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# Rigorous design of multiphase reactors: Identification of optimal conditions for mass transfer limited reactions

Mingquan Xie, Hannsjörg Freund*

*Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Lehrstuhl für Chemische Reaktionstechnik, Egerlandstrasse 3, 91058 Erlangen, Germany*

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ABSTRACT

Multiphase reaction systems are often complex due to the interaction of reaction and transport processes. To design optimal reactors for such systems, a rigorous optimization is necessary. In this regard, this work proposes extensions of a reactor design methodology based on rigorous optimization. Each phase is represented by one fluid element, subject to different mass and energy fluxes. While the unlimited external fluxes are optimally provided along the reaction route, sensitivity analysis of the parameters related to the limited external fluxes is performed. The extended methodology is applied in the reactor design for chemical absorption of $CO_2$ as an example for complex multiphase reaction systems with severe mass transfer limitation. An accurate model which is also numerically suitable for optimization has been set up and validated with pilot plant data from literature. Optimal temperature profiles which result from balancing the different temperature-dependent phenomena are identified for cases with different inlet conditions, and tailor-made heat control strategies are shown for these cases. The potential of the developments in improving mass transfer rates by, e.g., structural design or solvent design has been quantified. This model-based design methodology is generally applicable to different multiphase reaction systems with severe mass transfer limitation.

## 1. Introduction

In literature, many different reactor design methods exist including heuristics, attainable region approaches (e.g. [1,2]) and superstructure optimization (e.g. [3–5]). These design methods can be applied to single phase as well as multiphase reaction systems. For multiphase systems, Krishna and Sie [6] developed a strategy to choose between different multiphase reactors based on heuristics and with the aid of certain characteristics of the reaction systems. Mehta and Kokossis applied superstructure schemes to multiphase reactors [7] and eventually obtained homogeneous and multiphase reactor networks [8]. Kelkar and Ng [9] aggregated reactor attributes and constituent parts to form a reactor for the specific reaction under consideration.

Comprehensive descriptions of these reactor design methods can be found in previous works for homogeneous systems [10] and for multiphase systems [11]. These methods have in common that they are intended to guide the optimal selection from existing reactors or networks of existing reactors/reactor parts. It is then difficult with these methods to systematically include novel process intensification options in the design and to obtain tailor-made reactors. In order to allow for both, the identification of the maximum potential of the reaction system as well as the design of innovative reactor concepts, based on the concept of elementary process functions (EPF) [12] Freund, Peschel and Sundmacher recently proposed a new multi-level reactor design (MLRD) methodology [10,13]. The idea is to track a fluid element during the process, which travels through the reactor and changes its state within. On level 1, by continuously providing the fluid element with the optimal fluxes which are adjusted such that optimal states of the fluid element are achieved at all times, the optimal reaction conditions in the reactor can be identified. The most suitable fluxes to be further considered are determined by comparing the results of different cases including different combinations of fluxes, each representing different concepts for process intensification. On level 2, these fluxes obtained from level 1 are approximated by the optimal profiles of control variables such as the coolant temperature and the tube diameter by introducing the mass and heat transfer mechanisms, thereby checking the feasibility of realization of the most promising process intensification options. On level 3, the suitable control variables are further approximated using the detailed technical design.

This methodology has been successfully applied to different systems, including gas phase reaction systems [10,13–15] and multiphase reaction systems [11,16–19] (Table 1 except for $CO_2$ absorption). In those previously investigated systems, mass transfer limitations either can be completely neglected or have no significant influence. However,

* Corresponding author.
*E-mail address:* hannsjoerg.freund@fau.de (H. Freund).

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**Latin symbols**

| | |
|---|---|
| $a$ | specific area [$m^2/m^3$] |
| $A$ | cross-sectional area [$m^2$] |
| $c$ | concentration [$mol/m^3$] |
| $c_p$ | heat capacity [J/(kg K)] |
| $D$ | diffusion coefficient [$m^2/s$] |
| $H$ | Henry's law constant [Pa] |
| $J$ | mass transfer rate [$mol/(m^3 s)$] |
| $k$ | reaction rate coefficient, various units |
| $K$ | equilibrium constant, various units |
| $L$ | thickness of liquid film [m] |
| $M$ | molar mass [kg/mol] |
| $p$ | pressure [Pa] |
| $q$ | specific heat flux [$W/m^3$] |
| $r$ | reaction rate [$mol/(m^3 s)$] |
| $R$ | gas constant [J/(mol K)] |
| $t$ | time [s] |
| $T$ | temperature [K] |
| $u$ | velocity [m/s] |
| $w$ | mass fraction [–] |
| $X$ | mole fraction [–] |
| $z$ | length [m] |
| $Z$ | total length [m] |

*Greek symbols*

| | |
|---|---|
| $\epsilon$ | hold up [–] |
| $\delta$ | thickness of liquid segments [m] |
| $\nu$ | stoichiometric coefficient [–] |
| ρ | density [$kg/m^3$] |

*Abbreviations*

| | |
|---|---|
| EPF | elementary process functions |
| MEA | monoethanolamine |
| MLRD | multi-level reactor design |
| RMSE | root-mean-square error |

*Indices*

| | |
|---|---|
| C | carbon |
| for | forward |
| g | gas phase |
| gl | gas–liquid interface |
| in | inlet |
| l | liquid phase |
| rev | reverse |
| tot | total |
| 0 | operating point |

this assumption is of course not generally applicable since in many multiphase reaction systems severe mass transfer limitations exist. In these systems, one or more reactants diffuse from one phase into another phase where the reaction takes place, and the mass transfer rate is rather small compared to the reaction rate. Thus, a large concentration gradient is present. In order to consider the influence of the limited mass flux, the methodology is further extended for such systems in this present contribution. More specifically, it is the goal to rigorously consider multiphase reaction systems based on the EPF concept, by describing the system with fluid elements and fluxes as well as analyzing and optimizing different fluxes. For this, the tools of rigorous optimization and sensitivity analysis are applied, in order to obtain an optimal reactor design.

The extended methodology is applied to the chemical absorption of $CO_2$ with monoethanolamine (MEA) as example. Although based on the function of a $CO_2$ absorber in a chemical process the $CO_2$ absorber is a separator rather than a reactor, the design of $CO_2$ chemical absorber can represent the design of multiphase reactors. This system is chosen not only because it can represent the multiphase reaction systems with severe mass transfer limitation (see Table 1), but also because it is highly industrially relevant and many data are available. However, it should well be noted that the extended methodology is generally applicable to different multiphase reaction systems with severe mass transfer limitation, since it is only based on the balance equations, reaction kinetics, transfer kinetics, thermodynamics and system inherent boundaries.

**Table 1**
Summary of the reaction systems to which the MLRD methodology has been applied and comparison to the $CO_2$ absorption system in this work.

| System | Phase | Mass flux intensity |
|---|---|---|
| $SO_2$ oxidation [10,13] | Pseudo-homogeneous gas | Negligible |
| EO synthesis [14,15] | Pseudo-homogeneous gas | Negligible with constraints |
| Hydroformylation [11,16–19] | Liquid and gas | Considerable |
| $CO_2$ absorption, this work | Liquid and gas | Decisive |

## 2. The influence of transfer limitations and the extensions of the methodology

To apply the MLRD methodology to the multiphase system in which mass fluxes are limited, the types and influences of flux limitations need to be reviewed and discussed in the EPF framework.

### 2.1. The influence of transfer limitations

According to the EPF concept, when a fluid element is passing through a reactor, the state of the fluid element is changed by different types of fluxes. If each flux can be freely controlled, then each state in the operating range of the thermodynamic state space can be reached and kept in the reactor, i.e., possible species concentrations and temperature for the reaction are all attainable. The thermodynamic state determines the performance of the reaction (e.g. reaction rate or differential selectivity), and at least one state leading to maximum performance exists in the operating range of the state space. To keep this state, the corresponding fluxes of energy and all relevant components, which depend on the nature of the intrinsic reaction, need to be provided to counteract the effect of the reaction flux at this state (Fig. 1).

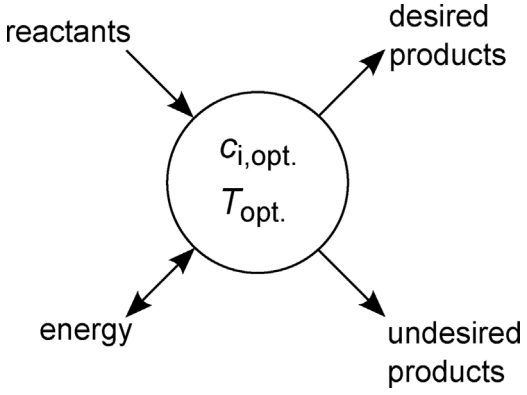


**Fig. 1.** The state in a fluid element (circle) leading to maximum performance and the corresponding fluxes (arrows).