

ECONOMICS AND EXERGY EFFICIENCY IN THE CONCEPTUAL DESIGN OF REACTIVE DISTILLATION PROCESSES

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Abstract

The interactions between economics and thermodynamic efficiency in the design of reactive distillation (RD) processes are explored. Our motivation derives from taking a sustainable lifespan perspective, where not only economics, but also exergy-efficiency and controllability should be borne in mind. Furthermore, novel process configurations might be generated and optimized (e.g. diabatic RD units) when an increased number of design variables is exploited. Our approach involves the development of rigorous dynamic, non-equilibrium model of a generic lumped RD volume element, comprising (species) mass, energy and entropy balances. The entropy production rate is important both for the exergy efficiency and a controllability analysis. As multiple conjugated fluxes and forces are considered, the classical theory of non-equilibrium thermodynamics is applied, to link fluxes with forces and to establish the entropy production rate. The key design variables considered for the lumped RD volume element are: liquid phase reaction volume (for homogeneously catalyzed reaction(s) or catalyst mass for heterogeneously catalyzed reactions(s)), external heating/cooling flow-rate and the areas for heat and mass transfer between the phases. A fundamental understanding of the strengths and shortcomings of this approach is developed by considering two applications: the simulation of a steady state MTBE column to analyze the contributions to entropy production rate; and the multiobjective optimization of a single diabatic RD stage. In the second application a trade-off has been found between economics and exergy criteria. Significant deviations from the utopia point have been encountered.

Keywords

Reactive distillation, conceptual design, entropy production rate, exergy efficiency.

Introduction

Advances in computing and information technology allow chemical engineers to solve more complex design problems, arising from the need to improve on the sustainability of the biosphere and human society. In such a context the performance of a chemical plant is to be optimized over its manufacturing life span, accounting for the use of multiple resources in the design and manufacturing stages. Since such resources are of a different nature (e.g. capital, raw materials, labor) with different degrees of depletion and rates of replenishment the performance of a chemical plant is characterized by multiple objectives with trade-off. This contribution offers

the results of a case study on the interactions between economics and exergy efficiency in the conceptual design of reactive distillation processes. Currently, design in chemical engineering is predominantly driven by (steady state) economic considerations, postponing to latter stages any issue related to exergy analysis and control performance. The importance of incorporating exergy efficiency in the early stages of the design cycle is stressed by the increasing depletion of non-renewable energy resources and the relatively low second law efficiencies (5-20%) for the majority of chemical processes. In spite of these facts, exergy analysis is exclusively performed as a

follow-up task to the process synthesis (de Koeijer, 2001). Controllability is important to maintain product quality and to avoid excessive use of utilities for control actions and reprocessing of off-spec material. An integrated unit operation like RD can offer significant benefits in resource utilization, when it is accompanied with the avoidance of chemical equilibrium limitations, enhancement of conversion, selectivity and yield and the reduction of both operational and capital costs. On the other hand, the non-linear coupling of chemical reaction, phase equilibria and transport phenomena leads to undesired, system-dependent features, such as multiple steady states and reactive azeotropes (Malone and Doherty, 2000). To study the interactions between economics, exergy efficiency and controllability three objective functions have been defined and solved simultaneously within an optimization problem. The functions include: f_{econ} representing the Total Annualized Costs of the process; f_{exergy} accounting for the process irreversibilities and expressed in terms of the entropy production rate by chemical reaction, heat and mass transfer; and $f_{control}$ being the settling time in the presence of representative disturbances as defined by Luyben et al. (1999).

Generic lumped RD volume element

To attain a fundamental understanding of the strengths and shortcomings of this approach a single lumped RD volume element is chosen as base case. This generic RD element has been selected to represent the governing phenomena involved in the combined process and to mimic the behavior expected in a whole (diabatic) RD column. Thus, mass transfer between phases and heat exchange are allowed in the stage and chemical reaction is triggered by the presence of an appropriate catalyst (Fig. 1). Each RD lumped element has its own complexities due to the many interacting phenomena. However, it does not account for the interactions between the stages in a real multi-stage column. The latter class of interactions could give rise to non-linear dynamic behavior and poor controllability if an unfortunate combination of reflux ratio and number of (non) reactive trays is chosen.

Mass/energy/entropy balances

Component, energy and entropy balances have been developed in the RD element. The entropy and, in particular, the entropy production rate are important to determine exergy losses and the controllability indicator. The balances lead to the following set of DAE's:

$$\frac{\partial C_i^{(\alpha)} V^{(\alpha)}}{\partial t} = \sum_{j=1}^{j=nst} F_{i,j}^{(\alpha)} - \Psi_i^{(\alpha)} + r_i^{(\alpha)} V^{(\alpha)} \quad (1)$$

$$\frac{\partial U^{(\alpha)}}{\partial t} = \sum_{i=1}^{i=nst} F_i^{(\alpha)} H_i^{(\alpha)} + \sum_{i=1}^{i=nc} J_i^{(\alpha)} g_i^{(\alpha)} + H_\psi + Q \quad (2)$$

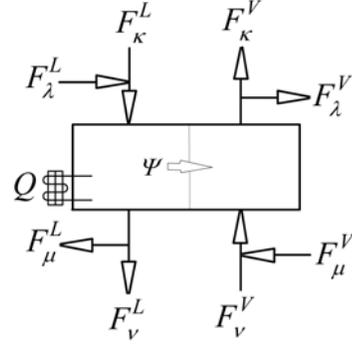


Figure 1. Generic lumped RD volume element

where: C_i is the molar concentration of component i ($i \in nc$) in the phase α ($\alpha \in np$), $F_{i,j}^{(\alpha)}$ is the convective flow of component i in phase α in the incoming or outgoing stream j ($j \in nst$), Ψ_j ($\equiv J_{\psi,j} a_\psi$) is the interphase molar flow of component j , $V^{(\alpha)}$ is the volume of phase α , J_j is the flux of component j per volume unit, r_j is the chemical reaction rate of component j per volume unit, U is the density of internal energy, F_j is the flowrate of stream j , $H_j^{(\alpha)}$ is the density of molar enthalpy of stream j , g_j is the external force exerted on component j per molar unit (including the contribution from electrical field), H_ψ is the energy flux associated with the interface mass and heat transfer, Q is the external heat exchange rate, nc is the number of components, nst is the number of incoming and outgoing streams and np is the number of phases. The entropy production rate σ at macroscopic level is derived from the contributions of mass-, heat diffusion in the liquid-vapour interphase, chemical reaction in the bulk of the liquid/vapour and heat conduction from external heat sources/sinks and the surrounding environment (Seider et al., 1999; Bedeaux and Kjelstrup, 2004). Hence, the entropy balance in the transient state at a *macroscopic* level is given by,

$$\frac{\partial S}{\partial t} = \sum_{i=1}^{i=nst} \Omega_i J_{s,i} + \Sigma_V \quad (3)$$

The entropy production rate Σ_V is obtained after integration of σ over the volume element, and elimination of the contributions of electric field, external forces ($g_j=0$) and diffusive momentum fluxes (Bird et al., 2003),

$$\iiint_V \sigma dV = \Sigma_V = \frac{1}{T} \sum_{i=1}^{i=nrx} A_i \varepsilon_i V_{RX} + J_q A_q X_q + \sum_{i=1}^{i=nc} J_i A_i H_i X_e + \left(- \sum_{i=1}^{i=nc} J_i A_i X_i \right) \quad (4)$$

where: S is the entropy of the system, $J_{s,j}$ is the convective flux of entropy of stream j ($j \in nst$), Ω_j is the cross sectional area orthogonal to the direction of flux j ($j \in nst$), A_j is the affinity of chemical reaction j ($j \in nrx$), ε_j is the extent of chemical reaction j , V_{RX} is the reaction volume, J_q is the measurable heat flux of the volume element, A_q is the heat transfer area of the measurable heat flux, H_j is the molar enthalpy of component j , X_q , X_e , and X_j are the conjugated driving forces for heat conduction, interfacial heat diffusion and interfacial mass diffusion of component j respectively (de Koeijer et al., 2002), T is the absolute temperature of the volume element, and nrx is the number of chemical reactions.

Design decision variables

For given operating pressure and feed(s) specifications the design variables under consideration are: liquid phase reaction volume for homogeneously catalyzed reaction(s) or catalyst mass for heterogeneously catalyzed reactions(s) (m_{cat}), external heating/cooling flow-rate (Q) and the areas for heat and mass transfer between the phases (a_{ψ}).

Economics/exergy efficiency and controllability objective functions

The economic performance indicator f_{econ} represents the TAC (investment and operation) of the process,

$$f_{econ} \equiv \sum_{i=1}^{i=nc} F_i^w c_i + F_{cu}^w c_{cu} + F_{hu}^w c_{hu} + c_{unit+catalyst} \quad (5)$$

where: F_j^w is the mass flow of component j , c_j is the cost of component j per unit of mass, $c_{unit+catalyst}$ is the investment cost of the unit and catalyst and cu and hu denote cool and hot utilities respectively. The exergy efficiency, f_{exergy} , is accounting for the process irreversibilities and is expressed in terms of the 2nd law thermodynamic efficiency, η^{II} ,

$$f_{exergy} \equiv \eta^{II} = \frac{W_{ideal}}{W_{ideal} - T_0 \Sigma_V} \quad (6)$$

where: W_{ideal} is the minimum work required by the process ($W_{ideal} < 0$), as given in Seider et al. (1999). The controllability index $f_{control}$ is chosen to be the settling time defined by Luyben et al. (1999),

$$f_{control} \equiv \tau = \frac{\Delta B(x(t))}{T_0 \Delta \Sigma_V(x(t))} \quad (7)$$

where: B is the availability or exergy function. At steady state conditions B is at its minimum value and increases when the system is perturbed by a disturbance. Since a similar situation holds for Σ_V , the response time τ measures the how fast a small $\Delta B(x(t))$ would dissipate due to an increased $\Delta \Sigma_V(x(t))$ (Luyben et al., 1999).

Two solving approaches have been adopted. (i) each objective function has been used independently, disregarding the other two; and (ii) a multi-objective problem has been formulated by using a weighted p -norm for the vector of three objectives, as given by Clark and Westerberg (1983),

$$\min f \equiv \left[\sum_i (w_i f_i)^p \right]^{\frac{1}{p}}, p \in [1, \infty) \quad (8)$$

A norm of $p \geq 2$ is used to localize non-inferior points in the non-convex regions (Clark and Westerberg, 1983). The first approach localizes the coordinates of the utopia point (i.e. such point given by the coordinates of the non-inferior points that solve independently the two scalar optimization problems) and subsequently, reduces the computational effort by limiting the search space. The second approach represents the interactions and trade-offs among the objectives.

Application 1: synthesis of Methyl *tert*-Butyl Ether

The esterification of isobutylene and methanol is used as case study. The presence of inerts is accounted for by a lumped-stream of n -butane (nC_4). The process is carried out at $11 \cdot 10^5$ Pa and 300K. The chemical reaction is represented by a pseudo-homogeneous kinetics. The gamma-phi thermodynamic model is used to predict phase equilibrium and the activity coefficients in the liquid phase are estimated by Wilson model (Güttinger and Morari, 1999).

Contributions to Σ_V in a complete MTBE column

In order to prepare for the optimization of a complete RD-column and to reduce complexity we identify the dominant contributions to entropy production rate over the MTBE column. The design parameters and conditions reported by Hauan et al. (1995), Jacobs and Krishna (1993) and Seader and Henley (1998) (see Table 1) are taken as nominal values. The results, Figure 2, show that mass diffusion is by far the dominant source of entropy production throughout the column, followed by the heat transfer. At the feed stages (9th-10th) the conjugated driving forces are considerably larger than elsewhere due to the difference of chemical potential and the temperature

between the entering streams and the mixture coexisting on the tray. External heat transfer plays a dominant role in the reboiler and condenser. In terms of entropy production, the separation function dominates over the reaction function for this MTBE column.

Table 1. Nominal values in the MTBE synthesis

Parameter	Value
Number of trays	15 (2-8-5)
Feed 1: location	iC_4+nC_4 : 10 th tray (G)
Feed 1: flowrate	455 mol/s
Feed 1: composition	iC_4 : 0.37; nC_4 : 0.63
Feed 1: temperature	350K
Feed 2: location	MeOH: 9 th tray (L)
Feed 2: flowrate	215.5 mol/s
Feed 2: composition	MeOH: 1.00
Feed 2: temperature	320K
Operating pressure	$11 \cdot 10^5$ Pa (top)
Column diameter	3.6 m
Heat duty/tray	0 W (except at reboiler/condenser)
Mass of catalyst/tray	204.1 kg

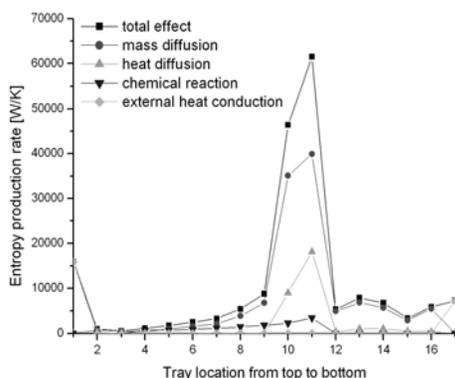


Figure 2. Entropy production rate for a 15 stage RD column for MTBE synthesis (Stage numbering: [1st: condenser]; [17th: reboiler]; [10th: feed MeOH]; [11th: feed C_4];)

Application 2: Pareto optimization

A multiobjective optimization problem is formulated for a single RD stage. The formulation includes Eqn. (1)-(4) and (5)-(8), together with the constraints imposed by operating conditions and product specifications. For the sake of simplicity the first approximation of this approach has been restricted to steady state operation. Under this assumption, the $f_{control}$ objective has been removed from the optimization formulation. The resulting optimization problem has been implemented and solved in gPROMS/gOpt. Significant deviations between optimal

designs and the utopia point are encountered (up to 60%) for the pair f_{econ} - f_{exergy} , stressing the importance of compromising both objectives (Figure 2).

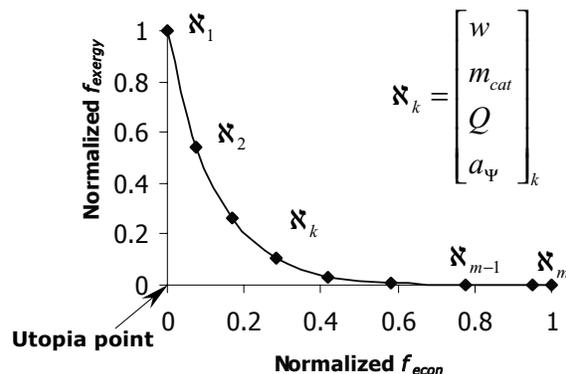


Figure 3. Pareto optimal curve depicting the trade-off between f_{econ} and f_{exergy} . Each point of the curve represents an optimal solution, x_k ($k \in \mathbb{R}^m$) in terms of the design variables $[m_{cat}, Q, a_p]$ and weighting factors $[w]$. The axes have been normalized so that the utopia point ($f_{exergy}=0.111$; $f_{econ}=6.25 \cdot 10^{-9}$) corresponds to the origin.

Conclusions and future research

The sources and the distribution of the entropy production rate in a complete MTBE column have been determined. It is believed that insight in such a distribution is helpful in assessing which column related design decision variables (feed tray location, reflux ratio, heat load distribution by means of diabatic operation) are key to optimize the column performance. In addition to economics and exergy objectives, this optimization will also cover controllability aspects in the future. The optimization studies of a single RD-stage already show that the designs based on an optimized individual objective (economics vs. exergy efficiency) differ significantly. The Pareto curve provides sensitivity information on the cost effects of improving the exergy efficiency.

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