GENERALIZED MODULAR REPRESENTATION FRAMEWORK FOR THE SYNTHESIS OF EXTRACTIVE SEPARATION SYSTEMS

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Abstract

In this work, a systematic process synthesis and intensification method is presented for extractive separation based on the Generalized Modular Representation Framework (GMF). GMF employs a mass/heat exchange module-based superstructure representation, incorporating detailed thermodynamic model, to investigate conventional or intensified process options for nonideal azeotropic separation without a pre-postulation of plausible unit/flowsheet configurations. Orthogonal Collocation is also applied to enhance GMF representation to obtain intra-module operation information and module dimensionality estimation while maintaining model size compactness. Thus, entrainer selection, process synthesis, design, and intensification are examined within a single mixed-integer nonlinear optimization (MINLP) problem. A case study on the separation of ethanol-water mixture is presented to highlight the potential of the proposed approach in deriving optimal and verifiable extractive separation systems.

Keywords

Process intensification, Process synthesis, Extractive separation, Distillation, Modular framework

Introduction

The separation of azeotropic mixtures is a frequent but challenging task in chemical processes (Mahdi et al., 2015). Conventional distillation, as the most widely utilized liquid separation technology, has limitations to achieve a higher purity beyond the azeotrope point in these systems. Extractive separation technologies based on process intensification principles (e.g., extractive distillation, membrane-assisted extraction) offer the solution to overcome the physical equilibrium by introducing an extra mass separating agent and by exploiting the synergy between multiple phenomena (Tian et al., 2018).

Extensive efforts have been made to investigate the synthesis and design of extractive separation systems, also with consideration of entrainer selection (Kossack et al., 2008). Recent advances in process synthesis for process intensification have been leveraging phenomenological representation methods to generate process options without the pre-postulation of plausible unit-operation-based flowsheets which may hinder the discovery of novel solutions (Tula et al., 2017; da Cruz and Manousiouthakis, 2017; Demirel et al., 2017). This provides the opportunity to synthesize chemical process from a lower aggregated level and to investigate the effect of functional materials from process fundamental perspective. However, key open questions remain for these phenomena-based synthesis approaches on how to systematically derive intensified processes and how to explore the combinatorial design space in a computationally efficient way.

As an attempt to address these challenges, in this work, we present a systematic framework for the synthesis of process intensification systems based on the Generalized Modular Representation Framework (GMF), with specific focus on extractive separation processes. The rest of the paper is organized as follows: In Section 2, the main principles and model formulation of the GMF, coupled with Orthogonal Collocation (OC) to enhance representation accuracy without sacrificing model size compactness, are introduced in detail. Section 3 showcases the proposed

GMF and GMF/OC approaches on an ethanol-water separation example.

Synthesis Framework

Originally proposed by Papalexandri and Pistikopoulos (1996), the Generalized Modular Representation Framework (GMF) is built on the idea that process operations can be characterized as a set of mass- and heat-transfer phenomena, such as the mass transfer of one component from one phase to another (e.g., distillation) or from one substance to another (e.g., reaction) due to the difference in their chemical potential. Thus, two types of phenomenological building blocks are used in GMF to represent chemical processes from a lower aggregated level than unit operations, namely a multifunctional mass/heat exchange module and a pure heat exchange module (Figure 1).

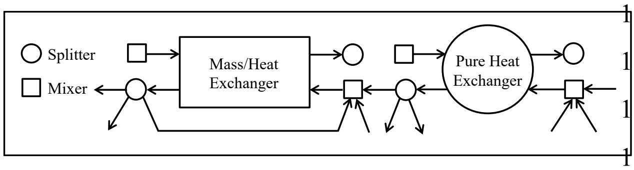

Figure 1. GMF modular building blocks

To ensure mass transfer feasibility within a mass/heat exchange module, "driving force constraints" are developed based on the change of total Gibbs free energy to exploit the "ultimate" thermodynamic space (see Ismail et al. (2001) for detailed derivation). Moreover, with a unified expression, the "driving force constraints" can systematically identify necessary reaction and/or separation phenomena taking place in each module without pre-postulation of plausible separation tasks, reaction tasks, or reactive separation tasks. However, since nonideal separation systems are of focus in the current work, readers are referred to Ismail et al. (2001) and Tian et al. (2019) for GMF application in reactive separation systems.

A superstructure network is constructed to allow for all possible interconnections between each GMF module via the use of auxiliary mixers and splitters. In this context, the GMF model consists of a physical model to represent underlying phenomena taking place in each module as well as a structural model to generate structural alternatives (Ismail, 1999). To further extract intra-module operation information and module design details while maintaining combinatorial compactness, the Orthogonal Collocation (OC) method (Seferlis and Hrymak, 1994) has been coupled with GMF physical model and has been demonstrated for the synthesis of advanced separation systems (Proios and Pistikopoulos, 2006; Algusane et al., 2006). In what follows, we present in detail the mathematical formulation for each sub-model.

GMF Physical Model

The physical model is applied to evaluate the physical feasibility in each GMF module and the overall flowsheet optimality with respect to design targets. Due to the space limitation, we present in the following section the major constraints and equations for the modeling of a GMF mass/heat exchange module, while the comprehensive mathematical formulation involving physical models for other GMF structural components (e.g., mixer, splitter, etc.) can be found in Ismail et al. (1999, 2001).

- Mass balances for each component around each mass/heat exchange module

$$f_e^{LI}x_{ei}^{LI} + f_e^{VI}x_{ei}^{VI} - f_e^{LO}x_{ei}^{LO} - f_e^{VO}x_{ei}^{VO} = 0 \tag{1}$$

- Energy balances around each mass/heat exchange module

$$f_e^{LI}h_e^{LI} + f_e^{VI}h_e^{VI} - f_e^{LO}h_e^{LO} - f_e^{VO}h_e^{VO} = 0 \tag{2}$$

- Energy balances around utility exchangers of module

$$Qh_e - f_e^{H}(h_e^{HO} - h_e^{HI}) = 0 \tag{3}$$

$$Qc_e - f_e^{C}(h_e^{CI} - h_e^{CO}) = 0 \tag{4}$$

- Summation of molar fractions

For streams $s = LI, LO, VI, VO$

$$\textstyle\sum_i x_{ei}^{s} - 1 = 0 \tag{5}$$

- Phase defining constraints

For liquid streams

$$\textstyle\sum_i (\gamma_{ei}^{s}P_{ei}^{sat,s}x_{ei}^{s})/(\phi_{ei}^{s}P_{tot}) \leq 1 \tag{6}$$

For vapor streams

$$\textstyle\sum_i (x_{ei}^{s}\phi_{ei}^{s}P_{tot})/(\gamma_{ei}^{s}P_{ei}^{sat,s}) \leq 1 \tag{7}$$

- Mass transfer driving force constraints for each component

$$G1_{ei} \times G2_{ei} \geq 0 \tag{8}$$

$$G1_{ei} = f_e^{LI}x_{ei}^{LI} - f_e^{LO}x_{ei}^{LO} \tag{9}$$

$$G2_{ei} = \ln\left[\frac{\gamma_{ei}^{LO}x_{ei}^{LO}P_{ei}^{sat,LO}}{\phi_{ei}^{VI}x_{ei}^{VI}P_{tot}}\right] \tag{10}$$

- Thermodynamic property calculation

Thermodynamic properties (e.g., saturated vapor pressure (P^{sat}), enthalpy (h), activity coefficient (γ), fugacity coefficient (ϕ)) are calculated via detailed thermodynamic models (e.g., NRTL, UNIQUAC) for accurate capture of nonideal mixture properties.

GMF/OC Physical Model

Each GMF mass/heat exchange module is highly compact in nature, featuring a certain mass/heat transfer pattern (e.g., component A transfer from liquid to vapor while component B and C vice versa). However, in practice, an aggregation of "intra-segments" inside these modules is often necessitated to overtake the transfer duty to achieve such “intensified” performances, in analogy to the distillation trays in a column section. To enhance intra-module representation while maintaining model size compactness, Orthogonal Collocation method is integrated with GMF physical model which obtains operation and design details at a minimum essential set of “intra-segments” defined by the “collocation points”. It is worth noting that, from computational perspective, the incorporation of OC approximation does not increase the combinatorial size of resulting synthesis problem, as continuous variables, instead of binary variables, are introduced for the description of “intra-segments”.

Based on OC principles, each mass/heat exchange module is discretized into nc interior and 2 exterior collocation points, as can be seen in Figure 2. The location, $s_{e,j}$, of each interior collocation point corresponds to a number of “intra-segments” and is determined by the roots of Hahn polynomials obeying orthogonality conditions as an explicit function of the total number of “intra-segments”, M_e, in the corresponding module (Stewart et al., 1985). After determining the discretization scheme (i.e., the number of nc), liquid and vapor component flowrate and enthalpy variables are approximated at these collocation points using Lagrange polynomials to further constitute intra-module physical constraints. The GMF/OC physical model thus comprises: (i) collocation point locations and Lagrange polynomial weighting functions, (ii) physical constraints enforced at interior collocation points (e.g., mass/energy balances, driving force constraints, phase defining constraints), and (iii) physical constraints to link discretized collocation points with the overall module inlet/outlet streams (Proios and Pistikopoulos, 2006). An indicative list of modeling constraints is as follows.

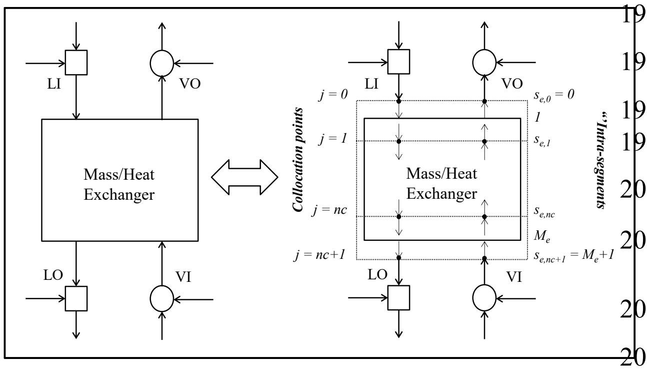

Figure 2. Mass/heat exchange module in GMF and GMF/OC representation (adapted from Proios and Pistikopoulos, 2006)

- Collocation point locations

$$s_{e,0} - 1 = 0 \tag{15}$$

$$s_{e,j} - s_j(M_e) = 0 \tag{16}$$

$$s_{e,nc_e+1} - (M_e + 1) = 0 \tag{17}$$

- Lagrange polynomial weighting functions

$$W_{j'}^{V}(s) - \prod_{z=1,z\neq j'}^{nc_e+1} \frac{s-s_{e,j}}{s_{e,j'}-s_{e,z}} = 0 \tag{18}$$

$$W_{j'}^{L}(s) - \prod_{z=0,z\neq j'}^{nc_e} \frac{s-s_{e,j}}{s_{e,j'}-s_{e,z}} = 0 \tag{19}$$

- Component mass and energy balances

$$\begin{aligned}&\sum_{j'=1}^{nc_e+1} W_{j'}^{V}\left(s_{e,j}+1\right) fc_c^V\left(s_{e,j'}\right) - fc_c^V\left(s_{e,j}\right)\\&+\sum_{j'=0}^{nc_e} W_{j'}^{L}\left(s_{e,j}-1\right) fc_c^L\left(s_{e,j'}\right) - fc_c^L\left(s_{e,j'}\right) = 0\end{aligned} \tag{20}$$

$$\begin{aligned}&\sum_{j'=1}^{nc_e+1} W_{j'}^{V}\left(s_{e,j}+1\right) f^V\left(s_{e,j'}\right) h^V\left(s_{e,j'}\right)\\&+\sum_{j'=0}^{nc_e} W_{j'}^{L}\left(s_{e,j}-1\right) f^L\left(s_{e,j'}\right) h^L\left(s_{e,j'}\right)\\&-f^V\left(s_{e,j}\right)h^V\left(s_{e,j}\right) - f^L\left(s_{e,j}\right)h^L\left(s_{e,j}\right) = 0\end{aligned} \tag{21}$$

- Conditions linking collocation points to module inlet/outlet streams

$$f_e^{VO} - \sum_c\left(\sum_{j=1}^{nc_e+1} W_j^V(1)\, fc_c^V\left(s_{e,j}\right)\right) = 0 \tag{22}$$

$$f_e^{VO} h_e^{VO} - \sum_{j=1}^{nc_e+1} W_j^V(1)\, f^V\left(s_{e,j}\right) h^V\left(s_{e,j}\right) = 0 \tag{23}$$

GMF Structural Model

The structural model generates structural alternatives via the use of logical constraints to denote the existence of GMF modules, process streams, and their interconnection schemes. Some indicative constraints are presented below.

- To define the existence of each module

$$yh_e - y_e \leq 0 \tag{24}$$

- To define the existence of module inlet/outlet streams (i.e., no streams exist if the module does not exist)

$$\left(f_e^{LI} + f_e^{LO} + f_e^{VI} + f_e^{VO}\right) - y_e F^{max} \leq 0 \tag{25}$$

- To define the existence of interconnecting streams between modules

$$f_{ee}^{s} - y_{ee}^{s} F^{max} \leq 0 \tag{26}$$

- To define that if a module exists, there will be an inlet/outlet flow

$$y_e - \left(\sum_{n^{liq}} yIl_{ne} + \sum_{e'} yll_{e'e} + \sum_{e'} ycl_{e'e}\right) \leq 0 \tag{27}$$

$$y_e - \left(\sum_{e'} yll_{e'e} + \sum_{e'} ylh_{e'e} + \sum_{p^{liq}} ylp_{ep}\right) \leq 0 \tag{28}$$

Objective Function

In this work, the objective function is formulated to optimize cost performances. Utility cost can be explicitly considered based on the utility consumption given by Eq. (3) and Eq. (4). However, capital costing correlations cannot be directly applied as no equipment is pre-postulated within the GMF and GMF/OC approaches. Thus a pseudo-capital module cost function is adapted based on the design information provided by OC approximations, as developed in Proios and Pistikopoulos (2006). The overall objective function is formulated as:

$$Obj = \sum_e C_{cw} Qc_e + \sum_e C_{st} Qh_e + \sum_e Cost_{mod,e}\, y_e \tag{29}$$

In this work, the resulting mixed-integer nonlinear programming (MINLP) problem is solved using the Generalized Benders Decomposition (GBD) method (Geoffrion, 1972) implemented in the General Algebraic Modeling System (GAMS). The primal NLP subproblem is solved with solver CONOPT and the master MIP with CPLEX. Nonetheless, due to the highly nonlinear and nonconvex nature of the model, the problem is not solved to global optimality. However, arguably even "intermediate" solutions can provide useful information on the process. Integer cuts can also be introduced to generate alternative solution structures.

Case Study: Separation of Ethanol and Water

In this section, the ethanol-water separation problem in Ismail et al. (1999) is revisited with GMF and GMF/OC approaches. The resulting optimal GMF configurations are also translated to equipment-based flowsheet alternatives and validated with steady-state simulation, thus closing the loop for the synthesis of intensified and verifiable process systems.

Problem Statement

Ethanol (EtOH) and water (H_2O) can form a minimum boiling azeotrope of 89.43 mol% ethanol at a temperature of 351.15 K and a pressure of 1 atm. Based on initial analysis of residue curve maps, ethylene glycol (EG), a heavy entrainer, and methanol (MeOH), a light entrainer, are selected as candidate mass separating agents, both of which can facilitate the separation by forming a homogenous mixture with the feed components.

An atmospheric ethanol-water liquid feed (EtOH 85mol%, H_2O 15 mol%) at a flow rate of 10 kmol/s and a temperature of 351.3 K is considered. The separation task is to obtain liquid ethanol at a rate of at least 8 kmol/s with a purity higher than 99 mol%. The system pressure is fixed at 1 atm. The NRTL equation is utilized to capture the nonideal liquid mixture properties using the thermodynamic parameters given in Ismail et al (1999). The synthesis objective is to identify a suitable entrainer and to determine a cost-optimal design configuration to meet the afore-mentioned production specifications.

Synthesis of EtOH-H_2O Separation System with GMF

In this case study, a maximum of 8 GMF mass/heat exchange modules and 16 associated pure heat exchange modules are allowed for the representation/synthesis of this process. The resulting synthesis model involves 4377 constraints, 4864 continuous variables, and 478 binary variables. Only operating cost, comprising hot and cold utility cost, is considered in the objective function to determine an optimal design configuration with respect to energy consumption. Capital cost estimation will be incorporated later in GMF/OC synthesis to capture the interaction of operating and capital cost in these systems.

The optimal separation scheme is illustrated in Figure 3 with an operating cost of $\$6.34\times10^7$/y. The heavy entrainer ethylene glycol is selected to facilitate the separation of desired ethanol product from overhead. Three mass/heat exchange modules are utilized, interconnected with two pure heat exchange modules, suggesting a configuration of extractive distillation (to be verified later with equipment-based simulation). This design is consistent with the optimal structure identified in Ismail et al. (1999).

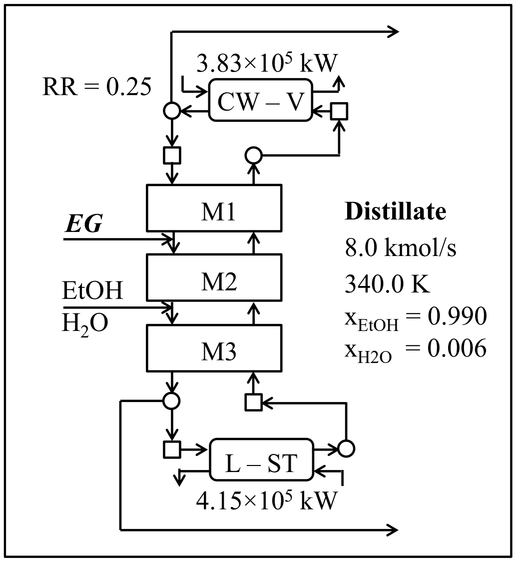

Figure 3. GMF configuration: EtOH-H_2O-EG extractive distillation

To illustrate the ability of GMF to identify versatile process alternatives, two intermediate solutions with higher operating costs are shown in Figure 4. Alternative 1 also employs EG as entrainer. However, instead of being intensified into a single "column" configuration as that in Figure 3, Alternative 1 consists of a side-module coupled with the main "column". Comparing to the optimal solution, larger reflux flowrates are necessitated in this system due to the less integrated and thus less efficient separation scheme, resulting in an operating cost of $\$6.98\times10^7$/y.

Alternative 2 in Figure 4(b) illustrates the process structure with MeOH as entrainer. In the ternary mixture of MeOH-EtOH-H_2O, ethanol is the intermediate component with respect to volatility. Therefore, two separation steps are identified in this process solution to obtain pure EtOH products. The first separation module removes water via the bottom liquid flow, while the vapor flow is directed to the other module for purification of ethanol from methanol. In a sequential manner of operation, this flowsheet requires an operating cost of $\$11.4\times10^7$/y.

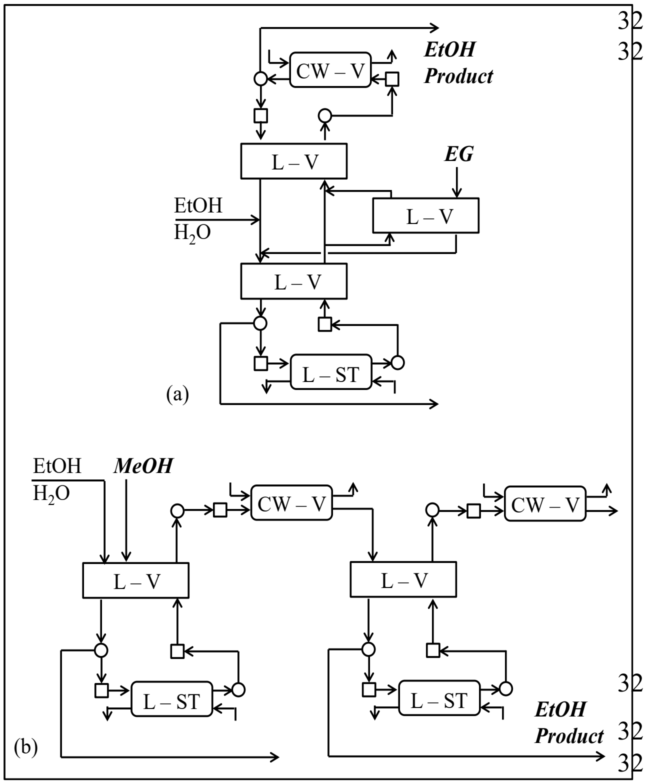

Figure 4. Intermediate GMF configurations: EtOH-H_2O extractive separation (a) Alternative 1 (b) Alternative 2

Synthesis of EtOH-H_2O Separation System with GMF/OC

In this section, GMF/OC approach is applied to investigate the afore-introduced ethanol-water separation problem. However, the synthesis task is driven by the minimization of total annualized cost (TAC) accounting for utility cost and capital cost.

The pre-specified discretization scheme (i.e., number of collocation points) in each mass/heat exchange module plays a key role to enhance physical representation accuracy as well as to monitor model size compactness. For this reason, different numbers of interior collocation points have been used to discretize each GMF module. As presented in Table 1, discretization with 2 interior collocation points provides the best cost performance for the design of this extractive separation process. The optimal number of "intra-segments" in each module is also given in Table 1.

The resulting optimal GMF/OC solution features the same modular configuration as the optimal GMF solution (Figure 3). This is consistent with the observation in Proios and Pistikopoulos (2006) for a broader scope of distillation systems, as operating cost constitutes the major part of TAC in these systems and thus serves as the dominant driving force for cost optimization.

Table 1. GMF/OC synthesis for EtOH-H_2O Separation with different discretization schemes

Interior collocation points	1	2	3
"Intra-segments"	M_1 = 10.0 M_2 = 2.0 M_3 = 10.0	M_1 = 2.9 M_2 = 6.0 M_3 = 2.4	M_1 = 3.3 M_2 = 3.0 M_3 = 3.0
Reflux ratio	0.30	0.25	0.27
Q^H (kW)	3.86×10^5	3.70×10^5	3.87×10^5
Q^C (kW)	4.12×10^5	4.03×10^5	4.05×10^5
Operating Cost ($/y)	6.37×10^7	6.13×10^7	6.38×10^7
Capital Cost ($/y)	0.73×10^7	0.63×10^7	0.63×10^7

Steady-state Simulation and Validation

In this step, we validate the above-derived optimal GMF and GMF/OC configurations with equipment-based simulation using Aspen Plus® to verify if extractive distillation is suggested as the process option for this ethanol-water separation problem. As per the estimation of "intra-segments" by the GMF/OC synthesis with 2 interior collocation points, the modular configuration is translated to an 11-tray extractive distillation column. Accordingly, EtOH-H_2O feed is introduced onto the 10th tray while EG entrainer enters the 4th tray.

The simulation results for the equipment-based flowsheet alternative are presented in Figure 5. Figure 6 shows the comparison profiles of column temperature and liquid composition between GMF, GMF/OC, and Aspen simulation. As shown, both GMF and GMF/OC match well with the major temperature and composition trends inside the extractive column, while GMF/OC provide further design and operation details within each column section. Up to this stage, the extractive distillation configuration shown in Figure 5 is identified as the optimal process solution in this case study.

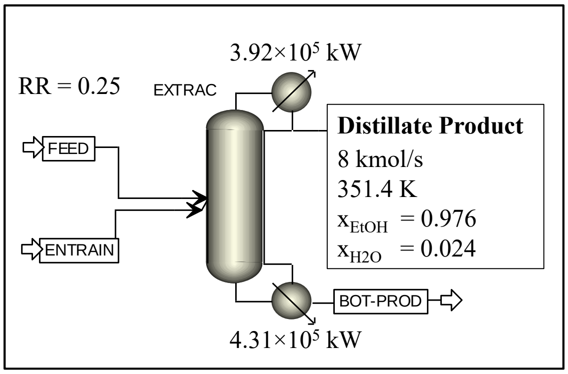

Figure 5. Aspen Plus simulation & validation of EtOH-H_2O-EG extractive distillation

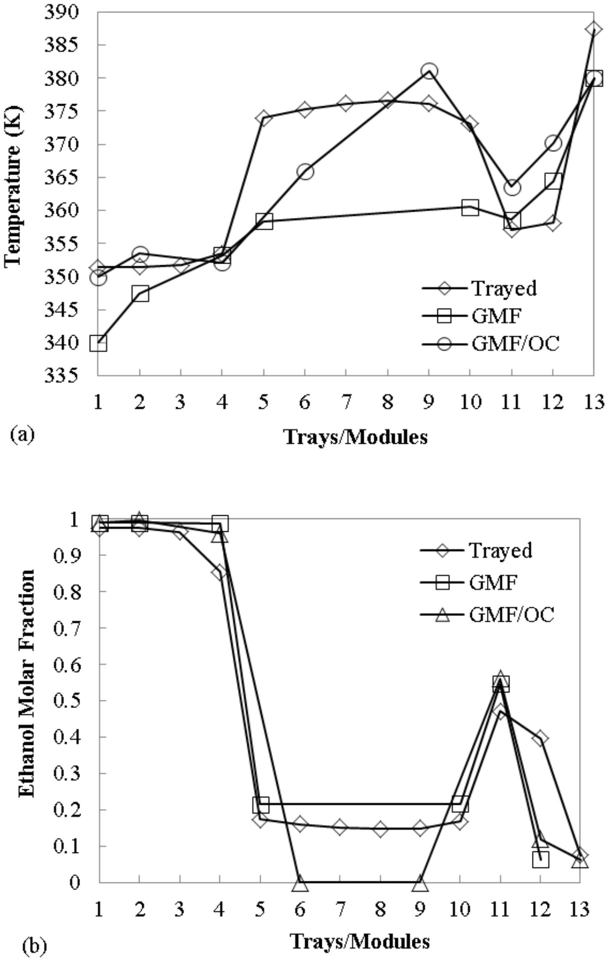

Figure 6. Steady-state validation: GMF & GMF/OC configurations (a)Temperature profile (b) EtOH composition

Conclusion

In this paper, we have presented a systematic framework, i.e. the Generalized Modular Representation Framework, for the synthesis of process intensification systems, with specific focus on extractive separation process. It is demonstrated, through the synthesis and design of an ethanol-water separation system, that GMF is able to simultaneous address entrainer selection, unit/flowsheet synthesis, design, and intensification in a single problem formulation. Moreover, GMF/OC allows for detailed intra-module physical representation and provides module dimensionality information, while maintaining the GMF's main advantage of combinatorial compactness. Ongoing work focuses on applying the GMF and GMF/OC approaches to membrane-assisted systems and cyclic operation systems. Extensions of the synthesis framework to include operability, safety, and dynamic controllability assessment are also under current investigation (Tian, 2019).

Acknowledgments

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