



Integrated exergy load distribution method and pinch analysis

M. Sorin ^{a,*}, J. Paris ^b

^a Energy Diversification Research Laboratory, CANMET, 1615 Lionel-Boulet, P.O. Box 4800, Varennes, Québec J3X 1S6, Canada

^b Chemical Engineering Department, Ecole Polytechnique, C.P.6079, succ. Centre-ville, Montréal, Québec H3C 3A7, Canada

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Abstract

A new thermodynamic criteria of chemical process performance, intended exergy yield is proposed. The criteria is used for the simultaneous assessment of the internal and external exergy losses and of the performance yield of a chemical process. The link between the overall intended exergy yield of a process and exergy yields of the unit operations which constitute the process is established using the exergy load distribution method. The integration of pinch analysis to the thermodynamic analysis of a process through the exergy load distribution method is demonstrated in the case of a process improvement study. The process used for the illustration of this combined approach is a typical hydrogen production unit by methane reforming. Pinch analysis with exergy targeting is used to treat the heat exchanger network (HEN) as a single unit operation, thus greatly simplifying the graphical representation of the exergy analysis and necessary computations. It is shown that this method of exergy analysis helps to identify process changes which are likely to produce a desired effect with minimum computational efforts. For the case treated, it is found that a reduction of 15°C of the high temperature shift reactor and a 0.05% purity improvement of the absorber effluent produce a 2% increase in hydrogen yield at the expense of 1.4% of the exportable steam without equipment modifications. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The exergy load distribution analysis method proposed by Sorin and Brodyansky (1992), provides an analytical expression of the relationship between the exergy efficiencies of the individual unit operations constituting a process and its overall efficiency. The graphical representation of this expression is a convenient tool to identify design and operating changes which may enhance the overall thermodynamic performance of the process. However there are two difficulties related to the application of the method. Firstly the expressions of exergy efficiencies used in the method do not account for the fact that exergy of all products produced in chemical reactors is no longer utilizable. In this work an alternative exergy coefficient which distinguishes between the exergies of desired products and unwanted by-products produced by a reactor, the intended exergy yield is introduced. A second difficulty is that the method is cumbersome with processes which

contain a large number of heat exchangers because they increase the number of unit operations to be taken into account and represented. This drawback can be overcome by the use of pinch technology to treat the entire exchanger network as a single lumped operation. The combined utilisation of pinch analysis and exergy load distribution method using the intended exergy yield is developed in this paper. The approach is illustrated in the case of the investigation of potential design improvements of an hydrogen production unit by methane reforming.

2. Background

Exergy optimisation of multi-operation processes can be difficult because the efficiencies of individual operations are interdependent in a way which was, heretofore, difficult to anticipate. Moreover a local improvement could result into an overall degradation of the process thermodynamic performance. Sorin and Brodyansky (1992), have shown that there is a simple relationship between local and overall efficiencies. It is

* Corresponding author. Tel.: +1-450-6523513; fax: +1-450-6520999.

E-mail address: msorin@nrcan.gc.ca (M. Sorin)

based on the concepts of primary and transformed exergies. Both primary and transformed exergies are consumed within the system but while primary exergy enters the system through its boundaries, transformed exergy is produced within its boundaries. A unit operation can consume either type of exergies or both. The primary exergy load of an operation, $\lambda_{p,i}$, is the fraction of the total primary exergy that it consumes. Its transformed exergy load, $\lambda_{t,i}$, is the ratio of the transformed exergy that it consumes to the total primary exergy. The following relationship between the individual efficiencies, η_i , and the overall efficiency, η , is then:

$$\eta = \sum_i [\lambda_{p,i}\eta_i - \lambda_{t,i}(1 - \eta)] \quad (1)$$

The primary exergy loads are subject, by their definition, to the following constraint:

$$\sum_i \lambda_{p,i} = 1 \quad (2)$$

Eq. (1) shows that by increasing a local efficiency, η_i or decreasing a transformed exergy load, $\lambda_{t,i}$ the overall efficiency, η of a process may increase as long as this does not trigger any opposite and larger effect through a change in other parameters in the equation. The efficiency η can also be increased by manipulating the primary loads $\lambda_{p,i}$. Nevertheless, because of the constraint (Eq. (2)), this can be practically achieved only by transferring part of a load from a unit operation to another. As observed by Sorin and Brodyansky (1992), it is easier to act upon $\lambda_{p,i}$ and $\lambda_{t,i}$ than upon η_i . An effective way to improve the overall exergy efficiency of a process is therefore to increase the primary load of the units with the largest efficiencies at the expense of those with the lowest efficiencies or to decrease the transformed exergy loads of the units with the lowest efficiencies which is also often achieved through load transfer, as will be seen in the case study, hence the name of the method. Eq. (1) lends itself to a simple graphical interpretation which is very useful in its practical application to process analysis (Sorin & Paris, 1995); each unit is represented by two rectangles of width $\lambda_{p,i}$ and $\lambda_{t,i}$ and height η_i and $(1 - \eta_i)$ respectively. When the primary load rectangles are drawn on the positive x -axis and the transformed load rectangles on the negative side, the difference between the total areas of the right and left rectangles is the overall process efficiency η given by Eq. (1). This means of visualisation of Eq. (1) will be utilized later in the example.

In the original work by Sorin and Brodyansky (1992), the exergy efficiency used to derive Eq. (1) was the efficiency according to the second law as introduced earlier by Grassman (1950):

$$\eta = \frac{E''}{E'} \quad (3)$$

As illustrated in Fig. 1, E' is the exergy input to the system and E'' its output. The total exergy input, E' , of a real system is always higher than its exergy output, E'' , because a certain amount of exergy is irreversibly destroyed within the system. This exergy generally referred to as the internal exergy losses, D^{int} , is directly linked to the thermodynamic irreversibilities in the system.

The formalism of Eq. (1) is independent of the way in which the efficiency is expressed provided that the equation be consistent within itself. Sorin, Bonhivers and Paris (1997) have shown that the efficiency according to the second law does not always represent adequately the thermodynamic performance of an operation and have proposed a different coefficient, the intended exergy efficiency, which takes into account the transiting exergy, $E^{tr,u}$ in the utilizable stream (Fig. 1) as well as external exergy losses, D^{ext} :

$$\eta_{in} = \frac{E'' - E^{tr,u} - D^{\text{ext}}}{E' - E^{tr,u}} = \frac{E^{pu}}{E^c} \quad (4)$$

The transiting exergy in the utilizable stream, $E^{tr,u}$ is that part of the exergy entering a unit operation which traverses it without undergoing any transformation and leaving it with the utilizable stream. External exergy losses, D^{ext} , are a part of the exergy output from the system which is dissipated into the environment as for example, heat losses, sewerage wastes or smokestack effluents. As illustrated on Fig. 1 there may also be transiting exergy, $E^{tr,D}$, in the external exergy losses stream, D^{ext} . For example exergy of the part of initial feed traversing the system without transformation and lost into environment. The transiting exergy which is the sum of those two terms ($E^{tr,u} + E^{tr,D}$), was first identified by Kostenko (1983). Brodyansky, Sorin and LeGoff (1994), have developed algorithms for the direct computation of the transiting exergy. To compute η_{in} according to Eq. (4) there is no need to evaluate the term $E^{tr,D}$. The term E^c includes two terms, the exergy actually consumed within the operation and $E^{tr,D}$. Therefore, $E^{tr,u}$ is not consumed by the operation but $E^{tr,D}$ is consumed. E^{pu} is the produced utilizable exergy and represents the part of E^p (Fig. 1.).

However, thermodynamic performance is generally not the most important factor in the chemical reactors design and analysis. Increase in productivity and waste minimisation are of primary concern (Douglas, 1988; Smith, 1995). A new coefficient, intended exergy yield, will be proposed in this work for the simultaneous assessment of thermodynamic and productivity performance of processes producing waste products. It will be demonstrated that the link between the intended exergy yields of unit operations $\eta_{y,i}$ and the overall intended exergy yield η_y is also expressed by Eq. (1).

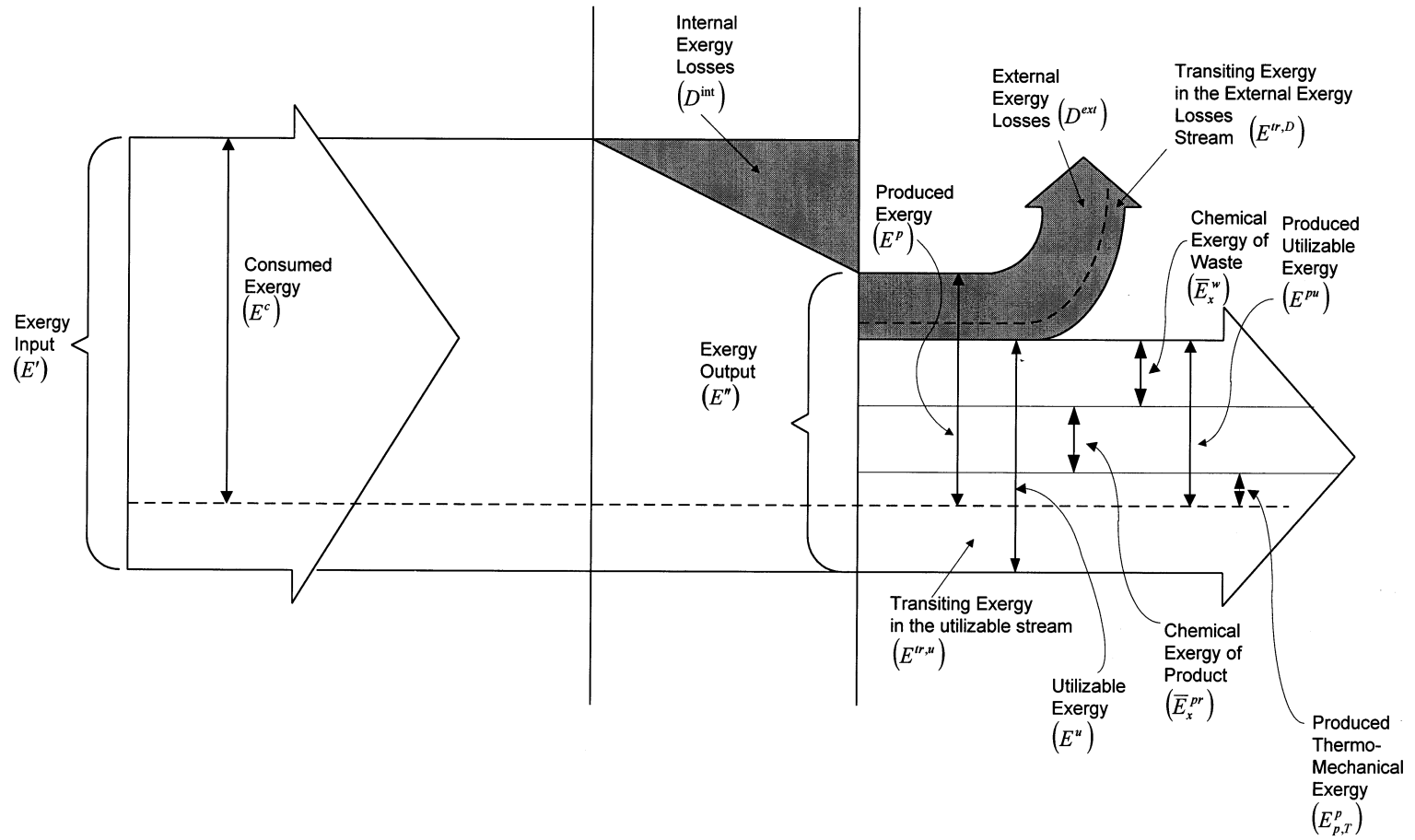


Fig. 1. Graphical presentation of the exergy balance of a system.

Linnhoff, Townsend and Boland (1994) have shown that an entire heat exchanger network (HEN) can be treated as a single heat transfer operation which can be characterised by its minimum overall heat supply and withdrawal requirements. Those minimum requirements, or exergy targets, can be determined by the now well established and widely used pinch analysis developed earlier by Linnhoff and Hindmarsh (1983). The interest of the method, known as exergy targeting, is that design of the HEN is not required. It can be done either graphically, by use of the heat exchange versus temperature composite profiles which are the basis of pinch analysis or, analytically, by use of the so-called problem table algorithm (Linnhoff & Flower, 1978). The analytical method has been used in this work. It consists of dividing the overall temperature interval of the HEN into elementary sub-intervals over which an exergy balance can be computed. The heat excess or deficit for each sub-interval is thus determined and, by summation, so are the overall requirements of the network.

3. Intended exergy yield of chemical reactors

The intended exergy yield of a chemical reactor introduced in this work is defined as:

$$\eta_y = \frac{E'' - E^{tr,u} - D^{ext} - E_x^W}{E' - E^{tr,u}} \quad (5)$$

where E_x^W is the chemical exergy of pure waste in the separated state. As illustrated in Fig. 1 the produced utilizable exergy is the sum of three terms:

$$E^{p,u} = \bar{E}_x^W + \bar{E}_x^{pr} + E_{p,T}^p \quad (6)$$

\bar{E}_x^W and \bar{E}_x^{pr} are, respectively, the exergy flow rates of waste and product in non separated states produced within the reactor. $E_{p,T}^p$ is produced thermo-mechanical exergy of the reactor effluent.

It has been shown by Szargut et al. (1988) that the link between chemical exergies of species in pure (separated) and mixed (non separated) states may be expressed as:

$$E_x^W = \bar{E}_x^W + \Delta E^W \quad (7)$$

$$E_x^{pr} = \bar{E}_x^{pr} + \Delta E^{pr} \quad (8)$$

where the sum $\Delta E^W + \Delta E^{pr}$ is the minimum thermodynamic work required to separate waste from product. Each of the terms $\Delta E^i (i = W, pr)$ may be computed from the molar flow rate n_i , activity coefficient γ_i and molar fraction x_i of component i in the effluent mixture.

$$\Delta E^i = n_i RT_0 \ln \left(\frac{1}{\gamma_i x_i} \right) \quad (9)$$

Combining Eqs. (5)–(8) the intended exergy yield may be expressed:

$$\eta_y = \frac{\bar{E}_x^{pr} - \Delta E^W + E_{p,T}^p}{E^c} \quad (10)$$

The intended exergy yield defined by Eq. (10) decreases with the unwanted by-product (waste) production. The larger the flow rate n_w the larger is the term ΔE^W in Eq. (9) and the smaller is exergy yield η_y . Moreover the reaction to unwanted byproducts increases the exergy consumption E^c due to the raw materials wasted in the byproducts formation. As a result η_y is penalized twice because of the poor reactor selectivity.

4. Relationship between local and overall intended exergy yields

The objective of this section is to demonstrate that Eq. (1) establishes also the relationship between the intended exergy yields of unit operations $\eta_{y,i}$ and overall intended exergy yield η_y . The reaction–separation–recycling system presented in Fig. 2 will be considered as an example. The reactor transforms the chemical exergy of the feed E_x^F into chemical exergies of product \bar{E}_x^{pr} and waste \bar{E}_x^W . Not all the feed reacts. Unreacted part of the feed is recycled to the reactor after the separation and mixed with product and waste within the reactor. The exergy of this feed $E_x^{\Delta F}$ decreases by the value $\Delta E^{\Delta F}$ because of the mixing and becomes $\bar{E}_x^{\Delta F}$ (see Fig. 2). The separation of the product from the unreacted feed and waste is achieved in a subsequent operation. E_q is exergy supplied to the separator by an external utility. The increase in exergies of the separated species by the values ΔE^W , ΔE^{pr} and $\Delta E^{\Delta F}$ are also illustrated in Fig. 2. To simplify the presentation it has been assumed that the temperature and pressure do not change in the process which means that there is no variation in thermomechanical exergy. It will be demonstrated in a later case study that this variation may also be included into the analysis. The intended exergy yield of the overall process is:

$$\eta_y = \frac{E_x^{pr}}{E_x^F + E_q} \quad (11)$$

The nomenclature is presented in Fig. 2. The intended exergy yields of the reactor and separator can be expressed by:

$$\eta_{y,r} = \frac{\bar{E}_x^{pr} - \Delta E^W}{E_x^F + \Delta E^{\Delta F}} \quad (12)$$

$$\eta_{y,s} = \frac{\Delta E^W + \Delta E^{pr} + \Delta E^{\Delta F}}{E_q} \quad (13)$$

Following the definition given in the previous section the primary exergy loads are:

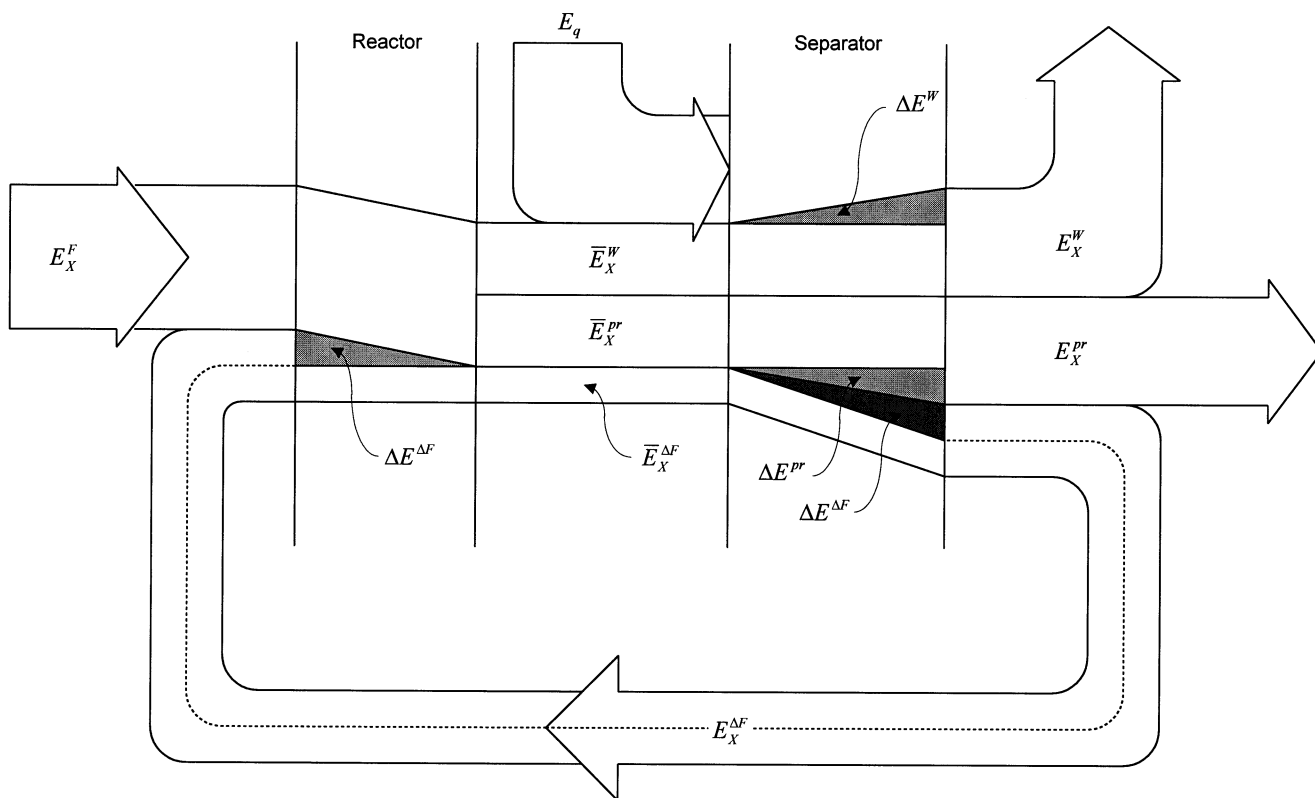


Fig. 2. Graphical presentation of the exergy balance of a reaction–separation–recycling system.

$$\lambda_{p,r} = \frac{E_x^F}{E_x^F + E_q} \quad (14)$$

$$\lambda_{p,s} = \frac{E_q}{E_x^F + E_q} \quad (15)$$

The consumption of the transformed exergy takes place only in the reactor; its value is $\Delta E^{\Delta F}$ and it is due to dilution of the unreacted feed by waste and product within the reactor. Then the transformed exergy load is:

$$\lambda_{t,r} = \frac{\Delta E^{\Delta F}}{E_x^F + E_q} \quad (16)$$

By means of Eq. (1), the relationship between the overall intended exergy yield and the intended exergy yields of the reactor $\eta_{y,r}$ and separator $\eta_{y,s}$ is:

$$\eta_y = \lambda_{p,r}\eta_{y,r} - \lambda_{t,r}(1 - \eta_{y,r}) + \lambda_{p,s}\eta_{y,s} \quad (17)$$

The substitution of the corresponding terms in Eq. (17) from Eqs. (12)–(15) gives the expression of η_y defined by Eq. (11). This is the proof that Eq. (1) is consistent with the definition of intended exergy yield expressed by Eq. (4).

Graphical interpretation of Eq. (17) is presented on the exergy yield–load diagram as an example (Fig. 3). Reactor is represented by two rectangles of widths $\lambda_{p,r}$ and $\lambda_{t,r}$ and heights $\eta_{y,r}$ and $(1 - \eta_{y,r})$ respectively. The separator is represented by one rectangle of width $\lambda_{p,s}$ and height $\eta_{y,s}$. The difference between the total areas of

the right and left rectangles is the overall intended exergy yield η_y given by Eq. (17). Acting upon $\lambda_{p,r}$, $\lambda_{p,s}$ and $\lambda_{t,r}$ accordingly to the exergy load distribution principles formulated above it is possible to increase the overall exergy yield. This manipulation may be achieved through variations in operating and design parameters, for example reactor conversion and topology of reaction–separation system.

5. Exergy analysis of a heat exchanger network

In order to apply the exergy load distribution analysis to a process in which the HEN is treated as a single unit, its intended exergy yield, $\eta_{y,HEN}$, primary exergy load, $\lambda_{t,HEN}$ and transformed exergy load, $\lambda_{p,HEN}$ must be computed and entered into Eq. (1). These coefficients can be computed by an exergy balance over the complete HEN as represented in Fig. 4. The large arrows represent the exergy flows corresponding to the heat supplied to the process and to the heat withdrawn. They are expressed

$$E'_q = Q_{Hmin} \left(1 - \frac{T_0}{T_H} \right) \quad (18)$$

respectively as:

$$E''_q = Q_{Cmin} \left(1 - \frac{T_0}{T_C} \right) \quad (19)$$

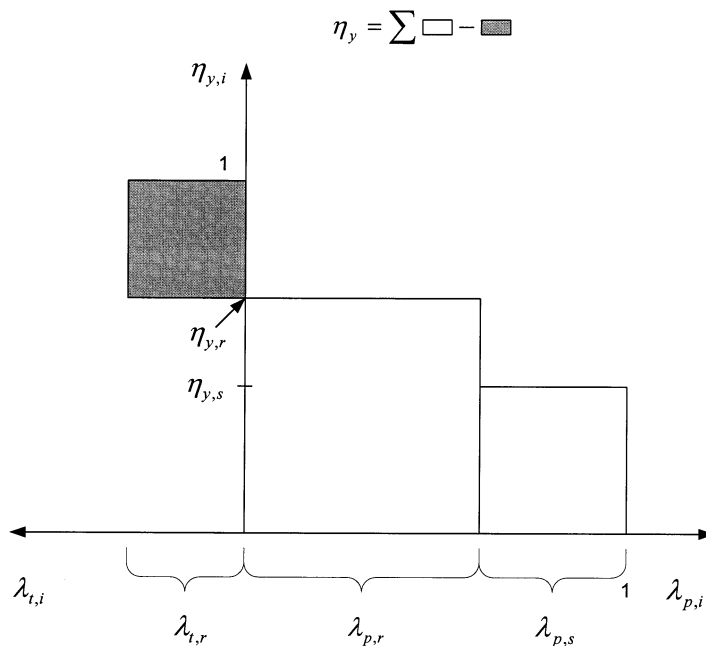


Fig. 3. Exergy yield versus load diagram for the reaction–separation–recycling system.

The terms Q_{Hmin} and Q_{Cmin} are the energy targets, T_H and T_C are the temperatures of the hot and cold utilities, T_0 is the temperature of the environment. Assuming $T_C = T_0$, the term E''_q becomes zero and the intended exergy yield takes the form:

$$\eta_{y,HEN} = \frac{\sum_i (E''_{i,c} - E'_{i,c})}{\sum_j (E'_{j,h} - E''_{j,h}) + E'_q} \quad (20)$$

The primary and transformed exergy loads are:

$$\lambda_{p,HEN} = \frac{E'_q}{E^c} \quad (21)$$

$$\lambda_{t,HEN} = \frac{\sum_j (E'_{j,h} - E''_{j,h})}{E^c} \quad (22)$$

The term E^c is the exergy consumed by the overall process.

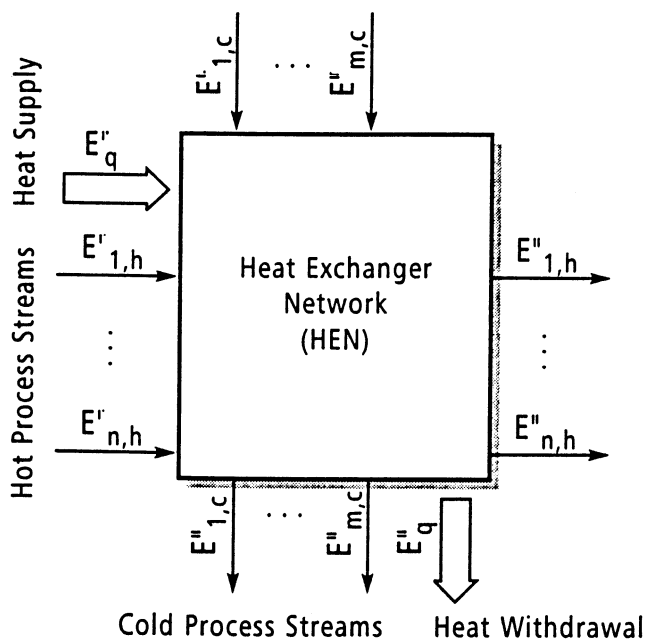


Fig. 4. HEN Representation as a single operation.

6. Case study

The application of the combined utilisation of exergy and pinch analyses is illustrated in a study of a typical refinery hydrogen production unit. The process is represented in Fig. 5 and includes five principal steps, which are CH_4 vapor reforming, high and low temperature shift conversions of CO, hot potassium carbonate absorption of CO_2 and finally methanation. The feed gas is composed of CH_4 and H_2 . In the flowsheet of Fig. 5, all heating and cooling duties are provided by utilities. The possibilities for exergy savings in this process by integrating the HEN while maintaining all other operating conditions unchanged have been identified in a previous study by Leroy, Sorin and Paris (1995). Important base case data of interest to this work are given in Table 1. All process computations for the base case and for this work have been performed with the ASPEN PLUS process simulator. For the purpose of this work, it is assumed that the objective of this new study is to determine process changes which would increase

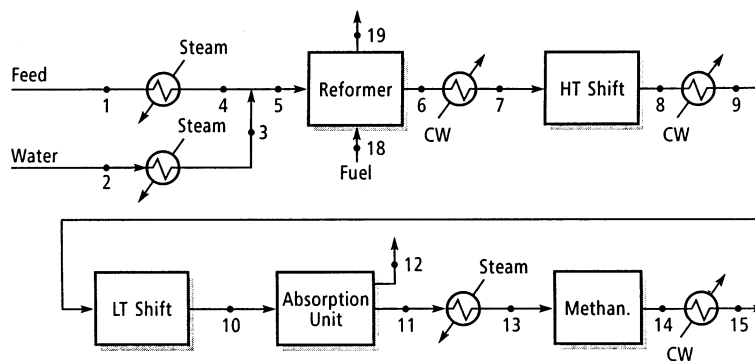


Fig. 5. Hydrogen production process (heating and cooling duties provided by utilities).

hydrogen yield and determine their effect on the HEN, and exergy requirements.

The first step in the analysis is to reduce the HEN to a single block as illustrated in Fig. 6, but without working out the details of the actual network. Energy targeting, subsequently performed, shows that there is no net external heat supply requirement, on the contrary some heat with exergy E''_q is withdrawn from the process to produce exportable steam. As a consequence, the term E'_q in Eqs. (20) and (21) is zero and the HEN primary load, $\lambda_{p,HEN}$, also reduces to zero.

The overall intended exergy yield for the process is:

$$\eta_y = \frac{[(\bar{E}_{H_2})_{1-13} - (\Delta E_{CH_4})_x + E''_q]}{[(\bar{E}_{CH_4})_{5-6} + (E_{CH_4})_{18} + (E_{H_2O})_{2-15}]^x} \quad (23)$$

In this equation $(\bar{E}_{H_2})_{1-13}$ is chemical exergy of produced hydrogen between the points 1 and 13 of the flowsheet (Fig. 6), $(\Delta E_{CH_4})_{13-14}$ is a part of the thermodynamic work required to separate methane produced within the methanation unit (computed using Eq. (9)). The terms $(\bar{E}_{CH_4})_{5-6}$ and $(\bar{E}_{H_2O})_{2-15}$ are the chemical exergies of methane and water consumed by the process. $(\bar{E}_{CH_4})_{18}$ is the chemical exergy of methane burned to supply heat for the vapor reforming. The overall intended exergy yield expressed through the exergy

yields of the individual unit operations is:

$$\eta_y = \lambda_{p,I} \eta_{y,I} + \sum_{i=II} [\lambda_{p,i} \eta_{y,i} - \lambda_{t,i} (1 - \eta_{y,i})] - \sum_{i=VI} [\lambda_{t,i} (1 - \eta_{y,i})] \quad (24)$$

The intended exergy yield and transformed exergy load of the HEN are computed by Eqs. (20) and (22). The exergy parameters ($\eta_{y,i}$, $\lambda_{p,i}$ and $\lambda_{t,i}$) for the other operations constituting the process have been computed for the base case conditions by equations given in the appendix. CO_2 produced in the vapor reformer, high and low temperature shift reactors as well as CH_4 produced by the methanation unit are considered as the waste products. The numerical values of the exergy parameters are given in Table 2. Process operation numbering in Table 2 and subsequent figures are as defined in Fig. 6. Fig. 7 gives the graphical representation of Eq. (24). The reforming unit is represented by a single rectangle (I) on the right hand side of the diagram because its transformed exergy load is zero and the HEN by a single rectangle (VI) on the left hand side because its primary exergy load is zero. The CO_2 absorption unit, and two temperature shift converters are represented each by a rectangle on the left hand side and a rectangle on the right hand side (rectangles II, III and IV). It should be noted that the HEN rectangle accounts for six separate heat exchangers. This underscores that, if the network had not first been lumped into a single operation, not only the figure, but also the computations necessary and the analysis would have been much more tedious and complicated. The diagram shows that the overall intended exergy yield of the process, η_y , is equal to 55.7%, is dominated by the performances of the reformer (larger rectangle on the primary load side) and of the HEN (larger rectangle on the transformed load side):

$$\lambda_{p,I} \eta_{y,I} - \lambda_{t,VI} (1 - \eta_{y,VI}) = 0.605 \quad (25)$$

All other terms are corrective factors which have a collective net contribution to the overall process efficiency of only about 10% of its value but, this contribu-

Table 1
Base case operating data

N ^a	T(°C)	Flow rate (kmol h ⁻¹)				
		CH ₄	CO ₂	CO	H ₂	H ₂ O
1	38	535	0	0	1790	0
5	340	535	0	0	1790	2140
6	788	285	104	145	2643	1786
7	380	285	104	145	2643	1786
8	405	285	216	33	2755	1674
9	220	285	216	33	2755	1674
10	227	285	245	5	2783	1645
10	76	285	5	5	2783	51
13	350	285	5	5	2783	51
14	370	295	0	0	2749	65

^a Points numbers as on Fig. 5.

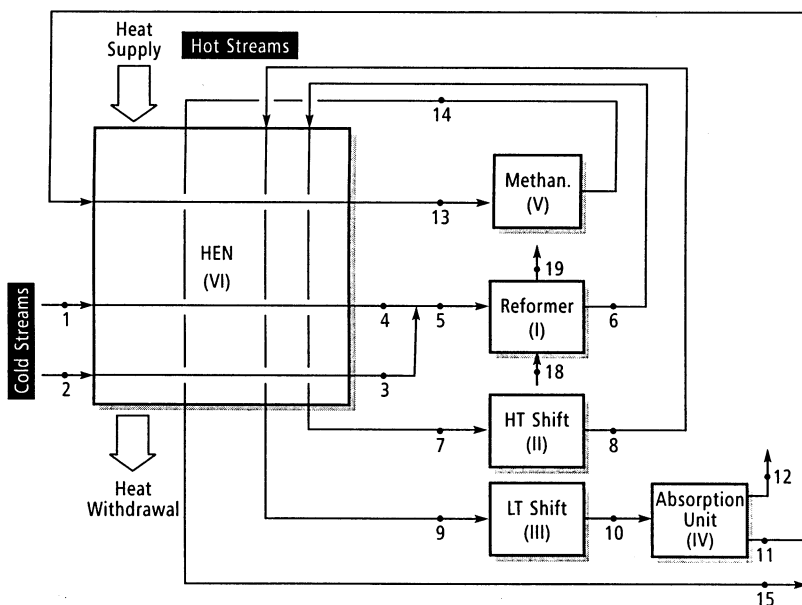


Fig. 6. Hydrogen production process with single block HEN representation.

tion is negative as is apparent on the diagram (sum of left rectangles II, III, IV and V larger than sum of right rectangles II, III, IV). It follows from those observations and an examination of Fig. 7 that the following changes could significantly improve the overall process exergy yield, η_y : increase the exergy yield of the reformer $\eta_{y,I}$, or increase its primary load $\lambda_{p,I}$ at the expense for instance of the CO_2 absorption unit (to further increase the largest rectangle on the right hand side), increase the efficiency of the HEN, $\eta_{y,VI}$, or decrease its transformed load $\lambda_{t,VI}$ (to reduce the area of the largest rectangle on the left hand side). All other changes in the diagram can only have a minor impact on the overall efficiency. However, prospective changes must also be judged on the basis of practicality and concordance with project objectives.

There are no general rules to improve the exergy yield of a unit operation. Potential changes which may lead to improvements, must be determined on a per case basis, by a heuristic approach. For example, as discussed by Leites, Sosna and Semenov (1988), improving the reformer and HEN exergy yields would require substantial investments. For those reasons, and following the general rules suggested by Sorin and Brodyansky (1992), the analysis will concentrate on load redistribution rather than exergy yield improvements. The redistribution of the primary exergy load from the absorption unit to the reforming unit is not practically achievable because the primary exergy loads of those two units are completely independent; reactants consumption affects $\lambda_{p,I}$ and water losses in the absorption unit affect $\lambda_{p,IV}$. The analysis of the left-hand side of the diagram indicates that the main transformed exergy load is concentrated in the HEN unit. Nevertheless there is no

possibility to act upon $\lambda_{t,VI}$ because the value of this parameter is determined by the exergy loads of the other processing steps.

Since those changes are not actually feasible one must consider other possibilities which, although they would have only minor effects on the overall efficiency, η_y , may be worthwhile from a process yield standpoint. Following the guidelines developed by Sorin and Brodyansky (1992), reducing the transformed load of the methanation unit which has the lowest efficiency or, transferring part of it to an other operation will now be examined. The analytical expression of $\lambda_{t,V}$ as well as $\lambda_{t,II}$ and $\lambda_{t,IV}$ can be found in the appendix. The terms \bar{E}_{H_2} , \bar{E}_{CO_2} and \bar{E}_{CO} represent the chemical exergy of the quantities of H_2 , CO_2 and CO which are chemically reacted in that unit. The quantities of reacted CO and CO_2 are independent parameters of which the quantity of reacted H_2 is a function. Therefore a reduction of $\lambda_{t,v}$ can be achieved by decreasing the feed in CO and CO_2 to the methaniser. The two possibilities are examined below.

6.1. Case I: reduction of CO to methaniser

This can be done by increasing the rate of CO conversion in one or both shift reactors. This will diminish the term E_{CO} in $\lambda_{t,V}$ but increase the corresponding terms in $\lambda_{t,II}$ or $\lambda_{t,III}$, thus being, in effect, a transfer of transformed load (Fig. 7). Increasing CO conversion can be done by lowering the temperature in the high temperature shift reactor, if feasible. This temperature has been fixed at 380°C in the base case, following the usual practice. However, lower temperatures can be used without affecting catalyst selectivity; Gary and Handwerk (1975) recommend a lower limit of

365°C. A process simulation was performed for that value. Key parameter values given in Table 2 show that the exergy yields of the process operations are unaffected except that of the methaniser which is further reduced and that of the HEN which is slightly increased. The primary loads are not modified; the transformed load of the methaniser is reduced and that of the high temperature shift reactor is increased as anticipated. The HEN transformed load is also decreased. A change in the methaniser exergy yield counterbalances any positive effect that the increased efficiency and decreased transformed load of the HEN might otherwise have had on the overall process efficiency, η_y . The net effect on this coefficient is indeed small (+0.7%) but it translates into a 1.6% increase in hydrogen production rate and a reduction of 1.2% of exportable steam.

6.2. Case II: reduction of CO₂ to methaniser

In order to reduce the flow rate of CO₂ to the methaniser, the CO₂ removal efficiency of the absorption unit must be improved. As in case I, this process

Table 2
Exergy parameters

	Base case	Case I	Case II
t_7^a (°C)	380	365	365
x_{CO_2} (%)	0.15	0.15	0.10
Intrinsic efficiency, $\eta_{in,i}$			
I	0.717	0.717	0.717
II	0.910	0.911	0.911
III	0.915	0.915	0.915
IV	0.181	0.181	0.180
V	0.082	0.076	0.070
VI	0.648	0.652	0.641
Primary load, $\lambda_{p,i}$			
I	0.977	0.977	0.977
II	0.020	0.020	0.020
III	0.010	0.010	0.010
IV	0.021	0.021	0.021
V	0.000	0.001	0.001
VI	0.001	0.001	0.001
Transformed load, $\lambda_{t,i}$			
I	0.000	0.000	0.000
II	0.060	0.062	0.062
III	0.015	0.015	0.015
IV	0.037	0.037	0.039
V	0.019	0.013	0.009
VI	0.271	0.267	0.2661
η_{in}	55.7	56.4	56.6
ΔH_2 (%)	0	+1.6	+0.4
ΔSt (%)	0	-1.2	-0.2

^a t_7 is temperature at point 7 on Fig. 6, x_{CO_2} is the fraction of CO₂ in purified gas, ΔH_2 is the rise in H₂ production, ΔSt is the decrease in steam production.

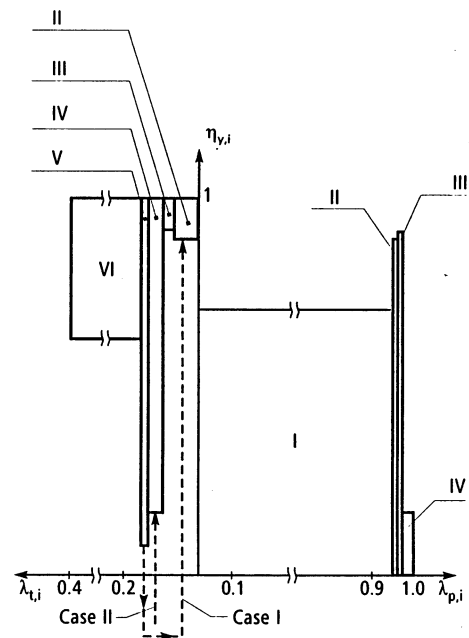


Fig. 7. Exergy yield versus load diagram (base case).

change will cause a reduction of the term E_{CO_2} in $\lambda_{t,V}$ and an increase of the term E_q in $\lambda_{t,IV}$ i.e. again, a redistribution of transformed load. A way to increase CO₂ removal in the absorption tower is through more complete stripping of the CO₂ in the desorber, which in effect produces a lower residual CO₂ concentration in the absorbing solution entering the tower. However, total removal is not feasible, and a CO₂ concentration of 0.1% molar in the gas tower effluent is generally accepted as a practical lower limit (Kohl & Reisenfeld, 1985). For the purpose of this study, it is assumed that from its base value of 0.15% molar the CO₂ concentration is lowered to 0.1% molar. The corresponding thermodynamic parameter values are also given in Table 2. The exergy yields of the process steps are again unaffected except for those of the methaniser (further reduced from case I) and of the HEN (reduced, on the contrary to case I). The primary exergy loads are unchanged; as expected, there is a transfer of load from the methaniser to the absorber and there is also a very slight reduction of the HEN transformed load. The net result on the overall exergy yield and hydrogen production rate are small but significant. There is a small drop in exportable steam.

6.3. Final design

Once the new process conditions which improve hydrogen yield have been fixed (case study II), a thermal design of the HEN is performed using the pinch design method (Linnhoff & Hindmarsh, 1983). The final process flowsheet is presented in Fig. 8. To complete the process enhancement study, an economic analysis

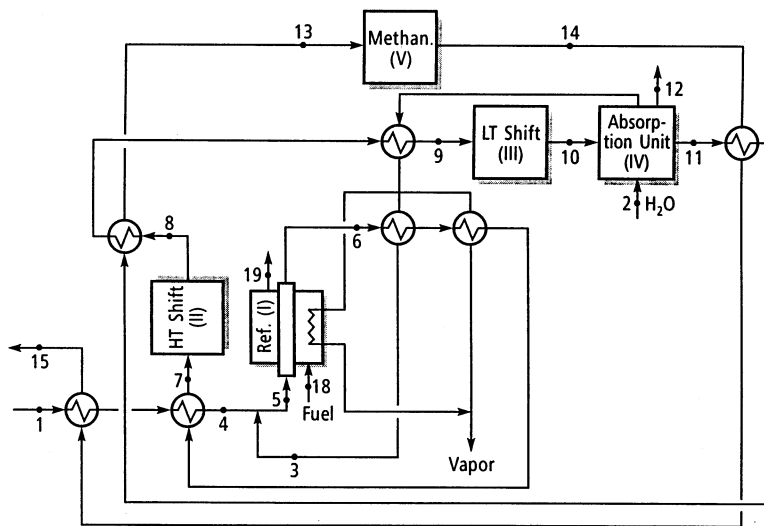


Fig. 8. Final flowsheet of the hydrogen production process.

should be performed. Such an analysis is beyond the scope of this work. However, it can be expected that the proposed changes in operating conditions, with an increase in hydrogen yield of 2%, can produce a significant economic return despite the reduction in exportable steam of 1.4%. In this industry, characterized by very large throughputs, a 2% production increase with no change in major equipments can give a competitive edge.

7. Conclusion

It has been shown in this example how pinch analysis can be advantageously combined with exergy analysis to reduce the number of unit operations for which the necessary thermodynamic parameters must be computed. Once this simplification is implemented, the exergy load distribution method can be effectively used to guide process analysis. In the example, the two changes which would be appropriate from the standpoint of process objectives and technically feasible have been rapidly identified in a broad initial choice without requiring any computations besides those already performed for the base case. The computing work was reduced to a minimum: two process simulations with only few parametric changes from the base case and a one step HEN thermal design. Using the combined method, an actual process which was already near optimized could be further improved without equipment changes.

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Appendix A. Appendix

Analytical forms of the exergy parameters

$$\eta_{y,I} = \frac{[\bar{E}_{H_2} + \bar{E}_{CO} - \Delta E_{CO_2}]_x + [\Delta E]_{p,T}}{[\bar{E}_{\Delta CH_4} + \bar{E}_{CH_4} + \bar{E}_{H_2O}]_x} \quad (A1)$$

$$\eta_{y,II} = \frac{[\bar{E}_{H_2}]_x}{[\bar{E}_{CO} + \bar{E}_{H_2O}]_x + [VE]_{p,t}} \quad (A2)$$

$$\eta_{y,III} = \frac{[\bar{E}_{H_2}]_x + [\Delta E]_{p,T}}{[\bar{E}_{CO} + \bar{E}_{H_2O}]_x} \quad (A3)$$

$$\eta_{y,IV} = \frac{[\Delta E_{CO_2} + \Delta E_{H_2}]_x}{\bar{E}_q + [\bar{E}_{H_2O}]_x} \quad (A4)$$

$$\eta_{y,V} = \frac{[\Delta E]_{p,T} - [\Delta E_{CH_4}]_x}{[\bar{E}_{H_2} + \bar{E}_{CO_2} + \bar{E}_{CO}]_x} \quad (A5)$$

$$\lambda_{p,I} = \frac{[\bar{E}_{\Delta CH_4} + \bar{E}_{CH_4} + \bar{E}_{H_2O}]_x}{E^c} \quad (A6)$$

$$\lambda_{p,II} = \frac{[\bar{E}_{H_2O}]_x}{E^c} \quad (A7)$$

$$\lambda_{p,III} = \frac{[\bar{E}_{H_2O}]_x}{E^c} \quad (A8)$$

$$\lambda_{p,IV} = \frac{[\bar{E}_{H_2O}]_x}{E^c} \quad (A9)$$

$$\lambda_{p,V} = 0 \quad (A10)$$

$$\lambda_{t,I} = 0 \quad (A11)$$

$$\lambda_{t,II} = \frac{[\bar{E}_{CO}]_x + [VE]_{p,T}}{E^c} \quad (A12)$$

$$\lambda_{t,III} = \frac{[\bar{E}_{CO}]_x}{E^c} \quad (A13)$$

$$\lambda_{t,IV} = \frac{E_q}{E^c} \quad (A14)$$

$$\lambda_{t,V} = \frac{[\bar{E}_{H_2} + \bar{E}_{CO_2} + \bar{E}_{CO}]_x}{E^c} \quad (A15)$$

Appendix B. Notation

E	Exergy flow rate
\bar{E}	Exergy flow rate of a component in a mixture
Q	Heat flow rate
T	Temperature
η	Exergy efficiency
λ_p	Primary exergy load
λ_t	Transformed exergy load

Subscripts

c	Cold streams
C	Cold utility
Cmin	Target for cold utility
h	Hot streams
H	Hot utility
HEN	Heat Exchanger Network
Hmin	Target for hot utility
q	Exergy of a heat flow
p, T	Termomechanical exergy
x	Chemical exergy

Superscripts

"	Output exergy flow
'	Input exergy flow
c	Consumed exergy
in	Intrinsic exergy efficiency
p	Produced exergy

tr	Transiting exergy
y	Intended exergy yield

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