

Executive Summary

The rate law equations were determined using two different methods which are the non-linear regression method and polynomial fit method by utilizing experimental data from the literature, such as the concentration of species A (acetic anhydride) at various times. The rate law equations that were derived by applying these two techniques show a few slight variations. Using the Arrhenius equation and data on rate constants at various temperatures taken from the literature, the value of the rate constant at 23°C is determined.

Next, the rate law that obtained will be compared with literature and the differences is discussed. Furthermore, the volume required for a CSTR and a PFR in a single reactor volume to achieve an 80 % conversion of acetic anhydride is determined by formula and graphical method. Lastly, an optimum isothermal reactor system is designed to achieve 80 % conversion of acetic anhydride with minimum reactor volume. The design will be further verified through HYSYS software.

Table of Contents

| | |
|--|----|
| Executive Summary | 2 |
| 1.0 Introduction | 4 |
| 1.1 Background..... | 4 |
| 1.2 Objective..... | 4 |
| 2.0 Two Methods Determine Rate Law, Reaction Order and Rate Constant | 5 |
| 2.1 Differential Method- Polynomial Fit..... | 5 |
| 2.2 Nonlinear Regression Method | 8 |
| 2.3 Rate Law..... | 9 |
| 3.0 Comparison of Rate Law..... | 11 |
| 3.1 Comparison of Rate Law Calculated with Literature Sources | 11 |
| 3.2 Factors Leading to Difference in k -values..... | 13 |
| 4.0 Calculation on Volume of CSTR and PFR to Achieve 80 % Conversion | 13 |
| 4.1 Formula Method | 14 |
| 4.2 Graphical Method | 15 |
| 4.3 Discussion..... | 17 |
| 5.0 Isothermal Reactor System to Achieved 80 % Conversion of Acetic Anhydride with Minimum Reactor Volume..... | 17 |
| 5.1 HYSYS Simulation Setup | 17 |
| 5.2 Parameter and Assumption..... | 18 |
| 5.3 Single CSTR Reactor System..... | 18 |
| 5.4 Single PFR Reactor System..... | 19 |
| 5.5 Double CSTR in Series..... | 20 |
| 5.6 Double PFR in Series | 22 |
| 5.7 CSTR and PFR in Series | 23 |
| 5.7.1 CSTR Followed by PFR in Series | 23 |
| 5.7.2 PFR Followed by CSTR in Series | 24 |
| 5.8 Double CSTR in Parallel | 25 |
| 5.9 Double PFR in Parallel..... | 27 |
| 5.10 CSTR and PFR in Parallel | 27 |
| 5.11 Comparison Between All Systems | 29 |
| Conclusion..... | 29 |
| References | 30 |

1.0 Introduction

1.1 Background

Acetic anhydride is a clear colourless liquid at standard conditions with a molecular formula of $C_4H_6O_3$ and a flash point of approximately $53.89\text{ }^{\circ}\text{C}$. It will react with water, including water vapour in the air, to form acetic acid, which is identifiable by its sharp odour. This happens through the reaction $(CH_3CO)_2O + H_2O \rightarrow 2 CH_3COOH$. This happens in a process known as hydrolysis with three overall irreversible steps: addition, elimination and proton transfer to the solvent (Asprey et al., 1996). The addition reaction is the rate-controlling process in this reaction and each of the reactants has first-order resulting kinetics (Asprey et al., 1996). According to Candruff (1978), since this reaction belongs to the SN_2 mechanism, it obeys the second-order kinetics. Hydrolysis of acetic anhydride is considered to have a pseudo-first-order rate constant k that is composed of a true second-order rate constant, k' (Asprey et al., 1996).

Although it is one of the simplest acid anhydrides, acetic anhydride is widely used for the production of a wide variety of products and is widely used in organic synthesis. It is used extensively in many industries including in the manufacture of industrial chemicals, pharmaceuticals, perfumes, synthetic fibres and even explosives. Moreover, it is used in the production of photographic film and other similar coated materials through the conversion of cellulose-to-cellulose acetate. Additionally, it is used in the production of aspirin in the acetylation of salicylic acid. Thus, it is justified to conclude that acetic anhydride plays a huge role in many industries.

This technical report will cover the overall understanding of the kinetics of acetic anhydride hydrolysis, mainly the rate law including the temperature dependence. This report will also determine reactor volumes necessary to achieve the necessary conversion in the system, as well as provide an optimum design of an isothermal reactor system.

1.2 Objective

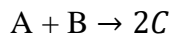
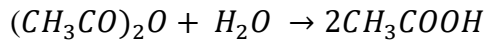
The objectives of this report are:

- To determine the rate law, reaction order and the temperature dependence of the rate constant with two methods using batch experimental data from literature provided.
- To compare the rate law obtained with literature.
- To determine and compare the reactor volume required for CSTR and PFR in single reactor system to achieve an 80 % conversion of acetic anhydride.
- To design an optimum reactor system to achieve an 80 % conversion of acetic anhydride by minimising the reactor volume.

2.0 Two Methods Determine Rate Law, Reaction Order and Rate Constant

2.1 Differential Method- Polynomial Fit

Chemical Equation of Hydrolysis of Acetic Anhydride:



*In this case, it is a pseudo-first-order reaction because water is an excess. Based on the excess method in batch reactor data analysis, the reaction runs in an excess of B which is the water, so that remains essentially unchanged during the reaction, therefore is treated dependently.

$$\text{Rate law: } -r_A = kC_A^\alpha C_B^\beta$$

Since $C_B = C_{B0}$ (H_2O) is an excess,

$$\text{Let } k' = kC_B^\beta \approx kC_{B0}^\beta$$

$$\text{Rate law: } -r_A = k'C_A^\alpha$$

From the mole balance batch reactor equation: $\frac{dN_A}{dt} = r_A V$

$$\text{Stoichiometry: liquid} \rightarrow N_A = C_A V$$

$$\begin{aligned} \frac{dN_A}{dt} &= \frac{dC_A V}{dt} r_A V \\ \frac{dC_A}{dt} &= r_A \end{aligned}$$

By combining mole balance, rate law, and stoichiometry:

$$\begin{aligned} -r_A &= k'C_A^\alpha \\ -\frac{dC_A}{dt} &= k'C_A^\alpha \end{aligned}$$

Taking the natural log of both sides,

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln(k') + \alpha \ln(C_A)$$

Which represent $y = c + mx$ in the graph

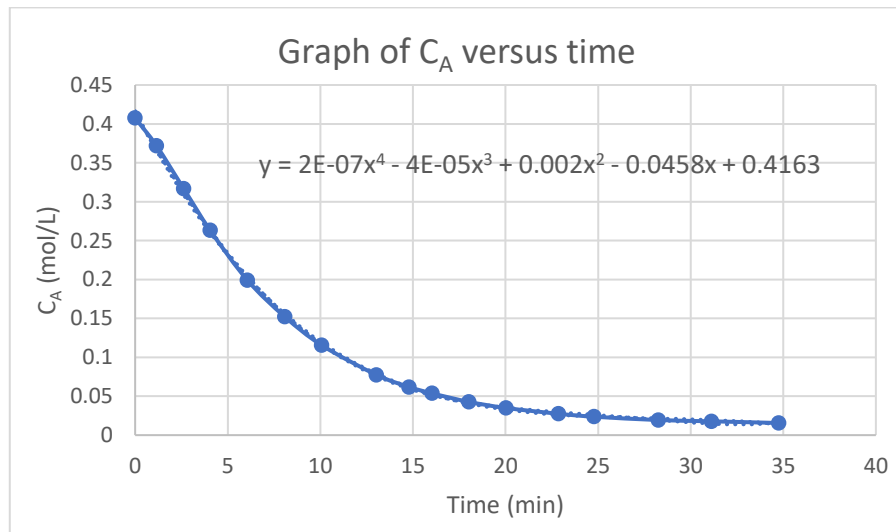
The slope of a plot of $\ln\left(-\frac{dC_A}{dt}\right)$ versus $\ln(C_A)$ will yield the reaction order α with respect to Acetic Anhydride, C_A by using the data from the literature.

Table 2.1.1: The Experimental Data at T=23°C

| t (min) | C_A (mol/L) |
|---------|---------------|
|---------|---------------|

| | |
|-------|---------|
| 0.00 | 0.40750 |
| 1.15 | 0.37199 |
| 2.62 | 0.31679 |
| 4.05 | 0.26323 |
| 6.07 | 0.19892 |
| 8.08 | 0.15222 |
| 10.08 | 0.11545 |
| 13.03 | 0.07749 |
| 14.80 | 0.06189 |
| 16.03 | 0.05369 |
| 18.02 | 0.04279 |
| 20.03 | 0.03490 |
| 22.87 | 0.02746 |
| 24.78 | 0.02371 |
| 28.25 | 0.01941 |
| 31.12 | 0.01779 |
| 34.75 | 0.01562 |

With the data from journal, a graph is plotted with C_A on y-axis and time on x-axis:



From the graph:

$$C_A = 2 \times 10^{-7} t^4 - 4 \times 10^{-5} t^3 + 0.002 t^2 - 0.0458 t + 0.4163$$

By differentiating with respect to time,

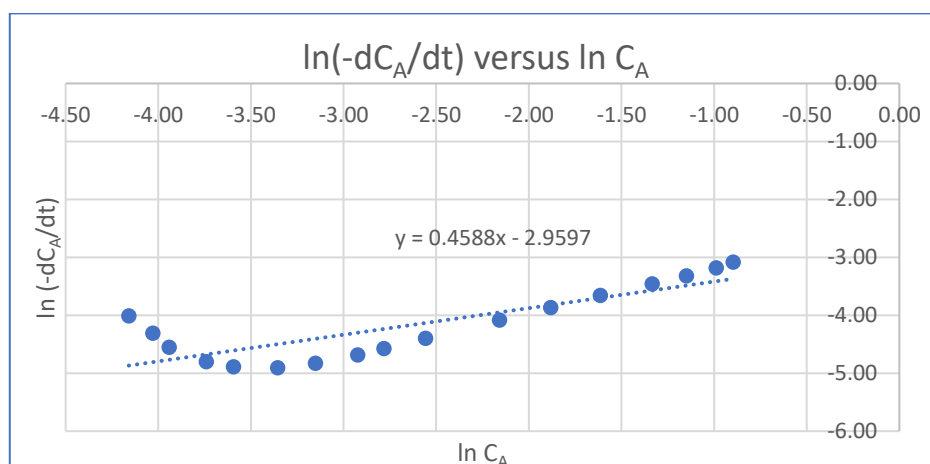
$$\frac{dC_A}{dt} = 8 \times 10^{-7} t^3 - 1.2 \times 10^{-4} t^2 + 4 \times 10^{-3} t - 0.0458$$

By substituting given time from Table 1.1 into $\frac{dC_A}{dt}$ using Excel Sheet, Table 2.2 is as below:

Table 2.1.2: The Experiment and Calculated Data for Polynomial Fit Graph Plotting

| t(min) | $C_A(\text{mol/L})$ | $-\frac{dC_A}{dt}$ | $\ln C_A$ | $\ln \left(-\frac{dC_A}{dt}\right)$ |
|--------|---------------------|--------------------|-----------|-------------------------------------|
| 0.00 | 0.40750 | 0.04580 | -0.89771 | -3.08347 |
| 1.15 | 0.37199 | 0.04136 | -0.98889 | -3.18550 |
| 2.62 | 0.31679 | 0.03613 | -1.14916 | -3.32065 |
| 4.05 | 0.26323 | 0.03152 | -1.33473 | -3.45729 |
| 6.07 | 0.19892 | 0.02576 | -1.61485 | -3.65884 |
| 8.08 | 0.15222 | 0.02089 | -1.88243 | -3.86837 |
| 10.08 | 0.11545 | 0.01685 | -2.15892 | -4.08320 |
| 13.03 | 0.07749 | 0.01228 | -2.55761 | -4.39946 |
| 14.80 | 0.06189 | 0.01029 | -2.78240 | -4.57645 |
| 16.03 | 0.05369 | 0.00922 | -2.92453 | -4.68638 |
| 18.02 | 0.04279 | 0.00801 | -3.15145 | -4.82765 |
| 20.03 | 0.03490 | 0.00740 | -3.35527 | -4.90692 |
| 22.87 | 0.02746 | 0.00751 | -3.59502 | -4.89086 |
| 24.78 | 0.02371 | 0.00819 | -3.74186 | -4.80449 |
| 28.25 | 0.01941 | 0.01053 | -3.94197 | -4.55340 |
| 31.12 | 0.01779 | 0.01342 | -4.02912 | -4.31072 |
| 34.75 | 0.01562 | 0.01814 | -4.15920 | -4.00979 |

The graph of $\ln \left(-\frac{dC_A}{dt}\right)$ versus $\ln C_A$ is plotted to determine the value for α (gradient) and k' (y-intercept) as shown on below:



From graph above,

Gradient, $m = \alpha = 0.4588$

$$\text{y-intercept} = \ln k' = -2.9597$$

$$k' = 0.0518$$

From the question, the overall order of the reaction is 2:

$$\alpha + \beta = 2$$

$$0.4588 + \beta = 2$$

$$\beta = 1.5412$$

$$\text{Rate law: } -r_A = k C_A^{0.4588} C_B^{1.4512}$$

2.2 Nonlinear Regression Method

From the derivation from section 1.1:

$$\frac{dC_A}{dt} = -k' C_A^\alpha$$

$$\int_{C_{AO}}^{C_A} -\frac{1}{k' C_A^\alpha} dC_A = \int_0^t dt$$

$$t_{calc} = \frac{1}{k'} \left[\frac{C_{AO}^{(1-\alpha)} - C_A^{(1-\alpha)}}{(1-\alpha)} \right]$$

By using the data provided in Table 1 and the initial concentration provided from the journal, time is calculated with the equation above with the guess of alpha and k'. After that, the equation shown below is used to calculate the sum of the squares of the differences between the measured value.

$$s^2 = \sum (r_{exp} - r_{calc})^2$$

After obtaining the sum of the s^2 , solver function is used to estimate the alpha and k' by minimise the sum of s^2 . The final value and table after applying the solver function in Excel is shown below:

Table 2.2.1: Table of Nonlinear Regression Method

| | |
|----------------|--------|
| Given C_{AO} | 0.4075 |
| Guess alpha | 1.299 |
| Guess k' | 0.223 |

| Time, t (min) | Concentration of A, C_A (mol/L) | Time calc (min) | s^2 |
|-----------------|-----------------------------------|-----------------|-------|
| 0 | 0.4075 | 0 | 0 |

| | | | |
|-------|---------|-------------------------------|----------|
| 1.15 | 0.37199 | 0.541059 | 0.370809 |
| 2.62 | 0.31679 | 1.530856 | 1.186235 |
| 4.05 | 0.26323 | 2.732632 | 1.735458 |
| 6.07 | 0.19892 | 4.681335 | 1.928391 |
| 8.08 | 0.15222 | 6.701249 | 1.900956 |
| 10.08 | 0.11545 | 8.965059 | 1.243092 |
| 13.03 | 0.07749 | 12.57663 | 0.205545 |
| 14.8 | 0.06189 | 14.81062 | 0.000113 |
| 16.03 | 0.05369 | 16.30249 | 0.07425 |
| 18.02 | 0.04279 | 18.81953 | 0.639251 |
| 20.03 | 0.0349 | 21.23033 | 1.440796 |
| 22.87 | 0.02746 | 24.26052 | 1.933541 |
| 24.78 | 0.02371 | 26.22626 | 2.091668 |
| 28.25 | 0.01941 | 29.0478 | 0.636489 |
| 31.12 | 0.01779 | 30.33033 | 0.623578 |
| 34.75 | 0.01562 | 32.30781 | 5.96429 |
| | | Total of s² | 21.97446 |

With nonlinear regression method, reaction order, α is estimated to be $1.299 \approx 1$ while k' is estimated to be 0.223 min^{-1} .

From the question, the overall order of the reaction is 2:

$$\alpha + \beta = 2$$

$$1 + \beta = 2$$

$$\beta = 1$$

Rate law: $-r_A = k C_A C_B$

2.3 Rate Law

By using the k' value from the literature, rate constant, k is calculated by the k' value with the equation below:

$$k' = k C_B ; C_B = C_{AO}(\theta_B - X)$$

With the value of $C_{AO} = 0.4075 \text{ mol/L}$; $X = 0.8$; $\theta_B = 131$, C_B is calculated to be 53.0565 mol/L .

With the value of k' from journal and C_B from calculation, the value needed for graph plotting is calculated at the Table 1.3 below:

Table 2.3.1: Rate Constant at Different Temperature

| Temperature, $T(^{\circ}\text{C})$ | Temperature, $T(\text{K})$ | Rate constant, k (L/mol.min) | $k'(\text{min}^{-1})$ | $1/T(\text{K}^{-1})$ | $\ln k$ |
|---------------------------------------|-------------------------------|-----------------------------------|-----------------------|----------------------|----------|
| 20 | 293 | 0.001998 | 0.106 | 0.003413 | -6.21567 |
| 23 | 296 | 0.002362 | 0.1253 | 0.003378 | -6.0484 |
| 26 | 299 | 0.003019 | 0.1602 | 0.003344 | -5.80269 |

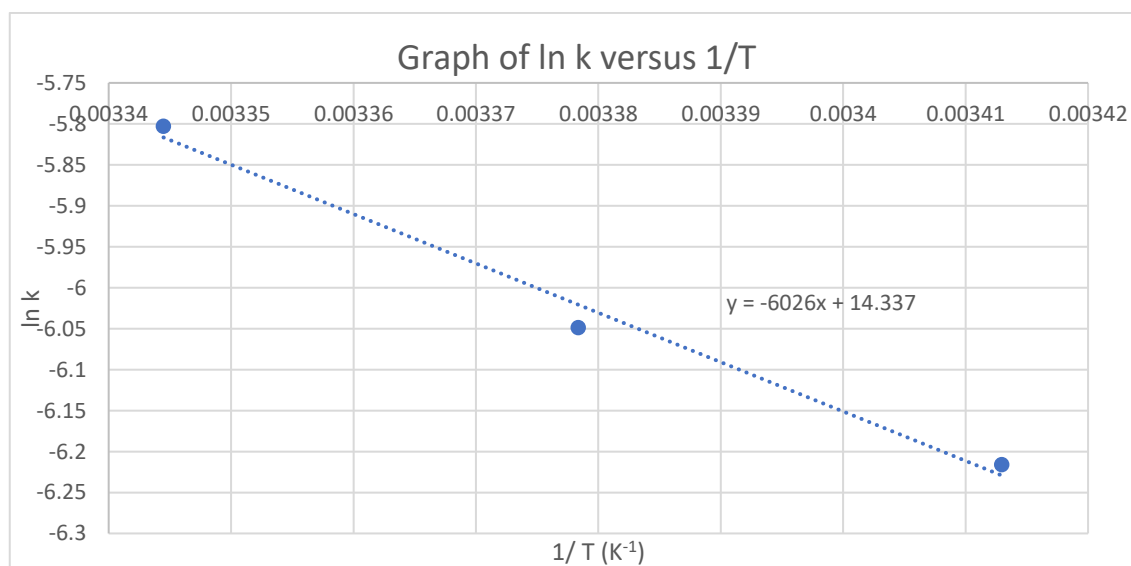
Arrhenius equation:

$$k = Ae^{-\frac{E}{RT}}$$

Taking natural log of both side:

$$\ln k = \ln A - \frac{E}{R} \left(\frac{1}{T} \right) ; \text{represented } y = mx + c$$

With data in Table 1.3.1, a graph with $\ln k$ on y-axis and $1/T$ on x-axis is plotted to find the value of frequency factor, A (y-intercept) and activation energy, E (gradient).



From the graph above:

$$-\frac{E}{R} = -6026$$

$$E = (-6026)(-R) = (-6026\text{K}) \left(-8.314 \frac{\text{J}}{\text{mol.K}} \right) = 50100.164 \frac{\text{J}}{\text{mol}}$$

$$\ln A = 14.337$$

$$A = e^{14.337} = 1684534.799$$

To calculate k with temperature of 23 $^{\circ}\text{C}$:

$$\ln k = \ln A - \frac{E}{R} \left(\frac{1}{T} \right) = 14.337 - 6026 \left(\frac{1}{23 + 273} \right) = -6.0211$$

$$k = e^{-6.0211} = 0.002427 \text{ L/mol.min}$$

Using rate law from nonlinear regression method:

$$-r_A = k C_A C_B$$

$$= 0.002427 C_A C_B$$

3.0 Comparison of Rate Law

3.1 Comparison of Rate Law Calculated with Literature Sources

The rate law for the reaction of acetyl anhydride was obtained using the non-linear regression method and the differential polynomial fit method. The rate law was calculated to be approximately $-r_A = 0.002427 C_A C_B$. This section will compare the rate law calculated in the previous section, with rate laws found in literature sources involving the hydrolysis of acetic anhydride. As each of the reaction orders, which are 1 for both acetic anhydride and water, for each species will not vary for a specific reaction, thus this section will be comparing the rate constant obtained from the literature sources and the calculation of part (1). The table below shows a number of rate constants and their respective operating temperatures obtained from different literature sources.

| No. | References | $\ln(k)$ | $k' (\text{min}^{-1})$ | $k(\text{L/mol.min})$ | $(\text{CH}_3\text{CO})_2\text{O}$ concentration (mol/L) | $T (^\circ\text{C})$ |
|-----|-----------------------------------|-------------|------------------------|-----------------------|--|----------------------|
| 1 | Amenaghawan et al., (2013) | -2.1802 | 0.1130 | - | NR | NR |
| 2 | Haji & Erkey (2005) | -1.7779 | 0.1690 | - | NR | 25 |
| 3 | Haji & Erkey (2005) | -1.8313 | 0.1602 | - | NR | 26 |
| 4 | Shatynski & Hanesian, (1993) | -2.2238 | 0.1082 | - | NR | NR |
| 5 | Lavertu, Darras & Bucshmann(2012) | -2.0010 | 0.1352 | - | NR | NR |
| 6 | Glasser and Williams (1971) | 7.95L/mol.s | - | 170134.497 | 0.25 | NR |
| 7 | Asprey et al. (1996) | 7.66L/mol.s | - | 127305.446 | 1.00 | 30 |
| 8 | Cleland and Wilhelm (1956) | 7.80L/mol.s | - | 146436 .119 | 0.02 – 0.06 | 25 - 35 |

*NR = not recorded

Since it is established that the reaction follows a second-order reaction, the values with the k units of L/mol.s are considered in the comparison. The rate constants obtained with the pseudo-first-order assumption have the unit of s^{-1} . In this report, by assuming water is in excess, the pseudo-first-order k values are also considered, as a pseudo-first-order rate constant involves a true second-order rate constant, k' .

The rate law obtained from part (1) yielded a k' value of 0.2230 min^{-1} at 23°C by using non-linear regression. This shows a large difference from the values obtained in literature sources. The values cited above generally fall within the range of 0.1000 min^{-1} to 0.1700 min^{-1} . The difference and variation of results are due to the varying concentration as well as the temperature of each of the experiments. The literature by Haji and Erkey (2005) yielded a k' value of 0.1690 min^{-1} at 25°C . In comparison, the calculated value has an approximate difference of 0.054 min^{-1} for a difference of 2°C . For a more accurate comparison, the k' values of a literature review by Toledo (2018) are taken into account and tabulated in the table below.

According to the research conducted by Toledo (2018), the result from an experiment using the titration method is as follows:

Table 3.1.: Experimental Data Obtained by Titration Method

| $T (^\circ\text{C})$ | $k (\text{min}^{-1})$ |
|----------------------|-----------------------|
| 5.1 | 0.0540 |
| 10.1 | 0.0900 |
| 15.1 | 0.1440 |
| 20.1 | 0.1680 |

By assuming water is in excess, at approximately 20.1°C the k' is recorded as 0.1680 min^{-1} . The value of k' obtained from the literature published is noticeably different than the value calculated manually from part (1) at 20°C . Furthermore, according to data by Haji and Erkey (2005), the k' values for temperatures 25°C and 26°C are 0.1690 and 0.1602 min^{-1} , which are close to the values achieved in the experiment carried out by Toledo (2018). Thus, confirming that the value obtained from Haji and Erkey (2005) are within acceptable range. Taking the results by Haji and Erkey (2005), the results of the calculation can be said to have approximately 32% error, without taking into account the slight temperature difference of 2°C and the concentration difference. Conversely, the k' obtained from the polynomial fit method was 0.0518 min^{-1} which is significantly lesser than the average from the literature sources and is also not fit for further calculations.

On the other hand, the rate constant, k , values obtained from literature sources and the calculation varies significantly. The k acquired by the calculation is approximately 0.002427

L/mol.min at 26 °C meanwhile it is recorded as 146 436 .119 L/mol.min for temperatures between 25 to 35 °C by Cleland and Wilhelm (1956). Taking the results from the literature as a basis, the error is approximately 99 %. Similar tests carried out by Asprey et al. (1996) and Glasser and Williams (1971) yielded results of 127304.446 and 170134.496 L/mol.min. This is a huge difference that can be attributed to the difference in temperature, concentration, error in recorded data or calculation and the presence of catalysts.

As the rate constant, k , value obtained are significantly smaller compared to literature sources, even if the k' values are similar, it is deduced that the rate equation obtained from manual calculation is not valid and cannot be applied for further calculations.

3.2 Factors Leading to Difference in k -values

Many factors could have influenced the difference of the k values between the calculated values and the values obtained from the literature. Among these, the most notable differences would be the inconsistent methodology. From the literature sources provided above, Toledo (2018) used the method of titration while Haji and Erkey (2005) experimented using FTIR. The data used in the calculation for part (1) was obtained through conductivity.

The difference between the rate equation from the literature and the manual calculation can also be attributed to the reactant concentrations. The values of the initial concentration of acetic anhydride used in the calculation was 0.4075 mol/L; the values used in the literature were ranging from 0.2000 to 1.0000 mol/L but does not have a similar value. The rate constant is directly proportional to the concentration of the reactants prepared.

Additionally, the temperature difference can be attributed to the difference in k and k' values. This is further supported by data from the literature by Toledo (2018), as the temperature increases from 5.1 °C to 20.1 °C, the value of the k' recorded tripled to 0.1680 min⁻¹ from 0.0540 min⁻¹. This inverse relationship is shown by the plotted graph of $\ln k$ vs $1/T$, whereas temperature increases from 20 °C to 26 °C, the k value obtained increases from 0.001998 to 0.003019 L/mol.min.

4.0 Calculation on Volume of CSTR and PFR to Achieve 80 % Conversion

The balance equation for hydrolysis of Acetic Anhydride:

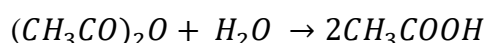


Table 4.0.1 Stoichiometric Table for Flow System

| Species | Symbol | Feed rate (mol/time) | Change (mol/time) | Effluent rate (mol/time) | Effluent (mol/volume.time) |
|---------|--------|-------------------------|----------------------|-----------------------------|-------------------------------|
|---------|--------|-------------------------|----------------------|-----------------------------|-------------------------------|

| | | | | | |
|---------------|---|----------------------------|------------|---|--|
| $(CH_3CO)_2O$ | A | F_{A0} | $-F_{A0}X$ | $F_A = F_{A0} - F_{A0}X$ $= F_{A0}(1-X)$ | $C_A = \frac{C_{A0}(1-X)}{(1+\varepsilon X)}$ |
| H_2O | B | $F_{B0} = \Theta_B F_{A0}$ | $-F_{A0}X$ | $F_B = \Theta_B F_{A0} - F_{A0}X$ $= F_{A0}(\Theta_B - X)$ | $C_B = \frac{C_{A0}(\Theta_B - X)}{(1+\varepsilon X)}$ |
| $2CH_3COOH$ | C | 0 | $2F_{A0}X$ | $F_C = 2F_{A0}X$ | $C_C = \frac{2C_{A0}}{(1+\varepsilon X)}$ |
| Total | | F_{T0} | | | |

Assume $F_{A0} = 100 \text{ kg mol/hr} = 1666.6667 \text{ mol/min}$

Assume there is no temperature change and no pressure drop.

$T = 23^\circ C$ $C_{A0} = 0.4075 \text{ mol/L}$ $\Theta_B = 131$ (journal)

$X = 0.8$ $v_0 = \frac{F_{A0}}{C_{A0}} = \frac{1666.6667}{0.4075} = 4089.9796 \frac{L}{min}$

$k' = 0.1253$ (journal) $k' = kC_B$ $\varepsilon = 2-1-1 = 0$

From section 1.3: $-r_A = 0.002427 C_A C_B$

4.1 Formula Method

Volume of CSTR

$$\begin{aligned}
 V_{CSTR} &= \frac{F_{A0}X}{-r_A}; -r_A = kC_A C_B \\
 &= \frac{F_{A0}X}{kC_A C_B} \\
 &= \frac{F_{A0}X}{kC_A C_B} \\
 &= \frac{F_{A0}X}{k[C_{A0}(1-X)][C_{A0}(\Theta_B - X)]} \\
 &= \frac{1666.6667 \frac{mol}{min} \times 0.8}{0.002427 \frac{L}{mol \cdot min} \times \left(0.4075 \frac{mol}{L}\right)^2 [(1-0.8)(131-0.8)]} \\
 &= \mathbf{127049.4423 \text{ L}}
 \end{aligned}$$

Volume of PFR

$$\begin{aligned}
 V_{PFR} &= F_{A0} \int_{X_{in}}^{X_{out}} \frac{dX}{-r_A}; -r_A = kC_A C_B \\
 &= C_{A0} v_0 \int_{X_{in}}^{X_{out}} \frac{dX}{kC_A C_B}; F_{A0} = C_{A0} v_0
 \end{aligned}$$

$$\begin{aligned}
&= C_{A0}v_0 \int_0^{0.8} \frac{dX}{k[C_{A0}(1-X)][C_{A0}(\Theta_B - X)]} \\
&= \frac{C_{A0}v_0}{k(C_{A0})^2} \int_0^{0.8} \frac{dX}{(1-X)(\Theta_B - X)} \\
&= \frac{v_0}{kC_{A0}} \int_0^{0.8} \frac{1}{(1-X)(\Theta_B - X)} dx ; \int_0^{0.8} \frac{1}{(1-X)(\Theta_B - X)} dx = \frac{1}{\Theta_B - 1} \ln \frac{\Theta_B - x}{\Theta_B(1-x)} \\
&= \frac{v_0}{kC_{A0}} \left[\frac{1}{\Theta_B - 1} \ln \frac{\Theta_B - x}{\Theta_B(1-x)} \right]_0^{0.8} \\
&= \frac{4089.9796 \frac{L}{min}}{0.002427 \frac{L}{mol \cdot min} (0.4075 \frac{mol}{L})} \left[\frac{1}{131-1} \ln \frac{131-x}{131(1-x)} \right]_0^{0.8} \\
&= \mathbf{51003.3297 \text{ L}}
\end{aligned}$$

4.2 Graphical Method

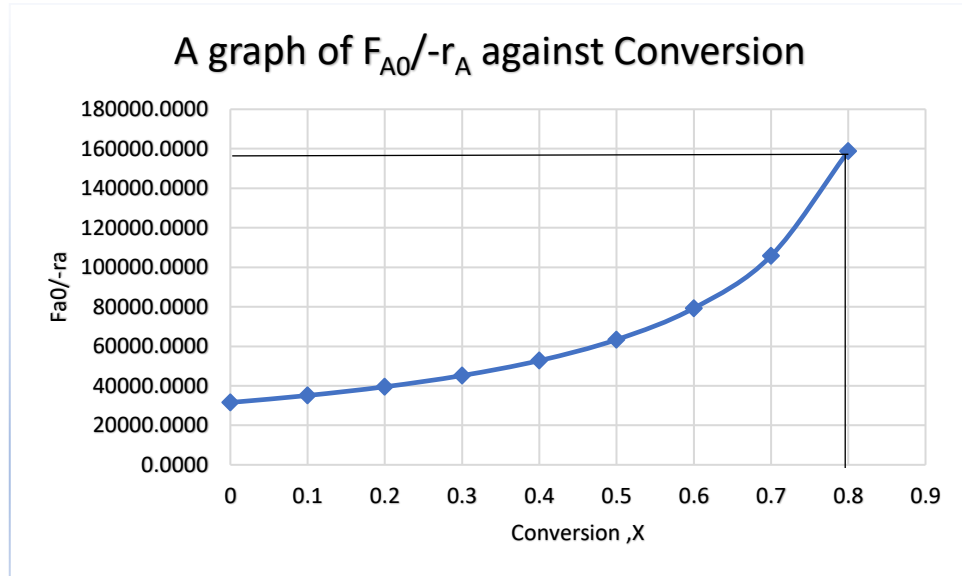
$$\begin{aligned}
\frac{F_{A0}}{-r_A} &= \frac{F_{A0}}{kC_A C_B} \\
&= \frac{F_{A0}}{k[C_{A0}(1-X)][C_{A0}(\Theta_B - X)]} \\
&= \frac{1666.6667 \frac{mol}{min}}{0.002427 \frac{L}{mol \cdot min} \left(0.4075 \frac{mol}{L}\right)^2 [(1-X)(\Theta_B - X)]}
\end{aligned}$$

Different value of conversion is substituted into above equation to get $\frac{F_{A0}}{-r_A}$. A graph of $\frac{F_{A0}}{-r_A}$ against Conversion is plotted to calculate the volume of CSTR and PFR by using Graphical Method.

Table 4.2.1: Data for Plotting Graph

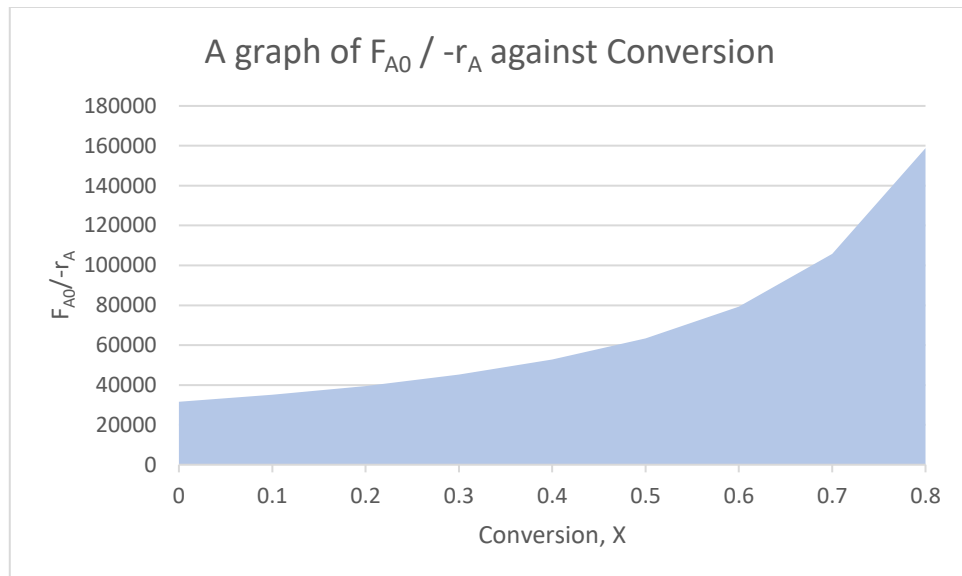
| Conversion, X | $\frac{F_{A0}}{-r_A}$ |
|---------------|-----------------------|
| 0 | 31568.3920 |
| 0.1 | 35102.7871 |
| 0.2 | 39520.8271 |
| 0.3 | 45201.2170 |
| 0.4 | 52775.1320 |
| 0.5 | 63378.6873 |
| 0.6 | 79284.1132 |
| 0.7 | 105793.2808 |
| 0.8 | 158811.8028 |

Volume of CSTR



$$\begin{aligned}\text{Volume of CSTR} &= \text{rectangular area of the curve} = 0.8 \times 158811.8028 \\ &= \mathbf{127049.4422 \text{ L}}\end{aligned}$$

Volume for PFR



$$\text{Volume of PFR} = \text{area under the curve}$$

Five-point Method Formula

$$V = F_{A0} \int_{X_{in}}^{X_{out}} \frac{dX}{-r_A}$$

$$= \int_0^{0.8} \frac{F_{A0}}{-r_A} dX$$

$$X_0 = 0, X_1 = 0.2, X_2 = 0.4, X_3 = 0.6, X_4 = 0.8$$

$$= \frac{h}{3} \left(\frac{FA_0}{-r_A(X=0)} + 4 \frac{FA_0}{-r_A(X=0.2)} + 2 \frac{FA_0}{-r_A(X=0.4)} + 4 \frac{FA_0}{-r_A(X=0.6)} + \frac{FA_0}{-r_A(X=0.8)} \right); h = \frac{X_4 - X_0}{4} = \frac{0.8 - 0}{4} = 0.2$$

$$= \frac{0.2}{3} [(31568.3920) + 4(39520.8271) + 2(52775.1320) + 4(79284.1132) + (158811.8028)]$$

$$= 51410.0147 \text{ L}$$

4.3 Discussion

The reactor volume required for a CSTR and a PFR in a single reactor system to achieve an 80 % conversion of acetic anhydride are obtained in the above calculation. There are two methods presented to calculate the reactor volume, which are by using Formula Method and Graphical Method. By comparing the volume of single CSTR and PFR in the Formula Method, the volumes are 127049.4423 L and 51003.3297 L respectively. For Graphical Method, the volume of single CSTR and PFR in Graphical Method is 127049.4422 L and 51410.0147 L respectively. It can conclude that both methods show that the single PFR has a smaller volume than CSTR when there is no temperature change and pressure drop. CSTR need a larger volume to hydrolyse acetic anhydride. So, PFR seems to be preferable to CSTR as PFR uses a smaller volume of the reactor and can save a lot of costs.

5.0 Isothermal Reactor System to Achieved 80 % Conversion of Acetic Anhydride with Minimum Reactor Volume

5.1 HYSYS Simulation Setup

In this section, HYSYS is used to modal the design of an isothermal reactor system to achieve an 80 % conversion of acetic anhydride by minimising the reactor volume. At first, component list is set up which include acetic anhydride, water and acetic acid. Next, UNIQUAC will be used as the fluid package and kinetic reaction is chosen as shown in Figure 5.1.1. Plug Flow Reactor (PFR) and Continuous-Stirred Tank Reactor (CSTR) will be used to simulate for different reactor systems and the total reactor volume for the same conversion will be compared.

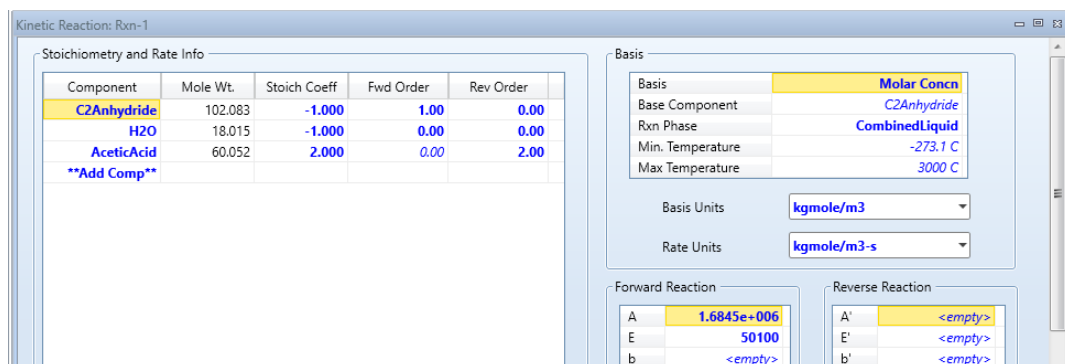


Figure 5.1.1: Kinetic Reaction

5.2 Parameter and Assumption

As discussed in section 4.0, the reactor is assumed to be isothermal and no pressure drop occurred with 23 °C and 1 atm throughout the modelling in HYSYS. The length of PFR is kept constant at 1.5 m. From section 2.3, the frequency factor, A and activation energy, E is obtained and input in HYSYS with the value of 1684534.799 and 50100.164 J/mol respectively. Besides, the inlet molar flow rate of acetic anhydride is assumed to be 100 kgmole/h while the inlet molar flow rate of water is assumed to be 13100 kgmole/h.

| Stream Name | Acetic Anhydride | Liquid Phase | Stream Name | Water | Aqueous Phase |
|-------------------------------|------------------|--------------|-------------------------------|-------------|---------------|
| Vapour / Phase Fraction | 0.0000 | 1.0000 | Vapour / Phase Fraction | 0.0000 | 1.0000 |
| Temperature [C] | 23.00 | 23.00 | Temperature [C] | 23.00 | 23.00 |
| Pressure [kPa] | 101.3 | 101.3 | Pressure [kPa] | 101.3 | 101.3 |
| Molar Flow [kgmole/h] | 100.0 | 100.0 | Molar Flow [kgmole/h] | 1.310e+004 | 1.310e+004 |
| Mass Flow [kg/h] | 1.021e+004 | 1.021e+004 | Mass Flow [kg/h] | 2.360e+005 | 2.360e+005 |
| Std Ideal Liq Vol Flow [m3/h] | 9.395 | 9.395 | Std Ideal Liq Vol Flow [m3/h] | 236.5 | 236.5 |
| Molar Enthalpy [kJ/kgmole] | -6.274e+005 | -6.274e+005 | Molar Enthalpy [kJ/kgmole] | -2.851e+005 | -2.851e+005 |
| Molar Entropy [kJ/kgmole-C] | -13.38 | -13.38 | Molar Entropy [kJ/kgmole-C] | 6.048 | 6.048 |
| Heat Flow [kJ/h] | -6.274e+007 | -6.274e+007 | Heat Flow [kJ/h] | -3.734e+009 | -3.734e+009 |
| Liq Vol Flow @Std Cond [m3/h] | 9.388 | 9.388 | Liq Vol Flow @Std Cond [m3/h] | 232.6 | 232.6 |
| Fluid Package | Basis-1 | | Fluid Package | Basis-1 | |
| Utility Type | | | Utility Type | | |

(a)

(b)

Figure 5.2.1: Material Stream of (a) Acetic Anhydride and (b) Water

5.3 Single CSTR Reactor System

In this section, one CSTR has been set up as shown in Figure 5.3.1 and the worksheet is shown in Figure 5.3.2. After keying in the inlet, outlet and estimated volume, a spreadsheet is created to calculate the conversion. After that, adjust function is used to fix the conversion as 80 % by changing the volume of the reactor as shown in Figure 5.3.3. Figure 5.3.4 showed the spreadsheet arrangement after the adjust function is applied. Figures 5.3.5 showed the reactor volume of a single CSTR reactor to achieve 80 % acetic anhydride conversion. The volume of CSTR to achieve 80 % conversion will be 109.9 m³ with an actual conversion of 79.94 % that shown in the spreadsheet.

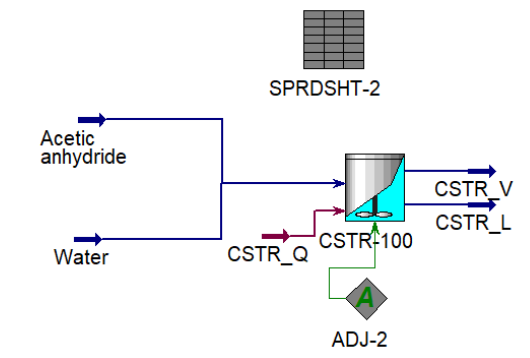


Figure 5.3.1: Design of Single Reactor CSTR

| Worksheet | Name | Acetic anhydride | Water | CSTR_L | CSTR_V | CSTR_Q |
|-------------|-------------------------------|------------------|-------------|-------------|-------------|-------------|
| Conditions | Vapour | 0.0000 | 0.0000 | 0.0000 | 1.0000 | <empty> |
| Properties | Temperature [C] | 23.00 | 23.00 | 23.00 | 23.00 | <empty> |
| Composition | Pressure [kPa] | 101.3 | 101.3 | 101.3 | 101.3 | <empty> |
| PF Specs | Molar Flow [kgmole/h] | 100.0 | 1.310e+004 | 1.320e+004 | 0.0000 | <empty> |
| | Mass Flow [kg/h] | 1.021e+004 | 2.360e+005 | 2.462e+005 | 0.0000 | <empty> |
| | Std Ideal Liq Vol Flow [m3/h] | 9.395 | 236.5 | 246.0 | 0.0000 | <empty> |
| | Molar Enthalpy [kJ/kgmole] | -6.274e+005 | -2.851e+005 | -2.877e+005 | -2.434e+005 | <empty> |
| | Molar Entropy [kJ/kgmole-C] | -13.38 | 6.048 | 7.428 | 155.6 | <empty> |
| | Heat Flow [kJ/h] | -6.274e+007 | -3.734e+009 | -3.798e+009 | 0.0000 | -7.189e+005 |

Figure 5.3.2: Worksheet of Single CSTR

Connections

Adjust Name: **ADJ-2**

Adjusted Variable

Object: CSTR-100 Select Var...

Variable: Tank Volume

Target Variable

Object: SPRDSHT-2 Select Var...

Variable: A3:

Target Value

Source

☒ User Supplied ☐ Another Object ☐ SpreadsheetCell Object

Specified Target Value: **0.8000**

Figure 5.3.3: Adjust Function of Single CSTR

| A | B |
|--------------------------|------------------------------------|
| 100.0000 kgmole/h | Feed of acetic anhydride |
| 20.0638 kgmole/h | Product of acetic anhydride |
| 0.7994 | Conversion |

Figure 5.3.4: Spreadsheet of Single CSTR after Applying the Adjust Function

Geometry

Orientation: ☒ Vertical ☐ Horizontal

☒ Cylinder ☐ Sphere

| | |
|--------------|--------------|
| Volume [m3] | 109.9 |
| Diameter [m] | 4.535 |
| Height [m] | 6.802 |

Figure 5.3.5: Volume of Single CSTR with 80 % Conversion

5.4 Single PFR Reactor System

In this section, single PFR is set up as shown in Figure 5.4.1 for the reaction of acetic anhydride. Similar to the modelling of single CSTR, inlet, outlet and estimated volume is set up for the PFR reactor. Figure 5.4.2 showed the workbook condition. After that, the spreadsheet function and adjust function are used which is similar to section 5.3 to estimate the volume to achieve 80 % conversion. Figure 5.4.3 show the spreadsheet condition after the adjust function is applied. In the spreadsheet, the actual conversion after applying the adjust tool is shown. Figure 5.4.4 showed the volume of PFR to achieve 80 % conversion. In a single PFR design, the volume estimated to achieve desire conversion will be 46.20 m³ with an actual conversion of 79.99 %.

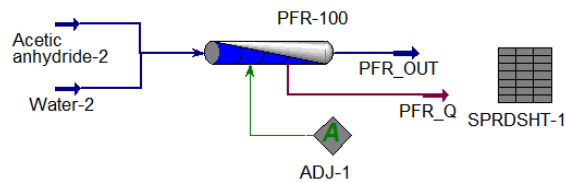


Figure 5.4.1: Design of Single Reactor PFR

| Worksheet | Name | Acetic anhydride | Water-2 | PFR_OUT | PFR_Q |
|-------------|-------------------------------|------------------|-------------|-------------|------------|
| Conditions | Vapour | 0.0000 | 0.0000 | 0.0000 | <empty> |
| Properties | Temperature [C] | 23.00 | 23.00 | 23.00 | <empty> |
| Composition | Pressure [kPa] | 101.3 | 101.3 | 101.3 | <empty> |
| PF Specs | Molar Flow [kgmole/h] | 100.0 | 1.310e+004 | 1.320e+004 | <empty> |
| | Mass Flow [kg/h] | 1.021e+004 | 2.360e+005 | 2.462e+005 | <empty> |
| | Std Ideal Liq Vol Flow [m3/h] | 9.395 | 236.5 | 246.0 | <empty> |
| | Molar Enthalpy [kJ/kgmole] | -6.274e+005 | -2.851e+005 | -2.877e+005 | <empty> |
| | Molar Entropy [kJ/kgmole-C] | -13.38 | 6.048 | 7.430 | <empty> |
| | Heat Flow [kJ/h] | -6.274e+007 | -3.734e+009 | -3.798e+009 | 7.216e+005 |

Figure 5.4.2: Worksheet of Single PFR

| | A | B |
|---|-------------------|-----------------------------|
| 1 | 100.0000 kgmole/h | Feed of Acetic Anhydride |
| 2 | 20.0085 kgmole/h | Product of Acetic Anhydride |
| 3 | 0.7999 | Conversion |

Figure 5.4.3: Spreadsheet of Single PFR

| Rating | Tube Dimensions |
|---------|-----------------------------|
| Sizing | Total Volume 46.20 m3 |
| Nozzles | Length 1.500 m |
| | Diameter 6.262 m |
| | Number of Tubes 1 |
| | Wall Thickness 5.000e-003 m |

Figure 5.4.4: Total Reactor Volume for Single PFR

5.5 Double CSTR in Series

In this design, two CSTR will be arranged in series to achieve the 80 % conversion of acetic anhydride as shown in Figure 5.5.1. Inlet, outlet and volume is set up. Next, the spreadsheet and adjust function is taken place. In this section, the first reactor will be assumed to achieve 40 % conversion by adjust function. With the same process, the second CSTR will be assumed to achieved 80 % of overall conversion with adjust tool. Figure 5.5.2 and 5.5.3 showed the worksheet of first and second CSTR reactor. Figure 5.5.4 showed the spreadsheet of first and second CSTR after adjust tool was applied. According to Figure 5.5.5, the first reactor reached a volume of 18.31 m³ with an actual conversion of 39.91 % while the volume estimated for the second CSTR will be 55.29 m³ with an actual overall conversion of 80 %. The total volume occupied for double CSTR in series will be 73.6 m³.

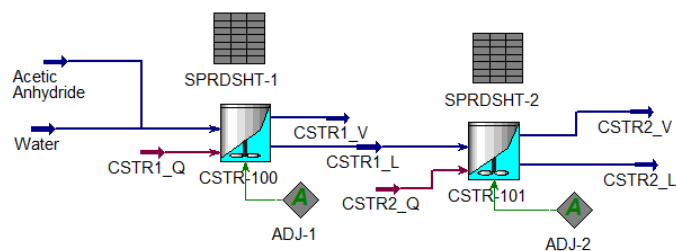


Figure 5.5.1: Design of Double Reactor CSTR

Cont. Stirred Tank Reactor: CSTR-100 - Set-1

DesignReactionsRatingWorksheetDynamics

Worksheet

ConditionsPropertiesCompositionPF Specs

| Name | Acetic Anhydride | Water | CSTR1_L | CSTR1_V | CSTR1_Q |
|-------------------------------|------------------|-------------|-------------|-------------|-------------|
| Vapour | 0.0000 | 0.0000 | 0.0000 | 1.0000 | <empty> |
| Temperature [C] | 23.00 | 23.00 | 23.00 | 23.00 | <empty> |
| Pressure [kPa] | 101.3 | 101.3 | 101.3 | 101.3 | <empty> |
| Molar Flow [kgmole/h] | 100.0 | 1.310e+004 | 1.320e+004 | 0.0000 | <empty> |
| Mass Flow [kg/h] | 1.021e+004 | 2.360e+005 | 2.462e+005 | 0.0000 | <empty> |
| Std Ideal Liq Vol Flow [m3/h] | 9.395 | 236.5 | 246.0 | 0.0000 | <empty> |
| Molar Enthalpy [kJ/kgmole] | -6.274e+005 | -2.851e+005 | -2.877e+005 | -2.427e+005 | <empty> |
| Molar Entropy [kJ/kgmole-C] | -13.38 | 6.048 | 6.893 | 155.4 | <empty> |
| Heat Flow [kJ/h] | -6.274e+007 | -3.734e+009 | -3.797e+009 | 0.0000 | -3.602e+005 |

Figure 5.5.2: Worksheet of First CSTR

Cont. Stirred Tank Reactor: CSTR-101 - Set-1

| Design | Reactions | Rating | Worksheet | Dynamics |
|-------------------------------|-------------|-------------|-------------|-------------|
| Worksheet | | | | |
| Name | CSTR1_L | CSTR2_L | CSTR2_V | CSTR2_Q |
| Vapour | 0.0000 | 0.0000 | 1.0000 | <empty> |
| Temperature [C] | 23.00 | 23.00 | 23.00 | <empty> |
| Pressure [kPa] | 101.3 | 101.3 | 101.3 | <empty> |
| Molar Flow [kgmole/h] | 1.320e+004 | 1.320e+004 | 0.0000 | <empty> |
| Mass Flow [kg/h] | 2.462e+005 | 2.462e+005 | 0.0000 | <empty> |
| Std Ideal Liq Vol Flow [m3/h] | 246.0 | 246.0 | 0.0000 | <empty> |
| Molar Enthalpy [kJ/kgmole] | -2.877e+005 | -2.877e+005 | -2.434e+005 | <empty> |
| Molar Entropy [kJ/kgmole-C] | 6.893 | 7.429 | 155.6 | <empty> |
| Heat Flow [kJ/h] | -3.797e+009 | -3.798e+009 | 0.0000 | -3.637e+005 |

Figure 5.5.3: Worksheet of Second CSTR

| A | B |
|-------------------|-----------------------------|
| 100.0000 kgmole/h | Feed of acetic anhydride |
| 60.0934 kgmole/h | Product of acetic anhydride |
| 0.3991 | Conversion |

(a)

| A | B |
|-------------------|-----------------------------|
| 100.0000 kgmole/h | Feed of acetic anhydride |
| 19.9987 kgmole/h | Product of acetic anhydride |
| 0.8000 | Conversion |

(b)

Figure 5.5.4: Spreadsheet of (a) First CSTR and (b) Second CSTR

Cont. Stirred Tank Reactor: CSTR-100 - Set-1

Worksheet Dynamics

Orientation: ☒ Vertical ☐ Horizontal

| | |
|--------------|-------|
| Volume [m3] | 18.31 |
| Diameter [m] | 2.496 |
| Height [m] | 3.743 |

(a)

Cont. Stirred Tank Reactor: CSTR-101 - Set-1

Worksheet Dynamics

Orientation: ☒ Vertical ☐ Horizontal

| | |
|--------------|-------|
| Volume [m3] | 55.29 |
| Diameter [m] | 3.607 |
| Height [m] | 5.410 |

(b)

Figure 5.5.5: Reactor Volume of (a) First CSTR and (b) Second CSTR

5.6 Double PFR in Series

In this section, two PFR reactors in series is designed as shown in Figure 5.6.1. The same flow from section 5.5 is taken place. Figure 5.6.2 and Figure 5.6.3 shows the worksheet of the first and second PFR. The first PFR is assumed to achieve 40 % conversion while second PFR is assumed to achieved overall conversion of 80 % with adjust tool. Figure 5.6.4 showed the spreadsheet after adjustment for the first and second PFR while Figure 5.6.5 show the volume of first and second PFR to achieve desire conversion. The volume of first PFR is 14.25 m³ with the actual conversion of 39.97 % while the volume for the second PFR will be 31.29 m³ with actual overall conversion of 80.10 %. The total volume occupied for two PFR in series will be 45.54 m³.

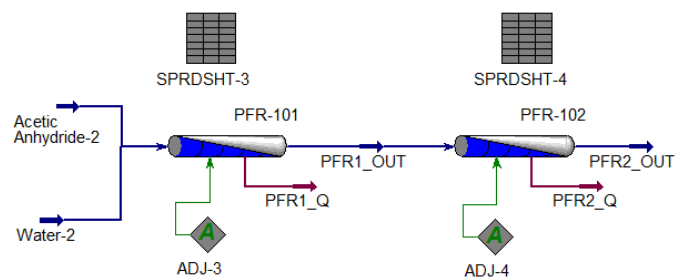


Figure 5.6.1: Design of Double Reactor PFR

| Worksheet | Name | Acetic Anhydride | Water-2 | PFR1_OUT | PFR1_Q |
|-------------|-------------------------------|------------------|-------------|-------------|------------|
| Conditions | Vapour | 0.0000 | 0.0000 | 0.0000 | <empty> |
| Properties | Temperature [C] | 23.00 | 23.00 | 23.00 | <empty> |
| Composition | Pressure [kPa] | 101.3 | 101.3 | 101.3 | <empty> |
| PF Specs | Molar Flow [kgmole/h] | 100.0 | 1.310e+004 | 1.320e+004 | <empty> |
| | Mass Flow [kg/h] | 1.021e+004 | 2.360e+005 | 2.462e+005 | <empty> |
| | Std Ideal Liq Vol Flow [m3/h] | 9.395 | 236.5 | 246.0 | <empty> |
| | Molar Enthalpy [kJ/kgmole] | -6.274e+005 | -2.851e+005 | -2.877e+005 | <empty> |
| | Molar Entropy [kJ/kgmole-C] | -13.38 | 6.048 | 6.894 | <empty> |
| | Heat Flow [kJ/h] | -6.274e+007 | -3.734e+009 | -3.797e+009 | 3.609e+005 |

Figure 5.6.2: Worksheet of First PFR

| Worksheet | Name | PFR1_OUT | PFR2_OUT | PFR2_Q |
|-------------|-------------------------------|-------------|-------------|------------|
| Conditions | Vapour | 0.0000 | 0.0000 | <empty> |
| Properties | Temperature [C] | 23.00 | 23.00 | <empty> |
| Composition | Pressure [kPa] | 101.3 | 101.3 | <empty> |
| PF Specs | Molar Flow [kgmole/h] | 1.320e+004 | 1.320e+004 | <empty> |
| | Mass Flow [kg/h] | 2.462e+005 | 2.462e+005 | <empty> |
| | Std Ideal Liq Vol Flow [m3/h] | 246.0 | 246.0 | <empty> |
| | Molar Enthalpy [kJ/kgmole] | -2.877e+005 | -2.877e+005 | <empty> |
| | Molar Entropy [kJ/kgmole-C] | 6.894 | 7.430 | <empty> |
| | Heat Flow [kJ/h] | -3.797e+009 | -3.798e+009 | 3.625e+005 |

Figure 5.6.3: Worksheet of Second PFR

| A | B | A | B |
|-------------------|-----------------------------|-------------------|-----------------------------|
| 100.0000 kgmole/h | Feed of acetic anhydride | 100.0000 kgmole/h | Feed of acetic anhydride |
| 60.0319 kgmole/h | Product of acetic anhydride | 19.9035 kgmole/h | Product of acetic anhydride |
| 0.3997 | Conversion | 0.8010 | Conversion |

(a)
(b)

Figure 5.6.4: Spreadsheet of (a) First PFR and (b) Second PFR

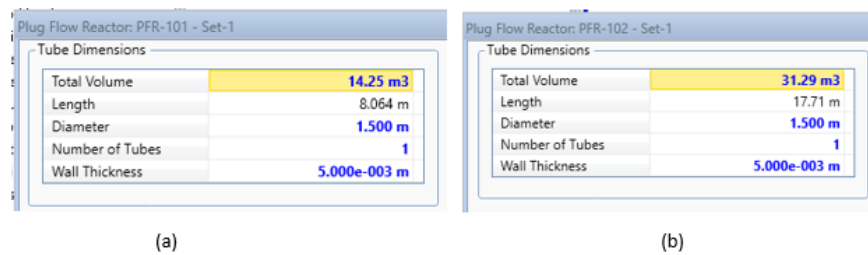


Figure 5.6.5: Total Volume of (a) First PFR and (b) Second PFR

5.7 CSTR and PFR in Series

5.7.1 CSTR Followed by PFR in Series

Similar with the section above, Figure 5.7.1.1 showed the design of CSTR followed by PFR in series while Figure 5.7.1.2 and 5.7.1.3 shows the worksheet of CSTR and PFR. CSTR is assumed to achieved 40 % conversion and PFR is estimated to achieve an overall conversion of 80 %. Figure 5.7.1.4 showed the spreadsheet of CSTR and PFR after adjustment and Figure 5.7.1.5 shows the total reactor volume of CSTR and PFR. The reactor volume for CSTR to achieve 40 % conversion will be is 18.38 m³ with an actual conversion of 40.01 %. The volume for PFR to achieve 80 % overall conversion is 31.13 m³ with an actual overall conversion of 79.99 %. The total volume occupied for this system will be 49.51 m³.

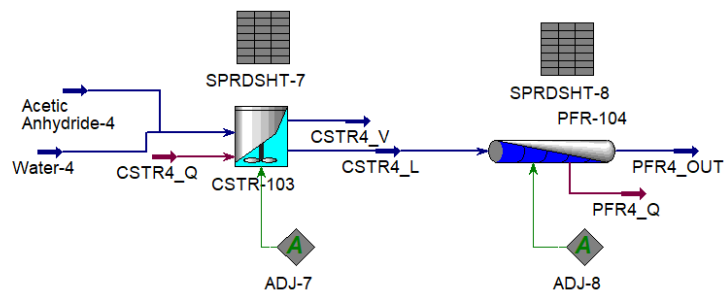


Figure 5.7.1.1: Design of CSTR Followed by PFR in Series

| Worksheet | Name | Acetic Anhydride | Water-4 | CSTR4_L | CSTR4_V | CSTR4_Q |
|-------------|-------------------------------|------------------|-------------|-------------|-------------|-------------|
| Conditions | Vapour | 0.0000 | 0.0000 | 0.0000 | 1.0000 | <empty> |
| Properties | Temperature [C] | 23.00 | 23.00 | 23.00 | 23.00 | <empty> |
| Composition | Pressure [kPa] | 101.3 | 101.3 | 101.3 | 101.3 | <empty> |
| PF Specs | Molar Flow [kgmole/h] | 100.0 | 1.310e+004 | 1.320e+004 | 0.0000 | <empty> |
| | Mass Flow [kg/h] | 1.021e+004 | 2.360e+005 | 2.462e+005 | 0.0000 | <empty> |
| | Std Ideal Liq Vol Flow [m3/h] | 9.395 | 236.5 | 246.0 | 0.0000 | <empty> |
| | Molar Enthalpy [kJ/kgmole] | -6.274e+005 | -2.851e+005 | -2.877e+005 | -2.427e+005 | <empty> |
| | Molar Entropy [kJ/kgmole-C] | -13.38 | 6.048 | 6.894 | 155.4 | <empty> |
| | Heat Flow [kJ/h] | -6.274e+007 | -3.734e+009 | -3.797e+009 | 0.0000 | -3.623e+005 |

Figure 5.7.1.2: Worksheet of CSTR

| Name | Acetic Anhydride | Water-3 | PFR3_OUT | PFR3_Q |
|-------------------------------|------------------|-------------|-------------|------------|
| Vapour | 0.0000 | 0.0000 | 0.0000 | <empty> |
| Temperature [C] | 23.00 | 23.00 | 23.00 | <empty> |
| Pressure [kPa] | 101.3 | 101.3 | 101.3 | <empty> |
| Molar Flow [kgmole/h] | 100.0 | 1.310e+004 | 1.320e+004 | <empty> |
| Mass Flow [kg/h] | 1.021e+004 | 2.360e+005 | 2.462e+005 | <empty> |
| Std Ideal Liq Vol Flow [m3/h] | 9.395 | 236.5 | 246.0 | <empty> |
| Molar Enthalpy [kJ/kgmole] | -6.274e+005 | -2.851e+005 | -2.877e+005 | <empty> |
| Molar Entropy [kJ/kgmole-C] | -13.38 | 6.048 | 6.895 | <empty> |
| Heat Flow [kJ/h] | -6.274e+007 | -3.734e+009 | -3.797e+009 | 3.617e+005 |

Figure 5.7.2.2: Worksheet of PFR

| Worksheet | Name | PFR3_OUT | CSTR3_L | CSTR3_V | CSTR3_Q |
|-------------|-------------------------------|-------------|-------------|-------------|-------------|
| Conditions | Vapour | 0.0000 | 0.0000 | 1.0000 | <empty> |
| Properties | Temperature [C] | 23.00 | 23.00 | 23.00 | <empty> |
| Composition | Pressure [kPa] | 101.3 | 101.3 | 101.3 | <empty> |
| PF Specs | Molar Flow [kgmole/h] | 1.320e+004 | 1.320e+004 | 0.0000 | <empty> |
| | Mass Flow [kg/h] | 2.462e+005 | 2.462e+005 | 0.0000 | <empty> |
| | Std Ideal Liq Vol Flow [m3/h] | 246.0 | 246.0 | 0.0000 | <empty> |
| | Molar Enthalpy [kJ/kgmole] | -2.877e+005 | -2.877e+005 | -2.434e+005 | <empty> |
| | Molar Entropy [kJ/kgmole-C] | 6.895 | 7.429 | 155.6 | <empty> |
| | Heat Flow [kJ/h] | -3.797e+009 | -3.798e+009 | 0.0000 | -3.623e+005 |

Figure 5.7.2.3: Worksheet of CSTR

| A | B | A | B |
|-------------------|-----------------------------|-------------------|-----------------------------|
| 100.0000 kgmole/h | Feed of acetic anhydride | 100.0000 kgmole/h | Feed of acetic anhydride |
| 59.9623 kgmole/h | Product of acetic anhydride | 19.9990 kgmole/h | Product of acetic anhydride |
| 0.4004 | Conversion | 0.8000 | Conversion |

(a)

(b)

Figure 5.7.2.4: Spreadsheet of (a) PFR and (b) CSTR

| Tube Dimensions | Geometry |
|-----------------|--------------|
| Total Volume | Volume [m3] |
| Length | Diameter [m] |
| Diameter | Height [m] |
| Number of Tubes | |
| Wall Thickness | |

(a)

(b)

Figure 5.7.2.5: Total Volume of (a) PFR and (b) CSTR

5.8 Double CSTR in Parallel

Two CSTR will be arranged in parallel as shown in Figure 5.8.1. Unlike arrangements in series, the two feed streams will go into a mixer before splitting by the tee to be fed in CSTR. Figure 5.8.2 show the worksheet for the mixer and the tee. The volume of both CSTR will be estimated by the adjust tool to achieve a conversion of 80 %. Figure 5.8.3 show the worksheet of the CSTR while Figure 5.8.4 show the spreadsheet of the first and second CSTR respectively. Figure 5.8.5 show the exact volume of both CSTR. The reactor volume of two CSTR to achieve 80 % conversion is nearly the same, 55.17 m³ with 80 % actual conversion and 54.91 m³ with 79.93 % actual conversion for the first and second reactor. There is some minor difference between

the two reactors because adjust function is used to estimate the volume, some discrepancy in value might happen. The total volume of two CSTR in parallel is 110.08 m³.

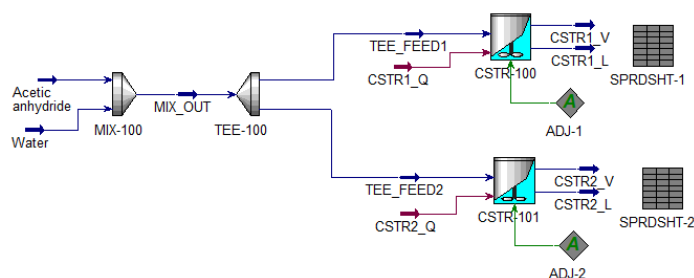


Figure 5.8.1: Design of Double CSTR in Parallel

| Name | Acetic anhydride | Water-3 | MIX3_OUT | Name | MIX3_OUT | TEE_FEED3-1 | TEE_FEED3-2 |
|-------------------------------|------------------|-------------|-------------|-------------------------------|-------------|-------------|-------------|
| Vapour | 0.0000 | 0.0000 | 0.0000 | Vapour | 0.0000 | 0.0000 | 0.0000 |
| Temperature [C] | 23.00 | 23.00 | 23.00 | Temperature [C] | 23.00 | 23.00 | 23.00 |
| Pressure [kPa] | 101.3 | 101.3 | 101.3 | Pressure [kPa] | 101.3 | 101.3 | 101.3 |
| Molar Flow [kgmole/h] | 100.0 | 1.310e+004 | 1.320e+004 | Molar Flow [kgmole/h] | 1.320e+004 | 6600 | 6600 |
| Mass Flow [kg/h] | 1.021e+004 | 2.360e+005 | 2.462e+005 | Mass Flow [kg/h] | 2.462e+005 | 1.231e+005 | 1.231e+005 |
| Std Ideal Liq Vol Flow [m3/h] | 9.395 | 236.5 | 245.9 | Std Ideal Liq Vol Flow [m3/h] | 245.9 | 122.9 | 122.9 |
| Molar Enthalpy [kJ/kgmole] | -6.274e+005 | -2.851e+005 | -2.876e+005 | Molar Enthalpy [kJ/kgmole] | -2.876e+005 | -2.876e+005 | -2.876e+005 |
| Molar Entropy [kJ/kgmole-C] | -13.38 | 6.048 | 6.271 | Molar Entropy [kJ/kgmole-C] | 6.271 | 6.271 | 6.271 |
| Heat Flow [kJ/h] | -6.274e+007 | -3.734e+009 | -3.797e+009 | Heat Flow [kJ/h] | -3.797e+009 | -1.898e+009 | -1.898e+009 |

(a)

(b)

Figure 5.8.2: Worksheet of (a) Mixer (b) Tee

| Worksheet | Name | TEE_FEED1 | CSTR1_L | CSTR1_V | CSTR1_Q |
|-------------|-------------------------------|-------------|-------------|-------------|-------------|
| Conditions | Vapour | 0.0000 | 0.0000 | 1.0000 | <empty> |
| Properties | Temperature [C] | 23.00 | 23.00 | 23.00 | <empty> |
| Composition | Pressure [kPa] | 101.3 | 101.3 | 101.3 | <empty> |
| PF Specs | Molar Flow [kgmole/h] | 6600 | 6600 | 0.0000 | <empty> |
| | Mass Flow [kg/h] | 1.231e+005 | 1.231e+005 | 0.0000 | <empty> |
| | Std Ideal Liq Vol Flow [m3/h] | 122.9 | 123.0 | 0.0000 | <empty> |
| | Molar Enthalpy [kJ/kgmole] | -2.876e+005 | -2.877e+005 | -2.434e+005 | <empty> |
| | Molar Entropy [kJ/kgmole-C] | 6.271 | 7.429 | 155.6 | <empty> |
| | Heat Flow [kJ/h] | -1.898e+009 | -1.899e+009 | 0.0000 | -3.611e+005 |

Figure 5.8.3: Worksheet of First CSTR

| A | B | A | B |
|------------------|-----------------------------|------------------|-----------------------------|
| 50.0000 kgmole/h | Feed of acetic anhydride | 50.0000 kgmole/h | Feed of acetic anhydride |
| 9.9975 kgmole/h | Product of acetic anhydride | 10.0351 kgmole/h | Product of acetic anhydride |
| 0.8000 | Conversion | 0.7993 | Conversion |

(a)

(b)

Figure 5.8.4: Spreadsheet of (a) First CSTR and (b) Second CSTR in Parallel

| | |
|------------------------|------------------------|
| Vessel Volume [m3] | 55.17 |
| Vessel Diameter [m] | 3.604 |
| Height [m] | 5.407 |
| Liq Volume Percent [%] | 100.00 |
| Level Calculator | Vertical cylinder |
| Fraction Calculator | Use levels and nozzles |

(a)

| | |
|--------------|--|
| Orientation: | <input checked="" type="radio"/> Vertical <input type="radio"/> Horizontal |
| Volume [m3] | 54.91 |
| Diameter [m] | 3.599 |
| Height [m] | 5.398 |

(b)

Figure 5.8.5: Volume of (a) First CSTR and (b) Second CSTR in Parallel

5.9 Double PFR in Parallel

In this section, 2 PFR will be arranged in parallel as shown in Figure 5.9.1. Similar to section 5.8, the Feed stream will be going through the mixer and tee before entering PFR. The volume of both PFR was estimated to achieve 80% conversion by the adjust tool. Unlike double CSTR in parallel, both PFR in this section achieves similar volume and actual conversion. Figure 5.9.2 show the spreadsheet of PFR, and Figure 5.9.3 show the actual volume of both PFR. The volume estimated for both PFR will be 23.10 m^3 with an actual conversion of 80 %. The total volume occupied by double PFR in parallel will be 46.20 m^3 .

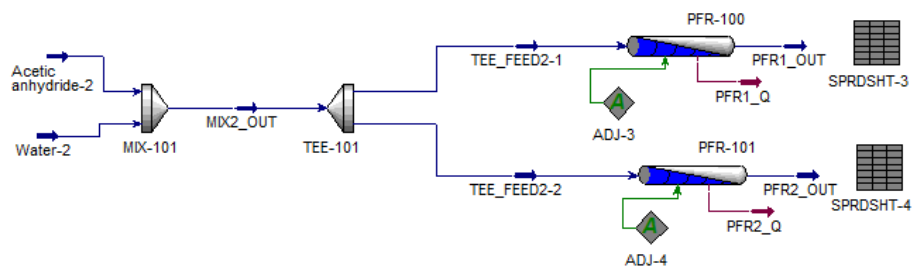


Figure 5.9.1: Design of Double PFR in Parallel

| A | B |
|------------------|-----------------------------|
| 50.0000 kgmole/h | Feed of acetic anhydride |
| 10.0022 kgmole/h | Product of acetoc anhydride |
| 0.8000 | Conversion |

Figure 5.9.2: Spreadsheet of Both PFR after Applying the Adjust Function

| Plug Flow Reactor: PFR-100 - Set-1 | |
|--|-----------------------------------|
| Design Reactions Rating Worksheet Performance Dynamics | |
| Rating | Tube Dimensions |
| Sizing | Total Volume 23.10 m ³ |
| Nozzles | Length 1.500 m |
| | Diameter 4.428 m |
| | Number of Tubes 1 |
| | Wall Thickness 5.000e-003 m |

Figure 5.9.3: Total Reactor Volume of Both PFR

5.10 CSTR and PFR in Parallel

The feed that goes through the mixer and tee will be fed into CSTR and PFR in parallel as shown in Figure 5.10.1. The worksheet of CSTR is shown in Figure 5.10.2 while the worksheet of PFR is shown in Figure 5.10.3. Figure 5.10.4 and 5.10.5 showed the spreadsheet and total volume of both reactors. The volume achieved by CSTR under estimation will be 55.17 m^3 with actual conversion of 80 % while the volume achieved by PFR under estimation will be 23.12 m^3 with actual conversion of 80.02 %. The total volume will be 78.29 m^3 .

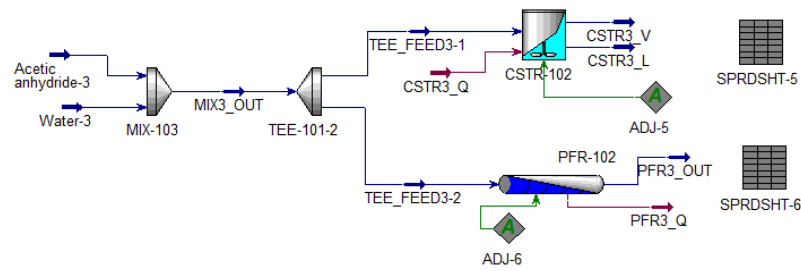


Figure 5.10.1 Design of CSTR and PFR in Parallel

| Worksheet | Name | TEE_FEED3-1 | CSTR3_L | CSTR3_V | CSTR3_Q |
|-------------|-------------------------------|-------------|-------------|-------------|-------------|
| Conditions | Vapour | 0.0000 | 0.0000 | 1.0000 | <empty> |
| Properties | Temperature [C] | 23.00 | 23.00 | 23.00 | <empty> |
| Composition | Pressure [kPa] | 101.3 | 101.3 | 101.3 | <empty> |
| PF Specs | Molar Flow [kgmole/h] | 6600 | 6600 | 0.0000 | <empty> |
| | Mass Flow [kg/h] | 1.231e+005 | 1.231e+005 | 0.0000 | <empty> |
| | Std Ideal Liq Vol Flow [m3/h] | 122.9 | 123.0 | 0.0000 | <empty> |
| | Molar Enthalpy [kJ/kgmole] | -2.876e+005 | -2.877e+005 | -2.434e+005 | <empty> |
| | Molar Entropy [kJ/kgmole-C] | 6.271 | 7.429 | 155.6 | <empty> |
| | Heat Flow [kJ/h] | -1.898e+009 | -1.899e+009 | 0.0000 | -3.611e+005 |

Figure 5.10.2: Worksheet of First CSTR

| Worksheet | Name | TEE_FEED3-2 | PFR3_OUT | PFR3_Q |
|-------------|-------------------------------|-------------|-------------|------------|
| Conditions | Vapour | 0.0000 | 0.0000 | <empty> |
| Properties | Temperature [C] | 23.00 | 23.00 | <empty> |
| Composition | Pressure [kPa] | 101.3 | 101.3 | <empty> |
| PF Specs | Molar Flow [kgmole/h] | 6600 | 6600 | <empty> |
| | Mass Flow [kg/h] | 1.231e+005 | 1.231e+005 | <empty> |
| | Std Ideal Liq Vol Flow [m3/h] | 122.9 | 123.0 | <empty> |
| | Molar Enthalpy [kJ/kgmole] | -2.876e+005 | -2.877e+005 | <empty> |
| | Molar Entropy [kJ/kgmole-C] | 6.271 | 7.429 | <empty> |
| | Heat Flow [kJ/h] | -1.898e+009 | -1.899e+009 | 3.610e+005 |

Figure 5.10.3: Worksheet of Second PFR

| A | B | A | B |
|------------------|-----------------------------|------------------|----------------------------|
| 50.0000 kgmole/h | Feed of acetic anhydride | 50.0000 kgmole/h | Feed of acetic anhydride |
| 9.9975 kgmole/h | Product of acetic anhydride | 9.9919 kgmole/h | Product of acetic anhyd... |
| 0.8000 | Conversion | 0.8002 | Conversion |

(a)

(b)

Figure 5.10.4: Spreadsheet of (a) CSTR and (b) PFR after Applying the Adjust Function

| Reactor: CSTR-102 - Set-1 | Plug Flow Reactor: PFR-102 - Set-1 |
|--|--|
| <div> <div>Conditions</div> <div>Rating</div> <div>Worksheet</div> <div>Dynamics</div> </div> <div> <div>Geometry</div> <div> <div>Orientation: <input checked="" type="radio"/> Vertical <input type="radio"/> Horizontal</div> <div> <div><input checked="" type="radio"/> Cylinder</div> <div><input type="radio"/> Sphere</div> </div> <div> <div>Volume [m3]</div> <div>Diameter [m]</div> <div>Height [m]</div> </div> <div> <div>55.17</div> <div>3.604</div> <div>5.407</div> </div> </div> </div> | <div> <div>Design</div> <div>Reactions</div> <div>Rating</div> <div>Worksheet</div> <div>Performance</div> <div>Dynamics</div> </div> <div> <div>Rating</div> <div> <div>Sizing</div> <div>Nozzles</div> </div> <div> <div>Tube Dimensions</div> <div> <div>Total Volume</div> <div>Length</div> <div>Diameter</div> <div>Number of Tubes</div> <div>Wall Thickness</div> </div> <div> <div>23.12 m3</div> <div>1.500 m</div> <div>4.430 m</div> <div>1</div> <div>5.000e-003 m</div> </div> </div> </div> |

(a)

(b)

Figure 5.10.5: Reactor Volume of (a) First CSTR and (b) Second PFR after 80% Conversion

5.11 Comparison Between All Systems

Table 5.11.1: Comparison between All Reactor Systems

| Reactor \ Arrangement | Volume (m ³) | | |
|---------------------------|--------------------------|--------|----------|
| | Single | Series | Parallel |
| CSTR | 109.9 | 73.6 | 110.08 |
| PFR | 46.2 | 45.54 | 46.2 |
| CSTR follow by PFR | - | 49.51 | 78.29 |
| PFR follow by CSTR | - | 69.35 | |

From Table 5.11.1, the volume of PFR in single, in series or even in parallel is almost the same. While for CSTR, the volume of a single CSTR has an approximate value for volume with two CSTR arranged in parallel to achieve 80 % conversion. Furthermore, it can be seen that PFR has a higher theoretical efficiency than CSTR to obtain a same conversion with smaller volume. From the table, the arrangement with minimum volume to achieve 80 % conversion of acetic anhydride will be two PFR in series with only 45.54 m³ when compared with other reactor systems.

Conclusion

In conclusion, two methods are used to determine the reaction order and k' which are the Polynomial Fit method and Nonlinear Regression Method. For the Polynomial Fit method, the reaction order obtained for the concentration of acetic anhydride and water will be 0.4588 and 1.5412 respectively with a k' value of 0.0518 min⁻¹. For Nonlinear Regression Method, the reaction order obtained for concentration of acetic anhydride will be 1.299 which approximates 1. By using this, the reaction order for water will be 1. While the k' value obtained from this method will be 0.223 min⁻¹. The k' value from the journal is used to plot a graph to determine the Frequency factor and Activation energy in this reaction. From the graph, the A and E value is determined to be 1684534.799 and 50100.164 J/mol respectively. With the A and E values with the Arrhenius equation, the rate constant at 23 °C is calculated to be 0.002427 L/mol.min. With Nonlinear Regression Method, the rate law will be $-r_A = 0.002427 C_A C_B$.

Next, the rate values obtained with relevant literature, and the rate equation obtained was determined to not be suitable for use due to the large difference with relevant literature sources. The error was theorized to have been due to the difference in temperature, concentration and method of testing among others.

Furthermore, manual calculation is applied to compare the reactor volume required for a CSTR and PFR in a single reactor system to achieve an 80 % conversion of acetic anhydride. Two

methods are applied which are formula method and graphical method. According to it, a single PFR in the reactor system required lesser reactor volume to achieve an 80 % conversion when compared with a single CSTR. The arrangement is furthered study by applying HYSYS to determine the design of the reactor system to achieve 80 % conversion with minimum reactor volume. According to the simulation of HYSYS, two PFR in a series required the lowest reactor volume to achieve the desired conversion when compared with other reactor systems.

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