**Butadiene to n-Butyraldehyde and n-Butanol**  
(recommended by Bruce Vrana, DuPont)

n-Butyraldehyde is conventionally produced from propylene and highly toxic synthesis gas in the so-called oxo process. The n-butyraldehyde is used to make 2-ethyl hexanol via aldol condensation as well as n-butanol. These oxo alcohols are frequently used, in either the alcohols or ester form, as solvents.

Because propylene is frequently quite expensive and in short supply, BASF has applied for a patent on a new route to n-butyraldehyde and/or n-butanol starting from butadiene. They found that a homogeneous palladium acetonylacetonate catalyst with phosphine ligands would allow butadiene to react with n-butanol to produce 1-n-butoxy-2-butene (nBB). nBB will then react with more n-butanol to produce the acetal, using a homogeneous phosphine modified ruthenium catalyst. The acetal can be hydrolyzed to n-butyraldehyde, or hydrogenated and hydrolyzed to n-butanol using the same Ru catalyst.

\[
\begin{align*}
CH_2=CHCH=CH_2 + BuOH & \rightarrow BuO-CH_2CH=CHCH_3 \quad [\text{nBB}] \\
nBB + BuOH & \rightarrow (BuO)_2CHCH_2CH_3 \quad [\text{Acetal}] \\
Acetal + H_2O & \rightarrow O=CHCH_2CH_2CH_3 + 2 BuOH \\
Acetal + H_2 + H_2O & \rightarrow 3 BuOH
\end{align*}
\]

Unfortunately, in the first reactor, a side reaction produces 2-butoxy-3-butene (iBB). The iBB can be isomerized to nBB using an acid ion exchange resin or a Pd catalyst. Unfortunately, this isomerization reaction is likely to be equilibrium limited.

BASF also found that while this reaction works well with pure butadiene, it will also work with "crude" butadiene, the C4 olefin cut from an ethylene cracker. The butenes in the C4 cut are inert under the reaction conditions.

Your company has asked your group to determine whether this new technology should be used in your Gulf Coast plant, and if so, what the economic optimum feedstock and product would be. The goal is to maximize the net present value (NPV) of the project. Based on past
experience, you know that you will have to be able to defend any
decisions you have made throughout the design, and the best defense is
economic justification.

Your company has 200 MM lb/yr of crude butadiene, which is currently
being burned for fuel value. Thus, one possible feedstock would be the
butadiene contained in the crude. You would receive a credit for the
unused C4’s in the stream, so you would only have to pay fuel value for
the butadiene you actually consume in the process. Of course, the inert
C4’s will dilute the reactor contents, making it larger, and complicate the
separation train. As an alternative, you could purchase pure butadiene for
$0.15/lb in 2001 dollars, which would result in smaller vessels.

The composition of your plant's C4 cut, which has already passed through
your MTBE plant to react away the isobutylene, is:

- 43% BD
- 28% 1-butene
- 10% cis-2-butene
- 10% trans-2-butene
- 6% n-butane
- 3% isobutene

For a product, you could produce n-butyraldehyde or n-butanol, or some
combination of the two. Your marketing organization believes they could
sell the aldehyde for $0.40/lb, and n-butanol for $0.40/lb also, both in
2001 dollars.

The plant design should be as environmentally friendly as possible.
Recover and recycle process materials to the maximum economic extent.
Also, energy consumption should be minimized, to the extent
economically justified. The plant design must also be controllable and
safe to operate.

Reference:

World Patent Application 98/41494 to BASF