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Relationships Creating Functionalities of a Process System and Their Representation by Process Vectors

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Abstract

Understanding of the target functionalities is the origin of creating systems. Those functionalities can be generated by the system structure. To examine both those functionalities and the system structure, we introduced the concepts of successional relationships among processes and mediative relationships between processes. Also the relation between inputs and outputs of the entire system is demonstrated. Process vectors were used to represent the above three kinds of relationships. These concepts were applied for methanol production to verify their usefulness.

Key words: energy & exergy analysis, functionality of a process system, successional relationship, mediative relationship, input and output relation, process vector

1. Introduction

When we want to grasp the characteristic features of an entire system, we look at its process flow diagram (PFD). To examine its energy features, we construct its energy flow diagram (*i.e.*, Sankey diagram). Similarly, to examine its exergy features, we draw its exergy flow diagram (*i.e.*, Grassmann diagram).

Then how can we discuss the functionalities of a system? The purpose of this paper is to graphically represent the functionalities of an entire system by use of process vectors. Process synthesis is the creation of the system structure that generates the target functionalities. In this paper, attention was paid to the relationships among processes to connect the creation of functionalities and the creation of the structure of the system.

2. Realization of Target Functionalities and Relationships among Processes

Figure 1 shows typical relationships among processes. Substance A changes to B, then to C, and finally to D. Change 1 from A to B is a process accepting intermediary energy, which is released by its coupled process (or coupler) 1. This intermediary energy may be heat, work or a mixture of the two.

On the other hand, change 2 from B to C releases intermediary energy, which is accepted by its coupled process 2. A similar relationship can be seen for change 3 from C to D and its coupled process 3.

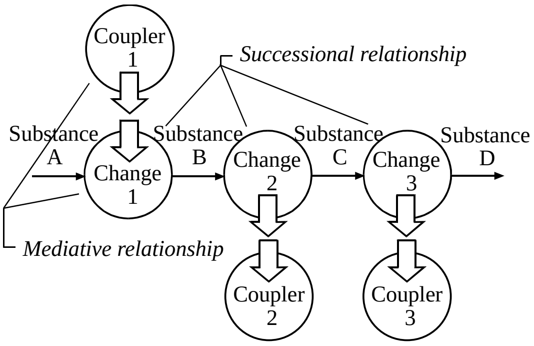


Figure 1. Relationships among processes in a system

We can find two kinds of relationships among the processes in this figure. The relationship between change 1 and its coupled process 1 belongs to the first category. Also the relationships between change 2 and its coupled process 2, and between change 3 and its coupled process 3 are in this category. For these relationships, the two processes are connected by the intermediary energy denoted by white arrows in *Figure 1*. Hence we may call them 'relationships through the intermediary energy' or 'mediative relationships' because the intermediary energy plays the role of mediator between the two processes.

TABLE I. CONNECTION BETWEEN FUNCTIONALITIES AND STRUCTURE OF A SYSTEM

Realization of target functionalities

Relationships among processes	
Relations through substances (Successional relationships)	Relations through intermediary energy (Mediative relationships)

Design of system structure

The relationship in the second category can be seen for the changes of substances from A through D, namely, the relationships between changes 1 and 2, and changes 2 and 3. For these relationships, the substance outputted from the previous process or a part of it becomes the substance inputted to the next process. For these relationships the two processes are connected by substances. Hence we may call them ‘relationships through the substances’ or ‘successional relationships’, stressing succession of the changes of substances.

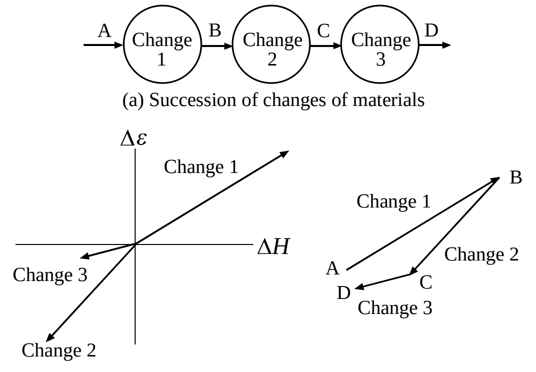
In this paper, we want to discuss the ‘creation of functionalities of a system’ or ‘creation of the structure of a system generating functionalities.’ Consideration of functionalities of a system seems to be quite different from that of structure of a system. However, since realization of functionalities of a system needs a proper structure, creation of functionalities and creation of a system structure are close to each other. Both subjects are very difficult, and we need a new methodology. TABLE I shows that the relationships among processes can make a connection between the functionalities of a system and the structure of a system.

3. Representation by Process Vectors

3.1. Successional relationships

A process vector on $(\Delta H, \Delta\varepsilon)$ domain can represent the feature of a process (Ishida 1983, 1995, 2002). Principally, a process vector is drawn on a thermodynamic compass, as shown in *Figure 2* (b). The abscissa, energy change ΔH, represents information on the first law, while the ordinate, $\Delta\varepsilon$, information on the second law.

The three vectors in (b) represent the three successive processes in (a). Substance B outputted from change 1 is the input for the next change 2. Hence it is reasonable to draw the process vector for change 2 from the tip of process vector 1, as shown in *Figure 2 (c)* (Ishida 1999, Ishida and Yamamoto 1999, Yamamoto and Ishida 1999). Similarly, the process vector for change 3 can be drawn from the tip of vector 2. Then the origin of the vector for change 1 corresponds to substance A, its tip substance B, the tip of the vector for change 2 substance C, and the tip of the vector for change 3 substance D. This connection of processes can be seen for power generation by a gas turbine, where change 1 indicates the heating of gas at an elevated pressure, change 2 the generation of power by the turbine, and change 3 the recovery of heat from the gas outputted from the turbine.

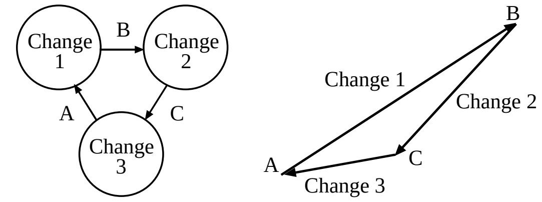


(a) Succession of changes of materials

(b) Vectors on thermodynamic compass (c) Translation of vectors

Figure 2. Successional relationships among processes

Figure 3 shows the case for which the three processes compose a loop: A is changed to B by change 1, to C by change 2, and back to A by change 3. Ignoring the small pump work, the working fluid, water, in the generation of power by a steam turbine, follows the above changes. Then the tip of process vector 3 reaches the origin of process vector 1. Hence, for the three processes composing a loop, their process vectors compose a loop, too. This means that the process vector precisely represent the changes of substances. This fact can hold because both energy H and exergy ε of substances are state properties.



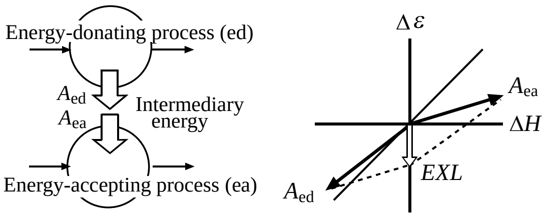
(a) Successional connection (b) Translated process vectors

Figure 3. Successional relationship for a loop

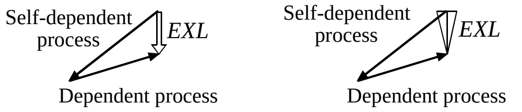
To be noted is that these successional relationships play quite important roles in generating functionalities in a system. Generation of power by a turbine, which is the functionality of a power plant, may be realized by a set of processes in *Figure 2 (c)* or *Figure 3 (b)*. Consequently, process vectors can be applied to represent the functionalities of a system. This will be discussed by use of other examples in Section 5.

3.2. Mediative relationships

Process vectors are useful also to represent the mediative relationship between an energy-donating process and an energy-accepting process shown in *Figure 4 (a)*. When the intermediary energy donated from the energy-donating process is received by the energy-accepting process, we have $-\Delta H_{ed} = \left|\Delta H_{ed}\right| = \Delta H_{ea}$, and the process vectors on a thermodynamic compass shown in (b) can represent the relationship between these processes. The subscripts ed and ea, respectively, refer to the energy donor and the energy acceptor. The exergy loss caused by this energy transformation, *EXL*, is given as the vector sum, $-\sum \Delta \varepsilon_j$, of these vectors, as shown in (b) (Ishida 1983, 1995, 2002).



(a) Energy exchange (b) Process vectors on compass



(c) Translation of a vector (d) Special notation for exergy loss

Figure 4. Mediative relationships

The slope of the process vector is called the energy level A ($=\Delta\varepsilon/\Delta H$), which indicates the quality of the intermediary energy released or accepted by the process (Ishida 2002, Ishida and Kawamura 1982, Ishida and Nakagawa 1985). For an energy transformation between two processes, the slope of the energy donor, A_{ed}, should be greater than or equal to that of the energy acceptor, A_{ea}, indicating that the quality of the energy donor should be higher than or equal to that of the energy acceptor.

A process with $\Delta\varepsilon<0$ can proceed spontaneously. Hence it is called a self-dependent process (Ishida 1995, 2002). On the other hand, a process with $\Delta\varepsilon>0$ is called a dependent process (Ishida 1995, 2002), because the proceeding of this process needs the help of a self-dependent process. When we move the origin of the vector of the dependent process to the tip of the vector of the self-dependent process by keeping its direction, we obtain (c). The vertical downward vector from the origin of the latter vector to the tip of the former vector is identical to the vector sum, which indicates the exergy loss *EXL* for this energy transformation. Although the shape of this triangle for the mediative relationship in (c) is similar to that for successional relationship in *Figure 3 (b)*, the meaning is quite different from each other. Hence we have introduced the special notation for the vector sum, as shown in (d). In this mediative relationship, this downward vector sum indicating the extent of the exergy loss *EXL* is quite important.

4. Relationship Between Inputs and Outputs in a System

So far we have concentrated our attention on the relationships among processes in a system. By examining them, we can find many important features of a system, as will be shown in a later example system. However, the substances inputted to an entire system or outputted from it have important meanings, too. At the start of the system synthesis, we first consider the resources and the products of the system. They are inputs or outputs for the entire system.

Figure 5 (a) represents the relationship between the inputs and outputs in an entire system. In this figure, a work source, a work sink, a heat source, and a heat sink are introduced to supply or accept heat or work. When we introduce the absolute values of the energy H and the exergy ε of the input and output substances, we can consider a substance vector (H, ε) for outputs and ($-H$, $-\varepsilon$) for inputs, and examine their relationships in an entire system, as shown in *Figure 5 (b)*, where we have assumed that W_{in}, Q_{in}, and Q_{out} are zero. The sum of these substance vectors represents the exergy loss EXL observed in this entire system.

5. Application of These Relational Expressions to Methanol Synthesis

5.1. A methanol plant as a model system

Figure 6 shows the PFD for a methanol plant (Ikawa et al. 1983). The resource is natural gas composed of 90% methane and 10% ethane on a molar basis. Natural gas is supplied by 365.1 mol/s for resource of reforming and 31.0 mol/s for additional fuel.

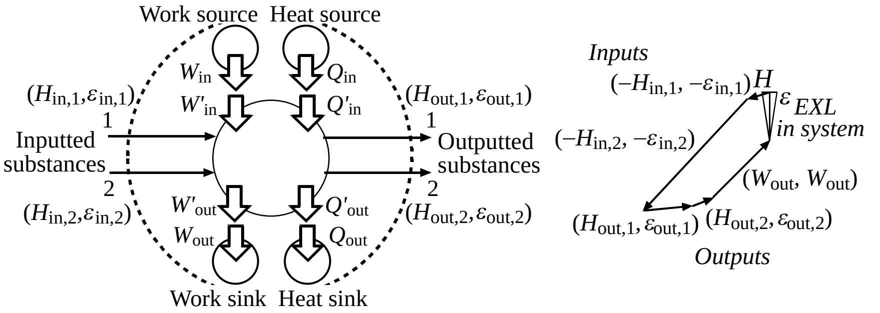
There are two reactors, R1 and R2. In R1, the following steam reforming reactions proceed:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (1)$$

$$C_2H_6 + 2H_2O \rightarrow 2CO + 5H_2 \qquad (2)$$

These reactions are endothermic. Hence supply of a large amount of heat at a high temperature is a key issue. Also the water-gas shift reaction may take place:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (3)$$



(a) Inputs and outputs of an entire system (b) Representation by substance vectors

Figure 5. Representation of inputs and outputs by substance vectors

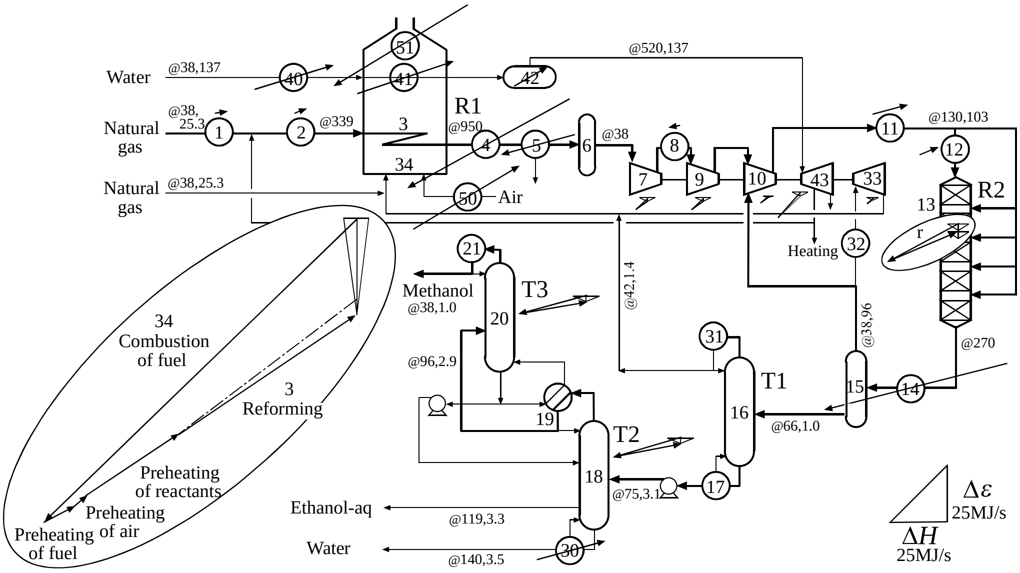


Figure 6. Process flow diagram with meditative relationships for a methanol plant

The product gas from R1 is cooled in 4 and excess water vapor is condensed in condenser 5.

In R2, methanol is produced by the following exothermic reactions:

$$CO + 2\ H_2 \rightarrow CH_3OH \qquad (4)$$

$$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O \qquad (5)$$

Since the equilibrium relation limits the concentration of methanol in the product stream, the product gas is cooled in 14 and product methanol is condensed in 15, recycling the rest gas fraction back to compressor 10. Its molar flowrate is 7838 mol/s. This rate is much larger than that of the reactant stream from R1, 1606 mol/s.

In R2, the heat released by the exothermic reaction is absorbed by the sensible heat of the introduced stream, giving rise to the increase in its temperature. Hence the cold reactant stream that has passed through preheater 11 is divided into five portions; one is fed from the top of the reactor, while the others from the side, making the temperature profile in the reactor uniform.

The liquefied fraction from 15 is sent to a refinery section. In T1, dimethyl ether (DME), a byproduct in R2, is separated. In T2, ethanol and water are separated. Methanol in 99.995% purity is discharged from T3 with its molar flowrate 363 mol/s.

5.2. Successional relationships in the system

We can observe various functionalities in this system. The main three functions are (1) the decomposition of the target reaction into two subtarget reactions, (2) the effect of the loop along unit 10 through 15, and (3) separation of impurities in T1 through T3. For the separation, the relationship between the function of the separation and the structural configuration of the sequence of distillation columns is clear. Hence, we discuss the former two.

The main target of this system is conversion of methane to methanol. Hence the target reaction of this system, **r**, may be written as

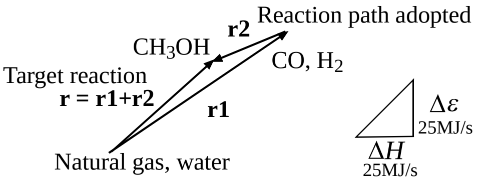
$$\mathbf{r}: 0.9CH_4+0.1C_2H_6+1.1H_2O \rightarrow 1.1CH_3OH+H_2 \quad (6)$$

At present, this direct reaction cannot be performed commercially and this reaction is divided into the following two reactions.

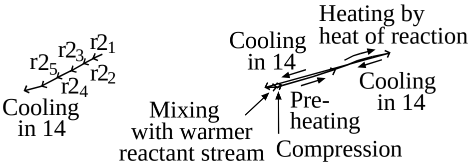
r1: $0.9CH_4+0.1C_2H_6+1.1H_2O \rightarrow 1.1CO+3.2H_2$ (7)

r2: $1.1CO+3.2H_2 \rightarrow 1.1CH_3OH+H_2$ (8)

The successional relationship between the thermal decomposition of natural gas (**r1**) and the methanol production (**r2**) constitutes the main frame of this system, and this relationship can be represented by the process vectors, as shown in *Figure 7 (a).* The slope of the original vector **r** for direct methanol production is very steep. Since this direct methanol production is unavailable, **r** is decomposed to endothermic reaction **r1** and exothermic reaction **r2**. The slope of a reaction vector is equal to the energy level of heat at its equilibrium temperature, $[1-(T_0/T_{eq})]$, where T_0 is an ambient environmental temperature. Hence, gentler slopes for **r1** and **r2** indicate that these reactions may proceed at temperatures much lower than that required for reaction **r**. Consequently, process vectors are very suited to represent this important functionality for this system. Although the above target reaction and the above scheme for its decomposition were selected, there may be other possibilities.



(a) Decomposition of the target reaction



(i) Change of reactants (ii) Recycle molecules

(b) Features of the open loop for methanol production

Figure 7. Functionalities represented by successional relationships

In the second reaction, the huge amount of gas is recycled to the inlet of R2. The flowrate of each component in the reactant gas supplied from R1 is 1200 for H_2, 271 for CO, 106 for CO_2 and 4.2 for H_2O in mol/s. On the other hand, the flowrate of each component in the recycled gas is 7130 for H_2, 103 for CO, 96 for CO_2, 484 CH_4, 20 for CH_3OH, and 5.1 for H_2O. Hence, the latter flowrate is much larger than the former.

This recycle forms a loop. Since it is an open loop with input and output of substances, we cannot apply the procedure for analyzing the functionality of a closed loop represented in *Figure 3*. However, the role of this open loop and its contribution to the reaction can be disclosed by dividing the molecules in each stream in the loop into reactant-stream molecules and recycle molecules. Namely we treat the reactant-stream molecules that came from compressor 9 and the recycle molecules that came from 15 separately. We assume that the reactant-stream molecules take part in the reactions in R2 and that the recycle molecules do not participate in those reactions. To trace both the reactant-stream molecules and the recycle molecules separately, we introduce the partial molar enthalpy $\bar{h}_j$ and partial molar exergy $\bar{\varepsilon}_j$ for a mole of molecule *j* in each stream in the loop. Then we can obtain energy H and exergy ε, for the reactant-stream molecules in each stream by

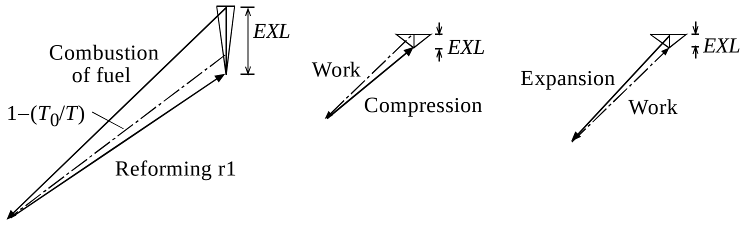
$$H = \sum_j n_j \bar{h}_j \tag{9}$$

$$\varepsilon = \sum_j n_j \bar{\varepsilon}_j \tag{10}$$

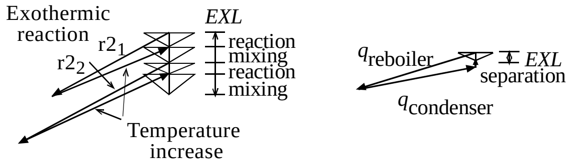
where n_j is the number of moles of reactant-stream molecule j. Similarly we may obtain H and ε for the recycle molecules, too, by regarding n_j as the number of moles of recycle molecule j. In this manner, we can draw the process vectors for (i) the reactant-stream molecules and (ii) the recycle molecules for each change, as shown in *Figure 7 (b).*

The successional relationships for the reactant molecules in (i) indicate that both energy H and exergy ε decrease with the progress of the reactions and in cooling in 14. Strictly speaking, there are three other vectors: for mixing with colder recycle stream with ΔH=−4.8 and Δε=−1.8 in MJ/s, for compression with ΔH=0.4 and Δε=0.3, and for preheating with ΔH=4.4 and Δε=1.1. Hence, the origin of $r2_1$ in (i) is located at (0, −0.4). On the other hand, the successional connection of the process vectors for the recycle molecules in (ii) gives a closed loop. The left-lower end corresponds to the state after cooling in 14. Then, mixing with the warmer reactant stream, compression, preheating and acceptance of heat of reaction follow. The right-upper end corresponds to this state. Finally the cooling in 14 makes the state back to the starting point. In this presentation, the fraction of purge that passes through 32 is neglected, for simplicity.

When we compare (i) and (ii), we find that the heat released by the reactions is absorbed by the abundant amount of the recycle molecules. Hence, it has become clear that the reactant stream acts as a heat donor and that the recycle molecules act as a heat acceptor. Also we find that the slopes of $r2_1$ through $r2_5$ in (i) are higher than that of the acceptance of the reaction heat in (ii). When the reaction takes place at the condition close to the equilibrium, the slope for the heat acceptance in (ii) approaches that for reaction in (i). The large difference in the slopes indicates that the recycle of



(a) Steam reforming in R1 (b) Compression (c) Expansion



(d) Production of methanol in R2 (e) Separation

Figure 8. Representation of various types of meditative relationships

large amount of hydrogen in the recycle molecules contributes to the increase in the driving forces for the progress of reactions (4) and (5). Hence the functionalities of an open loop can be disclosed by process vectors based on partial molar energy $\bar{h}_j$ and exergy $\bar{\varepsilon}_j$.

5.3 Mediative relationships

Most of the mediative relationships between energy-donating processes and energy-accepting ones in this system are shown by use of process vectors on PFD in *Figure 6*. The PFD is a suitable diagram to represent the structure of the system. It can represent the flows of substances and various kinds of apparatuses used in the system. The temperature and pressure of important streams are presented by @T,P with T in °C and P in bar. However, it has neither quantitative energy information nor exergy information. Hence the addition of mediative information by process vectors on PFD gives us quantitative and qualitative energy and exergy features of the system and makes PFD a very useful diagram. For example, at a glance we can observe large exergy loss for the reforming reaction in R1. The reforming reaction is endothermic and requires large amount of heat at a high temperature. This causes large exergy loss.

The part for the reforming reaction in reactor R1 is represented also in *Figure 8 (a)*. The heat required for this reaction is supplied by combustion of both the fuel natural gas and the purge gas. The dash-dotted line represents a thermal vector whose slope is equal to [1−(T_0/T)]. Hence, the exergy loss is divided into two parts: the lower part caused by the reforming and the upper part by the combustion. *Figures 8 (b)* and *(c)*, respectively, show the meditative relationships for a compressor and a turbine. The vectors for a work source and a work sink have the slope of 45°. Hence, the slope of the vectors for compression is less than 45°, while that for expansion is greater than 45°.

In reactor R2, methanol is produced in five steps. Only the first two steps $r2_1$ and $r2_2$ are shown in *Figure 8 (d)*. The reaction is exothermic and donates heat, which is accepted by the increase in the temperature of the reaction stream. This causes exergy loss. Then this stream is mixed with the cold reactant introduced from the side. This mixing causes exergy loss, too. Similar relationships are observed from the second through the fifth step. On PFD in *Figure 6*, the summed vectors for the exothermic reaction and for the temperature increase and the summed exergy loss by mixing are drawn. In (e), the meditative relationship for a distillation column is shown. The combination of supply of heat at a higher temperature in the reboiler and removal of heat at a lower temperature in the condenser can make the separation proceed with the exergy loss.

Since there are many heating and cooling processes in a chemical plant, each combination between them for heat exchange is not shown on PFD. Hence, for heat exchangers, the vectors of all heat donors are linked in the order of the high values of the slope, while those of all heat acceptors in the order of low values of the slope, as shown in *Figure 9*. Then, the total exergy loss for the heat exchangers is obtained, indicating that this value is also large.

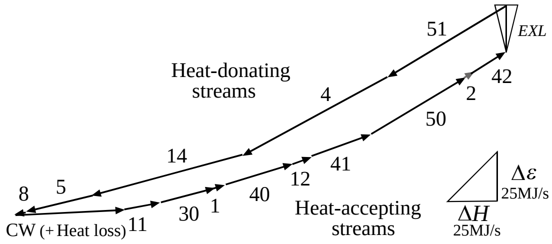


Figure 9. Mediative relationships for heat exchange

We can compare the exergy loss in the heat exchange network with other exergy losses in this system by *Figures 6* and *9*. However, the slope of the process vector represents the average energy level of the released or accepted heat. For a heat exchanger, the temperature differences at both the inlet and the outlet are key values. Hence, *T–Q* diagram (Hohman 1971) or *A–Q* diagram (Umeda et al. 1979) is more appropriate for detailed synthesis of the heat exchange network.

5.4. Relationship between inputs and outputs of the entire system

Figure 10 shows the inputs and outputs for the entire system. Most of the supplied natural gas is the reactant for reforming, but some is introduced as additional fuel. On the other hand, methanol is the product. This figure can disclose the roles of the resources and the products and the overall view of the entire system.

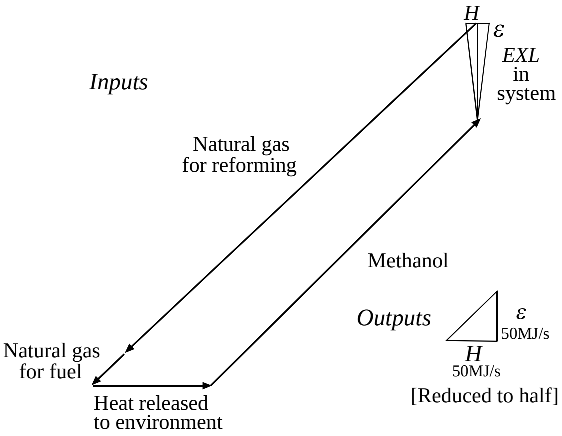


Figure 10. Relationship between inputs and outputs for an entire system

The size of this figure is reduced to half. This indicates that for a chemical reaction, ΔH and $\Delta \varepsilon$ for each change are much smaller than the absolute values of H and ε of the stream. Hence we have focused on ΔH and $\Delta \varepsilon$ for all processes in a system in *Figure 6*.

6. Comparison with Other Methods

The most popular diagram for the discussion on the features of an entire system is the energy-flow diagram (*i.e.*, Sankey diagram) or the exergy-flow diagram (*i.e.*, Grassmann diagram). The former is shown in *Figure 11*, while the latter in *Figure 12*. At a glance, we can find that these diagrams become very complex for chemical processes. There are disadvantages for these diagrams. The main disadvantage is the difficulty in drawing such a diagram. The second disadvantage is that each change in energy or exergy is so small as compared with the enthalpy or exergy of the natural gas or the methanol. This disadvantage is not so severe in energy systems in which almost all energy of the substance is converted to another form of energy, *e.g.*, power and/or heat. For chemical processes, however, some chemical substances are changed to other chemical substances, and the energy change or exergy change by this reaction is generally much less than the absolute value of H or ε of the chemical substance. The third disadvantage is that energy and exergy features are displayed on separate diagrams. Hence, the energy-flow and exergy flow diagrams cannot be recommended for analyses of chemical processes.

On the other hand, the combination of PFD and the process vectors has many advantages. For complicated systems, the clear representation of the functionalities generated by the system is quite important. So far these functionalities of a system have not been discussed in detail in the field of process system synthesis, because there was no appropriate method for representing functionalities. Hence the successional relationships represented by process vectors that can connect the functionalities generated by the system and the system structure are very important.

Moreover, the process vectors can display the mediative relationships between processes, too. They can disclose the locations with large exergy losses. The PFD is quite appropriate for compactly representing the system structure and the flow of substances in it. The process vectors are powerful to represent energy and exergy features simultaneously. They can give quantitative energy and exergy features by their size and qualitative features by their slopes. Further they can display exergy losses. Consequently, the synergic combination of PFD and process/substance vectors can give essential views useful for process analyses and syntheses.

7. Conclusions

(1) Process/substance vectors can represent three kinds of relationships: successional relationships among processes, mediative relationships between processes and the relationship between inputs and outputs of an entire system.

(2) The functionalities generated by a system or a subsystem are represented mainly by successional relationships. Even analyses of successional relationships for an open loop can be made by introducing the concepts of partial molar energy and exergy.

(3) The energy utilization can be represented by mediative relationships between energy donors and energy acceptors.

(4) The input and output relations represented by substance vectors can give overall view of the entire system.

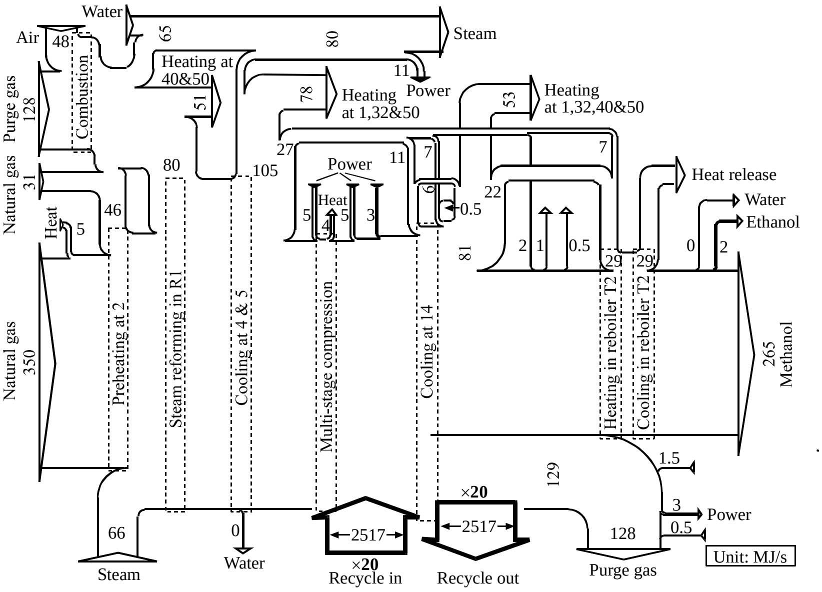


Figure 11. Energy-flow diagram for a methanol plant

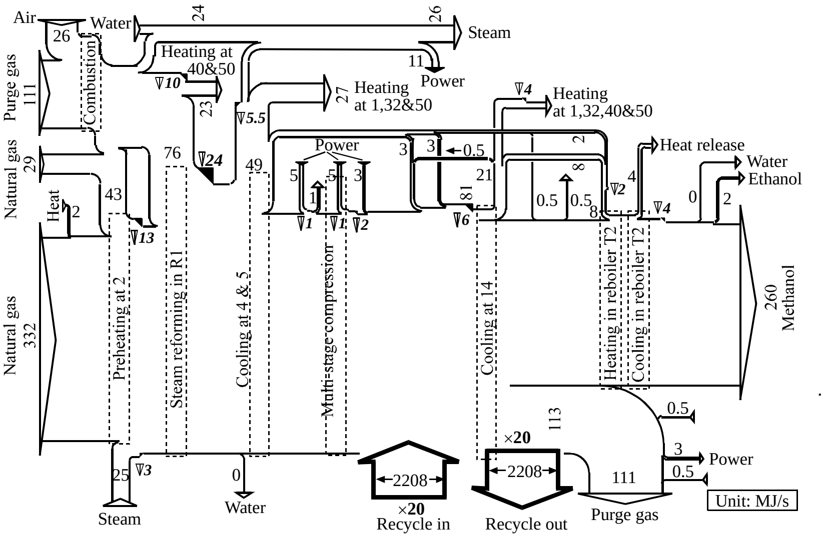


Figure 12. Exergy-flow diagram for a methanol plant

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