

Systematic Structure Synthesis of Distillation-Based Separation Processes

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1. Introduction

1.1. Basic technologies for energy-saving distillation

Distillation is the most popular separation operation in chemical industries. On the other hand, distillation is also well known as highly energy-consuming operation: e.g. distillation occupies approximately 40% of total energy consumption of chemical industry in Japan (NEDO, 2013). Thus, reduction of the energy consumed by distillation is crucial for energy conservation in chemical industries. From this viewpoint, various energy-saving techniques such as heat integration, thermal coupling, and combination with other unit operations such as membrane separation and reaction have been proposed and implemented.

Heat integration based on the pinch analysis has been widely implemented. The pinch analysis provides significant effect especially for the system consisting of many units, but further improvements can be achieved by globally optimizing the design and operation variables of each unit. For example, on the design of distillation processes consisting of many distillation columns, once the heat duties and operating temperatures of each reboiler and condenser are specified, the pinch analysis provides a heat exchange network between the reboilers and the condensers. Under the given heat duties and operating temperatures, the provided heat exchange network is the most efficient design. In other words, the efficiency may further become higher when optimizing the heat duties and the operating temperatures so as to enhance the overall efficiency of the whole distillation process. Such a technique is called multi-effect distillation.

Another key technology using heat integration is heat integrated distillation column (HIDiC). The feature of HIDiC is that the internal streams in the column are used for heat integration. HIDiC is usually applied for a distillation column which cannot exchange the heat with the other units. After the fundamental concept of HIDiC was proposed by Mah et al. (1977), many researchers adopted concentric column structures equipped with structured packing or trays (Lueprasitsakul et al., 1990; Nakaiwa et al., 2003). In such a structure of HIDiC, heat exchange between the stripping and rectifying sections at the same elevation is executed, and the temperature difference for heat exchange at each point is decided by the column design and the operating condition. For a double column system, Huang et al. pointed out the effectiveness of the external allocation of heat exchangers (Huang et al., 2010; Wang et al., 2010; Zhang et al., 2011). Wakabayashi and Hasebe (2011) showed that HIDiC having a limited number of side heat exchanges has the possibility of higher energy saving than that utilizing all stages for heat exchanges.

Thermal coupling is also intensively investigated as a technique for energy-saving

distillation since Petlyuk et al. (1965) presented a thermally coupled configuration for ternary distillation, called Petlyuk column. When considering thermal coupling, there are enormous number of potentially possible process structures. Various process structures were developed based on human experiences and trial and error. Rong et al. (2003) developed a systematic method for identifying functionally distinct thermally coupled configurations for quaternary distillation. They showed that there are many process structures which had not been examined before. In addition, the suitable process structure differs depending on the given design requirement such as the specifications of the feed, the products, and the available utility resources. Thus, there is a high possibility that better-performance process structures which have not conceptualized yet exist.

A popular research subject in terms of the combination of distillation and other unit operations is distillation/membrane hybrid separation. This hybrid separation is usually applied to the separations of azeotropic mixture and of mixtures with low relative volatility. As for these separation tasks, due to the unfavorable nature on vapor-liquid equilibrium (VLE) condition, separation only by distillation often results in large energy consumption. On the other hand, in membrane separation, the components in the mixture are separated depending on the affinity between membrane and each component instead of VLE condition. If a membrane with high selectivity is available, separation using the membrane can be a promising alternative to distillation. Actual applications of membrane separation systems to large scale plants however are limited because of the high membrane cost, limited available temperature and pressure ranges, the short life of membranes, and performance degradation by fouling. A possible solution for these difficulties in scale up is to combine membrane separation and distillation, which takes advantage of scale.

Reactive distillation is an attractive alternative to conventional processing scheme which consists of reactors and distillation columns. In addition to the reduction of the number of the processing units, reactive distillation possesses several potential advantages: e.g. direct heat integration between reaction and distillation can reduce utility usage; the continuous removal of products from the reaction zone can provide high conversion and selectivity over chemical-equilibrium limitations, which reduce raw material usage and undesired byproduct formation. These advantages were confirmed by many industrial applications such as the methyl acetate process presented by Agreda et al (1990), methyl tert-butyl ether (MTBE) process presented by Smith (1990). While there are significant potential advantages, design problems for reactive distillation processes are much more complicated than those of ordinary distillation processes. This is because reaction at each tray must be taken into account as well as vapor-liquid equilibrium (VLE)

on the design of a reactive distillation column.

While there are several basic technologies for energy-saving distillation, the consideration of these technologies complicates the resulting design problem. To obtain the optimal configuration, systematic methods for solving such complicated design problem is necessary.

1.2. Graphical methods for the process synthesis

On design of distillation columns, many graphical methods have been proposed. An advantage compared to numerical methods is to provide intuitive understanding of the process. On the other hand, graphical methods often introduce more assumptions than numerical methods in order to describe the configurations via the diagrams with two or three dimensions. The most basic methods are McCabe-Thiele method and Ponchon-Savarit method, and many graphical methods for the synthesis of advanced distillation columns are based on either of these methods. In this section, two typical extensions are introduced.

Wakabayashi and Hasebe (2013) developed a diagram for designing HIDiC. In their diagram, Ponchon-Savarit diagram (H-xy diagram) and T-xy diagram are combined. This method assume that high energy-efficiency should be achieved by emulating the reversible distillation in terms of thermodynamic properties. The involved thermodynamic properties are visualized on their diagram, and the design configuration such as heat-exchange combinations and heat transfer areas of each heat exchanger is determined through seeking similarity to reversible distillation on their diagram.

Daza et al (2003) extended the McCabe-Thiele method and Ponchon-Savarit method to the design of reactive distillation columns. They assume that equilibrium reaction is taken place at each tray. By assuming the chemical equilibrium in addition to vapor-liquid equilibrium, the degree of freedom in the state space is decreased: e.g. when two equilibrium reactions are taken place in four-component system, the degree of freedom is one. By utilizing this feature, they extended the traditional diagrams to reactive distillation in which the degree of freedom is one.

1.3. Synthesis methods over candidate process structures via nonlinear programming

As mentioned in section 1.1, when utilizing the energy-saving technologies, there are many possible process structures. The most primitive procedure to find the optimal configuration is examine each candidate structures individually. However, since there are many candidates, such a procedure results in too heavy computation. More

computationally efficient methodology is needed. The most popular approach is to formulate the process synthesis problem as a mathematical optimization problem based on a superstructure. Superstructure is a structure which contains all of the candidate structures under consideration. By solving the resulting optimization problem, the optimal configuration out of all considered structures is obtained as a part of the superstructure. Since the equations corresponding to the superstructures, such as material balances, heat balances, and thermodynamic relationships, are nonlinear, the optimization problem is usually formulated as a nonlinear programming (NLP) problem or a mixed integer nonlinear programming (MINLP) problem.

Novak et al. (1996) constructed a superstructure for designing multi-effect distillation. They adopted rectifying and stripping sections of a conventional column as a building block of their superstructure and formulated the process synthesis problem as a MINLP problem. Harwardt and Marquardt (2012) constructed a superstructure for designing HiDiC. In their superstructure, stripping and rectifying columns were installed in parallel, and heat exchange was allowed only between the stages at the same elevation of the stripping and rectifying sections. Based on the superstructure, they formulated the design problem as an MINLP problem. Synthesis problems involving thermally coupled columns have also been discussed by many researchers since Sargent and Gaminibandara (1976) firstly developed a basic method. In these researches, thermally coupled columns and/or their component structures are embedded as building blocks in the superstructure of the synthesis problem. Kookos (2003) developed a superstructure for the synthesis of distillation/membrane hybrid separation processes and formulated the synthesis problem as an MINLP problem. Jackson and Grossmann (2001) developed superstructure-based method for a reactive distillation column. Through solving the proposed MINLP problem, positions of feed trays and reaction zones, holdup of each tray in reaction zones, and the reflux and reboil ratios are optimized so as to minimize the total cost of a reactive distillation column.

By solving the formulated problems, we can obtain the most suitable process structure that is included in the adopted superstructures prepared in advance. In other words, a process structure which is not included in the superstructure is never obtained even if it actually can achieve much better performance. Therefore, the diversity of process structures included in the adopted superstructures is an important point for finding better configurations. Some researchers aimed at constructing more comprehensive superstructure as for thermally coupled distillation. Rong et al. (2003) developed a systematic method for generating functionally distinct thermally coupled configurations for quaternary distillation. Shah and Agrawal (2010) proposed a matrix-based method

that can efficiently enumerate the configurations for the cases involving higher components as well. Nallasivam et al. (2016) developed an algorithm in which many configurations are first enumerated, and the configuration with the least vapor duty is identified under minimum reflux condition. By simplifying the mathematical model using Underwood equations, the optimization problem is formulated only by linear and bilinear constraints. Thus, the global optimum can be obtained with reasonable computational burden.

1.4. Synthesis methods without any assumption on process structure via linear programming

When the diversity of candidate structures in the adopted superstructures increases, the size of the resulting optimization problem, which usually includes nonconvex nonlinear constraints, is increased. To solve the resulting optimization problem without heavy computational burden, many methods adopt simple VLE models and/or short-cut models such as the Underwood equation.

Drake and Manousiouthakis (2002ab) proposed the infinite-dimensional state-space (IDEAS) approach. In this approach, the state space is discretized with the infinitely

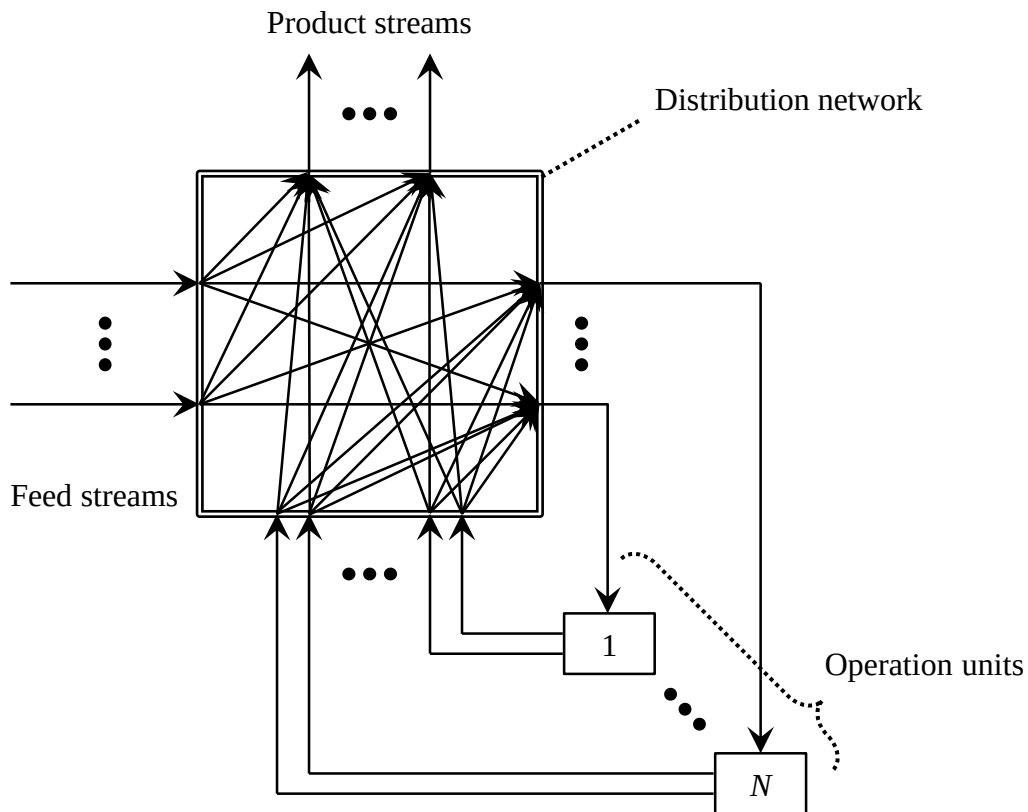


Figure 1.1 IDEAS representation of a general distillation network

small width, and each discretized state is assigned as the state of output or input flow of an operation unit. In this manner, the intensive variables concerning output and/or input flows of each operation unit are specified in advance. The distribution network connects the operation units, the feed flows, and the product flows so as to cover all possible flow connections. Figure 1.1 illustrates the IDEAS representation of a general distillation network. Based on this network, the global optimization over any possible process structures is formulated as an infinite dimensional linear programming (ILP) problem instead of nonlinear programming problem. The simplification of VLE model is also not required. The approximate solution of the ILP problem can be obtained by solving a finite dimensional linear programming problem where the state space is discretized with enough small finite widths instead of the infinitely small width.

The IDEAS approach was applied to the synthesis of various distillation processes such as ideal distillation processes (Drake and Manousiouthakis, 2002ab), heat/power integrated distillation processes (Holiastos and Manousiouthakis, 2004), azeotropic distillation processes (Ghougassian and Manousiouthakis, 2012), and reactive distillation processes (Burri and Manousiouthakis, 2004, Da Cruz and Manousiouthakis, 2017), as well as process synthesis of the other unit operations.

1.5. Overview of this thesis

While the IDEAS approach can quantify the limit of the performance, the result often consists of a quite large number of operation units and flow paths among the operation units. Thus, in many cases, it is difficult to generate a practical process structure from the obtained result. Indeed, the researches proposed by Manousiouthakis and coauthors focused on deriving a limit of a particular performance index rather than conceptualizing a process structure for practice. In contrast, the methods in this thesis focuses on synthesizing efficient process structures.

In chapter 2, synthesis of HIDiC is discussed. By adopting the state space discretization model used in the IDEAS approach, the synthesis procedure for deriving the process minimizing the total cost is developed. In order to evaluate the capital cost, the number of trays is incorporated in the objective function using 0-1 variable. Because of this treatment, the processes containing many trays, which tend to be obtained by the IDEAS approach is fairly penalized in the optimization.

In chapter 3, the method described in chapter 1 is extended to ternary distillation. Heat exchange and pressurization in the process is not considered. Under this condition, the optimization over any possible process structures including various thermally coupled configurations is carried out through the proposed procedure. For ternary distillation cases,

the formulation using 0-1 variables results in an MILP involving too many variables because the state space of three-component system is much larger than that of two-component system. Thus, from the viewpoint of computational burden, the approach using 0-1 variables cannot be applied to ternary distillation cases. To overcome this difficulty, an alternative heuristic procedure for simplifying the process structure is developed.

In chapter 4, the process synthesis procedure for reactive distillation involving three components are developed using the same concept. In the case study dealing with metathesis reaction of 2-pentene, the optimization result implied a new process structure. This new process structure was examined through the comparison with conventional structures using a process simulator. The result of the examination showed the superiority of the new process structure.

In chapter 5, an alternative method for formulating the process synthesis problems without nonlinear equations is proposed. The crucial disadvantage of the state space discretization adopted in the IDEAS approach is first described using a simple example. Then, the alternative method which overcomes the disadvantage is described. The alternative method was examined using a simple example, which is distillation of benzene-toluene mixture without heat integration.

In chapter 6, the method developed in chapter 5 is extended to the synthesis of distillation/membrane hybrid separation processes. The model of membrane separation unit is developed, and the superstructure considering membrane separation in addition to distillation is constructed. As for membrane separation model, the calculation involving differential equations and nonlinear equations is carried out before the optimization. Thus, the resulting optimization problem is still formulated only by linear equations. The proposed method was applied to a separation problem of propane and propylene.

Finally, this thesis is concluded in chapter 7. The accomplishments of this sequence of researches are summarized and the ideas for future development are addressed.

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2. Synthesis of Heat Integrated Distillation Processes Using the Discretization of Liquid Composition Space

2.1. Introduction

In many design procedures of HIDiC, the structure of internal heat integration is treated as a design variable, but the structure of vapor and liquid flow paths among stages, which is hereafter called "flow structure", are assumed to be the same as the conventional distillation column. Manousiouthakis and coauthors (Drake and Manousiouthakis, 2002a, 2002b; Holiastos and Manousiouthakis, 2004) treated the distillation process as a combination of stages, each of which executes mass exchange. Then, the mass exchange network was modeled by using a superstructure consisting of a variety of stages having different liquid compositions. The transshipment model presented by Papoulias and Grossmann (1983) was applied to model the heat exchange network. Under this model, the limit for a performance index is derived by the optimization over all possible flow structures. As the transshipment model was used, it is difficult to embed the heat exchanger cost into the objective function. In addition, number of trays was not considered in the objective function. As a result, complicated processes including a large number of trays were obtained as the optimal solutions.

For a better practical design of HIDiC, many kinds of costs should be considered, and not only the structure of internal heat integration, but also the flow structure should be treated as a design variable. For this purpose, we propose a new systematic procedure of deriving the optimal structure of HIDiC. In the proposed procedure, the method proposed by Manousiouthakis and coauthors (Drake and Manousiouthakis, 2002a, 2002b; Holiastos and Manousiouthakis, 2004) is extended, and HIDiC is treated as a combination of the stages, each of which executes mass and energy exchanges. By treating the material and energy balances at once, the compression cost and the heat exchanger cost can be embedded in the problem. In addition, the number of trays is incorporated into the objective function using 0-1 variables. Finally, the problem is formulated as an MILP problem. The optimization of the pressure is treated as the outer loop in the procedure.

In the rest of this chapter, in sections 2.2, the process synthesis problem discussed in this chapter is defined. In section 2.3 and 2.4, the configuration of the superstructure and the proposed optimization procedure are described, respectively. In section 2.5, proposed design procedure is demonstrated through the separation problem of a benzene-toluene mixture. Finally, this chapter is concluded in section 2.6.

2.2. Problem statement

In HIDiC, the rectifying section is operated at higher pressure than the stripping section. We consider the heat integration between the stages of the stripping and rectifying sections, i.e. we use the vapor flows of some stages in the rectifying section to vaporize the liquid flows of some stages in the stripping section.

In this chapter, the separation problem of binary mixtures is discussed. It is assumed that the flow rates, compositions and states of the feed and products are given in advance. The top and bottom products are assumed to be saturated liquid. The pressure of the feed is the same as that of the stripping section, and is given in advance. For the pressure of the rectifying section, some candidate pressures are assigned in advance. The pressure drop in a column is neglected.

For the above conditions, the optimal design problem which minimizes the design and operation costs is formulated as a mixed integer linear programming (MILP) problem.

2.3. Configuration of superstructure

2.3.1. Configuration of the modules

In the proposed design procedure, each stage, including the reboiler and condenser in a column, is treated as a separation module shown in Fig. 2.1, and the connection of these modules is assumed not to be decided in advance. First, the entire range of liquid composition between the feed and the distillate is divided into N_R different compositions, and the entire range of liquid composition between the feed and the bottom product is also divided into N_S different compositions. Then, each of the divided compositions is assigned to a separation module.

In the proposed method, the vapor-liquid equilibrium is assumed at each separation module. Figure 2.2 illustrates the assignments of the values of the intensive variables for each separation module. When the liquid composition and the pressure are given, other intensive variables such as temperature, vapor composition, and molar enthalpies of the vapor and the liquid can be calculated. For this calculation, any thermodynamic model can be used. Figure 2.1 shows the input and output relationship of a separation module in the stripping or rectifying section. There are two input nodes. One is the material flow, which consists of the mixture of vapor and liquid flows from other modules. The other is the heat flow from other modules of the rectifying section and/or outer utilities. There are three output nodes: liquid and vapor streams and the heat flow. The heat is transferred from the rectifying section to the stripping section. Thus, the separation modules in the rectifying section do not have input heat flow, and the separation modules in the stripping section do not have the output heat flow.

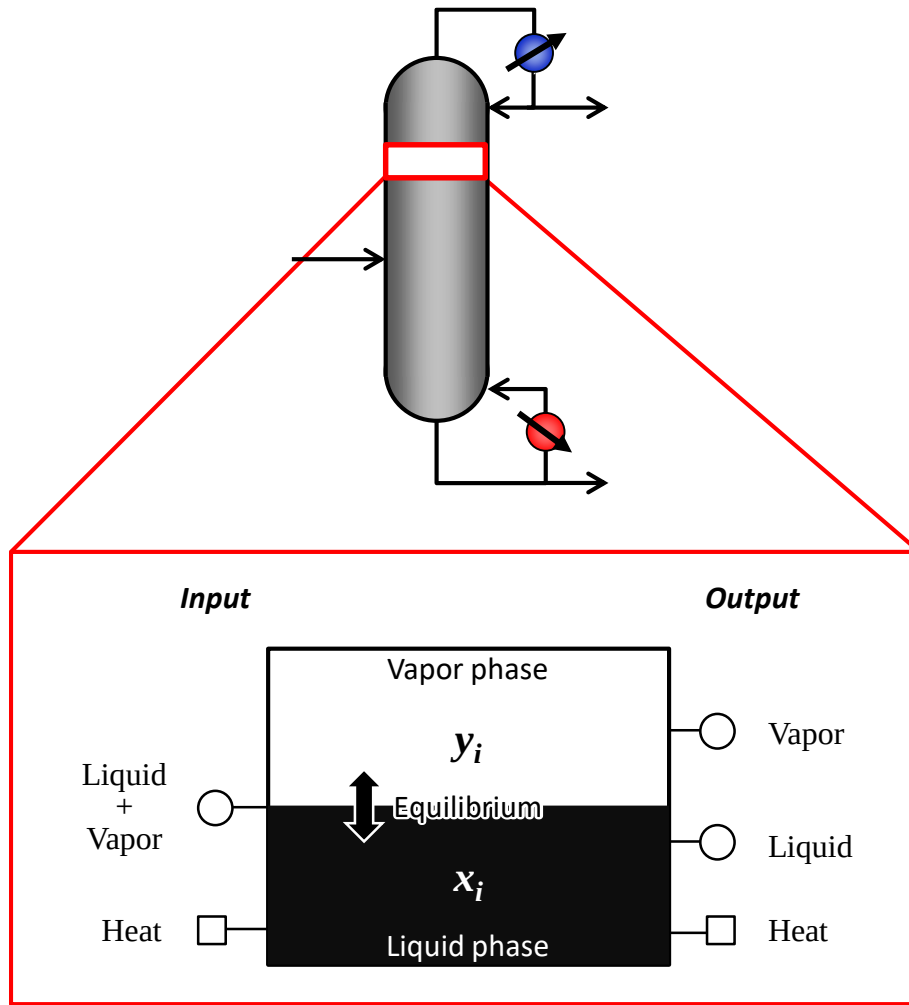


Figure 2.1 Separation module i in the superstructure, which corresponds to a theoretical tray with a specific equilibrium state

Feed and products are treated as special modules; the feed module contains no inputs and the material outputs while the product modules contain only the liquid inputs. Utilities for heating and cooling are also treated as special modules, which contain only the heat output and the heat input, respectively. The modules are named as follows: The feed is regarded as module 0, the module whose liquid composition is the same as that of the bottom product is module 1, the module whose liquid composition is the same as the feed composition is module N_S , the module whose liquid composition is closest to the feed composition in the rectifying section is module N_S+1 , the module whose liquid composition is the same as that of the distillate is module N_{SR} , the bottom product is module $N_{SR}+1$, and the distillate is module $N_{SR}+2$. Here, $N_{SR} = N_S + N_R$. Heating and cooling utilities are modules H and C, respectively.

The total material balance at module i is expressed by Eqs. (2.1) to (2.3).

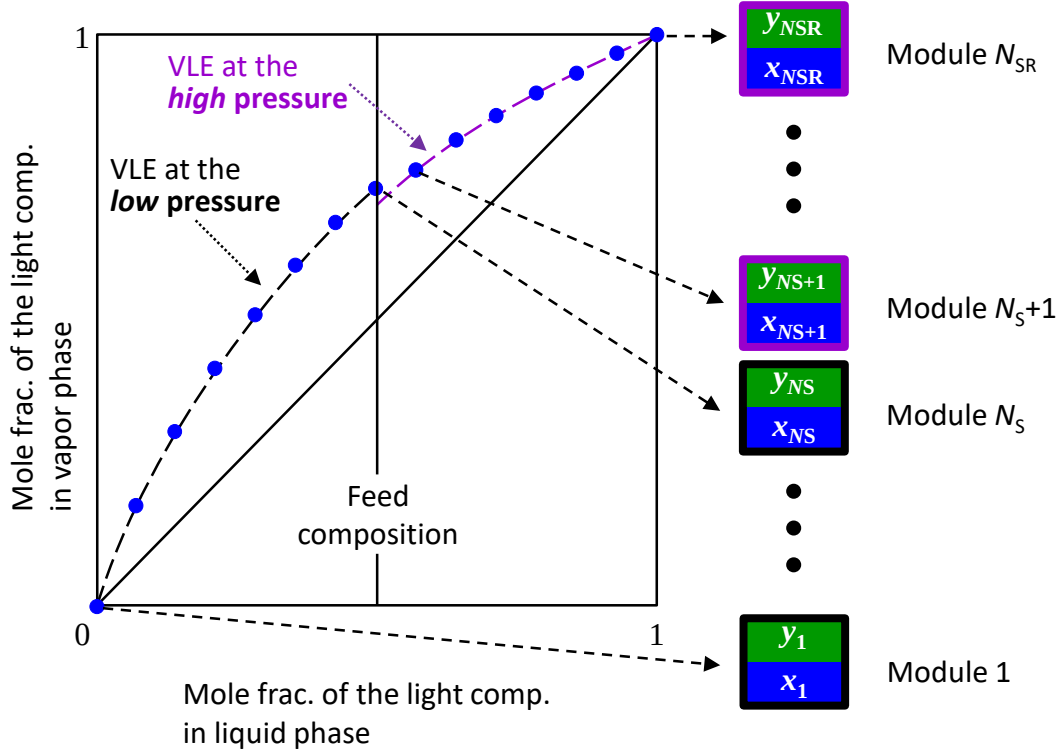


Figure 2.2 Preassignment of a specific equilibrium state to each separation module

$$\sum_{i=0}^{N_{SR}} L_{ij} + \sum_{i=0}^{N_{SR}} V_{ij} = \sum_{i=1}^{N_{SR}+2} L_{ji} + \sum_{i=1}^{N_{SR}+2} V_{ji}, \quad \forall j \in \{1, 2, \dots, N_{SR}\} \quad (2.1)$$

$$L_F = \sum_{i=1}^{N_{SR}} L_{0i}, \quad V_F = \sum_{i=1}^{N_{SR}} V_{0i} \quad (2.2)$$

$$L_{1, N_{SR}+1} = L_B, \quad L_{N_{SR}, N_{SR}+2} = L_D \quad (2.3)$$

Here, L_{ij} and V_{ij} are flow rates of liquid and vapor flows from module i to module j , respectively. L_F and V_F are liquid and vapor flow rates of feed, respectively. L_B and L_D are flow rates of bottom product and distillate, respectively. The first and second terms of the left hand side in Eq. (2.1) are the sum of liquid inlet flows to module j , and the sum of vapor inlet flows to module j , respectively. The first and second terms of the right hand side of Eq. (2.1) are the sum of liquid outlet flows from module j , and the sum of vapor outlet flows from module j , respectively. Equations (2.2) and (2.3) are the material balances of feed flow and product flows, respectively.

Since the composition of liquid phase is discretized in the proposed method, it is difficult to strictly satisfy the component balance at each module. Thus, except for the

product streams, the component balance of each module is given by inequality constraints.

$$-\varepsilon \leq \frac{\sum_{i=0}^{N_{SR}} L_{ij} x_i + \sum_{i=0}^{N_{SR}} V_{ij} y_i - x_j \sum_{i=1}^{N_{SR}+2} L_{ji} - y_j \sum_{i=1}^{N_{SR}+2} V_{ji}}{\sum_{i=1}^{N_{SR}} L_{ij} + \sum_{i=1}^{N_{SR}} V_{ij}} \leq \varepsilon, \quad \forall j \in \{1, 2, \dots, N_{SR}\} \quad (2.4)$$

Here, ε is a parameter which shows the maximum acceptable error on the composition. x_i is the molar fraction of the light component in the liquid of module i , and y_i is the molar fraction of the light component in the vapor of module i .

The enthalpy balances at module j are expressed by Eq. (2.5).

$$\sum_{i=0}^{N_{SR}} L_{ij} (h_i^L + \Delta h_{ij}^L) + \sum_{i=0}^{N_{SR}} V_{ij} (h_i^V + \Delta h_{ij}^V) + Q_j = \sum_{i=1}^{N_{SR}+2} L_{ji} h_j^L + \sum_{i=1}^{N_{SR}+2} V_{ji} h_j^V \quad (2.5)$$

$$\forall j \in \{1, 2, \dots, N_{SR}\}$$

Here, h_i^L and h_i^V are molar enthalpy of liquid and vapor flows from module i , respectively. As the pressure and composition of module i are given in advance, these values are also calculated before the optimization. Q_j is the sum of heat added to module j through heating (positive value) or cooling (negative value) by utilities or heat exchange with other process streams. Δh_i^L and Δh_i^V are compensation terms by pressure change, which is explained in section 2.3.3.

2.3.2. Configuration of liquid, vapor, and heat flow paths

The feature of the proposed design procedure is that the flow structure is treated as one of the design variables. Therefore, there is some possibility that a process structure which is different from the conventional distillation column will be obtained as the result of optimization. Figure 2.3 shows the superstructure which is adopted in this research. To show the flow structure easier, each separation module is divided into two parts: output part and input part. Thus, two boxes with the same number correspond to a separation module. The solid and dotted lines among the boxes are liquid and vapor flows, respectively. These lines connect output nodes of a module and input nodes of the other modules except the product modules. Only the liquid output node of module 1 is connected to the bottom product module, and only the liquid output node of module N_{SR} , is connected to the distillate module as shown in Fig. 2.3. When the internal heat integration is considered, some amount of heat may be supplied to modules in the stripping section, and some amount of heat may be removed from modules in the

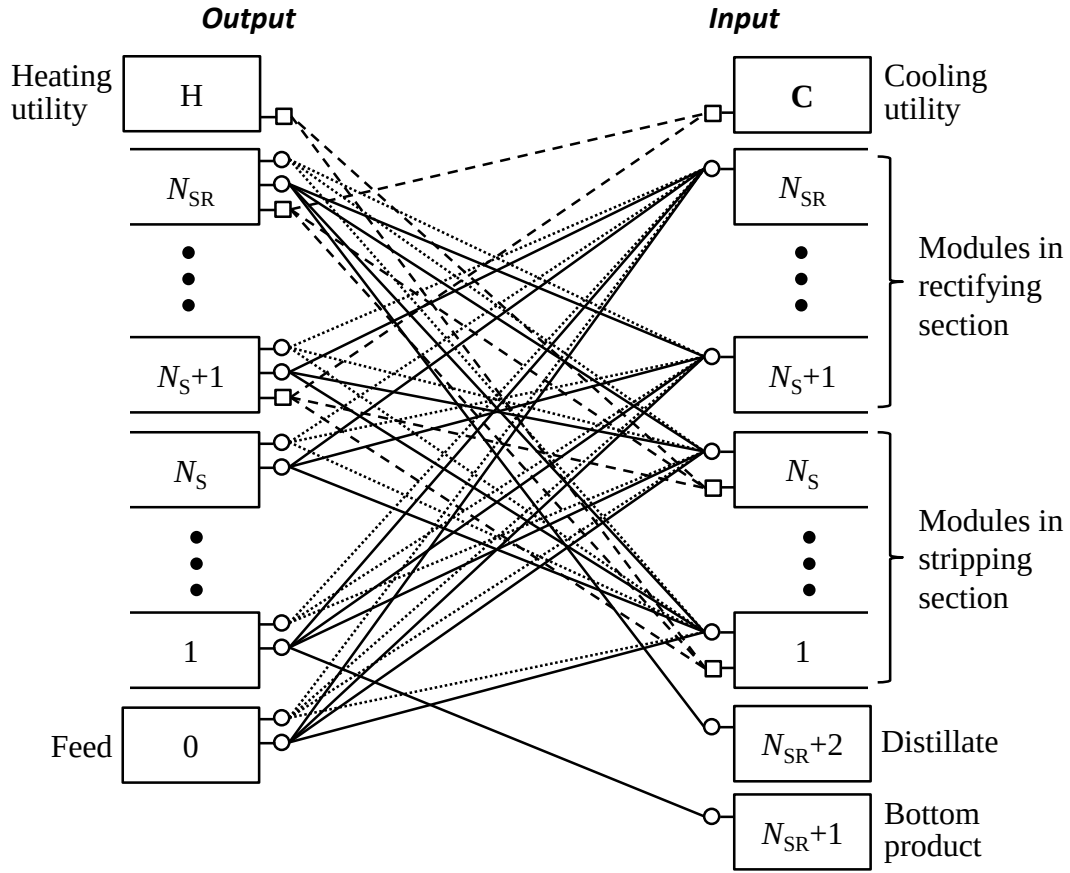


Figure 2.3 Configuration of the proposed superstructure

rectifying section. Such heat transfer is expressed by the heat flow between the modules, and is expressed by the broken line in Fig. 2.3.

2.3.3. Model of pressurization and depressurization

In the synthesis step, it is assumed that the pressures of both sections are given in advance. As the pressure of the rectifying section is higher than that of the stripping section, pumps or compressors are requested for the flows from the stripping section to the rectifying section (See Fig. 2.4). The molar enthalpy of the flow changes with the increase in the pressure. For the liquid flow, it is assumed that the power to compress the liquid is added to the enthalpy of the output flow. For the vapor flow, the output of the compressor is assumed to be saturated vapor. The molar enthalpy differences before and after the compression of the flow from module i in the stripping section to the rectifying section are expressed by Δh_i^V for vapor flow and Δh_i^L for liquid flow. These values are calculated in advance from the molar composition of the flow and the pressures of both sections, and are used in the enthalpy balance equation (Eq. (2.5)). The compressor and

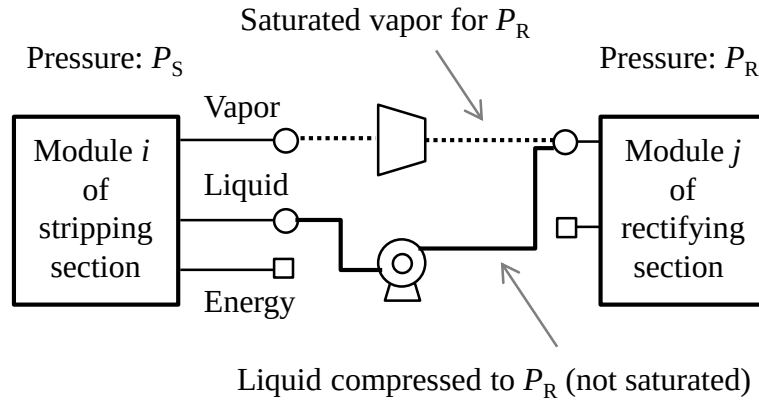


Figure 2.4 Model for the pressurization of the flows from the stripping section to the rectifying section

pump powers are also calculated using these values. It is assumed that the molar enthalpy of each flow is not changed by the depressurization.

2.3.4. Model of heat exchange

Consider the case where the vapor of module i in the rectifying section and the liquid of module j in the stripping section exchange heat. In this research, it is assumed that the vapor in the rectifying section condenses at the bubble temperature, and the liquid in the stripping section vaporizes at the dew temperature. The amount of heat transferred from module i in the rectifying section to module j in the stripping section, Q_{ij} , is expressed by Eq. (2.6).

$$Q_{ij} = UA_{ij}(T_i^b - T_j^d), \quad \forall i \in \{N_s + 1, \dots, N_{SR}\}, \forall j \in \{1, 2, \dots, N_s\} \quad (2.6)$$

Here, U is the overall heat transfer coefficient for heat exchanges between the process streams, A_{ij} is the heat transfer area of the heat exchanger assigned between module i and module j , T_i^b is the bubble point temperature of the vapor in module i , and T_j^d is the dew point temperature of the liquid in module j . In Eq. (2.6), non-negative condition is added to Q_{ij} and A_{ij} . Therefore, the heat transfer from the lower temperature to the higher temperature is automatically removed by this constraint.

Heat exchanges between the process streams and the heating (cooling) utility are similarly expressed by Eq. (2.7) (Eq. (2.8)).

$$Q_{Hi} = U_H A_{Hi}(T_H - T_i^d), \quad \forall i \in \{1, 2, \dots, N_s\} \quad (2.7)$$

$$Q_{iC} = U_C A_{iC} (T_i^b - T_C), \quad \forall i \in \{N_S + 1, \dots, N_{SR}\} \quad (2.8)$$

where U_H and U_C are overall heat transfer coefficients between the process streams and heating and cooling utilities, respectively. A_{Hi} (A_{iC}) is the heat transfer area of the heat exchange between the liquid (vapor) in module i and the heating (cooling) utility. T_H and T_C are temperatures of the heating and cooling utilities, respectively.

Consequently, the total amount of heat added to module i , Q_i , is given by Eq. (2.9).

$$Q_i = \begin{cases} \sum_{j=N_S+1}^{N_{SR}} Q_{ji} + Q_{Hi}, & \forall i \in \{1, 2, \dots, N_S\} \\ -\sum_{j=1}^{N_S} Q_{ij} - Q_{iC}, & \forall i \in \{N_S + 1, \dots, N_{SR}\} \end{cases} \quad (2.9)$$

2.3.5. Formulation of the design and operation costs

The objective function, TAC , consists of the design and operation costs. As the design cost, the capital cost of the column and the additional capital costs to equip the heat exchangers, compressors and pumps are considered. As the operation cost, the costs of heating and cooling utilities and electricity are considered. Thus, the objective function, TAC , is expressed by Eq. (2.10).

$$TAC = c_1 \sum_{i=1}^{N_S} Q_{Hi} + c_2 \sum_{i=N_S+1}^{N_{SR}} Q_{iC} + c_3 \left[\sum_{i=1}^{N_S} \left(A_{Hi} + \sum_{j=N_S+1}^{N_{SR}} A_{ij} \right) + \sum_{j=N_S+1}^{N_{SR}} A_{jC} \right] \\ + \sum_{i=0}^{N_S} \left(E_i^V \sum_{j=N_S+1}^{N_{SR}} V_{ij} \right) + \sum_{i=0}^{N_S} \left(E_i^L \sum_{j=N_S+1}^{N_{SR}} L_{ij} \right) + c_4 \sum_{i=1}^{N_{SR}} z_i \quad (2.10)$$

Here, c_1 to c_4 are coefficients of the cost function. The first and second terms of the right hand side of Eq. (2.10) represent the costs of heating and cooling utilities, respectively. It is assumed that the capital cost of heat exchangers is proportional to the sum of the heat transfer areas of the heat exchangers, and is expressed by the third term. The reboiler and condenser costs are also included in the third term. The fourth and fifth terms show the compressor costs and pump costs, respectively. E_i^V and E_i^L are the sums of capital and operating costs of compression for unit amounts of vapor and liquid flows from module i , and are assumed to be proportional to Δh_i^V and Δh_i^L , respectively. The sixth term represents the capital cost of the column, which is assumed to be proportional to the number of selected modules. z_i takes one when module i is selected, and takes zero when

it is not selected. z_i is also used to restrict the flow as in Eq. (2.11).

$$\sum_{j=1}^{N_{SR}+2} L_{ij} + \sum_{j=1}^{N_{SR}+2} V_{ij} \leq Mz_i, \quad \forall i \in \{1, 2, \dots, N_{SR}\} \quad (2.11)$$

Here, M is a sufficiently large number.

2.4. Optimization procedure

In the proposed method, it is assumed that the pressure of the feed and stripping section is fixed to P_s , and some candidate values of pressure of rectifying section are given. Then, process design is carried out by the following procedure:

1. The entire range of liquid composition is divided into $N_S + N_R$ different compositions.
2. The pressure of the rectifying section is set to one of the candidate values.
3. The values of intensive variables are calculated.
4. The problem of minimizing the total cost expressed by Eq. (2.10) under the constraints of Eqs. (2.1) to (2.9) and (2.11) is formulated as an MILP problem.
5. The formulated problem is solved by using an MILP solver.
6. The pressure of the rectifying section is changed to another candidate value, and returns to step 3. If all candidates are examined, go to step 7.
7. All cases are compared, and the best one is chosen as the optimal design.

2.5. Case study

The proposed method was demonstrated through the separation problems of a benzene-toluene mixture. The total flow rate and the molar fraction of benzene at the feed are 200 kmol h⁻¹ and 0.50. The pressure of the stripping section was assumed to be 101.3 kPa, and the candidate pressures of the rectifying section were 16 different pressures among 152.0 kPa to 303.9 kPa. Cost coefficients c_1 to c_4 in Eq. (2.10) are 1.1 ¥ MJ⁻¹, 2.5×10⁻² ¥ MJ⁻¹, 5.4 ¥ m⁻² h⁻¹, 40 ¥ h⁻¹, respectively. E_i^V in Eq. (2.10) is 3.1×Δ h_i^V ¥ MJ⁻¹. E_i^L is treated as zero in this case study. Steam at 473 K is used for heating and the water between 303 K and 313 K is used for cooling. The overall heat transfer coefficients between streams in the rectifying and stripping section, between process streams and the steam, and between process streams and the water are 5.4 MJ h⁻¹ m⁻² K⁻¹, 5.4 MJ h⁻¹ m⁻² K⁻¹, and 3.6 MJ h⁻¹ m⁻² K⁻¹, respectively. It is assumed that the steam is used only in module 1, the reboiler, and that the cooling water is used only at module N_{SR} , condenser. The values of intensive variables were calculated by the NRTL fluid package of Aspen

HYSYS® (Aspen Technology, Inc.).

In case 1, the specifications of distillate and bottom product are given by the molar fraction of benzene and are 0.95 and 0.05, respectively. The liquid composition was equally divided into 23 different compositions in the stripping section, and 22 compositions in the rectifying section.

In case 2, the specification of products is less severe than that in case 1. The molar fractions of benzene in distillate and bottom product are 0.80 and 0.20, respectively. The liquid composition was equally divided into 18 different compositions in the stripping section, and 17 compositions in the rectifying section.

The optimal structure shown in Fig. 2.5 was obtained for case 1. The number in each rectangular box shows the module number, and the value on each arrow shows the flow rate. The broken lines indicate the heat flows. In the stripping and rectifying sections, 15 and 10 modules are selected, respectively. The flow structure is almost the same as the conventional distillation column, i.e. the vapor of each stage flows into the stage just above, and the liquid of each stage flows into the stage just below. The result of internal heat exchange is summarized in Table 2.1. The change of costs against the pressure of the rectifying section is shown in Fig. 2.6. The optimal structure did not use any heating steam from outside the process. The reboiler duty of the conventional column with infinity number of stages without internal heat integration was 1849 kW. It is assumed that the primary energy consumption at the compressor is 2.73 times higher than the power needed for the compression. Thus, for the optimal case, it is 727 kW ($= 2.73 \times 261$ kW). This value is 39% of that for the conventional column of infinity number of stages without internal heat integration.

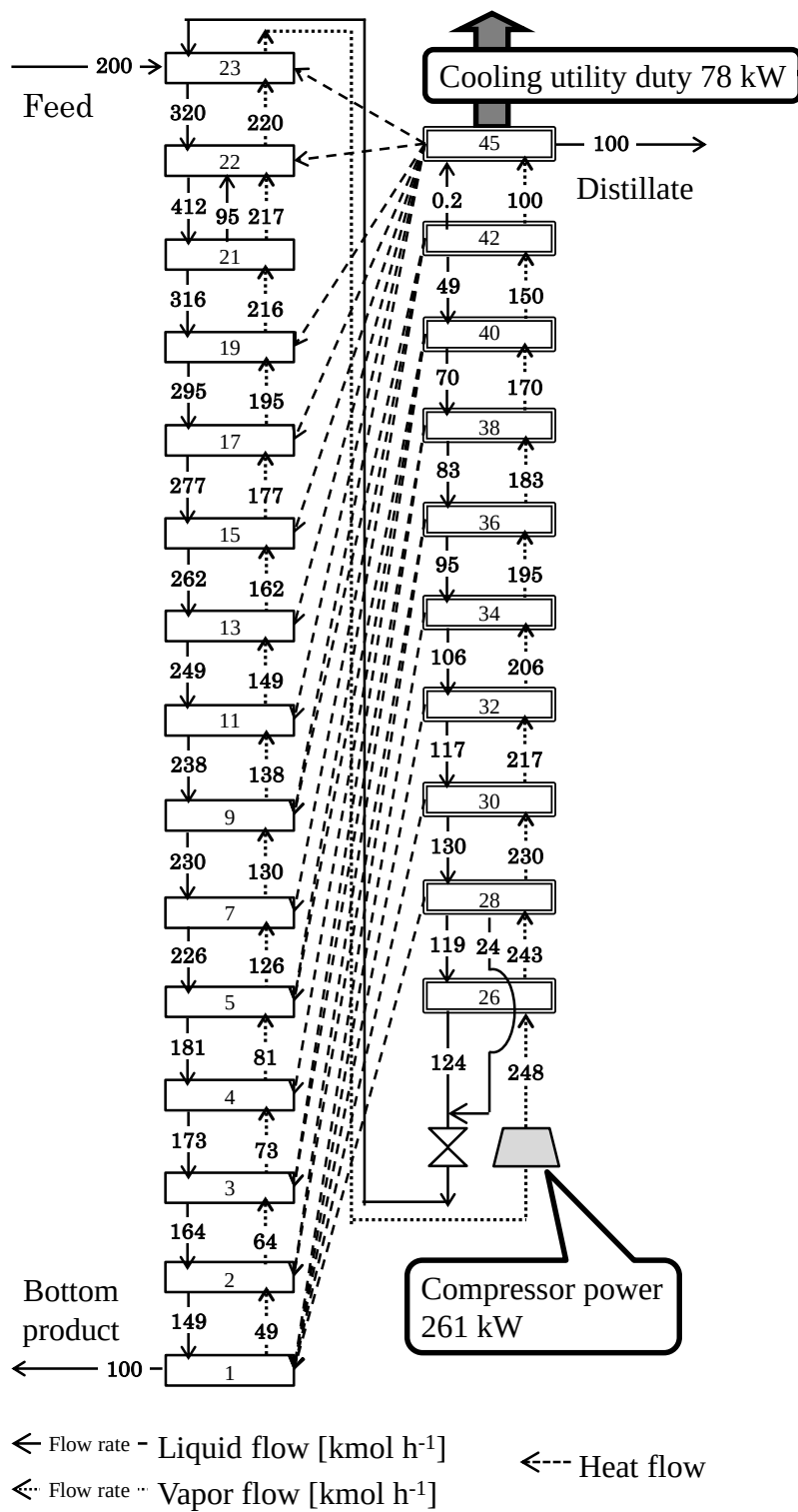


Figure 2.5 Optimal process obtained in case 1

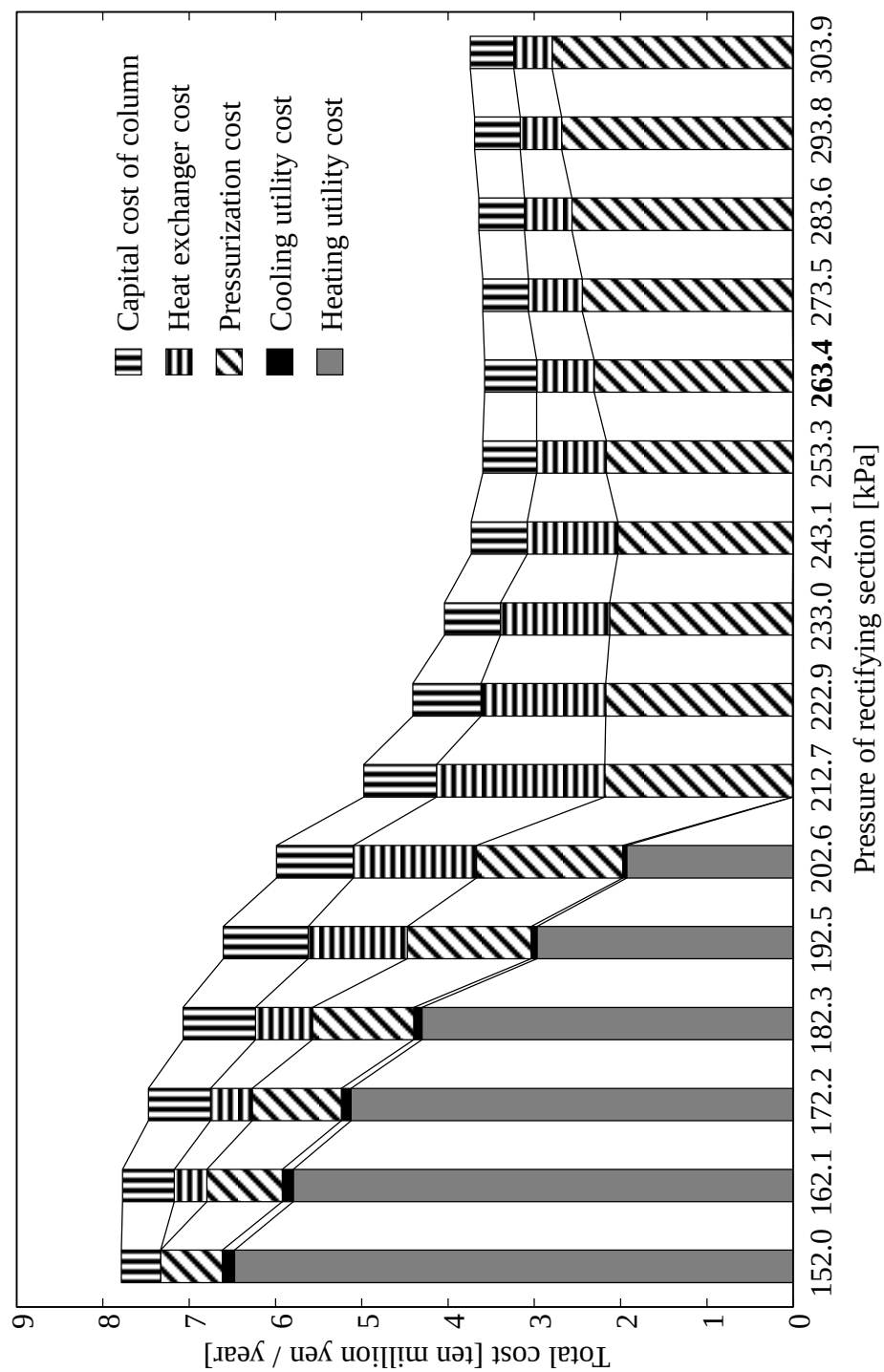


Figure 2.6 Transition of each cost over the varying operating pressures of rectifying section under the condition case 1

Table 2.1 Result of internal heat exchanges for case 1

Module numbers (Str. Sect.-Rec. Sect.)	Heat flow rate [MJ h ⁻¹]	Heat transfer area [m ²]
(23-45)	14	0.2
(22-45)	89	1.1
(19-45)	671	9.3
(17-45)	574	8.6
(15-45)	493	8.2
(13-45)	416	7.6
(11-45)	348	7.0
(9-45)	77	1.7
(9-42)	193	4.1
(7-42)	153	3.6
(5-42)	1149	30.4
(5-40)	365	9.0
(4-40)	239	6.3
(3-40)	25	0.7
(3-38)	284	7.4
(2-38)	156	4.4
(2-36)	359	9.2
(1-36)	23	0.6
(1-34)	366	9.2
(1-32)	380	8.7
(1-30)	415	8.7
(1-28)	454	8.8

In the optimal structure shown in Fig. 2.5, the directions of both vapor and liquid flows are the same between modules 42 and 45. Such a structure is not found in conventional distillation columns. This structure can be understood as a “stepwise condenser,” in which the vapor is condensed in multiple stages (Fig. 2.7). As illustrated in Fig. 2.7 and 2.8, the stepwise condenser can retrieve some heat at a higher temperature than the conventional single stage condenser. This means that the heat transfer area for internal heat exchange with a condenser can be reduced, and as a result, the heat exchanger cost can be reduced. On the other hand, the stepwise condenser increases the capital cost of the column which is proportional to the number of stages, because it uses more stages than the conventional single stage condenser. Consequently, the effectiveness

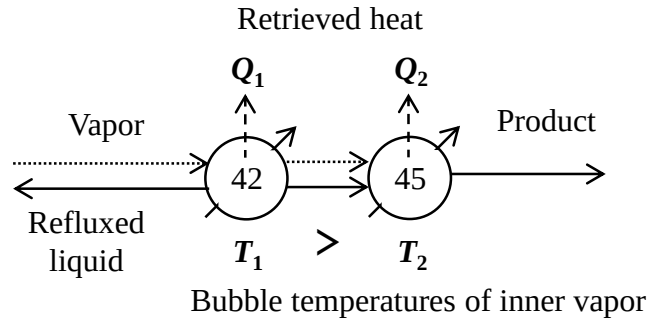


Figure 2.7 Stepwise condenser

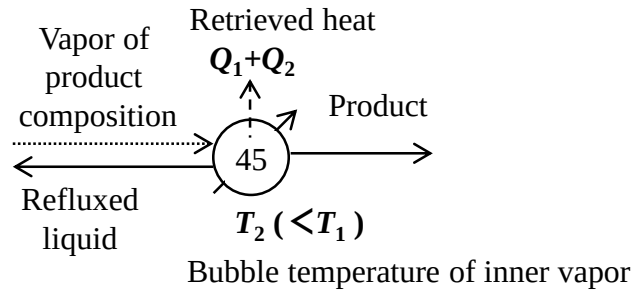


Figure 2.8 Conventional single-stage condenser

of this condenser is determined by taking the trade-off between the heat exchanger cost and the capital cost of the column. Whether the optimal structure has a stepwise condenser or not depends on the problem settings. As a qualitative feature, the stepwise condenser is suitable when the difference between the dew point temperature and the bubble point temperature of the distillate is large; in other words, the product specification is not so severe.

As an allowance is introduced in the component balance of each module (Eq. (2.3)), the feasibility of the result is verified by rigorous simulation using Aspen HYSYS®. In this simulation, the column design and the operation conditions are the same as the result shown in Fig. 2.5. For side heat exchange, the heat transfer rates are fixed to the obtained values and the heat transfer area of each side heat exchanger is recalculated. The pressures of both columns are fixed and the compressor power to achieve that pressure is recalculated. To simplify the structure, small heat exchanges (23-45), (22-45), (9-45), (3-40), (1-36) in Table 2.1 were merged to other heat exchanges. For the same reason, the liquid flows from modules 23 to 17 and from 21 to 22 were removed. Under the above conditions, the heat duty by utility, compressor power, total heat exchange area, and product compositions were calculated. The results shown in Table 2.2 illustrate that the

process designed by the proposed method can conduct the target production with almost the same cooling utility duty, compressor power, and total heat exchange area as those obtained by rigorous simulation.

For fair comparison of the result of the proposed method and that obtained by process simulator, pressure drop was neglected in the above discussion. The pressure drop affects the bubble and dew point temperatures. Thus, when the results obtained by the proposed method are applied to real problems, the results should be verified through process simulators by taking the pressure drop in the column into account.

For case 2, the optimal structure shown in Fig 2.9 was obtained. The optimal pressure of the rectifying section is 243.1 kPa, and the result of heat exchange is summarized in Table 2.3. In the optimal structure shown in Fig. 2.9, six and four modules are selected at the stripping and rectifying section, respectively. In the part of modules 27 to 35, the stepwise condenser was adopted again. The required compressor power is 148 kW, and the reboiler duty is 8 kW. Thus, the primary energy consumption of this optimal structure is 419 kW ($= 148 \times 2.73 + 8$ kW). This value is 34% of that for the conventional column

Table 2.2 Comparison of the results of HYSYS and proposed method

	HYSYS simulation	Proposed method
distillate composition	0.954	0.950
bottom product composition	0.047	0.050
cooling utility duty	81 kW	78 kW
compressor power	251 kW	261 kW
total heat exchange area	157.4 m ²	154.8 m ²

Table 2.3 Result of internal heat exchange for case 2

Module numbers (Str. Sect.-Rec. Sect.)	Heat flow rate [MJ h ⁻¹]	Heat transfer area [m ²]
(17-35)	16	0.2
(15-35)	204	3.0
(12-35)	386	6.4
(8-35)	1599	31.8
(5-35)	490	11.3
(1-35)	8	0.2
(1-27)	1288	28.0
(1-23)	790	14.9

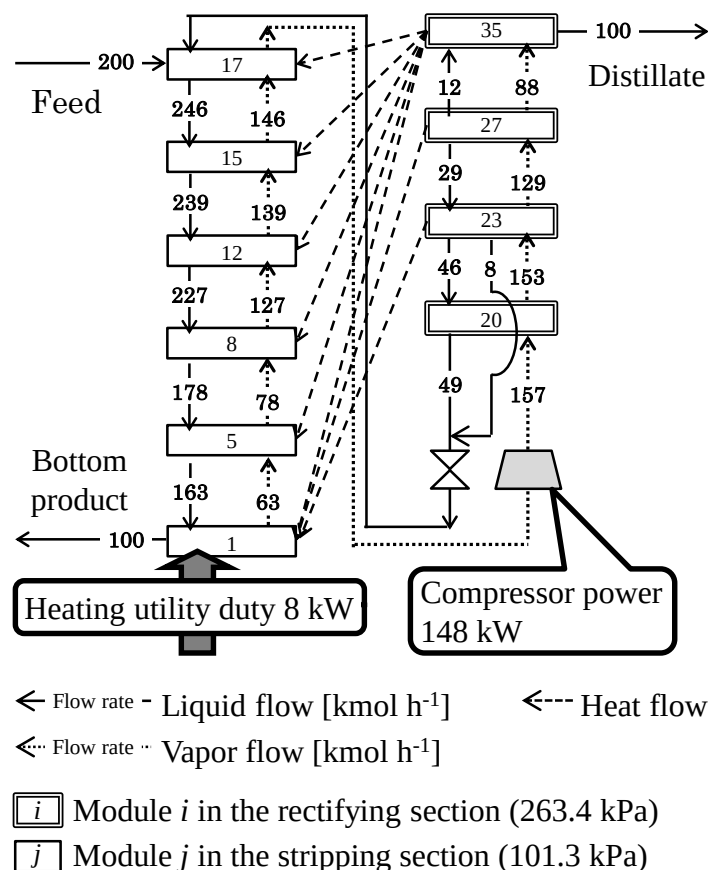


Figure 2.9 Optimal process obtained in case 2

of infinity number of stages without internal heat integration, 1227 kW.

2.6. Conclusion

A systematic design method of HiDiC was proposed. In this method, the column superstructure is introduced, and the optimal structure of the column is designed by route optimization. By giving liquid compositions and pressures of stages before the route optimization successfully, the route optimization could be formulated as MILP instead of MINLP. The results of case study problems separating benzene-toluene mixture indicated that the effective HiDiC design could be obtained by the proposed method. Furthermore, an innovative structure, "stepwise condenser," was derived by the proposed method. The feature of the proposed method is not to assign the flow structure in advance. Thus, the proposed method has high possibilities to generate innovative structures which are not derived by human experience.

Nomenclature

A_{ij}	Heat transfer area of the heat exchanger assigned between module i and module j [m^2]
c_1	Cost coefficient of heating utility cost [¥ MJ^{-1}]
c_2	Cost coefficient of cooling utility cost [¥ MJ^{-1}]
c_3	Cost coefficient of additional capital cost to equip heat exchangers [$\text{¥ m}^{-2} \text{h}^{-1}$]
c_4	Cost coefficient of capital cost of a column [¥ h^{-1}]
E_i^L	Sum of capital and operating costs of compression for unit amount of liquid flow from module i [¥ kmol^{-1}]
E_i^V	Sum of capital and operating costs of compression for unit amount of vapor flow from module i [¥ kmol^{-1}]
h_i^L	Molar enthalpy of liquid in module i [MJ kmol^{-1}]
h_i^V	Molar enthalpy of vapor in module i [MJ kmol^{-1}]
L_B	Flow rate of bottom product [kmol h^{-1}]
L_D	Flow rate of distillate [kmol h^{-1}]
L_F	Liquid flow rate of feed [kmol h^{-1}]
L_{ij}	Liquid flow rate from module i to module j [kmol h^{-1}]
M	Sufficiently big number [kmol h^{-1}]
N_R	Number of modules in the rectifying section [-]
N_S	Number of modules in the stripping section [-]
N_{SR}	Total number of modules in the rectifying and stripping sections [-]
P_R	Operating pressure of the rectifying section [kPa]
P_S	Operating pressure of the stripping section [kPa]
Q_i	Heat flow rate added to module i [MJ h^{-1}]
Q_{ij}	Heat flow rate transferred from module i to module j [MJ h^{-1}]
T_C	Temperature of cooling utility [K]
T_H	Temperature of heating utility [K]
T_i^b	Bubble point temperature of vapor in module i [K]
T_i^d	Dew point temperature of liquid in module j [K]
U	Overall heat transfer coefficient between streams in the rectifying and stripping sections [$\text{MJ h}^{-1} \text{K}^{-1}$]
U_C	Overall heat transfer coefficient between process streams and the cooling utility [$\text{MJ h}^{-1} \text{K}^{-1}$]
U_H	Overall heat transfer coefficient between process streams and the heating utility [$\text{MJ h}^{-1} \text{K}^{-1}$]
V_F	Vapor flow rate of feed [kmol h^{-1}]

V_{ij}	Vapor flow rate from module i to module j [kmol h ⁻¹]
x_i	Liquid molar fraction of the light component in module i [-]
y_i	Vapor molar fraction of the light component in module i [-]
z_i	0-1 variable which indicates the selection of module i [-]
Δh_i^L	Molar enthalpy increment on the pressurization of liquid flowing from module i in the stripping section to modules in the rectifying section [MJ kmol ⁻¹]
Δh_i^V	Molar enthalpy increment on the pressurization of vapor flowing from module i in the stripping section to modules in the rectifying section [MJ kmol ⁻¹]

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3. Synthesis of Ternary Distillation Processes Using the Discretization of Liquid Composition Space

3.1. Introduction

In this chapter, the framework described in chapter 2 is extended to ternary distillation. On this extension, the degree of freedom on the liquid composition space is increased from one to two. Due to this expansion, the number of the discretized liquid compositions, which is the same as the number of separation modules contained in the superstructure is significantly increased as shown in Fig. 3.1. In the formulation described in chapter 2, a 0-1 variable was assigned to each module. If this approach is simply applied to the synthesis problem of ternary distillation processes, the resulting MILP problem involves too many 0-1 variables. Thus, from the viewpoint of the computational cost, an alternative approach is needed for ternary distillation cases.

The proposed synthesis procedure consists of two steps. At the first step, the utility cost is minimized under the linear constraints on material and heat balances. Since the numbers of modules and flows are not included in the objective function, the result of the first step contains many tiny flows among the modules as the results obtained by IDEAS approach are (Conner and Manousiouthakis, 2014). Then, at the second step an evolutionary procedure for process simplification is executed. In this step, while a slight increase of the utility cost is permitted, the weighted sum of flow rates is minimized. By adjusting the weights of flow rates at each iteration, many tiny flows are gradually merged

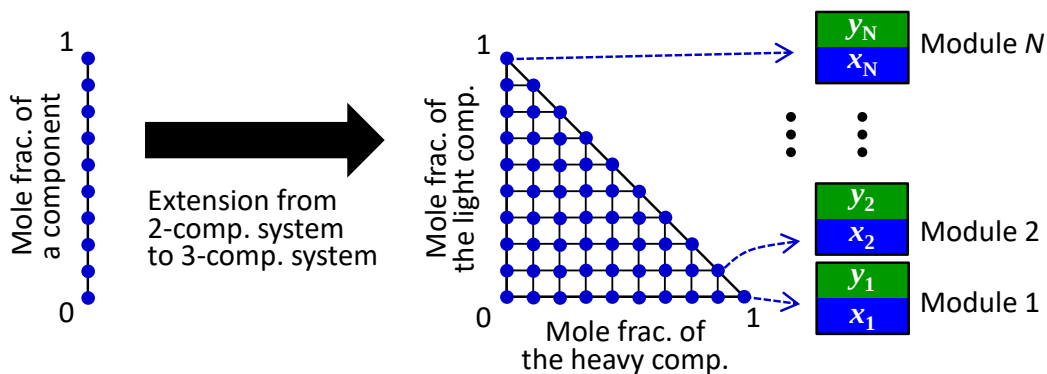


Figure 3.1 The number of the discretized liquid compositions and the separation modules contained in the superstructure are significantly increased through the extension from two-component system to three-component system.

to dominant flows. The practical process structure is finally determined from the result of the second simplification step.

In the rest of the chapter, the process synthesis problem discussed in this chapter is defined in section 3.2. In section 3.3 and 3.4, the configuration of the superstructure and the proposed synthesis procedure are described, respectively. A case study for the three-component system of benzene, toluene, and o-xylene is shown in section 3.5. Finally, this chapter is concluded in section 3.6.

3.2. Problem statement

In this research, a synthesis problem of distillation processes that separate ternary mixture is discussed under the following assumptions. The flow rate and composition of the feed are given in advance. The feed is separated into three products in the process. All products are withdrawn as saturated liquid or a mixture of saturated liquid, and the specification of each product is assigned as the lower bound of the concentration of its key component. The operating pressure in the process is given in advance, and the pressure drop in the process is negligible. The heat exchange among trays is not considered. Hot and cold utilities of different temperatures are available, and their costs per unit amount of heat are given in advance.

Under these assumptions, the optimal process is derived without any assumption on process structure. A tray in distillation columns is treated as a separation module, and all possible flow connections among the separation modules are considered. In the proposed procedure, first, the process of minimum utility cost is derived. Since equipment costs are not considered in this step, the obtained process has many trays and many liquid and vapor streams among the trays. Thus, as the second step, the process structure is simplified under the upper bound on the utility cost that is slightly larger than the minimum value obtained at the first step.

3.3. Configuration of superstructure

Regardless of the process structure, the liquid and vapor concentrations of the heaviest (lightest) component get very close to each other around zero at the high concentration region of the lightest (heaviest) component. Thus, in terms of the discretization width, in the dilute regions of the lightest and heaviest components, the concentration of the lightest and heaviest components is discretized more minutely than in the other region, for the sake of better emulation of the liquid composition trajectories in ternary distillation systems. Each of the defined liquid compositions is assigned to a separation module as the composition of its output liquid. Then, equilibrium is calculated

for each separation module, depending on the assigned liquid composition and the operating pressure given in advance. By the equilibrium calculation, all of the intensive variables of the output vapor and liquid flows, such as vapor composition, temperature, molar enthalpies, are determined. Since the equilibrium calculation is conducted before the optimization, any rigorous thermodynamic models can be applied.

Figure 3.2 illustrates a separation module used in the proposed superstructure. A separation module has material and heat input flows. The input material flow is the mixture of vapor and liquid. A separation module has three types of output flows: vapor, liquid, and heat flows. When a separation module has an input or output heat flow as a result of the optimization, the module functions as a reboiler or a condenser.

Figure 3.3 illustrates the superstructure adopted in this research. The boxes of the numbers from 1 to N_S are the separation modules. To identify the flow connection easily, each separation module is divided into two parts: output part and input part. Thus, two boxes of the same number correspond to the same separation module. The solid lines, dotted lines, and broken lines among the nodes are the liquid, vapor, and heat flow paths, respectively. The feed, products, and hot and cold utilities are treated as special modules. The feed module, module 0, has only material output flows. The product modules, module N_S+1 to N_S+3 , have only material input flows. As for the products, it is assumed that the boiling temperature of product 1 is the lowest and that of product 3 is the highest. The hot utilities of N_H different temperatures are treated as modules N_S+4 to N_S+N_H+3 , which have only heat output flows. The cold utilities of N_C different temperatures are treated as modules N_S+N_H+4 to $N_S+N_H+N_C+3$, which have only heat input flows.

Since the intensive variables of the material flows are determined in advance, all constraints can be expressed by the linear equations and inequalities shown in Eqs. (3.1) to (3.6). Equations (3.1) and (3.2) show the material balance of feed flows. As the

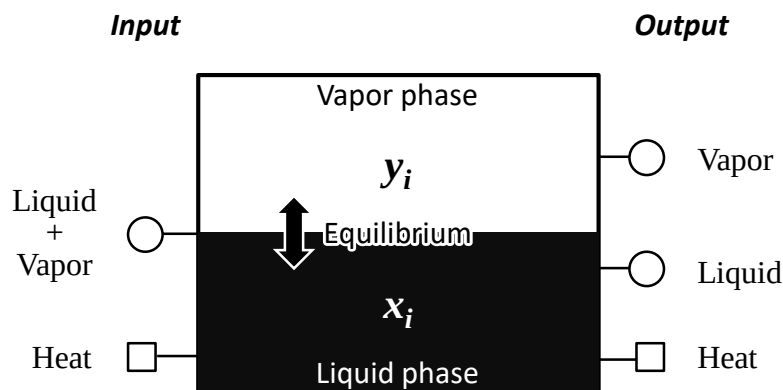


Figure 3.2 Separation module i

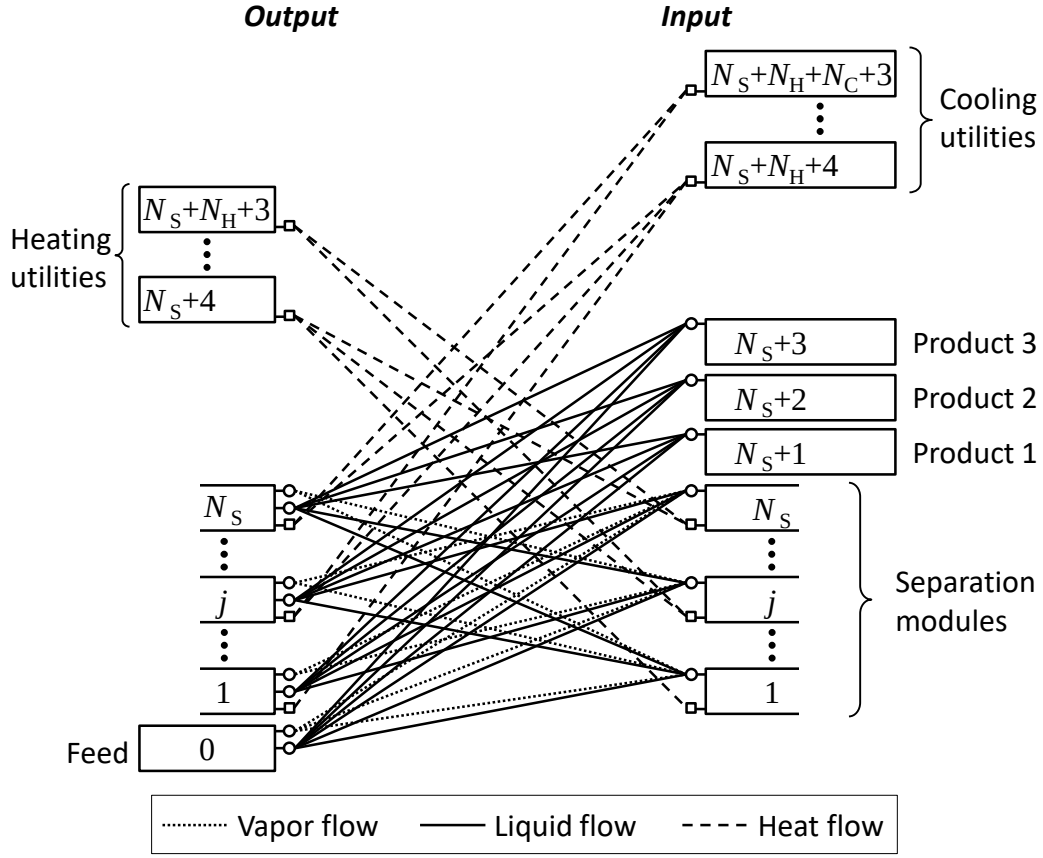


Figure 3.3 Configuration of the proposed superstructure

products are assumed to be liquid, the vapor flows are not connected to the product modules. The total material balance and component material balance at separation module j are expressed by Eqs. (3.3) and (3.4), respectively. In Eqs. (3.3) and (3.4), the left-hand side is the sum of inlet flows to module j , and the right-hand side is the sum of outlet flows from module j . The recycle flows from a separation module to the same separation module are excluded, because the corresponding terms are canceled out even when they exist. The specification of the product k is given as the lower bound of the concentration of its key component, x_k^P , and the corresponding constraint is expressed by Eq. (3.5).

$$\sum_{j=1}^{N_S+3} L_{0j} = L_F \quad (3.1)$$

$$\sum_{j=1}^{N_S} V_{0j} = V_F \quad (3.2)$$

$$\sum_{\substack{i=0 \\ i \neq j}}^{N_s} (L_{ij} + V_{ij}) = \sum_{\substack{i=1 \\ i \neq j}}^{N_s+3} L_{ji} + \sum_{\substack{i=1 \\ i \neq j}}^{N_s} V_{ji}, \quad \forall j \in \{1, 2, \dots, N_s\} \quad (3.3)$$

$$\sum_{\substack{i=0 \\ i \neq j}}^{N_s} (L_{ij} x_{ik} + V_{ij} y_{ik}) = x_{jk} \sum_{\substack{i=1 \\ i \neq j}}^{N_s+3} L_{ji} + y_{jk} \sum_{\substack{i=1 \\ i \neq j}}^{N_s} V_{ji}, \quad \forall j \in \{1, 2, \dots, N_s\}, \forall k \in \{1, 3\} \quad (3.4)$$

$$\sum_{i=0}^{N_s} L_{i, N_s+k} x_{i,k} \geq x_k^p \sum_{i=0}^{N_s} L_{i, N_s+k}, \quad \forall k \in \{1, 2, 3\} \quad (3.5)$$

where L_{ij} and V_{ij} are liquid and vapor flow rates from module i to module j , respectively. L^F and V^F are liquid and vapor flow rates of feed, respectively. x_{ik} is the liquid concentration of component k of module i . (y_{i1}, y_{i2}, y_{i3}) is the vapor composition which is in equilibrium with (x_{i1}, x_{i2}, x_{i3}) .

As the heat can be supplied by hot utilities and removed by cold utilities at arbitrary separation modules, the enthalpy balance at separation modules j is expressed by Eq. (3.6).

$$\sum_{\substack{i=0 \\ i \neq j}}^{N_s} L_{ij} h_i^L + \sum_{\substack{i=0 \\ i \neq j}}^{N_s} V_{ij} h_i^V + \sum_{m \in U_j^H} Q_{mj} = \sum_{\substack{i=1 \\ i \neq j}}^{N_s+3} L_{ji} h_j^L + \sum_{\substack{i=1 \\ i \neq j}}^{N_s} V_{ji} h_j^V + \sum_{m \in U_j^C} Q_{jm}, \quad (3.6)$$

$$\forall j \in \{1, 2, \dots, N_s\}$$

where h_i^L and h_i^V are molar enthalpies of liquid and vapor flows from module i , respectively, and are calculated in advance. Q_{ij} is the heat flow rate from module i to module j . U_j^H and U_j^C are index sets of heating and cooling utilities that can be used at module j , respectively. As the operating temperature of each module is calculated in advance, the elements of these sets can be determined by deciding the minimum approach temperature for heat exchange.

The number of flow paths among the modules is approximately proportional to the square of the number of modules. Thus, the size of the optimization problem increases when the composition space is discretized precisely. To reduce the size of the optimization problem, the connection among the modules is restricted by using the principle of distillation.

Let $\mathbf{x}_i (= [x_{i1}, x_{i3}])$ and $\mathbf{y}_i (= [y_{i1}, y_{i3}])$ be the vectors that show the liquid and vapor compositions of the output of module i , respectively. $\mathbf{x}_i - \mathbf{y}_i$ indicates the direction of residue curve. If the vapor of module i is fed to module j whose liquid composition, $\mathbf{x}_j$, satisfies Eq. (3.7), such mixing is regarded as being inefficient. Similarly, if the liquid of

module i is fed to module j whose liquid composition, $\mathbf{x}_j$, satisfies Eq. (3.8), such mixing is also regarded as being inefficient.

$$(\mathbf{x}_j - \mathbf{x}_i)^T (\mathbf{x}_i - \mathbf{y}_i) > 0 \quad (3.7)$$

$$(\mathbf{x}_j - \mathbf{x}_i)^T (\mathbf{x}_i - \mathbf{y}_i) \leq 0 \quad (3.8)$$

Figure 3.4 illustrates the regions of $\mathbf{x}_j$ satisfying the conditions of Eqs. (3.7) and (3.8), respectively. When a separation module is selected, the entire liquid composition space is divided into two regions, depending on its liquid and vapor compositions in this manner, and the remaining separation modules are classified into two subsets according to their liquid composition. Based on this classification, the vapor and liquid flow paths that cause the inefficient mixing mentioned above are prohibited:

$$V_{ij} = 0 \quad (3.9)$$

$$\forall (i, j) \in \{(i, j) \mid (\mathbf{x}_j - \mathbf{x}_i)^T (\mathbf{x}_i - \mathbf{y}_i) > 0, i \in \{1, 2, \dots, N_s\}, j \in \{1, 2, \dots, N_s\}\}$$

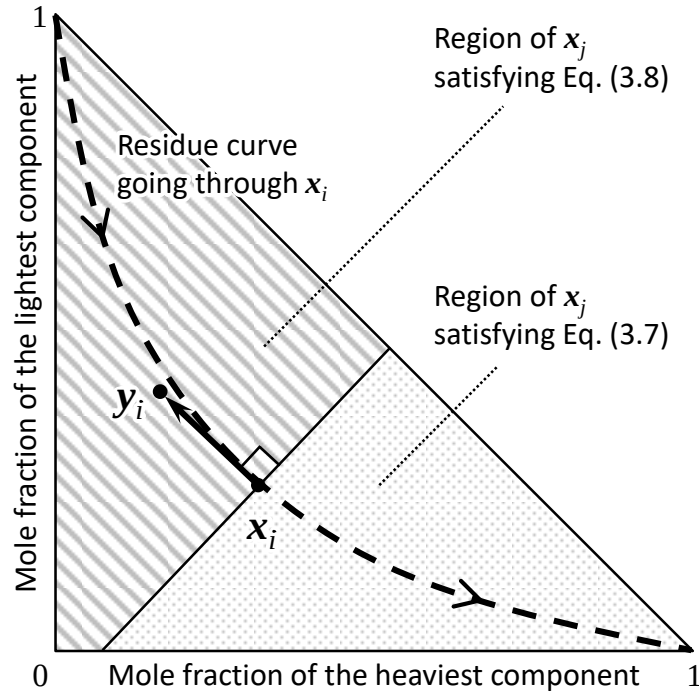


Figure 3.4 Division of the liquid composition space for the limitation of the modules which can accept liquid and vapor flows from module i

$$L_{ij} = 0$$

$$\forall (i, j) \in \{(i, j) \mid (\mathbf{x}_j - \mathbf{x}_i)^T (\mathbf{x}_i - \mathbf{y}_i) \leq 0, i \in \{1, 2, \dots, N_s\}, j \in \{1, 2, \dots, N_s\}\} \quad (3.10)$$

When optimization problems based on the proposed formulation are solved, the obtained processes tend to have many flow paths among the modules. Some of them are used only for satisfying the material and heat balances in the discretized composition space. By introducing Eqs. (3.9) and (3.10), the flow paths having little meaning can be avoided.

3.4. Optimization procedure

The proposed optimization procedure consists of two steps: utility cost minimization and process structure simplification. First, the utility cost, UC , expressed by Eq. (3.11) is minimized under the constraints of Eqs. (3.1) to (3.6), (3.9), and (3.10) as well as non-negativity constraint on all variables.

$$UC = \sum_{j=1}^{N_s} \sum_{m \in U_j^H} c_m^H Q_{mj} + \sum_{j=1}^{N_s} \sum_{m \in U_j^C} c_m^C Q_{jm} \quad (3.11)$$

where c_m^H and c_m^C are the costs of the unit amount of hot utility m and cold utility m , respectively.

Since the equipment cost is not considered in the first step, the obtained process tends to consist of many modules, and the vapor and liquid outputs of a module are supplied to many modules. It is difficult to actually construct such a complicated process. To simplify the process obtained in the first step, the second step introduces the mechanism of merging the flows with tiny flow rates into dominant flows of large flow rate. The idea is to add the material flow rates among the modules into the objective function, and to adjust the weight of each flow rate in the objective function so that the flows with tiny flow rates are gradually diminished. The objective at iteration k in the second step is minimization of SI^k given by Eq. (3.12). c_{Lij}^k , c_{vij}^k , and c_{Qj}^k are the weights to the liquid, vapor and heat flow rates, and are updated by Eqs. (3.13) to (3.15) depending on the latest solution. The utility cost is included not in the objective function but in the inequality constraint given by Eq. (3.16).

$$SI^k = \sum_{i=0}^{N_s} \sum_{j=1}^{N_s+3} c_{Lij}^k L_{ij}^k + \sum_{i=0}^{N_s} \sum_{j=1}^{N_s} c_{vij}^k V_{ij}^k + \sum_{j=1}^{N_s} c_{Qj}^k \left(\sum_{m \in U_j^H} Q_{mj}^k + \sum_{m \in U_j^C} Q_{jm}^k \right) \quad (3.12)$$

$$c_{Lij}^k = 1 / (\theta_L + L_{ij}^{k-1}), \quad \forall i \in \{0, 1, \dots, N_s\}, \forall j \in \{1, 2, \dots, N_s + 3\} \quad (3.13)$$

$$c_{vij}^k = 1 / (\theta_v + V_{ij}^{k-1}), \quad \forall i \in \{0, 1, \dots, N_s\}, \forall j \in \{1, 2, \dots, N_s\} \quad (3.14)$$

$$c_{Qj}^k = 1 / \left(\theta_Q + \sum_{m \in U_j^H} Q_{mj}^{k-1} + \sum_{m \in U_j^C} Q_{jm}^{k-1} \right), \quad \forall j \in \{1, 2, \dots, N_s\} \quad (3.15)$$

$$UC^k \leq (1 + \lambda) UC^0 \quad (3.16)$$

where superscript k refers to the iteration number, UC^0 is the minimum utility cost obtained at the first step, and λ is the allowable increase ratio of the utility cost. θ_L , θ_v , and θ_Q are prespecified positive constants that are introduced to adjust the effect of the flow rates to the objective function.

If a flow path has a large flow rate, a small value is assigned to the coefficient of that flow path, and vice versa. Then, in the next optimization, flow paths of the small coefficients, whose previous flow rate was large, tend to gain the flow rate, while those of the large coefficients lose the flow rate. Thus, some flow paths gradually absorb others and grow into the dominant flow paths by repeating of the optimization calculations. The large values of θ_L , θ_v , and θ_Q indicate that the coefficients in the objective function are not sensitive to the flow rate. In general, the great difference of digit between the coefficients in the objective function causes the LP to be numerically unstable. These coefficients also have the effect of keeping such numerical stability. θ_L , θ_v , and θ_Q are determined by estimating the largest flow rate in the process and the amount of heat duties needed for the process. There is no theoretical basis to select these coefficients. In the case study at the next section, the ratio of maximum value to the minimum value is used to determine these parameters.

The procedure of the second step is summarized in Fig. 3.5. At first, c_{Lij}^k , c_{vij}^k , and c_{Qj}^k are calculated by using the result of the first step optimization. Then, Eq. (3.12) is minimized under the constraints of material and heat balances, the limitation of flow paths,

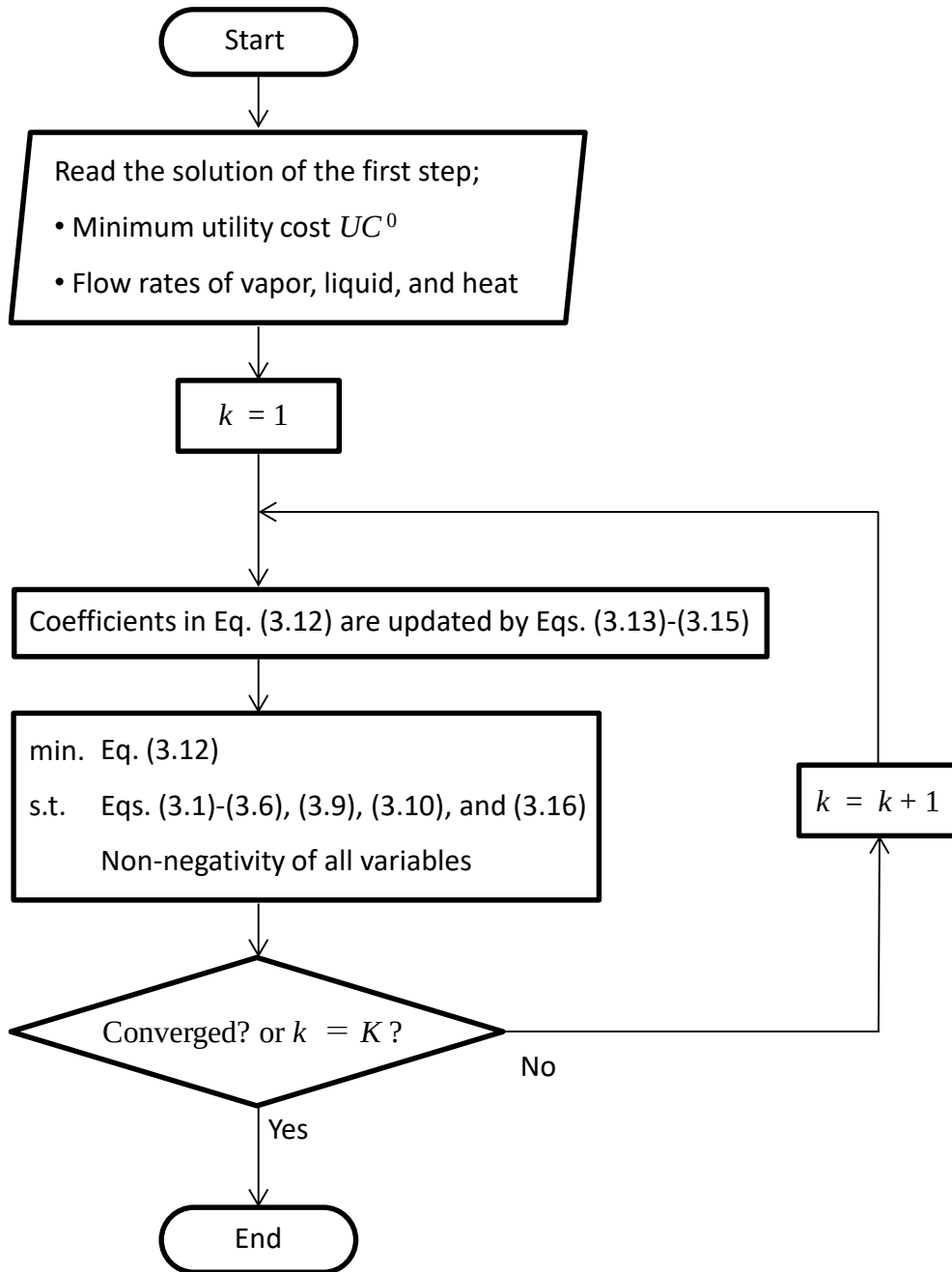


Figure 3.5 Procedure of process simplification

the limitation of utility cost expressed by Eq. (3.16), and non-negativity constraint on all variables. In every iteration, c_{Lij}^k , c_{vij}^k , and c_{Qj}^k are updated by Eqs. (3.13) to (3.15) by using the latest solution. The simplification procedure terminates when the convergence criterion given by Eq. (3.17) is satisfied or the iteration number reaches the prespecified upper limit K .

$$\left[\sum_{i=0}^{N_s} \sum_{j=1}^{N_s+3} c_{Lij}^k L_{ij}^{k-1} + \sum_{i=0}^{N_s} \sum_{j=1}^{N_s} c_{vij}^k V_{ij}^{k-1} + \sum_{j=1}^{N_s} c_{Qj}^k \left(\sum_{m \in U_j^H} Q_{mj}^{k-1} + \sum_{m \in U_j^C} Q_{jm}^{k-1} \right) \right] - SI^k \leq \epsilon \quad (3.17)$$

where ϵ is the convergence tolerance. As the global convergence of the proposed procedure is not proved, K is introduced to terminate the calculation for unexpected conditions. Thus, if the iteration reaches K , we will reevaluate the convergence criterion, some parameters and/or increase the value of K , and re-execute the simplification procedure.

3.5. Case study

The proposed method is applied to a separation problem of a benzene, toluene and o-xylene mixture. The feed is the saturated liquid of an equimolar mixture of three components and its flow rate is 300 kmol/h. The pressure is assumed to be 101.3 kPa in the entire system. The specification for each product is 90 mol% for key components. A single heating utility is available, and its cost coefficient c^H is 11.0 \$/GJ. A single cooling utility is available, and its cost coefficient c^C is 0.25 \$/GJ. As for the discretization of the liquid composition, each of the benzene and o-xylene concentrations is discretized with the width of 0.025 basically, but it is more minutely discretized with the width of 0.005 in a range from 0 to 0.025. To confirm the adequacy of the discretization width, the same problem is solved at different discretization widths. Figure 3.6 shows the optimization results. The basic discretization width is changed from 0.100 to 0.025, and the minimum range of the lightest and heaviest components is additionally discretized with one-fifth of the basic width. The number of resulting separation modules is shown in the abscissa, and for each case the minimum utility cost is calculated. Figure 3.6 shows that the minimum utility cost is well converged at the discretization width of 0.025. The vapor composition, temperature, and vapor and liquid enthalpies are calculated for each separation module, using the NRTL fluid package of Aspen HYSYS[®]. By the above discretization, 1197 feasible modules were defined. In the proposed optimization procedure, the barrier algorithm without crossover in CPLEX 12.6.1[®] was used as the solver of LP problems.

As the result of first optimization step, the minimum utility cost of 117 \$/h and the corresponding modules and flow path selections illustrated in Fig. 3.7 were obtained. The up-side figure and the down-side figure correspond to the liquid and vapor flow paths, respectively. The flow paths of more than 15 kmol/h, which is 5% of the feed flow rate, are illustrated by solid lines, those between 0.75 kmol/h and 15 kmol/h are dotted lines, and those less than 0.75 kmol/h are omitted. A box corresponds to a selected separation module, and the location refers to the liquid composition assigned to the separation

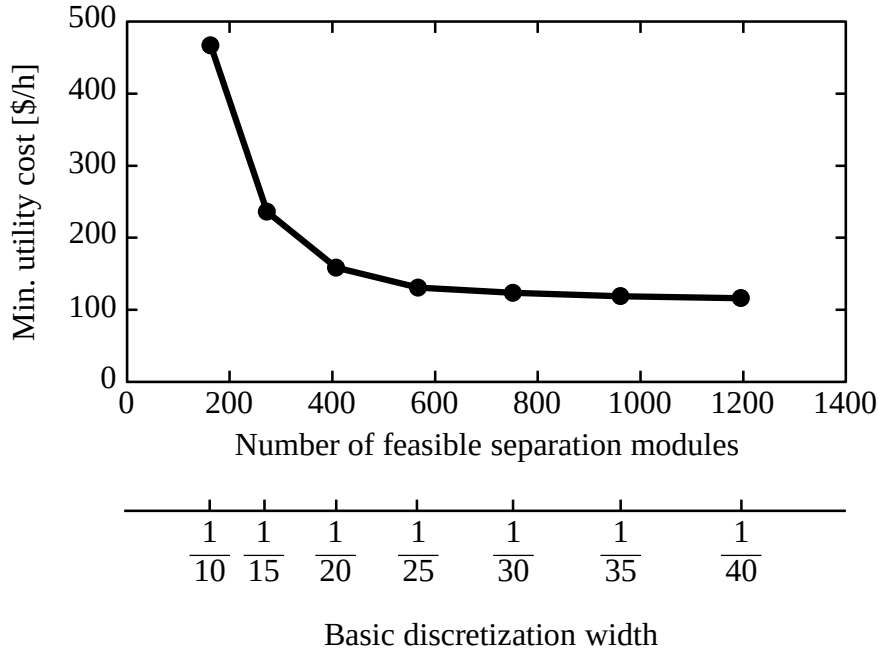


Figure 3.6 Convergence of minimum utility cost against level of the liquid composition discretization

module. In both the up-side and down-side figures, the modules which are associated only with the flows of less than 0.75 kmol/h are omitted.

Although the flows of less than 0.75 kmol/h have been omitted, the obtained process includes many flows and modules. It is difficult to imagine a practical design based on the result shown in Fig. 3.7. Thus, the second step of the procedure, the simplification of the structure, was executed. In this case study, the parameters, θ_L , θ_V , and θ_Q used in Eqs. (3.13) to (3.15) were determined by Eq. (3.18).

$$\theta_L = \alpha \left(\max_{ij} L_{ij}^0 \right), \quad \theta_V = \alpha \left(\max_{ij} V_{ij}^0 \right), \quad \theta_Q = \alpha \left(\max_{ij} Q_{ij}^0 \right) \quad (3.18)$$

where L_{ij}^0 , V_{ij}^0 , and Q_{ij}^0 are liquid, vapor, and heat flow rates from module i to module j , which are specified at the first optimization step. In this case study, 0.01 is assigned to α . This value means that the weight of the path with minimum flow rate is 101-times greater than that with maximum flow rate. In addition, 15% increase of the utility cost is permitted: $\lambda = 0.15$. The convergence tolerance in Eq. (3.17), ϵ , is set to be zero. Under this setting, the second step of the optimization procedure was carried out.

The algorithm converged at 11th iteration, and the result shown in Fig. 3.8 was obtained. We have not developed the procedure to automatically obtain a further simpler

process structure for practical design. The practical structure is derived by engineering experience. There are two dominant groups of flow paths in the region where the concentrations of lightest and heaviest components are not so pure: one is the group of paths crossing the feed composition and the other group crossing the intermediate product composition. Taking this fact into account, all the modules in Fig. 3.8 are classified into two groups. Figure 3.9 illustrates the liquid and vapor flow connections in and between two groups. In Fig. 3.9, the liquid and vapor flows of less than 15 kmol/h and heat flows of less than 1 GJ/h are omitted for ease of illustration.

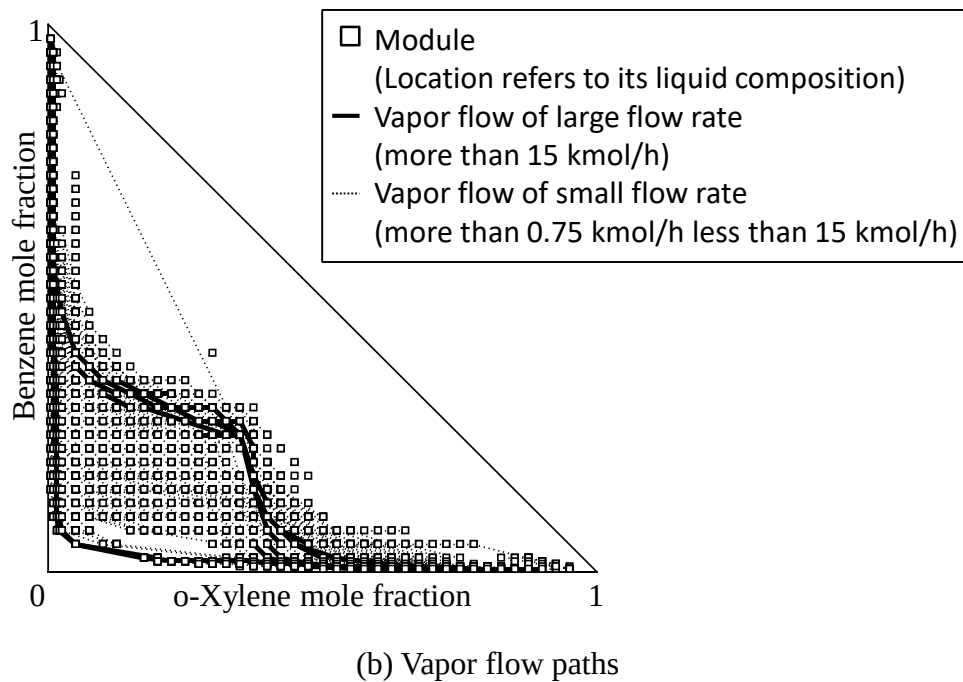
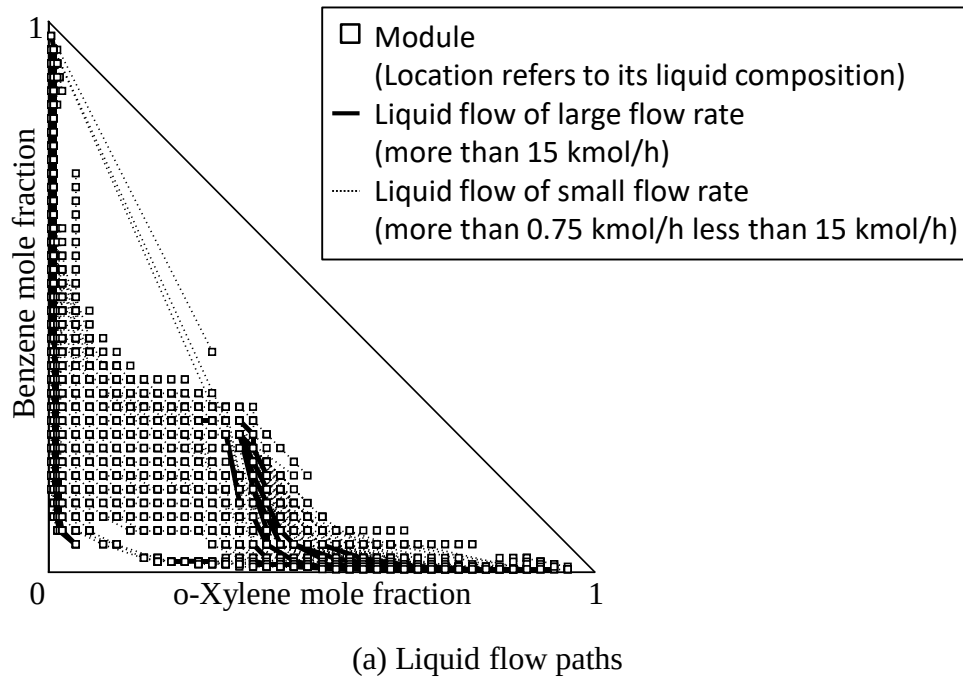


Figure 3.7 Selected modules and flow paths in the process obtained by utility cost minimization

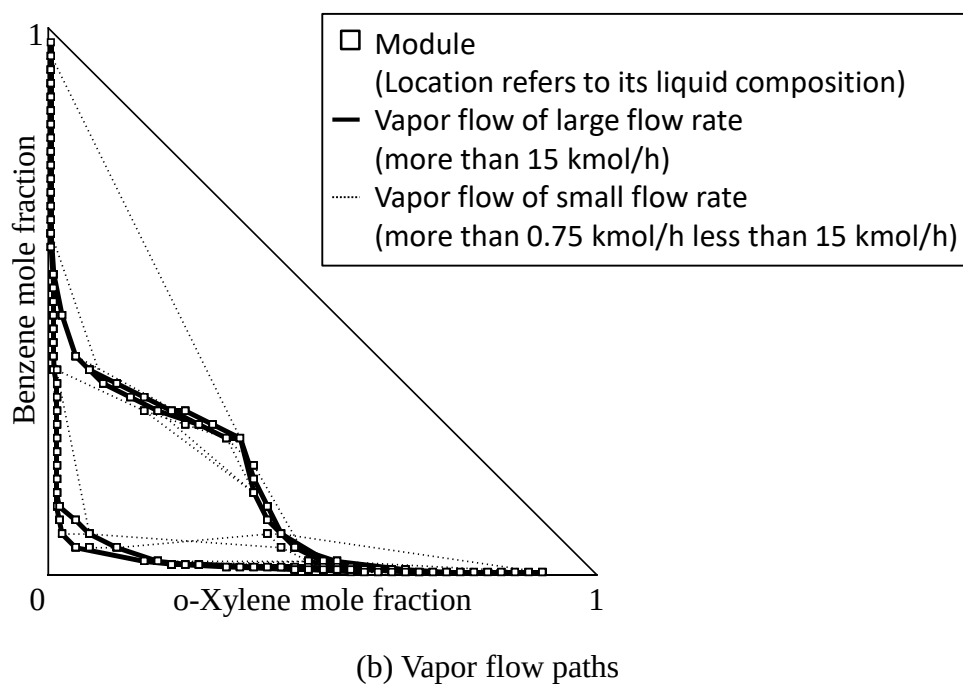
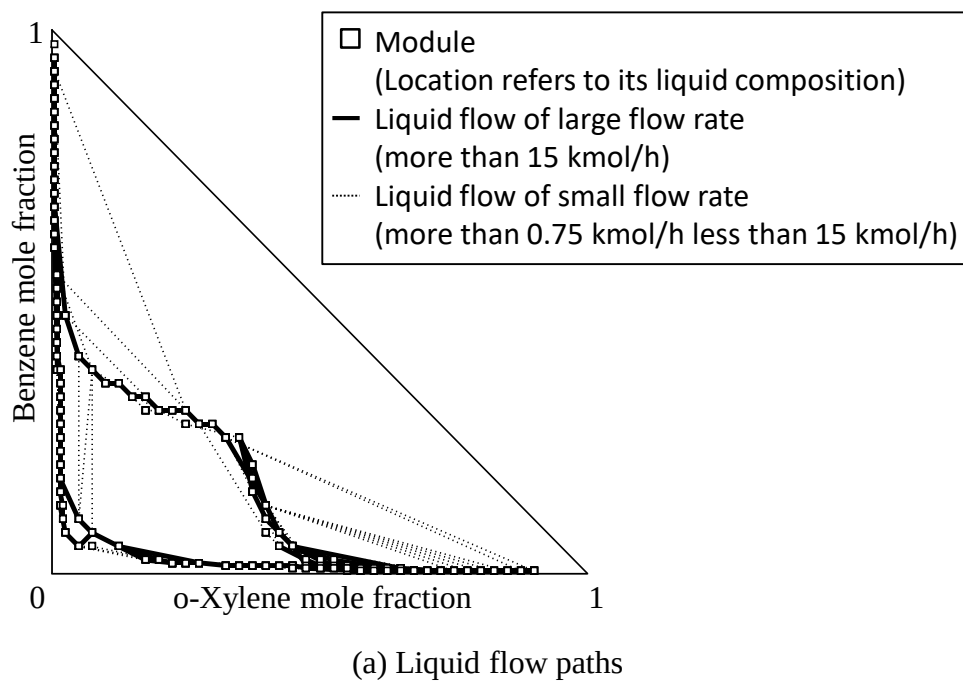


Figure 3.8 Selected modules and flow paths in the finally obtained process

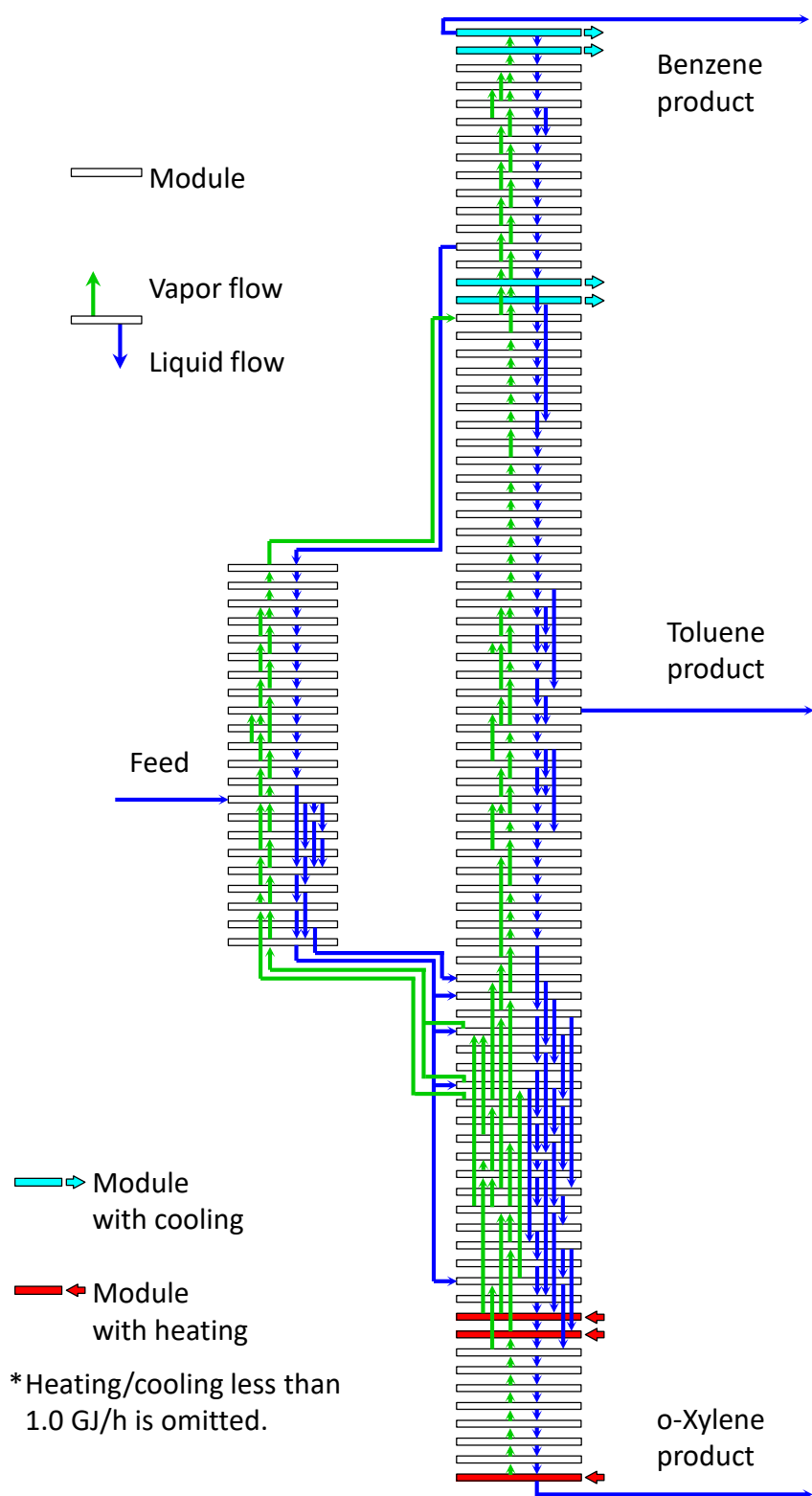
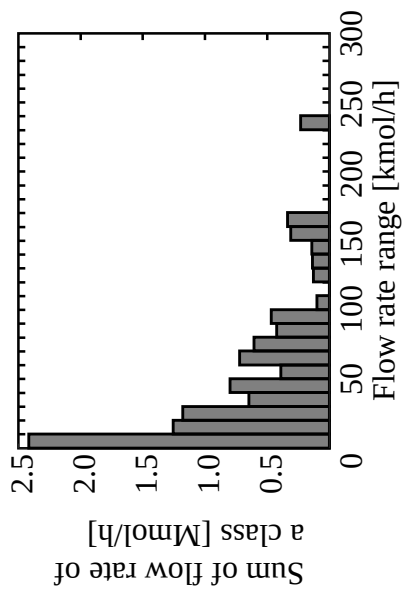


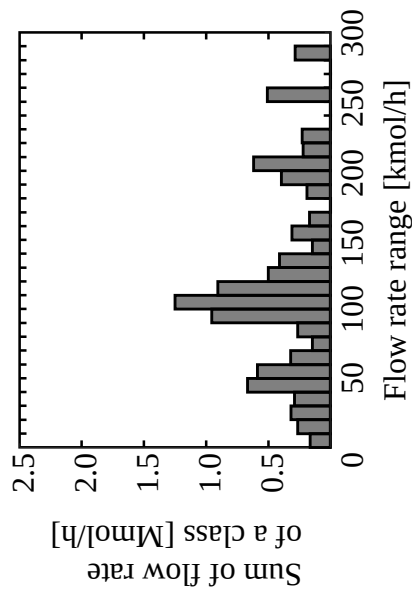
Figure 3.9 Significant flow connections of the finally obtained process

In Fig. 3.9, the group of modules that has feed flow is hereafter called the feed column, and the group having product flows is hereafter called the product column. When each group is treated as a distillation column, there are many bypass flows in the columns, especially at the bottom part of the product column. At that part, the composition of the lightest component is discretized in detail, and several modules have the same concentration of the heaviest component. Thus, the composition differences of those bypass flows are not so large compared with the tray model of the conventional distillation column. However, several bypass flows with large composition difference still exist in the final result. As some of the tiny flows were merged with each other in the process simplification procedure, there are some bypass flows of moderate flow rates that connect the modules of significantly different liquid compositions.

Figures 3.10 to 3.12 describe the progress in this second step, based on the distribution of liquid, vapor, and heat flow rates with the obtained processes. Figure 3.10 (a) and Fig. 3.10 (b) show the distribution of liquid flow rates before and after the second step simplification, respectively. Each of the selected liquid flow paths is categorized to a class of the corresponding flow rate range. The ordinate refers to the sum of flow rates of the liquid flow paths in a class. The classes of 0-10 kmol/h and 10-20 kmol/h in Fig. 3.10 (a) show high ordinate values compared to the other classes. This means the process obtained by utility cost minimization includes many liquid flow paths in the classes of 0-10 kmol/h and 10-20 kmol/h and a small number of liquid paths with larger flow rates. When comparing Fig. 3.10 (b) with Fig. 3.10 (a), the sum of the flow rates of small-flow-rate ranges decreases, and the sum of the flow rates of large-flow-rate ranges increases. This transition in the process simplification procedure suggests that, as expected, some flow paths absorbed many flow paths of small flow rates and gained their flow rates. Figure 3.11 describes the distributions of vapor flow rates in the same manner as Fig. 3.10. The transition described above is observed also in the distributions of vapor flow rate. Figure 3.12 describes the distributions of heat flow rates. As for each class, gray and black bars express the contributions of the heat flows from the hot utility to the separation modules and those from the modules to the cold utility, respectively. Through process simplification, the ordinate values of the classes of 0-0.25 GJ/h, 0.25-0.5 GJ/h, and 0.5-0.75 GJ/h are decreased, while the classes of larger flow rates gained their ordinate values. One large heat flow which used to be in the class of 3.75-4.0 GJ/h lost its flow rate, but the distribution of heat flow rate transits also in the expected way as a whole.

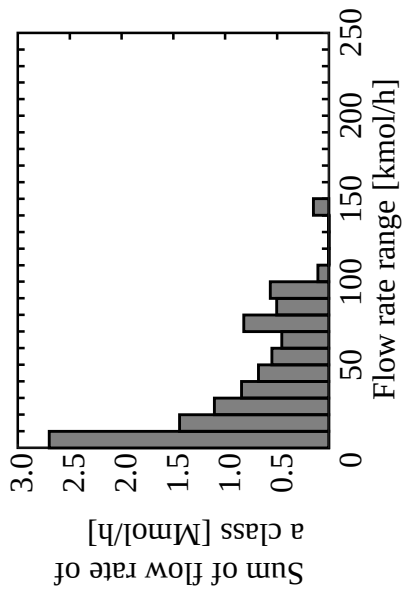


(a) Process obtained by the utility cost minimization

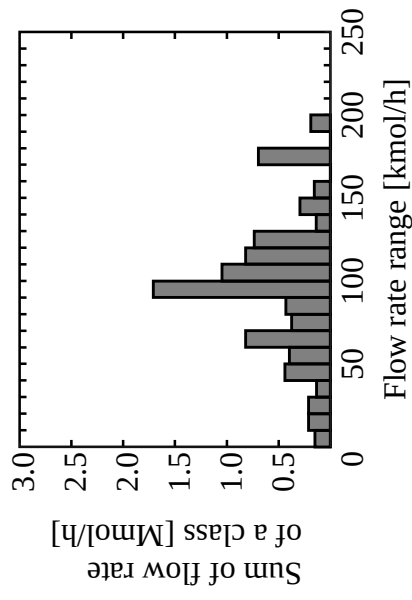


(b) Process after the simplification procedure

Figure 3.10 Liquid flow rate distribution

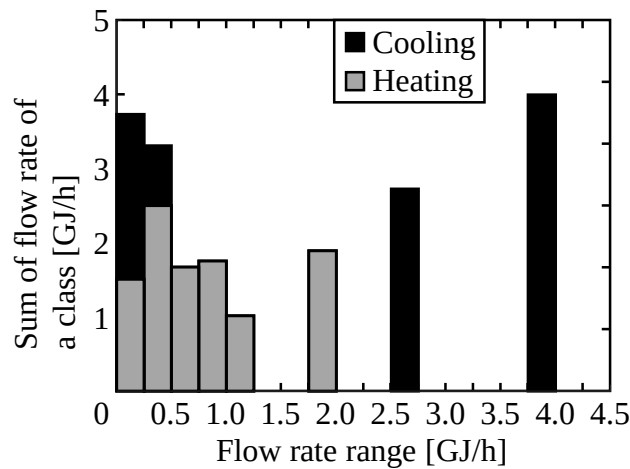


(a) Process obtained by the utility cost minimization

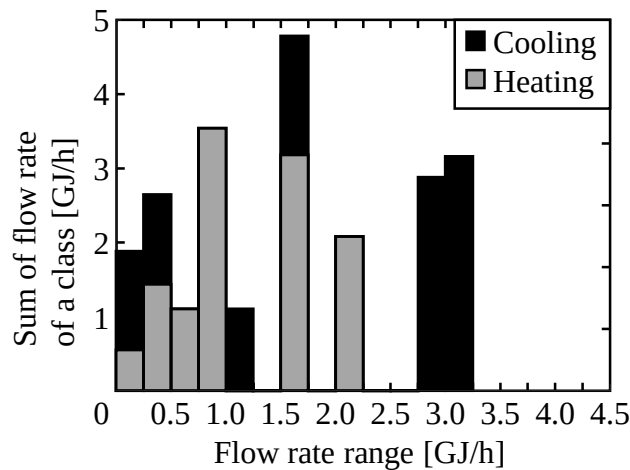


(b) Process after the simplification procedure

Figure 3.11 Vapor flow rate distribution



(a) Process obtained by the utility cost minimization



(b) Process after the simplification procedure

Figure 3.12 Heat flow rate distribution

Since the number of selected modules is significantly reduced through the process simplification, the liquid composition profile becomes much simpler. As distillation processes with similar liquid composition profiles are expected to show similar performance, a practical design with high performance can be conceptualized by considering a sufficiently simple process structure with similar liquid composition profile. In this case, the liquid composition profile shown in Fig. 3.8 is similar to that of a process of Petlyuk column structure, as shown in Fig. 3.13. This result surely suggests that the Petlyuk column structure will show excellent performance for the given design condition. Assuming a sufficient number of trays as shown in Fig. 3.13, the Petlyuk column was simulated by Aspen HYSYS® at the same condition of this case study. The utility cost of the simulation is 111 \$/h, and is 5.1 % smaller than the result of the first step optimization

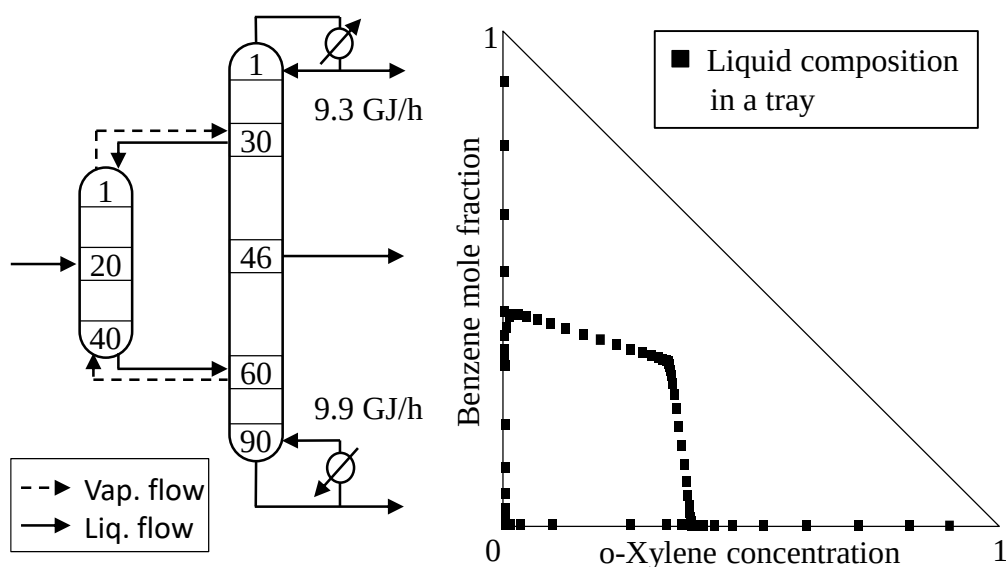


Figure 3.13 A process of Petlyuk column structure with plenty of trays (left) and its liquid composition profile (right)

of the proposed method. This difference is caused by the rough discretization of the composition space. The result in Fig. 3.6 indicates that discretization with a much smaller width is requested to obtain the theoretically optimal result, and needs heavy computational load. As the purpose of the proposed procedure is not to show the minimum utility cost but to derive effective process structures, we conclude that the preciseness of the discretization of this case study is sufficient for imaging a plausible process structure.

3.6. Conclusion

The framework proposed in chapter 2 is extended to ternary distillation cases. In chapter 1, the number of trays is incorporated into the objective function using 0-1 variables, in order to penalize the processes including many trays. For ternary distillation cases, such a formulation results in an MILP problem involving too many 0-1 variables. To avoid heavy computation, a two-step heuristic algorithm consisting of utility cost minimization and process structure simplification is developed. Because each optimization problem is formulated as an LP problem, even though a large number of design variables are involved, both steps of the optimization can be handled. The developed method was applied to the synthesis problem of a benzene, toluene and o-xylene mixture. Though the result of the first optimization step had a large number of tiny flows among the modules, such tiny flows were dramatically reduced through the second

simplification step. By grouping the modules that have large flow rates among them, a process structure similar to the Petlyuk column was finally obtained.

When considering the practical construction, the result of two step procedure is not sufficiently simple. Thus, the final process should be manually simplified by considering the similarity in liquid composition profile and/or the flow paths among the modules, and the final design should be examined by using a process simulator. When the obtained liquid composition profile is completely different from those of any familiar process structures, this reconciliation may need some engineering knowledge as well as some trial and error. The simple liquid composition profile obtained by the proposed procedure should still be a powerful reference for developing the underlying innovative design, which could not be conceptualized ever. There is some possibility that various process structures are obtained if the assumption of the number of distillation columns adopted in the final result is changed. Such uncertainty is unavoidable because the purpose of the procedure is to derive the plausible process structures for the given objective. However, we still need to seek systematic procedures for generating the practical process structures from the optimization result, and it is a remaining problem for future research.

The other remaining issue is to reduce the number of tiny flows that are still left over after the second optimization step. One reason why the obtained process is not so simple is that the compositions in the process are restricted to discrete values in the optimization, whereas discretization enables a linear formulation of the superstructure. An idea for overcoming this issue is to assign not a discrete liquid composition but a subregion in the composition space to a module. A new method for linear formulation of the process synthesis problem based on this idea is presented in chapter 5.

Nomenclature

c_m^H	Cost coefficient for heating utility m [\$ MJ ⁻¹]
c_m^C	Cost coefficient for cooling utility m [\$ MJ ⁻¹]
c_{Lij}^k	Weight to the liquid flow rate from module i to module j at iteration $k \in \{1, 2, \dots, K\}$ in the process structure simplification step [h kmol ⁻¹]
c_{vij}^k	Weight to the vapor flow rate from module i to module j at iteration $k \in \{1, 2, \dots, K\}$ in the process structure simplification step [h kmol ⁻¹]
c_{Qj}^k	Weight to the heat flow rates between the utilities and module j at iteration $k \in \{1, 2, \dots, K\}$ in the process structure simplification step [h MJ ⁻¹]
h_i^L	Molar enthalpy of liquid in module i [MJ kmol ⁻¹]
h_i^V	Molar enthalpy of vapor in module i [MJ kmol ⁻¹]
L_F	Liquid flow rate of feed [kmol h ⁻¹]

L_{ij}	Liquid flow rate from module i to module j [kmol h ⁻¹]
L_{ij}^0	Liquid flow rate from module i to module j obtained by the utility cost minimization step [kmol h ⁻¹]
L_{ij}^k	Liquid flow rate from module i to module j obtained by iteration $k \in \{1,2,\dots,K\}$ in the process structure simplification step [kmol h ⁻¹]
N_C	Number of available cold utilities [-]
N_H	Number of available hot utilities [-]
N_S	Number of separation modules in the superstructure [-]
Q_{ij}	Heat flow rate from module i to module j [MJ h ⁻¹]
Q_{ij}^0	Heat flow rate from module i to module j obtained by the utility cost minimization step [MJ h ⁻¹]
Q_{ij}^k	Heat flow rate from module i to module j obtained by iteration $k \in \{1,2,\dots,K\}$ in the process structure simplification step [MJ h ⁻¹]
SI^k	Value of the structure simplicity index calculated at iteration $k \in \{1,2,\dots,K\}$ in the process structure simplification step [-]
UC	Utility cost [\$ h ⁻¹]
UC^0	Utility cost obtained by the utility cost minimization step [\$ h ⁻¹]
UC^k	Utility cost obtained by iteration $k \in \{1,2,\dots,K\}$ in the process structure simplification step [\$ h ⁻¹]
V_F	Vapor flow rate of feed [kmol h ⁻¹]
V_{ij}	Vapor flow rate from module i to module j [kmol h ⁻¹]
V_{ij}^0	Vapor flow rate from module i to module j obtained by the utility cost minimization step [kmol h ⁻¹]
V_{ij}^k	Vapor flow rate from module i to module j obtained by iteration $k \in \{1,2,\dots,K\}$ in the process structure simplification step [kmol h ⁻¹]
x_{ik}	Liquid molar fraction of component k in module i [-]
x_k^P	Requested molar fraction of the key component for product k [-]
y_{ik}	Vapor molar fraction of component k in module i [-]
ϵ	Convergence tolerance for the process simplification step
θ_L	Prespecified positive constants for adjusting the effect of the liquid flow rates to the objective function [kmol h ⁻¹]
θ_V	Prespecified positive constants for adjusting the effect of the vapor flow rates to the objective function [kmol h ⁻¹]
θ_Q	Prespecified positive constants for adjusting the effect of the liquid flow rates to the objective function [MJ h ⁻¹]
λ	Allowable increase ratio of the utility cost in the process simplification step [-]

References

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4. Synthesis of Reactive Distillation Processes Using the Discretization of Liquid Composition Space

4.1. Introduction

On the design of reactive distillation processes, reaction, which is usually take place in liquid phase must be considered in addition to vapor-liquid equilibrium. When the reaction can be treated as equilibrium reaction, the system can be modeled by relatively simple expressions. On the other hand, when considering kinetically controlled reaction, the design problem become much more complicated: e.g. reaction rate must be precisely calculated depending on the composition, temperature, and pressure. Thus, the optimization and simulation of reactive distillation processes requests much more computational cost than those of ordinary distillation processes. Nevertheless, when using the state space discretization approach, the reaction at each module can be considered by minor modification of the configuration of the modules (Burri and Manousiouthakis, 2004, Da Cruz and Manousiouthakis, 2017).

In this chapter, the framework presented in chapter 3 is extended to reactive distillation in three-component system through modifying the configuration of the modules. As for reactive distillation involving metathesis reaction of 2-pentene, based on the optimization result obtained by the proposed method, a new process structure is conceptualized.

In the rest of this chapter, in section 4.2, the synthesis problem discussed in this chapter is defined. In section 4.3, the modified configuration of the modules is described. In section 4.4, the configuration of the superstructure is described and the utility cost minimization problem is formulated as a LP problem. The proposed method is applied to reactive distillation involving metathesis reaction of 2-pentene in section 4.5, and then, the new process structure is examined through the comparison with the conventional configuration consisting of a reactive distillation column.

4.2. Problem statement

The reaction treated in this research is shown in Eq. (4.1).



where A and C are the lightest and the heaviest components, respectively. It is a catalytic reaction, and the solid catalyst is assumed to be used. Thus, the reaction occurs in the liquid on the trays where catalyst is installed. Such stages are hereafter called the reactive

stages. Under the above conditions, a synthesis problem of deriving the best process structure that minimizes the utility cost is discussed. The following conditions are introduced to formulate the problem:

1. The flow rate, the temperature, and the composition of the feed are given in advance.
2. Both products are saturated liquid and the purity of each product is specified as the molar fraction of the key component.
3. The pressure is assigned in advance, and pressure drop in the process is negligible.
4. The vapor on each tray is in equilibrium with the liquid on the tray regardless of the degree of reaction.
5. The liquid holdup on each tray is an independent design variable. When the liquid holdup takes a positive value, that tray is treated as a reactive tray. The vapor holdup at each tray is assumed to be negligible. The upper bound on the total liquid holdup is imposed.
6. There is no restriction on the number of trays.
7. Heat can be supplied or removed at any tray by the hot or cold utility whose unit cost is given in advance.

4.3. Configuration of a separation module considering reaction in liquid phase

The state space discretization used in the IDEAS approach (Burri and Manousiouthakis, 2004) is adopted in this research. That is, first, the entire range of the liquid composition space is divided to enough number of sub-spaces, and a representative liquid composition is decided to each sub-space. Then, each sub-space is assigned to a separation module illustrated in Fig. 4.1. As the pressure is prespecified, the vapor composition and the temperature which satisfy VLE condition are calculated for each separation module. Based on the temperature specified by the VLE, the molar enthalpies of the liquid and the vapor are calculated. Furthermore, the reaction rate per unit volume of reactive holdup is calculated for each module by using a reaction model. Note that any rigorous models with complicated nonlinear equations can be used for the VLE, molar enthalpies, and the reaction rate equations because these calculations are completed before the optimization.

As illustrated in Fig. 4.1, a separation module possesses a material input and two material outputs. The material input accepts mixture of vapor and liquid, and the material outputs are vapor and liquid flows whose compositions and molar enthalpies are specified by the procedure mentioned above. A separation module possesses an input and output of heat. When heat is supplied to (removed from) a separation module as a result of the

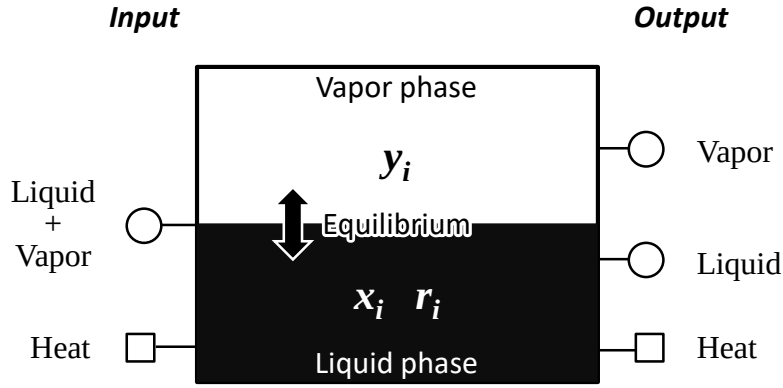


Figure 4.1 Separation module i in the superstructure

optimization, the module possesses the function of a reboiler (condenser).

4.4. Configuration of superstructure and formulation of the process synthesis problem

Figure 4.2 illustrates the distribution network adopted in this research. In Fig. 4.2, the boxes numbered from 1 to N are the separation modules. To identify the flow connection easily, each separation module is divided into two parts: output part and input part. Thus, two boxes of the same number correspond to a separation module. The solid lines, dashed lines, and dotted lines among the modules are the liquid, vapor, and heat flow paths, respectively. The products, feeds, and hot and cold utilities are treated as special modules. The product modules, which are numbered $N+1$ and $N+2$, possess only material inputs, and the feed module, which is numbered $N+3$, possesses only material outputs. As for the products, it is supposed that the boiling temperature of product 1 is lower than that of product 2. The hot and cold utilities possess only heat output flows and heat input flows, respectively, and are expressed by module H and module C.

In this research, all possible flow connections among the separation modules are considered. Since the intensive variables of the material flows are determined in advance, the material balances at each separation module and the feed module are expressed by linear equations shown in Eqs. (4.2) and (4.3).

$$\sum_{\substack{i=1 \\ i \neq j}}^N (L_{ij}x_i + V_{ij}y_i) + F_{N+3,j}x^F + H_j r_j v = \sum_{\substack{i=1 \\ i \neq j}}^{N+2} L_{ji}x_j + \sum_{\substack{i=1 \\ i \neq j}}^N V_{ji}y_j, \quad \forall j \in \{1, 2, \dots, N\} \quad (4.2)$$

$$\sum_{j=1}^{N+2} F_{N+3,j} = F_F \quad (4.3)$$

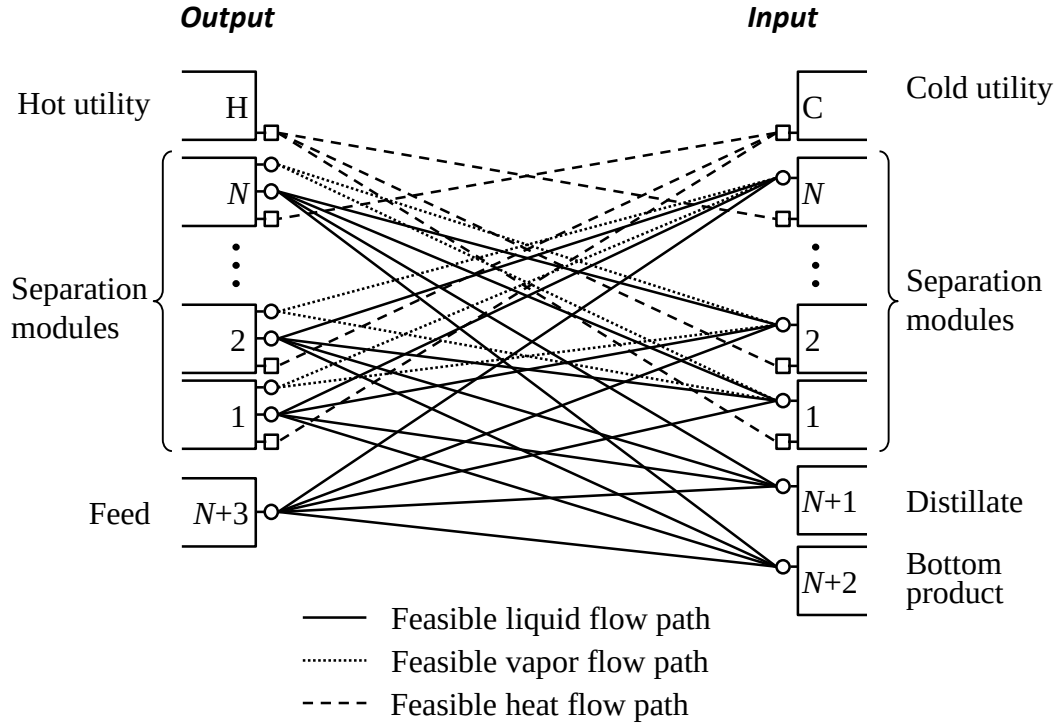


Figure 4.2 Superstructure adopted in this research

where L_{ij} and V_{ij} are liquid and vapor flow rates from module i to module j . $\mathbf{x}_i$ and $\mathbf{y}_i$ refer to the liquid and vapor compositions of module i . F^{Feed} and $\mathbf{x}^{\text{F}}$ are the feed flow rate and its composition, respectively. H_j is the liquid holdup at module j . r_j is the reaction rate at module j and is a function of $\mathbf{x}_j$ and the temperature of module j . $\mathbf{v}$ is a vector showing the stoichiometric coefficients of the reaction, and in this research it is $[1, -2, 1]^T$.

The heat balance at separation module j is expressed by Eq. (4.4).

$$\sum_{\substack{i=1 \\ i \neq j}}^N (L_{ij} h_i^{\text{L}} + V_{ij} h_i^{\text{V}}) + F_{N+3, j} h^{\text{F}} + Q_{\text{Hj}} = h_j^{\text{L}} \sum_{\substack{i=1 \\ i \neq j}}^{N+2} L_{ji} + h_j^{\text{V}} \sum_{\substack{i=1 \\ i \neq j}}^N V_{ji} + Q_{\text{Jc}}, \quad \forall j \in \{1, 2, \dots, N\} \quad (4.4)$$

where h_i^{L} and h_i^{V} are the liquid and vapor molar enthalpies of separation module i , respectively. h^{F} is the molar enthalpy of the feed. Q_{Hj} and Q_{Jc} are heat flow rates from the hot utility to separation module j and from separation module j to the cold utility, respectively. As the products are assumed to be saturated liquid, the vapor flows are not connected to the product modules in Eqs. (4.2) and (4.4).

The specification of the product k is given as the lower bound of the molar fraction of its key component, x_k^{P} , and the corresponding constraint is expressed by

$$\sum_{i=1}^N L_{i,N+k} \sigma_k^T \mathbf{x}_i + F_{N+3,N+k} \sigma_k^T \mathbf{x}^F \geq x_k^p \left(\sum_{i=1}^N L_{i,N+k} + F_{N+3,N+k} \right), \quad \forall k \in \{1, 2\} \quad (4.5)$$

where $\sigma_1^T = [1, 0, 0]$, $\sigma_2^T = [0, 0, 1]$.

The upper bound on the total liquid holdup on each tray is imposed:

$$\sum_{i=1}^N H_i \leq H^{\text{MAX}} \quad (4.6)$$

The reaction can take place at any separation module, and zero liquid holdup indicates that the reaction does not occur at that module. In Eqs. (4.2) to (4.6), the optimization variables are $L_{ij}, \forall i \in \{1, 2, \dots, N+2\}, j \in \{1, 2, \dots, N\}$, $V_{ij}, \forall i \in \{1, 2, \dots, N+2\}, j \in \{1, 2, \dots, N+2\}$, $F_{N+3,j}, \forall j \in \{1, 2, \dots, N+2\}$, $H_j, \forall j \in \{1, 2, \dots, N\}$, $Q_{Hj}, \forall j \in \{1, 2, \dots, N\}$, and $Q_{jC}, \forall j \in \{1, 2, \dots, N\}$, therefore, all of the constraints are linear for these variables. Thus, the problem that minimizes the utility cost expressed by Eq. (4.7) is obtained by solving the linear programming problem.

$$\min \quad c^H \sum_{i=1}^N Q_{Hi} + c^C \sum_{i=1}^N Q_{iC} \quad (4.7)$$

where c^H and c^C are cost coefficients. Note that the number of modules used in the separation is not included in the objective function.

4.5. Case study

The proposed method is applied to the synthesis problem of the reactive distillation involving metathesis reaction of 2-pentene to form 2-butene and 3-hexene studied by Okasinski and Doherty (1998). The reaction shown in Eq. (4.8) takes place in liquid phase and its kinetics and physical property at atmospheric pressure are given in Eqs. (4.9) and (4.10).



$$r_i = 0.5k_0 \exp\left(-\frac{E}{RT_i}\right) \left[(x_{i2})^2 - \frac{x_{i1}x_{i3}}{K_{\text{eq}}} \right] \quad (4.9)$$

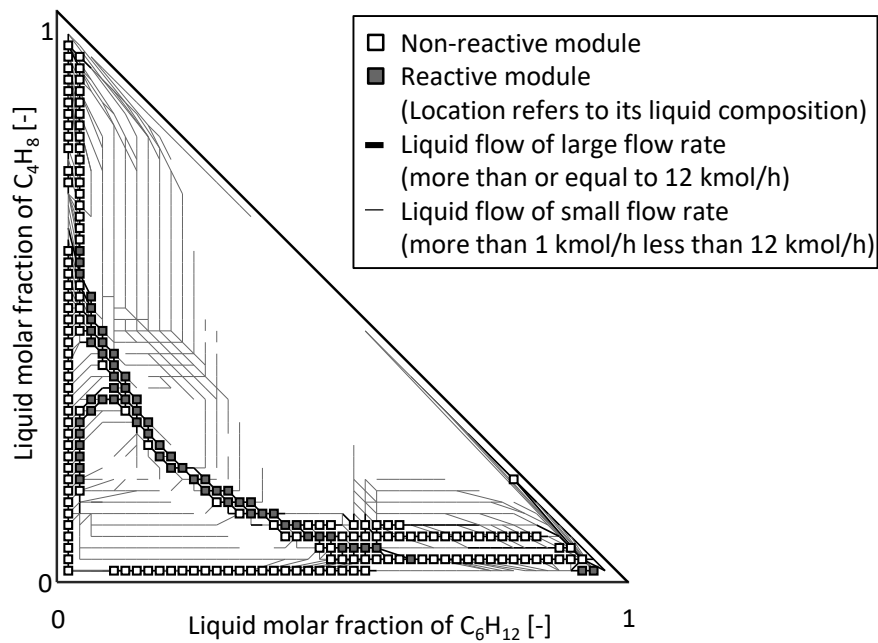
$$k_0 = 1.963 \times 10^6 \text{ kmol m}^{-1} \text{ h}^{-1}, \quad E = 27633 \text{ kJ/kmol}, \quad K_{\text{eq}} = 0.25 \quad (4.10)$$

where x_{i1} , x_{i2} and x_{i3} are liquid molar fractions of 2-butene, 2-pentene, and 3-hexene at module i , respectively; T_i is the temperature at module i . As this reaction model was

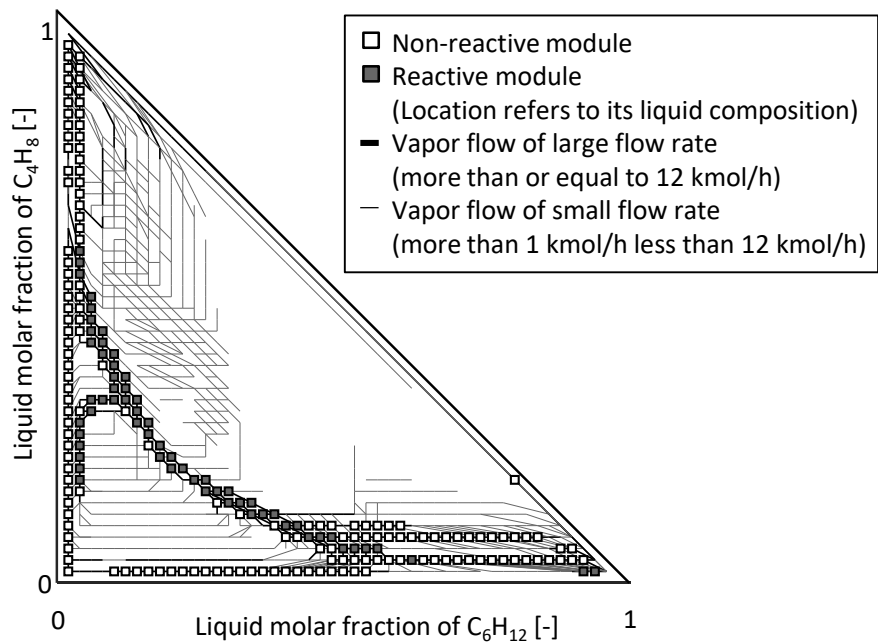
developed based on experiments under atmospheric pressure, in this case study, it is assumed that the reaction takes place at the atmospheric pressure. The feed is the saturated liquid of pure 2-pentene, and the feed flow rate is 120 kmol/h. The upper bound on the total liquid holdup is 36 m³. The purity requirements of both products, 2-butene and 3-hexene, are 95 mol%. The unit costs of hot and cold utilities are 10 \$/GJ and 5 \$/GJ, respectively. Since the normal boiling points of 2-butene of cis isomer and trans isomer are 3.7°C and 0.9°C, respectively, a refrigerant around -10°C is requested for cooling. Thus, the unit cost of cooling utility is higher than that of conventional systems that use cooling water as the cooling medium. The liquid composition space is discretized with the width of 2 mol%, and the obtained distribution network contains 1176 separation modules. Peng-Robinson package of Aspen HYSYS® V8.6 is used for VLE calculation.

Figure 4.3 show the result of optimization. In Fig. 4.3(a), the thick solid lines are liquid flows whose flow rate is larger than 12 kmol/h, which is 10% of the feed flow rate, and the thin solid lines are those of smaller flow rate. When the liquid flow rate is smaller than 1 kmol/h, such connections are not depicted. Selected separation modules are expressed by boxes whose locations correspond to the liquid composition. The modules where the reaction takes place are expressed by gray boxes. When the liquid inlet flow rate, the liquid outlet flow rate, the vapor inlet flow rate, or the vapor outlet flow rate is less than 12 kmol/h, such modules are not shown for ease of illustration. For the vapor flows, similar relationships are shown in Fig. 4.3(b). The locations of modules correspond to the liquid composition. The total holdup of reactive trays was 36 m³, and the holdup of 18 trays was larger than 0.72 m³, which is 2 % of the total holdup.

Since the material and heat balances must be satisfied with the discretized compositions and molar enthalpies, the obtained process includes many secondary flows of small flow rate and shows the complicated structure. The result shown in Fig. 4.3, however, gives us a hint of simple and efficient new structure. The arrows in Fig. 4.4 refer to directions of the liquid and vapor flows among the modules. In this case, by assigning a column to a part expressed by arrows 1L and 1V and the other column to the remaining part expressed by arrows 2L and 2V, a simple process structure can be obtained. The reaction takes place at the central part of the column corresponded to arrows 2L and 2V in Fig. 4.4. Thus, the induced reactive column has non-reactive trays around the top and bottom. Since the directions of arrows 1L and 1V in Fig. 4.4 are opposite of the conventional distillation, the inlet condition of the induced non-reactive column is unusual: the vapor rich in light component is fed to the bottom, and the liquid rich in heavy component is fed to the top of the column. By connecting these two columns, the process structure in Fig. 4.5 is obtained.



(a) Liquid flow paths



(b) Vapor flow paths

Figure 4.3 Selected modules and flow paths of the optimization result

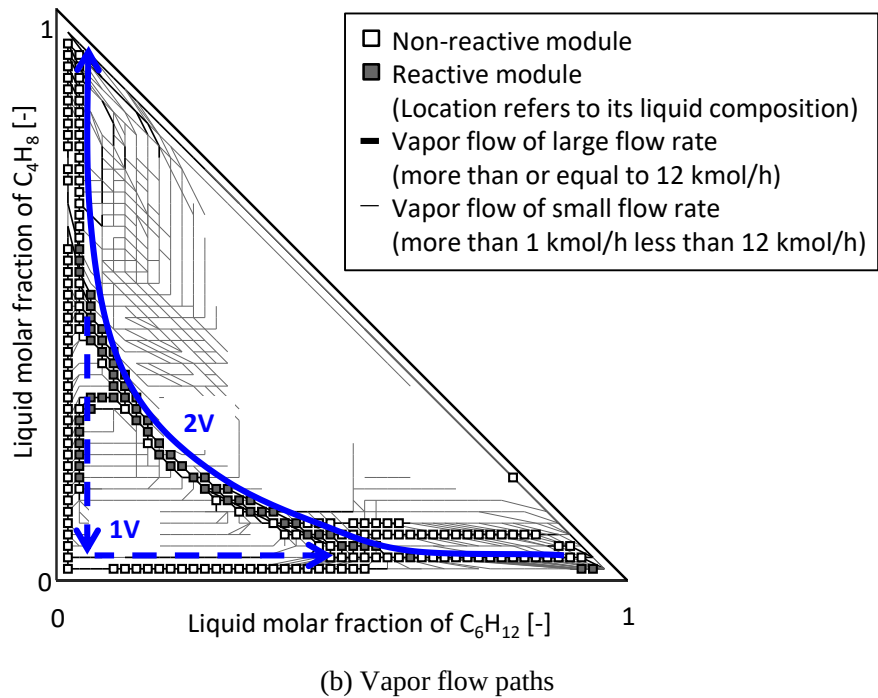
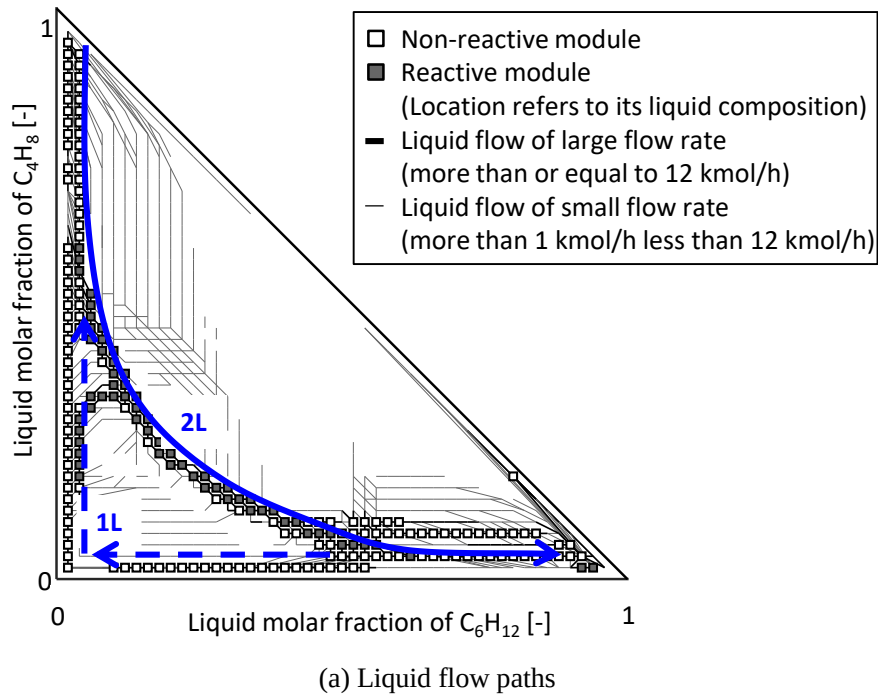


Figure 4.4 Directions of flow paths in the optimization result

The simulation of the process in Fig. 4.5 is carried out by Aspen HYSYS® V8.6. In the simulation, it is assumed that 21 trays are reactive, the total holdup is 36 m^3 , and the holdup on each reactive tray is identical, i.e. $36 \text{ m}^3 / 21 \text{ trays} = 1.71 \text{ m}^3/\text{tray}$. From the condenser duty of the optimization result, 1.0 is assigned to the reflux ratio. The number of non-reactive trays is decided by trial and error so as to satisfy the product specification. The obtained result is shown in Fig. 4.6. In this case, non-reactive column consists of 7 trays, and reactive column has 4 and 5 non-reactive trays above and below the reactive zone, respectively. The liquid composition of the obtained result is shown in Fig. 4.7. Gray circles in the figure indicate reactive trays and the dashed lines show the flow connection between two columns. The utility cost of the simulation was 44.8 \$/h, which is 11.5% smaller than the result indicated by the optimization of the proposed method. This slight discrepancy is caused by the rough discretization of the composition space. In theory, as decreasing the discretization width of the liquid composition, the resulting sequence of the minima of the performance index converges to its limit value. On the other hand, in practice, the complete convergence requires extremely small discretization width, which results in heavy computation corresponding to the superstructure with numerous separation modules. This is because, in the neighborhood of the exact limit, the approach of the sequence to its limit becomes very insensitive to increasing the number of the separation modules in the superstructure, as explained in chapter 3. As the purpose of the proposed procedure is not to show the minimum utility cost but to derive effective process structures, we conclude that the preciseness of the discretization of this case study

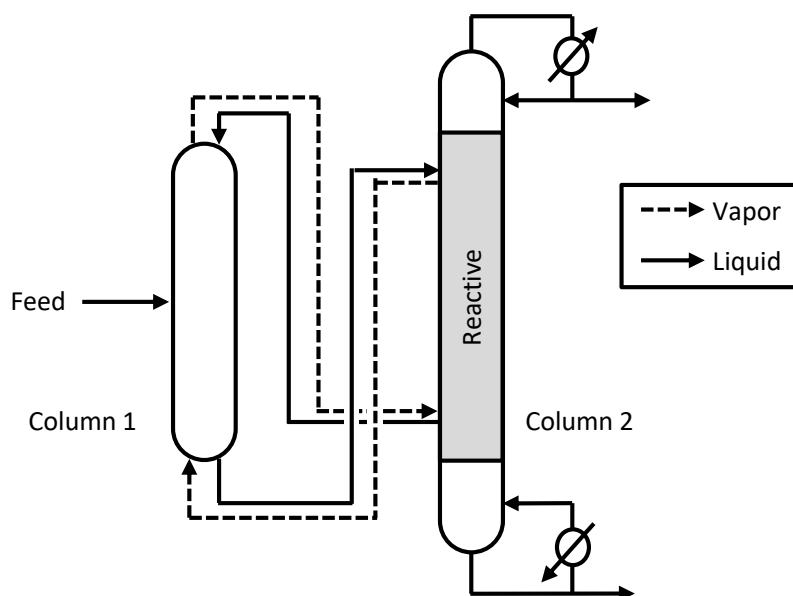


Figure 4.5 Schematic process structure implied by the optimization result

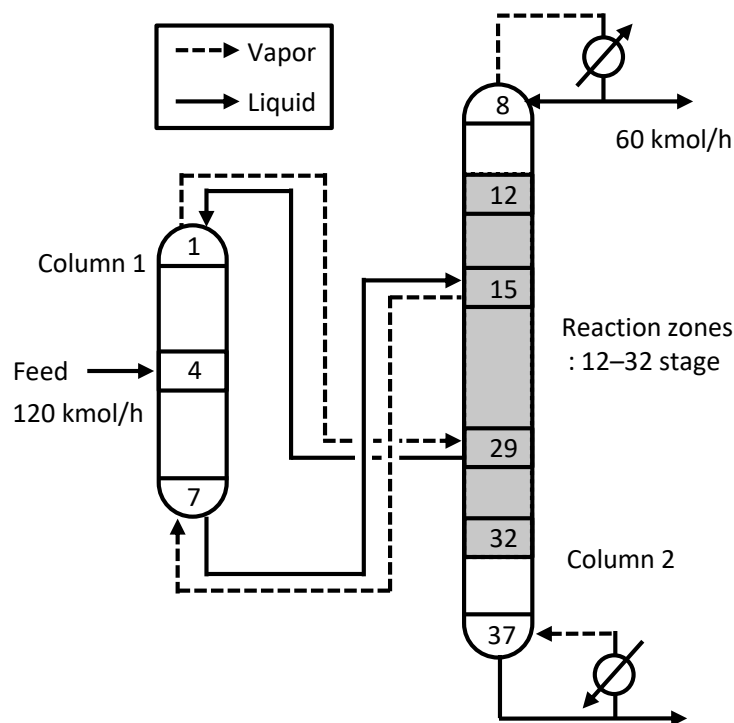


Figure 4.6 Specific process structure obtained by the HYSYS simulation based on the optimization result (Structure A)

is sufficient for imaging a plausible process structure.

In the next section, the implied process structure is compared with the conventional process structure, and the role of the unusual non-reactive column is discussed.

4.6. Comparison of the derived process structure and conventional structures

The effectiveness of the process structure shown in Fig. 4.6, which is implied by the result of the proposed method, is evaluated through the comparison with two conventional process structures shown in Fig. 4.8. The newly derived structure in Fig. 4.6 is hereafter called structure A. Structure B consists of single column and single feed, and structure C has double feeds. For all structures, the total number of trays is 37, and the total number of reactive trays is 21. The feed is the saturated liquid of pure 2-pentene, and the flow rates of feed and distillate are 120 kmol/h and 60 kmol/h, respectively. The unit utility costs are the same as those in the previous section, and are 10 \$/GJ for hot utility and 5 \$/GJ for cold utility.

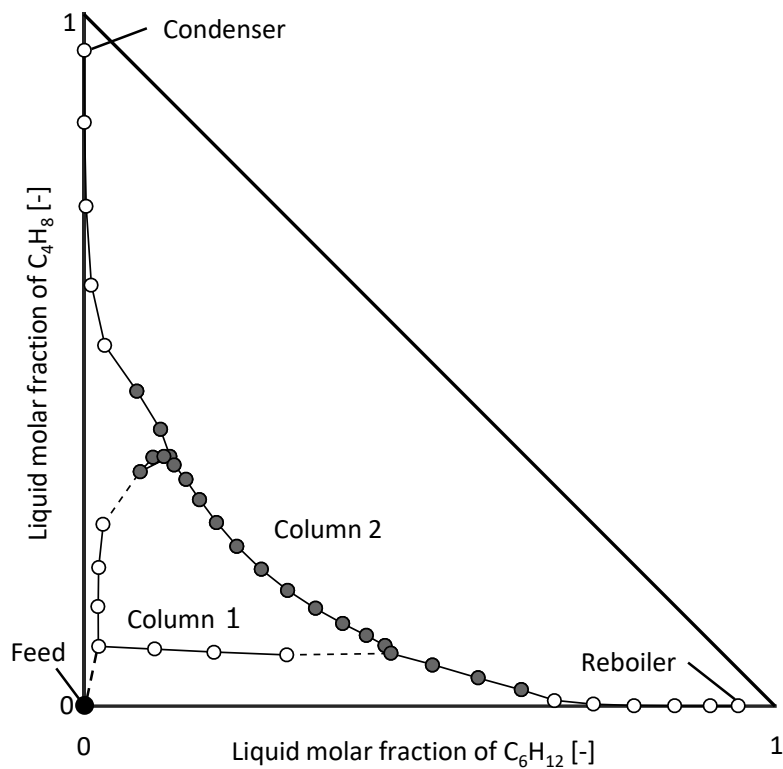


Figure 4.7 Liquid composition profile obtained by the HYSYS simulation of the new process structure shown in Fig. 4.6

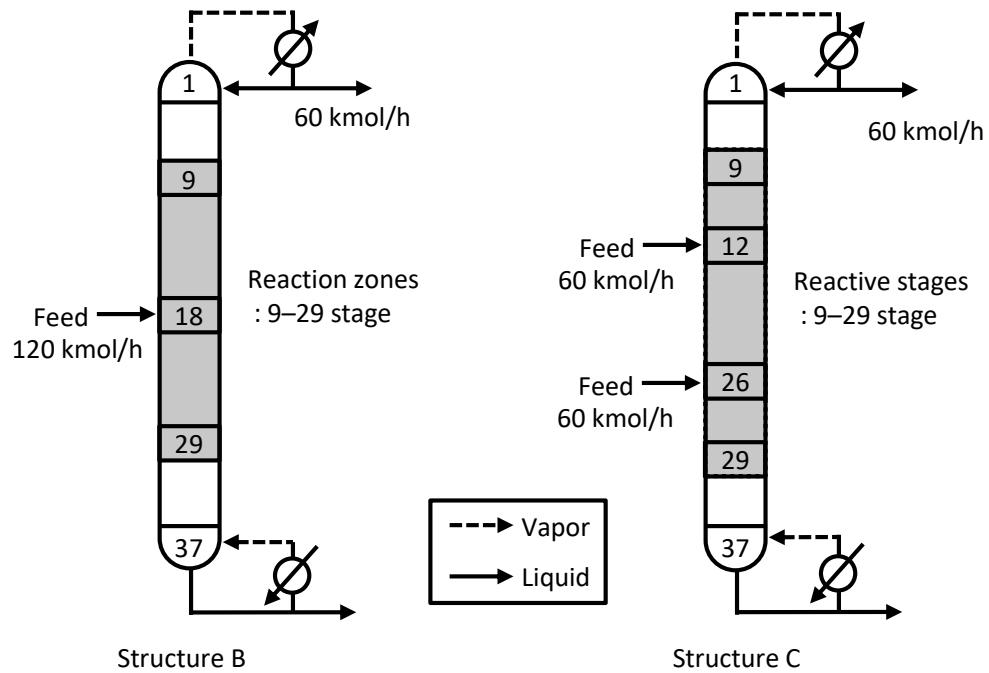


Figure 4.8 Conventional process structures adopted for the comparison

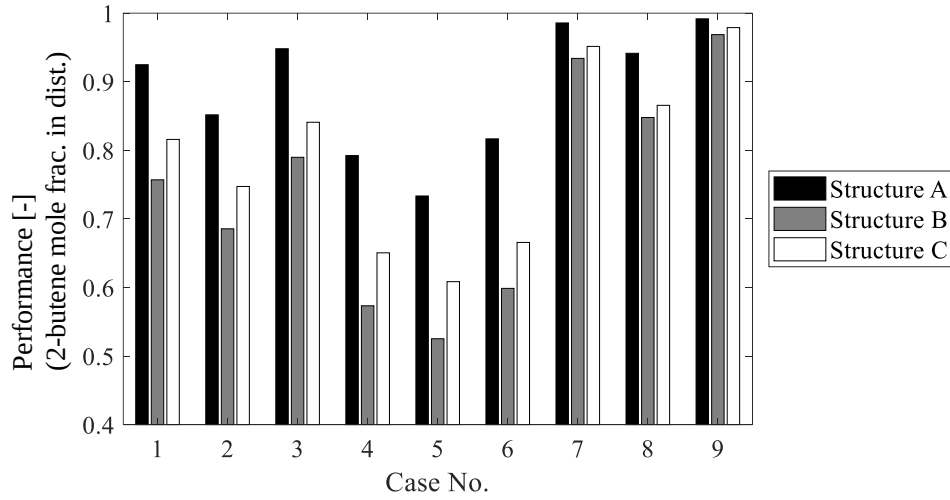
In addition to the base condition simulated above, eight different conditions are generated by altering the total liquid holdup in reaction zones and/or the reflux ratio of the reactive distillation column. For generated nine cases shown in Table 4.1, the product composition and the utility cost are compared. The holdup on each tray in the reaction zone is set to be identical for each case. The feed and side cut trays are decided as shown in Figs. 4.6 and 4.8, and these conditions are not changed for all cases. Structure A has two more degrees of freedom on the side cut flow rates from the reactive column to the non-reactive column. In terms of the liquid and vapor flows from the reactive column, each flow rate is assumed to take 0 kmol/h, 30 kmol/h, 60 kmol/h, or 90 kmol/h. As these flow rates have little effect to the reboiler and condenser duties, the values that maximize the product purity are selected. All simulations are carried out by Aspen HYSYS® V8.6.

The results of simulation are summarized in Fig. 4.9. Figure 4.9(a) shows the product concentration in the distillate, and Fig. 4.9(b) shows the utility cost. The amount of heats added to the reboiler and removed from the condenser are shown in Table 4.2. As the flow rate of the distillate and the reflux ratio are set to be common values among all structures in each case, the heating and cooling duties are almost same regardless of the structures. Thus, the performances of these three processes can be evaluated by the purity of the distillate. Figure 4.9(a) indicates that structure A achieved the highest performance for all cases.

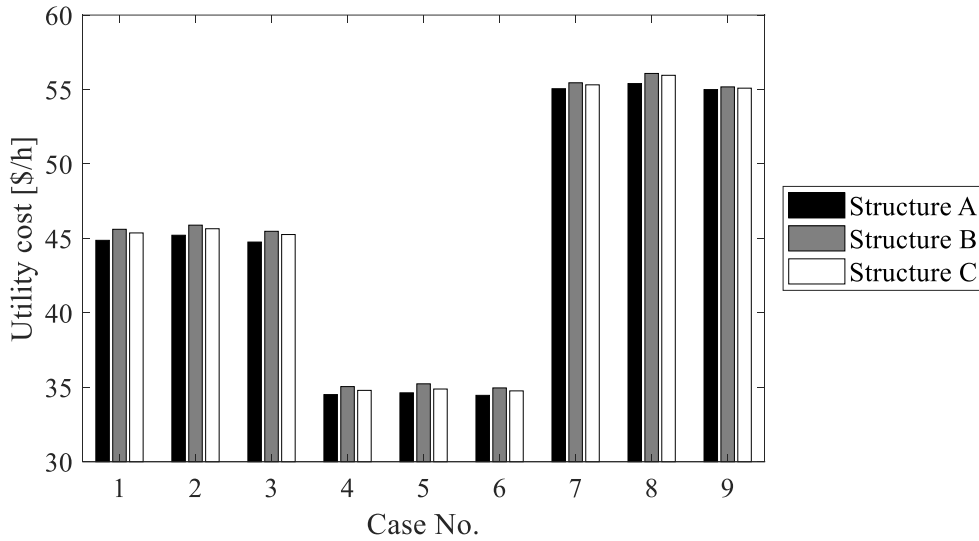
To explain the high performance of structure A, the profiles of reaction rate at each tray is calculated for case 1, and is shown in Fig. 4.10. The reaction rate is high values over the entire reaction zone of structure A, whereas there are regions of low reaction rate

Table 4.1 Condition of each case

Case No.	Reflux ratio [-]	Reactive hold-up [m ³]	
		Total	Per tray
1	1	24	1.143
2	1	12	0.571
3	1	36	1.714
4	0.5	24	1.143
5	0.5	12	0.571
6	0.5	36	1.714
7	1.5	24	1.143
8	1.5	12	0.571
9	1.5	36	1.714



(a) Product concentration in the distillate, which represents the performance of the processes



(b) Sum of the hot and cold utility cost

Figure 4.9 Simulation results for the structures A, B, and C in each cases

for structures B and C. Although only the profiles for case 1 are shown, similar profiles are observed in all cases.

This difference between the reaction rate profiles of structure A and the other structures primarily arises from the difference in backward reaction rate over reaction zone. The backward reaction rate is proportional to the term, $x_{i1}x_{i3}/K_{eq}$, where i is the tray number. The forward reaction rate is proportional to the square of molar fraction of 2-pentene, $(x_{i2})^2$. Figure 4.11 shows the values of these terms over the reaction zones. The average values of $(x_{i2})^2$ for the three structures are almost same, so that no structures show significant superiority in terms of the forward reaction rate. On the other hand, the average

Table 4.2 Cooling and heating duties for structures A, B, and C in each case

Case	Cooling duty [GJ/h]			Heating duty [GJ/h]		
	Str. A	Str. B	Str. C	Str. A	Str. B	Str. C
1	2.84	2.95	2.91	3.07	3.09	3.08
2	2.89	2.99	2.96	3.08	3.09	3.09
3	2.82	2.93	2.90	3.06	3.08	3.08
4	2.20	2.30	2.26	2.35	2.36	2.35
5	2.23	2.32	2.28	2.35	2.36	2.35
6	2.19	2.29	2.25	2.35	2.35	2.35
7	3.49	3.54	3.52	3.76	3.77	3.77
8	3.53	3.62	3.60	3.77	3.80	3.79
9	3.49	3.51	3.50	3.76	3.76	3.76

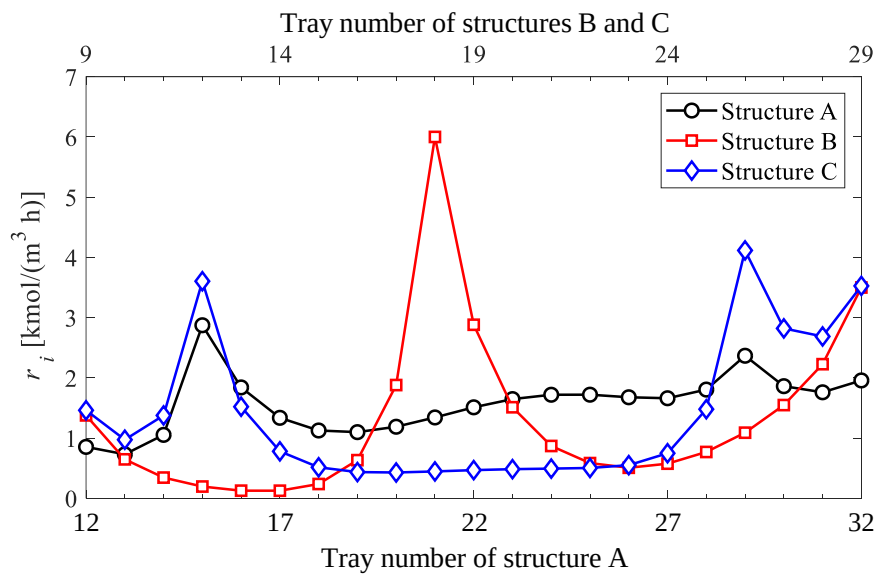


Figure 4.10 Profile of reaction rate in the reaction zones of structures A, B, and C for case 1

value of $x_{i1}x_{i3}/K_{eq}$ for structure A is clearly lower than that for structures B and C, so that the backward reaction rate is kept smaller in structure A than in the other structures. As a result, structure A can achieve better progress of the overall reaction than the other structures.

Figure 4.12 shows the profile of molar fraction of each component over the reaction zones of each structure. As for structures B and C, both concentrations of 2-butene or 3-hexene are relatively high in some regions, in which the resulting backward reaction rate

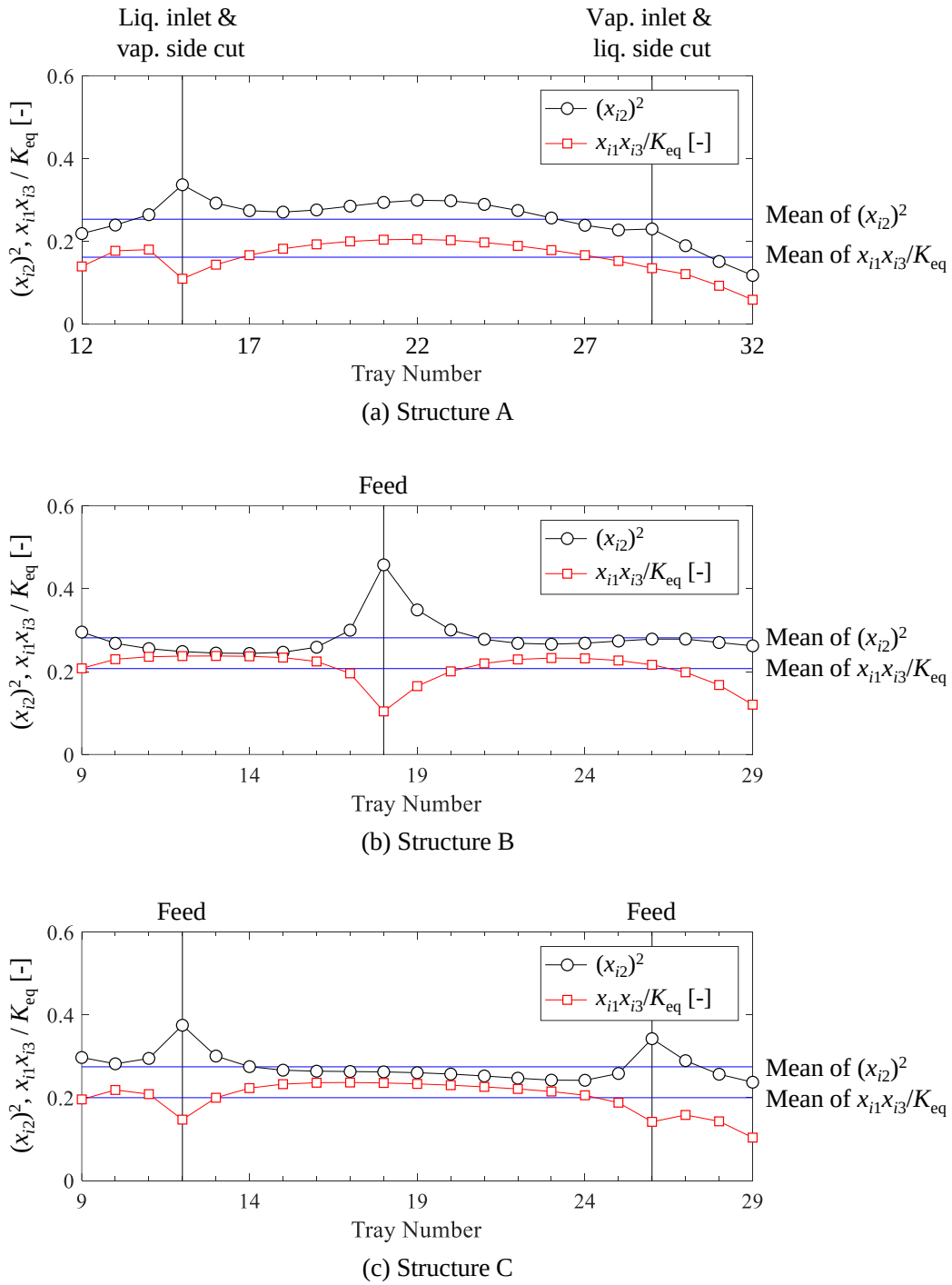


Figure 4.11 Profile of composition-dependent terms of forward and backward reaction rates in the reaction zones of structures A, B, and C for case 1

is high. In structure B, the molar fraction of 2-butene (3-hexene) keeps decreasing from the top (bottom) of the reaction zone to the feed tray, increases at several trays just below (above) the feed tray, and then decreases again around the bottom (top). Such local

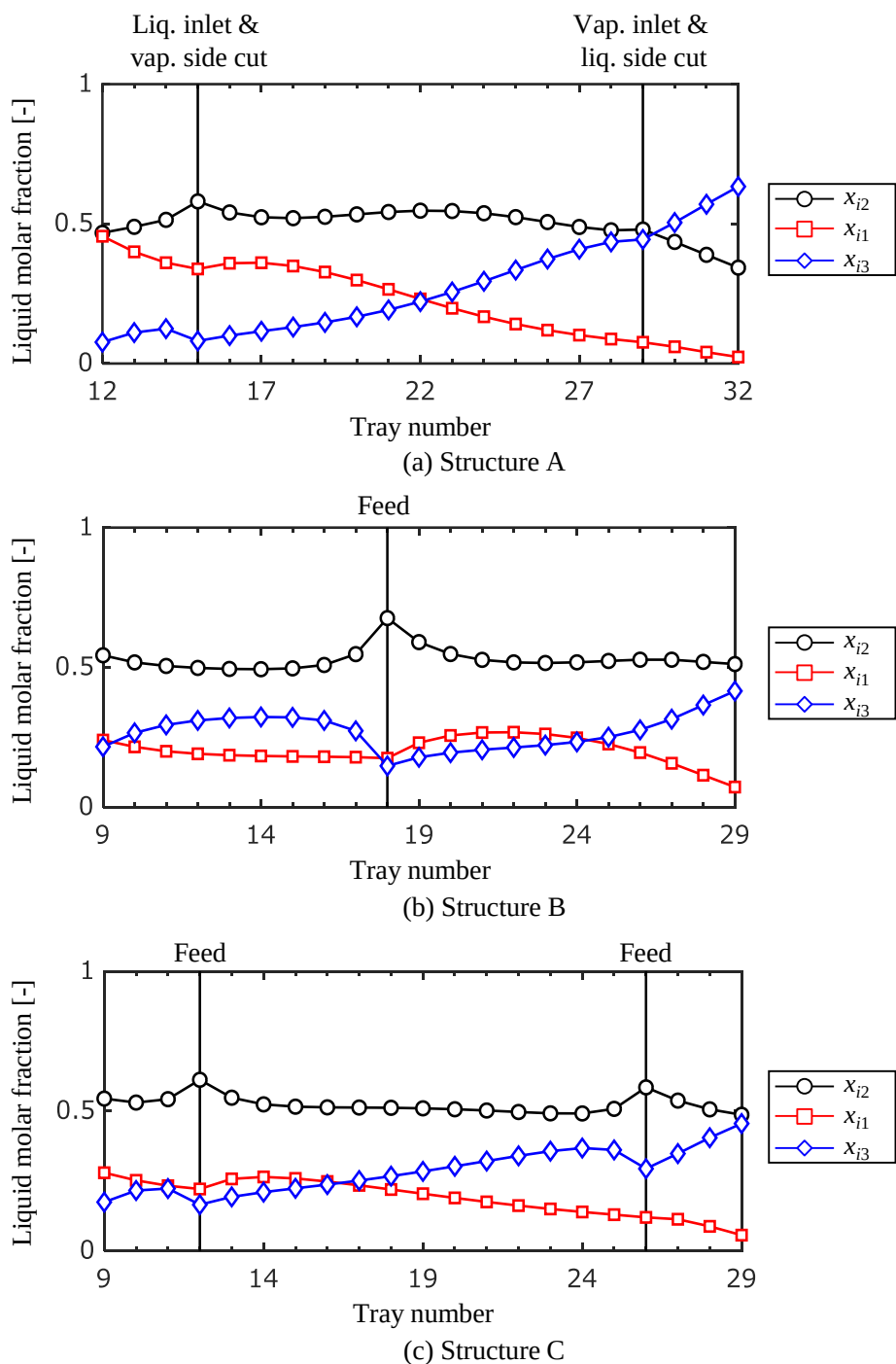


Figure 4.12 Profile of liquid-phase molar fraction of each component in the reaction zones of structures A, B, and C for case 1

increases of molar fractions of 2-butene and 3-hexene are observed also around the feed trays of structure C. In contrast, this local increases in the reactive column are suppressed in structure A. Accordingly, in the reaction zone of structure A, as both of molar fractions

of 2-butene and 3-hexene do not take large values at the same time, structure A can inhibit the backward reaction over the reaction zone.

Structure A can achieve such preferable liquid composition profile because the liquid and vapor are efficiently circulated through column 1. Because of this circulation, the liquid and vapor flow rates are large in most part of the reaction zone. By appropriately increasing the liquid and vapor flow rates in the reaction zone, the local increases of the molar fractions of 2-butene and 3-hexene can be avoided. Indeed, when those flow rates

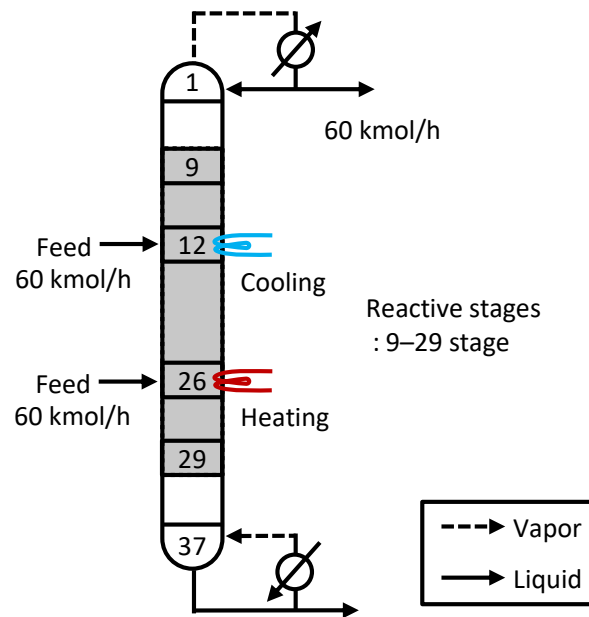


Figure 4.13 A process structure where a side heater and a side cooler are added to Structure C

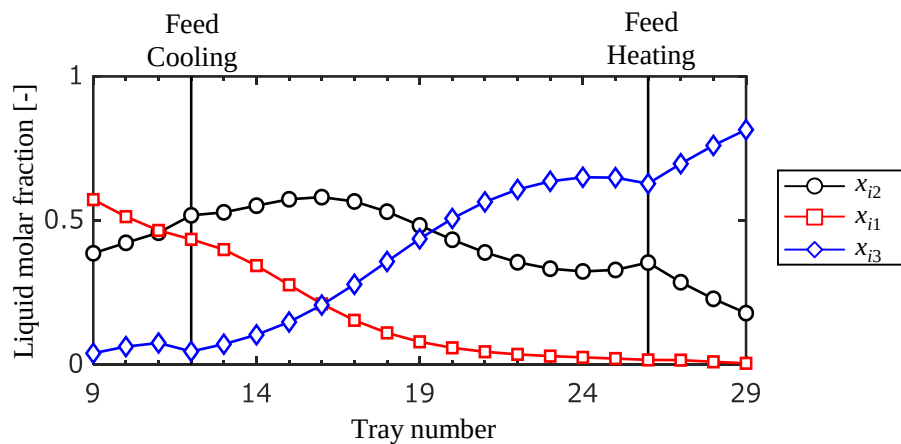


Figure 4.14 Profile of liquid-phase molar fraction of each component in the reaction zones of the structure in Fig. 4.13 for case 1

in structure C are increased up to the similar values to those of Structure A by incorporating the additional heating and cooling as shown in Fig. 4.13, high product purity is achieved. As shown in Fig. 4.14, the liquid composition profile also forms the preferable shape. On the other hand, the structure in Fig. 4.13 results in 77% increase of the utility usage because of the additional heating and cooling. Thus, some circulation of the liquid and vapor is needed to increase the flow rates in the reaction zone without extra

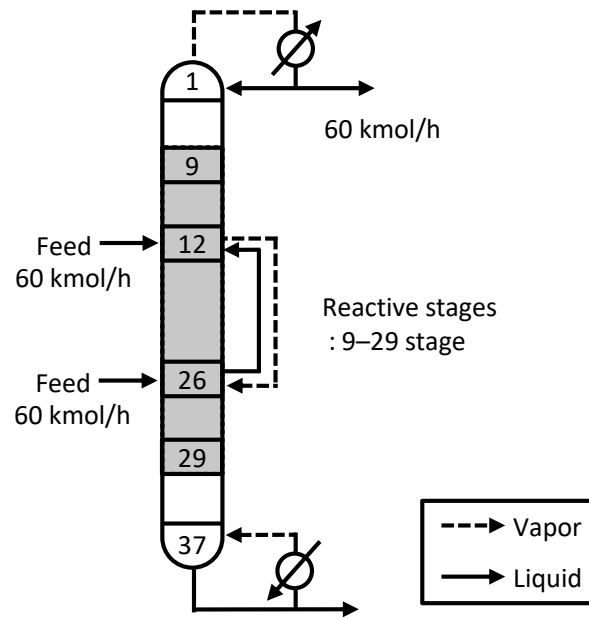


Figure 4.15 A process structure where the simple circulation of liquid and vapor are added to Structure C

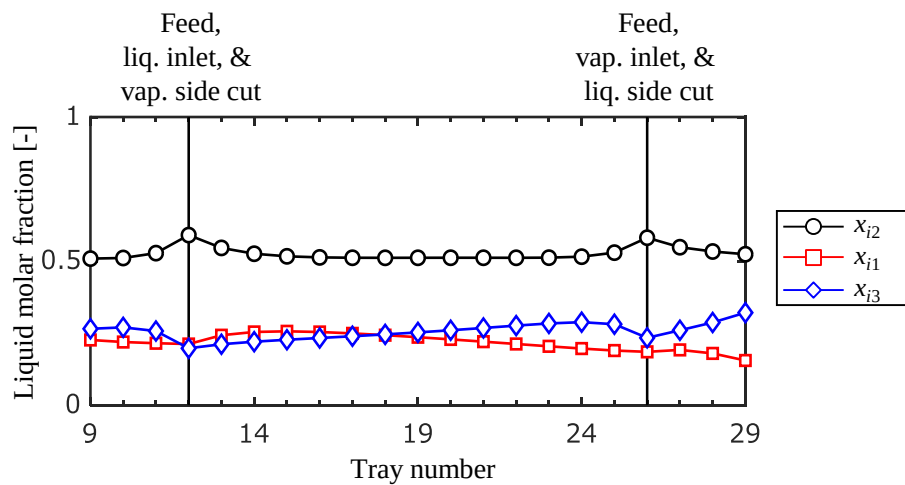


Figure 4.16 Profile of liquid-phase molar fraction of each component in the reaction zones of the structure in Fig. 4.15 for case 1

utility usage.

Figure 4.15 shows the process structure with the simplest circulation of liquid and vapor. When adopting this structure, the flow rates in the reaction zone can be increased up to those of Structure A without extra utility usage. Nevertheless, the preferable liquid composition profile and the high product purity cannot be achieved. Figure 4.16 shows the liquid composition profile in the reaction zone of the process shown in Fig. 4.15. Since the hexene-rich vapor is introduced in the top side of the reaction zone, the molar fraction of hexene does not become small over the entire reaction zone. Similarly, due to the introduction of butene-rich liquid at the bottom side, the molar fraction of butene also does not become small.

In structure A, the molar fraction of hexene (butene) in the circulated vapor (liquid) is decreased through the mass exchange in the mixing column, column 1. Consequently, the liquid and vapor are circulated without the inefficient mixing occurred in the structure shown in Fig. 4.15, so that the preferred liquid composition profile is achieved without extra utility usage. In addition, the process with structure A looks like a Petlyuk column, but the connection between two columns is different. In structure A, as the vapor at the upper part of the reactive column is fed to the bottom of the non-reactive column, the vapor compression of either of vapor flows between the columns is requested. However, the required compression is just the amount of overcoming the pressure drop of two columns. Thus, it does not become a serious drawback to introduce a new structure process.

4.7. Conclusion

The framework proposed in chapter 3 is extended to reactive distillation cases. At each module, VLE is assumed and the reaction is kinetically controlled. By discretizing liquid composition space and assigning each discretized composition to a module, the VLE calculation can be carried out prior to the optimization. The reaction rate at each module also can be calculated based on the assigned liquid composition and the temperature satisfying the VLE condition. Since these calculations are carried out before the optimization, without major increase of the overall calculation burden, any complicated equations can be used for the sake of accurate emulation of the thermodynamic behavior. The optimization problem corresponding to the proposed superstructure is formulated by using only linear equations and inequalities which include the pre-calculated intensive variables, as the coefficients. Because the optimization problem is formulated as an LP problem, even though a large number of design variables are involved, the solution can be obtained within reasonable calculation time. Thus, the

proposed method synthesizes the target reactive distillation process through minimizing utility cost without any assumptions concerning process structure.

The developed method was applied to the synthesis of reactive distillation process for the production of 2-butene and 3-hexene from 2-pentene. Although the structure of the obtained process was complicated, it was demonstrated that a simple structure for practical design can be easily conceptualized based on the liquid composition profile suggested by the optimization result. The induced process structure, which includes a non-reactive column in addition to a reactive column, was compared with the conventional structures consisting of a reactive column using a rigorous process simulator. The performances achieved by the processes of these structures were simulated for nine cases where holdup at a tray in reaction zone and reflux ratio are different. As a result, the structure implied by the optimization result outperformed the conventional structures in all cases. The comparison regarding the profiles of reaction rate and liquid composition revealed that the non-reactive column in the new structure works for keeping high reaction rate over the entire reaction zone.

Nomenclature

c^H	Cost coefficient for hot utility [$\$ \text{ MJ}^{-1}$]
c^C	Cost coefficient for cold utility [$\$ \text{ MJ}^{-1}$]
F_F	Feed flow rate [kmol h^{-1}]
$F_{N+3,j}$	Flow rate of the feed supplied to module j [kmol h^{-1}]
h_i^L	Molar enthalpy of liquid in module i [MJ kmol^{-1}]
h_i^V	Molar enthalpy of vapor in module i [MJ kmol^{-1}]
h^F	Molar enthalpy of the feed [MJ kmol^{-1}]
H_i	Liquid hold up of module i where the reaction is take place [m^3]
H^{MAX}	Upper bound of total liquid hold up of reactive trays [m^3]
L_{ij}	Liquid flow rate from module i to module j [kmol h^{-1}]
N	Number of the separation modules in the superstructure [-]
Q_{ij}	Heat flow rate from module i to module j [MJ h^{-1}]
r_i	Reaction rate of module/tray i [$\text{kmol m}^{-3} \text{ h}^{-1}$]
T_i	Temperature at module i [K]
V_{ij}	Vapor flow rate from module i to module j [kmol h^{-1}]
$\mathbf{x}^F$	Feed composition [-]
$\mathbf{x}_i$	Liquid composition of module i [-]
x_{ik}	Molar fraction of component k in the liquid of module/tray i [-]
x_k^P	Requested molar fraction of the key component for product k [-]

- y_i Vapor composition of module i [-]
 ν Stoichiometric-coefficient vector of the reaction [-]

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5. Linear Formulation of Structure Synthesis Problems Using Stepwise VLE Description

5.1. Drawbacks of the discretization of liquid composition space

In the methods described in chapters 2 to 4, the liquid composition space is, first, discretized and each discretized liquid composition is assigned to a separation module. Because of this assignment, all of the involved intensive variables can be calculated using a thermodynamic model before the optimization and they are treated as constants in the optimization. As the result, the optimization problem can be formulated only with linear constraints, so that the optimal solution can be obtained efficiently. However, as the composition can take only the discretized values, the optimization result usually has many secondary flows of small flow rate among the trays so as to satisfy the material and energy balances at the trays. In other words, even though arbitrary flow connection among the modules is covered in the adopted superstructures, many processes of simple structures are actually not treated as feasible solutions in the optimizations where the constraints on material and heat balances at each module are imposed.

As a typical example of simple process structures, let us consider a distillation column separating a binary mixture. Figure 5.1 describes why processes consisting of a distillation column are infeasible in the optimization. As liquid composition space is discretized, the feasible values of vapor and liquid compositions in equilibrium are only the discrete values plotted in the x-y diagram. According to the McCabe-Thiele method, the profile of vapor and liquid compositions in a distillation column is identified by drawing a stair between the corresponding operating line and the equilibrium curve. Consequently, if and only if all points at which the stair and the equilibrium curve meet are included as the feasible values of the vapor and liquid compositions, that distillation column is a feasible solution in the optimization. Even when the liquid composition space is discretized with very small width, as for most of the operating lines, some of the requested equilibrium points are usually missing. Thus, the processes consisting of a distillation column alone are usually not treated as feasible solutions in the optimization. Similarly, processes of other simple structures are also regarded as being infeasible when the feasible liquid compositions are given as a set of discrete values. Since the configurations with simple structures cannot satisfy the constraints of material and heat balances, some secondary flows are requested for compensating the errors in the balances.

To reduce such secondary flows, an alternative methodology for linear formulation of the process synthesis problem is needed. For this purpose, the alternative methodology, stepwise VLE description, is proposed in this research. As the primal purpose is the

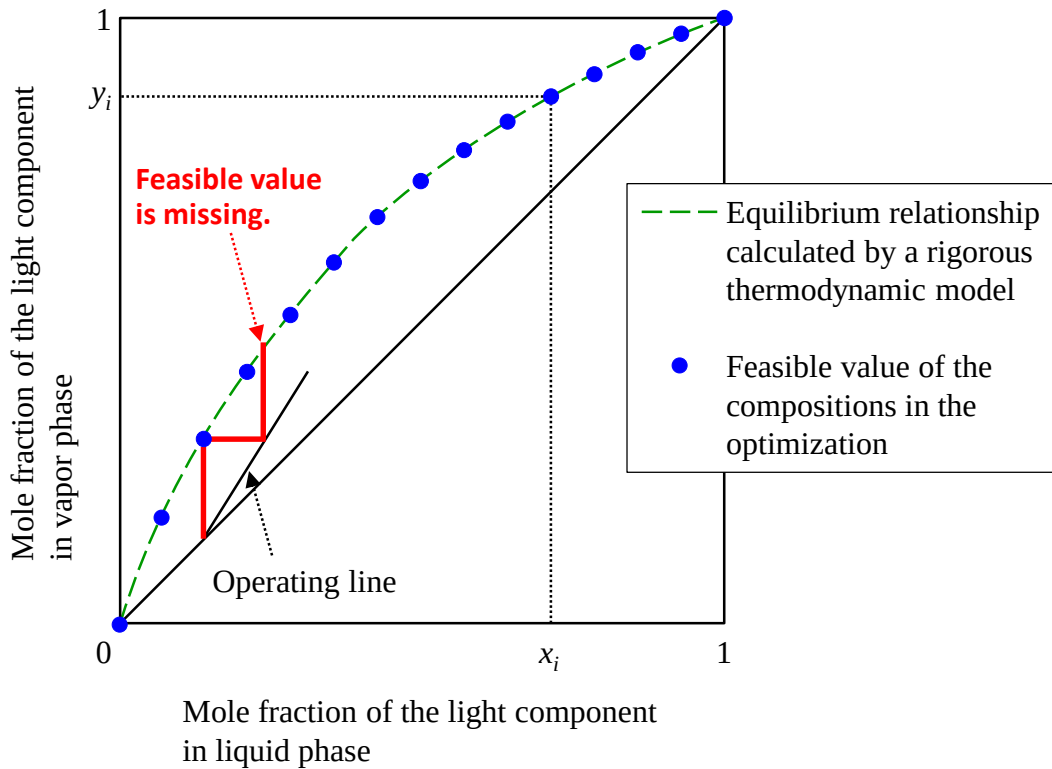


Figure 5.1 Illustration of the reason why a distillation column is not a feasible solution in the optimization where liquid composition space is discretized

development of the new linear formulation, this research deals with binary distillation without heat integration, which is a simple system.

5.2. Problem statement

Process synthesis problem of binary distillation without heat integration is discussed under the following assumptions. The flow rate and composition of the feed are given as the design requirement. The products are saturated liquid, and their compositions are specified. The operating pressure in the process is determined in advance, and the pressure drop in the process can be neglected.

5.3. Linear formulation based on stepwise VLE description

5.3.1. Configuration of the modules

Figure 5.2 illustrates the module adopted in the new formulation. As is the case for the approach based on the liquid composition discretization, a module corresponds to a tray in distillation columns. A module has two types of input flows, which are material flows and energy flow. The input material flows are the mixture of liquid and vapor. A

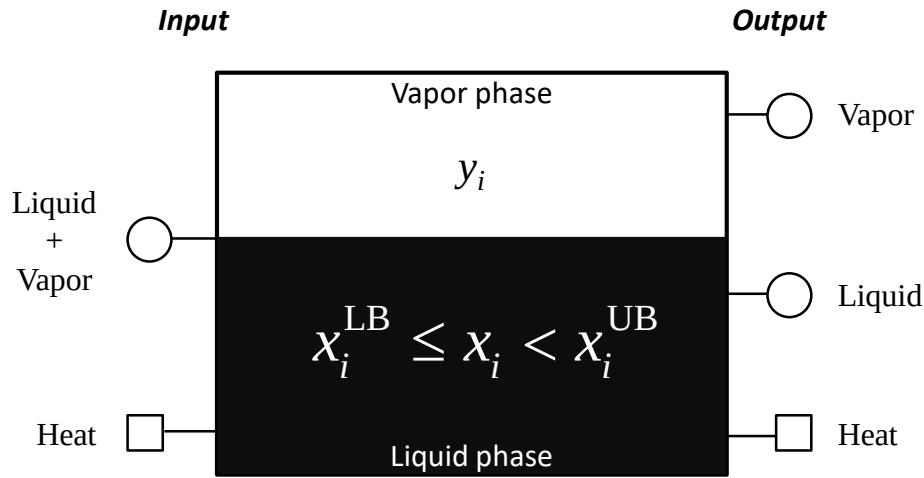


Figure 5.2 Configuration of separation module i based on the stepwise VLE description

module has three types of output flows, which are vapor flows, liquid flows, and energy flow. When a module has an input (output) energy flow as a result of optimization, the module functions as a reboiler (condenser).

The primal difference between the approach adopted in chapters 2 to 4 and the new approach is in the specification of the output liquid. In the previous works including the methods developed by Manousiouthakis and coauthors (Drake and Manousiouthakis, 2002a, 2002b), the composition of the output liquid of a module was restricted to a single value. On the other hand, in this work, it is assumed that the output liquid can take any composition in the subregion that is decided in advance. In order to decide this subregion, first, liquid composition space is divided into many subregions, and each subregion is assigned to a module. It is still assumed that the composition of the output vapor of a module takes a certain value. The molar enthalpy of output liquid is calculated by linear interpolation between the values at the endpoints of each subregion, while the molar enthalpy of output vapor is decided to be a particular value corresponding to the vapor composition.

When adopting this assignment, the resulting superstructure considers trays of arbitrary liquid compositions via selecting the module of appropriate liquid composition domains and adjusting the liquid composition in those domains. Since liquid compositions are optimized not over the set of discrete values but over the entire continuous space, processes with simple structures are included in the set of feasible solutions. For example, an ordinary distillation column is a feasible solution. As the vapor composition of a module is constant, the equilibrium relationship between liquid

composition and vapor composition becomes a step function as shown in Fig. 5.3. Under this surrogate equilibrium relationship, a stair can be drawn in the manner of the McCabe-Thiele method. This stair does not encounter lack of feasible liquid composition values because liquid composition space is not discretized. Thus, a distillation column based on the surrogate equilibrium relationship is a feasible solution in the optimization.

5.3.2. Configuration of superstructure

Figure 5.4 illustrates the superstructure adopted in this research. Each module is divided into two sections to identify the flow connection easily. The input and output parts are shown in right-hand side and left-hand side, respectively. Thus, two boxes with the same number represent a module. The solid lines, dotted lines, and broken lines among the nodes are the liquid flow paths, vapor flow paths, and heat flow paths, respectively.

The feed and hot utility are treated as special modules that have only output flows and are expressed by F and H, respectively. The distillate, bottom product, and cold utility are treated as special modules that have only input flows and are expressed by D, B, and

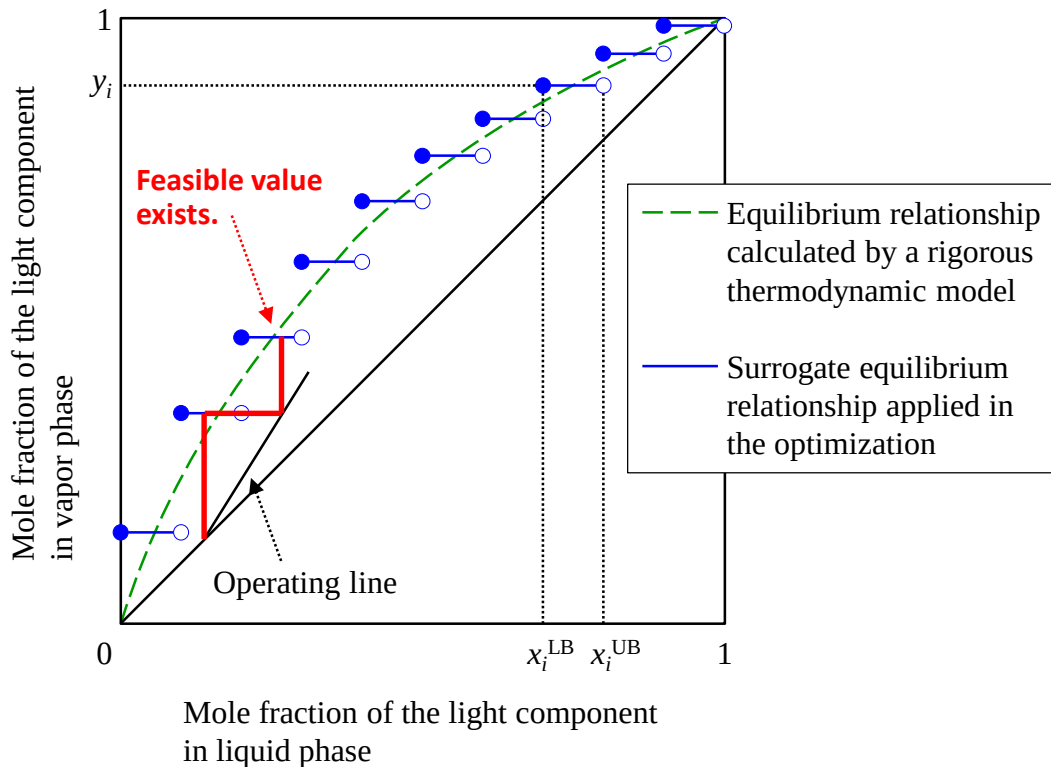


Figure 5.3 Surrogate equilibrium relationship applied in the optimization based on the stepwise VLE description, on which the configurations consisting of just a distillation column is a feasible solution

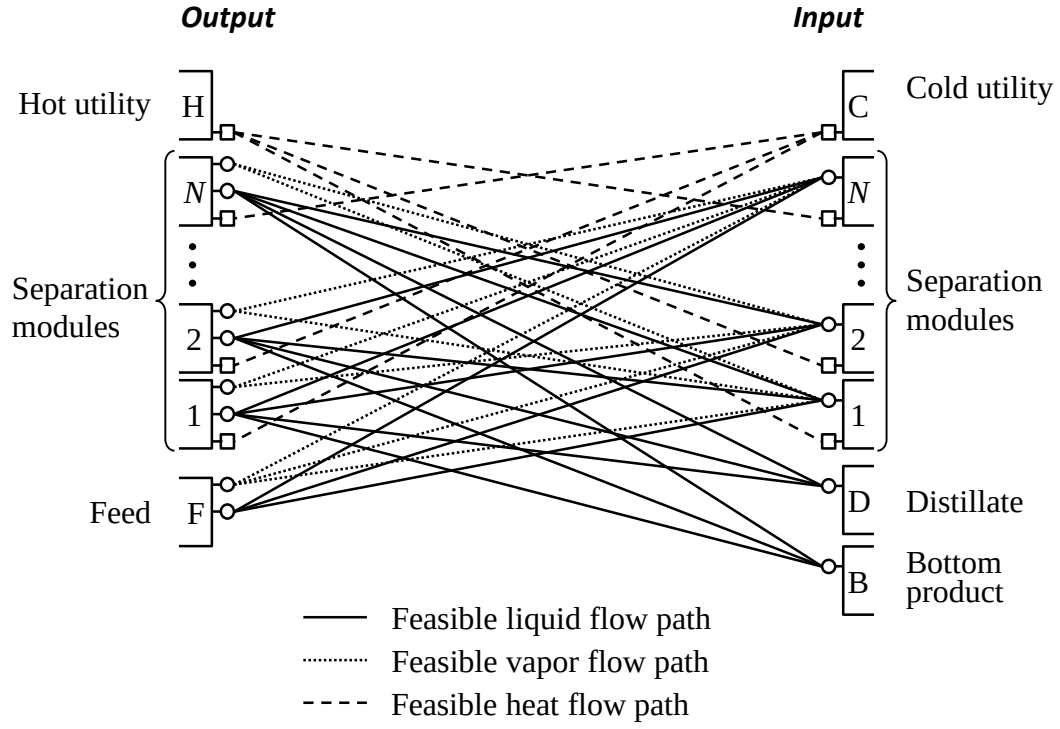


Figure 5.4 Superstructure adopted in this research

C, respectively. In principle, vapor and liquid can flow from any modules to any modules. However, some meaningless connections are omitted in advance. For example, the feed is not connected to product flows, and vapor flows from tray modules are not connected to product modules because of the assumption that the products are liquid.

From the superstructure shown in Fig. 5.4, the material balances and component material balances at the modules are expressed by the following equations.

$$\sum_{j \in S_{out}} (L_{ji} + V_{ji}) - \sum_{j \in S_{in}} (L_{ij} + V_{ij}) = 0, \quad \forall i \in S \quad (5.1)$$

$$\sum_{j \in S} L_{Fj} = L_F \quad (5.2)$$

$$\sum_{j \in S} V_{Fj} = V_F \quad (5.3)$$

$$\sum_{j \in S} L_{jD} = L_D \quad (5.4)$$

$$\sum_{j \in S} L_{jB} = L_B \quad (5.5)$$

$$V_{jD} = V_{jB} = 0, \quad \forall j \in S_{out} \quad (5.6)$$

$$\sum_{j \in S_{out}} (x_j L_{ji} + y_j V_{ji}) - \sum_{j \in S_{in}} (x_i L_{ij} + y_i V_{ij}) = 0, \quad \forall i \in S \quad (5.7)$$

$$\sum_{j \in S} x_j L_{jD} = x_D L_D \quad (5.8)$$

$$\sum_{j \in S} x_j L_{jB} = x_B L_B \quad (5.9)$$

$$x_i^{LB} \leq x_i < x_i^{UB}, \quad \forall i \in S, \quad \forall j \in S_{in} \quad (5.10)$$

where S , S_{in} , and S_{out} are sets of suffixes that indicate tray modules, modules having material inflow, and modules having material outflow, i.e. $S = \{1, 2, \dots, N\}$, $S_{in} = \{1, 2, \dots, N, D, B\}$, and $S_{out} = \{1, 2, \dots, N, F\}$. L_{ij} and V_{ij} are liquid and vapor flow rates from module i to module j , respectively. L_F , V_F , L_D , and L_B are the flow rates of liquid feed, vapor feed, distillate and bottom product, respectively, and these values are given in advance. x_F , x_D , and x_B are the molar fractions of the light component in the feed, distillate, and bottom product, respectively. x_j and y_j are the molar fractions of the light component of the liquid and vapor output flows from module j , respectively. x_i^{UB} and x_i^{LB} are the upper and lower bounds of x_i .

x_i is a variable whereas y_i is a constant. Equations (5.7) to (5.9) include bilinear terms of x_i and L_{ij} . To avoid such nonlinearity, $x_i L_{ij}$ in Eqs. (5.7) to (5.9) is replaced by l_{ij} as shown in Eqs. (5.11) to (5.13).

$$\sum_{j \in S} (l_{ji} + y_j V_{ji}) + (x_F L_{Fi} + y_F V_{Fi}) - \sum_{j \in S_{in}} (l_{ij} + y_i V_{ij}) = 0, \quad \forall i \in S \quad (5.11)$$

$$\sum_{j \in S} l_{jD} = x_D L_D \quad (5.12)$$

$$\sum_{j \in S} l_{jB} = x_B L_B \quad (5.13)$$

The composition of the liquid flowing from module i is restricted by Eq. (5.14) instead of Eq. (5.10).

$$L_{ij}x_i^{\text{LB}} \leq l_{ij} < L_{ij}x_i^{\text{UB}}, \quad \forall i \in S, \quad \forall j \in S_{\text{in}} \quad (5.14)$$

The molar enthalpy of the liquid flowing from module i , h_i^{L} , is assumed to be expressed by an affine function of x_i , as shown in Eq. (5.15). In Eq. (5.15), a_i and b_i are constants that are decided from the molar enthalpies at the endpoints of each subregion. The vapor molar enthalpy of module i , h_i^{V} , is constant as the vapor composition is uniquely determined at each module. By using Eq. (5.15) and the relationship of $x_i L_{ij} = l_{ij}$, the heat balance at each module can be expressed by Eq. (5.16).

$$h_i^{\text{L}} = a_i x_i + b_i \quad x_i \in [x_i^{\text{LB}}, x_i^{\text{UB}}), \quad \forall i \in S \quad (5.15)$$

$$\begin{aligned} & \sum_{j \in S} (a_j l_{ji} + b_j L_{ji} + h_j^{\text{V}} V_{ji}) + (h_{\text{F}}^{\text{L}} L_{\text{Fi}} + h_{\text{F}}^{\text{V}} V_{\text{Fi}}) + Q_{\text{Hi}} \\ & - \sum_{j \in S_{\text{in}}} (a_i l_{ij} + b_i L_{ij} + h_j^{\text{V}} V_{ij}) - Q_{\text{Ci}} = 0, \quad \forall i \in S \end{aligned} \quad (5.16)$$

where Q_{Hi} and Q_{Ci} are heat flow rates from the outer heat source to module i and from module i to the outer heat sink, respectively.

It should be noted that all the constraints including the material and heat balances at each module are expressed by linear equations and inequalities by assuming the stepwise VLE description.

5.4. Examination of the new formulation based on the stepwise VLE description

5.4.1. Purpose

This examination demonstrates that processes with simple structures can be fairly considered by adopting a new formulation based on the stepwise VLE description. As described in section 5.1, when liquid composition space is discretized, many secondary flows are requested so as to satisfy the material and heat balances. When the new formulation is adopted, the balances can be satisfied without such secondary flows by adjusting the compositions of the output liquid of the modules. Thus, if the simplicity of process structure is evaluated in the applied optimization procedure and if no better performance can be achieved by adopting more complicated structures, a process with a simple structure should be derived. This feature is illustrated through a simple case study dealing with a benzene-toluene distillation without heat integration in the process. The next subsection describes the optimization procedure applied to this examination where the simplicity of process structure is evaluated.

5.4.2. Optimization procedure

The optimization procedure consists of three steps: the minimization of utility cost, the minimization of the number of modules, and the simplification of the process structure.

First, the utility cost UC expressed by Eq. (5.17) is minimized under the constraints of Eqs. (5.1) to (5.6), and (5.11) to (5.16) as well as the non-negativity constraints on all variables.

$$UC = \sum_{i \in S} (c^H Q_{Hi} + c^C Q_{Ci}) \quad (5.17)$$

where c^H and c^C are the cost coefficients of the hot and cold utilities, respectively.

The first problem is formulated as a linear programming problem, and can easily be solved even if the number of modules are large. However, the derived optimal structure uses many modules because the equipment cost is not included in the objective function. Thus, at the second step, the number of necessary modules is minimized under a particular upper bound of the utility cost. This minimization problem is formulated as an MILP problem where N_{selected} in Eq. (5.18) is minimized. On the minimization, the constraints of Eqs. (5.1) to (5.6), (5.11) to (5.16), and (5.19) to (5.20) are imposed. The integrality constraints and the non-negativity constraints are also imposed on all 0-1 variables and all continuous variables, respectively.

$$N_{\text{selected}} = \min \sum_{i \in S} z_i \quad (5.18)$$

$$\sum_{j \in S_{\text{in}}} (L_{ji} + V_{ji}) \leq M_{\text{flow}} z_i, \quad \forall i \in S \quad (5.19)$$

$$\sum_{i \in S} (c^H Q_{Hi} + c^C Q_{Ci}) \leq (1 + \lambda) UC^* \quad (5.20)$$

where λ is a nonnegative constant which specifies the allowable increase of the utility cost from the minimum value UC^* obtained at the first step. M_{flow} is a sufficiently large value for flow rate. z_i is a 0-1 variable which indicates whether module i is selected or not. When z_i takes zero, module i is not selected.

By solving the second optimization problem, a process with the minimum number of modules can be obtained. Due to the degeneracy, there are usually multiple optimal solutions for the minimization problem in the second step. The process obtained in the second step is not necessarily the simplest process of those optimal solutions. In the third

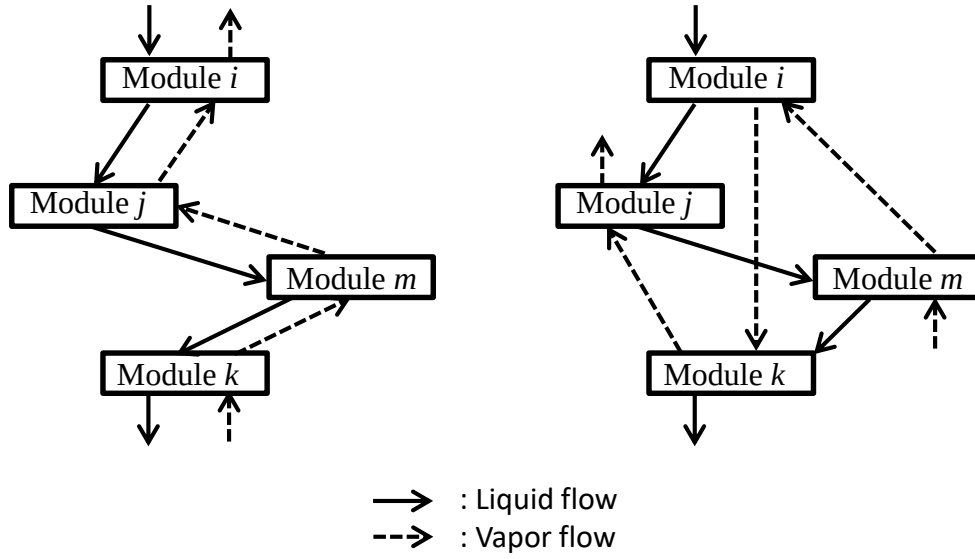


Figure 5.5 Simple structure (left) and complicated structure (right)

step, this simplest process is identified by solving another MILP problem.

Figure 5.5 shows two different process structures. Both structures have the same number of flows among modules. However, Fig. 5.5 (right) is more difficult to construct as an actual device. In Fig. 5.5 (left), when the liquid flow from module i to module j exists, the vapor flow from module j to module i exists. This relationship is used to measure the simplicity of the structure. A new 0-1 variable, w_{ij} , and the constraints of Eqs. (5.21) and (5.22) are introduced as for each combination of two modules.

$$L_{ij} \leq M_{\text{flow}} w_{ij}, \quad \forall i \in S_{\text{out}}, \forall j \in S_{\text{in}} \quad (5.21)$$

$$V_{ji} \leq M_{\text{flow}} w_{ij}, \quad \forall i \in S, \forall j \in S_{\text{out}} \quad (5.22)$$

If the liquid flow from module i to module j and/or vapor flow from module j to module i exists, w_{ij} must take one. Under a particular number of liquid and vapor flows, the sum of w_{ij} can be decreased by increasing the countercurrent combinations of liquid and vapor flows. The number of heat flows is also considered by introducing a new 0-1 variable z_i^q and the constraint

$$Q_{Hi} + Q_{iC} \leq M_{\text{heat}} z_i^q \quad \forall i \in S \quad (5.23)$$

where M_{heat} is a sufficiently large value for heat flow rate. z_i^q must take one when heat

flow from hot utility to module i and/or from module i to cold utility exists. Consequently, the simplest process in the set of optimal solutions for the problem in the second step is derived by minimizing the complexity index defined by Eq. (5.24) under the constraints of Eqs. (5.1) to (5.6), (5.11) to (5.16), (5.19) to (5.20), (5.21) to (5.23), and (5.25). The integrality constraints and the non-negativity constraints are also imposed on all 0-1 variables and all continuous variables, respectively.

$$\min CI = \left(c_q \sum_{i \in S} z_i^q + \sum_{i \in S_{out}} \sum_{j \in S_{in} \cup S_{out}} w_{ij} \right) \quad (5.24)$$

$$\sum_{i \in S} z_i = N_{selected}^* \quad (5.25)$$

where c_q is a constant that represents the weight of a heat flow to a countercurrent combination of a liquid flow and a vapor flow, and $N_{selected}^*$ is the minimum number of necessary modules obtained in the second step.

5.4.3. Optimization condition

The target mixture is the equimolar mixture of benzene and toluene. The feed is the saturated liquid and its flow rate is 200 kmol/h. The specification for the product purity is 99 mol%, and the flow rate of each product is 100 kmol/h. The pressure is assumed to be 1 atm in the entire system. In terms of the cost coefficients, the hot utility cost coefficient c_h was 13 \$/GJ, and the cold utility cost coefficient c_c was 0.13 \$/GJ. At the minimization of the number of modules, 1% of utility cost increase ($\lambda = 0.01$) is permitted. As for the structure simplification, the weight for a heat flow to a combination of countercurrent combination of a liquid flow and a vapor flow, c_q , is 10. In the optimization procedure, IBM ILOG CPLEX V12.6.1 was used as a solver. The CPU of the applied computer was Intel® Core™ i7-4770K 3.50GHz and the memory capacity was 32.0 GB.

There are no settled rules to divide the composition space. In this examination, the width for a subregion of the liquid composition is decided by taking into account the driving force of the distillation. First, the whole region of the molar fraction of benzene, which is between 0 and 1, is equally divided into certain subregions. Suppose that x_i^L and x_i^U are the lowest and the highest benzene molar fractions of the liquid phase in the subregion of module i . The average value of the driving force at the total reflux operation in this region is assumed to be given by $\{y(x_i^U) - x_i^U + y(x_i^L) - x_i^L\}/2$. $y(x)$ is benzene molar fraction in the equilibrium vapor when the benzene molar fraction in the liquid is x , and is calculated by using a rigorous thermodynamic model. When $\{y(x_i^U) + y(x_i^L)\}/2$

is taken as the representative value for the benzene molar fraction of vapor in the module, the maximum error of the molar fraction of vapor phase becomes $\{y(x_i^U) - y(x_i^L)\}/2$. If this error is large in the region of small driving force, it affects the result of distillation calculation. By taking into account this fact, Eq. (5.26) is used to determine if the width of each subregion is small enough.

$$\frac{\{y(x_i^U) - y(x_i^L)\}/2}{\{(y(x_i^U) - x_i^U) + (y(x_i^L) - x_i^L)\}/2} \leq \theta, \quad (5.26)$$

The numerator of the left-hand side of Eq. (5.26) represents the maximum error of vapor concentration, while the denominator represents the potential driving force. θ is the threshold for the maximum error normalized with the potential driving force. If a subregion does not satisfy Eq. (5.26), the subregion is bisected. This procedure is repeated until each subregion satisfies Eq. (5.26) or the width of the subregion becomes smaller than a prespecified value.

In this examination, the minimum width of liquid concentration intervals was set to be 1/256, and the threshold θ was 0.1. As the rigorous thermodynamic model, Pen Robinson fluid package of Aspen HYSYS® V8.6 was applied. After the width of the subregions of benzene molar fraction in the liquid phase was initialized to be 1/32, each subregion was further divided based on the procedure described above. As a result, 72 separation modules were defined in addition to the feed, products and utility modules. The resulting stepwise VLE description is shown in Fig. 5.6.

5.4.4. Result

The first step required 0.17 seconds of CPU time and a process consisting of 70 separation modules were obtained. Heat is supplied to 13 modules and is removed from one module. The minimum utility cost, UC^* was 109 \$/h. This result was used as the initial condition for solving the MILP problem in the second step. The second step required 1.1 minutes of CPU time. The minimum number of necessary separation modules, N_{selected}^* , was 25, which is almost one-third of the number of separation modules contained in the superstructure. The obtained process is illustrated in Fig. 5.7. In this figure, thin lines indicate that the flow rate is less than 20 kmol/h. The result of the second step still involves many bypass flows. Thus, at the third step, the structure was simplified. The third step required 35 minutes of CPU time, so that the overall CPU time was 36 minutes. Figure 5.8 illustrates the obtained process, whose structure is the same as a conventional distillation column. This result suggests that, for the target distillation

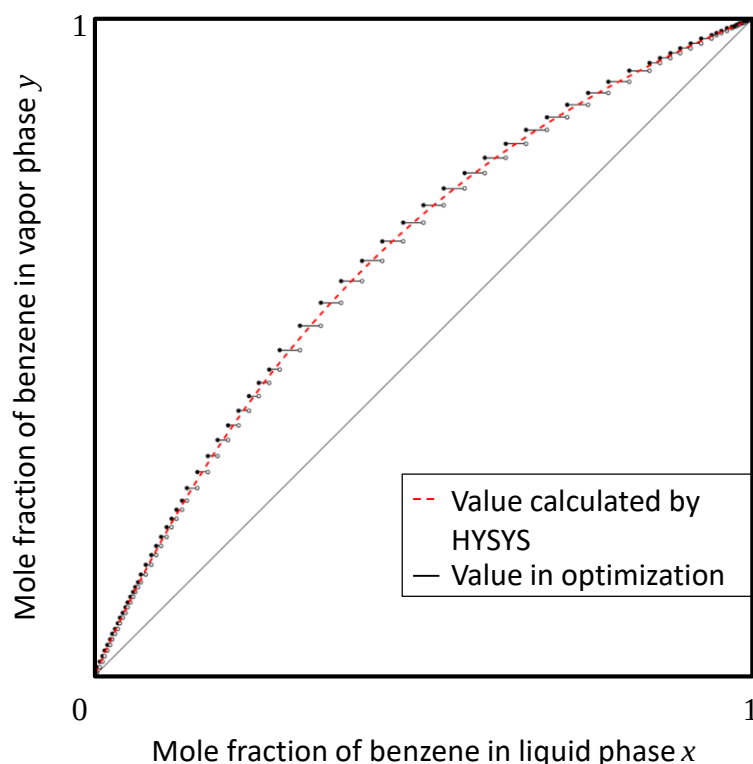


Figure 5.6 Stepwise VLE description applied in the examination

operation, we can hardly reduce the utility cost further by changing the structure: i.e. the possible reduction is just 1%.

It should be noted that such a process whose structure is a simple distillation column is usually not a feasible solution on the optimization based on state space discretization as described in the beginning of this chapter. This result demonstrates that the optimization based on the stepwise VLE description can provide a process of a simple structure properly if no better performance can be achieved by complicating the structure.

The approximation error of using stepwise VLE was verified by comparing the result with that of process simulation. The required reflux ratio to obtain the same product condition with the same number of trays as the solution in Fig. 5.8 was calculated using Aspen HYSYS® V8.6, and was compared with the result obtained by the optimization via proposed method. The value of the rigorous simulation was 1.67, whereas the reflux ratio of the process shown in Fig. 5.8 was 1.70. The relative error between them is less than 2%. This result shows that the use of stepwise VLE does not affect the result if the widths of the subregions are properly configured.

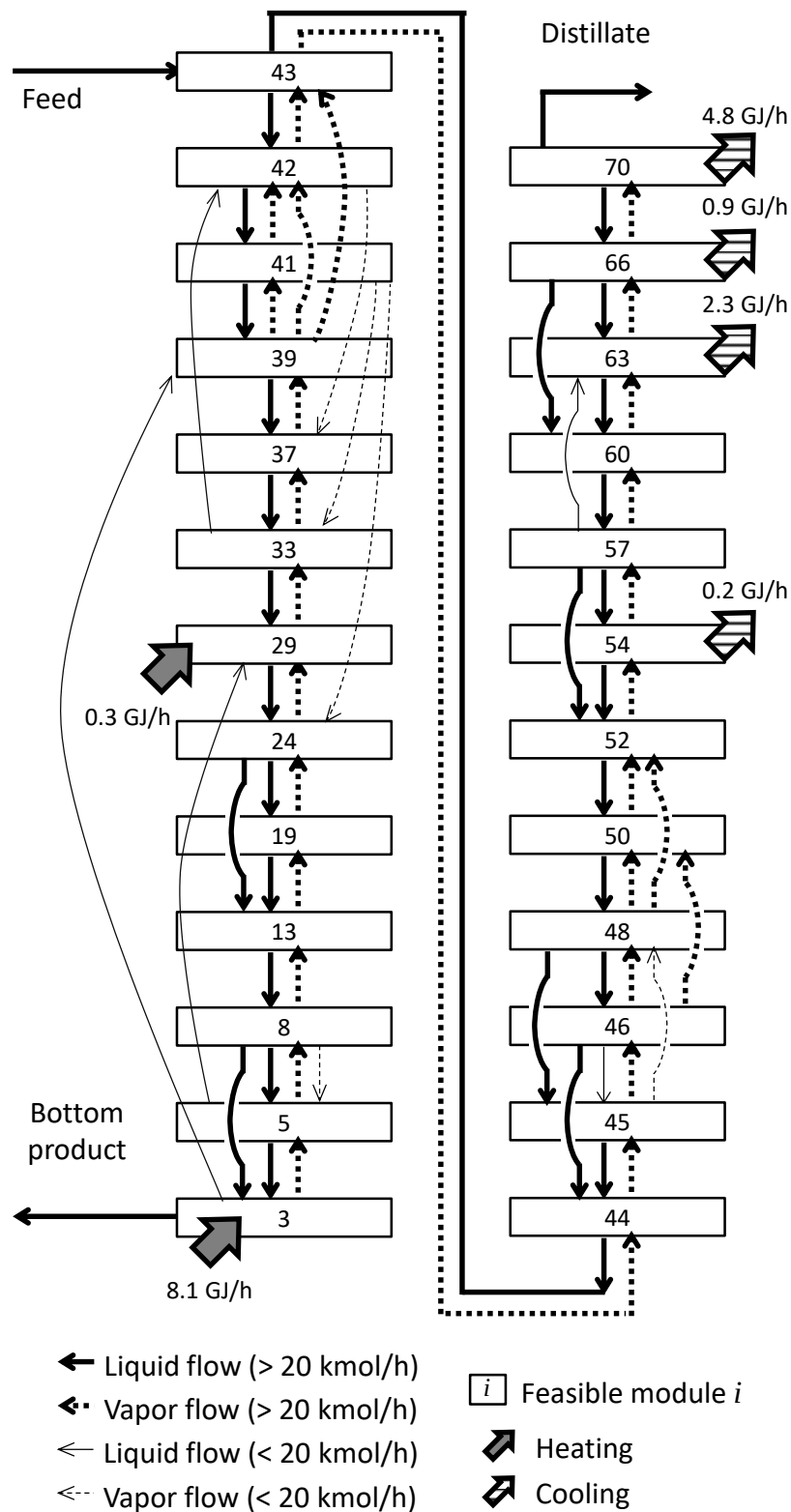


Figure 5.7 Process obtained in the second step

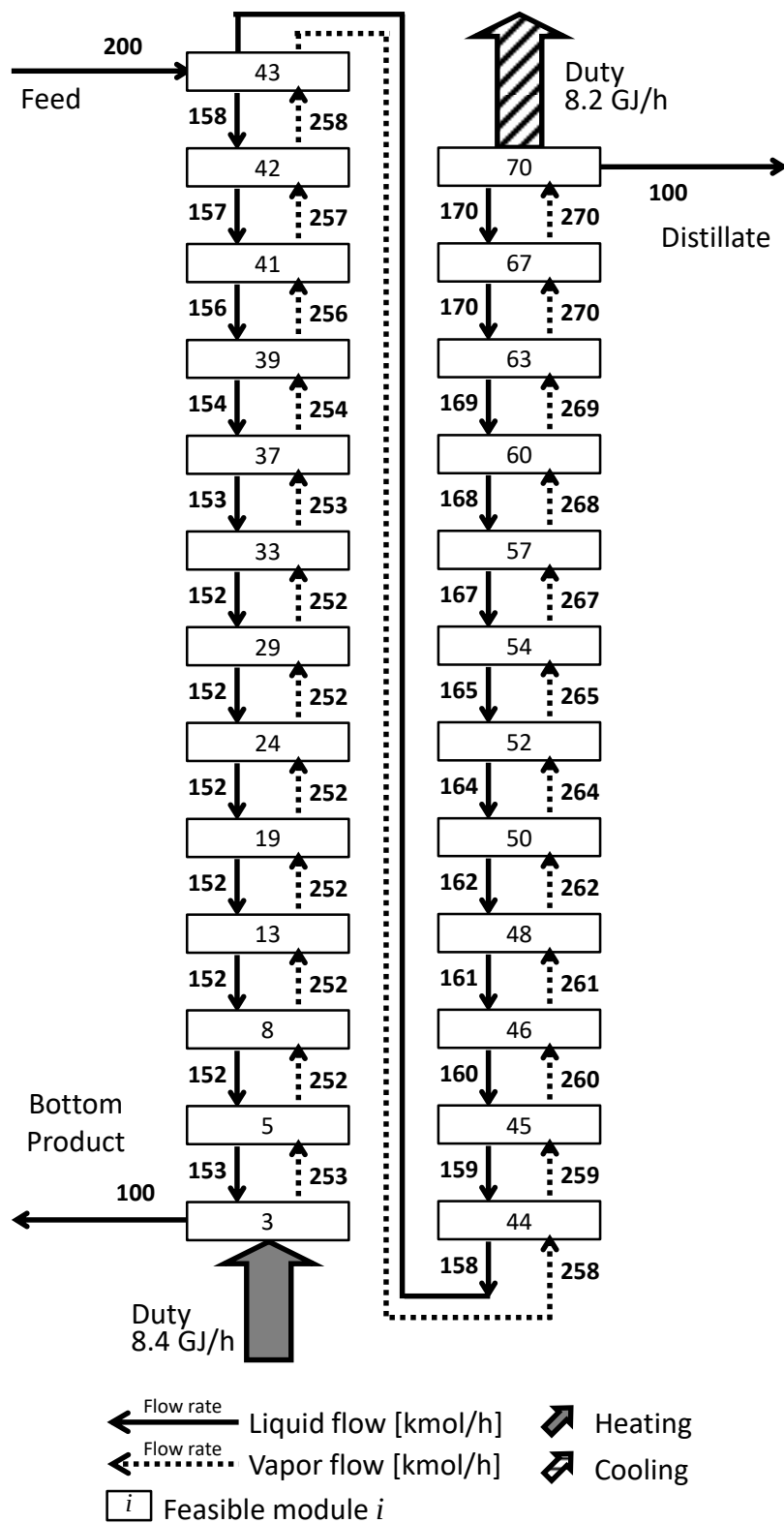


Figure 5.8 Finally obtained process

5.5. Conclusion

A new method for linear formulation of the process synthesis problem, stepwise VLE description is developed as an alternative to state space discretization. In the proposed method, the composition of the output liquid of each module is treated as a continuous variable whereas it was treated as a constant in the previous works. Because of this feature, on the optimization based on the stepwise VLE description, the material and heat balances can be satisfied without involving the secondary flows with small flow rates. In terms of the computational cost, there is no significant difference between the stepwise VLE description and the state space discretization because all constraints are linear in both approaches. The stepwise VLE description is examined through a case study dealing with the separation of benzene and toluene. The optimization is carried out through a three-step procedure, which evaluates simplicity of the process structures as well as the utility cost and the number of trays. As a result, the process structure that was the same as the conventional column was obtained. Thus, it was confirmed that simple processes without the secondary flows can be obtained when adopting the stepwise VLE description.

In this chapter, to establish the basis of a new method for the linear formulation, the design target was one of the simplest separation problem of binary mixtures. Hence, in the case study, the structure of a conventional distillation column was obtained as the optimal structure. When considering the process synthesis problems of ternary mixtures, it is expected to obtain unknown structures that are difficult to be obtained by human experiences.

Nomenclature

a_i	Slope for the linear interpolant of liquid molar enthalpy at module i [MJ kmol ⁻¹]
b_i	Intercept for the linear interpolant of liquid molar enthalpy at module i [MJ kmol ⁻¹]
c^H	Cost coefficient for hot utility [\$ MJ ⁻¹]
c^C	Cost coefficient for cold utility [\$ MJ ⁻¹]
h_i^L	Molar enthalpy of liquid flowing from module i [MJ kmol ⁻¹]
h_i^V	Molar enthalpy of vapor flowing from module i [MJ kmol ⁻¹]
L_B	Flow rate of bottom product [kmol h ⁻¹]
L_D	Flow rate of distillate [kmol h ⁻¹]
L_F	Liquid flow rate of feed [kmol h ⁻¹]
L_{ij}	Liquid flow rate from module i to module j [kmol h ⁻¹]

l_{ij}	Flow rate of the key component flowing on the liquid stream from module i to module j [kmol h ⁻¹]
M_{flow}	Sufficiently big number for material flows [kmol h ⁻¹]
M_{heat}	Sufficiently big number for heat flows [MJ h ⁻¹]
N	Number of the separation modules contained in the superstructure [-]
N_{selected}^*	Minimum number of necessary modules under the allowable utility cost [-]
Q_{ij}	Heat flow rate transferred from module i to module j [MJ h ⁻¹]
S	Set of suffixes {1, 2, ..., N }
S_{in}	Set of suffixes {1, 2, ..., N , D, B}
S_{out}	Set of suffixes {1, 2, ..., N , F}
UC^*	Minimum utility cost [\$ h ⁻¹]
V_F	Vapor flow rate of feed [kmol h ⁻¹]
V_{ij}	Vapor flow rate from module i to module j [kmol h ⁻¹]
x_i	Molar fraction of a key component in the liquid of module i [-]
x_{ij}	Molar fraction of a key component in the liquid flowing from module i to module j [-]
x_i^L	Lower bound of the molar fraction of a key component in the liquid flowing from module i [-]
x_i^U	Upper bound of the molar fraction of a key component in the liquid flowing from module i [-]
y_i	Molar fraction of a key component in the vapor of module i [-]
z_i	0-1 variable which indicates the selection of module i [-]
z_i^q	0-1 variable which indicates the equipment of a reboiler/condenser at module i [-]
w_{ij}	0-1 variable which indicates the selection of the liquid flow from module i to module j and/or the vapor flow from module j to module i [-]
θ	Allowable increase ratio of the utility cost from the minimum value [-]
λ	Threshold the maximum error normalized with the potential driving force, used on the liquid composition division [-]

References

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6. Synthesis of Distillation/Membrane Hybrid Separation Processes Using the Stepwise VLE Description

6.1. Introduction

On distillation/membrane hybrid separation, the difference in characteristics between distillation and membrane separation should be exploited in order to achieve high performance as a whole process. From this point of view, the synthesis methods for distillation/membrane hybrid separation processes are intensively investigated. Kookos (2003) proposed a superstructure-based method where the problem is formulated as an MINLP problem. In order to consider a larger number of candidate structures, Marquardt (2008) and Caballero et al. (2009) adopted two-step approach. First, some promising process structures are found out from many candidate structures using shortcut models, and then the optimal configuration is determined using MINLP models which consider only those promising structures. If the shortcut models can estimate the performances of the candidates with sufficient accuracy, this framework provides the best process of the candidates prepared in advance.

In this chapter, the synthesis procedure for distillation/membrane hybrid processes is developed using the stepwise VLE description proposed in chapter 5. In addition to the modules in chapter 5, which corresponds to a tray in distillation columns and is hereafter called D-module, membrane separation modules, which are hereafter called M-modules, are incorporated into the superstructure. Based on the state space discretization approach, the compositions of the input flow and the retentate-side output flow are assigned to each M-module, and all of the other intensive variables concerning the input and output flows are calculated before the optimization. Thus, the material and heat balances at each M-module as well as each D-module are expressed by linear equations, and the process synthesis problem is formulated as an MILP problem.

In the rest of this chapter, in section 6.2, the synthesis problem discussed in this chapter is defined. In section 6.3, the configuration of the modules is described. In sections 6.4 and 6.5, the configuration of the superstructure and the proposed optimization procedure are described. The proposed method is applied to the separation of propane-propylene in section 6.6, and the optimization result is examined using a process simulator in section 6.7. Finally, this chapter is concluded in section 6.8.

6.2. Problem statement

This research deals with the hybrid separation processes involving distillation and gas membrane separation. The synthesis problem of the hybrid processes that separate binary mixture is discussed under the following assumptions.

The flow rate and composition of the feed are given in advance. The feed is separated into two products in the process. Both products are saturated liquid and the composition of each product is given in advance. The pressure of the products is supposed to be the same as that of the feed, and is given in advance. The available membrane is characterized by the permeability and the selectivity. The thickness of the membrane and the equipment cost for the unit area of the membrane are given in advance.

In the processes, the non-negligible pressure drop occurs only when the vapor permeates the membrane. The operating pressure for the distillation is the pressure of the feed. The retentate side of the membrane separation unit is also operated at the pressure of the feed. The operating pressure of the permeate-side is optimized over the given candidate values. The permeate-side outlet stream is compressed to the operating pressure for the distillation before flowing to the distillation part or to the product stream. Since the equipment cost of a compressor is usually expensive regardless of its capacity, the hybrid processes involving more than one compressor are not considered. The membrane separation unit is supposed to be operated with the isothermal condition at the temperature of the inlet stream. The heat exchange in the process is not considered.

Under these assumptions, the process minimizing the sum of the utility cost and the membrane cost is derived without any assumption on process structure.

6.3. Configuration of the modules

6.3.1. Distillation module (D-module)

Distillation in the process is modeled by using the D-modules, which are the modules presented in chapter 5. Figure 6.1 illustrates D-module i in the superstructure. A D-module possesses two types of input flows, which are material flows and an energy flow. The input material flows are the mixture of liquid and vapor. A module has three types of output flows, which are vapor flows, liquid flows, and an energy flow. When a module has an input (output) energy flow as a result of optimization, the module functions as a reboiler (condenser).

A unique liquid composition domain is assigned to each D-module. The composition of the output liquid can change within the assigned domain, and the molar enthalpy of the output liquid is expressed by the affine function of the liquid composition. The composition and molar enthalpy of the output vapor are constants which are the mean

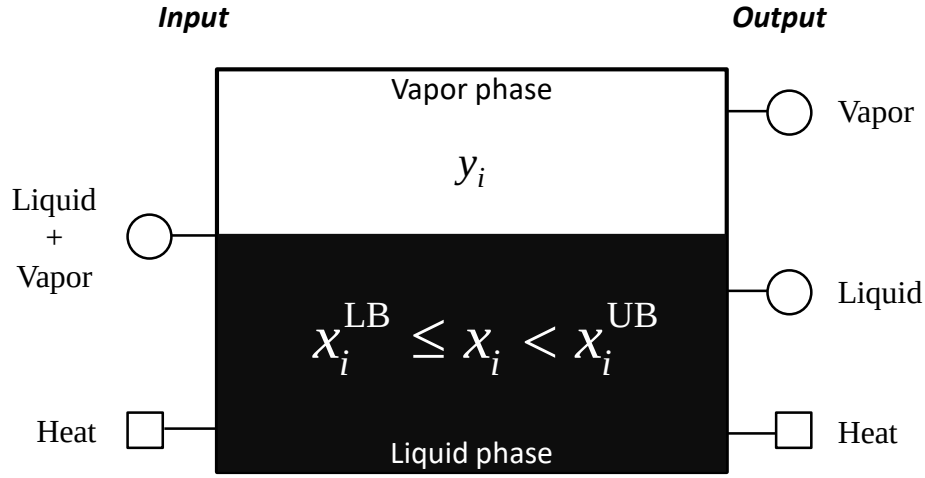


Figure 6.1 D-module i in the superstructure

values of the equilibrium values at the boundary of the assigned liquid composition domain. The more detailed description is provided in section 5.3.1.

6.3.2. Membrane separation module (M-module)

A membrane separation module (M-module) corresponds to a membrane separation unit. For the purpose of the linear formulation of the resulting optimization problem, the values of the intensive variables concerning the input and output vapor streams are specified before the optimization. By considering different input and output conditions, a set of M-modules is defined. The input to an M-module is assumed to be the vapor output of a particular D-module. It means that the input composition of each M-module is decided in advance. Even when the input composition is given, the output compositions vary with the membrane area and the operating condition. In this research, it is assumed that the retentate-side output composition of an M-module is the same as the vapor composition of one of the D-modules. Thus, the specification of an M-module is defined by assigning an ordered pair of compositions of vapor flows that are outputs of two D-modules. When considering the arbitrary ordered pair, some pairs represent impossible input-output conditions because the magnitude relationship between the input and output concentrations of each component is determined by the membrane characteristics. Such inappropriate pairs are excluded when defining the M-modules.

Figure 6.2 illustrates M-module (i, j) in the superstructure. There are two types of inputs, which are vapor input and heat input. The vapor input of M-module (i, j) is connected with the output vapor of D-module i . There are three types of outputs, which are permeate-side vapor output, retentate-side vapor output, and heat output. The vapor

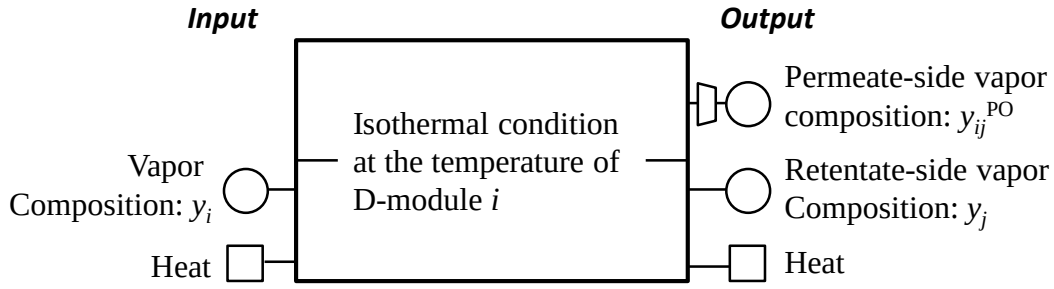


Figure 6.2 M-module (i, j) in the superstructure

composition of retentate-side output of M-module (i, j) is the same as that of the output vapor of D-module j . The pressure of the input vapor and the retentate-side vapor is the same as the operating pressure for distillation, while the pressure of the permeate-side vapor is one of its candidate values. Heat is supplied to (removed from) the M-module when heating (cooling) is needed to keep the isothermal condition on the membrane separation.

On modeling the behavior in the membrane separation unit, the countercurrent configuration shown in Fig. 6.3 is adopted and the following assumption adopted in Kookos (2003) is introduced: 1) flow conditions both in retentate side and permeate side are plug flow; 2) vapor can be treated as ideal gas; 3) permeability is independent of temperature and composition; 4) effects of condensation are negligible. Under the above assumptions, the solution-diffusion model (Wijmans and Baker, 1995) is applied to the permeation across the membrane:

$$u^1(z) = \frac{\rho^1}{\phi} [P_e^p y^p(z) - P^R y^R(z)] \quad (6.1)$$

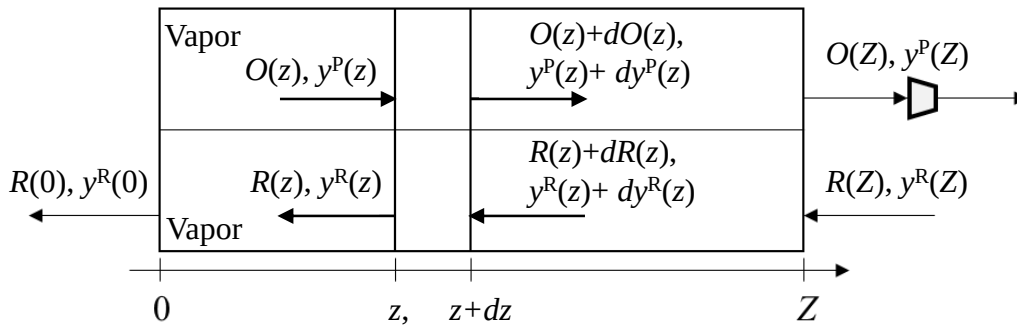


Figure 6.3 Counter-current model of membrane separation unit and a compressor

$$u^2(z) = \frac{\rho^2}{\phi} \left[P_e^p (1 - y^p(z)) - P^R (1 - y^R(z)) \right] \quad (6.2)$$

where $u^k(z)$ is the flux of component k through the membrane at position z , ρ^k is permeability of component k . Components 1 and 2 refer to the light and heavy components, respectively. ϕ is the thickness of the membrane, P_e^p is candidate permeate-side pressure, P^R is the retentate-side pressure, $y^p(z)$ is the vapor molar fraction of the light component at position z in the permeate side, $y^R(z)$ is the vapor molar fraction of the light component at position z in the retentate side. To avoid the confusion of description, the subscripts that identify the module are not shown for these variables in this section.

The total material balances for the permeate and retentate sides in the shell between z and $z + dz$ are expressed as

$$dO(z) = \left[\sum_{k=1}^2 u^k(z) \right] \omega dz \quad (6.3)$$

$$dR(z) = \left[\sum_{k=1}^2 u^k(z) \right] \omega dz \quad (6.4)$$

where ω is the width of the membrane, $O(z)$ and $R(z)$ are the flow rates at position z in the permeate and retentate sides, respectively. The corresponding light-component balances are expressed as

$$y^p(z) dO(z) + O(z) dy^p(z) = u^1(z) \omega dz \quad (6.5)$$

$$y^R(z) dR(z) + R(z) dy^R(z) = u^1(z) \omega dz. \quad (6.6)$$

In addition, the total material balance and the light-component balance between positions 0 and z in retentate side is expressed as

$$R(z) = R(0) + O(z) \quad (6.7)$$

$$R(z) y^R(z) = R(0) y^R(0) + O(z) y^p(z) \quad (6.8)$$

Equations (6.9) to (6.11) are derived from Eqs. (6.3) to (6.8).

$$O(z) dy^p(z) = \left[u^1(z) - y^p(z) \sum_{k=1}^2 u^k(z) \right] \omega dz \quad (6.9)$$

$$R(z) dy^R(z) = \left[u^1(z) - y^R(z) \sum_{k=1}^2 u^k(z) \right] \omega dz \quad (6.10)$$

$$\frac{O(z)}{R(z)} = \frac{y^R(z) - y^R(0)}{y^P(z) - y^R(0)} \quad (6.11)$$

From these three equations, the Eq. (6.12) is obtained.

$$\frac{dy^P(z)}{dy^R(z)} = \frac{[y^P(z) - y^R(0)] \left[u^1(z) - y^P(z) \sum_{k=1}^2 u^k(z) \right]}{[y^R(z) - y^R(0)] \left[u^1(z) - y^R(z) \sum_{k=1}^2 u^k(z) \right]} \quad (6.12)$$

Since $u^k, k \in \{1,2\}$, can be regarded as a function of y^P and y^R , Eq. (6.12) can be treated as an ordinary differential equation with y^P and y^R :

$$\frac{dy^P}{dy^R} = \frac{[y^P - y^R(0)] \left[u^1(y^P, y^R) - y^P \sum_{k=1}^2 u^k(y^P, y^R) \right]}{[y^R - y^R(0)] \left[u^1(y^P, y^R) - y^R \sum_{k=1}^2 u^k(y^P, y^R) \right]} \quad (6.13)$$

Thus, through numerically solving Eq. (6.13) with the boundary condition of Eq. (6.14), the light-component molar fraction of the permeate-side output of M-module (i, j), y_{ij}^{PO} , can be calculated from the light-component molar fractions for the vapor of D-modules i and j , y_i and y_j , which are assigned as the input and the retentate-side output compositions, respectively.

$$\begin{cases} y^P = \frac{u^1(y^P, y^R)}{\sum_{k=1}^2 u^k(y^P, y^R)} & \text{when } y^R = y_j \\ y^P = y_{ij}^{PO} & \text{when } y^R = y_i \end{cases} \quad (6.14)$$

Since the operating pressures of both sides and the operating temperature are already specified, the vapor molar enthalpies of the input and the outputs can be calculated based on their compositions. By using a process simulator, the molar enthalpy of the permeate-side output vapor after the compression can be calculated as well based on the composition, temperature, and pressures.

The differential equation for calculating the membrane area per unit flow rate of retentate-side output, $\omega Z / R(0)$, also can be derived from Eqs. (6.7) to (6.9). First, Eq. (6.15) is obtained from Eqs. (6.7) and (6.8).

$$R(z) = \frac{y^P(z) - y^R(0)}{y^P(z) - y^R(z)} R(0) \quad (6.15)$$

From this equation and Eq. (6.9) , the following ordinary differential equation is obtained.

$$\left(\frac{\omega}{R(0)} \right) dz = \frac{y^P(z) - y^R(0)}{\left[y^R(z) - y^R(0) \right] \left[u^1(z) - y^R(0) \sum_{k=1}^2 u^k(z) \right]} \quad (6.16)$$

For M-module (i, j) , the boundary condition is specified with the light-component molar fraction for the vapor of D-modules i and j ; $z = 0$ when $y^R = y_j$, and $z = Z$ when $y^R = y_i$. Consequently, by calculating Eq. (6.16) together with Eq. (6.13), the membrane area requested for the unit flow rate of retentate-side output, α_{ij} , is obtained.

6.4. Configuration of the superstructure

Figure 6.4 describes the adopted superstructure. Each of the D-modules and M-modules is divided into two sections to identify the flow connection easily. For the same purpose, only the flow paths related to D-module i and/or M-module (i, j) are depicted

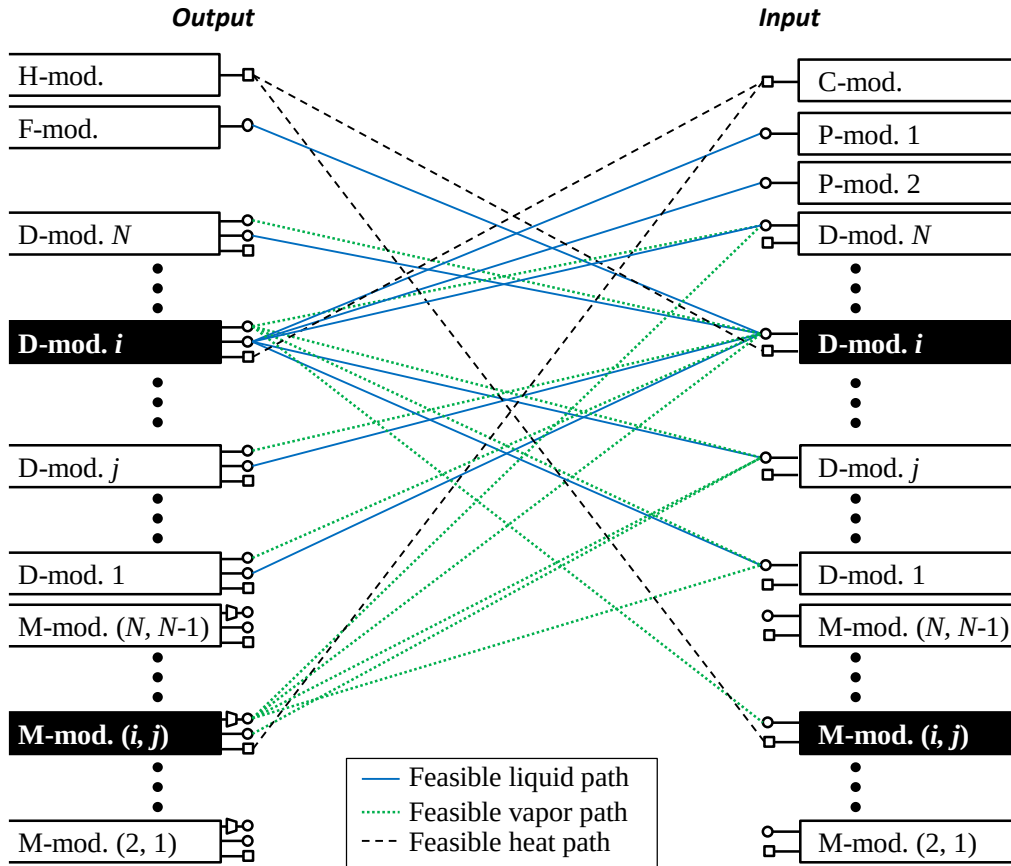


Figure 6.4 Superstructure adopted in this research

and the other flow paths are omitted. The input and output parts of the modules are shown in right-hand side and left-hand side, respectively. The solid lines, dotted lines, and dashed lines among the nodes are liquid flows, vapor flows, and energy flows, respectively. The hot (cold) utility is treated as a special module, H-module (C-module), which possesses only a heat output (input). The feed and products are also treated as special modules, F-module and P-modules, respectively. F-module possesses only a material output while P-modules possesses only a material input.

The material input of D-module i is connected with the material output of the F-module, the liquid and vapor outputs of the other D-modules, the permeate-side outputs of all M-modules. The retentate-side vapor outputs of the M-modules whose composition is the same as the output vapor composition of D-module i is also connected with the material input of D-module i . The vapor output of D-module i is connected with the material input of the P-modules, the material inputs of the other D-modules, and the vapor inputs of the M-modules whose compositions are the same as the output vapor composition of D-module i . The heat input and output of D-module i is connected with the H-module and the C-module, respectively. Thus, the total material balance, the light-component balance, and the heat balance at D-module i are expressed as

$$\begin{aligned} \sum_{j \in S} (L_{ji} + V_{ji}) + \left(\sum_{j \in \bar{S}_i} V_{ji}^R + \sum_{i' \in S} \sum_{j' \in \bar{S}_{i'}} V_{i'j'}^P \right) + F_{Fi} \\ - \sum_{j \in S} (L_{ij} + V_{ij}) - \sum_{j \in \bar{S}_i} V_{ij}^I - \sum_{k=1}^2 L_{i,P(k)} = 0, \quad \forall i \in S \end{aligned} \quad (6.17)$$

$$\begin{aligned} \sum_{j \in S} (l_{ji} + y_j V_{ji}) + \left(\sum_{j \in \bar{S}_i} y_j V_{ji}^R + \sum_{i' \in S} \sum_{j' \in \bar{S}_{i'}} y_{i'j'}^{PO} V_{i'j'}^P \right) + F_{Fi} x_F \\ - \sum_{j \in S} (l_{ij} + y_i V_{ij}) - \sum_{j \in \bar{S}_i} y_i V_{ij}^I - \sum_{k=1}^2 l_{i,P(k)} = 0, \quad \forall i \in S \end{aligned} \quad (6.18)$$

$$\begin{aligned} \sum_{j \in S} (a_j l_{ji} + b_j L_{ji} + h_j^V V_{ji}) + \left(\sum_{j \in \bar{S}_i} h_{ji}^{V,R} V_{ji}^R + \sum_{i' \in S} \sum_{j' \in \bar{S}_{i'}} (h_{i'j'}^{V,P} + \Delta h_{i'j'}^{V,P}) V_{i'j'}^P \right) + F_{Fi} h_F \\ - \sum_{j \in S} (a_i l_{ij} + b_i L_{ij} + h_j^V V_{ij}) - \sum_{j \in \bar{S}_i} h_j^V V_{ij}^I - \sum_{k=1}^2 (a_i l_{i,P(k)} + b_i L_{i,P(k)}) \\ + Q_{Hi} - Q_{Ci} = 0, \quad \forall i \in S \end{aligned} \quad (6.19)$$

where S is the set of suffixes that indicate the set of D-modules; i.e. $S = \{1, 2, \dots, N\}$. $\bar{S}_i$

and $\bar{S}_i$ are subsets of S . S_i and $\bar{S}_i$ contain only the suffixes for which M-modules (i, j) and (j, i) exist, respectively. L_{ij} and V_{ij} for $j \in S$ are liquid and vapor flow rates from D-module i to D-module j , respectively. V_{ji}^R and V_{ij}^I are the vapor flow rate from the retentate-side output of M-module (j, i) to D-module i and that from D-module i to M-module (i, j) , respectively. V_{ij}^{PO} is the vapor flow rate from the permeate-side output of M-module (i, j') to D-module i . Q_{Hi} and Q_{iC} are the heat flow rate from the H-module to D-module i and from D-module i to the C-module, respectively. l_{ij} for $j \in S$ is the flow rate of the light component transported by liquid stream from D-module i to D-module j . y_j is the molar fraction of the light component in the output liquid from D-module j . y_j^{PO} is the molar fraction of the light component of the permeate-side output flows from M-module (i, j) . h_i^V is the molar enthalpy of output vapor from module i , $h_{ij}^{V,R}$ and $h_{ij}^{V,P}$ are the molar enthalpies of retentate-side and permeate-side output vapor from M-module (i, j) , respectively. a_i and b_i are the coefficients for describing the liquid molar enthalpy of D-module i as an affine function of the liquid molar fraction. The suffixes F and P(k) represents the F-module and P-module k , so that F_{Fi} , $L_{i,P(k)}$, and $l_{i,P(k)}$ are the flow rate of the feed supplied to D-module i , the liquid flow rate from D-module i to P-module k , and the flow rate of the light component transported by the liquid stream from D-module i to P-module k . Inequality constraints are imposed on l_{ij} based on the liquid composition domain assigned to D-module i :

$$L_{ij}x_i^{LB} \leq l_{ij} < L_{ij}x_i^{UB}, \quad \forall i \in S, \quad \forall j \in S \cup \{P(1), P(2)\} \quad (6.20)$$

where x_i^{UB} and x_i^{LB} are the upper and lower bounds of the liquid molar fraction of the light component specified by the liquid composition domain.

The vapor input and retentate-side output of M-module (i, j) are connected only with the vapor output of D-modules i and the material input of D-module j , respectively, while the permeate output is connected with the material inputs of all D-modules. The heat input and output of M-module (i, j) is connected with the H-module and the C-module, respectively. Thus, the total material balance, the light-component balance, and the heat balance at M-module (i, j) are expressed as

$$V_{ij}^I - V_{ij}^R - \sum_{i' \in S} V_{iji'}^P = 0, \quad \forall i \in S, j \in S_i \quad (6.21)$$

$$y_i V_{ij}^I - y_j V_{ij}^R - \sum_{i' \in S} y_j^{PO} V_{iji'}^P = 0, \quad \forall i \in S, j \in S_i \quad (6.22)$$

$$h_j^V V_{ij}^I + Q_{Hij} - h_{ij}^{V,R} V_{ij}^R - \sum_{i' \in S} h_{ij}^{V,P} V_{iji'}^P - Q_{ijC} = 0, \quad \forall i \in S, j \in S_i \quad (6.23)$$

where Q_{Hij} and Q_{ijC} are the heat flow rates from the H-module to M-module (i, j) and from M-module (i, j) to C-module. Since the number of compressors are supposed to be one or zero, the number of M-modules selected by the optimization is restricted to be one or zero using 0-1 variables z_i^I and z_i^R :

$$\sum_{j \in S_i} V_{ij}^I \leq M z_i^I, \quad \forall i \in S \quad (6.24)$$

$$\sum_{i \in \bar{S}_j} V_{ij}^I \leq M z_j^R, \quad \forall j \in S \quad (6.25)$$

$$\sum_{i \in S} z_i^I = \sum_{j \in S} z_j^R = 1 \quad (6.26)$$

where M is a sufficiently large number. When M-module (i, j) is selected, both z_i^I and z_i^R take one and the other 0-1 variables take zero, so that the other M-modules cannot be selected.

The material output of the F-module is connected with the material inputs of all D-modules. The material input of the P-modules are connected with the liquid outputs of all D-modules. Thus, the total material balance at the F-module is expressed by Eq. (6.27) while the total material balance and the light-component balance at P-module k are expressed by Eqs. (6.28) and (6.29), respectively.

$$\sum_{j \in S} F_{Fj} = F_F \quad (6.27)$$

$$\sum_{j \in S} L_{j,P(k)} = L_{P(k)} \quad (6.28)$$

$$\sum_{j \in S} l_{j,P(k)} = x_{P(k)} L_{P(k)} \quad (6.29)$$

where F_F , $L_{P(k)}$, and $x_{P(k)}$ are the flow rate of the feed, flow rate of product k , and the molar fraction of the light component for product k , which are given as the design condition.

Finally, the process synthesis problem where the permeate-side pressure for membrane separation is specified to be one of the candidate values is formulated as an

MILP problem:

$$\begin{aligned}
\min \quad & c_H \sum_{i \in S} \left(Q_{Hi} + \sum_{j \in S_i} Q_{Hij} \right) + c_C \sum_{i \in S} \left(Q_{iC} + \sum_{j \in S_i} Q_{ijC} \right) \\
& + c_E \sum_{i \in S} \sum_{j \in S_i} \sum_{i' \in S} \Delta h_{i',j}^{V,P} V_{iji'}^P + c_M \sum_{i \in S} \sum_{j \in S_i} \alpha_{ij} V_{ij}^R
\end{aligned} \tag{6.30}$$

s.t. Eqs. (6.17) to (6.29)

where the non-negativity constraints on all continuous variables and the integrality constraints on all 0-1 variables are imposed. c_H , c_C , c_E , and c_A are the cost coefficients for the hot utility, the cold utility, the electricity, and the membrane. Thus, the objective function expresses the sum of the hot and cold utility costs, the cost of electricity for the compressor, and the membrane equipment cost.

6.5. Optimization procedure

The MILP problem expressed by Eq. (6.30) needs long computational time due to its size while its LP relaxation can be solved much more quickly. For solving the MILP problem in terms of all candidate values of the permeate-side pressure on the membrane separation, very long calculation time is required. To obtain the optimal process over all of the candidate pressures more efficiently, the following procedure is adopted in this research.

- 1) Solve the LP relaxations of the MILP problems of Eq. (6.30) as for all candidate pressures.
- 2) Rank the candidate pressures in ascending order of the obtained objective values.
- 3) $m = 1$.
- 4) Solve the MILP problem of Eq. (6.30) for the m th-rank candidate pressure and regard the result as the tentative optimal solution. $m = m+1$.
- 5) If the objective value of the LP relaxation problem for the m th-rank candidate pressure is worth than the tentative optimal value, stop the calculation. The current tentative optimal solution is the best solution.
- 6) Solve the MILP problem of Eq. (6.30) for the m th-rank candidate pressure. If the result is better than the current tentative optimal solution, regard the obtained result as the current tentative optimal solution.
- 7) If m is equal to the number of candidate pressures, stop the calculation. The current tentative optimal solution is the best solution. Otherwise $m = m + 1$ and

go back to step 5.

By adopting this procedure, the final solution is expected to be obtained by solving a fewer number of the MILP problems, especially when the objective value strongly depends on the permeate-side pressure.

6.6. Case study

The proposed method is applied to the separation of propane and propylene, which is a typical separation with low relative volatility. The design condition adopted by Kookos (2003) and Kanezashi et al. (2012) shown in Table 6.1 is applied. The candidates for the permeate-side pressure on the membrane separation are 2 bar, 4 bar, 6 bar, and 8 bar. In the superstructure, 172 of feasible D-modules and 14706 of M-modules were contained.

First, the LP relaxation of the MILP problem in Eq. (6.30) was solved for each candidate pressure. The obtained objective values are plotted by white circles in Fig. 6.5. The results of the relaxation problems showed that 6 bar is the first-rank candidate. Thus, the MILP problem for 6 bar was solved. As the obtained objective value plotted by a cross mark in Fig. 6.5 was better than the results of the other relaxation problems, the solution of 6 bar is adopted as the final result. Figure 6.6 illustrates the structure of the finally obtained process, which includes 169 D-modules. In this figure, the liquid flows are

Table 6.1 Design condition

Feed flow rate	100 kmol/h
Propylene concentration in the feed	91.2 mol%
Feed temperature	43.3°C
Pressure for distillation	20.4 bar
Propylene concentration in product 1	98.0 mol%
Propylene concentration in product 2	16.0 mol%
Unit cost of hot utility (130°C steam)	5.0×10^{-3} \$/kg
Unit cost of cold utility (input 25°C, output 35°C)	1.5×10^{-5} \$/kg
Unit cost of electricity	0.04 \$/kWh
Unit cost of membrane	100 \$/m ²
Life time of membrane	2.5 years
Membrane selectivity of propylene against propane (ρ^1 / ρ^2)	30
Membrane permeability coefficient of propylene including the membrane thickness (ρ^1 / ϕ)	1.78×10^{-2} kmol m ⁻² h ⁻¹ bar ⁻¹

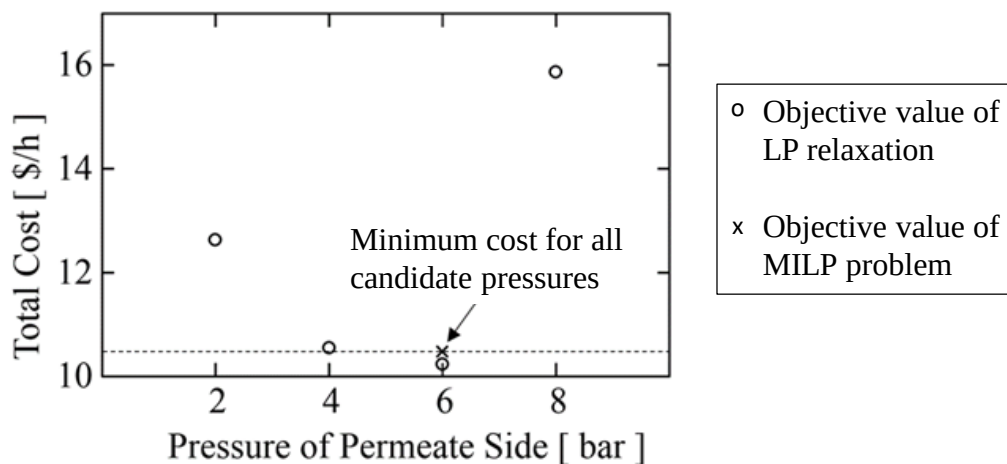


Figure 6.5 Result of optimization concerning permeate-side pressure of membrane separation unit

shown at the left-hand side of D-modules, and the vapor flows are shown at the right-hand side. Bold lines indicate that the flow rate is larger than 40 kmol/h, and thin lines indicate that the flow rate is between 40 kmol/h and 5 kmol/h. When the flow rate is less than 5 kmol/h, such flows are not depicted in the figure.

6.7. Conceptualization of a new process structure based on the optimization result

In Fig. 6.6, the structure consisting of D-modules can be classified into two groups. By omitting some flows among the D-modules, the structure shown in Fig. 6.6 can be simplified to the structure shown in Fig. 6.7. The simplified structure consists of two columns and one membrane unit with a compressor. The numbers of trays of columns 1 and 2, and the membrane area of the membrane separation unit were specified based on the optimization result as 147, 18, and 1160 m², respectively.

The simplified process was simulated by using Aspen HYSYS® V8.6. The comparison of the optimization result and the simulation result is summarized in Table 6.2. The total cost consisting of the utility costs and the membrane equipment cost obtained by HYSYS simulation is 0.6 % larger than that obtained by the proposed optimization procedure.

To evaluate the performance of newly obtained structure, the total cost of the simplified hybrid process shown in Fig. 6.7 was compared with that of the conventional distillation process consisting of a single distillation column. As shown in Table 6.2, the total cost of the hybrid process is significantly smaller than that of a single distillation column.

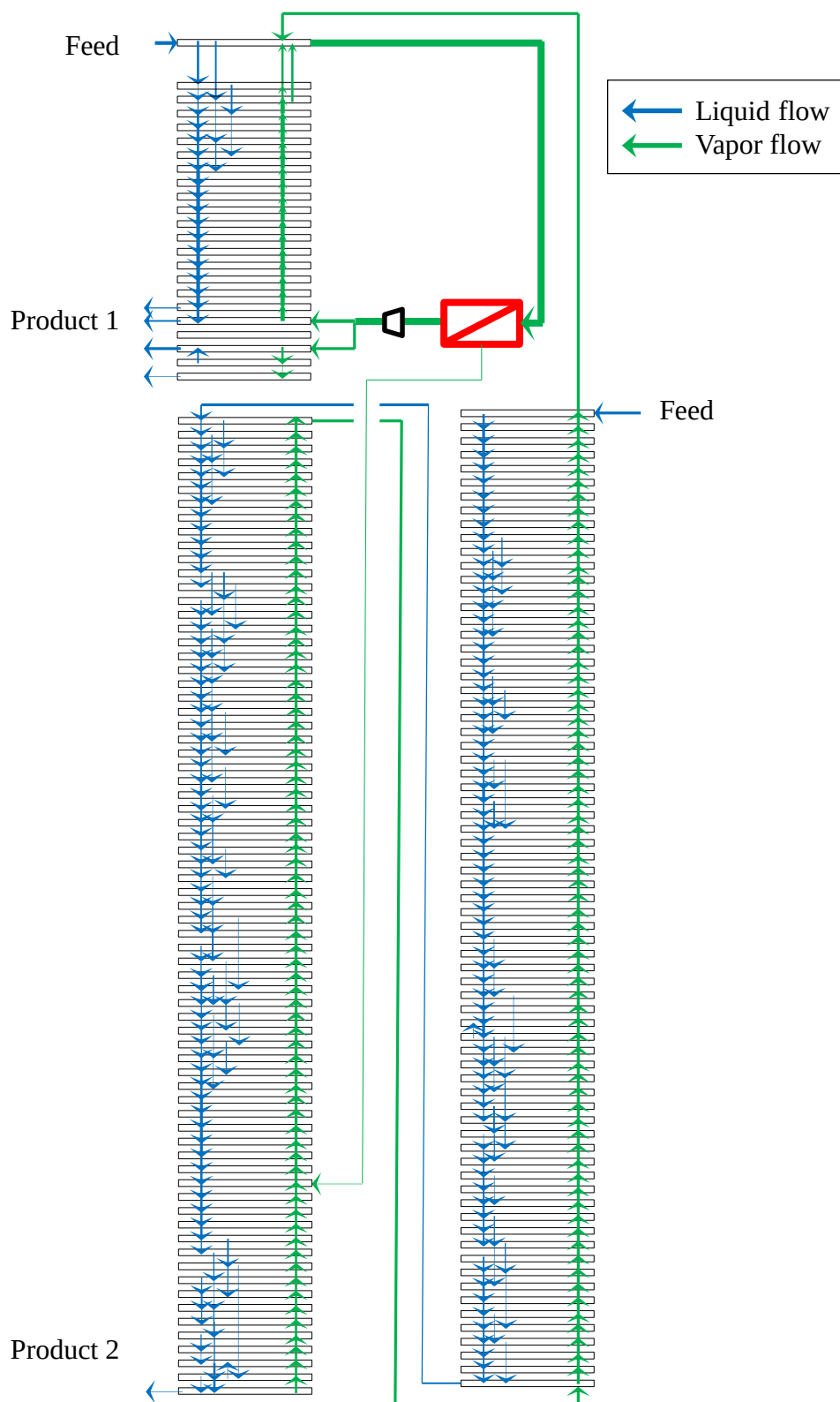


Figure 6.6 Process obtained by the optimization

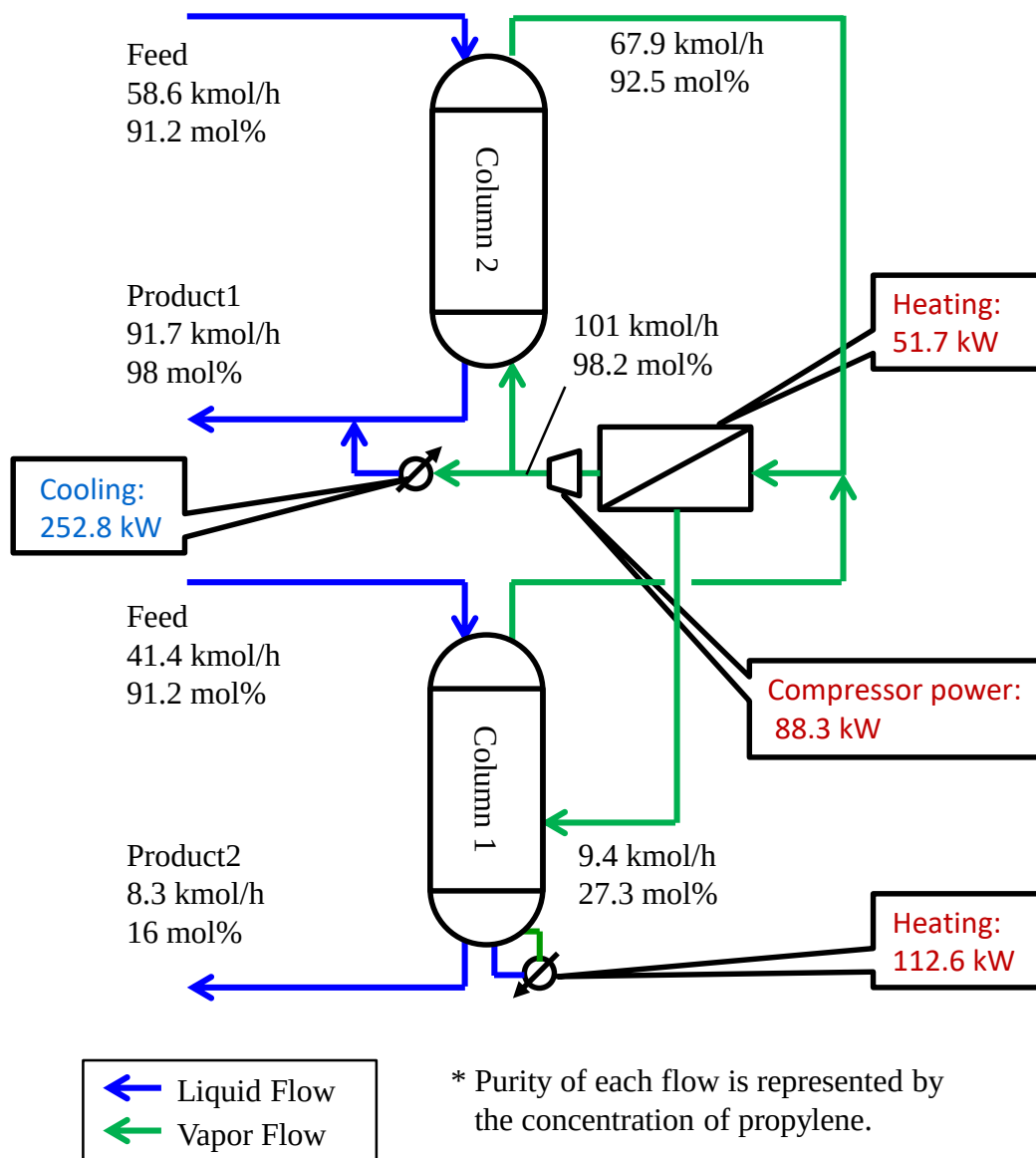


Figure 6.7 A process conceptualized based on the optimization result in Fig. 6.6

When using only distillation, a large number of trays are needed to obtain a high purity product. On the other hand, if the product specification is not so severe, the product can be easily obtained with a small number of trays. In this case study, as the specification of product 2 is loose, product 2 is withdrawn directly from column 1 in the proposed hybrid structure. It is impossible to achieve the specifications of product 1 and product 2 simultaneously only by using a membrane separation unit in this case study. Thus, distillation is needed in addition to the membrane separation unit. Figure 6.8 illustrates a possible configuration which consists of a membrane separation unit and a distillation column. Column 3 supplies product 2, while the membrane separation unit purifies

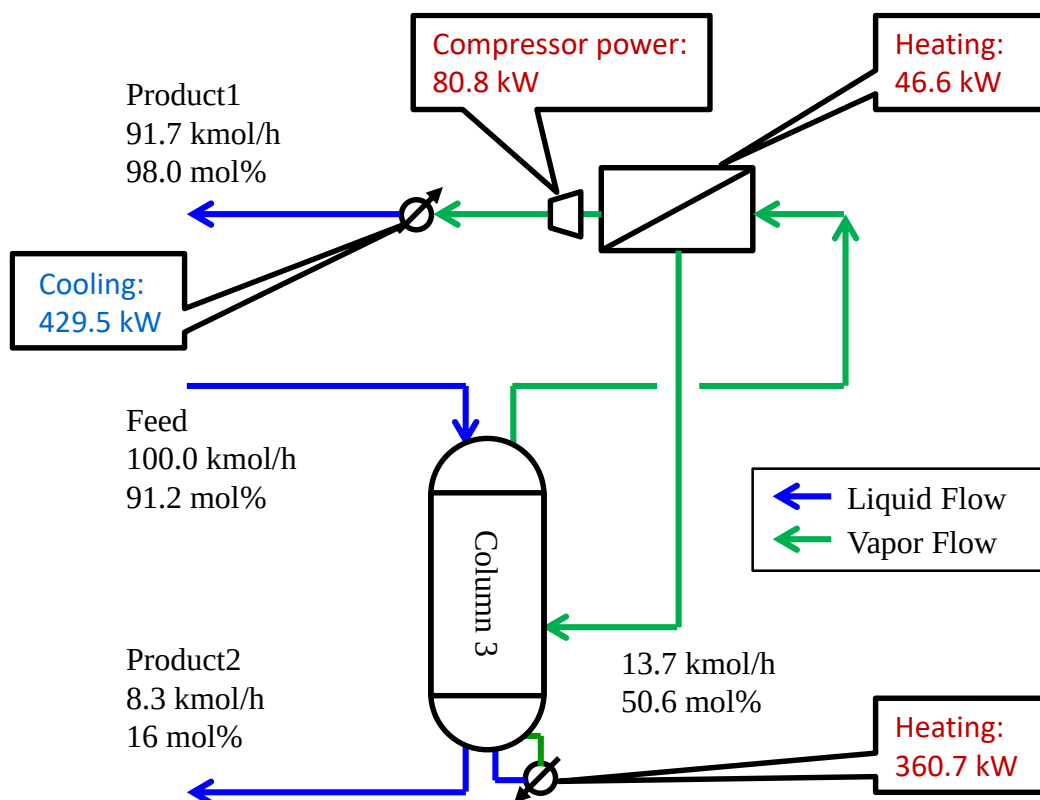
Table 6.2 Comparison of costs of a conventional distillation process simulated by HYSYS, the optimization result, and the conceptualized hybrid process simulated by HYSYS

	Distillation only		Optimization result		Simulation by HYSYS	
	quantity	cost	quantity	cost	quantity	cost
Steam	13.3	29.5	0.59	1.31	0.61	1.36
cooling water	13.3	4.73	0.91	0.32	0.93	0.33
electricity	—	—	0.32	3.53	3.18	3.53
membrane	—	—	1160	5.32	1160	5.32
area						
total cost	—	34.2	—	10.5	—	10.5
Unit; quantity [GJ/h or m ²] cost [\$/h]						

propylene and supplies product 1. The number of trays of column 3 is the same as that of column 2 in Fig. 6.7, 147, and the membrane area is also same as that of the process in Fig. 6.7.

In contrast to the process in Fig. 6.8, as shown in Fig. 6.7, the process induced by the optimization result includes column 2, in addition to column 1 which supplies product 2. The inlets of column 2 are the feed to the hybrid separation process and the permeate-side outlet vapor of the membrane separation unit. The feed is saturated liquid and is introduced at the top of column 2. The super-heated vapor from the membrane separation unit is introduced at the bottom. Both the purity and the flow rate of the vapor are slightly greater than those of product 1. Because of this unusual inlet condition, in column 2, the concentration of the light component, propylene, increases from the top to the bottom instead of from the bottom to the top. The outlet vapor from the top of column 2 is saturated vapor which is slightly richer in propylene than the feed. The outlet liquid from the bottom is retrieved as a part of product 1. Thus, column 2 “mixes” the feed and the over-purified vapor. Hereafter, this column is referred to as a “mixing column”.

The operation in the mixing column can be visualized in the manner of the McCabe-Thiele method. Figures 6.9 and 6.10 illustrate the input-output condition of the mixing column and the corresponding operating line on the x - y diagram, respectively. It should be noted that the operating line in Fig. 6.10 is positioned over the VLE curve on the x - y diagram. The gradient of the line depends on the composition of liquid and vapor, and it is also equal to the ratio of liquid flow rate to the vapor flow rate, i.e. L/V . As the relative volatility is smaller, the gradient of the operating line can be larger. In other words, the



* Purity of each flow is represented by the concentration of propylene.

Figure 6.8 A process consisting of a membrane separation unit and a distillation column

liquid flow rate per unit vapor flow rate can be larger. Thus, the mixing column is suited for systems with low relative volatility. This is one of the primal reasons why the process structure containing a mixing column was implied in this case study, which deals with a typical separation of low relative volatility.

The mixing through column 2 is seemingly inefficient because the objective of the process is the separation of the components. The incorporation of column 2, however, improves energy efficiency under the condition of this case study. With assuming the primary energy consumption for the compression is 2.73 times larger than the compressor duty, the process in Fig. 6.7 saves 35% of energy compared to the process in Fig. 6.8. The mixing column contributes the reduction of energy consumption with its function as a heat pump. On the condition of this case study, the membrane separation unit can process only vapor while the feed and the products of the process are liquid. In other words, the feed must be vaporized before being introduced into the membrane separation unit and the outlet vapor must be condensed before being retrieved as a product. In Fig. 6.8, the

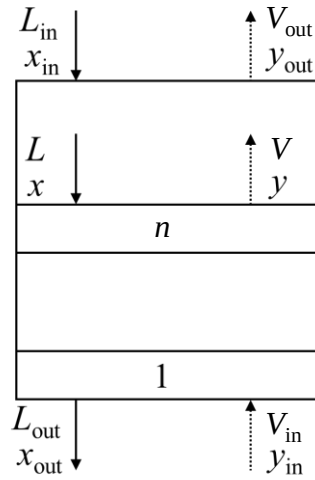


Figure 6.9 Liquid and vapor flow connections in the mixing column

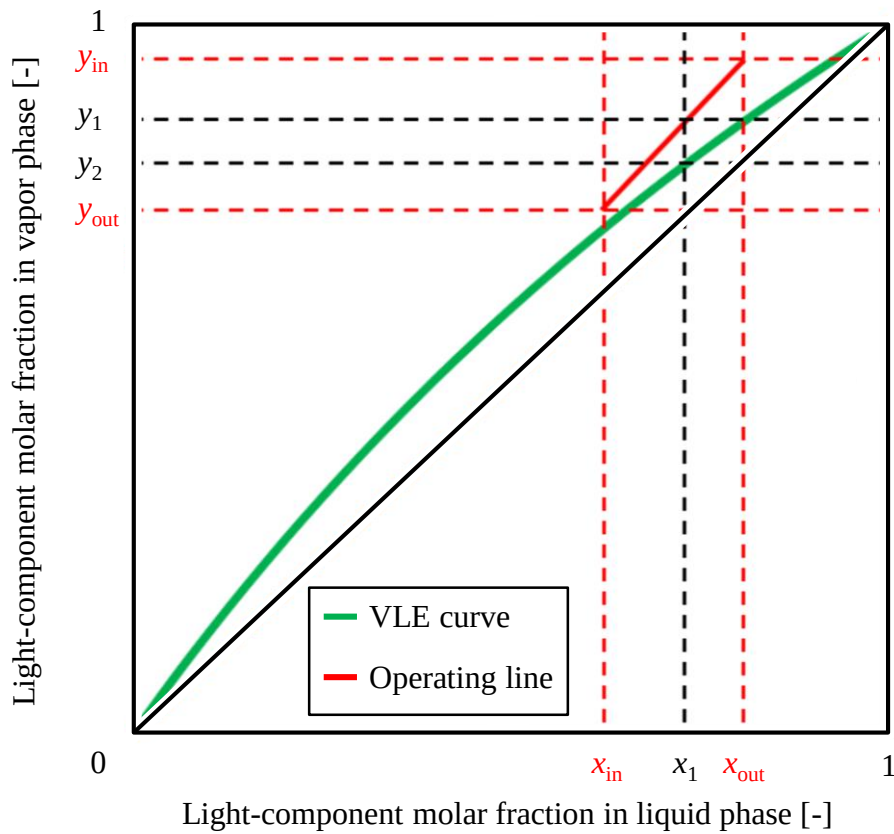


Figure 6.10 Operating line of the mixing column (red line)

feed is vaporized by the heat originally supplied at the reboiler of column 3, and product 1 is obtained through cooling the permeate-side outlet vapor. It should be noted that, without heat pumps, the latent heat of the permeate-side outlet vapor cannot be directly

utilized for the vaporization of the feed. This is because the permeate-side outlet vapor is richer in the light component than the feed and the pressure of the vapor after the compression is identical to the pressure of the feed. In contrast, by incorporating the mixing column, the liquid feed and the permeate-side outlet vapor are converted to the vapor and liquid with similar compositions, respectively, without any heating and cooling. Thus, by adopting the mixing column, although the permeate-side outlet vapor is needed to be slightly over-purified, the overall energy efficiency of the hybrid separation process is improved as a result of the significant decrease of the heating duty.

6.8. Conclusion

The synthesis procedure of distillation/membrane hybrid separation processes is developed using the stepwise VLE description, which is proposed in chapter 5. D-modules are generated based on the stepwise VLE description approach. The membrane separation process is modeled using a set of M-modules. The superstructure is constructed using these modules, and the process synthesis problem under a particular set of operating pressures is formulated as an MILP problem. The operating pressure for the permeate side of the membrane separation unit is optimized over the given candidate values in the outer loop. A computationally efficient procedure for this outer-loop optimization is also developed.

The developed method was applied to the separation problem of a propane-propylene mixture. The result of case study showed a new process structure containing a mixing column, which functions as a heat pump and improves the energy efficiently as a whole separation process. The feasibility of the obtained process and its efficiency on the energy conservation were validated using a process simulator. The simulation result showed that the proposed process may potentially reduce the 68 % of energy consumption compared with a conventional process consisting of a single distillation column.

The result involving a mixing column indicated the importance of the heat exchange between the liquid feed and the permeate-side outlet of the membrane separation unit. Such a heat exchange can be realized not only by incorporating the mixing column but also by compressing the outlet vapor to a higher pressure than the pressure of the liquid feed. The consideration of such an operation is beyond the contents of this paper and is regarded as an important issue for future research.

Nomenclature

a_i	Slope for the linear interpolant of liquid molar enthalpy at D-module i [MJ kmol ⁻¹]
b_i	Intercept for the linear interpolant of liquid molar enthalpy at D-module i [MJ kmol ⁻¹]
c_H	Cost coefficient of the hot utility [\$ MJ ⁻¹]
c_C	Cost coefficient of the cold utility [\$ MJ ⁻¹]
c_E	Cost coefficient of the electricity [\$ MJ ⁻¹]
c_M	Cost coefficient of the membrane equipment [\$ m ⁻² h ⁻¹]
F_F	Flow rate of the feed [kmol h ⁻¹]
F_{Fi}	Flow rate F-module to D-module i [kmol h ⁻¹]
h_F	Molar enthalpy of the feed [MJ kmol ⁻¹]
h_i^V	Molar enthalpy of the output vapor of D-module i [MJ kmol ⁻¹]
$h_{ij}^{V,P}$	Molar enthalpy of the permeate-side output vapor of M-module (i, j) before the compression [MJ kmol ⁻¹]
$h_{ij}^{V,R}$	Molar enthalpy of the retentate-side output vapor M-module (i, j) [MJ kmol ⁻¹]
$\Delta h_{ij}^{V,P}$	Increment of the molar enthalpy through the compression of the permeate- side output vapor of M-module (i, j) [MJ kmol ⁻¹]
L_{ij}	Liquid flow rate from D-module i to D-module j [kmol h ⁻¹]
$L_{i,P(k)}$	Liquid flow rate from D-module i to P-module k [kmol h ⁻¹]
$L_{P(k)}$	Flow rate of Product k [kmol h ⁻¹]
l_{ij}	Flow rate of the light component flowing on the liquid stream from D-module i to D-module j [kmol h ⁻¹]
$l_{i,P(k)}$	Flow rate of the light component flowing on the liquid stream from D-module i to P-module k [kmol h ⁻¹]
M	Sufficiently large number for the vapor flow rate to a M-module [kmol h ⁻¹]
N	Number of D-modules in the superstructure [-]
$O(z)$	Vapor flow rate at position z in the permeate side [kmol h ⁻¹]
P_e^P	Candidate e for the pressure in the permeate side of the membrane separation unit [bar]
P^R	Pressure in the retentate side of the membrane separation unit [bar]
Q_{Hi}	Heat flow rate from H-module to D-module i [MJ h ⁻¹]
Q_{Hij}	Heat flow rate from H-module to M-module (i, j) [MJ h ⁻¹]
Q_{Ci}	Heat flow rate from D-module i to C-module [MJ h ⁻¹]
Q_{Cij}	Heat flow rate from M-module (i, j) to C-module [MJ h ⁻¹]

$R(z)$	Vapor flow rate at position z in the retentate side [kmol h^{-1}]
S	Set of suffixes $\{1, 2, \dots, N\}$
$u^k(z)$	Flux of component k permeating the membrane at position z . [$\text{kmol m}^{-2} \text{h}^{-1}$]
V_{ij}	Vapor flow rate from D-module i to D-module j [kmol h^{-1}]
V_{ij}^I	Vapor flow rate from D-module i to M-module (i, j) [kmol h^{-1}]
$V_{i'j'}^P$	Vapor flow rate from the permeate-side output of M-module (i', j') to D-module i [kmol h^{-1}]
V_{ij}^R	Vapor flow rate from the retentate-side output of M-module (i, j) to D-module j [kmol h^{-1}]
x_F	Light-component molar fraction of the feed [-]
x_i^L	Lower bound of the molar fraction of the light component in the liquid flowing from D-module i [-]
x_i^U	Upper bound of the molar fraction of the light component in the liquid flowing from D-module i [-]
$x_{P(k)}$	Light-component molar fraction in product k [-]
y_{ij}^{PO}	Light-component molar fraction of the permeate-side output of M-module (i, j) [-]
y_i	Light-component molar fraction of the output vapor of D-module i [-]
y^P	Molar fraction of the light component at position z in the permeate side of the membrane separation unit [-]
y^R	Molar fraction of the light component at position z in retentate side of the membrane separation unit [-]
z_i^I	0-1 variable which takes one when vapor flows from D-module i to the M-modules [-]
z_i^R	0-1 variable which takes one when vapor flows from the M-modules to D-module i [-]
α_{ij}	Membrane area requested for the unit flow rate of retentate-side output of M-module (i, j) [$\text{m}^2 \text{kmol}^{-1} \text{h}$]
ρ^k	Permeability of component k of the membrane [$\text{kmol h}^{-1} \text{bar}^{-1}$]
ϕ	Thickness of the membrane [m]
ω	Width of the membrane [m]

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7. Conclusions and Final Remarks

In this thesis, first, basic technologies for energy-saving distillation is introduced. Then, process synthesis methods developed in previous researches are reviewed. This review revealed that the IDEAS framework developed by Manousiouthakis and coauthors enables the optimization without any assumption on process structure whereas the other approaches need preassignment of the candidate structures. The previous researches on the synthesis of distillation processes using the IDEAS framework focused on deriving the limit of a certain performance index rather than synthesizing the process structures for practice. This is because the optimization results obtained by the IDEAS framework tend to include many trays and flow paths.

The research of this thesis aims at developing the synthesis methods for energy-saving distillation processes which do not introduce any assumptions concerning process structure. This research focused on finding high-performance processes for practice or providing useful references for conceptualizing such processes instead of deriving the limit of a particular performance index.

In chapters 2 to 4, using the state space discretization approach adopted in the IDEAS framework, synthesis methods for binary distillation with heat integration, ternary distillation, and reactive distillation are developed, respectively. In the adopted approach, a tray in distillation columns is treated as a module, and the connections of the vapor and liquid flows among the trays are treated as design variables. By discretizing the composition space and assigning each discretized composition to a module, the material and heat balances of the proposed superstructures are expressed only by linear equations.

In chapter 2, the minimization problem of the total annual cost is formulated as an MILP problem. The number of trays is incorporated into the objective function using 0-1 variables, so that complicated processes including many trays are fairly penalized on the optimization. As a result of the optimization, a process including a new partial structure, stepwise condenser, was obtained. In terms of the thermodynamic efficiency, the effectiveness of the stepwise condenser was confirmed.

In chapter 3, this framework is extended to ternary distillation cases. To avoid heavy computation of large-scale MILP, the two-step approach consisting of utility cost minimization and heuristic process structure simplification is adopted instead of incorporating the number of trays into the objective function. Since each optimization problem in both steps is formulated as an LP problem, the calculation does not require so heavy computation.

In chapter 4, the proposed framework using liquid composition discretization is extended to the synthesis of reactive distillation processes. In the case study dealing with

metathesis reaction of 2-pentene, the optimization result implying a new process structure was obtained. Based on the optimization result, a new process structure was conceptualized, and examined through the comparison with the conventional process structures. The results of the simulation using a process simulator showed the superiority of the new structure.

In chapter 5, stepwise VLE description, which is a new concept for a linear formulation of the process synthesis problem is developed as an alternative to the liquid composition discretization. After a fundamental drawback of the discretization approach is addressed, the effectiveness of the stepwise VLE description to the addressed difficulty is illustrated. The stepwise VLE description is examined in a case study dealing with a simple binary distillation.

In chapter 6, synthesis of distillation/membrane hybrid separation processes is investigated using the stepwise VLE description. As for membrane separation, by adopting state space discretization approach, a model without nonlinear equations is developed. Using a superstructure which consists of distillation modules based on the stepwise VLE description and the membrane separation modules, the process synthesis problem is formulated as an MILP problem.

As future developments, there should be four dimensions of extensions. The first dimension is the extension to the systems involving more components such as quaternary distillation. As more components are involved, the synthesis based on human experiences becomes more difficult because the visualization of the underlying nature of the system requires the related properties to be more compressed. In contrast, the extension via the proposed methodology can be applied without fundamental modification. Thus, the proposed methodology should show more explicit advantages when extended to multi-component systems. A crucial issue for such extension is the significant increase in the size of the resulting optimization problem. For the extension to multi-component systems, some decomposition technique of the optimization problem is needed to avoid too heavy computation. Some possible implementations of a decomposition technique, which should be published in a paper followed by this thesis were investigated through the collaboration with the group of Professor Richard D. Braatz in Massachusetts Institute of Technology.

The second dimension is the extension to the systems of more complicated VLE behavior, such as non-ideal distillation and azeotropic distillation. By adopting the stepwise VLE description, the complexity of the thermodynamic models for describing the VLE behavior does not affect the mathematical structure of the resulting optimization problem but just changes the values of the parameters. Thus, the systems involving

complicated VLE behavior is expected to be handled without the significant increase in computational cost. Once the first dimension of extension mentioned above is accomplished, the second dimension of extension should be carried out without great difficulty.

The third dimension of extension is to expand the types of unit operations combined with distillation. In this thesis, reaction and membrane separation are addressed. When the first dimension of extension is accomplished, the proposed methodology should be able to handle more variety of industrially important design targets, including other possible unit operations such as extraction. This extension is expected to be realized by the modification of the configuration of a module or by introducing another type of the modules as proposed in chapters 4 and 6, respectively.

Finally, the fourth dimension of extension is consideration of the controllability. Throughout this thesis, the methodology was developed as a new tool for the conceptual design of the target distillation processes, and only steady state is discussed. When considering controllability, the optimization involves many more variables and constraints, which causes heavy computation. A practical solution to the consideration of controllability is to implement a sub calculation block for the assessment of controllability into the optimization procedure.

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Publication List

Journal

1. Takase H, Hasebe S. Optimal structure synthesis of internally heat integrated distillation column. *J Chem Eng Japan*. 2015; 48(3): 222-229. [Chapter 2].
2. Takase H, Hasebe S. Optimal Structure Synthesis of Ternary Distillation System. *Comput Aided Chem Eng*. 2015; 37: 1097-1102. [Chapter 3].
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4. Takase H, Hasebe S. Optimal Structure Synthesis of Reactive Distillation Processes Using a Liquid Composition Discretization Approach. In preparation. [Chapter 4].
5. Takase H, Hasebe S. Synthesis of Distillation/Membrane Hybrid Separation Process Structures Using a Stepwise VLE description. In preparation. [Chapter 6].

Conference proceedings

1. Takase H, Hasebe S. Optimal Structure Synthesis of Distillation Processes Using Stepwise VLE Description. *Proceedings of PSE Asia 2016*. 2016: paper C123. [Chapter 5].
2. Tsuji T, Takase H, Hasebe S. Optimal Structure Synthesis of Distillation/Membrane Hybrid Processes. *Proceedings of PSE Asia 2016*. 2016: paper C131. [A part of chapter 6].