Problems with specifying $\Delta T_{\min}$ in design of processes with heat exchangers

Jørgen Bauck Jensen* Sigurd Skogestad†

Department of Chemical Engineering, Norwegian University of Science and Technology, Trondheim, Norway

Abstract

We show in this paper that the common method of specifying $\Delta T_{\min}$ in design of heat exchanger systems may lead to wrong decisions and should be used with care. Although specifying $\Delta T_{\min}$ is reasonable for heat exchanger networks synthesis with given stream data, it should not generally be used for obtaining optimal design data - and especially not stream data (temperatures). An alternative simple TAC method is suggested and compared with the $\Delta T_{\min}$-method on three vapour compression (refrigeration) cycle case studies.

Keywords: $\Delta T_{\min}$, vapour compression cycle, heat exchanger, design.

1 Introduction

In process design one seeks to optimize the future income of the plant. This might be realized by minimizing the total annualized cost (TAC), $J_{\text{TAC}} = J_{\text{operation}} + J_{\text{capital}}$ [\$ year^{-1}]. However, this requires information of the capital cost, which is often too detailed in a preliminary study.

†Author to whom correspondence should be addressed: e-mail: skoge@chemeng.ntnu.no, Tel: +47 73 59 41 54, Fax.: +47 73 59 40 80

*Current affiliation: ABB Enhanced Operations & Production, Advanced Process Control, Oslo, Norway

An alternative simple and common approach for design of processes with heat exchangers, especially at an early design stage, is to specify the minimum approach temperature (ΔT_{min}) in each heat exchanger. The idea is that this specification gives a reasonable balance between minimizing operating costs (favored by a small ΔT_{min}) and minimizing capital costs (favored by a large ΔT_{min}). As an example, Figure 1 shows a hot stream (T_2) transferring heat to a cold stream with constant temperature (T_1). Stream 2 is hot exhaust gas that one would like to cool to capture its energy and this is done by vaporizing water in stream 1. A low value of ΔT_{min} means that a lot of the energy is recovered, but it requires a large heat exchanger. On the other hand, a higher value of ΔT_{min} will require less area, but the outlet temperature T_2 will be higher and less energy is recovered. There exists many rules of thumb for the value of ΔT_{min}. For example Turton et al. (1, page 250) recommends 10 °C for fluids and 5 °C for refrigerants.

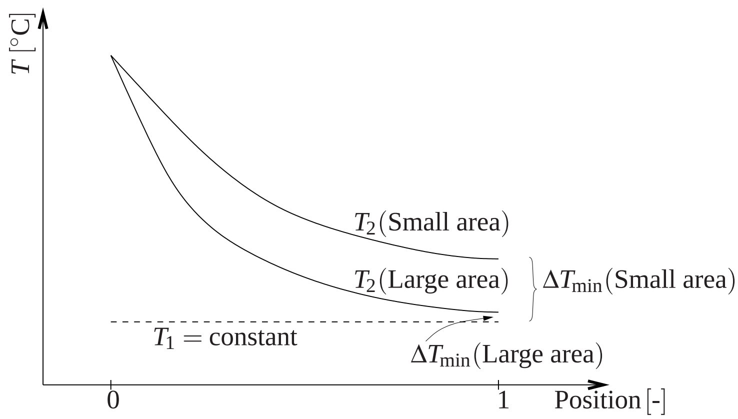


Figure 1: The effect of different values for ΔT_{min}

Note here that we are referring to *design* as it is reasonably well known that we should never specify ΔT_{min} during operation where the heat exchanger areas are given and should be used as constraints rather than ΔT_{min}. However, even when it comes to design, specifying ΔT_{min} (and maybe varying it in an outer loop), does not always result in a good design, except for simple cases. To understand why specifying ΔT_{min} in design may not be correct, consider the following three problems:

Problem 1 Detailed optimal design *based on minimizing TAC* $[\$\,\text{year}^{-1}]$ *(e.g. 2):*

$$\min\left(J_{operation} + J_{capital}\right) \tag{1}$$

where $J_{capital} = \sum_{i\in Units}\left(C_{fixed,i} + C_{variable,i}\cdot S_i^{n_i}\right)$. *Here* S_i *is the characteristic size for the unit (area in* m^2 *for heat exchangers), and the cost factors (*$C_{fixed,i}$ *and*

$C_{variable,i}$) and cost scaling factor n_i are constants for each unit (e.g. heat exchangers). T is the capital depreciation time, e.g. $T = 10\,\text{years}$.

Problem 2 Simplified optimal design *with specified ΔT_{min}:*

$$
\begin{aligned}
& \min(J_{operation}) \\
\textit{subject to} \quad & \Delta T_i - \Delta T_{\min,i} \geq 0
\end{aligned} \tag{2}
$$

After solving this problem one can obtain the heat exchanger areas ($A_{\max}$). Note that the capital costs (heat exchanger area) are not included, so the only factor to optimize (minimize) is the operating cost. Thus, provided there are degrees of freedom available, for example if the stream data are not fixed, optimization will favor designs where the temperature difference ΔT is close to $\Delta T_{\min}$ throughout the heat exchangers because this improves energy efficiency but does not cost anything. Specifying $\Delta T_{\min}$ will therefore tend to give designs with large heat exchanger areas.

Problem 3 Optimal operation *with given heat exchanger areas, A_{max}, (e.g. found from Problem 1 or 2):*

$$
\begin{aligned}
& \min(J_{operation}) \\
\textit{subject to} \quad & A_i - A_{\max,i} \leq 0
\end{aligned} \tag{3}
$$

The solution to Problem 3 in terms of optimal stream data (temperatures) will be the same as to Problem 1, but not generally the same as to Problem 2. To understand this, note that with the areas given (Problem 3), there is no particular incentive to make the temperature difference ΔT "even" throughout the heat exchangers. Provided there are degrees of freedom, we will therefore find that ΔT from Problem 3 varies more through the heat exchangers than ΔT from Problem 2. In particular the $\Delta T_{\min}$ obtained from Problem 3 is usually smaller than that specified in design (Problem 2) even when the areas A_i are obtained by solving Problem 2 (see the introductory example below). Thus, the optimal nominal operating point (solution to Problem 3) is not the same as the nominal simplified design point (solution to Problem 2). From this it is clear that specifying $\Delta T_{\min}$ in design cannot be optimal.

Note that we are here discussing the use of $\Delta T_{\min}$ for individual heat exchangers and *not* for heat exchanger networks. $\Delta T_{\min}$ is often used in design of heat exchanger networks (e.g. see the review paper by 3), but here $\Delta T_{\min}$ refers to the "pinch" temperature for the entire network. Thus, $\Delta T_{\min}$ is used to set the target for energy recovery and the stream data (temperatures) are assumed given so the use of $\Delta T_{\min}$ may be justified.

The objective of this paper is to study the $\Delta T_{\min}$-method (Problem 2) in more detail and suggest an alternative simple design method for heat exchanger systems.

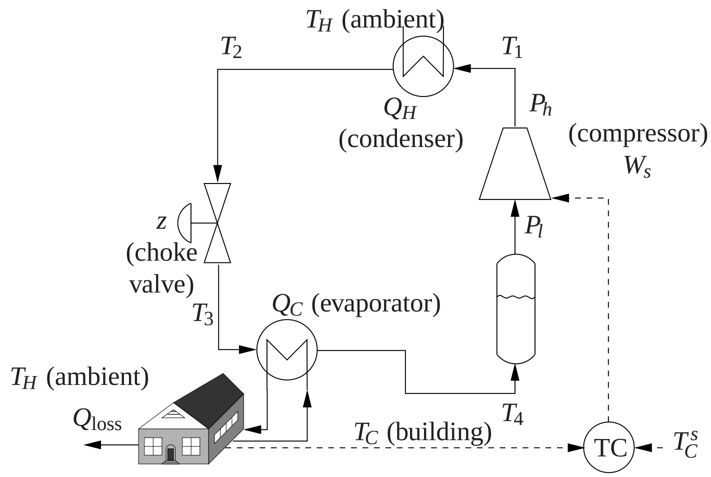


Figure 2: An ammonia refrigeration system

2 Introductory example: Ammonia refrigeration cycle

The ammonia refrigeration cycle for cold storage presented in (4) is shown in Figure 2. We use the following conditions:

- $Q_{\text{loss}} = 20\,\text{kW}$
- Ambient temperature $T_H = 25\,^\circ\text{C}$
- Cold storage (indoor) temperature set point $T_C^s = -12\,^\circ\text{C}$
- Heat transfer coefficient for the evaporator and condenser, $U = 500\,\text{W}\,\text{m}^{-2}\,^\circ\text{C}^{-1}$

The temperature controller adjust the compressor power to maintain $T_C = T_C^s$ which indirectly gives $Q_C = Q_{\text{loss}}$. The main model equations are given in Table 1.

Table 1: Structure of model equations for the ammonia case study

Heat exchangers (condenser and evaporator)
$Q = U \cdot \int \Delta T \, \mathrm{d}A = \dot{m} \cdot (h_{out} - h_{in})$
$P = P_{sat}(T_{sat})$
$m = \rho / V$
Valve
$\dot{m} = z \cdot C_V \sqrt{\Delta P \cdot \rho} \qquad h_{out} = h_{in}$
Compressor
$W_s = \dot{m}(h_{out} - h_{in}) = \dot{m} \cdot (h_s - h_{in}) / \eta$

2.1 $\Delta T_{\mathbf{min}}$-method

The operational cost is given by the compressor power ($J_{\text{operation}} = W_s$), so with the ΔT_{min}-method, the optimal design problem, see Problem 2, becomes:

$$\begin{aligned} & \min(W_s) \\ \text{such that} \quad & \Delta T_{\text{vap}} - \Delta T_{\text{min, vap}} \geq 0 \\ & \Delta T_{\text{con}} - \Delta T_{\text{min,con}} \geq 0 \end{aligned} \tag{4}$$

We choose $\Delta T_{\text{min}} = 10\,^\circ\text{C}$ in both the evaporator and the condenser (5). The resulting heat exchanger areas A are then obtained from $Q = \int (U \cdot \Delta T) \, \mathrm{d}A$.

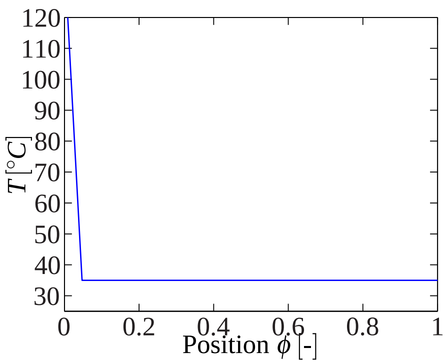
As noted in the introduction the solution to Equation 4 does not give optimal operation with the resulting areas. The re-optimized operation problem with given areas, see Problem 3, becomes:

$$\begin{aligned} & \min(W_s) \\ \text{such that} \quad & A_{\text{vap}} - A_{\text{vap}}^{\text{design}} \leq 0 \\ & A_{\text{con}} - A_{\text{con}}^{\text{design}} \leq 0 \end{aligned} \tag{5}$$

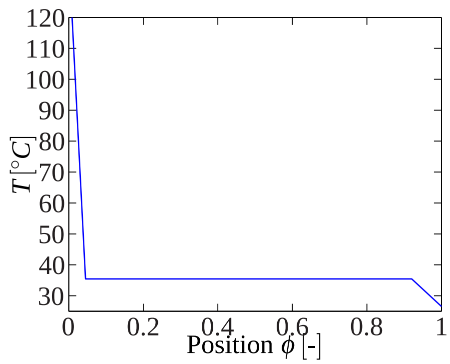
where $A_{\text{vap}}^{\text{design}}$ and $A_{\text{con}}^{\text{design}}$ are the result of the ΔT_{min}-method design problem (Equation 4).

The results for the two problems are summarized in the two left columns of Table 2 and we note that re-optimization reduces the operating cost (W_s) by 3.2%. Figure 3 shows the corresponding temperature profiles in the condenser.

- In the design case (with fixed ΔT_{min}) there is no sub-cooling in the condenser. In the re-optimized operation however, there is a sub-cooling of $8.9\,^\circ\text{C}$. The optimality of sub-cooling in simple refrigeration cycles is discussed in detail in (6).



(a) Optimal design with specified $\Delta T_{\min}$



(b) Re-optimized operation with specified A

Figure 3: Temperature profile in the condenser for the $\Delta T_{\min}$-method

- The high pressure P_h is increased by 0.7 % in the re-optimized case, but this is more than compensated for by a 3.7 % reduction in flowrate.

In summary, we find that the $\Delta T_{\min}$-method is not suitable for the optimal design of vapour compression cycles.

3 Proposed simplified TAC method

The cost function for Problem 1 is complicated as it requires quite detailed cost data. Therefore, the idea is to replace equipment cost in Problem 1 with a simplified expression. First, we assume that the structure of the design is given such that we need not consider the fixed cost terms (i.e. we set $C_{\text{fixed,i}} = 0$). Second, we only consider heat exchanger costs. For a vapour compression cycle this is justified if we assume the exponent $n_i = 1$ for the compressor. Then we have $C_{\text{com}} \cdot S_{\text{com}} = k \cdot W_s$ and we can include the capital cost for the compressor in the operating cost. Third, we assume that all heat exchangers have the same cost factors ($C_{\text{variable,i}} = C_0$ and $n_i = n$).

The resulting "simplified TAC" optimal design problem becomes:

$$\min \left(J_{\text{operation}} + C_0 \cdot \sum_i A_i^n \right) \tag{6}$$

where $J_{\text{operation}} = W_s$ for a refrigeration cycle.

Table 2: Ammonia case study

	$\Delta T_{\min}$-method		Simplified TAC (Eq. 7)	
	Design (4)	Operation (5)	$C_0 = 818^*$	$C_0 = 8250^\dagger$
	$\Delta T_{\min} = 10\,^\circ$C	Re-optimized		
$\Delta T_{\min}^{\mathrm{vap}}$ [°C]	**10.0**	10.0	9.13	26.7
$\Delta T_{\min}^{\mathrm{con}}$ [°C]	**10.0**	1.53	1.84	**10.0**
A_{con} [m^2]	4.50	**4.50**	4.12	1.47
A_{vap} [m^2]	4.00	**4.00**	4.38	1.50
A_{tot} [m^2]	8.50	8.50	**8.50**	2.97
HX cost [-]	1.00	1.00	1.00	0.51
P_l [bar]	1.74	1.74	1.81	0.77
P_h [bar]	13.5	13.6	14.0	28.4
ΔT_{sub} [°C]	0.0	8.9	9.6	28.5
$\dot{m}$ [$\mathrm{mol\,s^{-1}}$]	1.07	1.03	1.03	1.10
$\mathbf{W_s}$ [W]	6019	5824	5803	12479
COP [-]	3.32	3.43	3.45	1.60

$^*C_0$ adjusted to get same total heat exchanger area as the $\Delta T_{\min}$-method
$^\dagger C_0$ adjusted to get same $\Delta T_{\min}$ as used in the $\Delta T_{\min}$-method

In the examples, we choose $n = 0.65$ for the heat exchangers and use C_0 as the single adjustable parameter (to replace $\Delta T_{\min}$). There are several benefits compared with the $\Delta T_{\min}$-method:

- The optimal design (Equation 6) and the optimal operation (Problem 3) have the same solution in terms of optimal stream data. This follows since the term $C_0 \sum_i A_i^n$ is constant in operation.
- The assumption of using the same C_0 for all heat exchangers is generally much better than assuming the same $\Delta T_{\min}$.

3.1 Ammonia case study

The optimization problem becomes*:

$$\min(W_s + C_0 \cdot (A_{\mathrm{con}}^n + A_{\mathrm{vap}}^n)) \tag{7}$$

The right two columns of Table 2 shows the optimal design with $n = 0.65$ and two different values of C_0. $C_0 = 818$ gives the same total heat exchanger area, and

*In a more realistic design, one may also consider additional constraints such as maximum compressor suction volumes and pressure ratio, but this is not discussed here.

almost the same capital cost as the ΔT_{min}-method, but the area is better distributed between the evaporator and condenser. This results in a 3.60 % reduction in W_s compared with the ΔT_{min}-method (0.36 % after re-optimizing the ΔT_{min}-method). Using $C_0 = 8250$ gives $\Delta T_{\text{min}} = 10.0\,^{\circ}\text{C}$. The compressor work is increased with 107 % (114 %), but the heat exchanger area is reduced by 60 %, and this is the only design that truly satisfies the ΔT_{min} we selected initially.

The simplified TAC method confirms that sub-cooling is optimal, and we see that the degree of sub-cooling increases with decreasing heat transfer area (increased C_0).

Note that the heat transfer coefficients are assumed to be equal, but the simplified TAC method will automatically distribute the heat transfer area optimally, also if the heat exchangers have different heat transfer coefficients. For example, with $U_{\text{evaporator}} = 2U_{\text{condenser}}$ the energy savings (for the same heat exchangers cost) are even larger (6 %) using the simplified TAC method compared with the ΔT_{min}-method.

4 Other case studies

We here briefly present results from two other case studies.

4.1 CO_2 air-conditioner

CO_2 as a working fluid in air-conditioners and heat-pumps is gaining increased popularity because of its low environmental impact (7, 8). We consider a trans-critical CO_2 air-conditioning unit with the following data:

- Heat transfer coefficient: $U = 500\,\text{W}\,\text{m}^{-2}\,\text{K}^{-1}$ for the evaporator, condenser and internal heat exchanger
- Ambient temperature: $T_H = 30\,^{\circ}\text{C}$
- Set point for room temperature: $T_C = 20\,^{\circ}\text{C}$
- Heat loss into the room: $Q_{\text{loss}} = 4.0\,\text{kW}$

The details about the model are found in Jensen and Skogestad (4). In the optimization we have included an internal heat exchanger that transfers heat from before the compressor to before the valve. Otherwise the flowsheet is as for the ammonia cycle shown in Figure 2.

Table 3: CO_2 air-conditioner

	$\Delta T_{\min}$-method		Simplified TAC		
	Design $\Delta T_{\min} = 5\,^\circ\mathrm{C}$	Operation Re-optimized	$C_0 = 253^*$	$C_0 = 185^\dagger$	$C_0 = 877^\ddagger$
$\Delta T_{\min}^{\mathrm{gco}}$ [°C]	**5.00**	3.56	2.41	2.07	**5.00**
$\Delta T_{\min}^{\mathrm{vap}}$ [°C]	**5.00**	5.00	5.78	5.01	11.5
$\Delta T_{\min}^{\mathrm{ihx}}$ [°C]	**5.00**	4.75	-	-	-
A_{gco} [m^2]	1.31	**1.31**	1.76	2.02	0.92
A_{vap} [m^2]	1.60	**1.60**	1.38	1.60	0.70
A_{ihx} [m^2]	0.23	**0.23**	0	0	0
A_{tot} [m^2]	3.14	3.14	**3.14**	3.62	1.61
HX cost [-]	1.00	1.00	0.91	**1.00**	0.59
P_h [bar]	87.8	91.6	92.8	91.0	107.0
P_l [bar]	50.8	50.8	49.9	50.8	43.3
$\dot{m}$ [mol s^{-1}]	0.65	0.59	0.69	0.70	0.67
$\mathbf{W_s}$ [W]	892	859	871	814	1328
COP [-]	4.49	4.65	4.59	4.92	3.01

$^*C_0$ adjusted to get same total area as $\Delta T_{\min}$-method
$^\dagger C_0$ adjusted to get same heat exchanger cost as the $\Delta T_{\min}$-method
$^\ddagger C_0$ adjusted to get same $\Delta T_{\min}$ as used in the $\Delta T_{\min}$-method

For solving Problem 2, we use a design $\Delta T_{\min} = 5.0\,^\circ\mathrm{C}$ in all heat exchangers. Again we find that re-optimizing for operation (Problem 3) gives a better operating point with 3.70 % less compressor power. The results given in Table 3 are similar to the ammonia cooling cycle, although there is no sub-cooling since $P_h > P_c$.

Interestingly with the simplified TAC method $A_{\mathrm{ihx}} = 0.0\,\mathrm{m}^2$, which means that it is not optimal from an economical point of view to pay for the area for the internal heat exchanger (although the internal heat exchanger would of course be used if it were available free of charge). This is a bit surprising since we have not included the fixed cost of installing a heat exchanger, which would make it even less desirable to invest in an internal heat exchanger. On the other hand, if a lot of super-heating before the compressor is required then it might be better to achieve this super-heating in an internal heat exchanger, but this is not discussed here.

With $C_0 = 253$ we get the same total heat transfer area as for the $\Delta T_{\min}$-method, but the shaft work is reduced by 4.26 % (0.58 % compared to re-optimized). $C_0 = 185$ gives the same cost of heat exchanger area (without even considering the savings of completely removing a heat exchanger) and W_s is reduced by 12.22 % (8.85 %). With $C_0 = 877$ we get the only design with $\Delta T_{\min} = 5.0\,^\circ\mathrm{C}$. The heat exchanger cost is reduced by 41 % and the compressor power is increased by 49 % (55 %)

Table 4: PRICO LNG process

	$\Delta T_{\min}$-method		Simplified TAC		
	Design	Operation	$C_0 =$	$C_0 =$	$C_0 =$
	$\Delta T_{\min} = 2\,^{\circ}\mathrm{C}$	Re-optimized	2135*	2090†	7350‡
$\Delta T_{min,HOT}$ [°C]	**2.00**	0.89	0.90	0.86	**2.00**
$\Delta T_{min,NG}$ [°C]	**2.00**	0.98	1.09	1.08	2.22
$A_{HOT} \cdot 10^{-3}$ [m^2]	98.2	**98.2**	101.2	102.7	43.1
$A_{NG} \cdot 10^{-3}$ [m^2]	29.9	**29.9**	26.9	27.2	14.5
$A_{Tot} \cdot 10^{-3}$ [m^2]	128.1	128.1	**128.1**	129.9	57.7
HX cost [-]	1.00	1.00	0.99	**1.00**	0.60
P_h [bar]	20.1	27.1	27.0	26.8	37.8
P_l [bar]	2.7	2.9	2.9	2.9	1.91
$\dot{m}$ [kmol s^{-1}]	3.0	2.5	2.5	2.5	2.3
$\mathbf{W_s}$ [MW]	18.94	18.14	18.17	18.12	22.16

*C_0 adjusted to get same total area as $\Delta T_{\min}$-method
†C_0 adjusted to get same heat exchanger cost as the $\Delta T_{\min}$-method
‡C_0adjusted to get same $\Delta T_{\min}$ as used in the $\Delta T_{\min}$-method

compared with the $\Delta T_{\min}$-method.

4.2 PRICO LNG process

The PRICO LNG process (9) is the simplest configuration utilizing mixed refrigerants. Note that we are not considering constraints on compressor suction volume and pressure ratio for the compressor. This will be important in an actual design, but we have tried to keep the case study simple to illustrate the effect of specifying $\Delta T_{\min}$.

A design $\Delta T_{\min}$ of $2.0\,^{\circ}\mathrm{C}$ is used for the $\Delta T_{\min}$ method. From Table 4 we see that re-optimizing reduces the energy usage (W_s) by 4.8 %. This is achieved by increasing the pressure ratio (by 25.5 %) and reducing the refrigerant flowrate (by 16.7 %). The composition of the refrigerant is also slightly changed, but this is not shown in Table 4. We were quite surprised by the rather large improvement obtained by re-optimizing with fixed heat transfer areas considering the relatively low value for the initial $\Delta T_{\min}$.

With the simplified TAC method we get a 4.1 % reduction (0.2 % increase compared to re-optimized) in W_s for the same total heat transfer area ($C_0 = 2135$). The small increase in W_s compared with the re-optimized $\Delta T_{\min}$ design is because the simplified TAC method minimizes the heat exchanger cost and not the total area.

With the same cost ($C_0 = 2090$), the TAC-method gives a reduction in compressor power of 4.3% (0.1%). The saving compared with the re-optimized case is small because of the small ΔT_{min} resulting in very large heat exchangers. A more reasonable design is achieved with $C_0 = 7350$, which gives a design with a true ΔT_{min} of 2.0°C. The heat exchanger capital cost is reduced by 40% but the compressor power is increased by 17.0% (22.2%).

5 Discussion

There are some main points that are important to note from this analysis of the ΔT_{min}-method

1. ΔT_{min} is treated as an important parameter in heat exchangers, but the theoretical basis seems weak "Violating" ΔT_{min} in operation gives lower operating cost.
2. The ΔT_{min}-method will not give the optimal operating point, so sub-optimal setpoints might be implemented.
3. The size distribution between the heat exchanger will not be optimal, but this may be corrected for by adjusting the value of ΔT_{min} for each heat exchanger.
4. More seriously, the results might lead to wrong structural decisions and this can not be changed by iterating on the ΔT_{min}-values. In the ammonia case study one would incorrectly conclude that sub-cooling is not optimal and thus implement a liquid receiver after the condenser. This would during operation achieve no sub-cooling. From the true optimum however, we see that some sub-cooling is optimal.
5. One potential advantage with the ΔT_{min}-method is that it only requires an overall energy balance for the heat exchangers. However, for more complex cases a more detailed model of the heat exchangers is needed so in the general cases this advantage is lost.

In summary, the ΔT_{min}-method is not satisfactory for realistic design problems. The question is whether there are other ways of specifying temperature differences. In terms of area, it would be better to specify the mean temperature difference $\overline{\Delta T} = \frac{1}{A}\int \Delta T\, dA$, since $\overline{\Delta T}$ is directly linked to the heat transfer area by (assuming constant heat transfer coefficient):

$$Q = UA\overline{\Delta T} \tag{8}$$

This method has several drawbacks that makes it unattractive to use. First, it might be cumbersome to calculate the integral of the temperature and second, and more importantly there are no general rules in selecting values for $\overline{\Delta T}$. We therefore propose to use the simplified TAC-method.

6 Conclusion

We have shown that the method of specifying $\Delta T_{\min}$ for design of heat exchangers, $\min J$ subject to $\Delta T \geq \Delta T_{\min}$, may fail for cases where the stream data are not fixed. In the ammonia refrigeration case study the $\Delta T_{\min}$-method fails to find that sub-cooling in the condenser is optimal. As a simple alternative we propose the simplified total annualized cost (TAC) method, $\min(J + C_0 \sum_i A_i^n)$, where C_0 replaces $\Delta T_{\min}$ as the adjustable parameter.

Another important conclusion is related to the temperature difference profile in the heat exchanger. According to exergy or entropy minimization rules of thumb (e.g. 10) it is optimal to have even driving forces, which suggests that ΔT should be constant in heat exchangers. The results presented here however, suggest that this is not true. The $\Delta T_{\min}$ approach (Problem 2) favors a constant ΔT profile, but in optimal operation (Problem 3) we find that the temperature difference is less constant.

References

(1) R Turton, R. C. Bailie, W. B. Whiting, and J. A. Shaeiwitz. *Analysis, synthesis, and design of chemical processes*. Pearson Education Ltd., 1998.

(2) L. T. Biegler, I. E. Grossmann, and A. W. Westerberg. *Systematic Methods of Chemical Process Design*. Prentice Hall, 1997.

(3) T. Gundersen and L. Naess. The synthesis of cost optimal heat exchangers networks. *Comput. Chem Eng.*, 12(6):503–530, 1988.

(4) J. B. Jensen and S. Skogestad. Optimal operation of a simple refrigeration cycles. Part II: Selection of controlled variables. *To appear in Comput. Chem Eng.*, 2007.

(5) M. R. Shelton and I. E. Grossmann. Optimal synthesis of integrated refrigeration systems—i : Mixed-integer programming model. *Comput. Chem. Eng.*, 10(5):445–459, 1986.

(6) J. B. Jensen and S. Skogestad. Optimal operation of simple refrigeration cycles. Part I: Degrees of freedom and optimality of sub-cooling. *Comput. Chem. Eng.*, 31:712–721, 2007.

(7) G. Lorentzen. The use of natural refrigerants: a complete solution to the CFC/HCFC predicament. *Int. Journal of Refrigeration*, 18:190–197, 1995.

(8) P. Neksaa. CO_2 heat pump systems. *Int. J. Refrigeration*, 25:421–427, 2002.

(9) B. C. Price and R. A. Mortko. PRICO - a simple, flexible proven approach to natural gas liquefaction. In *GASTECH, LNG, Natural Gas, LPG international conference , Vienna*, 1996.

(10) E. Sauer, S. K. Ratkje, and K. M. Lien. Equipartition of forces: A new principle for process design and optimization. *Ind. Eng. Chem. Res.*, 35: 4147–4153, 1996.