

Butanol Make vs Buy Problem Statement

ABC Acrylate Company has formed a team to evaluate the justification for the construction of a 200 kta Butyl Acrylate plant in China as part of a large integrated Olefin Petrochemical complex which is in the planning phase by the parent company. A key decision in the economic analysis of the site investment is whether to make (in-situ), or buy (externally), n-butanol as a feedstock for the Butyl Acrylate Facility. You have been assigned the task to develop an economic analysis of the Butanol supply choice.

The basis for the Butanol Plant evaluation will be the Dow Low Pressure Oxo Process (LPOSM), which produces n-butanol via a 3 stage process :

- 1) Hydroformylation of propylene and synthesis gas to butyraldehydes.
- 2) Hydrogenation of butyraldehydes to crude butanol.
- 3) Product purification to refined to n-butanol via distillation.

The Hydroformylation of propylene produces both normal and iso-butyraldehydes in an N/I ratio of approximately 10 using the LPO technology. The “iso” molecule can either be removed upstream of the hydrogenation step as a refined isobutyraldehyde product stream, or, it can be hydrogenated to isobutanol and separated during product refining. Your project analysis should develop a recommended outlet for the co-product iso-molecule.

Scope of work required.

Prepare a process diagram for the Butanol plant showing major items of equipment.

Develop an Aspen model of the process incorporating reaction kinetics.

Prepare a material & energy balance for the Butanol process.

Provide a Butanol major equipment list indicating materials of construction and normal operating temperature and pressure.

Estimate the total manufacturing cost (\$/lb) for n-Butanol from this design.

Develop an economic analysis to guide a make vs buy decision for Butanol based on the proposed Butanol plant design. Include raw material sensitivities to reflect the uncertainty of raw material price forecasting.

Develop a recommended market strategy for the by-product iso-molecule, together with end-uses for other plant residue streams.

Develop an economic analysis of the size and number of LPO reactors.

Prepare a detailed Engineering Design (including Aspen Simulation) of the Isomer Distillation Column.

Document the Process Safety Concerns for the process and describe how these risks will be mitigated.

Conduct a Hazop on the Hydrogenation Reactor and define a basic control strategy for the safe operation of the Hydrogenation Reactor.

Economic Data

YEAR/COMPONENT	1	2	3	4	5	6	7	8	9	10
Chemical Grade Propylene, USD/lb	0.468	0.432	0.383	0.356	0.356	0.354	0.373	0.381	0.396	0.412
Syn Gas, USD/lb	0.170	0.167	0.161	0.160	0.159	0.158	0.160	0.163	0.165	0.169
Hydrogen, USD/lb	0.864	0.846	0.819	0.815	0.807	0.805	0.813	0.827	0.837	0.858
Purchased Butanol USD/lb (Cost & Freight SE Asia)	0.612	0.505	0.435	0.427	0.442	0.458	0.470	0.485	0.523	0.539
Isobutanol Sale Price, USD/lb (Cost & Freight SE Asia)	0.558	0.484	0.372	0.388	0.376	0.408	0.410	0.433	0.491	0.497
Isobutyraldehyde Sale Price, USD/lb	0.402	0.477	0.448	0.435	0.430	0.431	0.443	0.452	0.460	0.476

(USD =US \$)

Butanol/Butyl Acrylate Unit Ratio = 0.6 lbs of Butanol/lb of Butyl Acrylate

A minimum of 15% DCF must be attained for any capital investment.

References

Oxo Process, Billig & Bryant, Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley and Sons, 2001.

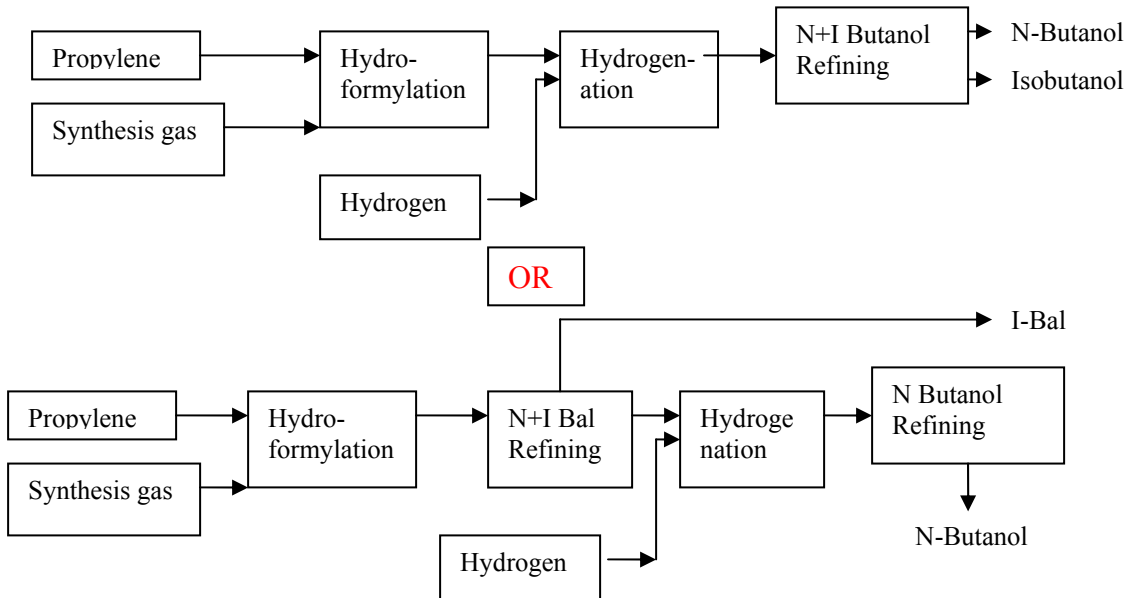
Rhodium Catalyzed Hydroformylation, edited by Van Leeuwen and Claver, Kluwer Academic Publishers, 2002. (ISBN: 978-1-4020-0421-6).

Kirkpatrick Award for Low Pressure Oxo, Chemical Engineering Magazine, 12/5/1977, page 110 (*the Gas Recycle technology described in this article was a precursor of the Liquid Recycle Catalyst Technology shown below*).

Butanol Process Information Summary

Information Needed For Process Design / Simulation

Overall Process Flows:



Feedstock Specifications

1. Chemical Grade Propylene

Characteristic	Unit	Design Value
Propylene	wt%	92.0
Propane	wt%	7.998
Ethylene	wt%	0.002
Sulfur	ppmw	1

Propylene Purification

- Sulfur removal from 1 ppmw inlet to 0.1 ppmw outlet is required as LPO feed gas, solid phase Zinc Oxide adsorbent, liquid propylene.
- Operating Temperature ambient; Design Propylene Loading 100 lb/hr/ft³.
- Maximum Bed Loading: 1 wt.% sulfur

Notes :

1) The following side reaction should be considered in design.

Ethylene + 2 H₂ + CO → propanol (assume complete conversion of ethylene).

2) For details on typical Chemical Grade Components see :

<http://www.mrw.interscience.wiley.com/emrw/9780471238966/kirk/article/propcala.a01/current/pdf>.

2. Synthesis gas

Characteristic	Unit	Design Value
Hydrogen	mol%	52.0
Carbon Monoxide	mol%	47.0
Methane	mol%	0.7
Carbon Dioxide	mol%	0.27
Water	mol%	0.03

3. Hydrogen

Characteristic	Unit	Design Value
Hydrogen	mol%	90.0
Methane	mol%	10.0

Product Specifications

n-Butanol

Charateristic	Unit	Spec Limit
Butanol	wt%	≥ 99.8
Isobutanol	wt%	≤ 0.1000
DiButyl Ether	wt%	≤ 0.025
2-Ethylhexanol	ppmw	≤ 150
Total Butyrates	ppmw	≤ 50.00
Water	wt%	≤ 0.05
Color	PtCo	≤ 5
Total Carbonyl	wt%	≤ 0.005

Isobutanol

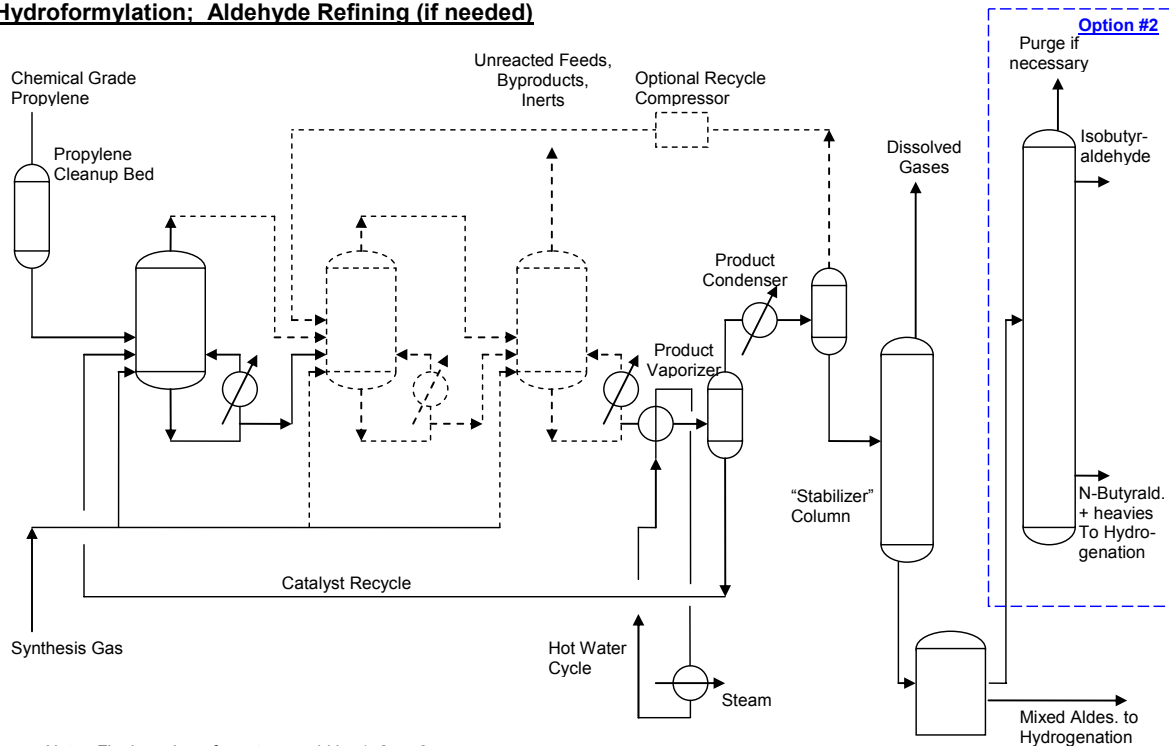
Characteristic	Unit	Spec Limit
Isobutanol	wt%	≥ 99.5
Butanol	wt%	≤ 0.1
Propanol	wt%	≤ 0.1
Water	wt%	≤ 0.05
Total Carbonyl	wt%	≤ 0.07
Color	PtCo	≤ 5

Isobutyraldehyde

Characteristic	Unit	Spec Limit
Isobutyraldehyde	wt%	≥ 99.5
n-butyraldehyde	Wt%	≤ 0.4
Water	wt%	≤ 0.05
Color	PtCo	≤ 10

Hydroformylation Process

Hydroformylation: Aldehyde Refining (if needed)



Note: Final number of reactors could be 1, 2, or 3, with or without the recycle compressor

- The system can be designed as a low-conversion system with propylene recycle, or a high conversion system with more reactors and catalyst, and no recycle, or something in between. So, the size and number of CSTRs in series, and whether or not a compressor is used to recycle unreacted propylene, must be determined. Choose 2-3 representative cases and compare their economics to determine the best arrangement. Considerations should include capital cost, catalyst costs, and operating costs.

- Assume the following reaction conditions for each reactor:

Temperature = 95°C

Pressure = 240 – 340 psig, include 20 psig drop between reactors

MOC = 304 SS or 304 SS Clad

Reactor volume = Catalyst must not occupy more than 3/4 of total reactor Volume

Triphenylphosphine Concentration = 12 wt.% in the liquid phase of the first reactor.

Hydrogen partial pressure must be at least 40 psi in each reactor vent.

Carbon Monoxide must be between 5 and 15 psi in each reactor vent

- Assume the heat of reaction is removed via an external heat exchanger cooled with cooling water.

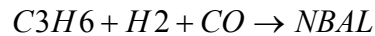
- Butyraldehyde trimer is a common byproduct that is not in most physical property sets. You can model “trimer” using 1-dodecanol instead (you

must change its molecular weight to $72.1 \times 3 = 216.3$).

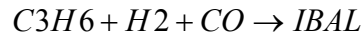
- Hydroformylation Reactions, Kinetics

(time units are seconds, concentration is in gmol/L)

CO partial Pressure (psi)	N/I	k, propane
5	13	0.0046
10	10	0.0045
15	7	0.0040



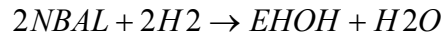
$$\frac{d[NBAL]}{dt} = 1.65 \frac{N/I}{N/I + 1} [C_3H_6][H_2]^{0.2}[CO]^{0.4}$$



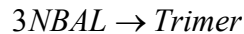
$$\frac{d[IBAL]}{dt} = 1.65 \frac{1}{N/I + 1} [C_3H_6][H_2]^{0.2}[CO]^{0.4}$$



$$\frac{d[C_3H_8]}{dt} = k[C_3H_6][H_2]^{0.2}$$



$$\frac{d[EHOH]}{dt} = 1.0 \times 10^{-6} [NBAL][H_2]^{0.2}$$



$$\frac{d[Trimer]}{dt} = 2.0 \times 10^{-6} [NBAL]$$

Ethylene + 2 H₂ + CO → n-Propanol - assume complete conversion

Hydroformylation Catalyst:

The catalyst is TPP-modified rhodium. Fresh catalyst costs \$50/liter, lifetime is 2 years, and for \$5/Kg of spent catalyst solution processing fee, 50% of the rhodium can be recovered from a spent catalyst.

Product Removal

Use a simple shell/tube heat exchanger with a knockout pot; hot water on shell side to minimize delta T to limit thermal exposure.

Assume the flash that removes the product operates at a low pressure (above atmospheric). Note that the triphenylphosphine concentration in the catalyst recycle to the reactor should not exceed 40 wt.% (solubility concerns).

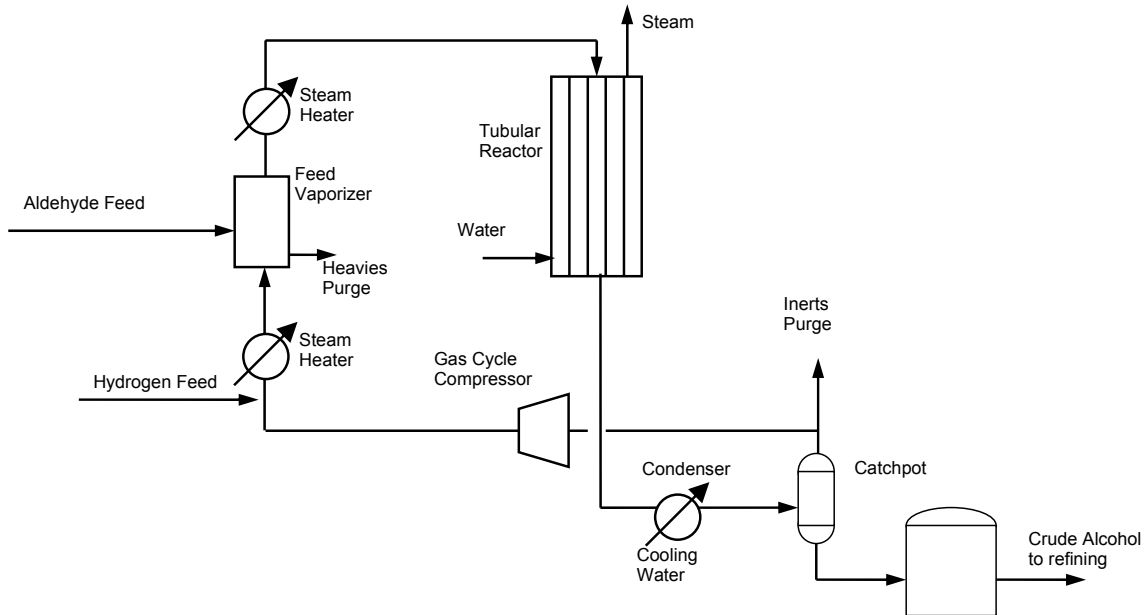
“Stabilizer”

- The primary purpose of the “Stabilizer” is to remove CO from the crude product to avoid personnel exposure issues in the crude product tanks. For this exercise, use a specification limit of 10 ppmv CO in the liquid product. The purity specification on the mixed aldehydes from the Stabilizer should be assumed to be 99.9 wt.%.

Compressor

Depending on the single pass raw material conversion selected, a compressor can be used to recycle unreacted propylene back to the reactor.

Hydrogenation Process:



Design Assumptions:

The reactor design is similar to a shell-and-tube heat exchanger, with catalyst in the tubes and water on the shell. Heat is removed by converting the water to steam.

$$\text{Rate, (gmol/hr/gm unreduced catalyst)} = k \{P_{\text{ald}}/(P_{\text{H}_2})^{0.5}\}$$

P_{ald} = Partial press of aldehyde (psi)

P_{H_2} = Partial press of Hydrogen (psi)

$$\ln k = -E/RT + \ln A \quad \text{where } R = \text{Gas Constant, } T = \text{Temp K}$$

$$E = 7800, \ln A = 5.31$$

Target Conversion: 98%

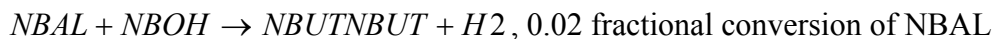
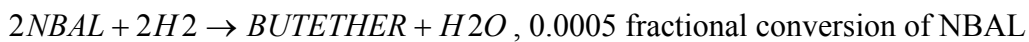
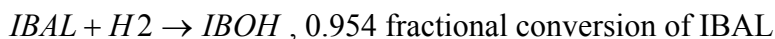
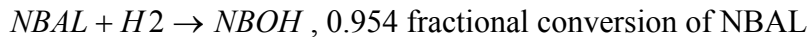
Byproduct selectivities:

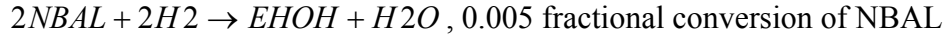
n-Butyl n-Butyrate: 2.0 %

di-n-butyl ether: 0.1%

2-ethylhexanol: 0.5 %

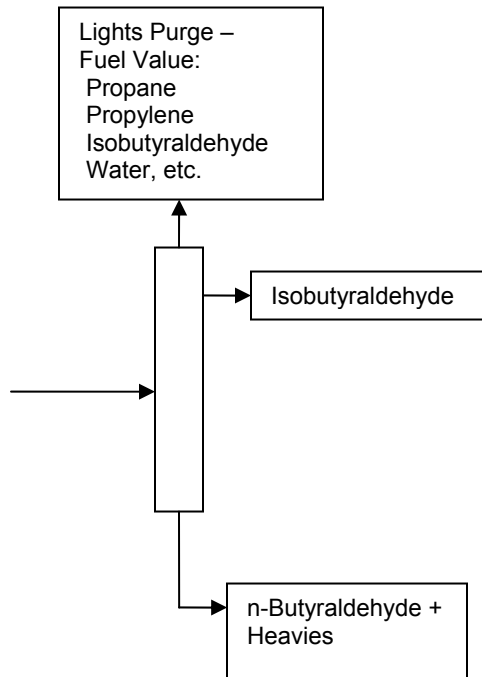
Reactions, Kinetics, etc.:



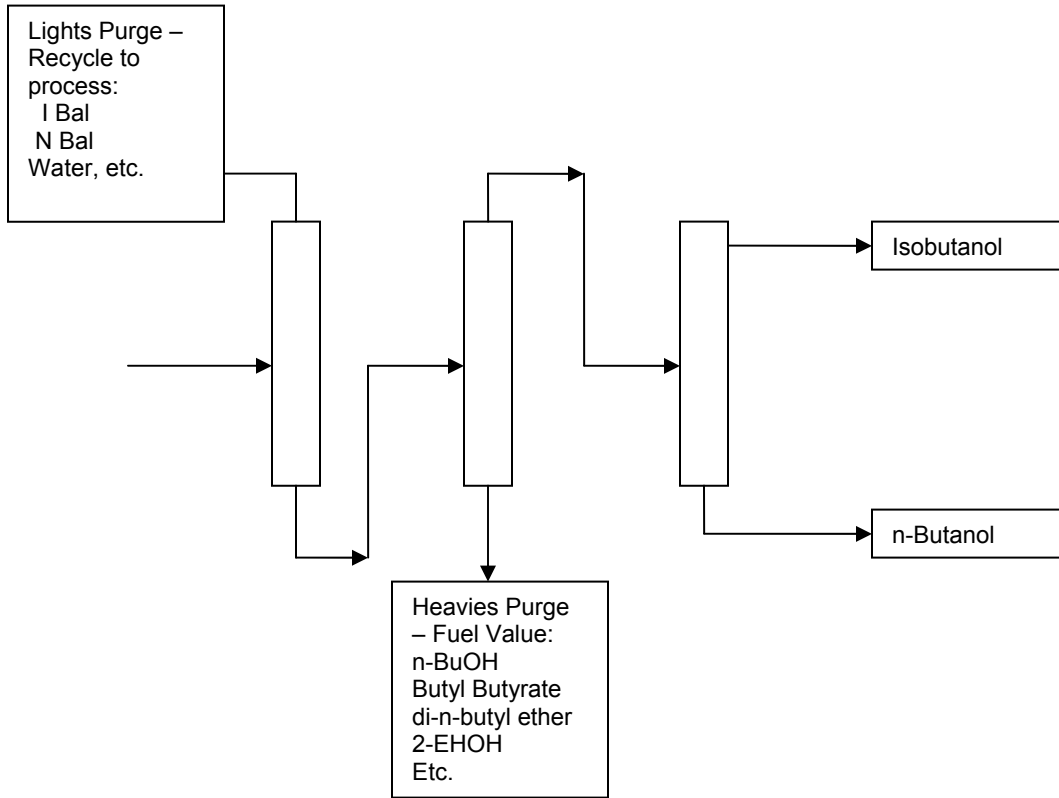


- Catalyst: Copper-based catalyst of size/shape 1/8" tablet
- Operating Temperature: 145 – 190°C
- Reaction pressure: 100-200 psig
- Reactor inlet composition: hydrogen / aldehyde mole ratio should be 10:1
- Reactor inlet temperature should be at least 10°C above the dew point of the stream
- Losses of hydrogen out the “inerts purge” should be 10% of the hydrogen feed or less
- Heavies are purged from the aldehyde feed using the vaporizer as a single stage flash

Butyraldehyde Refining:



Butanol Refining:



Run the columns at the lowest practical pressure above atmospheric.

Component List and Physical Properties

Use the following component list:

<i>Component Name</i>	<i>Trivial Formula in Aspen Plus</i>
N-BUTYRALDEHYDE	C4H8O-1
ISOBUTYRALDEHYDE	C4H8O-2
N-BUTANOL	C4H10O-1
ISOBUTANOL	C4H10O-3
HYDROGEN	H2
CARBON-MONOXIDE	CO
PROPANE	C3H8
PROPYLENE	C3H6-2
N-BUTYL-N-BUTYRATE	C8H16O2-D1
2-ETHYLHEXANOL	C8H18O-3
BUTYL-ETHER	C8H18O-4
BUTYRALDEHYDE TRIMER*	C12H24O3
METHANE	CH4
CARBON-DIOXIDE	CO2
WATER	H2O
ETHYLENE	C2H4
1-PROPANOL	C3H8O-1
TRIPHENYLPHOSPHINE	C18H15P

*Use 1-DODECANAL as a substitute for butyraldehyde trimer

Nearly all of these components are available in the PURE13 database available in Aspen Plus version 12.1. The exception is butyraldehyde trimer – use 1-dodecanal as a substitute molecule. Supply the correct molecular weight for trimer as 216.32076 g/mol in the *Pure Component Properties* folder.

Use the NRTL-RK property method for this system. Treat hydrogen, carbon monoxide, propane, carbon dioxide, methane, ethylene, and propylene as Henry components. Use the default Henry parameters from the HENRY database. Also, use the NRTL binary interaction parameters available in the VLE-RK database.

If Aspen Plus gives an error regarding missing Henry constants, use the databank values for hydrogen in n-butanol.