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A novel methodology for the modeling of CO_2 absorption in monoethanolamine (MEA) using discrimination of rival kinetics

Rameshwar Hiwale [a], Robin Smith [a], Sungwon Hwang [b,*]

[a] Centre for Process Integration, School of Chemical Engineering and Analytical Science, The University of Manchester, P.O. Box 88, Manchester, M60 1QD, UK
[b] Department of Chemistry and Chemical Engineering, Inha University, 253, Yonghyun-Dong, Nam-Gu, Incheon, 402-751, South Korea

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ABSTRACT

This paper suggests a new approach for the design of a multi-phase reactor and its optimization, focusing on close interaction among the laboratory experiments, rigorous modeling of reaction system, and design of reactors. A new methodology of "discrimination of rival kinetics" was developed to obtain a set of accurate kinetics for the identified reaction mechanisms, and this approach allowed us to develop more robust reactor design by making full use of the experimental data, avoiding unnecessary laboratory experiments. A case study of 'CO_2 absorption in an aqueous monoethanolamine solution' in a packed bed reactor was used to illustrate the methodology.

Introduction

When a new chemical process design is developed, a reactor design is generally one of the first tasks to be considered because catalyst and reactor design and operating parameters such as reactor type, reactor configuration, selection of catalysts, operating condition of a reactor and so on affect overall scheme of chemical process design. Major unit operation of chemical process typically includes reaction, separation, treating and utility systems. Among these units, appropriate design of reaction system leads to economic benefits in terms of process design, and equipment and process operation, in addition to producing less unwanted by-products that often have a negative environmental impact.

Most reactions in the petrochemical, biological, and pharmaceutical industries take place in a multi-phase system. Contacting pattern is mainly used as a basis to classify reactors in multi-phase reaction system, and typical types of multi-phase reactors in industry include (1) packed bed reactor, (2) moving bed reactor, (3) fluidized bed reactor, (4) trickle bed reactor, and (5) bubbling bed reactor. From the perspective of reactor design, the design of multi-phase reactors has much greater complexity than a homogeneous reactor because mass transfer between phases and inter-phase reactions must be considered simultaneously.

Typically, the following irreversible procedures have been adopted for the design of a multi-phase reactor along the project timeline.

(1) Laboratory experiments to identify the reaction mechanism, often with selected catalysts
(2) Analysis of experimental data to develop the reaction mechanisms and kinetics
(3) Modeling of the reaction system for reactor design and its optimization, considering the followings:
   A. Mass and energy balance including transport phenomena,
   B. Chemical reaction,
   C. Operating condition including concentration, pressure, temperature and catalyst deactivation, etc., and
   D. Computational fluid dynamics (CFD)
(4) Scale up to a pilot plant

The first and second tasks are carried out mainly by chemists at the early stages of the project without considering reactor design aspects, whereas the third and the fourth tasks are undertaken by chemical engineers. Mechanical engineers and metallurgists become involved in the task of determining the final reactor design.

The above four steps must be considered simultaneously in an ideal situation, and iteration of the entire procedure must be performed throughout the project. In reality, however, each step is

Abbreviations: CFD, Computational Fluid Dynamics; LCS, Linear Cooling Schedule; MINLP, Mixed Integer Non-linear Programming; SA, Simulated Annealing; SQP, Successive Quadratic Programming.

* Corresponding author. Tel.: +82 32 8607461; fax: +82 32 8720959.
E-mail address: sungwon.hwang@inha.ac.kr (S. Hwang).

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Notations

a	Interfacial area (m^2)
C_i	Concentration of component i, (kmol/m^3)
C_P	Heat capacity (KJ/kg K)
E_{act}	Activation energy (KJ/mol)
h_G	Heat transfer coefficient (Kcal/s m^2 K)
i	Number of experimental runs
j	Number of experimental samples
k	Reacting species
k_g or k_G	Gas phase mass transfer coefficient (Kmol/m^2 s kPa)
L_k	Markov chin length
L_M	Mass liquid flow rate (kg/m^2 s)
P	Total pressure (kPa)
p	Number of data points
r	Reaction rate (1/s)
R	Absorption rate (kmol/s)
T	Temperature (K, °C)
T_0	Initial temperature (K, °C)
T_k	Annealing temperature (K, °C)
Y_i	Concentration of gas component i (Kmol i/kmol B)
y_i	Gas concentration of gas component i (Kmol i/kmol B)
Z	Height of packing in packed bed column (m)

Greek letters

α	CO_2 loading (mol/mol)
γ	Cooling parameter
σ	Standard deviation of the objective function
ΔH_R	Latent heat of vaporization (kJ/kg)

completed individually without much interaction with the other steps, and sometimes step three is easily overlooked. As a result, the reactor design and its operating conditions are not properly optimized, and it causes negative effects on the overall process design downstream for the following reasons.

(1) The laboratory experiment is often performed randomly without a systematic approach. As a result, experimental settings such as temperature, pressure, and concentration ratio of the reactants are not properly optimized. Furthermore, there is no basis to indicate that a range of all feasible reactions are covered appropriately through laboratory experiments, particularly, in line with the reactor design.
(2) The effect of mass transfer and its interaction with chemical reactions tend to be neglected for reactor design.
(3) No methodology is available to measure the accuracy of developed kinetics from laboratory experiments unless it is proven by both simulation and experimental data. The developed kinetics should be compared with experimental data through the simulation. Hence, the most accurate kinetics must be chosen based on the analysis results.

For the reasons above, a new methodology was developed in this study by adopting the following approaches.

(1) Rigorous modeling was developed to increase the accuracy of the simulation results by considering the following aspects simultaneously.
   A. Physical properties of the major key components in a reaction system
   B. Mass and heat transfer phenomena of the system
   C. Chemical reaction and its effect on the mass and heat transfer coefficients
(2) Stochastic optimization was used to develop the reaction kinetics. This allowed an engineer to identify multiple sets of feasible kinetics based on the available laboratory data that met the user-specified criteria, such as the maximum standard deviation between the simulation results and experimental data.
(3) These obtained rival kinetic models were analyzed further through simulation under a wider range of operating conditions. In addition, if needed, the experimental scopes were explored further to identify the most accurate kinetics among the set of developed kinetics.

Following the approaches suggested above, an optimum reactor design can be achieved by making full use of the experimental information, avoiding redundant laboratory or pilot plant experiments.

In this study, a case study of 'carbon dioxide absorption in aqueous monoethanolamine (MEA) solution in a packed bed reactor' was performed. This paper discusses the modeling of the reactor, focusing on the application of stochastic optimization to the development of the reaction kinetics based on the experimental data.

Application of simulated annealing algorithm to "discrimination of rival kinetics"

Model discrimination

A simulated annealing algorithm was used to search the feasible reaction kinetics. One of the major advantages of using the algorithm is to find multiple optimum solutions that satisfy all the specified constraints for the objective. Owing to the nature of simulated annealing, multiple sets of individual kinetics that agree with the same experimental results are often produced from the search. In such a case, a researcher needs to identify which model represents the reactions most accurately. For example, different ranges of operating conditions need to be explored further to determine what condition can provide the maximum deviation among the sets of kinetics identified. The experimental study was performed under the same conditions, and the results were compared with the simulation results to reduce the number of nominated kinetics. Fig. 1 presents the above strategic procedure for the development of reaction kinetics [1].

This methodology provides effective guidelines to find the accurate kinetics, minimizing the unnecessary pilot plant testing or experiments. The next two sections illustrate how the optimization algorithm is applied to the methodology.

Simulated annealing

Many different types of optimization algorithms have been developed and applied to process design in engineering. Each optimization algorithm has its own advantages and disadvantages. Therefore, it is important to understand the nature of each algorithm and determine if a tool is suitable for design of a system. In broad, an optimization algorithm can be divided into two different categories – deterministic and stochastic optimization. Most well-known algorithms for deterministic optimization involve successive quadratic programming (SQP) for non-linear problems. Meanwhile, a range of stochastic optimizations, such as simulated annealing, genetic algorithms, neural networks, tabu search, target analysis, etc., have been developed.