The object of this column is to enhance our readers' collections of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and which elucidate difficult concepts. Please submit them to Professor James O. Wilkes (e-mail: wilkes@engin.umich.edu) or Mark A. Burns (e-mail: maburns@engin.umich.edu), Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.

# CSTR OPTIMIZATION WITH BY-PRODUCT DISPOSAL COSTS

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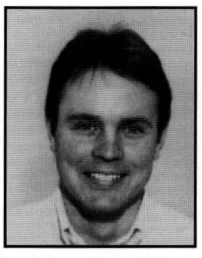
Reactor optimization problems are commonly encountered in the study of chemical reaction engineering. These problems become particularly interesting and challenging when product distribution is a concern. The simplest series reaction scheme

$$A \rightarrow R \rightarrow S \tag{1}$$

where the intermediate R is the desired product, is often analyzed. While discussing this reaction with a group of environmentally conscious chemical engineering students, concern for the fate of the undesired by-product S arose. What if species S is hazardous and presents disposal problems? How would this influence optimization of the reactor? An example of this type of reaction scheme is the successive chlorination of benzene to produce monochlorobenzene and dichlorobenzene. The ortho and para isomers of dichlorobenzene are health hazards[1] that may entail immediate disposal costs and/or future liability costs.[2] Fogler[3] has suggested that this reaction sequence can be carried out in a continuous stirred tank reactor (CSTR), and if the liquid phase is saturated with chlorine, then the reaction kinetics can be taken as first-order in nature.



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## A TRADITIONAL ANALYSIS

A diagram of the reactor is shown in Figure 1. Note that the feed concentrations of the product species R and S will be taken to be zero ($C_{Ro} = C_{So} = 0$). Before considering our analysis of this problem, a quick review of the typical approach to optimizing the performance of a CSTR for this reaction scheme will be given. When disposal of the by-product S is not a concern, the effluent concentration of species R is usually maximized to optimize reactor performance.[4] For the case of first-order reaction kinetics

$$-r_A = k_1 C_A \qquad r_R = k_1 C_A - k_2 C_R \qquad r_s = k_2 C_R \tag{2}$$

the CSTR design equation for constant-density conditions

$$\tau = \frac{V}{Q} = \frac{C_{Ao} - C_{Af}}{-r_A} = \frac{C_{Rf} - C_{Ro}}{r_R} \tag{3}$$

can be solved for the effluent concentrations of species A and R

$$\frac{C_{Af}}{C_{Ao}} = \frac{1}{1 + k_1 \tau} \tag{4a}$$

$$\frac{C_{Rf}}{C_{Ao}} = \frac{k_1\tau}{(1+k_1\tau)(1+k_2\tau)} \tag{4b}$$

The effluent concentration of species S can be determined from the reaction stoichiometry

$$\frac{C_{Sf}}{C_{Ao}} = 1 - \frac{C_{Af}}{C_{Ao}} - \frac{C_{Rf}}{C_{Ao}} \tag{4c}$$

Maximizing the effluent species R concentration with respect to the reactor space time by setting $dC_{Rf}/d\tau$ equal to zero indicates that the optimal reactor space time is

$$\tau_{max} = \left(\frac{1}{k_1 k_2}\right)^{1/2} \tag{5a}$$

The corresponding maximum effluent concentration of species R is

$$\frac{C_{Rf,max}}{C_{Ao}} = \frac{1}{\left[\left(\frac{k_2}{k_1}\right)^{1/2} + 1\right]^2} \tag{5b}$$

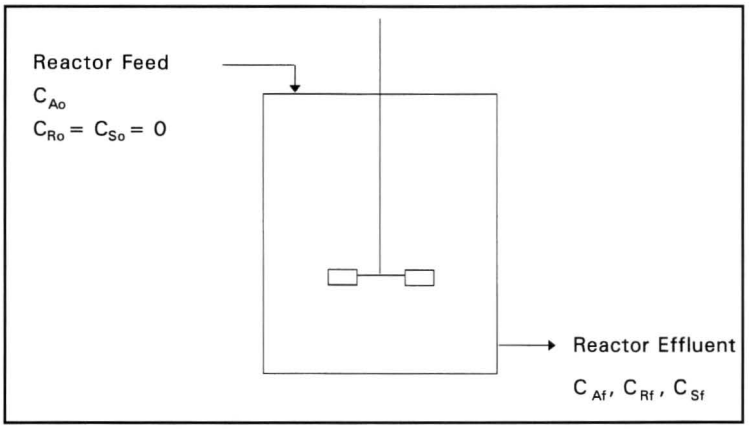


***Figure 1.*** *CSTR diagram.*

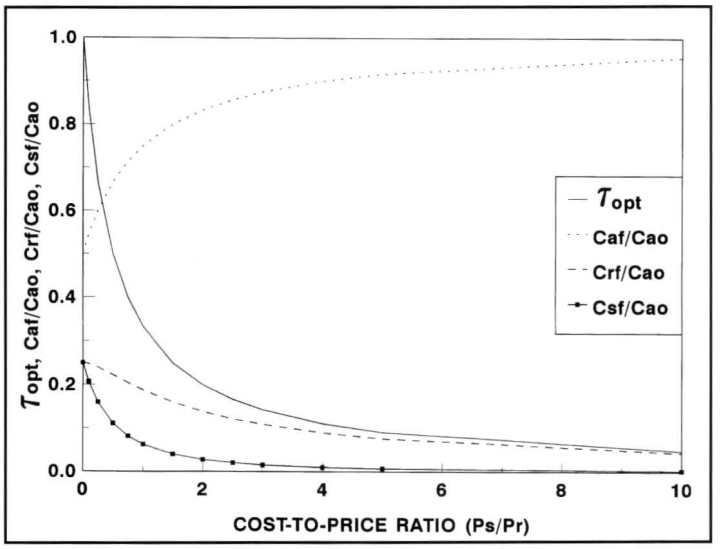


***Figure 2.*** *Influence of the cost-to-price ratio on the optimal reactor space time and corresponding effluent concentrations when the value of the effluent stream is maximized and* $k_1=k_2=1$ *time*$^{-1}$.

## A DIFFERENT APPROACH

Now reconsider this reactor optimization problem when there are disposal costs associated with the production of species S. In this case, the problem becomes one of pollution prevention.[2] First, it is necessary to choose an objective function that is to be optimized. We chose an economic objective function, the value of the effluent stream per unit volume ($\$_f$), which can be expressed as the difference between the income that can be obtained from selling the desired product (species R) and the cost required to dispose of the undesired by-product (species S)

$$\$_f = P_R C_{Rf} - P_S C_{Sf} \tag{6}$$

$P_R$ represents the income per mole that can be obtained from the sale of species R while $P_S$ is the cost per mole associated with the disposal of species S. To keep the analysis straightforward, this objective function does not include any costs associated with species A (perhaps species A is inexpensive or can readily be separated from the effluent and recycled to the reactor). But this consideration could also be included in a more detailed analysis.

The objective function of Eq. (6) can be maximized with respect to the reactor space time using the effluent concentrations of Eq. (4) (note that these expressions are not influenced by the change in objective function). Setting $d\$_f/d\tau$ equal to zero yields the reactor space time that maximizes the value of the effluent stream per unit volume

$$\tau_{opt} = \frac{1}{k_2}\left[\frac{\left(\beta - \alpha\beta + \alpha\beta^2\right)^{1/2} - 1}{1+\alpha\beta}\right] \tag{7}$$

The parameter $\alpha$ is the ratio of the reaction rate constants, while the parameter $\beta$ characterizes the relation between the selling price of species R and the disposal cost of species S,

$$\alpha = \frac{k_1}{k_2} \qquad \beta = \frac{P_S + P_R}{P_S} = 1 + \frac{P_R}{P_S} \tag{8}$$

The expression for the optimal reactor space time in this instance is rather unwieldy, but can be combined with Eq. (4) to yield the corresponding effluent concentrations.

Figure 2 illustrates the variation of the optimal reactor space time and effluent concentrations with respect to the cost-to-price ratio $P_S/P_R$ for the specific case of

$k_1 = k_2 = 1$ time$^{-1}$ (any arbitrary time units can be used). In the limit of the income from selling species R far exceeding the cost of disposing species S ($P_R >> P_S$ such that $P_S/P_R \rightarrow 0$) the present solution reduces to that found previously when the effluent concentration of species R was maximized (Eq. 7 reduces to Eq. 5a as $\beta$ approaches infinity).

As the cost of disposing species S increases, the amount of S produced must be decreased to maximize the value of the effluent stream. This is done by decreasing the reactor space time, which in turn decreases the effluent concentration of the desired product (species R) such that the driving force for the production of species S is decreased (refer to Eq. 2). This also increases the effluent concentration of the raw material (species A).

In the limit of very high disposal costs ($P_S >> P_R$), the process cannot be profitable and the optimal reactor space time tends to zero so that no reaction occurs and the formation of species S is avoided.

## VARIATIONS AND EXTENSIONS

This problem also leads to related exercises:

- Students can find examples of industrially relevant reaction schemes that fit this scenario. This should include finding selling prices and disposal costs to quantify the optimum reactor space time.
- Students can demonstrate that the results of the new analysis reduce to the results of the traditional analysis when the cost of disposing of species S is negligible (that is, show that Eq.7 reduces to Eq. 5a as $\beta$ approaches infinity).
- The technique of maximizing the value of the product stream can be modified to account for species S being a marketable product, but with a lower selling price than the intermediate species R. Fogler[5] cites the successive hydrodealkylation of mesitylene to produce m-xylene and toluene as an example of this situation. Both species have selling value, but m-xylene is preferred because of its higher selling price. Westerterp, et al.[6] discussed the successive chlorination of methane to form methyl chloride, methylene chloride, chloroform, and carbon tetrachloride. In this more complex reaction scheme, methylene chloride and carbon tetrachloride have the higher selling prices.
- As shown in Figure 2, large amounts of species A may remain in the effluent stream. This indicates that the simplifying assumption that the costs associated with species A are negligible may not be valid. A more complex optimization problem would include the cost of the species A raw material and/or the cost of separating species A from the product stream.[7]


## ACKNOWLEDGMENT

The author would like to acknowledge the encouragement and suggestions provided by the editor of the "Class and Home Problems" and the reviewer of this article.


## NOMENCLATURE

| | |
|---|---|
| $C_i$ | Concentration of species i (mole/m$^3$) |
| $C_{if}$ | Effluent concentration of species i (mole/m$^3$) |
| $C_{io}$ | Feed concentration of species i (mole/m$^3$) |
| $C_{Rf,max}$ | Maximum effluent concentration of species R (mole/m$^3$) |
| $k_i$ | First-order reaction rate constants (s$^{-1}$) |
| $P_R$ | Selling price of species R ($/mole) |
| $P_S$ | Disposal cost of species S ($/mole) |
| Q | Volumetric flow rate (m$^3$/s) |
| $r_i$ | Rate of production of species i per unit volume (mole/m$^3$s |
| V | Reactor volume (m$^3$) |
| $\$_f$ | Value of the effluent stream per unit volume ($/m$^3$) |
| $\alpha$ | Kinetic parameter $k_1/k_2$ (-) |
| $\beta$ | Cost parameter $(P_S+P_R)/P_S$(-) |
| $\tau$ | Reactor space time (s) |
| $\tau_{max}$ | Reactor space time that maximizes the effluent concentration of the desired product (s) |
| $\tau_{opt}$ | Reactor space time that maximizes the value of the effluent stream (s) |

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