

Value Proposition and Modeling of Solvent Changes

Recall from the introductory article the steps to a well-framed value proposition:

- Describe the situation
- Identify the need
- Develop a model
- Probe for solutions
- Identify value points
- Quantify pricing and cost assumptions
- Evaluate proposed solutions

This example applies these principles to a simple operational debottleneck.

Background to this Example

Solvents and additives are used in numerous industrial reactions, for example:

- Homogeneous catalysis for hydroformylation of olefins (“Oxo process”)
- Air oxidation of p-xylene to terephthalic acid
- Butadiene hydrocyanation to adiponitrile
- Methanol carbonylation to acetic acid
- Hydrogen peroxide via anthraquinone

The solvents may improve solubility of a reactant or catalyst; an additive may increase catalytic selectivity or activity. However, the recovery and recycle of the solvent can consume significant energy and limit the capacity of an existing facility. In general, two approaches can be taken to address this issue:

- Replace the solvent
- Modify the reaction conditions or catalyst to accommodate less solvent

Example Reaction in Solvent

Consider a hypothetical reaction $A + B \rightarrow C$ with a solvent S of some concentration. The catalyzed reaction essentially goes to completion and the product is recovered by vaporization along with some solvent. The catalyst stays in the liquid phase. Product C and solvent S are then separated in a distillation column. Figure 1 shows such a process.

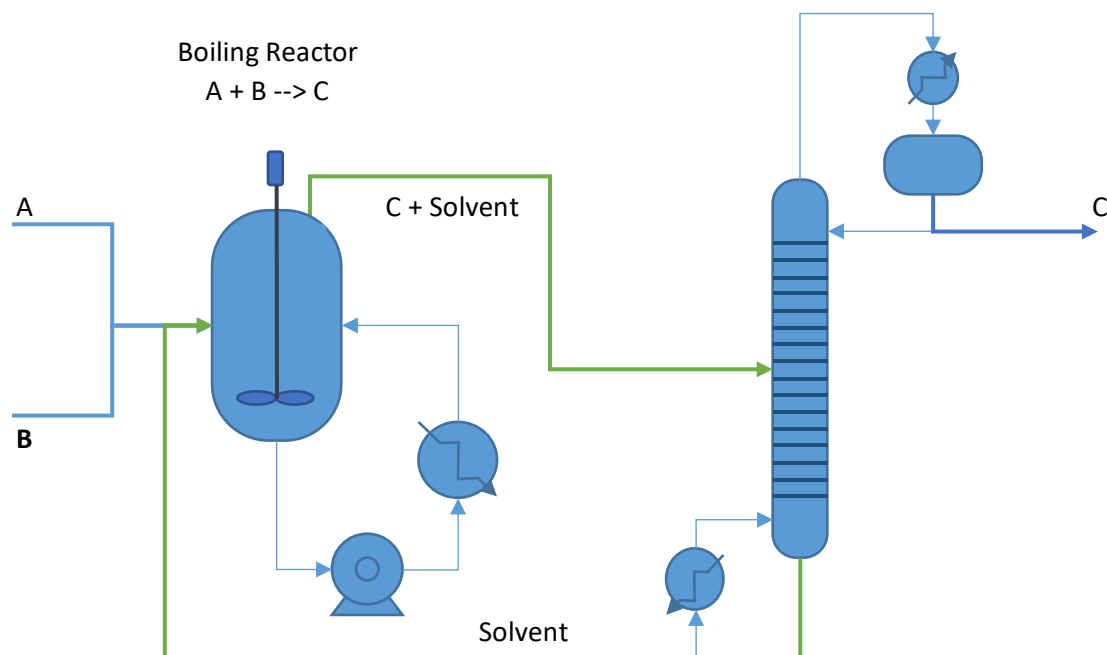


Figure 1 Hypothetical $A + B \Rightarrow C$ with Solvent in Boiling Reactor

To better illustrate an example of such a process, consider the hydroformylation of propylene to butyraldehyde in a solvent such as toluene¹. *As this is an illustrative example, the values and conditions used herein are fictitious and chosen by the author to demonstrate an approach for determining value proposition.*

This example assumes the following current operating conditions:

- Essentially complete conversion of propylene, H₂, and CO in stoichiometric amounts in the reactor
- Atmospheric operation
- 20,000 lb/hr of butyraldehyde produced
- Reaction conditions:
 - 60 wt% toluene in the reactor
 - One hour residence time
- Distillation Design
 - 99.95% Butyraldehyde purity with 90% recovery in the distillate
 - 17 theoretical stages
- Utilities
 - Cooling water available at 90F, returned at 110F
 - Low pressure steam available at 300 F

The reaction is exothermic at -926 BTU/lb butyraldehyde. It should be noted that this is sufficient to boil material overhead and the reactor requires net cooling.

¹ See, for example, US patent 4041082 A

Identify the Need

To set the stage, the business is contemplating a grass-roots investment to meet growing demand. The R&D department is first asked if there is anything they can do to debottleneck the existing process. Their efforts identify candidates for new solvents and catalyst additives that yield equivalent conversion (near 100%) at reduced residence times and solvent concentrations. These results are given to the process engineer to determine if there is any incremental plant capacity available with these conditions. These hypothetical results are shown in Table 1.

Table 1 Hypothetical Development of New Catalyst/Solvent Systems for Propylene Hydroformylation

Solvent:	Benzene	Toluene	Ethylbenzene	p-Xylene
Wt% Solvent	60%	50%	45%	45%
Residence time, hr	0.65	0.7	0.75	0.8

The researchers note that operating pressure was kept constant at 1 atmosphere, allowing reaction temperature to fluctuate with solvent and concentration.

A simplified model

The simplified model described here is no substitute for rigorous simulation, but it serves to illustrate the concepts involved with analyzing the options in Table 1.

Two key assumptions allow this process to be easily modeled with a spreadsheet:

- Only butyraldehyde and solvent exist in the reactor, for the purposes of enthalpy and VLE calculations. This condition is based on the assumption of near complete conversion of reactants.
- Butyraldehyde and solvent behave as ideal VLE. The distillation is modeled using Fenske-Underwood shortcut design.

The current conditions and those in Table 1 are modeled for 20,000 lb/hr product, with two degrees of freedom in the process design:

- The recovery of butyraldehyde in the distillate, the remainder returned with solvent to the reactor
- The reflux ratio, or more specifically, the ratio relative to the minimum to achieve design.

These are subject to the constraint that the required number of stages, $N_{stage} \leq 17$, given the current distillation column.

Equipment capacity ratios, R_{ec} , compare the equipment utilization in the proposed case versus current operation:

- For exchangers: $R_{ec} = UA_{proposed}/UA_{current}$, where $UA = Q/\Delta T$
- For the reactor: $R_{ec} = (\omega T)_{proposed} / (\omega T)_{current}$
 - Where ω = reactor throughput = distillation feed, lb/hr

- T = residence time, hr
- For the distillation column: $R_{ec} = (\text{Diameter}_{\text{proposed}} / \text{Diameter}_{\text{current}})^2$
 - Where Diameter is calculated using the Kister and Haas correlation ²

The degrees of freedom, butyraldehyde recovery and reflux ratio, are optimized to minimize equipment utilization with 20,000 lb/hr product for each of the conditions in Table 1. The new capacity C available with the new catalyst/solvent system is thus

$$C = 20,000 / R_{ec}^{max}$$

where ^{max} refers to the maximum of all the equipment ratios.

Probe for Solutions

The process engineer in our hypothetical example prepares the following table.

Table 2 Model Results: Process Design and Capacity Potential for Hypothetical Changes in Hydroformylation Catalyst. See also Table 1.

	Current	Benzene	Toluene*	Ethylbenzene	p-Xylene	
Distillation Design						
Benzaldehyde Recovery	90%	N/A	67%	58%	56%	
R/R _{min}	1.4	N/A	1.3	2.8	3.3	
Intermediate Values						
$\alpha_{\text{butyraldehyde/solvent}}$	2.97	1.18	2.97	6.77	7.25	
Temperatures, °F						
Reactor	194	Insufficient Stages to meet Distillation Specs	188	189	189	
Reboiler	213		188	177	176	
Condenser	167		167	167	167	
Duties, MMBTU/hr						
Reactor	12.5		11.3	11.4	11.2	
Reboiler	5		1	0	0	
Condenser	11		9	7	7	
Distillation Feed, lb/hr	33448		40013	38362	36938	
Equipment Capacity Ratio, R_{ec}						
Reactor			0.91	0.92	0.94	
Reactor Cooler		0.91	0.92	0.94		
Distillation Column		0.84	0.72	0.70		
Distillation Reboiler		0.16	Not needed	Not needed		
Distillation Condenser		0.83	0.72	0.70		
Capacity, lb/hr Butyraldehyde		22001	21696	21184		

* Toluene is also used in "current conditions" but with different catalyst system

² Henry Kister, "Distillation Design", McGraw-Hill, 1992. See 6.5.3.

A few points about the above results:

- Relative volatility of the product benzaldehyde to benzene, at 1.18, requires more stages to affect the required product purity than is available with the current distillation column, designed with a relative volatility of 2.97 for benzaldehyde to toluene. Thus, the benzene option is not viable as a retrofit.
- Benzaldehyde is easier to separate from the C8 aromatics than from toluene, thus requiring a smaller reflux ratio. In fact, no reboiler is required and the distillation is a simple rectifying section with vapor feed at the bottom. Note this would require some piping rearrangements.
- The proposed cases are compared to the current design, not to the actual equipment constraint. If the equipment is not uniformly sized for the current design, there may be additional capacity due to oversized equipment in the current design.

Identify Value Points and Quantify Pricing and Cost Assumptions

The value propositions for changing catalyst system include:

- Incremental capacity with little or no capital cost
- Potential utility reduction (\$5/MMBTU steam by way of example)
- Lower capital cost for new plant of similar production

The incremental capacity realizes incremental revenue at raw material margin along with any adjustments for changes in utilities. For this hypothetical example, we will use 10 cents/lb butyraldehyde as the raw material margin, and plant operation at 8300 hours per year.

In addition, the new catalyst system would lower capital costs on future plants. For this hypothetical example, we will use \$50 million as the installed cost for a plant identical to the current case, and use a 0.6 exponent on capital scaling.

Some considerations not taken into account here should be identified as well. These include:

- Operation at pressures other than atmospheric were not explored and may enhance value.
- The cost of any new catalyst is not addressed, nor is solvent makeup.
- Incremental capacity may not be sufficient to forego a new plant investment.
- Full development of the new technology will require R&D and engineering costs and may delay when new capacity is available.

Evaluate the Value Proposition of each Alternative

The engineer prepares the following Table 3 showing incremental revenues for selling incremental capacity available with the proposed cases. The table also summarizes the capital savings on new plants of the same 20,000 lb/hr capacity.

Table 3 Value Proposition for Hypothetical Debottleneck with new Solvent / Catalyst Systems

	Current	Toluene	Ethylbenzene	p-Xylene
Variable Margin, \$MM/yr	16.6	18.3	18.0	17.6
Energy (reboiler), \$MM/yr	-0.2	-0.0	0	0
Proposed Retrofit Value, \$MM/yr		1.8	1.6	1.2
New Plant Capital, \$MM	50	47.2	47.6	48.3
Proposed New Capital Savings, \$MM		2.8	2.4	1.7

In Summary

This example shows the thought process to generate a value proposition for changing solvents in a boiling reactor, such as might be the case for hydroformylation of olefins. A simple spreadsheet model helps to analyze the impact of a solvent change on equipment capacity, given the effects on reaction conditions, and on relative volatility with the product. Product recycle from the distillation section is a free variable to optimize existing equipment capacity. Incremental capacity gained by the new solvent is valued at the variable margin of the product sold. Energy differences in design are also accounted for.