

Model-based hybrid reaction-separation process design

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Abstract

The design of hybrid processes takes into account the performance of each constituent element and the optimisation of the design must take into consideration their interdependency. In this paper, we focus on hybrid process systems consisting of a reactor and a membrane separation unit whose design is usually carried out through trial-and-error approaches involving experiments. Through a model-based computer-aided technique it is possible to identify reliable and feasible design alternatives, saving valuable resources. The technique to be presented in this work consists of an efficient and systematic approach that generates and test design alternatives by avoiding duplication of work and by efficient decomposition of the problem into integrated sub-problems.

Keywords

Hybrid process, membrane separation, solvent selection, model-based design

1. Introduction

Many chemical and biochemical products are obtained in processes where reactions are equilibrium or kinetically controlled. These types of reactive processes can be usually characterized by low process yield or by low selectivity to the desired product, when parallel reactions occur. Irrespective of the controlling factor of reaction(s), on-site removal of product(s) enhance the yield, leading to reduced processing times and may also reduce undesired side

reaction(s) if they occur.

Conventional separation processes like distillation can be efficiently integrated with reaction as well known reactive distillation. However, specific “knock-off” criteria with respect to the reaction phase, catalyst, residence time and operating temperature and pressure need to be satisfied. One available option to remove products, in case when products of the reactions of interest are heat sensitive and separation technique requires operation at temperatures below the degradation temperature (reactants and/or catalyst), is to introduce some membrane-based separation processes. The membrane imparts selectivity to specific components based on either the difference in size or the chemical potential of the molecules. Solvents are playing a significant role in the reaction-separation systems not only as a reaction medium (e.g. solvent bring reactants together) or as a solubilization agent but also as a separation agent. Solvents are widely use in such processes like liquid-liquid extraction, extractive distillation and crystallization.

Combination of at least two processes is called a hybrid process since the two processes influence the performance of each other and the optimisation of the design must take into account that interdependency. Two types of hybrid processes are generally distinguished in literature [1]. The first group consists of processes which essentially perform the same function, for instant separation and separation (S-S). The second group contains “off-springs” of processes which combine processes originally different in nature, for example, combination of reactor and separator (R-S).

Based on a model-based framework for systematic analysis, it is possible to design hybrid process systems to find improved process design alternatives in terms of process output parameters such as reaction yield, selectivity, processing time and environmentally friendly solvents.

2. Design methodology of hybrid reaction – separation processes

2.1. Design algorithm

A systematic model-based framework presented in [2] has been extended to analyze not only hybrid reaction-separation (R-S) but also hybrid separation-separation (S-S) systems. The objective is to identify the best possible process set-ups for (R-S) and (S-S) systems with desired constraints of process parameters like yield, reaction time, selectivity and product purity. The design algorithm is depicted in Figure 1 and consists of four mains steps where new features are indicated in “bold” letters and only these are discussed below. Step 1 has been expanded to analyze separation tasks, which includes identification of azeotrope points, phase split, etc. Step 3 now combines all collected knowledge from step 1 with appropriate membrane separation models to generate the feasible hybrid process (design) alternatives. If an identified

separation technique requires use of solvents, the solvent selection method of Gani et. al [3] is used. In the last step (step 4), the generated hybrid process alternatives are tested under different operational scenarios. Based on which feasible alternatives are identified.

2.2. Process alternatives

The methodology as described above requires the analysis of different process scenarios in order to satisfy the process demands defined in step 2. Depending on batch or continues processes, various process scenarios can be derived. All scenarios need to be investigated qualitatively and quantitatively in order to explore and propose the best possible process scenario or at least the feasible operational window where the optimal design may exist. The superstructure of possible alternatives from which various process scenarios can be derived is depicted on Figure 2.

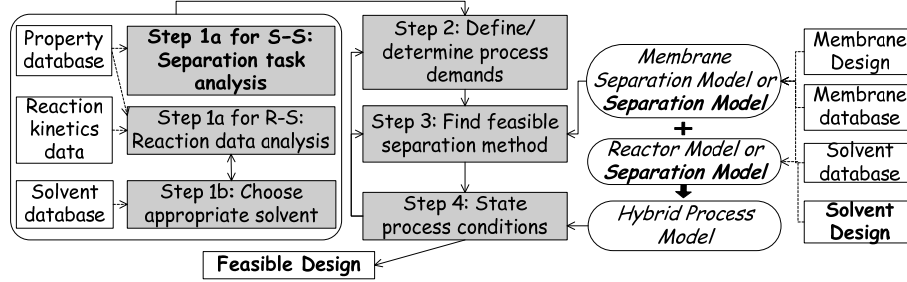


Figure 1 Methodology of design/analyze hybrid process system

2.3. Generic model of the hybrid process

A generic model giving the balance equations ((1)-(2)) for hybrid process are derived based on scheme given in Figure 2. The differential equations represent the states of the system at discrete time points while the algebraic equations are the constitutive and control equations. The process and property sub-models for both processes are not listed here but can be obtained from the corresponding author.

$$\begin{aligned} \left[\frac{\partial n_i}{\partial t} \right] = & \left[F_i \right] + \left[F_i^{(1\alpha R)} \right] + \left[F_i^{(1\beta R)} \right] + \left[F_i^{(2\alpha R)} \right] + \left[F_i^{(2\beta R)} \right] - \left[F_i^{(1\alpha P)} \right] \\ & - \left[F_i^{(1\beta P)} \right] - \left[F_i^{(2\alpha P)} \right] - \left[F_i^{(2\beta P)} \right] + \left[\sum_{k=1}^{NKR} v_{i,k}^{1\beta} r_k^{1\beta} V^{1\beta} \right] \end{aligned} \quad (1)$$

$$\begin{aligned} \left[\frac{\partial H}{\partial t} \right] = & \left[F_h(F) \right] + \left[F_i^{(1\alpha R)}_h(1\alpha R) \right] + \left[F_i^{(1\beta R)}_h(1\beta R) \right] + \left[F_i^{(2\alpha R)}_h(2\alpha R) \right] + \left[F_i^{(2\beta R)}_h(2\beta R) \right] \\ & - \left[F_i^{(1\alpha P)}_h(1\alpha P) \right] - \left[F_i^{(1\beta P)}_h(1\beta P) \right] - \left[F_i^{(2\alpha P)}_h(2\alpha P) \right] - \left[F_i^{(2\beta P)}_h(2\beta P) \right] + \left[\sum_{k=1}^{NKR} r_k^{1\beta} \Delta H_k^R \right] + [Q] \end{aligned} \quad (2)$$

In Equations (1)-(2): F_i – component molar flow, r – reaction rate, t – reaction

time, V – reaction volume, $\nu_{i,k}$ – stoichiometric coefficient, superscript: R – recycle, P – product, α – “bottom sub-product”, β – “top sub-product”.

For hybrid process design, the objective is to combine Flow out and Recycle terms of (Eq.1) into a single term representing the effluent from the hybrid system. Advantage of such a reformulated model is simplicity to investigate the performance of the hybrid system. Moreover, this reformulation reduces the number of variables and the degrees of freedom. Using the generic model and the particular details of any problem, the specific hybrid reactor-membrane process can be generated and tested.

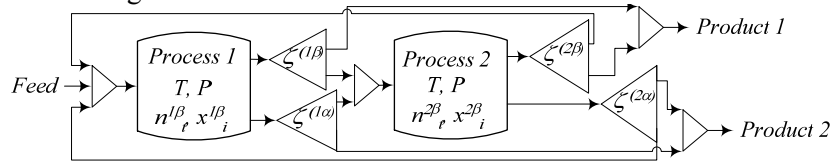


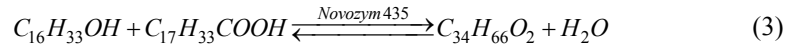
Figure 2 The general scheme of hybrid process

3. Case study

Application of the model-based framework is illustrated through an enzymatic esterification reaction of cetyl oleate, a sperm whale oil analogue. This ester has important applications in the cosmetics, lubricants, food and pharmaceutical industries. Objective of this study is to analyze the esterification process in order to identify hybrid process configurations with higher process yields.

Step 1a: Reaction data collection

The esterification of cetyl alcohol with oleic acid is carried out over Novozym 435 (commercially available *Canadia antarctica* immobilized lipase on acrylic resin) in the liquid phase. The kinetic model published by Garcia et. al. [4] considers competitive inhibition between substrates and products. However, the overall reaction can be represented as follows:



Operational window for this reaction with respect to temperature is between 332.3 K and 353 K (melting point temperature of 1-hexadecanol and the temperature of denaturation of lipase, respectively). Reaction is limited by the stability of the catalyst, which depends on water activity and is set to 0.11 based on information obtained from literature [5]. Since reported kinetic data [4] were obtained in solvent free system with reasonable conversion (at atmospheric pressure conversion is 0.8), it is considered that a solvent is not required.

Step 2: Process demands

Esterification reaction, which is kinetically controlled, has a conversion around 80mol%. The objective is to increase the process productivity by removing water from the reaction medium.

Step 3: Separation method selection

Pervaporation (PV) is selected as the membrane-based separation technique because of the possibility of introducing hydrophilic membranes that would allow only water to permeate. Several authors [6] had reported PV membranes to dehydrate organic mixtures, even with very small water concentration.

Step 4: Process conditions and feasible design

Two operational alternatives are presented in this paper: batch and semi-batch hybrid since small production rate is considered. In this case reactor and PV can be combined together in one unit since feed to PV unit does not need to be pre-heated ($T_R = 348.15K$). All set-ups are investigated under assumptions that: reactor is well mixed and activity of enzyme does not change during operation. From the generic hybrid model (Eq. (1)), the problem specific hybrid process model is generated (Eq.(4)). With respect to membrane, water flux depends on molar fraction of water (Eq.(5))[6] and fluxes for all other components present in the system are neglected.

$$\frac{dn_i}{dt} = -J_i A_m + V \sum_{k=1}^{NKR} \nu_{i,k} r_k \quad (4)$$

$$J_w = P_w x_w \quad (5)$$

Reaction kinetics is described by reversible Michaelis-Menten kinetics. Conversion of process is defined as ratio of moles of desired product (cetyl-oleate) to initial amount of reactant, ($X = N_{Es}/N_{Ac}$), and has a limiting value of 0.988. The full process model of the hybrid process consists of 4 ordinary differential equations, 31 algebraic equations with 91 variables, plus the equations for the constitutive model (Mod. UNIFAC (Lyngby)), and it is solved and analyzed through ICAS-MoT[7]. With the generated problem specific hybrid process model, five scenarios (with five different membrane areas) have been investigated in terms of process yield and superiority of the hybrid process over batch reaction. All simulations have been performed with the same initial conditions with respect to reactor: $C_{Al} = 1.58 \text{ mol/dm}^3$, $C_{Ac} = 1.58 \text{ mol/dm}^3$, $C_{Es} = 0 \text{ mol/dm}^3$, $C_w = 0.005 \text{ mol/dm}^3$ and $V = 0.6 \text{ dm}^3$. Performance of the hybrid system is strongly dependent on the membrane area (A_m) and component fluxes (J_i). The conversion-time behaviour is shown on Figure 3 while design variables are given in Table 1.

Table 1 Process parameters and process conversions

	Batch	RCPV1	RCPV2	RCPV3	RCPV4	RCPV4	RCPV5
$A_m [\text{m}^2]$	-	0.0036	0.0144	0.0288	0.0432	0.0144	0.0576
$t [\text{min}]$	300	300	300	300	300	900	300
$X [-]$	0.841	0.872	0.917	0.927	0.929	0.967	0.930

For operations carried out for 5h, yield is improved from 0.84 (batch) to 0.927 (RCPV3) by removing water from the system using a reasonable design for a PV-unit ($A_m = 0.0288 \text{ m}^2$). However, in 15h with RCPV3 it is possible to achieve conversion close to the limiting value. What is important to observe is that the increase of A_m from 0.0288 m^2 to 0.0576 m^2 does not give significant

improvement. The feasible membrane which would meet that design is a commercially available polyvinyl alcohol membrane (PERVAP1005, GFT).

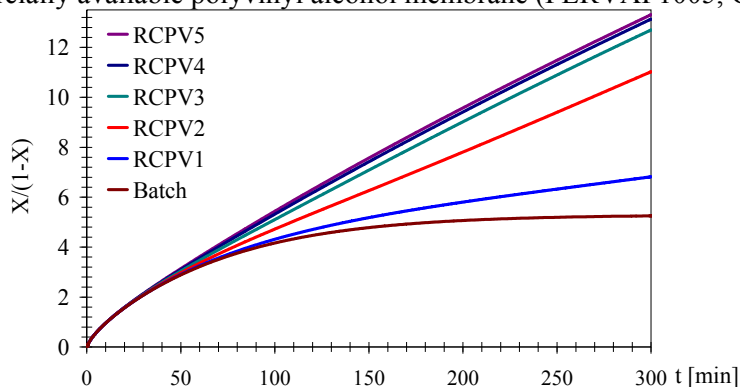


Figure 3 Comparison of hybrid process systems with batch in terms of conversion

4. Conclusions

A model-based computer-aided technique for systematic investigation of hybrid systems has been presented along with the application of the technique to the study of a enzymatic esterification reaction – separation system. The work-flow and the corresponding data-flow for the design methodology and the corresponding computer aided tools needed by the model-based technique have been developed and tested. Problem specific hybrid process models were generated from the generic model for the illustrated and other case studies. From this work, it is clear that hybrid processes consisting of a reactor and a membrane unit show advantages with respect to achieving increased product yield by overcoming limitations of kinetically controlled reactions and without additional process constraints.

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