Chapter 09.00B

Physical Problem for Optimization Chemical Engineering

Problem Statement

Very often, undesirable reactions occur along with desirable ones in chemical reactors. To improve the efficiency when such multiple reactions occur, it is important to maximize the yield of desired products and minimize the formation of undesired products. The separation cost increases proportionally to the rate of undesired product formation. We can improve the conversion efficiency of any reaction by wisely choosing the concentration of precursors and properly designing the reactor. Multiple reactions can be series, parallel or combinations of both types of reactions. Following are some examples of industrially significant multiple reactions:

Parallel Reactions

$$\text{Ethylene} + \text{Oxygen} \rightarrow \underset{\text{(undesired)}}{\text{Carbon dioxide} + \text{water}}$$

$$\downarrow$$

$$\text{Ethylene dioxide}$$

Series Reactions

$$\text{Ethylene oxide} + \text{Ammonia} \rightarrow \text{Mono} - \text{ethanolamine} \rightarrow \underset{\text{(desired)}}{\text{Di} - \text{ethanolamine}} \rightarrow \text{Tri} - \text{ethanolamine}$$

Complex Reactions

Reaction kinetics for the production of maleic anhydride by the air oxidation of benzene using a vanadium pentoxide catalyst [1]

$$\text{Benzene} \xrightarrow{O_2} \text{Maleic anhydride (desired)}$$

$$O_2 \downarrow \qquad\qquad\qquad \downarrow O_2$$

$$\text{Carbon dioxide} + \text{water}$$

Selectivity in multiple reactions indicates how one product is favored over another. It is defined as follows:

$$selectivity = \frac{rate\ of\ formation\ of\ desired\ product}{rate\ of\ formation\ of\ undesired\ products}$$

By maximizing selectivity, one can increase the efficiency of the process. Selectivity can be increased by choosing the optimal concentration of reactants, and by optimizing the configuration of the reactor. With this background, two problems for optimization are suggested below:

Problem 1.

The following are parallel reactions with the appropriate rate equations. This reaction scheme was given by Trambouze *et al.* [2]

$A \rightarrow X$ (undesired) Rate of formation of X: $r_X = 0.025$ mol/(liter.sec)

$A \rightarrow Y$ (desired) Rate of formation of Y: $r_y = 0.2C_A$ mol/(liter.sec)

$A \rightarrow Z$ (undesired) Rate of formation of Z: $r_z = 0.4C_A^{\ 2}$ mol/(liter.sec)

C_A is the concentration of A. Selectivity of this reaction in terms of desired product is

$$S_{Y/XZ} = \frac{r_y}{r_x + r_z}$$

Determine the concentration of reactant A at which the reactor should be operated to achieve maximum conversion to the desired product Y.

Problem 2.

Electro oxidation of methanol on planar platinum in alkaline electrolytes is carried out in packed bed electrochemical reactors [3]. Suggest the optimum volume V of catalyst in the reactor to maximize the yield of desired product.

$$\mathrm{CH_3OH} \xrightarrow{-4e} \underset{\text{(desired)}}{\mathrm{HCOO-}} \xrightarrow{-2e} \mathrm{CO_3 2-}$$

This equation can be represented as:

$$\mathrm{A} \rightarrow \underset{\text{(desired)}}{\mathrm{B}} \rightarrow \mathrm{C}$$

Rate of formation of B:

$$r_B = v_0 \frac{dC_B}{d\tau} = k_1 C_A - k_2 C_B$$

Rate of reaction for A:

$$r_A = v_0 \frac{dC_A}{d\tau} = -k_1 C_A$$

Where τ is the space-time, which can be related to volume V of catalyst using the following equation

$$\tau = V / v_0$$

$$k_1 = 0.33\,\mathrm{hr}^{-1}$$

$$k_2 = 0.15\,\mathrm{hr}^{-1}$$

When $V = 0, C_{A0} = 0.04$ mol/liter

The volumetric flow rate (v_0) of the reactants in the reactor is 7200 liters/hr.

Solutions

Solution Scheme for problem 1

Selectivity of the reaction

$$S_{Y/XZ} = \frac{r_y}{r_x + r_z} = \frac{0.2C_A}{0.25 + 0.4C_A^{\ 2}} \tag{1}$$

This selectivity is to be maximized to maximize the production of the desired product.

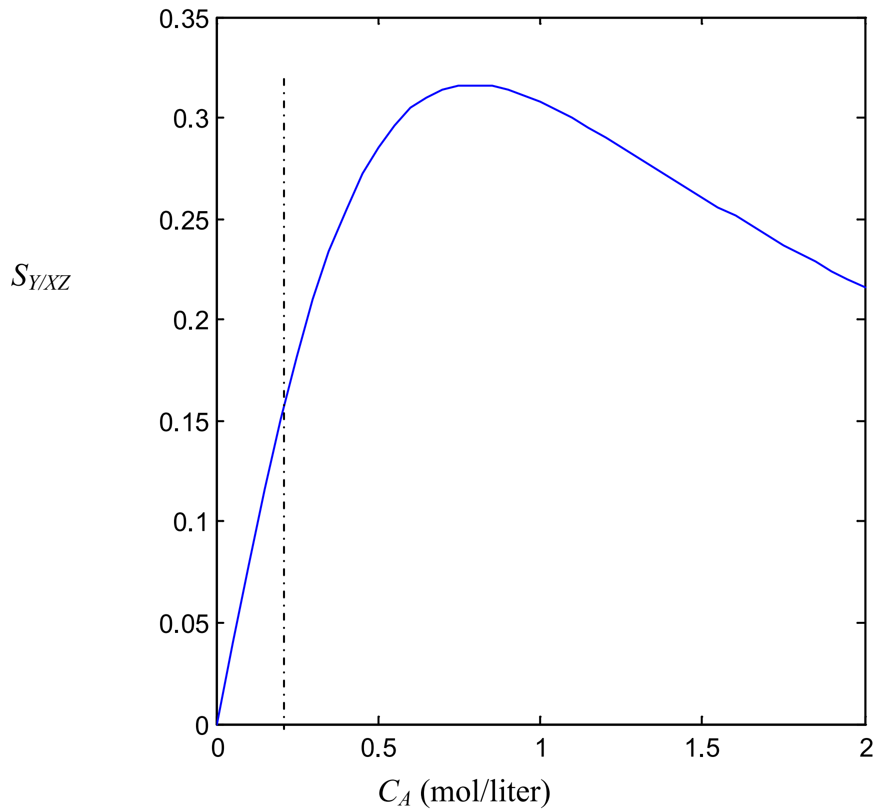

Figure 1: Selectivity as a function of the concentration of A

By observing Figure 1, it can be easily seen what value of C_A maximizes the selectivity of the desired product. This problem can be solved by both gradient search and direct search methods.

Solution scheme for problem 2

$$r_A = v_0 \frac{dC_A}{d\tau}$$

$$= -k_1 C_A \tag{2}$$

Integrating Equation (2)

$$C_A = C_{A0} e^{-k_1 \tau} \tag{3}$$

Putting this expression for C_A in following equation

$$r_B = v_0 \frac{dC_B}{d\tau}$$

$$= k_1 C_A - k_2 C_B \tag{4}$$

We get

$$\frac{dC_b}{d\tau} + k_2 C_B = k_1 C_{A0} e^{-k_1 \tau} \tag{5}$$

At the entrance of reactor

$$V = 0, C_B = 0, \tau = 0$$

Integrating Equation (5)

$$C_B = k_1 C_{A0} \left[\frac{e^{-k_1 \tau} - e^{-k_2 \tau}}{k_2 - k_1} \right] \tag{6}$$

We have to find out the optimal value of τ for which C_B will be maximized.

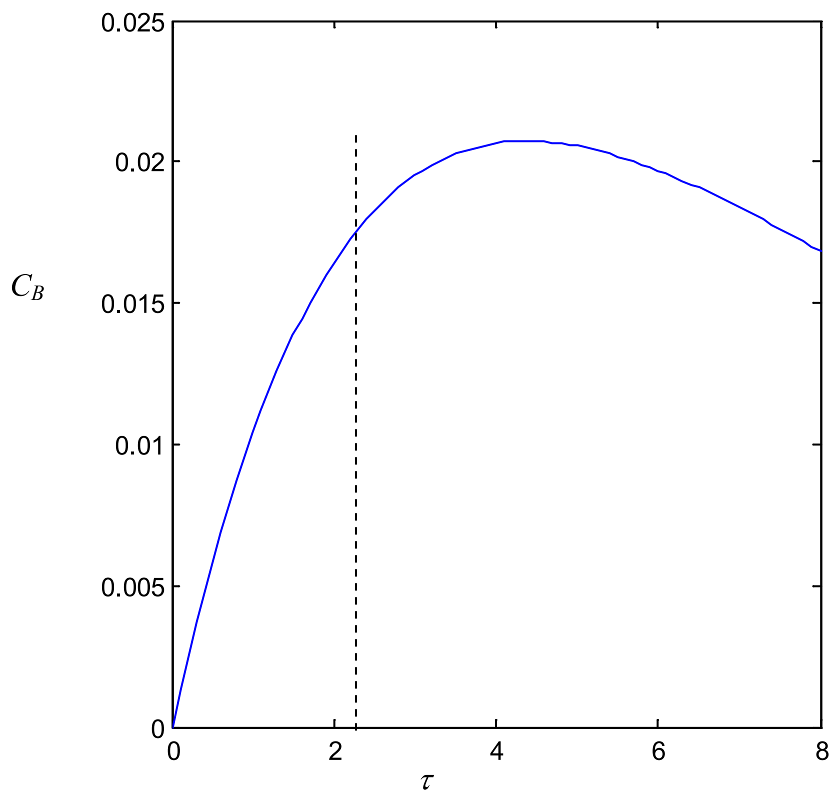

Figure 2: Concentration profile of B with respect to space-time in a packed bed reactor.

Referring to Figure 2, it can be seen that the optimal space-time is approximately 4.40 hours. Using the gradient search method, the optimal space-time and consequently the volume of catalyst can be calculated.
Differentiating Equation (6) we get

$$\frac{dC_B}{d\tau} = 0$$

$$\frac{k_1 C_{A0}}{k_2 - k_1}(-k_1 e^{-k_1\tau} + k_2 e^{k_2\tau}) = 0 \quad (7)$$

Solving Equation (7) we get

$$\tau_{opt} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2} \quad (8)$$

The optimum volume of the catalyst can be calculated from the optimal space time by using the following equation

$$V_{opt} = \tau_{opt} v_0 \quad (9)$$

Using Equation (8), the value for the space time obtained is 4.38 hour.
The optimum volume of the catalyst is: $V_{opt} = 31536$ liters.

References

1. Westerink EJ, Westerterp KR. Safe design of cooled tubular reactors for exothermic multiple reactions: multiple reaction networks. Chem Eng. Sci. 1988; 43, 1051.
2. Trambouze PJ, Piret EL. Continuous stirred tank reactors: design for maximum conversions of raw material to desired product. homogeneous reactions. AIChE J. 1959; 5, 384.
3. George PS. Criteria for selective path promotion in electrochemical reaction sequences. AIChE Journal, 1979; 25, 781.

OPTIMIZATION	
Topic	Physical optimization problem for chemical engineering
Summary	A physical problem of maximizing the yield of chemical products
Major	Chemical Engineering
Authors	Venkat Bhethanabotla
Date	December 5, 2011
Web Site	http://numericalmethods.eng.usf.edu