Chemical Process Research Lab.

압력 변환 증류를 이용한 메탄올-아세톤의 분리공정 모델링 및 최적화 연구

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Abstract

Acetone-methanol system forms an azeotrope at 77.6% by mole of acetone in acetone-methanol mixture under atmospheric pressure. Acetone can be purified from water by pressure swing distillation process since the azeotropic composition is very sensitive to the system pressure. Pressure swing distillation process is more environmental-friendly than azeotropic or extractive distillation process because azeotropic distillation process uses an entrainer and extractive distillation process utilizes a solvent.

In this study, modeling and comparison works have been performed for low-high columns and high-low columns configurations. Optimal operating conditions that minimize the total reboiler heat duty were determined by using feed stage locations and reflux ratios as manipulated variables for each distillation column. Overhead vapor stream of high pressure distillation column was used as a reboiler heating source for the low pressure column to reduce high temperature and low temperature utility consumptions.

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A. Introduction and Basic Principles

If a binary **azeotrope** changes composition over a moderate range of pressure, consideration should be given to using two ordinary distillation columns operating in series at different pressures.*

This process is referred to as pressure-swing distillation.

- **Azeotrope** ~ mixture of two or more liquids wherein its components cannot be altered by simple distillation because they share a common boiling point and vaporization point.

- **Methods to separate an Azeotropic Mixture:**
  - Extractive Distillation
  - Azeotropic Distillation
  - Vacuum Distillation
  - Pressure-Swing Distillation

Pressure swing distillation process is more *environmental-friendly* than azeotropic or extractive distillation process because azeotropic distillation process uses an entrainer and extractive distillation process utilizes a solvent.

Reference:
*Seader, J. D., Henley, E. J. & Roper, D. K. *Separation process principles: chemical and biochemical operations*, 3rd ed., John Wiley & Sons, Inc., United State of America, 2011. pp. 429-442

A.1 Pressure Swing Distillation

- **Pressure-swing distillation** is a method for separating a pressure-sensitive azeotrope that utilizes two columns operated in sequence at two different pressures.

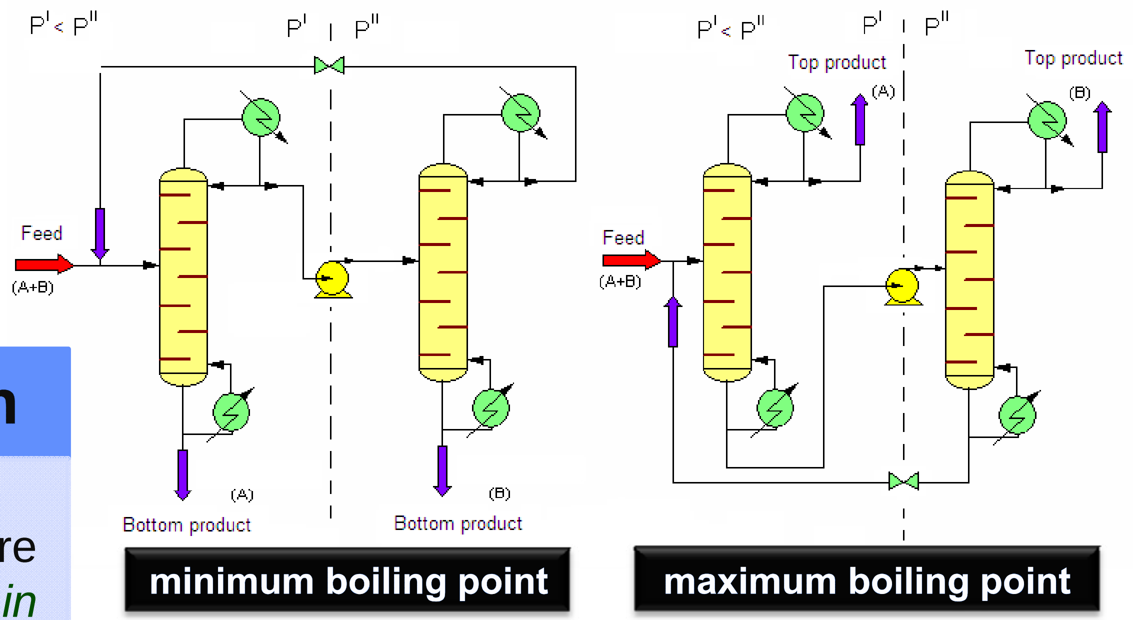


Figure A.1 Types of Separation of Azeotropic Mixtures

Principle of Separation

- simple *change in pressure* can alter relative volatility of the mixture
- can result to a significant *change in the azeotropic composition* or *enlarging the relative volatility* of the components with very close boiling points
- allows the recovery of feed mixture *without adding a separating agent*.

Equilibrium relationship

$$K_i = \frac{y_i}{x_i} = \frac{P_i^{vap}(T)}{P}$$

Relative Volatility

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{y_i/x_i}{y_j/x_j}$$

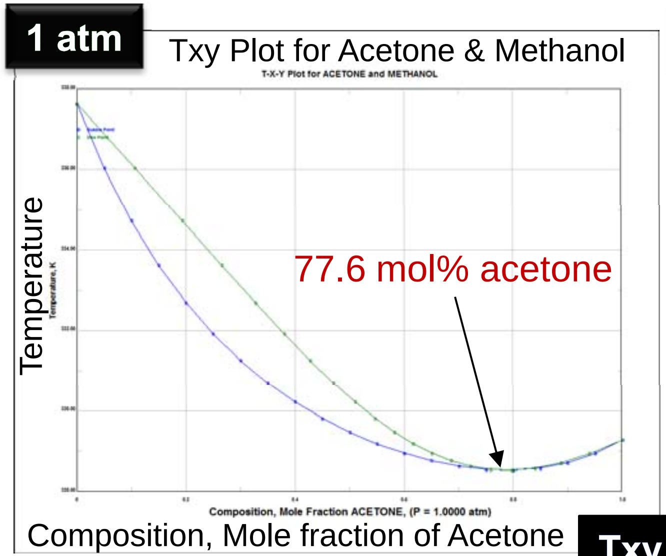
Figure A.2 Equilibrium relationship for relative volatility

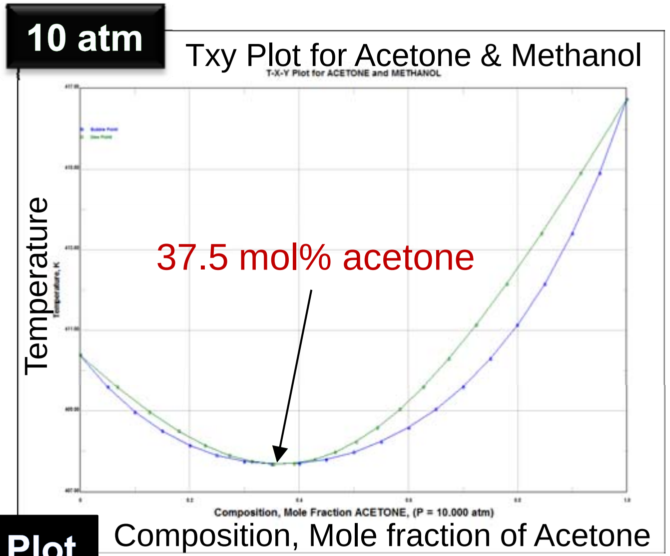
Reference:
Figure A.1: http://users.atw.hu/distillation/processes_us.html
Figure A.2: http://en.wikipedia.org/wiki/Relative_volatility

A.2 Acetone-Methanol System

Acetone and methanol are widely used as solvents and reagents in the pharmaceutical and fine industries.	The acetone-methanol mixture forming a minimum azeotrope is a frequent waste in the pharmaceutical industry.	This mixture cannot be separated into pure components by conventional rectification, but a special distillation method.

- Acetone and methanol have very similar normal boiling points (329.2 and 337.5 K)
- Forms a homogeneous minimum-boiling azeotrope at 1 atm with a composition 77.6 mol% acetone at 328 K.
- At 10 atm the azeotropic composition is 37.5 mol% acetone at 408 K





Txy Plot

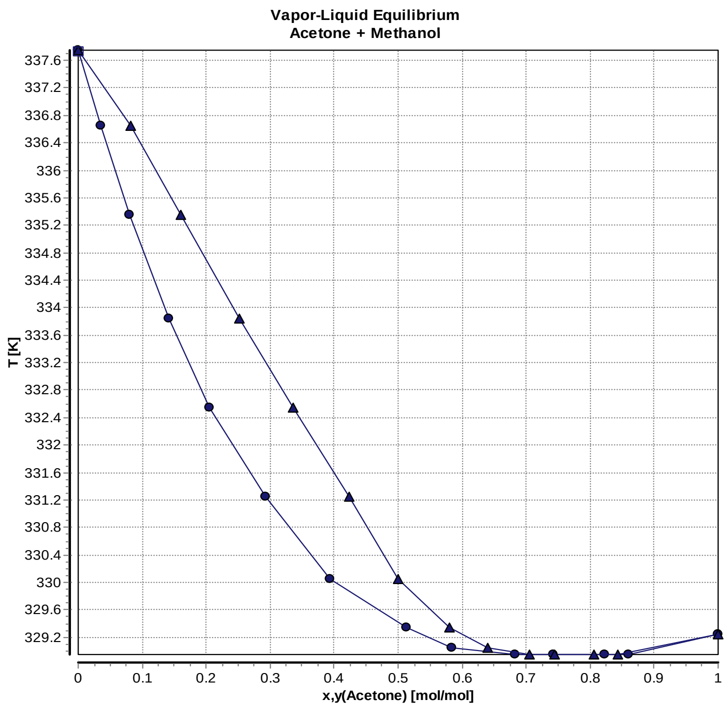
Reference:
Simsci PRO/II 9.1, Invensys System Inc., 1994-2011

Blue – T-x Plot or Bubble point
Green – T-y Plot or Dew point

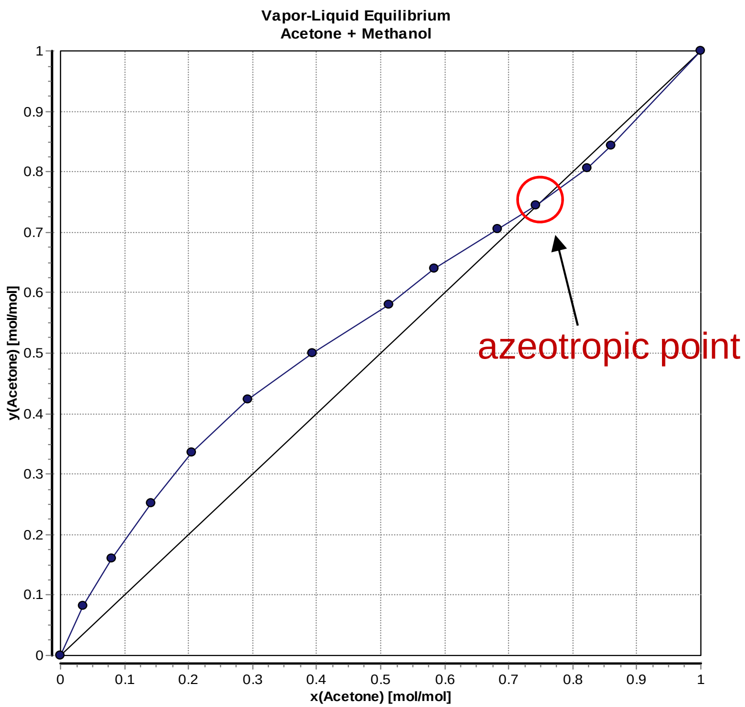
The large shift in the azeotropic composition from 77.6% to 37.5 mol % acetone indicates that a pressure-swing separation should be feasible.

A.2 Acetone-Methanol System

T-X-Y Plot for ACETONE and METHANOL Systemat 1 atm



Vapor-Liquid Equilibrium Plot of Acetone-Methanol System at 1 atm



- Experimental Data Plot from Dortmund Data Bank (DDB)

A.3 Thermodynamic Theory

Liquid Activity Method

<u>Universal Quasi-chemical (UNIQUAC)</u>

K-values: UNIQUAC method

Enthalpies, entropies, densities, vapor fugacities: Ideal method

$$\ln \gamma_i = \ln \gamma_i C + \ln \gamma_i R$$

Combinatorial part → $\ln \gamma_i C$

Residual part → $\ln \gamma_i R$

combinatorial part	residual part
• depends only on the sizes and shapes of the individual molecules	• accounts for the energy interactions, has two adjustable binary parameters.

g^E/RT	$\ln\gamma_i$
$\frac{g^E(\text{combinatorial})}{RT} + \frac{g^E(\text{residual})}{RT}$	$\ln \gamma_i^{comb} + \ln \gamma_i^{res}$
$= \sum_i x_i \ln \frac{\Phi_i}{x_i} - \frac{Z}{2} \sum_i q_i x_i \ln \frac{\Phi_i}{\vartheta_i} - \sum_i x_i q_i \ln S_i$	$\ln \gamma_i^{comb} = \ln \left(\frac{\Phi_i}{x_i}\right) + 1 - \left(\frac{\Phi_i}{x_i}\right)$
$S_i = \sum_j \vartheta_j \tau_{ji}$	$- \frac{Z}{2} q_i \left(\ln \frac{\Phi_i}{\vartheta_i} + 1 - \frac{\Phi_i}{\vartheta_i}\right)$
$\Phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad \vartheta_i = \frac{q_i x_i}{\sum_j q_j x_j}$	$\ln \gamma_i^{res} = q_i \left(1 - \ln S_i - \sum_j \frac{\tau_{ij} \vartheta_j}{S_j}\right)$
$Z = 10$	

Reference:
Simsci PRO/II 9.1,
Invensys System Inc.,
1994-2011

Simulation Objectives

Modeling of the Pressure Swing Distillation Process using PRO/II

- Low-High Pressure Column Configuration (1atm ~ 10atm)
- High-Low Pressure Column Configuration (10atm ~ 1atm)

Determining the Optimum Feed Stage Location

- For Low Pressure Column and High Pressure Column

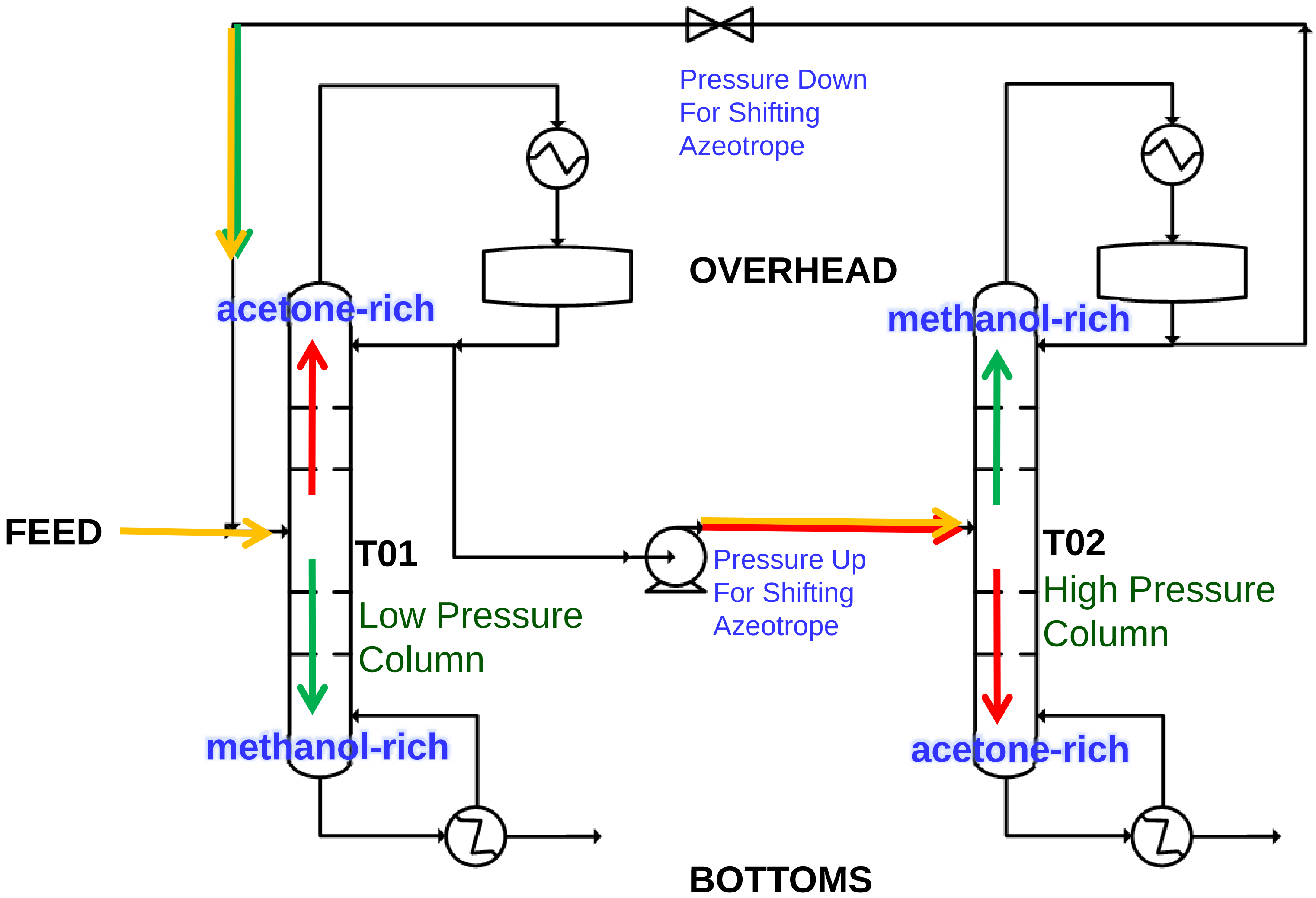
Determining the Optimum Reflux Ratio

- For Low Pressure Column and High Pressure Column

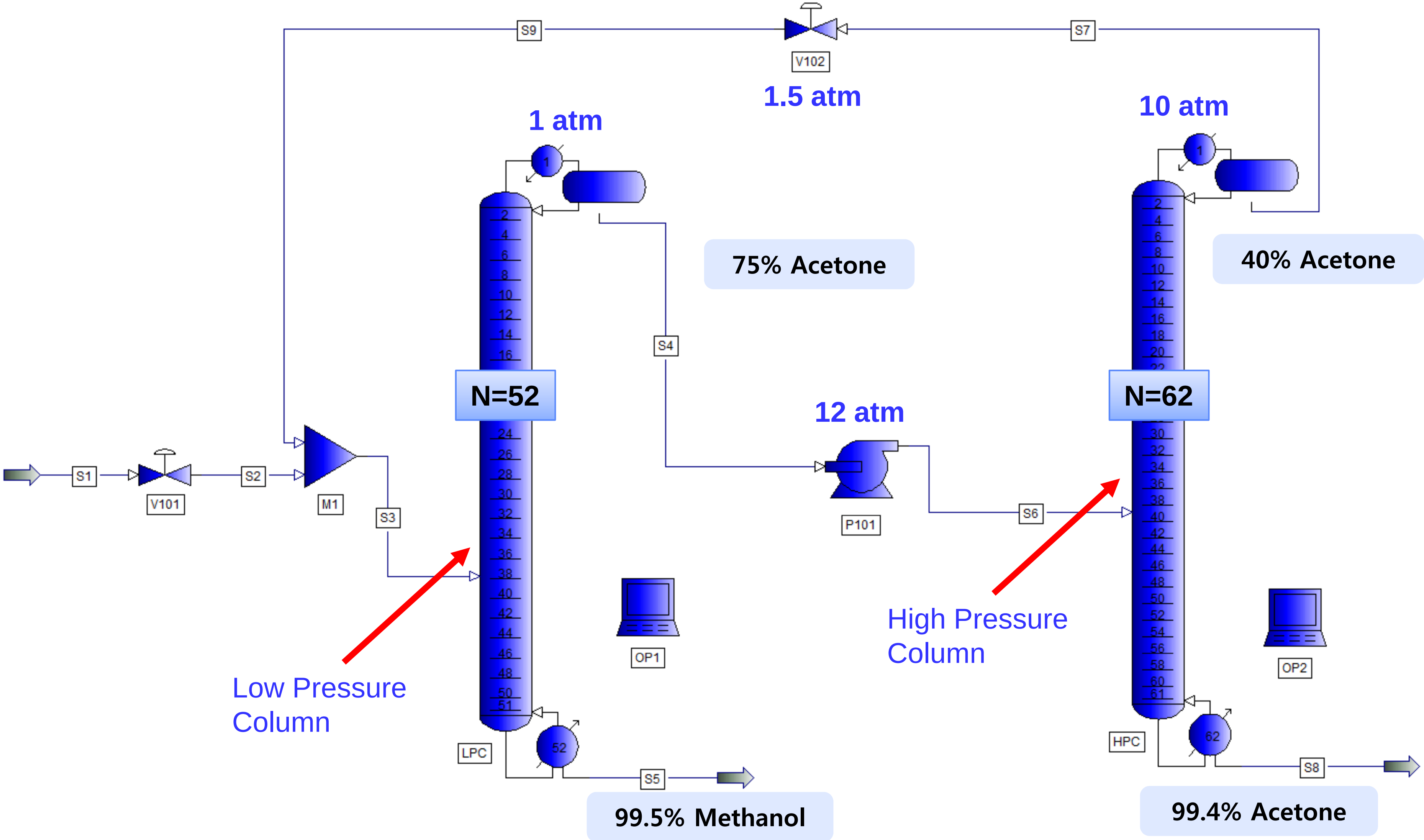
Determining the Minimum Total Reboiler Heat Duties

- Comparison between the two configurations (LP+HP and HP+LP)

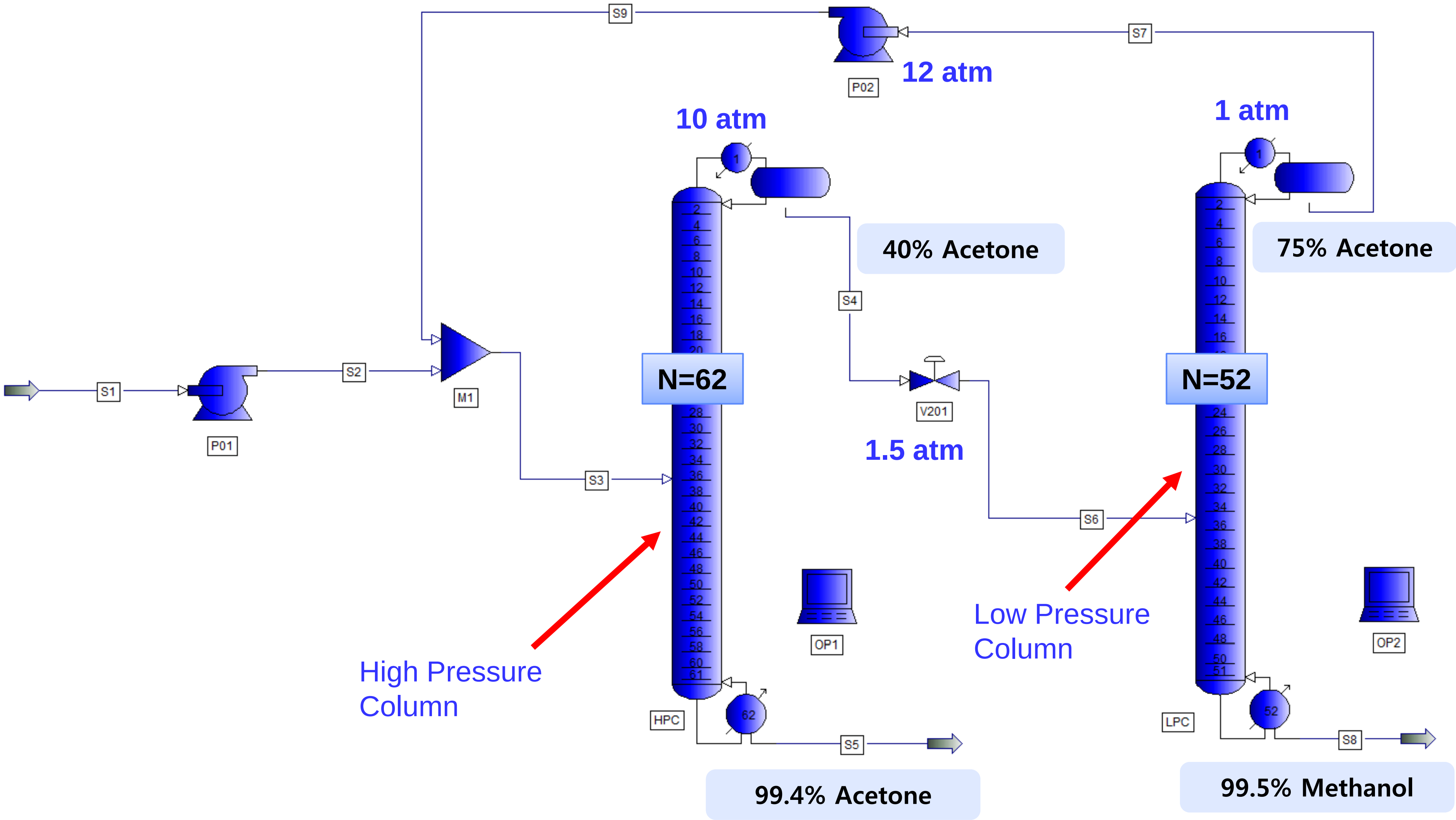
Acetone-Methanol Separation using Pressure Swing Distillation



A. Low-High Pressure Column Configuration



B. High-Low Pressure Column Configuration



Acetone-Methanol System Steady-State Design Inputs

Reference: Luyben, William L. & I-Lung Chien. *Design and control of distillation systems for separating azeotropes*..

C.1 Feedstock Characterization

FEED

Component	composition (%mole)
Acetone	50
Methanol	50
Total Flow Rate (kg-mol/hr)	540
Temperature (K)	320
Pressure (atm)	2.5

C.2 Product Specifications

PRODUCT

Specs	Low-Pressure Column	High-Pressure Column
Bottoms	99.5% methanol	99.4% acetone
Distillate	75% acetone	40% acetone

C.3 Equipment Specifications and Operating Conditions

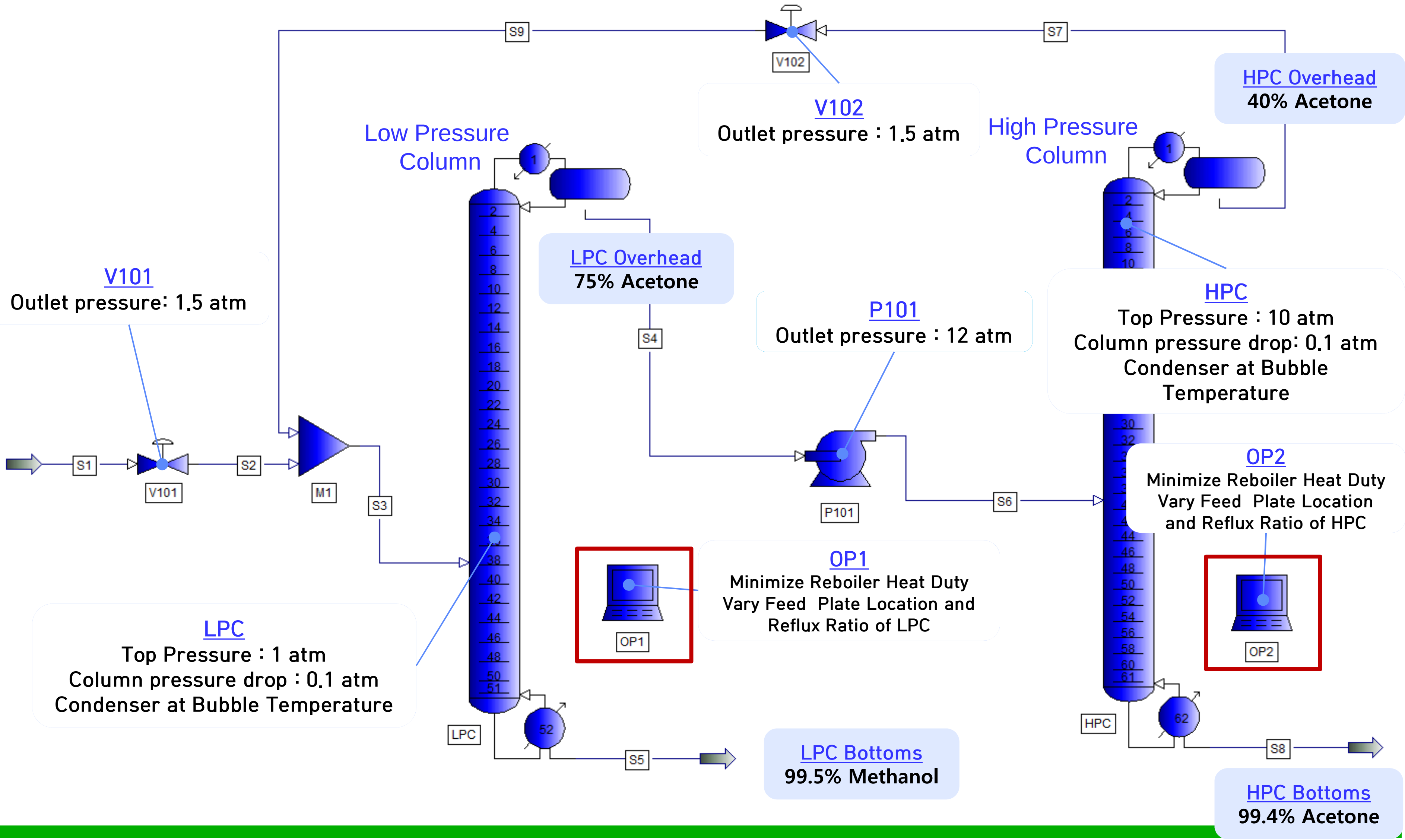
Distillation Column

Specs	Low-Pressure Column	High-Pressure Column
Pressure (atm)	1	10
N stage	52	62
Column pressure drop	0.1 atm	0.1 atm
Condenser condition	at Bubble Temperature	at Bubble Temperature

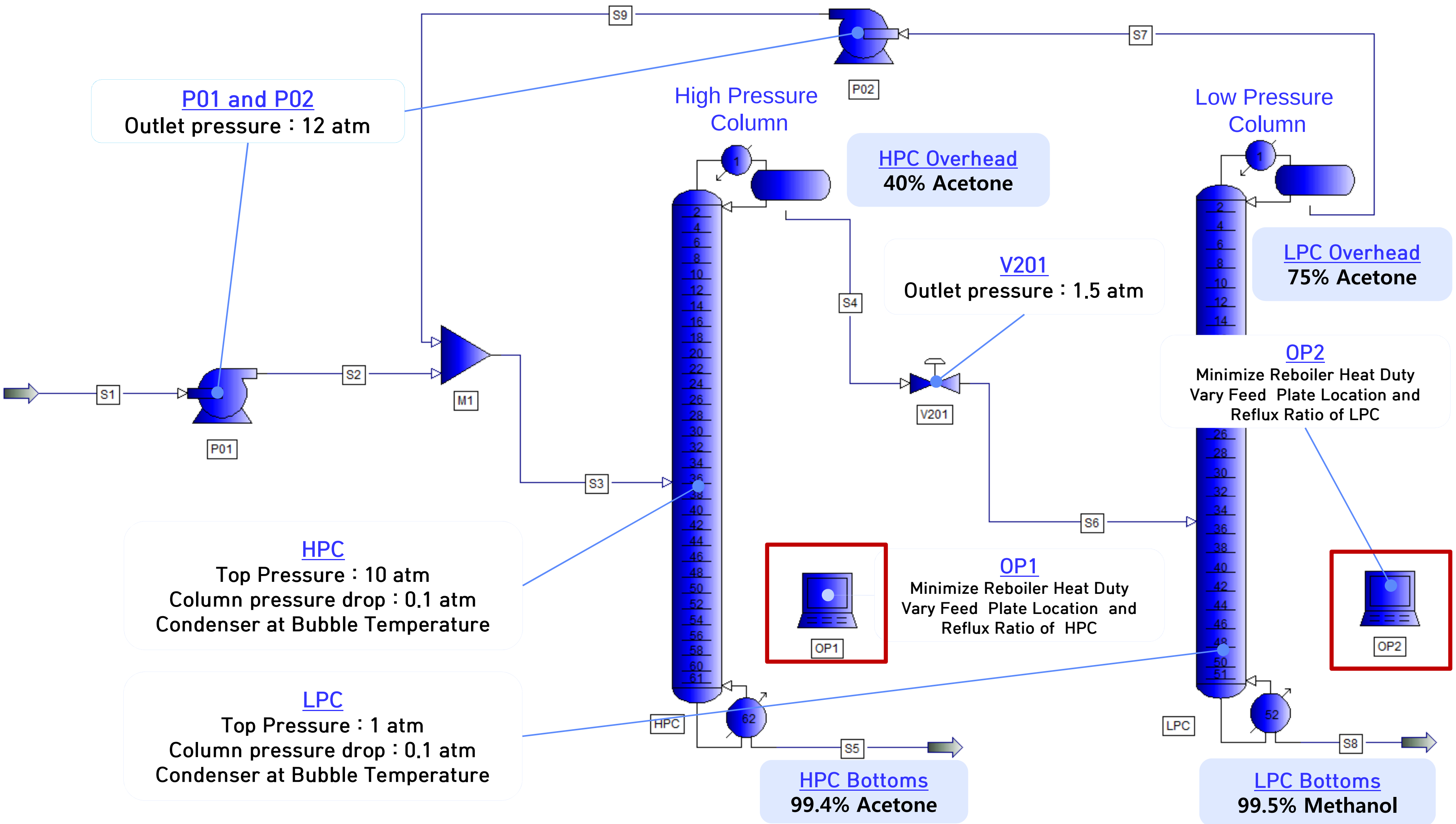
Pressure Changer

Equipment	Outlet Pressure
Valve (V01)	1.5
Valve (V02)	1.5
Pump (P01)	12

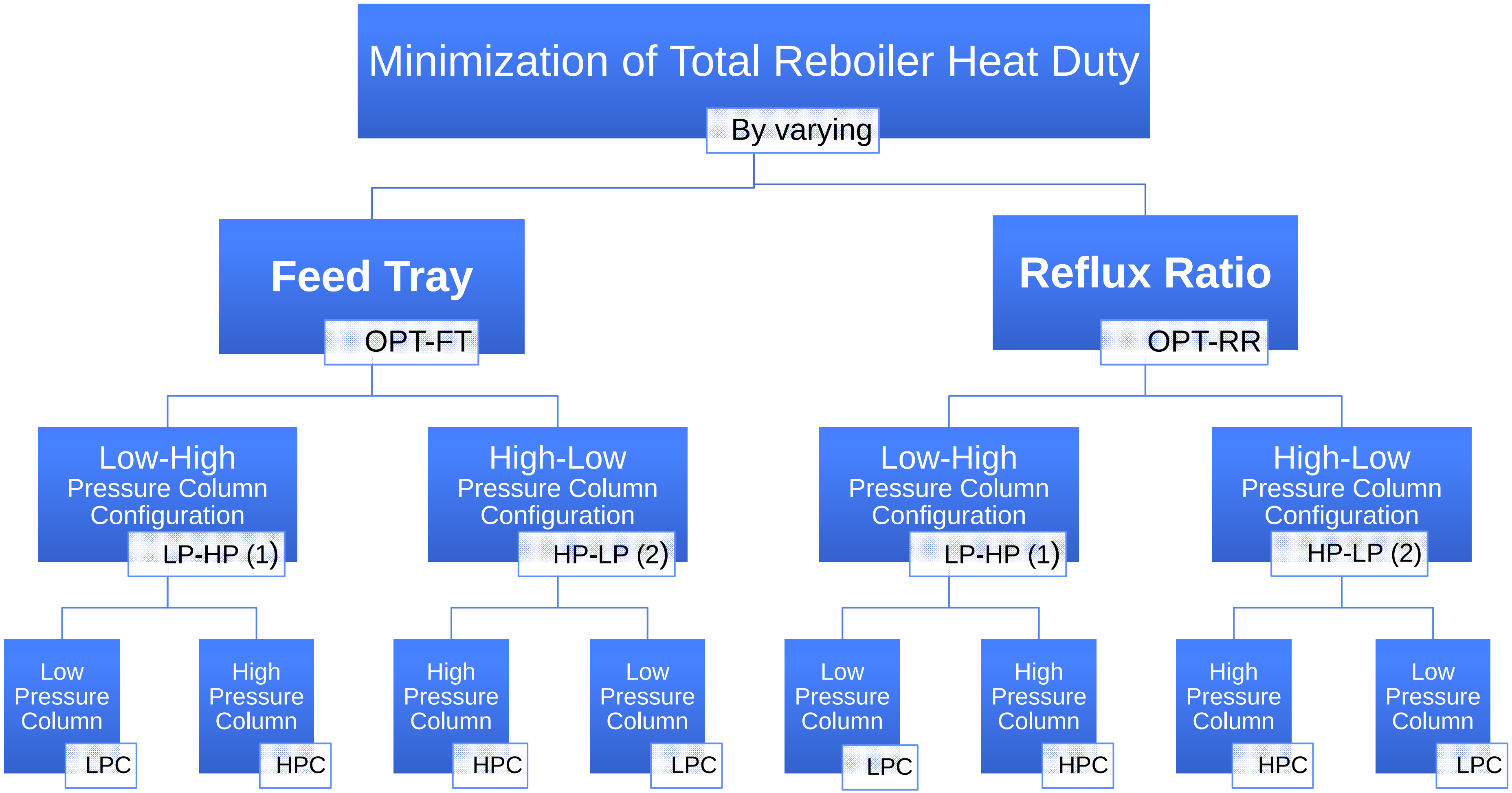
Low-High Configuration Specifications Summary



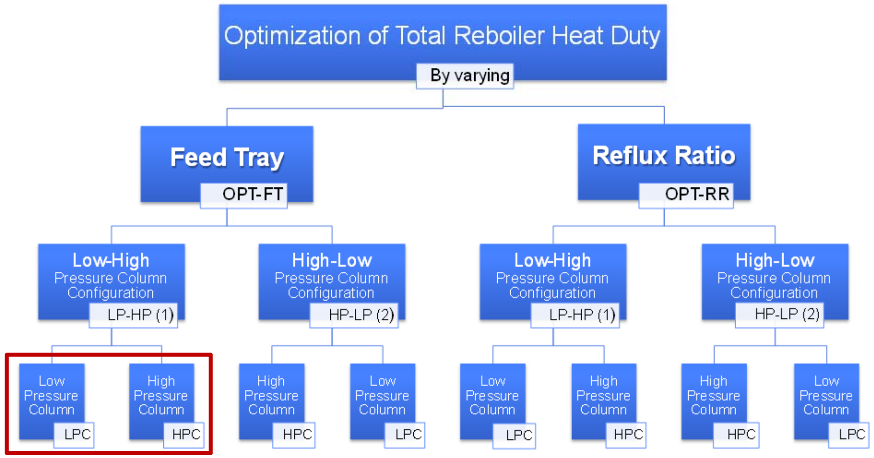
High-Low Configuration Specifications Summary

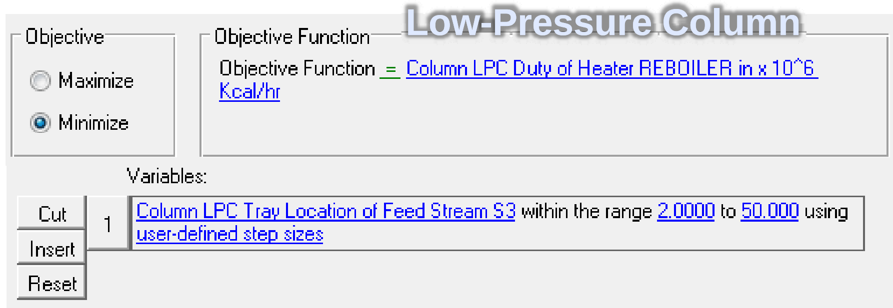


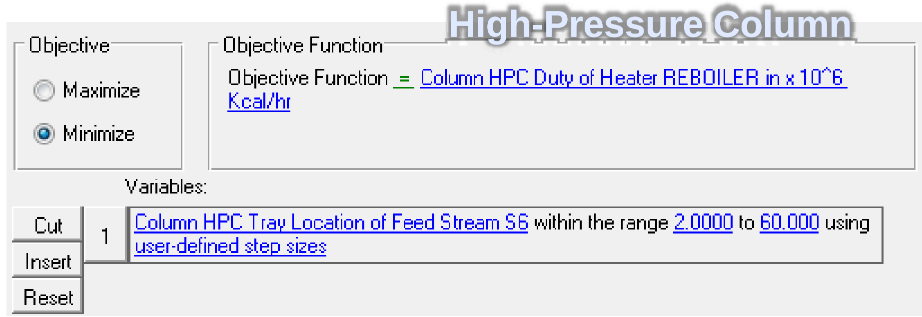
Optimization Objectives and Variables



Feed Tray Optimization for Low-High Configuration



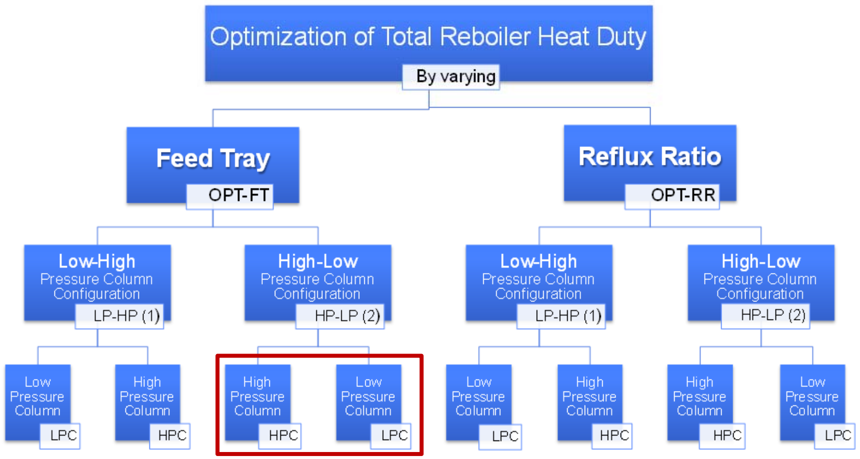


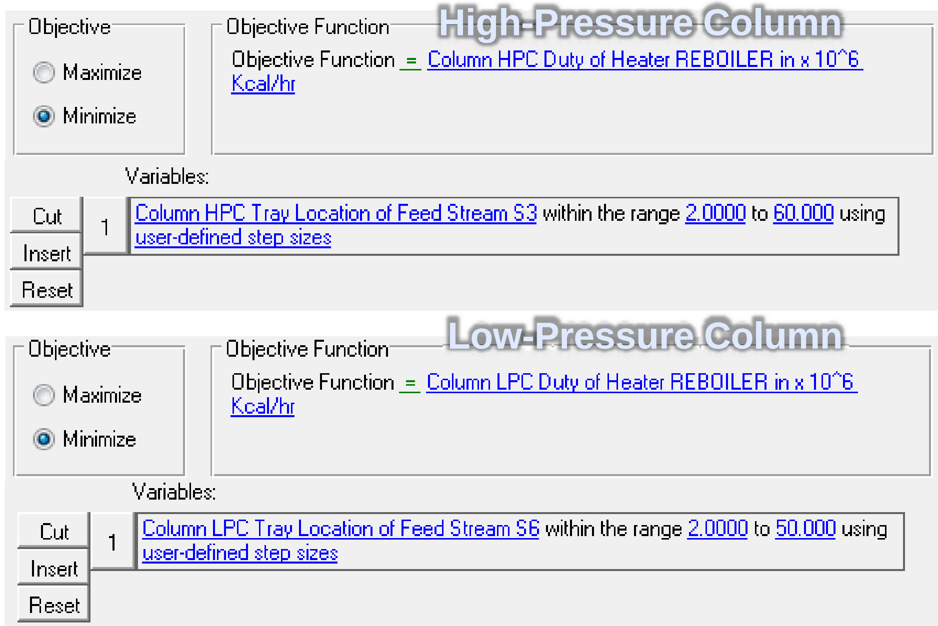


Optimization Results				Vary	Objective	Vary	Objective	
				2 ~ 50		2 ~ 60		
Initial Bottoms Flow Rate		Initial Feed Tray Location		Feed Tray Location	Reboiler Heat Duty	Feed Tray Location	Reboiler Heat Duty	Total
				Low-High Pressure Configuration				
LPC	HPC	LPC	HPC	Low Pressure		High Pressure		
460	190	26	31	37.887	11.550	39.700	6.208	17.758
460	190	37	39	37.739	11.551	39.000	6.207	17.758
460	190	38	39	38.000	11.549	39.000	6.207	17.756
460	190	38	40	**38.000**	11.549	**40.000**	6.202	**17.751**

Optimum		Minimum	
Feed Stage Location		Reboiler Heat Duty	
LPC	HPC	LPC	HPC
38	40	11.549	6.202
Total Reboiler Heat Duty		**17.751** M*KCAL/HR	

Feed Tray Optimization for High-Low Configuration



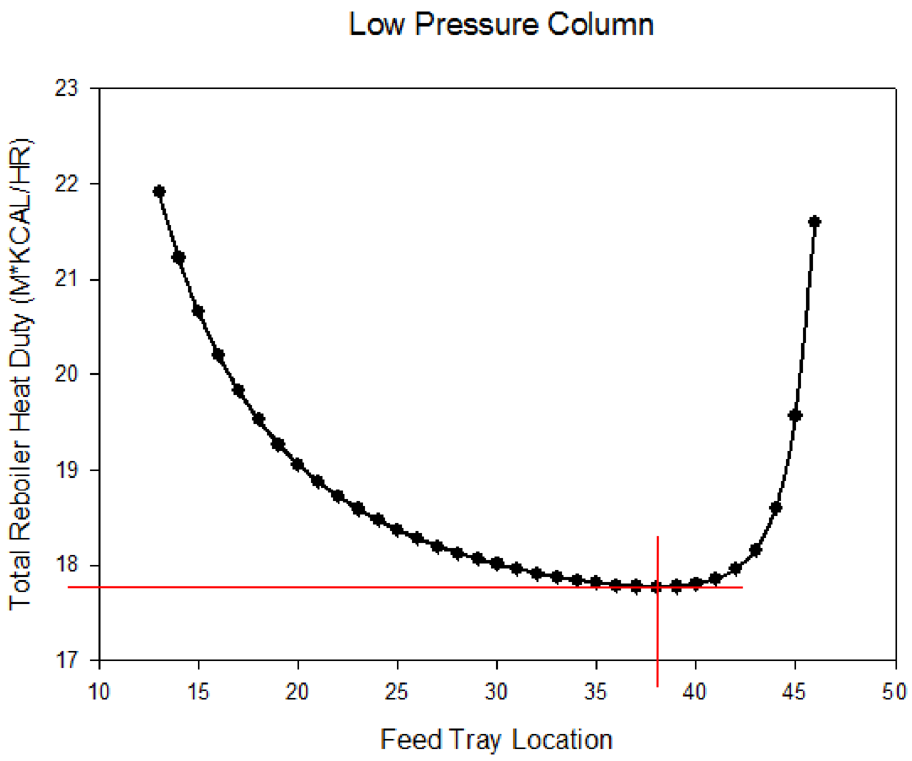


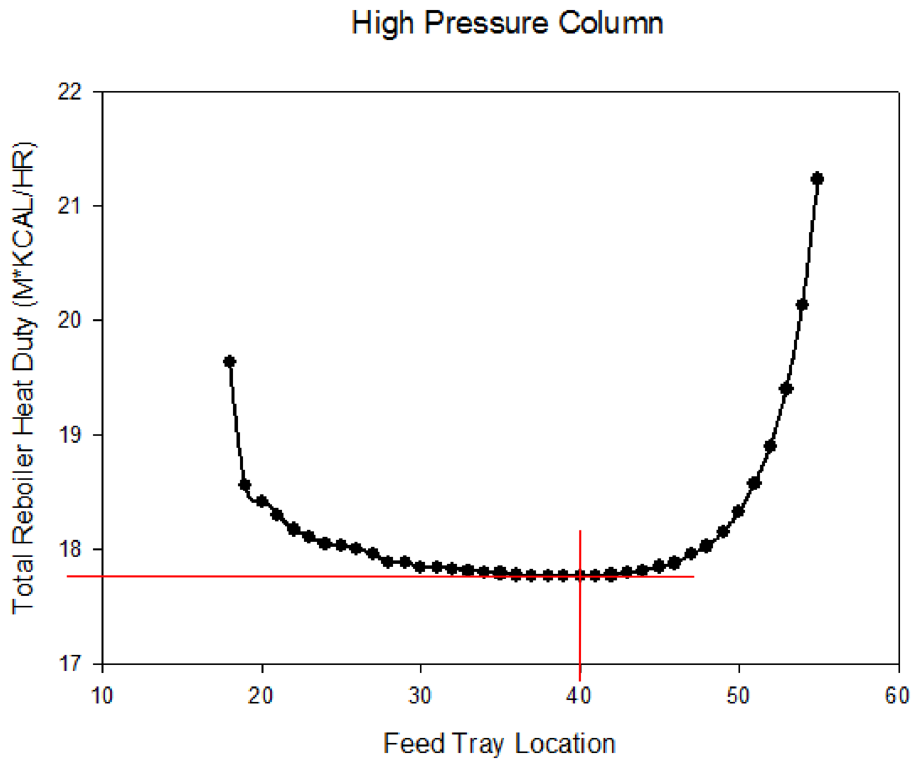
Optimization Results

Initial Bottoms Flow Rate		Initial Feed Tray Location		Vary 2 ~ 60 Feed Tray Location	Objective Reboiler Heat Duty	Vary 2 ~ 50 Feed Tray Location	Objective Reboiler Heat Duty	Total
				High-Low Pressure Configuration				
HPC	LPC	HPC	LPC	High Pressure		Low Pressure		
190	460	31	26	41.966	14.595	37.073	7.0885	21.684
190	460	42	37	**39.039**	14.585	**37**	7.0884	**21.673**
190	460	39	37	40	14.596	37	7.0884	21.6844
190	460	37	35	39.258	14.584	35	7.1153	21.699
190	460	39	35	38.876	14.585	35	7.1153	21.7003
190	460	36	35	38.74	14.587	35	7.1153	21.702

Optimum		Minimum	
Feed Stage Location		Reboiler Heat Duty	
HPC	LPC	HPC	LPC
39	37	14.585	7.0884
Total Reboiler Heat Duty		**21.673** M*KCAL/HR	

Feed Tray Case Study for Low-High Configuration





Modifying Column Specification

Low Pressure Column

	Specifications:	Active:
1	LPC_BOTTOM - Stream S5 Composition of component METHANOL on a Wet basis in Mole percent = 99.500 within an absolute tolerance of 1.0000e-006	☑
2	REFLUX_LPC - Column LPC Reflux Ratio on a Mole basis = 2.0000 within the default tolerance	☑

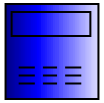
	Variables:
1	Column LPC Duty of Heater CONDENSER
2	Column LPC Duty of Heater REBOILER

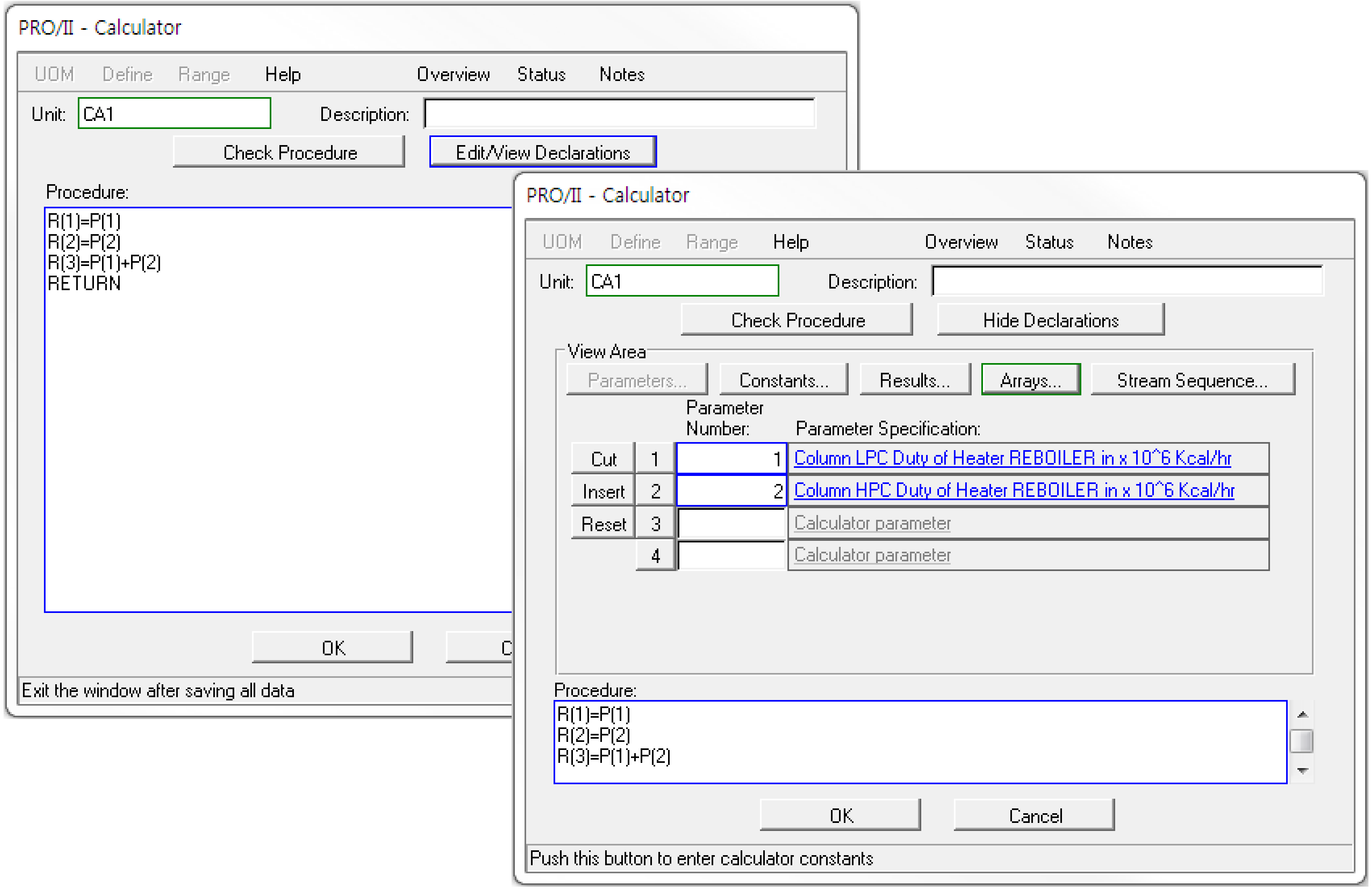
High Pressure Column

	Specifications:	Active:
1	HPC_BOTTOM - Stream S8 Composition of component ACETONE on a Wet basis in Mole percent = 99.400 within an absolute tolerance of 1.0000e-006	☑
2	REFLUX_HPC - Column HPC Reflux Ratio on a Mole basis = 2.0000 within the default tolerance	☑

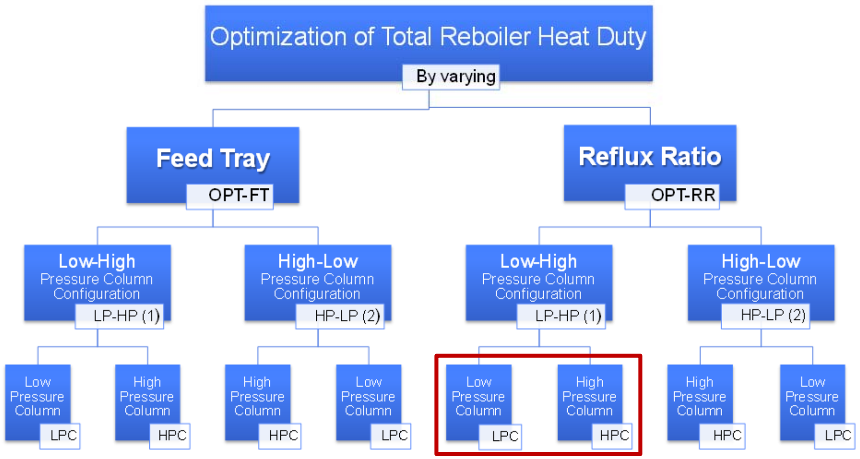
	Variables:
1	Column HPC Duty of Heater CONDENSER
2	Column HPC Duty of Heater REBOILER

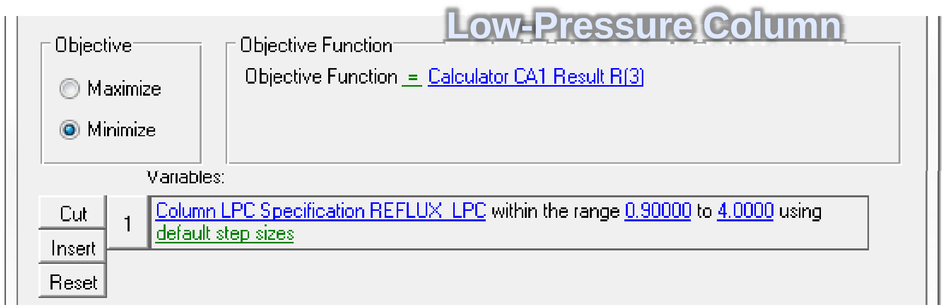
Calculator Input

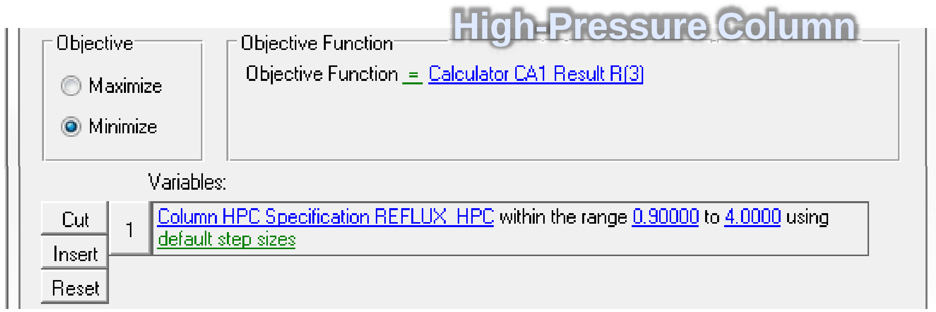




Reflux Ratio Optimization for Low-High Configuration



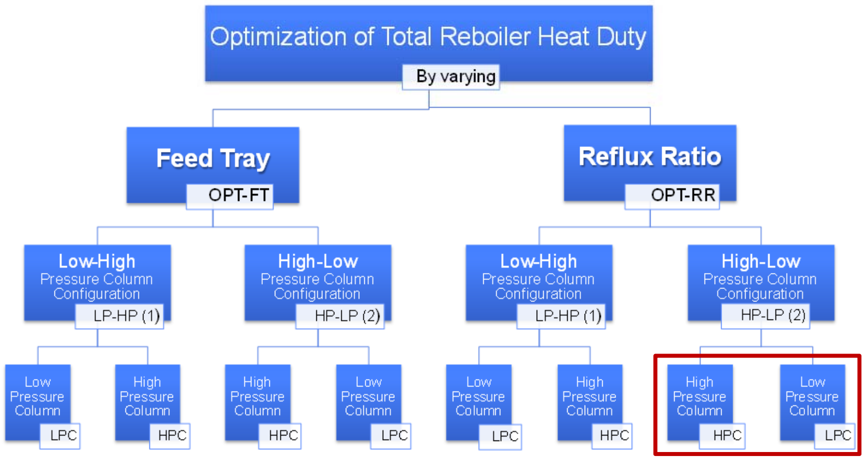


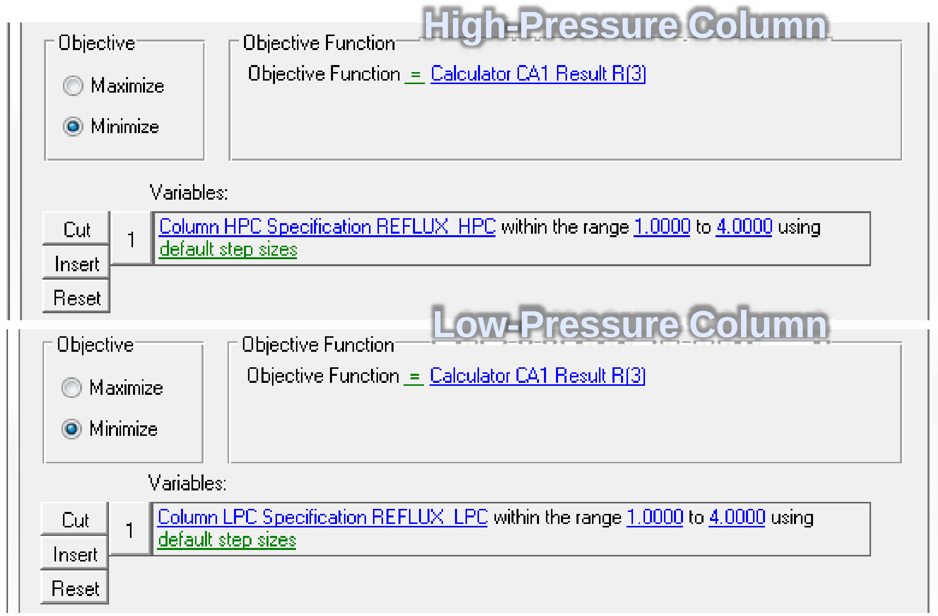


Optimization Results				Vary	Objective	Vary	Objective	
				0.1 ~ 10		0.1 ~ 10		
Initial Bottoms Flow Rate		Initial Feed Tray Location		Reflux Ratio	Reboiler Heat Duty	Reflux Ratio	Reboiler Heat Duty	Total
				Low-High Pressure Configuration				
LPC	HPC	LPC	HPC	Low Pressure		High Pressure		
460	190	26	31	2.2543	11.2527	3.2385	6.7758	18.0285
460	190	37	40	2.1214	12.3097	2	6.6384	18.9481
460	190	38	39	2.1308	11.0642	3	6.7575	17.8217
460	190	38	40	**2.2853**	11.0847	**3.3494**	6.5622	**17.6469**

Optimum		Minimum	
Reflux Ratio		Reboiler Heat Duty	
LPC	HPC	LPC	HPC
2.2853	3.3494	11.0847	6.5622
Total Reboiler Heat Duty		**17.6469** M*KCAL/HR	

Reflux Ratio Optimization for High-Low Configuration



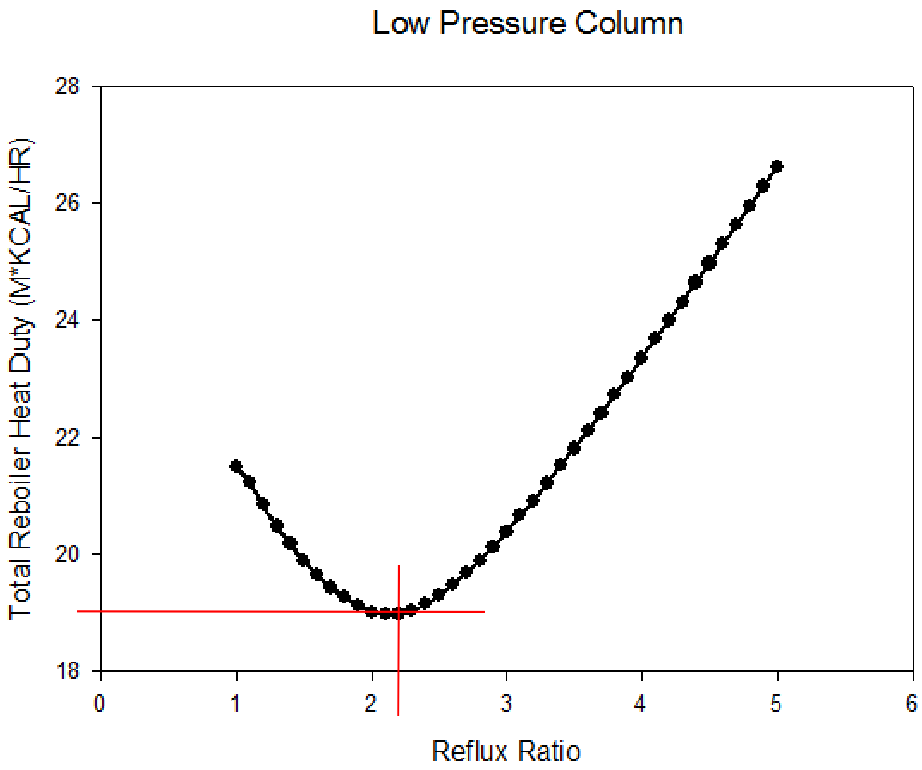


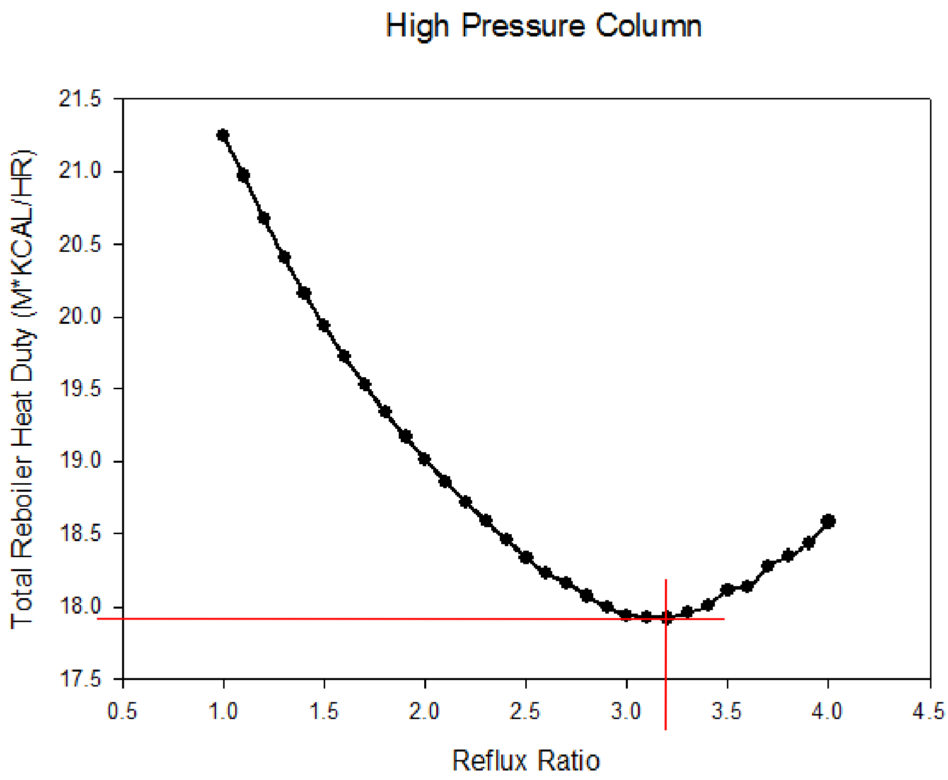
Optimization Results

					Vary	Objective	Vary	Objective	
					0.1 ~ 10		0.1 ~ 10		
RR Range	Initial Bottoms Flow Rate		Initial Feed Tray Location		Feed Tray Location	Reboiler Heat Duty	Feed Tray Location	Reboiler Heat Duty	Total
					High-Low Pressure Configuration				
	HPC	LPC	HPC	LPC	High Pressure		Low Pressure		
0.1 ~ 10	300	575	36	35	1.5696	14.0609	2	8.306	22.3669
1 ~ 10	575	300	37	35	1.7	14.3651	2	7.9834	22.3485
1 ~ 4	575	300	37	35	**2.1772**	14.2902	**2.6**	7.3762	**21.6664**
1 ~ 4	575	300	39	37	1.7	13.5078	2.5064	8.45512	21.9629

Optimum		Minimum	
Reflux Ratio		Reboiler Heat Duty	
HPC	LPC	HPC	LPC
2.1772	2.6	14.2902	7.3762
Total Reboiler Heat Duty		**21.6664** M*KCAL/HR	

Reflux Ratio Case Study for Low-High Configuration





Comparison of the Results

Optimization of Total Reboiler Heat Duty

- **Feed Tray**
  - Low-High Pressure Column Configuration
  - High-Low Pressure Column Configuration
- **Reflux Ratio**
  - Low-High Pressure Column Configuration
  - High-Low Pressure Column Configuration

	LPC	HPC	HPC	LPC	LPC	HPC	HPC	LPC
No. of stages	52	62	62	52	52	62	62	52
Operating Pressure (atm)	1	10	10	1	1	10	10	1
Overhead Flowrate (KMOL/HR)	458.467	188.327	574.133	304.406	461.357	190.770	589.185	319.584
Bottoms Flowrate (KMOL/HR)	269.528	270.141	270.273	269.727	269.899	270.587	269.875	269.602
Optimum Values	**38**	**40**	**39**	**37**	**2.2853**	**3.3494**	**2.1772**	**2.600**
Reboiler Heat Duty (M*KCAL/HR)	11.549	6.202	14.585	7.0884	11.0847	6.5622	14.2902	7.3762
Total Reboiler Heat Duty	**17.751 M*KCAL/HR**		21.673 M*KCAL/HR		**17.6469 M*KCAL/HR**		21.6664 M*KCAL/HR	

Conclusion

- ✓ After running the PSD simulation and optimization, different results are obtained from varying the feed stage locations and reflux ratios.
- ✓ In order to make the simulation converged, some parameters are varied such as the initial bottoms flowrates, initial feed stage locations, and reflux ratio range.
- ✓ Several runs should be done to make the simulation converged for some cases since it changes results little by little.
- ✓ After running the simulation for several times, it will reach a point wherein the results are constant.
- ✓ Comparing all the obtained result from the simulation, by varying the feed stage location and reflux ratio, it was shown that the Low-High pressure configuration can give a lower Total Reboiler Heat Duty than the High-Low pressure configuration for both cases.
- ✓ Therefore we can conclude that the Low-High Pressure Configuration is more economical than the High-Low Pressure Configuration.

F. References

[1] Seader, J. D., Henley, E. J. & Roper, D. K. *Separation process principles: chemical and biochemical operations*, 3rd ed., John Wiley & Sons, Inc., United State of America, 2011. pp. 429-442

[2] Klein, Andreas. *Azeotropic Pressure Swing Distillation*. Berlin University of Technology Dissertation. Berlin, 2013. pp. 6-16

[3] Luyben, William L. & I-Lung Chien. *Design and control of distillation systems for separating azeotropes*. John Wiley & Sons, Inc., Hoboken, New Jersey, 2010. pp. 149-164.

[4] Hong-Mei Wei, Feng Wang, Jun-Liang Zhang, Bo Liao, Ning Zhao, Fu-kui Xiao, Wei Wei, & Yu-Han Sun. *Design and control of dimethyl carbonate–methanol separation via pressure-swing distillation*. Industrial & Engineering Chemistry Research Article ASAP. American Chemical Society, 2013.

[5] Luyben, William L. *Pressure-swing distillation for minimum- and maximum-boiling homogeneous azeotropes*. Industrial & Engineering Chemistry Research. American Chemical Society, 2012, 51 (33), pp. 10881–10886.

[6] Kontogeorgis, Georgios M. & Folas, Georgios K. *Thermodynamic Models for Industrial Applications: From Classical and Advanced Mixing Rules to Association Theories*, John Wiley & Sons, Ltd., United Kingdom, 2010. pp. 109-154

감사합니다!