*Distillation Absorption 2010*
*A.B. de Haan, H. Kooijman and A. Górak (Editors)*

# METHODOLOGY FOR DESIGN AND ANALYSIS OF REACTIVE DISTILLATION INVOLVING MULTIELEMENT SYSTEMS

Amnart Jantharasuk[1], Rafiqul Gani[2], Andrzej Górak[3] and Suttichai Assabumrungrat[1]
[1] Dept. of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand, Email: suttichai.a@chula.ac.th
[2] Dept. of Chemical and Biochemical Engineering, Technical University of Denmark, DK-2800 Lyngby, Denmark, Email: rag@kt.dtu.dk
[3] Dept.of Biochemical and Chemical Engineering, TU Dortmund University, 44221 Dortmund, Germany, Email: Andrzej.Gorak@bci.tu-dortmund.de

## Abstract

This work presents a new methodology for design and analysis of reactive distillation. The methodology employing the element-based approach coupled with a driving force diagram for two-element systems is extended to multielement systems commonly involved in most chemical processes. The multielement system is transformed to an equivalent binary (key) element system, and consequently graphical design is carried out to determine the number of stages, the feed stage, the minimum reflux, etc., corresponding to minimal energy consumption, based on a driving force diagram. Two case studies including methyl acetate (MeOAc) synthesis and methyl tertiary butyl ether (MTBE) synthesis are presented. It is shown that the designed column is able to satisfy desired targets with a minimum energy requirement. In addition, an improvement in design is obtained compared to the design without any considerations about nonkey components.

**Keywords**: reactive distillation, design methodology, multielement-based approach, driving force diagram

## 1. Introduction

Reactive distillation (RD) has been proven industrially as an efficient alternative over conventional sequential operations as it offers several benefits such as avoidance of reaction equilibrium restrictions, higher conversion, selectivity and yield, and, reduction of investment costs and energy demands. Because the experimental design of RD is expensive and time consuming, several design methodologies have been proposed by a number of researchers. Available techniques dealing with optimization of RD column are ordinarily related to intensively complicated computations while graphical design are more rapid but difficult to reach the optimized requirement.

Pérez-Cisneros et al.[1] employed a method of chemical elements defined as the part of molecule remaining invariant along the reaction, rather than using actual components to solve a chemical-physical equilibrium (CPE) problem. The distinctive advantages of this approach are the reduction in dimension of governing equations since the number of elements is always less or equal to the number of components and the CPE system can be treated like a nonreactive system of components. In a graphical design method for RD[2], the number of stages is calculated in a similar manner to classical McCabe-Thiele diagram at a given reflux ratio. This method delivers also a driving force diagram allowing for identifying an optimal feed location based on the hypothesis that the largest driving force refers to the minimum energy consumption and the easiest operation. Although it is promising, the current application of the element based approach coupled with a driving force diagram for RD design has the limitation that only two-element systems can be handled whereas most chemical processes involve multielement systems.

Consequently, the objective of this work is to propose a new design methodology relating to the use of "reactive" driving force diagrams to design RD columns containing multielement systems. This methodology is restricted to single feed system and chemical equilibrium is attained on each reactive stage. The design is expected to represent, at least, a near optimal solution with respect to energy consumption.

## 2. Design methodology

As shown in Figure 1, the proposed methodology consists of 4 main steps: (1) data/information collection, (2) determination of RD design target specification, (3) analysis, and (4) RD design.

### *2.1 Data/information collection*

Before applying the methodology, all data and information about an interested process have to be collected in order to clarify if an integrated, reactive process is superior over the sequential one of reaction and separation units.

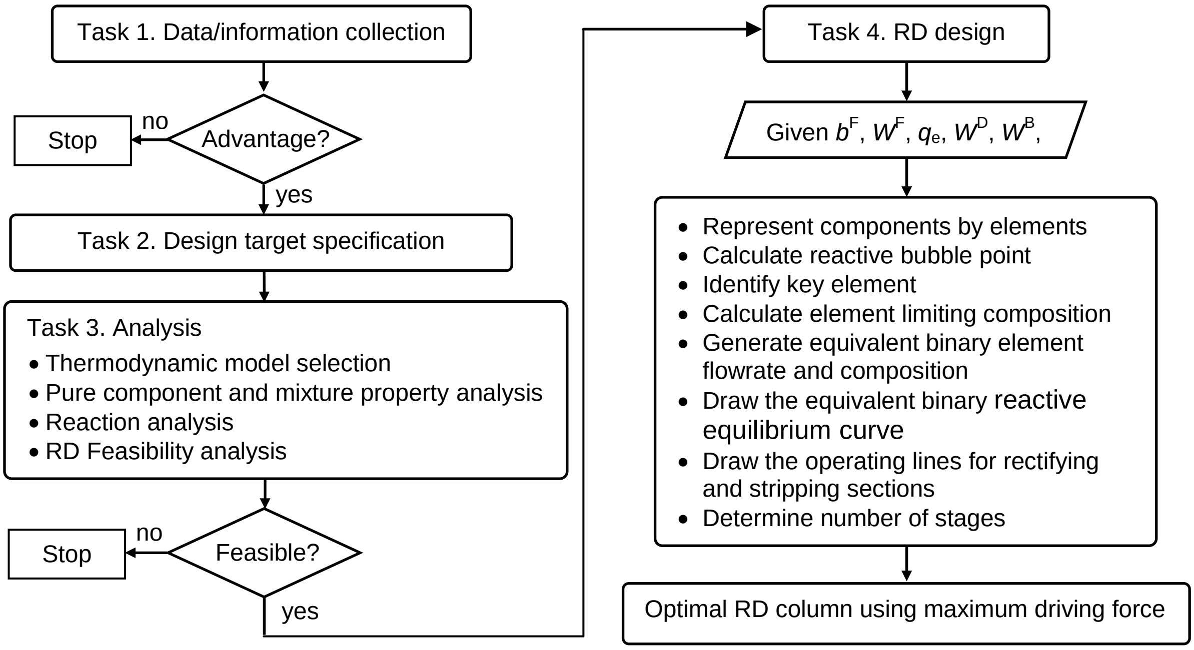


**Figure 1.** Design methodology for RD containing multielement system

### *2.2 Determination of RD design target specification*

When the advantages of RD application are realized, design targets have to be identified or selected from the main propose of using RD process. Generally, the increasing conversion and selectivity, a shorter process-time, improved energy efficiency, and heat integration, and the process simplification are set as the design targets of RD application. In this work the minimum energy consumption is considered as the design target for given values of conversion and product purities.

### *2.3 Analysis*

After the targets are established, the system has to be analyzed in terms of thermodynamic model selection, pure component and mixture property analysis, reaction analysis, and RD feasibility analysis. If all steps are passed, the design of RD column configuration will be performed to achieve the specified design targets as mentioned in Section 2.2.

- *Thermodynamic model selection*

If reliable experimental data is not available, appropriate thermodynamic models need to be used to predict the system behavior at various mixture compositions and operating conditions. In this work, ICAS-TML, a tool for thermodynamic model selection, is utilized by defining components and composition range in an expected operating condition. The chosen models are used afterward in the reactive bubble point calculation step and RD process simulation.

- *Pure component and mixture property analysis*

Pure components properties are analyzed to investigate the system boundary; for example, the liquid region and separation temperature at a given operating pressure. Azeotropic information in terms of composition and boiling temperatures is also important as it can refer to the possible distillation products. By considering both component boiling points together with azeotropic boiling points, an expected distillation temperature is obtained and verified for liquid miscibility. In this analysis, necessary component property data is retrieved from ICAS-database.

- *Reaction analysis*

The reaction condition has to be analyzed together with the selection of the proper separation window because the combination between reaction and separation exists for the case that there is an overlapping of reaction and separation windows[3]. According to the Le Chatelier's principle, a reversible-equilibrium limited reaction is preferred to carry out by RD, and for the case of reaction network one reaction product is properly selected among all components to be a separating component in order to obtain the advantages provided by in-situ distillation. In case of heterogeneously catalyzed RD, availability and catalyst lifetime has to be carefully checked. Short-life catalyst results in frequent catalyst replacement or regeneration problem which are undesired for real operation.

- *Feasibility of reactive distillation*

All information is analyzed to check the feasibility of using RD. For example, it is not advisable to use RD when the relative volatility of the key-components is less than 1.05[4], when overall reaction system is highly endothermic, when there is no overlap of operation windows between reaction and separation[4], and when only a short-life catalyst is available.

### *2.4 Reactive distillation design*

The methodology proposed in this work relies on application of multielement reactive system that allows for treating the reactive process as a separation between two key elements, light key (LK) and heavy key (HK). To attain this goal, all components are transformed to elements and then the reactive bubble point calculations are performed (see[1] for more detail) to construct the reactive equilibrium curve.

In order to transform the multielement system to an equivalent binary element system, the method of Hengstebeck and Jenny, typically employed for designing a distillation column to fractionate multicomponent mixture, is applied[5,6]. In this method the concept of 'limiting compositions' is used which assumes constant light and heavy component concentrations in a rectifying and stripping part of the column, respectively. That concept is also true even if components are represented by elements because the volatility of components truly refers to the element volatility[2]. From the nonkey element balance around the RD column, those limiting compositions of nonkey elements, classified as light nonkey (LNK) and heavy nonkey (HNK), are derived. As the summation of key element flowrate equals to the total element flowrate depleted by summation of limiting nonkey element flowrate, the flowrate of equivalent binary keys can be calculated. Consequently, the complex multielement system can be represented by LK and HK. All equations obtained in this work are provided in Table 1,

**Table 1.** Liquid and vapor phase limiting element composition and equivalent binary element flowrate for rectifying and stripping section

| | Rectifying section | Stripping section |
|---|---|---|
| Liquid phase composition | $W^{l,\lim}_{LNK,R}=\frac{W^{D}_{LNK}\left(b^{D}/b^{l}_{R}\right)}{\left(K_j/K_{HK}\right)-1}$ (1) | $W^{l,\lim}_{HNK,S}=\frac{W^{B}_{HNK}\left(b^{B}/b^{l}_{S}\right)}{1-\left(K_j/K_{LK}\right)}$ (2) |
| Vapor phase composition | $W^{v,\lim}_{LNK,R}=\frac{W^{D}_{LNK}\left(b^{D}/b^{v}_{R}\right)}{1-\left(K_{HK}/K_j\right)}$ (3) | $W^{v,\lim}_{HNK,S}=\frac{W^{B}_{HNK}\left(b^{B}/b^{v}_{S}\right)}{\left(K_{LK}/K_j\right)-1}$ (4) |
| Liquid phase flowrate | $b^{l}_{eq,R}=b^{l}_{R}\left(1-\sum W^{l,\lim}_{LNK,R}\right)$ (5) | $b^{l}_{eq,S}=b^{l}_{S}\left(1-\sum W^{l,\lim}_{LNK,S}\right)$ (6) |
| Vapor phase flowrate | $b^{v}_{eq,R}=b^{v}_{R}\left(1-\sum W^{v,\lim}_{LNK,R}\right)$ (7) | $b^{v}_{eq,S}=b^{v}_{S}\left(1-\sum W^{v,\lim}_{LNK,S}\right)$ (8) |
| $K_j$: the ratio of nonkey composition in vapor phase to nonkey composition liquid phase<br>$K_{LK}$: Equilibrium ratio of the light key element in the stripping section, $K_{LK}=b^{l}_{S}/b^{v}_{S}$<br>$K_{HK}$: Equilibrium ratio of the heavy key element in the rectifying section, $K_{HK}=b^{l}_{R}/b^{v}_{R}$ | | |

Following the algorithm, given in Figure 1, the design is started by transforming all components appearing in the system to elements[1,2] and then the reactive bubble point calculations are carried out using the chosen thermodynamic model (Section 2.3). A suitable pair of key element is selected and further used to represent the whole component system employing the calculated limiting nonkey composition.

The overall element balances around the column are performed for both rectifying and stripping sections (Figure 2B). Then the equations are transformed into the form of equivalent binary element system using all equations shown in Table 1. Finally the operating equations of rectifying and stripping sections are obtained as shown by Eqs. (9) and (10), respectively. Note that the form of operating equations is similar to the conventional McCabe-Thiele equations. It means that the reactive system can be treated like nonreactive when the element-based approach is applied.

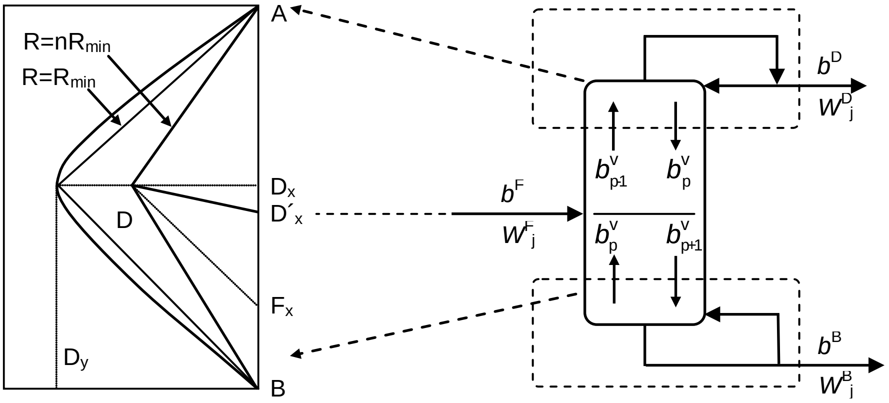
$$W^v_{LK,R,eq} = \frac{b^l_{eq,R}}{b^v_{eq,R}} W^l_{LK,R,eq} + \frac{b^D}{b^v_{eq,R}} W^D_{LK} \tag{9}$$

$$W^v_{LK,S,eq} = \frac{b^l_{eq,S}}{b^v_{eq,S}} W^l_{LK,S,eq} + \frac{b^B}{b^v_{eq,S}} W^B_{LK} \tag{10}$$

Basing on the knowledge of chemical-physical equilibrium resulting from the calculated reactive bubble points, end points for distillate and bottom products (calculated by Eq. 11), and the slope for two operating lines, $b^l_{eq,R} \big/ b^v_{eq,R}$ and $b^l_{eq,S} \big/ b^v_{eq,S}$ (for rectifying section and stripping section, respectively) a diagram is constructed for the equivalent binary element system and used to determine the number of stages needed to achieve the targets given in the Section 2.2.

$$W^p_{LK,eq} = W^p_{LK} \Big/ \left( W^p_{LK} + W^p_{HK} \right) \tag{11}$$

Driving force (DF) is defined as the difference in composition between two separating phases[7,8]. From this definition, it can also be noted that at fixed *P* or *T*, the plot of driving force, $F_{ij}$, the composition difference between liquid and vapour phases in RD, versus liquid composition, can be made and the location of maximum DF is easily identified (Figure 2A). Then a near optimal feed location is identified based on the assumption that the design employing the largest driving force leads to a minimum of energy consumption. For two products (A and B), the maximum driving force is employed when the operating lines from points A and B intersect on the line $D_x$-D and extended to the vertex[8]. Note that in this work the DF diagram is constructed by the plot of $\left| W^v_{eq} - W^l_{eq} \right|$ versus $W^l_{eq}$ whereas operating lines, for both minimum reflux ($R=R_{min}$) and operating reflux condition ($R=nR_{min}$), are constructed similar to the method described by Gani and Bek-Pedersen[8]. The difference in feed condition plays a role in the deviation of optimal feed location in the range of $D_x$ to $F_x$ as illustrated in Fig. 2A, where $F_x$ is the saturated vapor feed and $D_x$ is the saturated liquid feed.



(A) (B)

**Figure 2.** Driving force diagram (A) and element balance around RD column (B)

## 3. Case studies

The application of the developed design methodology is illustrated through two case studies involving the synthesis of methyl acetate (MeOAc) synthesis and the synthesis of MTBE in RD columns.

### *3.1 Methyl Acetate Synthesis*

In this case study, the entirely reactive RD column experimentally reported in literature[9] to synthesize MeOAc from methanol (MEOH) and acetic acid (HOAc) is compared with the design configuration obtained by the developed design methodology. Finally, the optimal design is validated by varying feed location.

- *Information collection, design target specification and analysis*

The MeOAc synthesis is one of the most classic examples showing several advantages of process intensification technique in which the system of one reactor and several separation units is replaced by single RD unit[10]. In order to verify the methodology, the design targets are set at product purity of 54% of MeOAc in the distillate and 50% MeOH conversion taken from the experimental work[9]. For this system, the suitable thermodynamic model, declared from ICAS-TML, is UNIFAC-ideal gas. From Table 2, the pure component and mixture properties are collected and it is clear that the separation by distillation is possible due to high relative volatility of each component pair. It should be noted that the heat of reaction is useful to vaporize the separating component-MeOAc, and moreover, there is no side reaction present in this system.

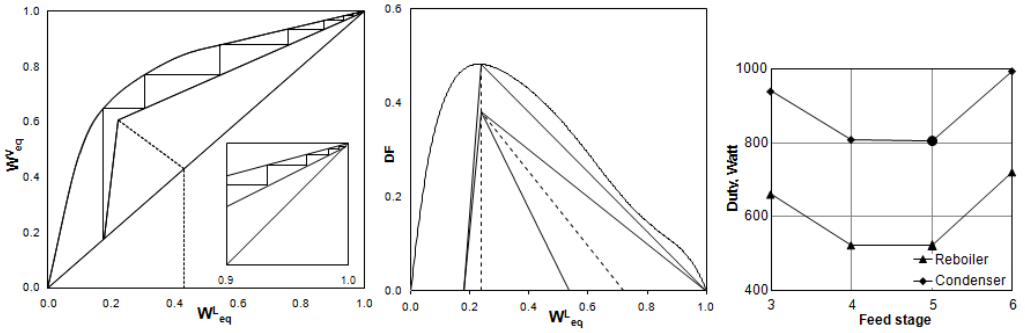
**Table 2.** Pure component and mixture properties for MeOAc synthesis at 399 mbar

| Component | Element | $T_b$ [K] | $\alpha_{i,HOAc}$ | $T_m$ [K] | Solubility Parameter [MPa$^{½}$] |
|---|---|---|---|---|---|
| MeOAc | AB | 305.9 | 13.8 | 175.15 | 17.59 |
| MeOH | A | 315.8 | 6.8 | 175.55 | 44.81 |
| $H_2O$ | C | 348.9 | 3.0 | 273.15 | 47.81 |
| HOAc | AC | 363.2 | 1.0 | 289.75 | 22.10 |

| Azeotrope | T [K] | Molar composition | | | |
|---|---|---|---|---|---|
| | | MeOAc | MeOH | $H_2O$ | HOAc |
| MeOAc/MeOH | 304.0 | 0.75 | 0.25 | - | - |
| $H_2O$ /HOAc | 347.6 | - | - | 0.82 | 0.18 |

- *RD design*

Firstly, all components are represented by elements (Table 2), and then the reactive bubble point calculations are performed. The HNK element for this system is B, while A and C are selected as LK and HK, respectively. From calculations, the values of $W_{HNK,S}^{l,\lim}$ and $W_{HNK,S}^{v,\lim}$ are obtained as 0.64 and 0.95, respectively.



(A) (B) (C)

**Figure 3.** $W^v_{eq}$-$W^l_{eq}$ diagram (A), driving force diagram (B), column duty at various feed locations (C)

As shown in Figures 3A and 3B, the RD column consisting of 10 reactive stages is obtained from this design methodology while the driving force diagram identifies that the optimal feed stage is 5. By comparison to the work of Pöpken et al. (2000)[9], a good agreement in total number of stages and feed location are achieved. At fixed MeOH conversion of 50% as the design target, the feed stage is varied in order to justify the optimal feed stage obtained from driving force diagram. From Figure 3C, 522.9 W and 804.3 W are required for reboiler duty and condenser duty, respectively to reach the desired conversion when the feed plate is located at stage 5 or 4. All other feed plate locations require greater energy demand. This indicates that the design methodology proposed in this work can provide a single feed RD column which is able to reach the design targets and optimal feed location.

### *3.2 MTBE Synthesis*

In this case study, MTBE is synthesized from isobutene (IB) and methanol (MeOH). Butane (*n*C4) is present as an inert component in the system. With given design targets[11], two column designs are performed; i.e. (i) design based on the methodology proposed in this work and (ii) graphical design method with no consideration of nonkeys[2]. Table 3 shows that the design (i) obtained from this work can reach all design targets, but not for the case (*ii*) with no consideration of nonkeys in the design steps. It proves that the new graphical design methodology presented in this work can successfully be used for feasibility studies of reactive distillation column design.

**Table 3.** The comparison of RD column configuration for MTBE synthesis containing *n*C4 inert

| Design | Number Stages | Feed stage | Distillate | | | Bottom | | | Conversion (%) |
|---|---|---|---|---|---|---|---|---|---|
| | | | IB | *n*C4 | MTBE | IB | *n*C4 | MTBE | |
| i | 15 | 7 | 0.037 | 0.958 | 0.004 | 0 | 0.001 | 0.988 | 95.9 |
| ii | 12 | 5 | 0.103 | 0.885 | 0.012 | 0 | 0.011 | 0.894 | 87.8 |
| Target | - | - | - | >0.90 | - | - | - | >0.95 | >90 |

Reflux ratio = 3, *B*/*F* = 0.32, Column pressure = 8 atm, Thermodynamic model: UNIFAC-SRK

## 4. Conclusions

The new methodology for design and analysis of single-feed RD column involving multielement systems is proposed in this work. The whole multielement system is represented by equivalent binary element of two keys and then the driving force diagram is applied in order to identify the optimal feed location. From two case studies of MeOAc synthesis and MTBE synthesis, it was demonstrated that this proposed work provides the RD column achieving design targets with minimal energy consumption. Furthermore, it has been shown that the accuracy in design is improved if nonkey elements are taken into account during the column design.

## Acknowledgements

This work is sponsored by Thailand Research Fund (TRF) and SCG Chemical Co. LTD.

## References

1. E.S. Pérez-Cisneros et.al., *Chem. Eng. Sci.*, 52(1997) 527-543
2. O. Sánchez-Daza et.al., *AIChE J.*, 49(2003) 2822-2841
3. G. Schembecker and S. Tlatlik, *Chem. Eng. Process.*, 42(2003) 179-189
4. P.T. Mitkowski et.al., *Comput. and Chem. Eng.*, 33 (2009) 551-574
5. R.J. Hengstebeck, *Distillation-Principles and Design Procedures*, Reinhold Publishing (1961)
6. P.J. Jenny, Trans. *Am. Inst. Chem. Engrs.*, 35(1939), 635
7. E. Bek-Pedersen and R. Gani, *Chem. Eng. Process.*, 43(2004) 251-262
8. R. Gani and E. Bek-Pedersen, *AIChE J.*, 46(2000) 1271-1274
9. T. Pöpken et.al., *Ind. Eng. Chem. Res.*, 40(2001) 1566-1574
10. V.H. Agreda et.al., *Chem. Eng. Prog.*, 86(1990) 40-46
11. R.M. Dragomir and M. Jobson, *Chem. Eng. Sci.*, 60(2005) 4377-4395

*Nomenclature*
*W*: Element molar fraction
*b*: Element molar flowrate
*R*: Reflux ratio
*B/F*: Bottom to feed ratio

*Subscript*
LK: Light key element
HK: Heavy key element
eq: Equivalent binary
R: Rectifying section
S: Stripping section

*Superscript*
F: Feed stream
D: Distillate stream
B: Bottom stream
lim: Limiting composition stage
p: Phase condition, e.g. liquid (l) or vapor (v)