EXTENSION OF IDEAL MIXED REACTOR (CSTR) CONCEPTS: SIMULTANEOUS REACTION AND SEPARATION

Multifunctional reactors perform more than one function (e.g. reaction and separation) and are a good example of process intensification (e.g. achievement of increased volumetric productivity and selectivity from a reactor vessel).

a) Classical CSTR Model
We illustrate the concept of in-situ selective product removal through the example of a CSTR used to perform a simple reversible reaction $A = R$. Assuming a constant density system and a first order reversible process for a CSTR of volume $V$ and constant volumetric flow rate $\dot{V}$ the standard CSTR design equation yields:

$$\tau = \frac{V}{\dot{V}} = \frac{C_{A0} - C_A}{-R_A} = \frac{C_{A0} - C_A}{k_1 C_A - k_2 C_R} \quad (A)$$

Using the stoichiometry and definition of the reaction equilibrium constant expressed in concentrations we have

$$K = \frac{k_1}{k_2} = \frac{C_{eq}}{C_{eq}} = \frac{C_0 - C_{eq}}{C_{eq}} \quad (B)$$

where

$$C_0 = C_{A0} + C_{B0} \quad (C)$$

Thus,

$$C_{eq} = \frac{C_0}{K+1} \quad (B')$$

Using the relationship between the equilibrium and rate constants and equilibrium concentration of $A$, $C_{eq}$, the reaction rate can be rewritten as follows:

$$-R_A = k_1 C_A - k_2 C_R = (k_1 + k_2)(C_A - C_{eq}) = \frac{k_1 (K + 1)}{K} (C_A - C_{eq}) \quad (I) = (II) = (III)$$

Substitution of form II into equation (A) yields

$$\tau = \frac{V}{\dot{V}} = \frac{C_{A0} - C_A}{(k_1 + k_2)(C_A - C_{eq})} \quad (A*)$$

which can now be solved for the reactor exit concentration $C_A$:

$$C_A = \frac{C_{A0} + (k_1 + k_2)\tau C_{eq}}{1 + (k_1 + k_2)\tau} \quad (1)$$

or

$$C_A = \frac{(1+k_2\tau)C_{A0} + k_2\tau C_{B0}}{1 + (k_1 + k_2)\tau} \quad (1*)$$

From eq (1) note that the reactor exit concentration is always limited by the equilibrium one, i.e. $C_A > C_{eq}$, and the larger the space time $\tau$ the smaller the difference between the exit and equilibrium concentration. In the limit of $\tau \rightarrow \infty$ (i.e. of an infinitely large reactor) we approach $C_{eq}$ from above.
b) **In Situ Product Removal in Ideal CSTR**

Now assume that the product $R$ can also leave the reactor via another stream and to illustrate the case of maximum efficiency, reactant $A$ cannot enter that stream at all. For example, if $A$ is nonvolatile and $R$ is highly volatile, $R$ is removed by the stream of vapor. Or consider $R$ being removed via a selective membrane and being carried away by a purge stream. Consider other possibilities such as $R$ being removed as solids, etc.

The key concept of the equilibrium separation stage is now applied so that the concentration of $R$ in the new phase by which it is removed, $C_{R1}$, is considered equilibrated with concentration $C_R$ in the previous phase in the CSTR.

$$C_{R1} = K_s C_R$$  \tag{2}

The mass balance for $R$ on the overall CSTR must now acknowledge the removal of $R$ via two streams (the new one has flow rate $\dot{V}_1$) as shown below

$$\dot{V}(C_R - C_{R0}) + \dot{V}_1 C_{R1} = \dot{V}(C_{A0} - C_A)$$

so that the concentration of $R$ in the exit stream of the CSTR is

$$C_R = C_0 - C_A - \frac{\dot{V}_1}{V} C_{R1}$$

Using equation (2) we get the final concentration of $R$ in the reactor and in the original exit stream:

$$C_R = \frac{C_0 - C_A}{1 + \frac{\dot{V}_1}{V} K_s}$$  \tag{3}

Since reactant $A$ only leaves via the original outlet stream the balance for $A$ yields

$$\dot{V}(C_{A0} - C_A) = (k_1 C_A - k_2 C_R)V$$

Solving this for $\tau$ and substituting equation (3) for $C_R$ one gets

$$\tau = \frac{C_{A0} - C_A}{k_1 C_A - \frac{k_2 (C_0 - C_A)}{1 + \frac{\dot{V}_1}{V} K_s}}$$

Solving for the exit concentration $C_A$ one gets

$$C_A = \frac{(1 + k_2 \tau)C_{A0} + \frac{\dot{V}_1}{V} K_s C_{A0} + k_2 \tau C_{R0}}{1 + (k_1 + k_2) \tau + \frac{\dot{V}_1}{V} K_s (1 + k_1 \tau)}$$  \tag{4}

Let us examine eq (4). When $K_s = 0$ or $\dot{V}_1 = 0$, eq (4) becomes identical to eq (1*). Thus there is no selective product removal. Also eq (3) is then eq (C).

In general, when $\tau \to 0$ ($\dot{V} \to \infty$), $C_A = C_{A0}$; when $\tau \to \infty$ eq (4) reduces to

$$C_A = \frac{k_2 C_{A0}}{k_1 + k_2 + \frac{\dot{V}_1}{V} K_s}$$  \tag{4'}
If $\frac{\dot{V}}{V} K_s \rightarrow 0$, there is no selective product removal and the classical CSTR formula for equilibrium exit concentration is recovered (eq B'), i.e.

$$C_A = C_{A_{eq}} = \frac{C_0}{K+1}$$

But when $\frac{\dot{V}}{V} K_s > 0$ at $\tau \to \infty$

$$C_{A_{exit}} = \frac{C_0}{K+1} \left( \frac{1}{1 + \frac{\dot{V}}{V} K_s \frac{K}{K+1}} \right) = C_{A_{eq}} \left( \frac{1}{1 + \frac{\dot{V}}{V} K_s \frac{K}{K+1}} \right)$$

Clearly $C_{A_{exit}} < C_{A_{eq}}$.

We are now able to overcome equilibrium limitations and move the reaction to the right. Volumetric productivity is increased as

$$\frac{\dot{V}(C_{A_{0}} - C_A)}{V} = \frac{C_{A_{0}} - C_A}{\tau}$$

or a given $\tau$ is now increased by reducing $C_A$.

The effect of various parameters is as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Effect</th>
<th>$C_{A_{exit}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_S$</td>
<td>↑</td>
<td>↓</td>
</tr>
<tr>
<td>$K$</td>
<td>↑</td>
<td>$C_{A_{exit}}$</td>
</tr>
<tr>
<td>$\frac{\dot{V}}{V}$</td>
<td>↑</td>
<td>$C_{A_{exit}}$</td>
</tr>
</tbody>
</table>

**Numerical Example**

Let $k_1 = k_2 = 1$ (min$^{-1}$), $K = 1$, $C_{A_{0}} = 1$ (mol/L), $C_{R_{0}} = 0$. Then

$$C_{A_{eq}} = \frac{C_0}{K+1} = 0.5\text{ (mol/L)}$$

**a) Classical CSTR**

Given $\tau = 1\text{ min}$, use eq (1)

$$C_A = \frac{1 + 2 \times 0.5}{1 + 2 \times 1} = \frac{2}{3} = 0.667\text{ (mol/L)}$$

Given $\tau = 10\text{ min}$,

$$C_A = \frac{1 + 2 \times 10 \times 0.5}{1 + 2 \times 10} = \frac{11}{21} = 0.524\text{ (mol/L)}$$

As $\tau \to \infty$,

$$C_A = C_{A_{eq}} = 0.5\text{ (mol/L)}$$

**b) CSTR with selective product removal**

Let $\frac{\dot{V}}{V} K_s = 1$, $C_{R_{0}} = 0$, use eq (4).

$\tau = 1\text{ min}$
\[ C_{\text{exit}} = \frac{(1+1) \times 1 + 1 \times 1}{1 + 2 \times 1 + 1 \times (1 + 1)} = \frac{3}{5} = 0.6 \text{(mol/L)} \]

We have already achieved a better performance that with a classical CSTR. \( \tau = 10 \text{ min} \)

\[ C_{\text{exit}} = \frac{(1+10) \times 1 + 1 \times 1}{1 + 2 \times 10 + 1 \times (1 + 10)} = \frac{12}{32} = \frac{3}{8} = 0.375 \text{(mol/L)} \]

\[ C_{\text{eq}} = 0.5 \text{(mol/L)} \]

We have already gone beyond equilibrium concentration in a finite size (finite \( \tau \)) reactor. As \( \tau \rightarrow \infty \), we improve the performance further

\[ C_{\text{exit}} = \frac{1 \times 1}{1 + 1 \times 1 \times 1} = \frac{1}{3} = 0.333 \text{(mol/L)} \]

Additional improvement can be achieved by increasing \( (\dot{V}_i / \dot{V})K_s \).