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Design and optimization of batch reactive distillation processes with off-cut

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ABSTRACT

Although off-cut is commonly applied in non-reactive batch distillation, reports of the application of off-cut for batch reactive distillation (BREAD) are quite rare. In order to systematically investigate the use of off-cut in BREAD systems, we develop the optimal BREAD process design with and without off-cut for a canonical set of hypothetical reaction systems and a process for the hydration of methyl lactate. The results show that using off-cut can significantly improve performance, especially when both reactants have boiling points between those of the two products (for a quaternary system), when the product purity specification is high, and when the reaction equilibrium constant is low. The optimal batch recipe including off-cut can also be understood based on the normal boiling point ranking of the reactants and products.

1. Introduction

Reactive distillation is an intensified chemical process in which reaction and distillation are combined in a single operation. It can save capital and operating costs compared to traditional processes with reaction and separation separately and is especially attractive for equilibrium-limited reactions. Many researchers have investigated the feasibility, design, operation, control and optimization of continuous reactive distillation processes.

However, reactive distillation can also be carried out batch-wise, which is attractive for low-volume products such as pharmaceuticals or fine/specialty chemicals. Much less research has been conducted on the operation and optimization of batch reactive distillation (BREAD). Mujtaba [1] states: "An extensive literature survey shows that very little attention has been given to modeling and simulation of batch reactive distillation, let alone optimization of such process." Cuille and Reklaitis [2], Wajge *et al.* [3] and Bollyn and Wright [4] discuss the development and numerical solution of dynamic models for BREAD systems. Venimadhaven *et al.* [5], Bruggermann *et al.* [6], Huerta-Garrido *et al.* [7], and Qi and Malone [8] discuss design and operation of BREAD systems. Lee and coworkers [9–12] and Steger *et al.* [13] discuss the feasibility of batch reactive distillation. Malone and coworkers [14,15] discuss the selectivity of batch reactive distillation processes. Only a few authors [16–18] consider the optimization of BREAD processes. This is in part because the flexibility and inherently time-varying nature of the operation increase the complexity and difficulty of optimal BREAD process design.

A common strategy for improving the performance of batch distillation processes is the collection of off-cut (slop cut), that is material that does not meet the product purity specifications of any product and therefore must be either disposed of safely, recycled to the next batch, or collected for further processing in a separate batch operation. The off-cut is usually produced between two successive valuable product cuts. However, most researchers that investigated the operation of batch reactive distillation have assumed that only a single valuable product is collected and therefore the batch stops once it is no longer feasible to collect that product, and the processing of the remaining contents of the reactive reboiler (which does not meet any product purity constraint) is not considered. We are only aware of a few articles [5,19] which include off-cut collection in their BREAD processes.

In order to investigate the use of off-cut in BREAD process design, we determine the optimal batch recipe with off-cut for a canonical set of reversible quaternary reactions A + B ⇔ C + D, with different rankings of the normal boiling points of reactants and products. This set of reactions is the same as that used by Tung and Yu [20] to investigate the design of continuous reactive distillation processes. Trends in the efficacy of off-cut removal as well as reflux ratio profile, length of batch time and maximum possible batch capacity can be understood in terms of the normal boiling point ranking. The utility of off-cut in BREAD processes is also illustrated by the optimization of a real process for the hydrolysis of methyl lactate.

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2. Model development and optimization

2.1. Ideal quaternary reaction system

Tung and Yu [20] investigated the design of continuous reactive distillation systems using a canonical set of quaternary reversible reactions A + B ⇔ C + D. For this system, there are 24 (4!) possible boiling point rankings. Considering that the two reactants and two products are interchangeable, this reduces to six distinct possibilities, as shown in Table 1. LLK (lighter-than-light key), LK (light key), HK (heavy key) and HHK (heavier-than-heavy key) are used to denote the four components in the system in an increasing order of boiling point. The thermodynamic and kinetic parameters used in the ideal quaternary system are listed in Table 2. Further details about the reaction classification, kinetic and thermodynamic models are given in Tung and Yu [20] and in the web-published supplement.

2.2. Methyl lactate hydrolysis process

The hydrolysis of methyl lactate is an important step in the purification of lactic acid. The reaction is: water + methyl lactate ⇔ methanol + lactic acid. Edreder *et al.* [21] presented a case study of BREAD process design for this chemistry but did not consider the use of off-cut to improve process performance. Details of the kinetics and thermodynamics of this process are given in the web-published supplement [22,23].

2.3. BREAD column model

The BREAD column models used in this work are based on the work of Cuille and Reklaitis [2]. The main assumptions of the model include constant molar holdup on each stage, no reaction on the stages, and constant molar overflow. Two different column configurations, conventional batch distillation (CBD) and inverted batch distillation (IBD), are considered in this work and depicted in Fig. 1. For the CBD process, the feed is charged to a reactive reboiler and product and off-cut are collected at the top of the column. For the IBD process, reactants are charged to a feed drum, which in this case functions as a reactive distillate receiver, and product and off-cut are collected at the bottom of the column. Further details about the dynamic model and the assumptions that underlie it is available in the web-published supplement.

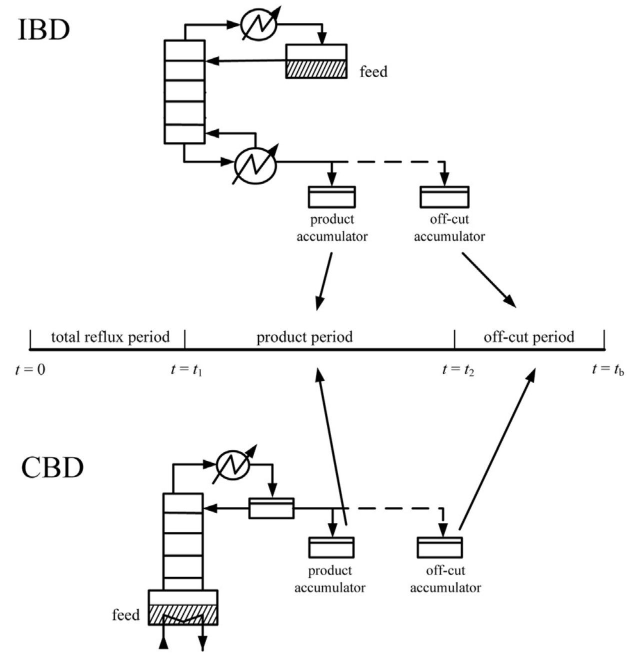

Fig. 1. Illustration of sub-periods for a quaternary BREAD process.

Table 1
Summary of chemistries and feasibility in BREAD processes for the quaternary system of Tung and Yu [20].

Type	Chemistry A + B ⇔ C + D	Feasibility[a]	
		CBD[b]	IBD[c]
I_p	LLK + HK ⇔ LLK + HHK	O	O
I_r	LLK + HHK ⇔ LK + HK	X	X
II_p	HK + HHK ⇔ LLK + LK	O	X
II_r	LLK + LK ⇔ HK + HHK	X	O
III_p	LK + HHK ⇔ LLK + HK	O	X
III_r	LLK + HK ⇔ LK + HHK	X	O

[a] O: feasible X: infeasible.
[b] Conventional batch distillation.
[c] Inverted batch distillation.

Table 2
Thermodynamic and kinetic parameters in the ideal system.

Activation energy (cal/mol)	Forward (E_F)			12,000
	Backward (E_B)			17,000
Specific reaction rate at 366 K (kmol/s/kmol)	Forward (k_F)			0.008
	Backward (k_B)			0.004
Heat of reaction (cal/mol)	λ			−5000
Heat of vaporization (cal/mol)	ΔH_V			6944
Relative volatilities	(LLK/LK/HK/HHK)			8/4/2/1
Component	LLK	LK	HK	HHK
Vapor pressure constants A_{VP}	13.04	12.34	11.65	10.96
$\ln P^S_i = A_{VP,i} - B_{VP,i}/T$ B_{VP}	3862	3862	3862	3862

From Tung and Yu [20].

2.4. Feasibility

Guo *et al.* [9] discussed the feasibility of BREAD processes. They showed that a BREAD process is feasible if and only if one of the product species is the lightest (CBD) or heaviest (IBD). For the quaternary system studied in this work, the feasibility of systems for CBD and IBD columns is given in Table 1. Infeasible designs are not considered for optimization.

3. Process operation and optimization

3.1. BREAD process operation

In general, for batch distillation process without reaction, separating a mixture composed of *NC* components requires ($NC - 1$) product cuts, and different product cuts are collected in separate accumulators sequentially. An off-cut may also be collected between two successive product cuts to achieve product with the desired purity in a reasonable amount of time. BREAD processes are similar except that the liquid mixture contains both reactants and products and there is a reaction taking place at the same time as the separation process. Therefore, the number of product cuts is also ($NC - 1$), but here *NC* means the number of products because the number of reactants is not important if they are almost completely consumed and not collected. The ideal quaternary system considered in this work contains two products, thus only one product cut is needed and an off-cut after the product cut may be used to improve the performance (achieve the purity specification of the other product which remains in the column in a shorter time). As a result, the total batch time is divided into three sub-periods for a reactive system with two products: total reflux period, product period and off-cut period. The lower diagram in Fig. 1 is an illustration of the operation of the CBD column. At $t = 0$,