

A Critical Review of Chemical Reactors Design for Reversible Reactions (I)

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Abstract

The aim of this paper is to present the correct relations of some chemical reactors design written for reversible reaction. Our discussion start from a paper of R. Levine where this subject is analysed, but a series of errors made by this author led to wrong solutions. This paper follows the presentation proposed by Levine, but in each situation where an error is occurred we try to repair and finally to propose a correct solution for each type of analysed reaction.

Key words: reactor, reversible reaction, volumetric efficiency

Introduction

Continuous stirred tank reactors (CSTR) are applied in different situations when: the reaction rate is quite low; the liquid reactants are immiscible or their viscosity is high and a higher agitation rate is required. The agitation system is also used in batch reactors and for this reason these two reactors are in discussion in this work.

We will put in discussion a design approach for CSTR made by Ralf Levine in his article “CSTR Design for Reversible Reactions” published in *Chemical Engineering*, Sept. 2009 [2].

The author intention is to discuss the volumetric efficiency of multiple CSTRs applied to the reversible second-order reactions and we will present the multiple errors made by Ralf Levine in the paper named above.

We will analyse the article exactly in the manner of the presentation, using the same chemical reactions and the same number for the equation proposed by author, but we added a small star (*) for each equation corrected by us. Finally, all the equations with the sign (*) are those that are proposed to replace the equations with the same number from the original article.

The first part of this review will put in discussion the 2nd order, reversible reaction carried out in a CSTR or in a plug-flow reactor. Finally, the volumetric efficiency is calculated in order to compare the performance of these two types of reactors.

Analysis of the 2nd Order, Reversible Reaction

The first case discussed by authors is the kinetic process: $2A \Leftrightarrow G + H$

where:

$$-r = k_F C_A^2 - k_R C_G C_H \quad (1)$$

$$k_R = \frac{k_F}{K} \quad (2)$$

$$(C_{A0} X_f)^2 = (C_{A0} - C_{Af})^2 = (C_{G0} - C_{Gf}) \cdot (C_{H0} - C_{Hf}) \quad (2a)$$

A first error is made in the equation (2a) because G and H are products of chemical reaction and their production will increase the final quantity of each product, thus the equation (2a) must be changed and the correct equation will be (2a*):

$$(C_{A0} X_f)^2 = (C_{A0} - C_{Af})^2 = 4 \cdot (C_{Gf} - C_{G0}) \cdot (C_{Hf} - C_{H0}) \quad (2a^*)$$

Because, the author did not explained how was calculated C_{Gf} and C_{Hf} we introduced equations (aa*, ba* and ca*) in order to explain this and to highlight where are the author's errors.

$$C_{Gf} = C_{G0} + \frac{1}{2} C_{A0} X_f \quad (aa^*)$$

$$C_{Hf} = C_{H0} + \frac{1}{2} C_{A0} X_f \quad (ba^*)$$

$$C_{A0} X_f = 2(C_{Gf} - C_{G0}) = 2(C_{Hf} - C_{H0}) \quad (ca^*)$$

Assuming that G and H are not present in the feed, therefore C_{G0} and C_{H0} are equal to zero.

At this moment, we found a new error in the equations (2b) and (2c), written by author as follows:

$$C_{Gf} = C_{A0} X_f \quad (2b)$$

$$C_{Hf} = C_{A0} X_f \quad (2c)$$

The error consists in the non-application of mass conservation law because there are 2 mols of reactant A which are transformed in 1 mol of G and 1 mol of H, thus the correct equations are (2b*) and (2c*):

$$C_{Gf} = \frac{C_{A0} X_f}{2} \quad (2b^*)$$

$$C_{Hf} = \frac{C_{A0} X_f}{2} \quad (2c^*)$$

From these equations it was obtained the following expression:

$$(C_{A0} X_f)^2 = 4 C_{Gf} C_{Hf} \quad (2d^*)$$

From the equations (2b*) and (2c*) we can observe that the final concentrations for G and H are equals and the expression “the concentration of G in the product may be five times that of H” is wrong because it is outside of the mass conservation law.

The reaction rate, written by the author, as a function of conversion has the following expression:

$$-r = k_F C_A^2 - k_R C_G C_H = k_F C_{A0}^2 (1 - X_f)^2 - \left(\frac{k_F}{K}\right) (C_{A0} X_f)^2 \quad (3a)$$

But, taking into account the expression (2d*), the correct form of the reaction rate is:

$$-r = k_F C_A^2 - k_R C_G C_H = k_F C_{A0}^2 (1 - X_f)^2 - \frac{1}{4} \left(\frac{k_F}{K}\right) (C_{A0} X_f)^2 \quad (3a^*)$$

$$-r = k_F C_{A0}^2 \left(1 - 2X_f + X_f^2 - \frac{1}{4K} X_f^2\right) \quad (3b^*)$$

$$-r = k_F C_{A0}^2 \left(\frac{4K-1}{4K} X_f^2 - 2X_f + 1\right) \quad (3c^*)$$

At equilibrium the net reaction rate will equal zero:

$$\frac{4K-1}{4K} X_e^2 - 2X_e + 1 = 0 \quad (4a^*)$$

Solving the equation (4a*), it was obtained:

$$X_e = \frac{1 \pm \sqrt{1 - \frac{4K-1}{4K}}}{\frac{4K-1}{4K}} = \frac{1 \pm \sqrt{\frac{1}{4K}}}{\frac{4K-1}{4K}} \quad (4b^*)$$

And, written in the same manner as the author we will have the following expression:

$$X_e = \frac{2 \pm \sqrt{1/K}}{(4K-1)/2K} = \frac{4K \pm \sqrt{4K}}{4K-1} \quad (4c^*)$$

The solution of the quadratic equation (3c*), can be written as following:

$$X_f = \frac{2 \pm \sqrt{1/K}}{(4K-1)/2K} = \frac{4K \pm \sqrt{4K}}{4K-1} \quad (5a^*)$$

The reaction rate expressions (5b) and (5c) are wrong because the author changed the reaction order from 2 to 1, without any explanation.

$$-r = k_F C_{A0}^2 (X_e - X_f) \quad (5b)$$

$$-r = k_F C_{A0}^2 X_e \left(1 - \frac{X_f}{X_e}\right) \quad (5c)$$

The correct expression for reaction rate can be written if the constant of equilibrium K is calculated as a function of X_e :

$$K = \frac{(C_G)_e \cdot (C_H)_e}{(C_A)_e^2} = \frac{\left(\frac{1}{2} C_{A0} X_e\right) \cdot \left(\frac{1}{2} C_{A0} X_e\right)}{C_{A0}^2 (1 - X_e)^2} = \frac{1}{4} \cdot \frac{X_e^2}{(1 - X_e)^2} \quad (da^*)$$

$$\frac{4K-1}{4K} = \frac{\frac{X_e^2}{(1-X_e)^2} - 1}{\frac{X_e^2}{(1-X_e)^2}} = \frac{X_e^2 - (1-X_e)^2}{X_e^2} = \frac{2X_e - 1}{X_e^2} \quad (\text{ea}^*)$$

Thus, the correct rate of reaction obtained from equation (3c*) is:

$$-r = k_F C_{A0}^2 \left(\frac{2X_e - 1}{X_e^2} X_f^2 - 2X_f + 1 \right) \quad (\text{5c}^*)$$

This expression of reaction rate shows that the reaction rate depends on the conversion and for $X_f = X_e$ the reaction rate becomes zero.

Batch reactor or plug-flow reactor

The analysis of the batch reactor and plug-flow reactor is made by author by using the incorrect equation (5c).

The reaction time t_r for batch reactor is equal with the spatial (residence) time V/v for the continuous plug-flow reactor:

$$t_r = V/v = C_{A0} \int_0^{X_f} \frac{dx}{-r} \quad (6)$$

Substituting the correct equation (5c*) in the equation (6) and rearranging gives the following expression:

$$\frac{V}{v} (k_F C_{A0}) = \int_0^{X_f} \frac{dX}{\frac{2X_e - 1}{X_e^2} X^2 - 2X + 1} \quad (\text{6a}^*)$$

The equation (6a*) is solved by integration for known values of conversion at equilibrium X_e .

Volume of each CSTR stage

The equation (7) is the expression of the mass balance, written for the first stage of a CSTR battery connected in series:

$$\frac{V_1}{v \cdot C_{A0}} = \frac{X_1}{-r} \quad (7)$$

The author [2] considers that for a battery of CSTR where each reactor has the same volume and volumetric flow rate (Temperature being equal for all the reactors) the conversion will be the same for each stage, thus: $X_1 = X_2 = \dots = X_n$.

But we cannot accept this judgement because the conversion is a function of reaction rate which is different from a reactor to other, $X_1 \neq X_2 \neq \dots \neq X_n$.

In this case, the mass balance written for reactor "i" has the following expression [1]:

$$\frac{V_i}{v \cdot C_{A0}} = \frac{X_i - X_{i-1}}{-r_i} \quad (7^*)$$

Substituting equation (5c*) into (7) it was obtained equation (7a*):

$$\frac{V_1}{v} (k_F C_{A0}) = \frac{X_1}{\frac{2X_e - 1}{X_e^2} X_1^2 - 2X_1 + 1} \quad (7a^*)$$

Number of stages

The discussion regarding the number of stages has some mistakes, which will be underlined at that moment.

So, the conversion for the first stage is:

$$X_1 = \frac{C_{A0} - C_{A1}}{C_{A0}} \quad (8)$$

And, the equilibrium conversion has a similar expression:

$$X_e = \frac{C_{A0} - C_{Ae}}{C_{A0}} \quad (9)$$

Subtract equation (9) from (8) and divide by (9) obtains equations (10a) and (10b):

$$X_e - X_1 = \frac{C_{A1} - C_{Ae}}{C_{A0}} \quad (10)$$

$$\frac{X_e - X_1}{X_e} = \frac{C_{A1} - C_{Ae}}{C_{A0} - C_{Ae}} \quad (10a)$$

$$1 - \frac{X_1}{X_e} = \frac{C_{A1} - C_{Ae}}{C_{A0} - C_{Ae}} \quad (10b)$$

Making a similar judgement for C_{A2} , based on volume for all stages are equals and are working in the same conditions, we cannot accept the equation (10c), because X_2 is calculated as “conversion at the exit of the second reactor” and this value is not equal with the conversion made in the second reactor (Δx_2). The correct expression is presented in equation (10c*).

$$1 - \frac{X_2}{X_e} = \frac{C_{A2} - C_{Ae}}{C_{A1} - C_{Ae}} \quad (10c)$$

$$X_2 = X_1 + \frac{C_{A1}}{C_{A0}} \Delta x_2 \quad (fa^*)$$

where:

$$\Delta x_2 = \frac{C_{A1} - C_{A2}}{C_{A1}} \quad (ga^*)$$

$$1 - \frac{X_2}{X_e} = 1 - \frac{C_{A0} - C_{A1}}{C_{A0} - C_{Ae}} - \frac{C_{A1} - C_{A2}}{C_{A0} - C_{Ae}} = \frac{C_{A2} - C_{Ae}}{C_{A0} - C_{Ae}} \quad (10c^*)$$

Thus the equation (11a) is wrong because the author consider that $X_1=X_2$ and it is easy to observe that they are not equals. Also, the equation (10c*) has the same result al equation (11a), showing another mistake of the application of chemical rules.

$$\left(1 - \frac{X_1}{X_e}\right)^2 = \frac{C_{A1} - C_{Ae}}{C_{A0} - C_{Ae}} \cdot \frac{C_{A2} - C_{Ae}}{C_{A1} - C_{Ae}} = \frac{C_{A2} - C_{Ae}}{C_{A0} - C_{Ae}} \quad (11a)$$

The remaining expressions (12 – 12b) are wrong for the same reasons.

Total volume of all stages

For the calculation of total volume of all stages, the author use a wrong equation based on equation (5c). The correct solution will be obtained by substituting equation (7a*) into (13a):

$$V_T = nV_1 \quad (13a)$$

$$\frac{V_T}{v} (k_F C_{A0}) = n \frac{V_1}{v} (k_F C_{A0}) = n \left(\frac{X_1}{\frac{2X_e - 1}{X_e^2} X_1^2 - 2X_1 - 1} \right) \quad (13b^*)$$

The discussion regarding the replacement of conversion X_f with concentration C_{An} is also wrong, because: $X_f \neq n \cdot X_1$ and equations (13c-13d) are wrong.

Volumetric efficiency

The plug-flow reactor and CSTR are operated with the same volumetric flowrate and they are working at the same temperature in isothermal conditions. Thus, the volumetric efficiency is obtained if the volume V for plug-flow operation is compared to total volume V_T for multiple CSTRs. This ratio (V/V_T) is expressed as equation (14a*) and is derived from the equations (6a*), (13b*) and (14*):

$$\frac{\frac{V}{v} k_F C_{A0}}{\frac{V_T}{v} k_F C_{A0}} = \frac{\int_0^{X_f} \frac{dX}{\frac{2X_e - 1}{X_e^2} X^2 - 2X + 1}}{\frac{nX_1}{\frac{2X_e - 1}{X_e^2} X_1^2 - 2X_1 + 1}} \quad (14^*)$$

$$\frac{V}{V_T} = \frac{\int_0^{X_f} \frac{dX}{\frac{2X_e - 1}{X_e^2} X^2 - 2X + 1}}{\frac{nX_1}{\frac{2X_e - 1}{X_e^2} X_1^2 - 2X_1 + 1}} \quad (14a^*)$$

If the author [2] concludes that the volumetric efficiency is “dependent on only the ratio of the first stage conversion compared to the equilibrium conversion”, the equation (14a*) shows that volumetric efficiency also depends of final conversion X_f in plug-flow reactor and number of stages n for a series of CSTR.

Conclusion

This study presented a critical analysis of CSTR design for reversible reactions. The aim of the author was to “create” short equations for different chemical reactions in order to obtain very easy to interpret equations of volumetric efficiency for CSTR and plug-flow reactors.

Unfortunately, the author made some errors and these “short” equations didn’t respect the fundamental laws of chemistry, so that we made the corrections and the “short” equations became longer, but in respect of all the chemical laws.

References

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2. Levine, R. – CSTR Design for Reversible Reactions, *Chemical Engineering*, Vol. 116, No. 9, Sept. 2009, p.46.

O analiză critică a proiectării reactoarelor chimice pentru reacții reversibile (I)

Rezumat

Scopul acestei lucrări este să prezentăm relațiile corecte pentru proiectarea unor reactoare chimice scrise pentru reacții reversibile. Analiza noastră are la bază un articol scris de R. Levine care se ocupă de acest subiect, dar face o serie de erori care conduc la soluții greșite. Lucrarea noastră urmărește prezentarea făcută de Levine, dar acolo unde apar greșeli, noi încercăm să le corectăm și în final propunem o soluție corectă pentru fiecare tip de reacție analizată.