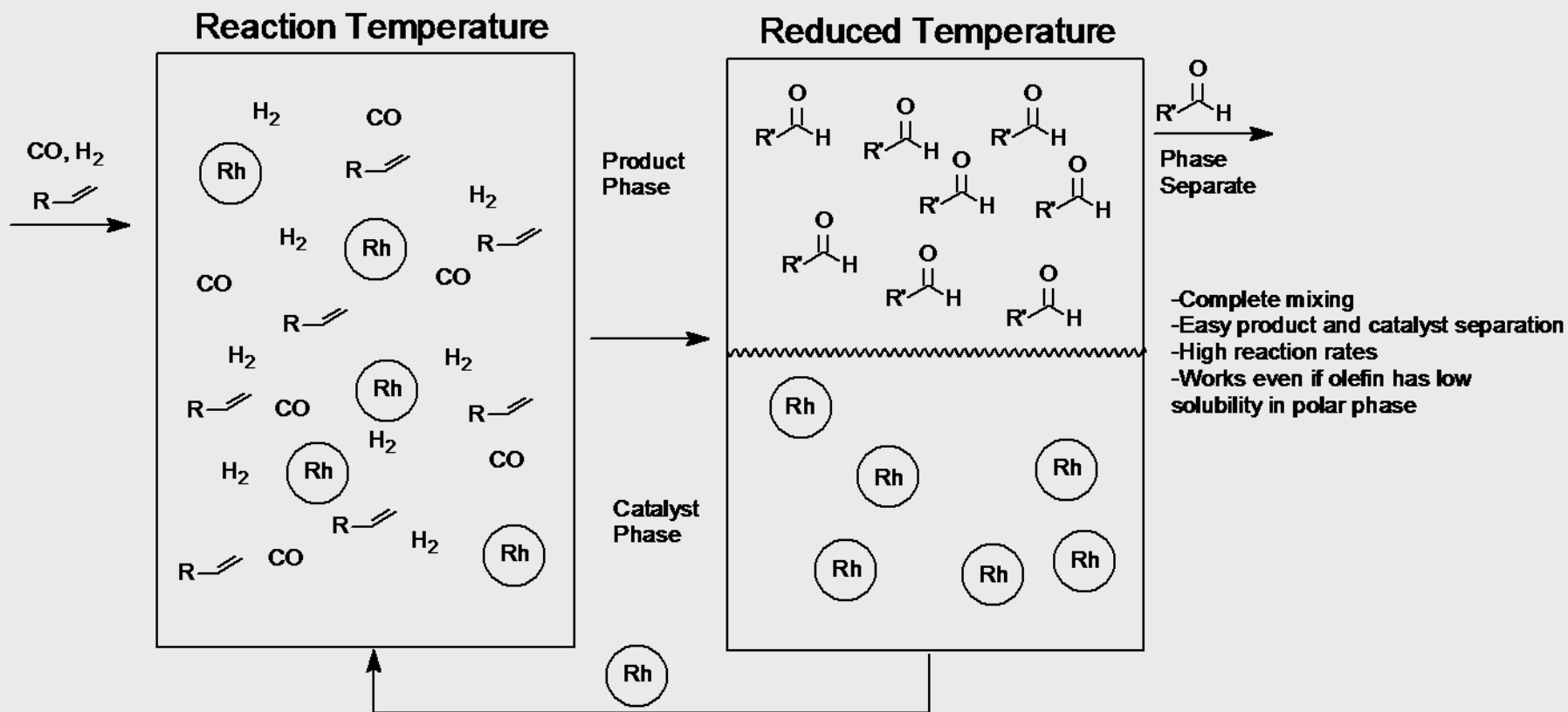
- **The higher boiling points of higher aldehydes result in catalyst decomposition**
- **Higher aldehydes are produced using less efficient cobalt catalysts because there is no effective means to separate the rhodium phosphine catalyst from the reaction mixture**

Biphasic Hydroformylation (Ruh Chemie/Rhône Poulenc)



Wiebus, E., and B. Cornils (1996). "Water-soluble catalysts improve hydroformylation of olefins," *Organic Processing*, March 63-66.

Thermomorphic Hydroformylation



Fluorous Thermomorphic Hydroformylation

- Hydroformylation has been done using perfluoromethylcyclohexane/toluene thermomorphic solution with fluorinated phosphine ligands (Exxon)
- Catalyst: $\text{HRh}(\text{CO})\text{-}(\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3)_3$
- Problem is that fluorinated solvents and ligands are very expensive

Horváth, I.T., and J. Rábai (1994). "Facile Catalyst Separation Without Water: Fluorous Biphasic Hydroformylation of Olefins," *Science* **266**, 72-75

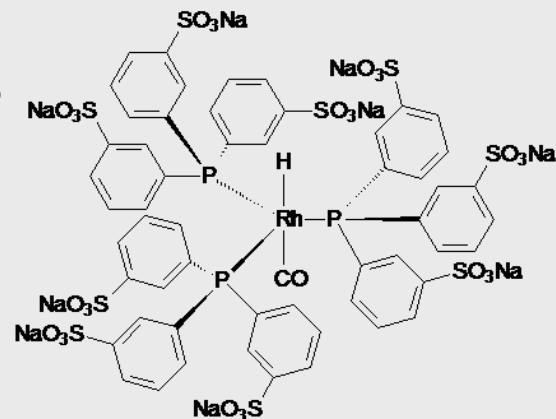
Non-Fluorous Thermomorphing Solutions

- **Common solvent pairs that reversibly change from being biphasic to monophasic as a function of temperature**
 - Methanol/cyclohexane (49°C)
 - *n*-butanol/water (125°C)
 - Heptane/90:10 ethanol:water (70°C)
- **TDA's approach is to use conventional solvents and ligands for thermomorphing hydroformylation**

Thermomorphic Hydroformylation at TDA

Thermomorphic System

- Catalyst soluble in aqueous phase
- Olefin/aldehyde soluble in nonpolar phase
- Tested various aqueous cosolvents and a surfactant (cetyltrimethylammonium bromide (CTAB))
- Catalyst: $\text{H}(\text{CO})\text{Rh}(\text{TPPTS})_3$
 - Ruhrchemie/Rhône Poulenc



Thermomorphing Catalyst Solution (90:10 EtOH:Water/Heptane + CTAB)



25°C



70°C

Hydroformylation of 1-Octene (Batch)

Sample	Surfactant	Aq. Phase	Time (h)	Conversion (%)	L/B ^b ratio
R39 ^a	-	-	2.0	20	4.4
R4	CTAB ^c	-	2.5	0.3	-
R13	-	90% EtOH	2.0	0.2	-
R14	-	50% EtOH	2.0	12	1.7
R15A	CTAB	90% EtOH	2.0	19	1.7
R29A	CTAB	50% EtOH	2.0	20	5.8

Reaction conditions: Catalyst H(CO)Rh(TPPTS)₃, Rh 0.089 mmol, 1-octene/Rh = 426, CO/H₂ (molar ratio) = 1, P(CO/H₂) 400 psi, T = 100°C. ^aSingle phase heptane only solvent, catalyst H(CO)Rh(PPh₃)₃.

^bLinear/branched, ^ccetyltrimethylammonium bromide

Hydroformylation of 1-Dodecene (Batch)

Sample	Surfactant	Aq. Phase	Time (h)	Conversion (%)	L/B ratio
R33	CTAB	-	2	0	-
R24	-	50% EtOH	2	0	-
R27	CTAB	50% EtOH	4.6	26	5.3

Reaction conditions: Catalyst $\text{H}(\text{CO})\text{Rh}(\text{TPPTS})_3$, Rh 0.089 mmol, 1-octene/Rh = 426, CO/H₂ (molar ratio) = 1, $P(\text{CO}/\text{H}_2)$ 400 psi, $T = 100^\circ\text{C}$. ^bLinear/branched.

Comparison of Water Soluble Solvents (1-Octene)

Aqueous Phase Components	Olefin Conversion (mol. %)	Linear/Branch Aldehyde Ratio
50:50 THF/Water	9.6	5.0
50:50 Acetone/Water	13	3.8
50:50 Acetonitrile/Water	7.3	5.6
50:50 1,4-dioxane/Water	16	6.0
50:50 Ethanol/Water	20	5.8

Reaction conditions: Catalyst = $\text{H}(\text{CO})\text{Rh}(\text{TPPTS})_3$, CO/H_2 (molar ratio) = 1, $P(\text{CO}/\text{H}_2)$ = 500 psi, $T = 100^\circ\text{C}$, Rxn Time = 2h, nonpolar phase = heptane, surfactant = CTAB.

Continuous Reactor

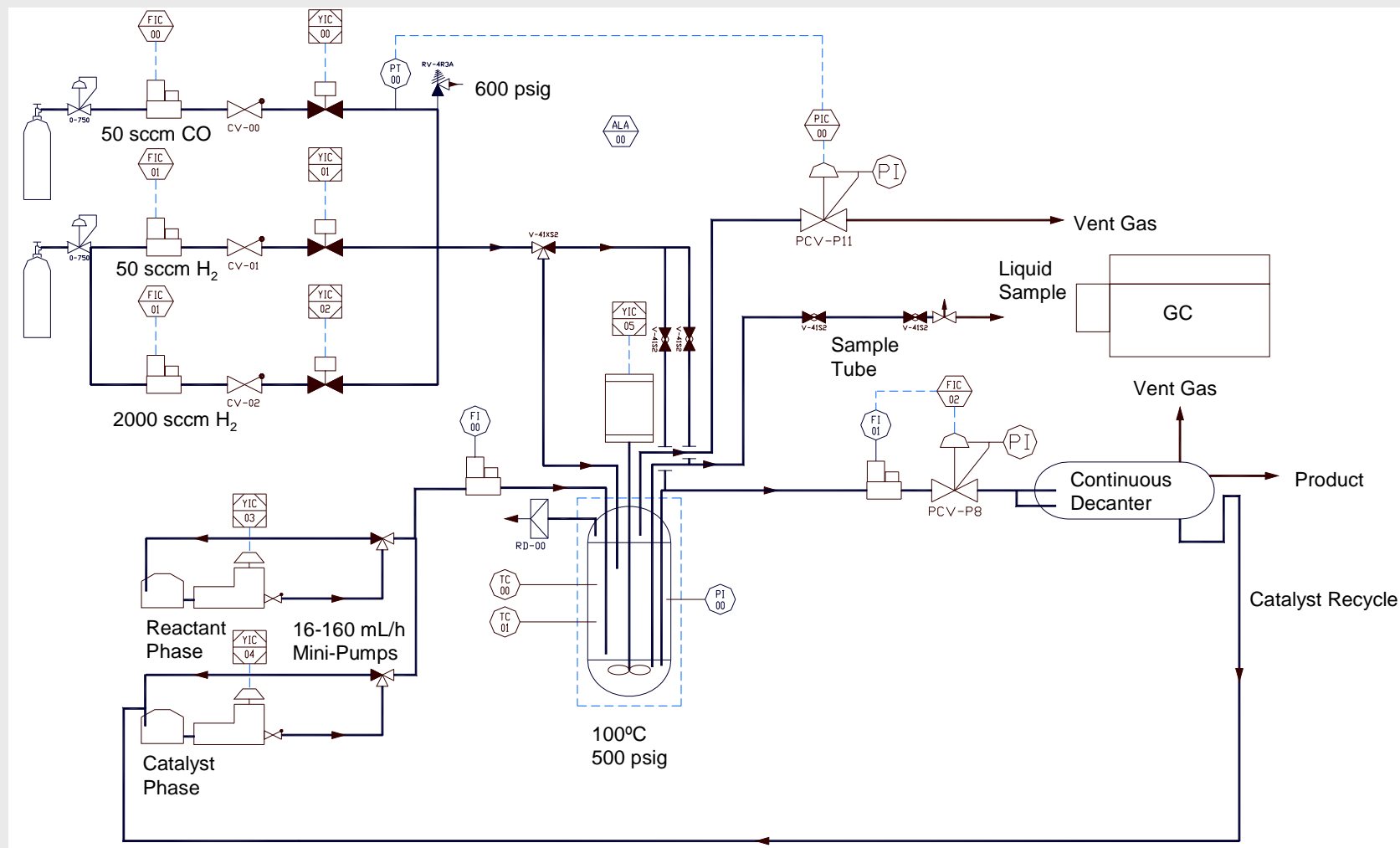
- **Show that our catalyst system can produce higher aldehydes in a continuous reactor with:**
 - High selectivity (linear/branched ratio)
 - Reasonable rates
 - Long catalyst lifetime
 - Low rhodium loss
- **How issue was addressed**
 - Built a bench-scale continuous reactor
 - Did process optimization and long-term testing

Bench-Scale Continuous Reactor



- Reactor body manufactured by Autoclave Engineers
- 300 ml volume
- Fitted with Magnedrive stirrer and Dispersimax™ impeller for improved gas dispersion in liquid
- Rated up to 4700 psig at 200°C
- Computer controlled (OptoControl software)

P&ID of Bench-Scale Continuous Reactor

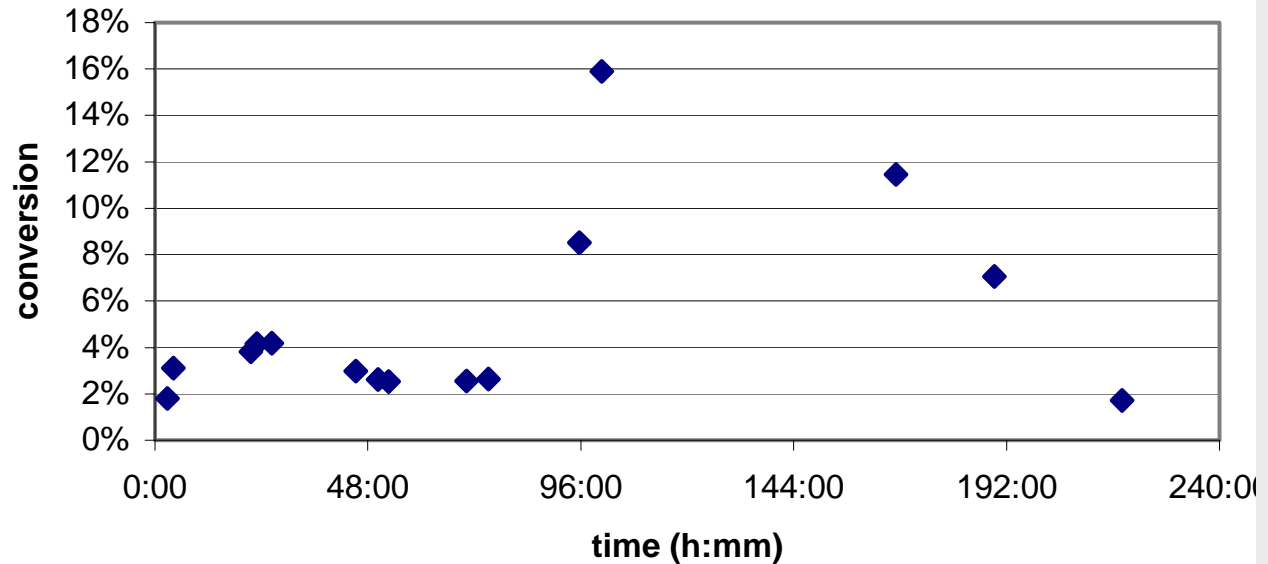


Catalyst System Tested

- **Catalyst: $\text{H}(\text{CO})\text{Rh}(\text{TPPTS})_3$, $4.5 \times 10^{-3} \text{ M}$**
- **Aqueous phase: 1,4-dioxane/water, 1:1 v/v**
- **Surfactant: CTAB, $3 \times 10^{-3} \text{ M}$**
- **Organic solvent: Heptane**
- **Olefin/Rh molar ratio, 500**
- **CO/H_2 (molar ratio), 1**
- **$P(\text{CO}/\text{H}_2)$, 500 psi**
- **Reaction temperature: 100°C**

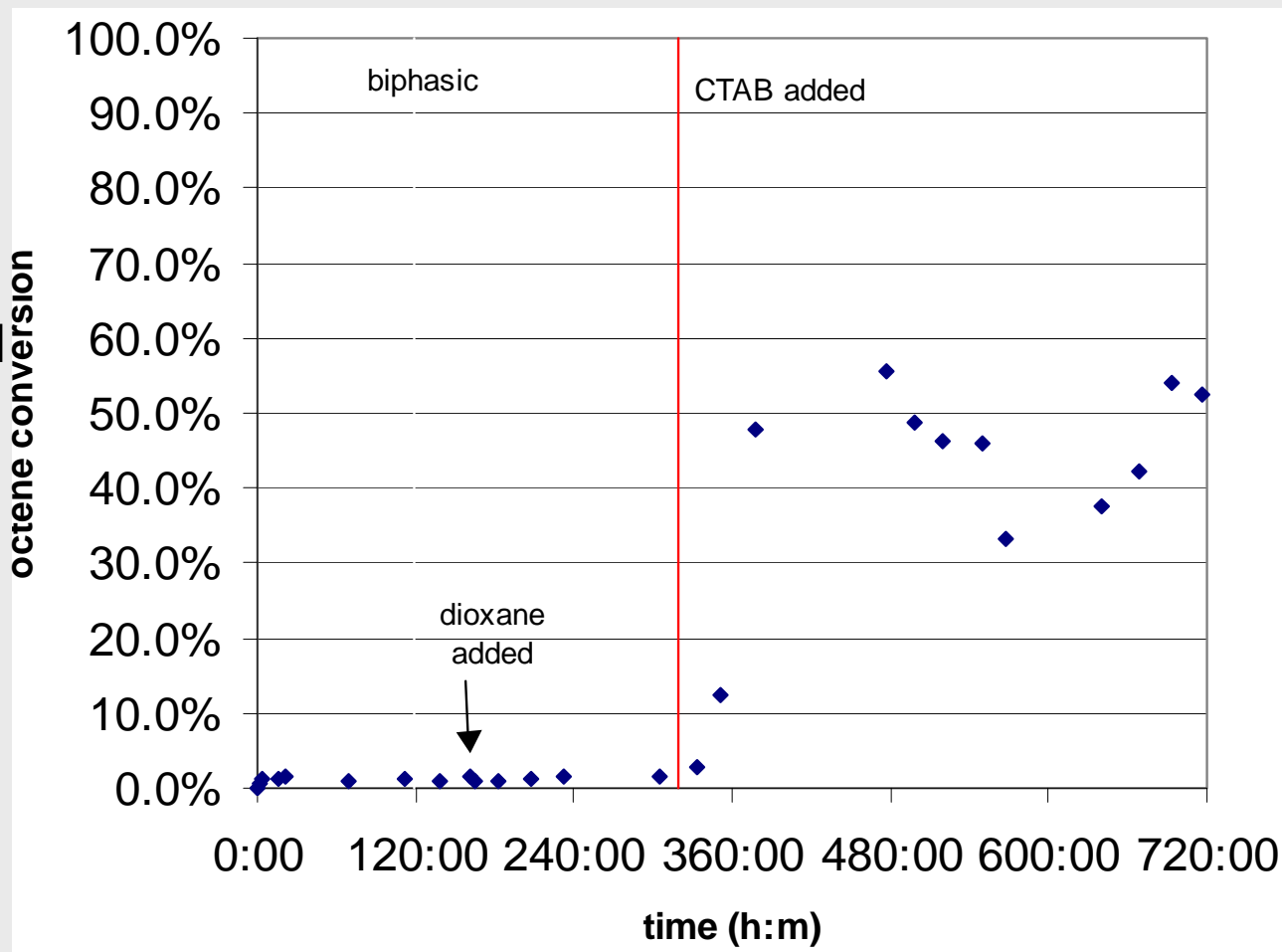
Hydroformylation of 1-Octene in Continuous Reactor

- Linear/branched ratio – 7:1
- Significant loss of catalyst solvent



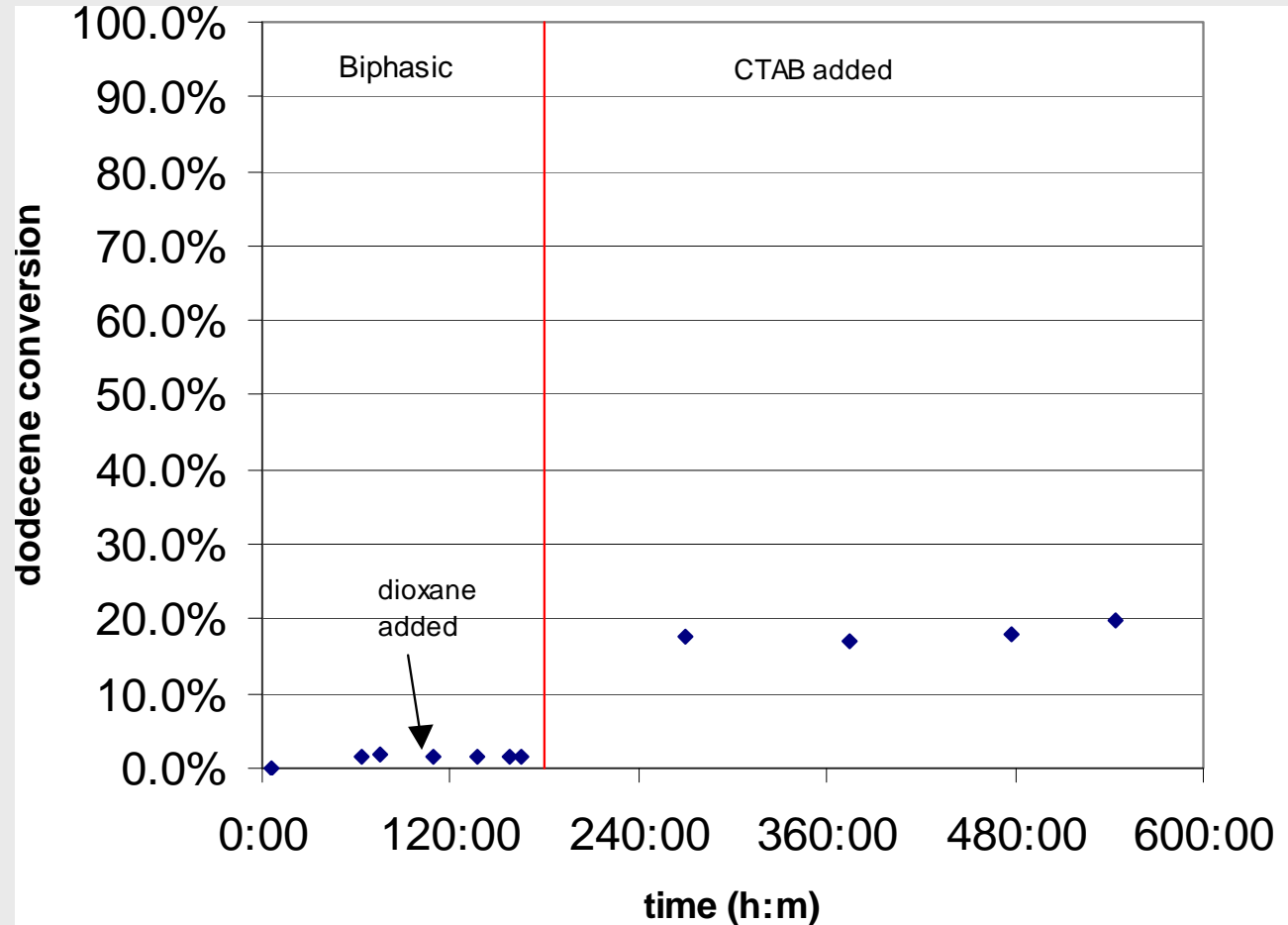
Hydroformylation of 1-Octene in Continuous Reactor

- 1,4-dioxane added to feed 10% v/v
- Linear/branched ratio – 5:1



Hydroformylation of 1-Dodecene in Continuous Reactor

- 1,4-dioxane added to feed 10% v/v
- Linear/branched ratio – 5:1

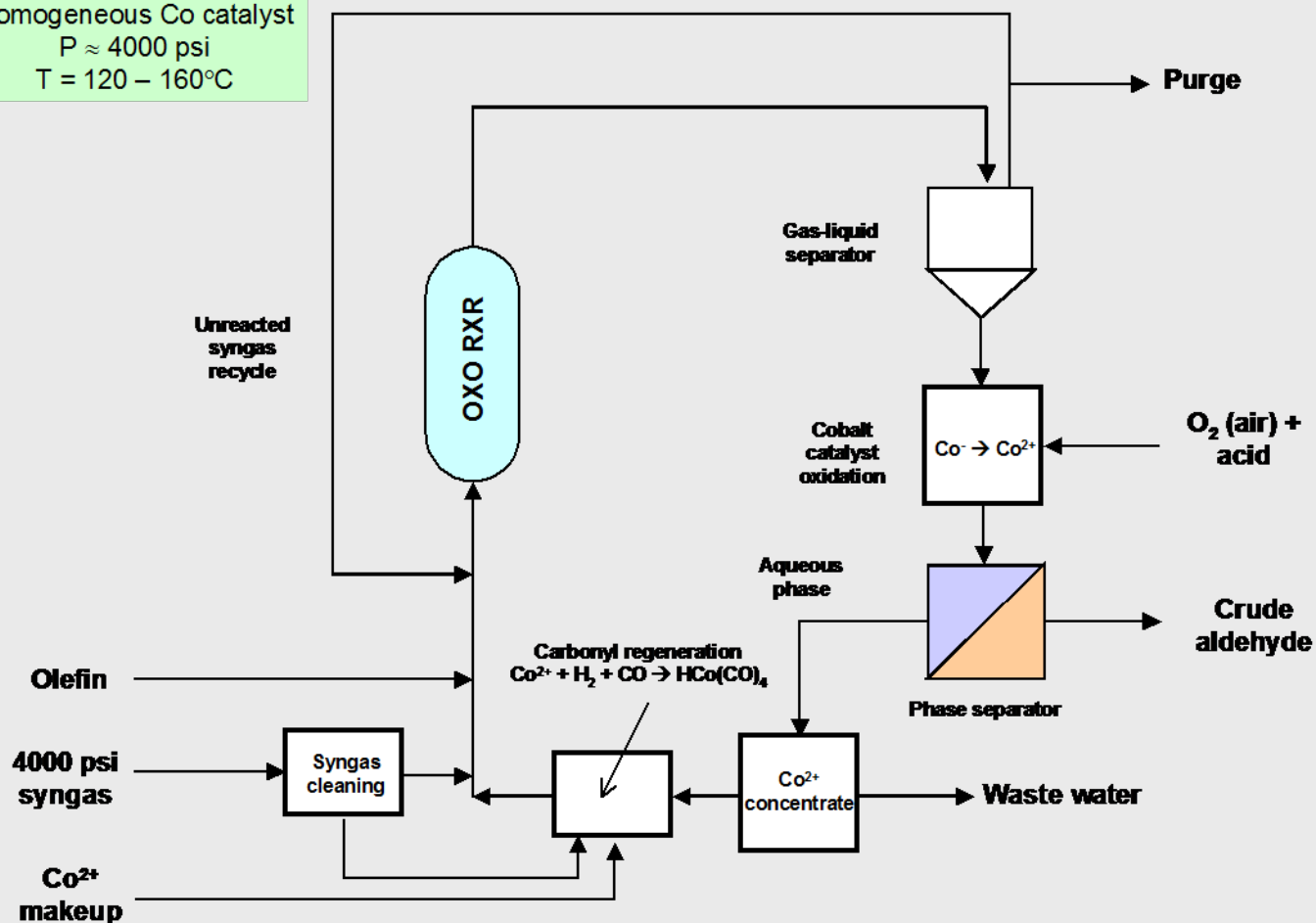


Process Comparisons

- **TDA Thermorphic vs. BASF Higher Olefin**

BASF Higher Olefin Process

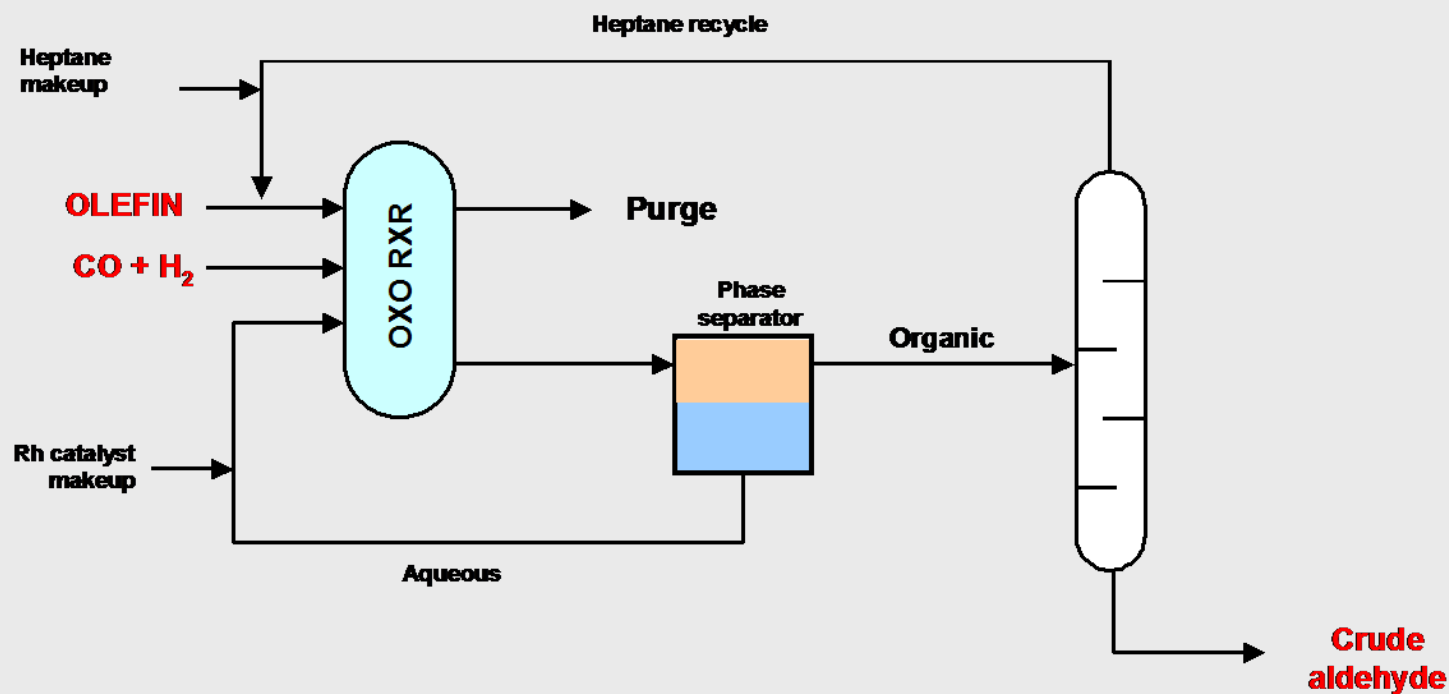
**BASF Higher Olefins
Hydroformylation**
Homogeneous Co catalyst
P ≈ 4000 psi
T = 120 – 160°C



C.D. Frohning, C.W. Kohlpaintner and H.-W. Bohnen in Applied Homogeneous Catalysis with Organometallic Compounds (eds. B. Cornils and W.A. Herrmann)

Wiley-VCH: Weinheim (2002), vol. 1, p. 69

TDA Higher Olefin Process



TDA Higher Olefins Hydroformylation
Thermomorphic Solvent System
Rh catalyst
P ≈ 500 psi
T < 100°C

Cost Comparison of TDA and BASF Higher Olefin Processes

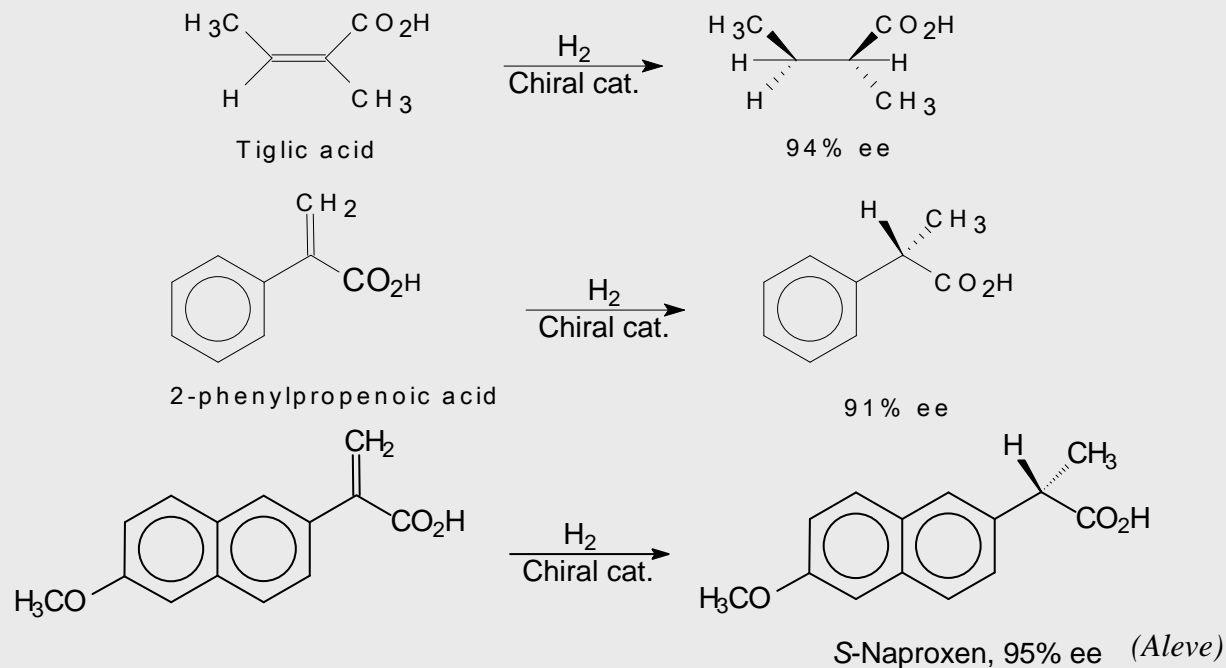
- Higher linear/branch selectivity (5:1 vs. 3:1)
- Over 50% reduction in capital investment costs
 - Fewer unit operations
 - Lower pressure operation (500 psi vs. 4000 psi)

REVENUE SUMMARY	BASF	TDA Thermomorphic
Gross Annual Sales (\$)	15,000,000	15,000,000
Total CAPEX (\$)	15,049,560	6,145,035
Total OPEX (\$)	13,452,521	9,994,744
Capital recovery (20% of CAPX/yr) (\$)	3,009,912	1,229,007
Net Profits (\$)	1,547,479	5,005,256
OPEX (\$/lb product)	0.4484	0.3332
Net Revenue (\$/lb)	0.0516	0.1668
TDA Revenue/BASF Revenue		3.234

Related Work

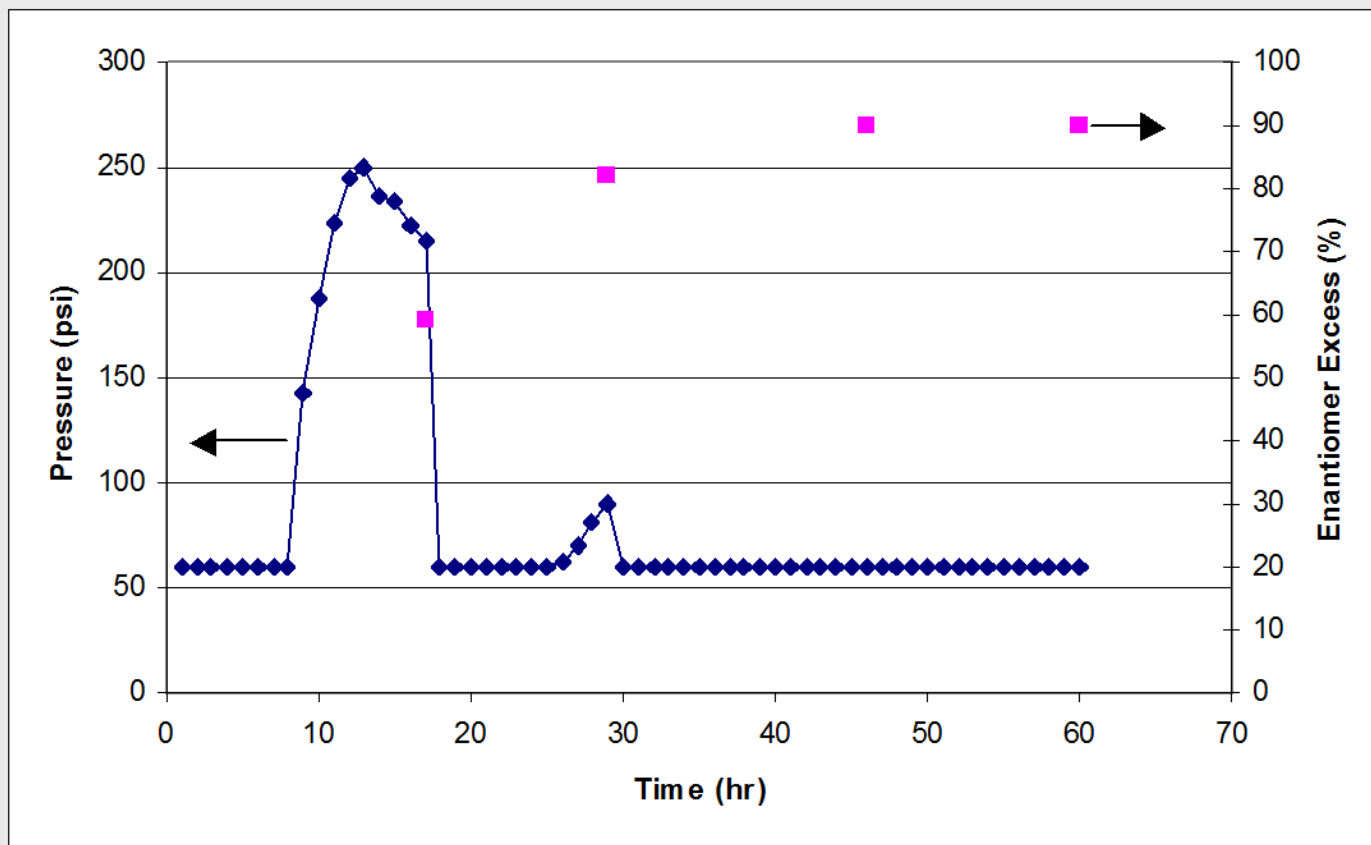
Asymmetric Hydrogenation

- TDA is developing a similar process to make enantiomerically pure products from unsaturated carboxylic acids using a modified ruthenium BINAP catalyst



Ohta, T, H. Takaya, M. Kitamura, K. Nagai, and R. Noyori (1987). "Asymmetric Hydrogenation of Unsaturated Carboxylic Acids Catalyzed by BINAP-Ruthenium(II) Complexes," *J. Org. Chem.* **52**, 3174-3176

Asymmetric Hydrogenation of Tiglic Acid in Continuous Reactor



- >95% conversion
- Catalyst can be easily removed from product
- Catalyst can be reused

Summary

- **Successfully developed thermomorphic catalyst system for hydroformylation**
- **To be successful, an aqueous soluble solvent and a surfactant are needed**
- **Separation of the product aldehyde from the catalyst by simple room temperature decantation**
- **Suitable for conversion of higher olefins to higher aldehydes**
- **High conversion rates and high selectivity**
- **Little catalyst leaching and high catalyst recyclability**
- **Process also applicable to asymmetric hydrogenation**

Acknowledgement

- **This work was funded by the DOE SBIR program**
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