



The role of equilibrium thermodynamics in process synthesis

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Abstract

The role of classical thermodynamics in generating design options in a systematic way is emphasised. Two thermodynamic approaches to solving this problem, the pinch and exergy methods, are compared. It is demonstrated that both approaches are based on analysis of exergy losses within a designed system. The difference is that in pinch analysis knowledge of exergy losses precedes design, while the latter allows us to establish energy targets prior to design. In conventional exergy analysis, losses may be evaluated only after the configuration of the process has been chosen. As a result, the conventional exergy approach remains trial-and-error. In order to overcome this limitation, this paper proposes a new exergy-based approach to generating design alternatives. A special graphic presentation of exergy balance around the ideal processes, where exergy losses are nil, allows us to generate alternatives with predetermined targets in a systematic way. In the next design step, real processes with the same structure as the selected ideal ones are identified. The final solution is carried out through optimization of a superstructure embedding the limited number of real process alternatives. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

One of the most widespread approaches to process synthesis is mathematical optimization of a superstructure containing all the alternatives to be considered for a design [5]. It was also emphasized [9] that with increasing numbers of alternatives, the likelihood of determining the global optimum diminishes. Therefore, it is essential to find a systematic way to generate the limited number of most promising design alternatives to be embedded within a superstructure. It was

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pointed out that classical thermodynamics may be helpful [8]. Two thermodynamic approaches, pinch analysis [7] and exergy analysis [6], aim to generate design alternatives in a systematic way. Pinch analysis is not as general as exergy analysis, but it has found many more applications in industrial practice. This paper will explain this situation from a thermodynamic point of view. A new approach to generating design alternatives based on the exergy concept will also be presented. Application of the proposed approach to the generation of design alternatives for sorption refrigeration systems will be demonstrated as an example. The final procedure of embedding these alternatives within a superstructure, like their further mathematical optimization, is beyond the scope of the paper.

2. Application of pinch analysis and exergy analysis to generation of process structures

Two interrelated problems in the design of process structures might be solved by using the methods of classical thermodynamics [1,7]:

- setting energy targets prior to design,
- identifying design options in order to meet these targets.

Pinch analysis and exergy analysis try to solve these problems differently. Pinch analysis is mainly concerned with the design of heat exchanger networks (HEN) and utilities. The key concept of the analysis is composite curves presented on diagrams of temperature (T) vs. enthalpy (H) (Fig. 1).

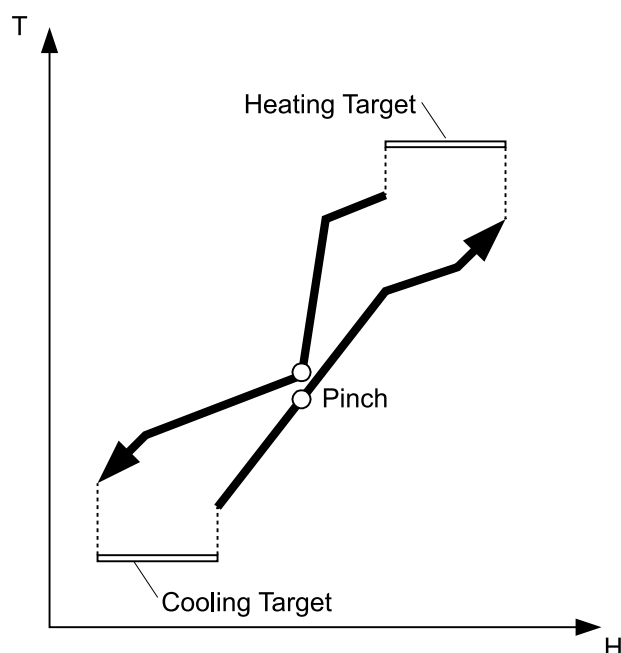


Fig. 1. Composite curves in traditional pinch analysis.

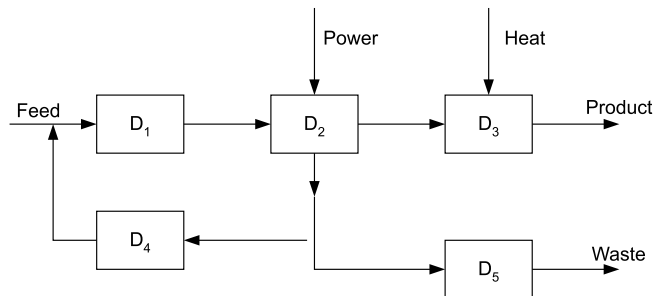


Fig. 2. Local exergy losses, D in a process.

They are used to set energy targets prior to design and to predict the location of pinch(es). Certain rules have been formulated [7] for the design to meet energy targets. The most important among them is the statement that the targets cannot be met if there is any “cross-pinch” heat transfer from above the pinch to below the pinch. This analysis has become a widespread methodology for targeting and design of thermal processes. Evidence of its practical application comes from more than 1000 projects worldwide.

Exergy analysis allows us to indicate the major causes of thermodynamic imperfection in any process, not only thermal ones. In this sense, it is more general than pinch analysis. Conventional exergy analysis compares the performance of a real process and the corresponding ideal one by computing the local exergy losses in every unit operation of the process, as presented in Fig. 2. The most widely quoted design rule is “tackle the biggest loss first” [4]. Sometimes this rule works, and sometimes it does not due to the interrelation among local exergy losses [13]. As a result, exergy analysis is still less practical and remains mainly of academic interest. Which thermodynamic features make pinch analysis so practical compared to conventional exergy analysis? The question deserves special investigation.

3. Exergy losses and pinch analysis

Coming back to the origin of pinch analysis, we can interpret the composite curves on a Carnot factor (θ) vs. enthalpy (H) diagram, presented for the first time by Umeda et al. [14]. As shown in Fig. 3, the composite curves from Fig. 1 can be converted into exergy composite curves. The hatched area indicates the overall exergy losses associated with HEN and utilities. As was indicated by Umeda et al. [14], and later by Linnhoff [8], the above exergy losses are predetermined by thermal sources, sinks and just one variable: minimum temperature difference, ΔT_{\min} , at the pinch point. Instead of the widespread notion that the energy targets in Figs. 1 and 3 are defined by the shape of the composite curves and ΔT_{\min} , a more profound thermodynamic explanation is as follows: energy targets are determined by overall exergy losses, and the energy targeting procedure in pinch analysis is built on the exergy concept. The logical sequence of analysis and design stages is presented in Fig. 4. Knowledge of overall exergy losses prior to design allows us to define targets and formulate the main guidelines by using pinch analysis.

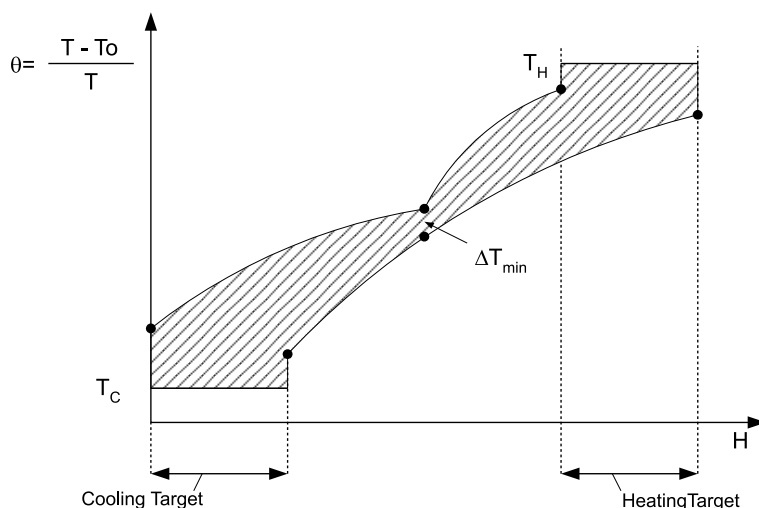


Fig. 3. Exergy composite curves.

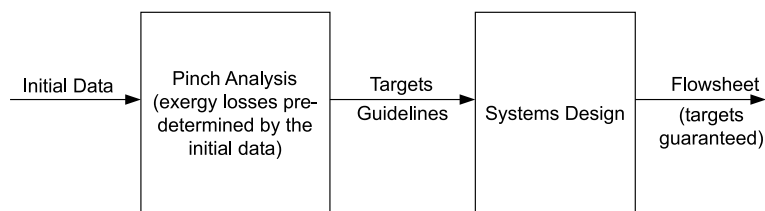


Fig. 4. The knowledge of exergy losses precedes design in traditional pinch analysis.

4. Conventional exergy analysis and new developments

As indicated in Fig. 5, the logical sequence of the analysis and design stages in the conventional exergy approach is the opposite of that presented in Fig. 4. Exergy losses may be computed only after the process structure and equipment have been chosen. As a result, conventional exergy analysis gives important, but merely iterative feedback to process design. How can this limitation be overcome? Two directions might be sketched. The first one follows the tradition of thermal

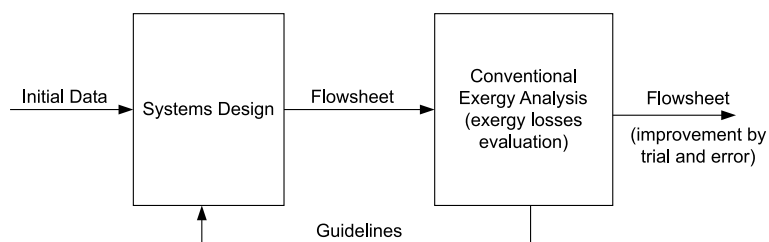


Fig. 5. Losses may be evaluated only after design in classical exergy analysis.

pinch analysis by formulating the design problems in a way that predetermines exergy losses from the initial data. Recent developments in water pinch analysis for just one contaminant [2,15], as well as developments in the pinch approach to mass-exchange networks [3], may serve as examples.

The second direction is the search for new concepts in exergy analysis and their interpretation in a context of practical design. One possible approach was recently proposed by Sorin et al. [11]. The main premises of this approach are:

1. design options will be systematically generated with predetermined targets for *ideal* processes (no exergy losses) and their combinations;
2. the structures selected for ideal processes will be *the same* as for the real ones;
3. technical and economical feasibility of the chosen design options should be checked through traditional modeling (in the case of a limited number of design options) or through mathematical programming (in the case of numerous design options and their combinations).

Application of the proposed approach to the conceptual design of thermochemical refrigerators is presented in the next section.

5. Solid/gas thermochemical refrigerator: design problem statement

Thermochemical refrigeration (TR) systems are based on the thermal effect of one or more reversible chemical transformations involving a solid and a gas. The basic unit of the process presented in Fig. 6 comprises a solid/gas reactor coupled with a condenser and evaporator. The

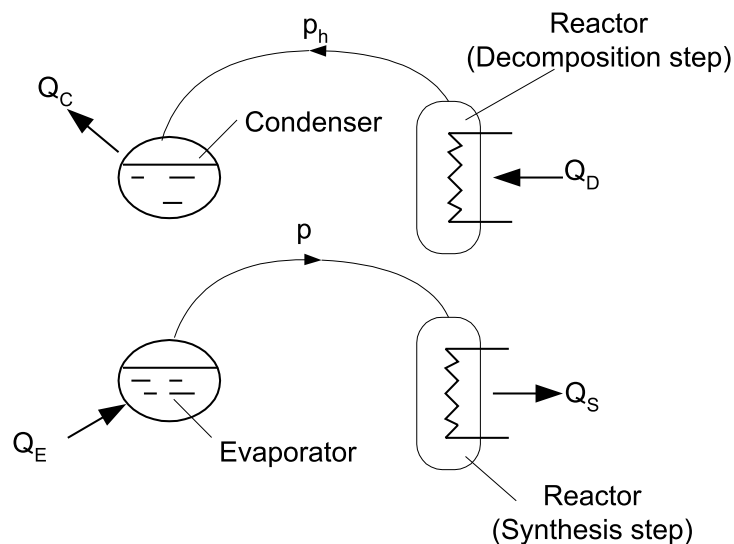


Fig. 6. Single-effect solid-gas TR.

reactor contains a salt, S , which reacts with the gas, G , (usually ammonia) present in its liquid form in the condenser/evaporator. The reactions used are of the type:



where ΔH_r is the enthalpy of solid/gas transformation. The two main successive phases of the cycle are demonstrated in Fig. 6.

- (a) Low pressure phase: the reactor is linked to the evaporator, which produces cold Q_E at low temperature T_E and pressure p_l (the evaporation step); the resultant vapor is absorbed by the salt in the reactor, thus producing heat Q_S at intermediate temperature T_S (the synthesis step).
- (b) High pressure phase: the reactor is linked to the condenser, which imposes its pressure p_h . Gas desorption requires heat input Q_D at high temperature T_D (the decomposition step). The gas condenses in the condenser at T_C , producing heat Q_C (the condensation step).

The above single-effect TR system works discontinuously. The problem of efficient TR design may be formulated as follows:

The working fluid is ammonia; the amount of Q_E and temperature level T_E of cold production, as well as the ambient temperature T_0 , are fixed. This does not exclude the possibility of producing additional cold, $(Q_E)_{\text{new}}$, at the range of temperature level, $(T_E)_{\text{new}} < T_0$. Temperature T_D of the disposed energy sources for salt decomposition varies in the range of $(T_D)_{\text{max}} \geq T_D \geq (T_D)_{\text{min}}$. The heat produced, Q_S , is a waste product. The salt materials should be chosen in order to simultaneously improve the COP value of the designed machine and minimize the temperature, T_S , of waste heat. The value T_S satisfies the condition $T_S \geq T_0$, where T_0 is the ambient temperature.

Before proposing an approach to solving the problem, the energy and exergy flow distribution within the TR system should be understood and quantified.

6. Energy and exergy flow distribution within a single-effect thermochemical refrigerator system

Within a four-temperature (T_D , T_E , T_S and T_C) single-effect thermochemical sorption process, there are three possible connections between the points corresponding to the energy inlets and outlets [12]. They are presented in Fig. 7. Two inlet points, D and E, are connected with two outlet points, S and C, in three ways. These ways will be named “energy shortcuts”. The external heat flow Q_D is split into two parts, Q_{D-C} and Q_{D-S} . Each of them moves along the energy shortcuts D–C and D–S. The heat flow $Q_E = Q_{E-S}$ moves along the shortcut E–S. Therefore, six external heat substreams (three inputs and three outputs) cross the control surface of the system.

It is important to emphasize that the flow rates of the heat streams remain unchanged along the shortcuts. The upgrading of the heat flow from low to high temperatures along the shortcut E–S is due to the thermal degradation of two heat flows along the shortcuts D–S and D–C. In order to quantify the variations in thermodynamic potential of upgrading and degrading heat flows, application of the exergy balance around an ideal TR system is required. On condition that the exergy losses, D , are nil, the exergy balance of the sorption system in Fig. 7 takes the form:

$$Q_{D-C}\theta_D + Q_{D-S}(\theta_D - \theta_S) = Q_{E-S}(\theta_S + (-\theta_E)) \quad (2a)$$

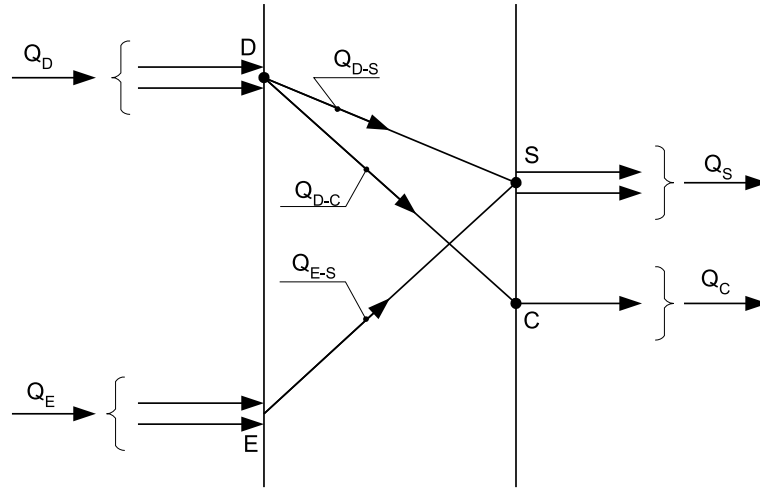


Fig. 7. Energy shortcuts within a single-effect TR.

Dividing Eq. (2a) by the value $Q_D \theta_D$, the equation may be presented as:

$$\lambda_{D-C} + \lambda_{D-S} \left(1 - \frac{\theta_S}{\theta_D} \right) = \lambda_{E-S} \left(\frac{\theta_S}{\theta_D} + \left(-\frac{\theta_E}{\theta_D} \right) \right) \quad (2b)$$

where $\lambda_{in-out} = Q_{in-out}/Q_D$ (in = D, E and out = C, S) is the ratio between an energy flow and Q_D . Taking into account that:

$$\lambda_{D-C} + \lambda_{D-S} = 1 \quad (3)$$

and

$$\lambda_{E-S} = \text{COP}_i \quad (4)$$

Eq. (2b) may be presented on a modified Carnot factor vs. heat diagram in coordinates θ/θ_D vs. Q_{in-out}/Q_D , as presented in Fig. 8. The diagram illustrates the fundamental fact that the sum of the areas (1–2–6–7 and 2–3–4–5), corresponding to the degradation of two parts of energy flow Q_D , is equal to the area (7–9–12–11), corresponding to the upgrading of energy flow Q_{E-S} . The diagram allows us to target the COP_i value directly (segment 11–12). The geometric figure 1–3–4–8 is a square with the base equal to 1.

Two important observations follow from the analysis of the diagram in Fig. 8. The first is that the thermodynamic potential of a relative heat flow (λ_{D-S}) to produce work is not realized completely. Indeed, the temperature barrier θ_S/θ_D prevents the further degradation of the flow. According to the balance (2b), the latter prevents an increase in energy upgrading within the given temperature conditions. Hence, it may be concluded that more cold would be produced for the same energy input, Q_D , if the remaining part of the outlet exergy flow $\lambda_{D-S}\theta_S/\theta_D$ (the shaded area 5–6–7–8 in Fig. 4) was reduced. The latter would cause a rise in the COP_i value. The shaded rectangle 5–6–7–8 in Fig. 8 is the relative value of so-called transiting exergy (see Ref. [11]). The second observation is that the exergy of waste heat $\lambda_{E-S}\theta_S/\theta_D$ is represented by the shaded area

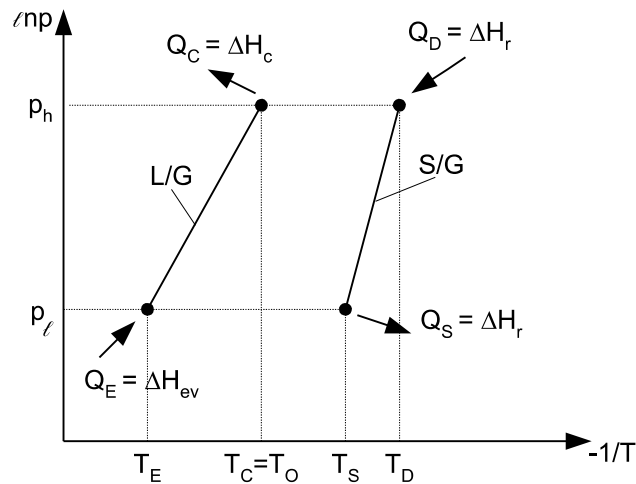


Fig. 9. TR cycle on Clausius–Clapeyron diagram.

7. Synthesis of new structures for thermochemical refrigerators

As was illustrated by Sorin et al. [11], room for energy improvement of single-effect machines through salt selection only is too narrow. In order to overcome this problem, more complex configurations of thermochemical processes are required. The synthesis of new configurations is achieved through manipulation of the energy shortcuts presented in Fig. 7. By way of example, Fig. 10 illustrates the case where a new energy shortcut between points E and C has been added.

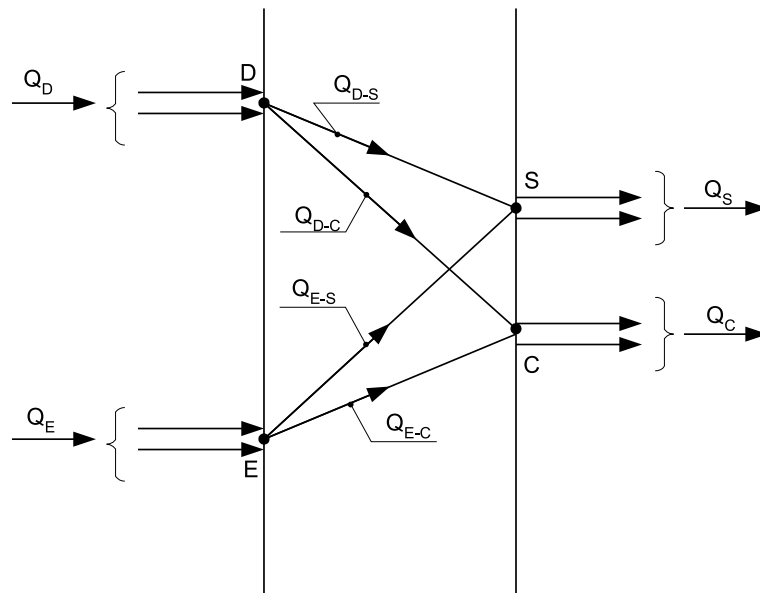


Fig. 10. Addition of a new energy shortcut within a TR process.

The corresponding exergy-based diagram is presented in Fig. 11. As has been discussed previously, any energy TR improvement is indicated on the diagram by reduction in areas corresponding to the transiting exergy as well as exergy of waste heat. The case corresponding to the total elimination of the areas is presented in Fig. 12. The geometric figure 1–3–4–6 is a square

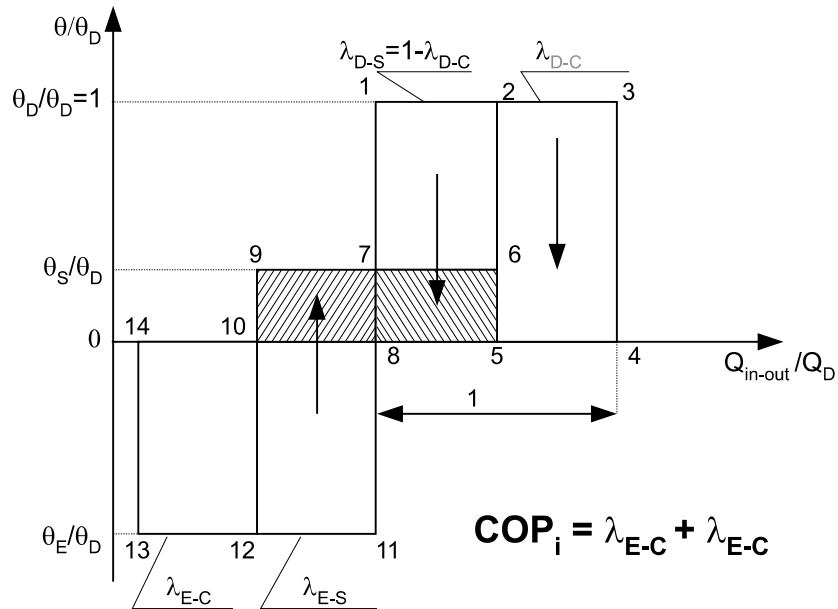


Fig. 11. Modified Carnot factor vs. heat diagram for a newly synthesized TR process.

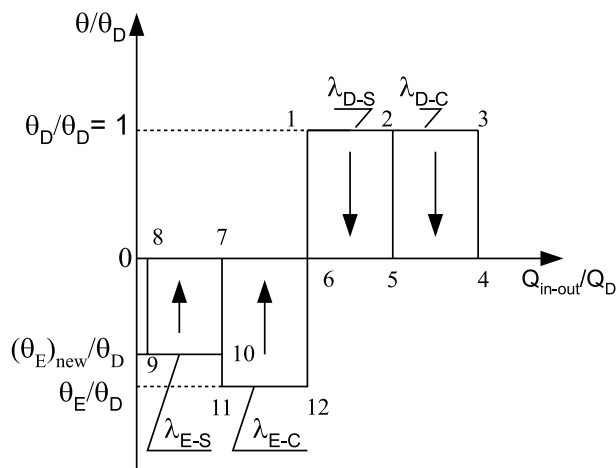


Fig. 12. Elimination of areas corresponding to transiting exergy and exergy of waste heat on a modified Carnot factor vs. heat diagram.

with the base equal to 1. Fixing the values T_D and ΔH_r defines the parameters θ_E/θ_D , $\lambda_{E-S} = \lambda_{E-C} = \Delta H_{ev}/\Delta H_r$. Then the height $(\theta_E)_{new}/\theta_D$ of the rectangle 7–8–9–10 may be easily computed from the equality of the areas 1–3–4–6 and 6–8–9–10–11–12 as:

$$\frac{(\theta_E)_{new}}{\theta_D} = \left(1 - \lambda_{E-S} \left(-\frac{\theta_E}{\theta_D}\right)\right) / \lambda_{E-C} \quad (6)$$

The Claperon–Clausius diagram corresponding to the exergy-based diagram in Fig. 12 may be automatically built as shown by the arrows in Fig. 13. In contrast to previously discussed single-effect TR, Fig. 13 illustrates the process using two different salts, placed in two different reactors. The operating principle of the new process is presented on a Claperon–Clausius diagram where the unit operations are visualized (see Fig. 14). The synthesis heat from one reactor is used to fire decomposition in the other. The principle of heat recovery between two reactors is known and is used in so-called double-effect machines [10]. By comparison to this classical case, the originality of the process structure presented in Fig. 14 consists in the fact that cold is produced on two levels, T_E and $(T_E)_{new}$. As a result, two evaporators are required.

As an example of further T_D variation on condition that ΔH_r keep its value constant, the procedure of TR synthesis is presented in Figs. 15 and 16. Using Eq. (6), the new value of the parameter $(\theta_E)_{new}/\theta_D$ may be defined. It identifies the height of the rectangle in Fig. 15 corresponding to the energy shortcut E–C. The response to this modification is presented on the Claperon–Clausius diagram, combined with a presentation of process unit operations (Fig. 16). An important distinction between Figs. 16 and 14 is that $(T_E)_{new} < T_E$. The list of design options produced by the proposed approach may be continued, and the design procedure may be summarized.

By changing the values T_D or/and ΔH_r , the exergy-based diagram may be identified. By eliminating the areas corresponding to the transiting exergy as well as the exergy of waste heat, the

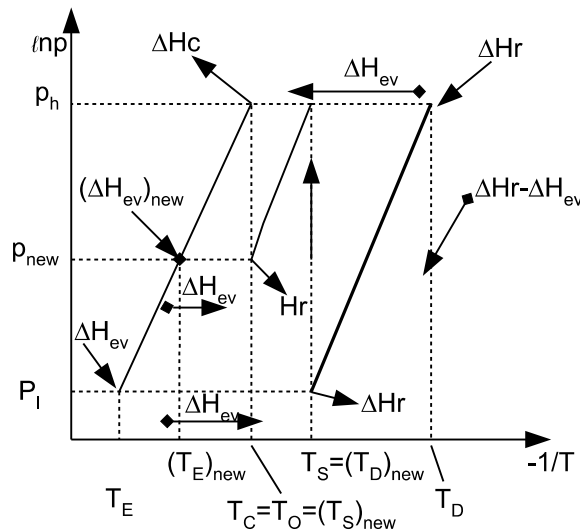


Fig. 13. Claperon–Clausius diagram corresponding to the exergy-based diagram in Fig. 12.

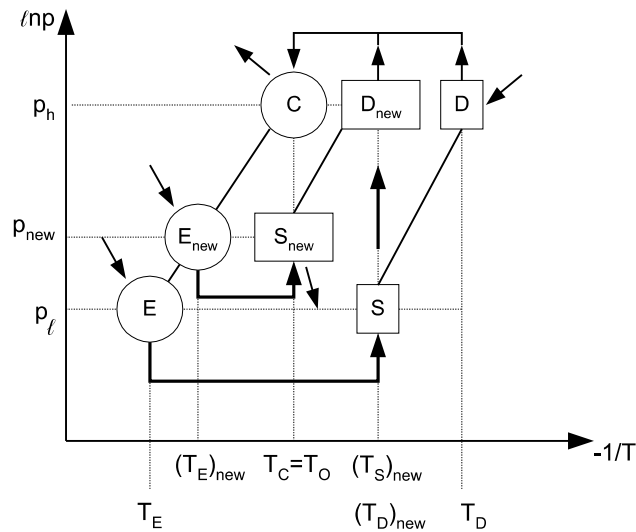


Fig. 14. Synthesis of new TR process on a Claperon–Clausius diagram (design option N.1).

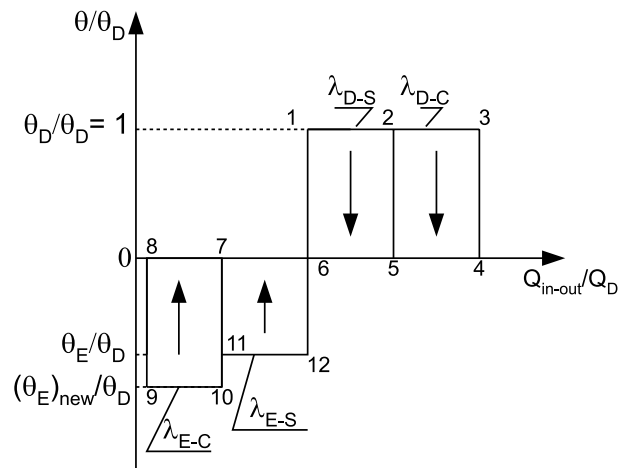


Fig. 15. Modification of the exergy-based diagram due to variations in temperature for salt decomposition.

diagram may be modified. The appropriate equilibrium lines on the Claperon–Clausius diagram, as well as the points corresponding to T_D , T_E , T_S and T_C , may be immediately targeted as a response to these modifications. The latter unambiguously identify the TR structure. The technical feasibility of generated options embedded within a special superstructure should be carried out through an optimization procedure where cost is minimized. This part of the TR design problem is beyond the scope of this paper.

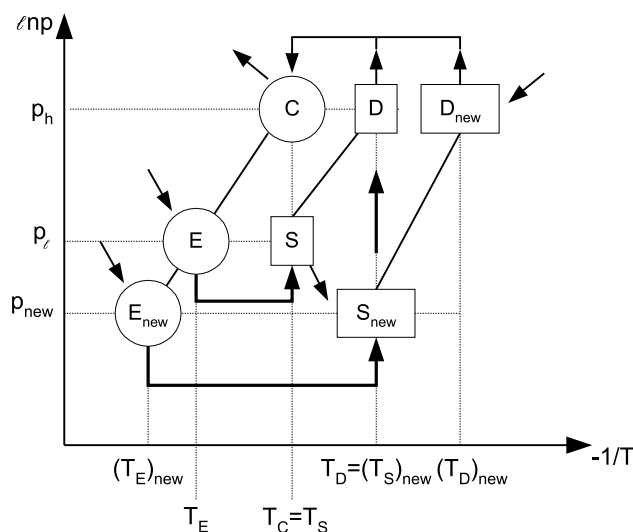


Fig. 16. Synthesis of new TR process on a Claperon–Clausius diagram (design option N.2).

8. Conclusion

The energy targets in pinch analysis are defined by the value of the overall exergy losses. Knowledge of these losses prior to design is based on a special formulation of the design problem as a combination of predetermined sources and sinks. Assuming that this kind of design problem formulation is suited only to a special group of problems, such as HEN, water re-use networks, etc, another thermodynamically sound approach to process synthesis has been proposed. It is based on a special graphic presentation of exergy balance around ideal processes, where exergy losses are nil. The approach allows systematic generation of the design alternatives for the ideal processes with predetermined targets. In the next design step, the corresponding real processes, having the same structure as the selected ideal ones, are identified. The final solution is carried out through optimization of a superstructure embedding the real process alternatives.

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