Design, simulation and pilot verification of a coupled azeotropic and extractive distillation process for the production of propylene oxide with high purity

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List of the impurities to be removed and the related extractant, comparison between experimental and calculated results for saturated temperature and compositions and some binary mixtures, residue curve maps for mixtures containing NC4, sequential iterative strategy for sensitive analysis, process diagram with operation parameters, TAC calculation model.

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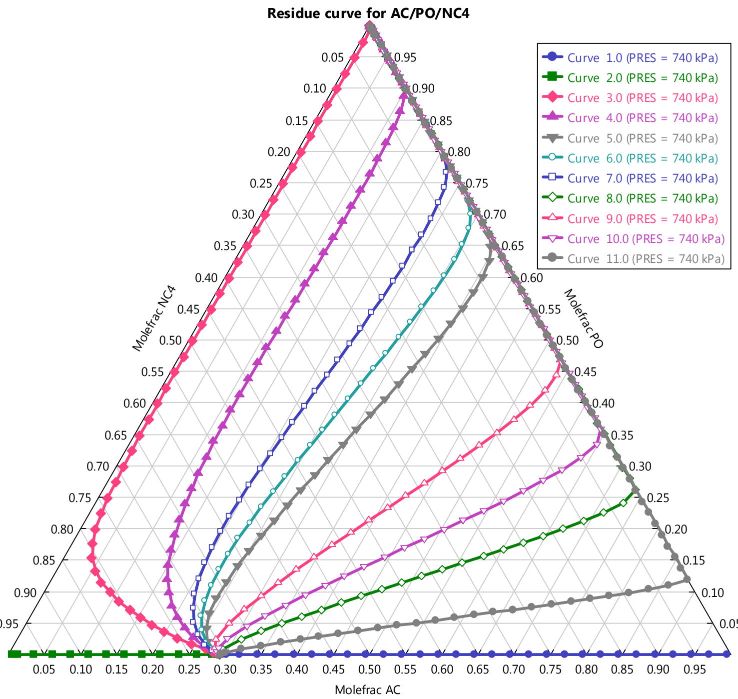
Table S1. The impurities to be removed and related extractant

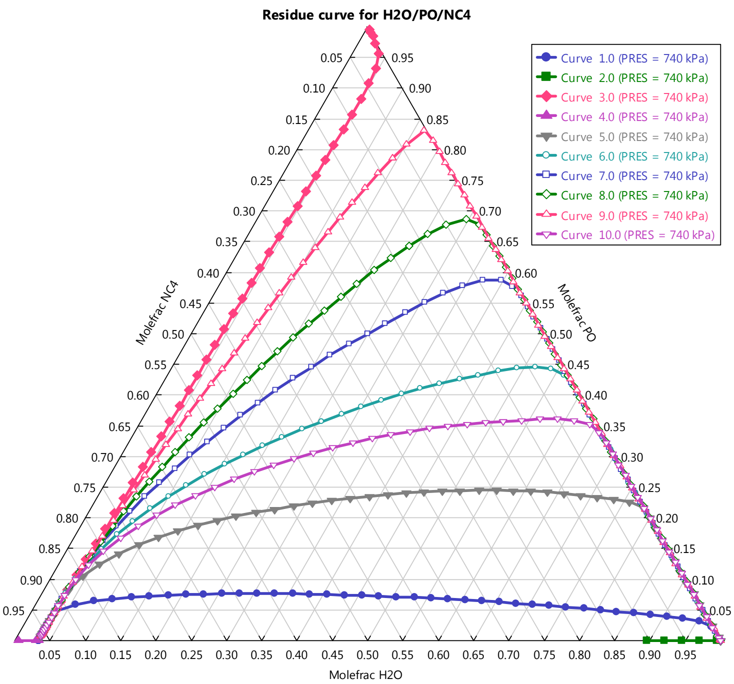
Impurities	Extractant	Ref.
C_5-C_7 hydrocarbons	C_8-C_{20} open chain or cyclic paraffin	1-3
	T-butyl alcohol/water	4
	C_8-C_{10} paraffinic hydrocarbon/water	5
Water	2-Hydroxyethyl 2-hydroxyethylcarbamate	6
	Sulfolane	7
	Ethylene carbonate, propylene carbonate or a mixture	8
	C_5-C_8 monohydroxy alkoxyalkanol	9
Aldehyde	T-butyl alcohol/water	4
	C_6-C_{18} acyclic paraffinic hydrocarbons	10 11, 12
Water, acetone, methanol	1-Methyl-2-pyrrolidone	13
	Triethylene glycol	14
	Dipropylene glycol	14
	1-Propanol	15
	Mixture of triethylene glycol with 2-methyl- 2,4-Pentanediol, or tertiary butyl alcohol or ethylene glycol	16
ethyl formate	C_6-C_{18} acyclic paraffinic hydrocarbons	10, 11
	T-butyl alcohol/water	4
	Octane	11

Table S2. Boiling point and azeotropes of PO systems under 101.325kPa (°C). Comparison between experimental and theoretical results

Comp.*i*	Experimental data[17]		Computed data		Azeotrope type
	Mole fraction	Boiling point	Mole fraction	Boiling point	
NC4	1	0	1	-0.53	
NC4 (740 kPa)	1		1	66.11	
PO	1	35.0	1	34.48	
2MC5	1	60.4	1	60.21	
H_2O	1	100	1	100.02	
NC8	1	125.75	1	125.69	
PG	1	187.8	1	187.72	
NC4- H_2O			0.9943:0.0057	-0.67	MIH
NC4- H_2O (740 kPa)			0.9667:0.0333	64.73	
NC8- H_2O	0.3152:0.6847	89.60	0.3194:0.6806	89.57	MIH
PG- NC8			0.0844:0.9156	122.65	MIH
PO-2MC5			0.9451:0.0549	34.37	MI
PO-2MC5 (175.8 kPa)	0.9250:0.0750	50	0.9460:0.0540	50.71	MI
PO- H_2O	0.9685:0.0315	33.80	0.9685:0.0315	33.81	MIH



(a) AC-PO-NC4 at 740kPa



(b) H2O-PO-NC4 at 740kPa

Figure S1. Residue curve maps for ternary mixtures containing NC4

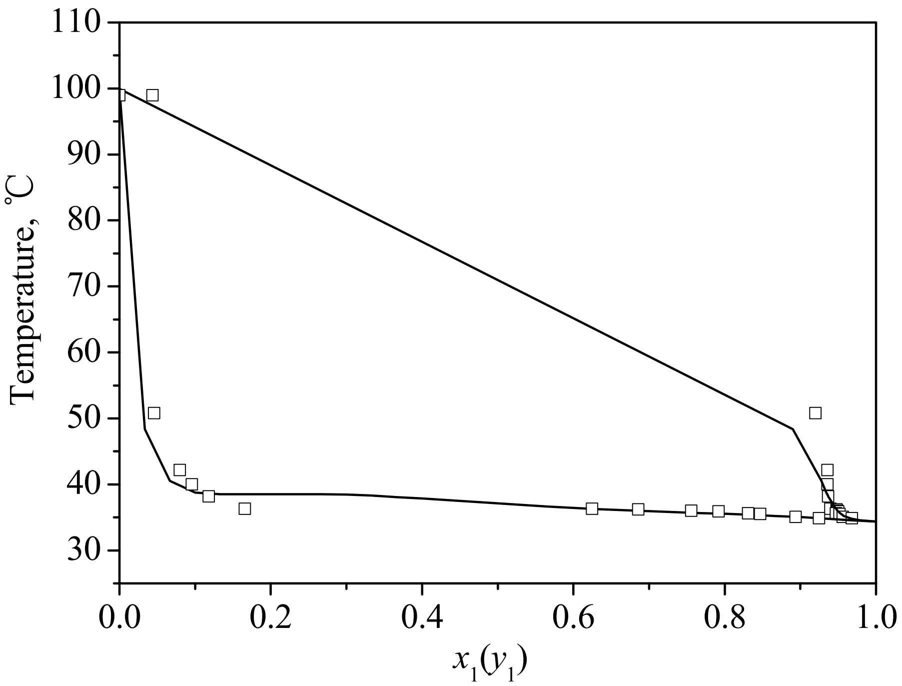


Figure S2. Comparison between experimental[18] and theoretical VLE data for PO and water at 101.325 kPa. (Symbols: experiment; Lines: NRTL)

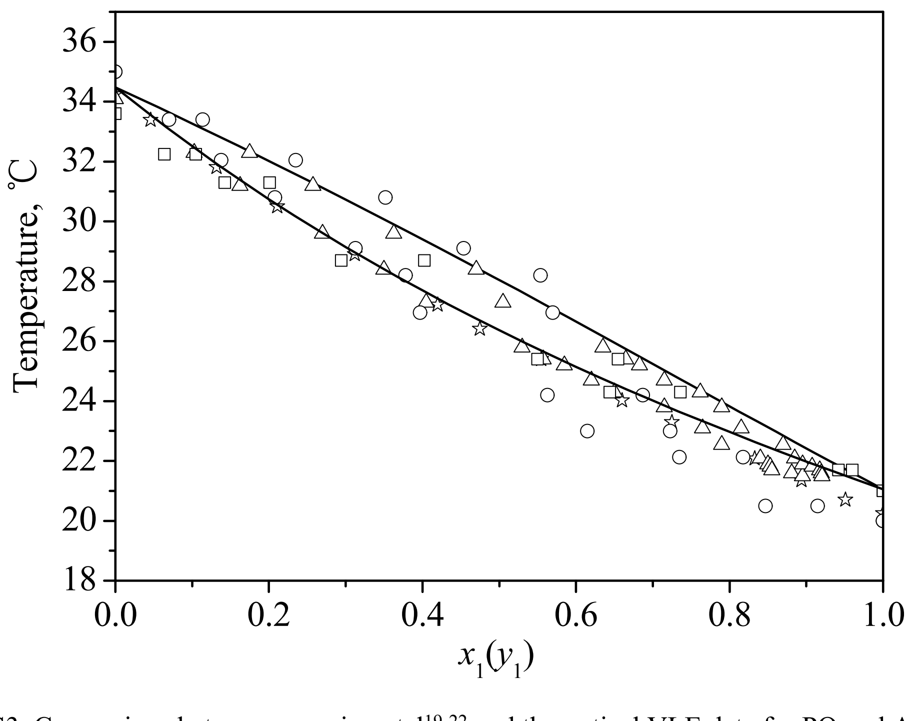


Figure S3. Comparison between experimental[19-22] and theoretical VLE data for PO and AC (AC) at 101.325 kPa. (Symbols: experiment; Lines: NRTL)

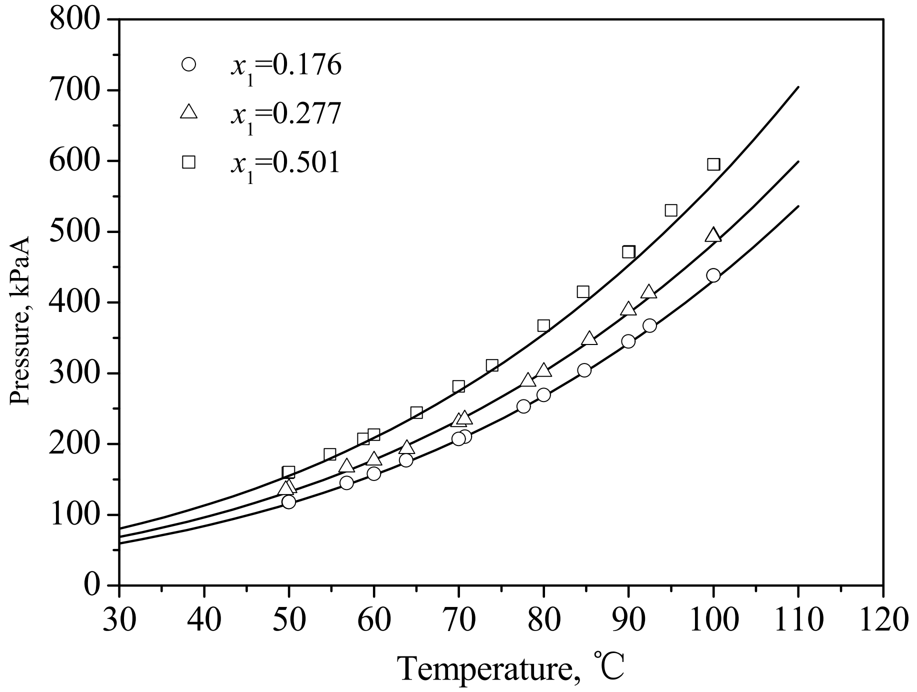


Figure S4. Comparison between experimental[23] and theoretical VLE data for PO + 2-methyl-pentane. (Symbols-experiment; Lines-NRTL)

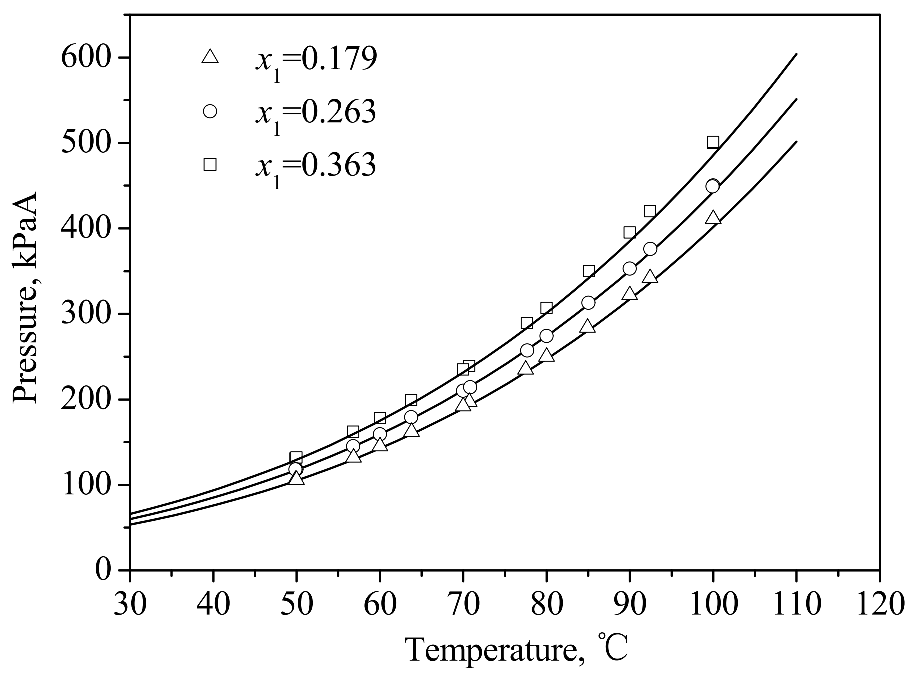


Figure S5. Comparison between experimental[23] and theoretical VLE data for PO + 2-methyl-pentene. (Symbols-experiment; Lines-NRTL)

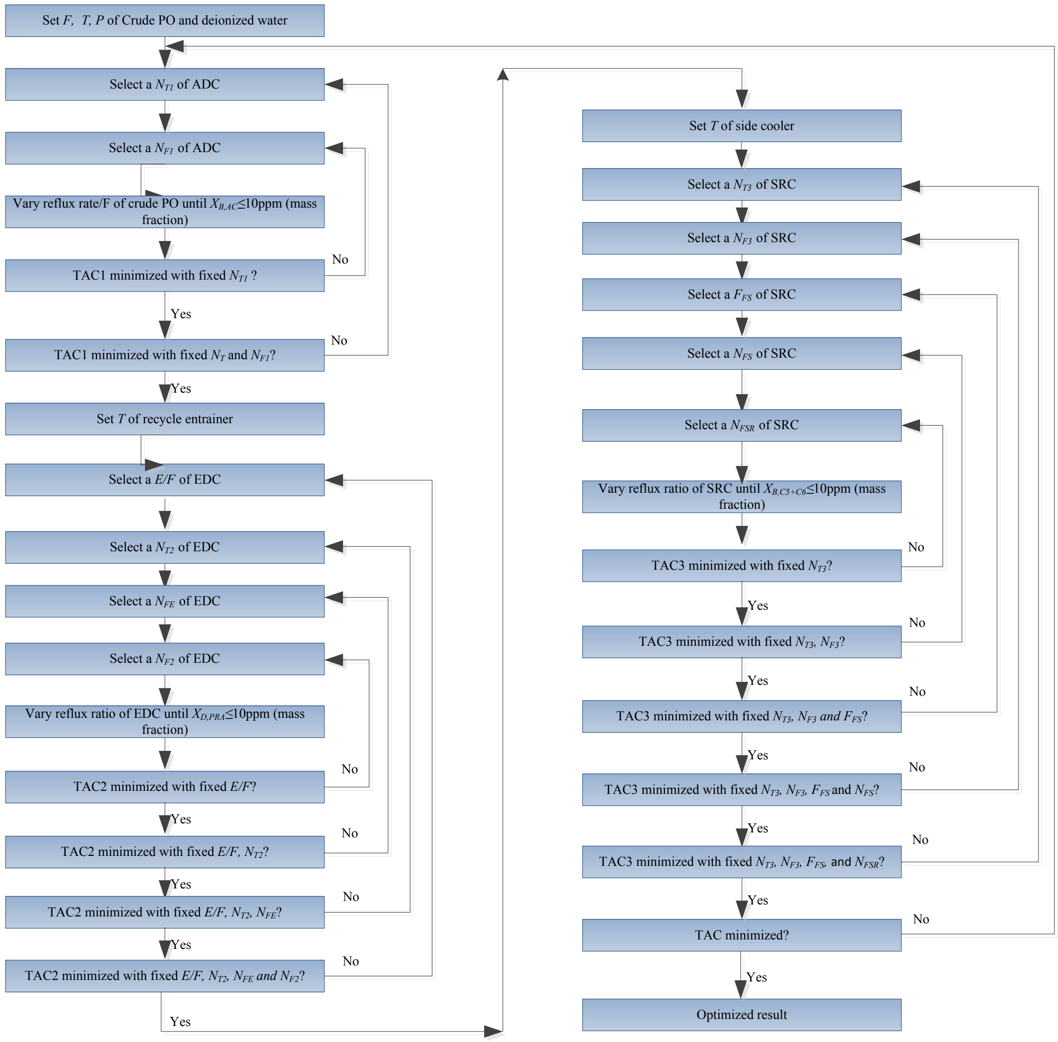


Figure S6. Sequential iterative strategy for sensitive analysis

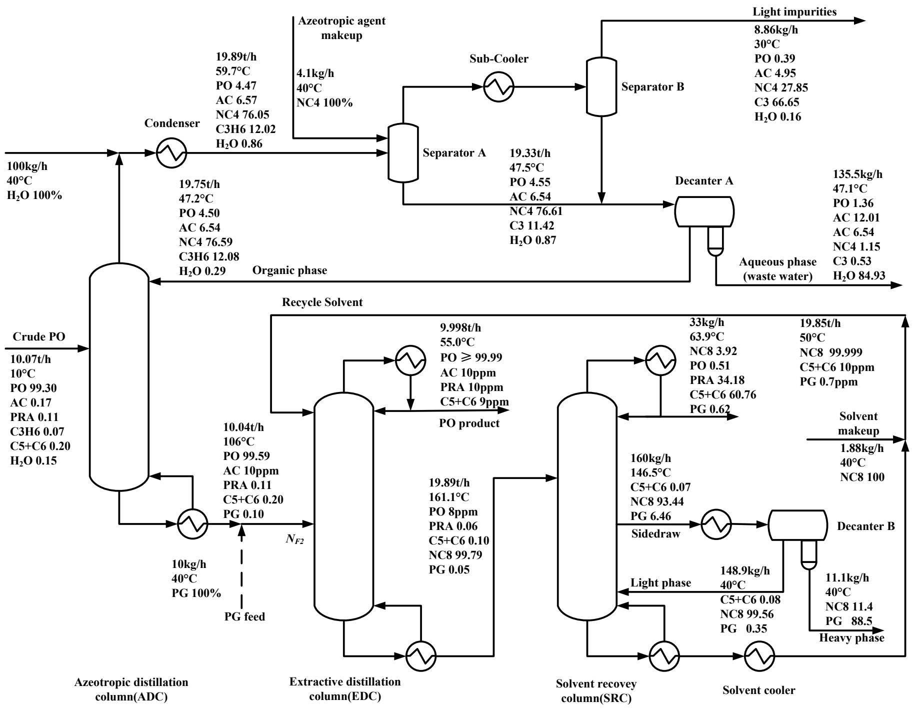


Figure S7. The optimal steady state design flowsheet of PO purification process (The unit for the composition is wt%)

Information of TAC Optimization

In this work, the evaluation of equipment cost followed the procedure of Douglas[24] and the specific equations were from ones in a previous work[25]. A payback period of 3 years was assumed and a M&S index of 1611.7 was applied in calculation. Materials of construction were stainless steel. The equipment was sized as follows.

(1) Reboiler heat transfer area (A_R)

$$A_R[\text{ft}^2] = \frac{Q_R}{U_R \cdot \Delta T_R} \tag{S1}$$

where Q_R [Btuh] is the reboiler duty, the overall heat-transfer coefficient U_R is assumed to be 250 Btu/(h.ft^2), and the temperature driving force ΔT_R [°F] in the reboiler depends on the steam temperature:

$$\Delta T_R = T_{steam} - T_R \tag{S2}$$

(2) Condenser heat-transfer area (A_C)

$$A_C[\text{ft}^2] = \frac{Q_C}{U_C \cdot \Delta T_C} \tag{S3}$$

where Q_C [Btuh] is the condenser duty, the overall heat-transfer coefficient U_C is assumed to be 150 Btu/(h.ft^2), and the log-mean temperature driving force ΔT_C [°F] depends on the dew points and bubble points (T_b) for a total condenser:

$$\Delta T_C = \frac{(107.6 - 89.6)}{\ln\left(\frac{T_b - 89.6}{T_b - 107.6}\right)} \tag{S4}$$

(3) Column length (L_C)

$$L_C[\text{ft}] = 2.4 N_T \tag{S5}$$

where N_T is the total number of trays? The capital and operating costs are calculated according to:

A *Column cost and reactor cost*

$$column\ cost[\$] = \frac{\text{M\&S}}{280}(101.9 D_C^{1.066} L_C^{0.802}(2.18 + F_C)) \tag{S6}$$

where $F_C = F_m F_p = 3.67$.

B *Tray cost*

$$tray\ cost[\$] = \frac{\text{M\&S}}{280}(4.7 D_C^{1.55} L_C F_C) \tag{S7}$$

where $F_C = F_s + F_t + F_m = 1 + 1.8 + 1.7$.

C *Heat exchanger cost*

$$heat\ exchanger\ cost[\$] = \frac{\text{M\&S}}{280}(A^{0.65}(2.29 + F_{\text{C}})) \quad \text{(S8)}$$

where $F_{\text{C}} = (F_{\text{d}} + F_{\text{p}})F_{\text{m}} = (1.35 + 0)3.75$ for the reboiler and $F_{\text{C}} = (F_{\text{d}} + F_{\text{p}})F_{\text{m}} = (1 + 0)3.75$ for the condenser and cooler.

D *Steam cost*

$$steam\ cost[\$/year] = P_{\text{steam}}(\frac{Q_{\text{R}} * 3600}{10^9})\left(8150\frac{\text{h}}{\text{year}}\right) \quad \text{(S9)}$$

where P_{steam} is the price of steam.

E *Cooling water cost*

$$cooling\ water\ cost[\$/year] = P_{\text{CW}}(\frac{Q_{\text{C}} * 1055.06}{c_{\text{p}}\frac{(107.6 - 89.6)}{1.8}})\left(8150\frac{\text{h}}{\text{year}}\right) \quad \text{(S10)}$$

where Cp is the heat capacity of water, equal to 4200J/kg/K, P_{CW} is the price of cooling water.

F *Chilled water cost*

$$Chilled\ water\ cost[\$/year] = P_{\text{ChW}} * Q_{\text{C}} * \frac{1055.06}{10^9}\left(8150\frac{\text{h}}{\text{year}}\right) \quad \text{(S11)}$$

(4) Cooler heat-transfer area (A_{Cooler})

$$A_{\text{Cooler}}[\text{ft}^2] = \frac{Q_{\text{Cooler}}}{U_{\text{Cooler}} \cdot \Delta T_{\text{Cooler}}} \quad \text{(S12)}$$

where Q_{Cooler} [Btuh] is the cooler duty, the overall heat-transfer coefficient U_{C} is assumed to be 50 Btu/(h.ft^2), and the log-mean temperature driving force ΔT_{Cooler} [°F] depends on the inlet and outlet temperature of cooler. The difference of temperature for heat transfer for cooling water and chilled water were calculated by:

Cooling water

$$\Delta T_{Cooler} = \frac{(T_{hot,in} - 107.6) - (T_{hot,out} - 89.6)}{\ln\left(\frac{T_{hot,in} - 89.6}{T_{hot,out} - 107.6}\right)} \quad \text{(S13)}$$

and

$$\Delta T_{Cooler} = \frac{(T_{hot,in} - 59) - (T_{hot,out} - 41)}{\ln\left(\frac{T_{hot,in} - 41}{T_{hot,out} - 59}\right)} \quad \text{(S14)}$$

Other parameters like price and energy were listed as following:

- Low-pressuresteam (6 bar, 87 psia, 160 ºC/433K/320°F) =$7.78/GJ
- Medium-pressure steam (11 bar, 160 psia, 184 ºC/457K/363°F) =$8.22/GJ

- High-pressure steam（42 bar, 611 psia, 254 ^{o}C/527K/490°F）=$9.88/GJ
- Electricity = $16.8/GJ

For the refrigeration, the following parameters were used:

- Chilled water at 5℃，returned at 15℃=4.43/GJ
- Refrigerant at -20^{o}C=7.89/GJ
- Refrigerant at -50^{o}C =13.11/GJ

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