

## Analysis of Chemical Reactors for Saponification



Project: Final Report

Date: 19 April 2018

Class: CHE 0401

Section: Thursday B-3

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### Nomenclature

Symbol	Definition	Units
$K_{eq}$	The equilibrium constant	Unitless
$X$	Conversion of reactant	Unitless
$\kappa$	Measured conductivity	mS
$\lambda$	Specific conductance	mS-L/mol
$\alpha$	Alpha value	mS/C
$C_0$	Initial concentration	mol/L
$C$	Final concentration	mol/L
$k$	Reaction rate coefficient	L/mol-sec
$u$	Linear velocity	m/s
$L$	Reactor tube length	m
$F$	Volumetric flow rate	mL/min
$D$	Reactor tube inner diameter	m
$E_a$	Activation energy	kJ/mol
$R$	Ideal gas constant	J/mol-K
$k_0$	Pre-exponential factor	L/mol-sec
$T$	Temperature	C
$P$	Productivity	mol/L-min
$\tau$	Residence Time	min
$V$	Reactor Volume	L
$t$	Time	sec
$\bar{x}$	Mean of Data Set	Shares units of data it is describing

S	Standard Deviation	Unitless
$\bar{Sx}$	Standard Error of Mean	Unitless
$t_{\text{stat}}$	t-statistic	Unitless
NaOH	Sodium Hydroxide	N/A
EtAc	Ethyl Acetate	N/A
NaAc	Sodium Acetate	N/A
EtOH	Ethanol	N/A

## 1.0 Introduction and Background

According to the United States census, a staggering 274 million people use bar soap to bathe [1]. Soap is a commodity that many residents of first-world countries take for granted, as it is not readily available. In some countries like Ethiopia, a mere 0.1% of the population has access, which could be a result of the complex technology involved in the soap making process. Soap is made from a process called saponification which, in a nutshell, involves turning an acid and a base into a salt. More specifically, some sort of ester is mixed with a strong base to form a salt that is used in soap. While soap is an important product of this process, it is not the only product which is why saponification is an integral part of the chemical industry and is studied often in a laboratory setting.

In the laboratory, the reaction of ethyl acetate and sodium hydroxide to form ethanol and the sodium acetate salt is observed through the use of six different reactors. These reactors, which include three batch reactors at various temperatures, one plug flow reactor (PFR), and two continuously stirred tank reactors (CSTR) with one as a single tank and one as a cascade, are studied and compared through two or three technical objectives for each system. Each reactor functions differently and can be analyzed by calculating their conversions and productivities.

The first of the reactors, the batch reactor, is the simplest of the three reactors. It is a closed system reactor that processes a singular batch of reactants at a time. By manipulating the initial concentrations of the reactants as well as the system temperature, the reaction is modified and observed. The technical objectives involving the batch reactor run the reaction at various temperatures ranging from room temperature (22C) to 45C to measure the effect of temperature on the conversion. By measuring concentration over time, the progress of the reaction, and therefore the conversion, can be calculated.

The second reactor, the CSTR, is an open system which has a continuous feed flow and continuous exit flow. The CSTR is always assumed to function at the exit conditions of the reactor since it is a continuously stirred reactor that is considered well mixed. For the single tank reactor, this means that the feed stream is assumed to be entering an environment with equal concentrations to that of the exit stream. For the CSTR cascade, which is two or more CSTRs in series, each feed flow enters an environment like the exit stream of the tank it is entering. This

means that the feed of the second is the exit stream of the first and so on. Like the Batch reactor, the operation of a CSTR is affected by initial concentrations and temperature. Because it is an open system with streams entering and exiting, the CSTR is also affected by the volume of the tanks themselves as well as the feed flow rate as described by the residence time or the time that it takes for a desired conversion to be reached. This means that the technical objectives for the single tank CSTR involve the manipulation of the flow rate to study the effect of flow rate on conversion. The technical objectives for the cascade on the other hand involve a comparison between the cascade and the single tank to study the volumetric efficiency of a CSTR cascade versus the single tank.

The third and final system is the PFR which is another open system reactor. The PFR functions like a chain of differentially small CSTRs which means that length plays a role in the reaction as well as the variables discussed with the CSTR. While the length will not be adjusted during testing, the temperature and flow rate will be changed for the PFR like they are for the CSTR to study the effects on conversion and productivity. Essentially, through the methodical adjustment of the temperature, flow rates, or the initial concentration in the case of the batch reactor, the effects of these variables as well as the functionality of each reactor are studied and quantified through a series of technical objectives in the lab.

## 2.0 Experimental Methodology

### 2.1 Equipment and Apparatus

As mentioned previously, six main pieces of equipment were utilized during testing. Three of these six were batch reactors with each batch reactor being set to a different temperature. Having multiple batch reactors is easy since the reactors are quite simple, and it allows for easy experimentation on the effects of temperature without changing other aspects of the reactor or reaction.

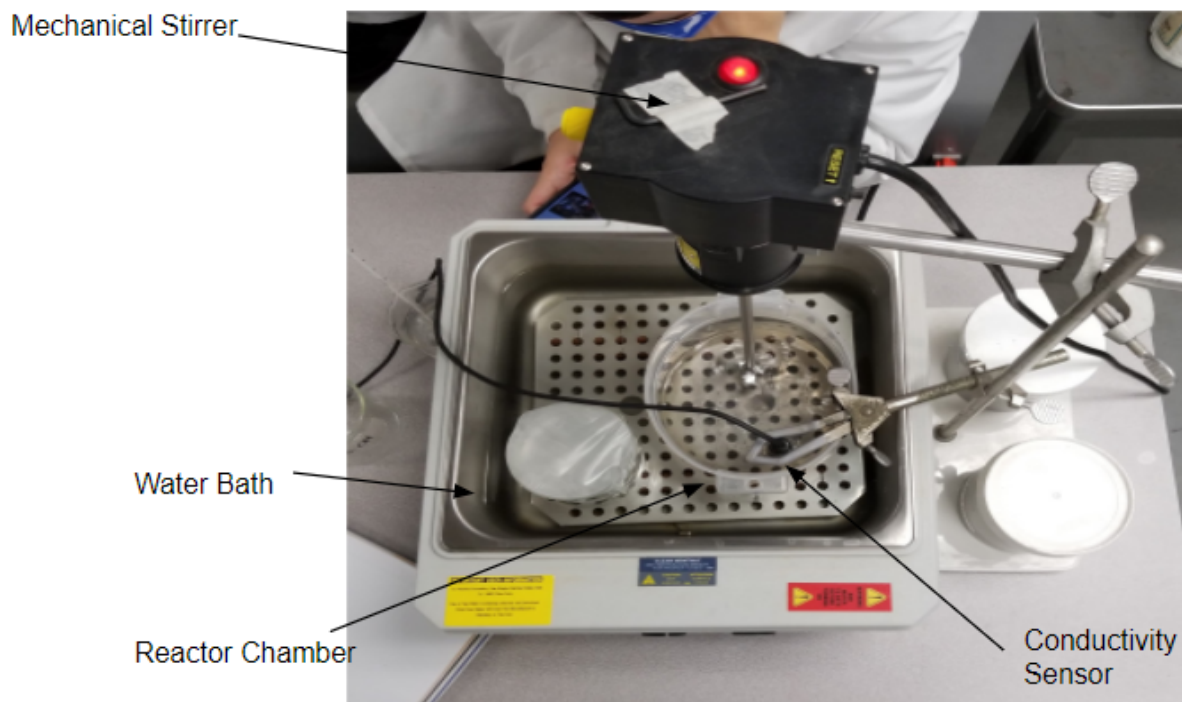


Figure 1: Diagram of a heated batch reactor

The overall setup of the batch reactor is as shown in the Figure 1. A vessel that is used as the reaction chamber sits in a heated water bath so that the temperature stays controlled and constant throughout testing. The vessel is 2L in volume and is filled to 1L for the experiments. In the vessel, the chosen reactants are combined and mixed continuously with the stirrer shown at the top of the figure. The reaction progress is documented and calculated using measurements

from the conductivity sensor seen in the bottom right corner of Figure 1. Each reading is taken at strict time intervals of ten or twenty seconds so that the data is accurate and able to be plotted on a graph with a time axis.

The next reactor used in the study is the CSTR. Both the old CSTR and the new CSTR are used in the study to compare results between the reactors. Having these two reactors helps present how innovation and modifications to the basic reactor design can improve productivity. The first and simplest of the two CSTRs is the old CSTR displayed in the diagram below.

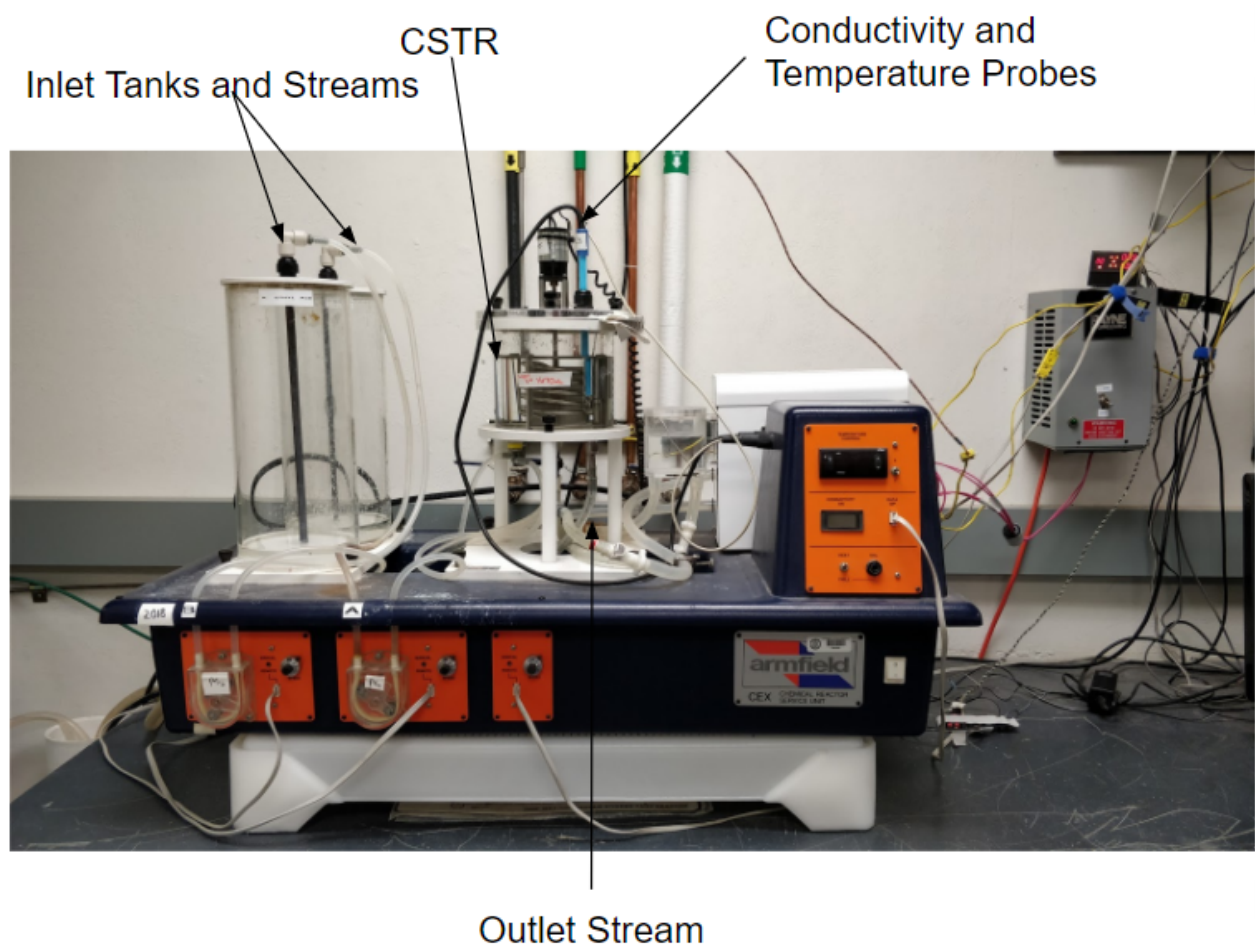


Figure 2: Diagram of the old CSTR

As seen in Figure 2, the reactor has a mixing tank in the center where the reaction takes place. The volume of this tank is 1.67L. This chamber has a stirrer and a heater so that the



reaction remains well mixed at the intended temperature. On the left, the reactant tanks can be seen as a feed for the reaction chamber in the center. At the top of the figure, the conductivity and temperature probes are labeled so that temperature can be monitored and conductivity can be measured in the same manner as the batch reactor. Lastly, the orange device on the right is a display panel for the mixer speed, reactor feed rates, and reaction temperature to be read.

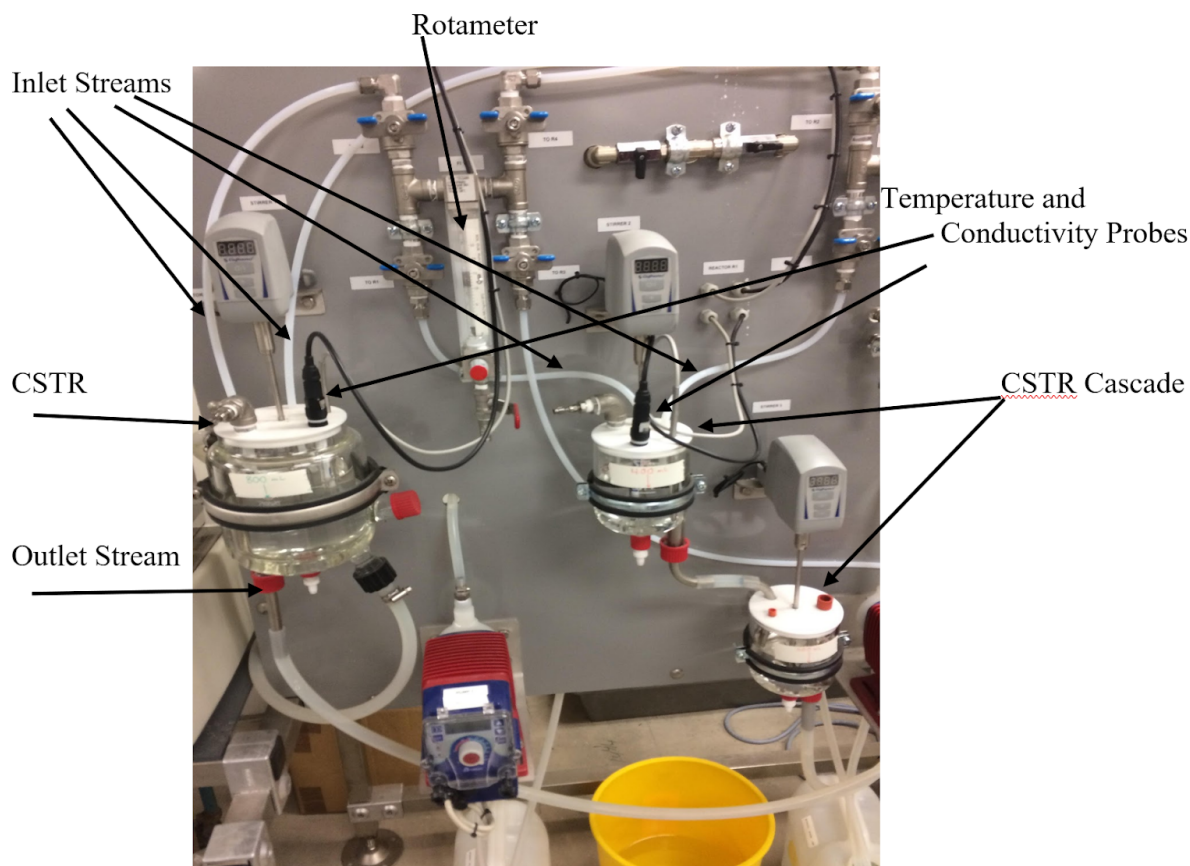


Figure 3: Diagram of the new CSTR

The new CSTR is similar to the old CSTR with the added depth of a cascade as well as the single tank reactor. Figure 3 shows the New CSTR and illustrates the distinct parts and mechanisms that are attached. The CSTR cascade has a 400 mL volume in each reactor and probes attached to them. The black probe reads the conductivity, and the silver probe reads the temperature. Both probes send the readings to a mechanism to the right of the New CSTR mechanism (not shown in picture). The lone CSTR, the reactor above the outlet stream and

below the inlet stream, has an 800 mL volume and also has the same probes attached. The flow rate is controlled by the rotameter which is located in between the reactors. These two CSTRs are analyzed and compared to see which performs better.

## PFR

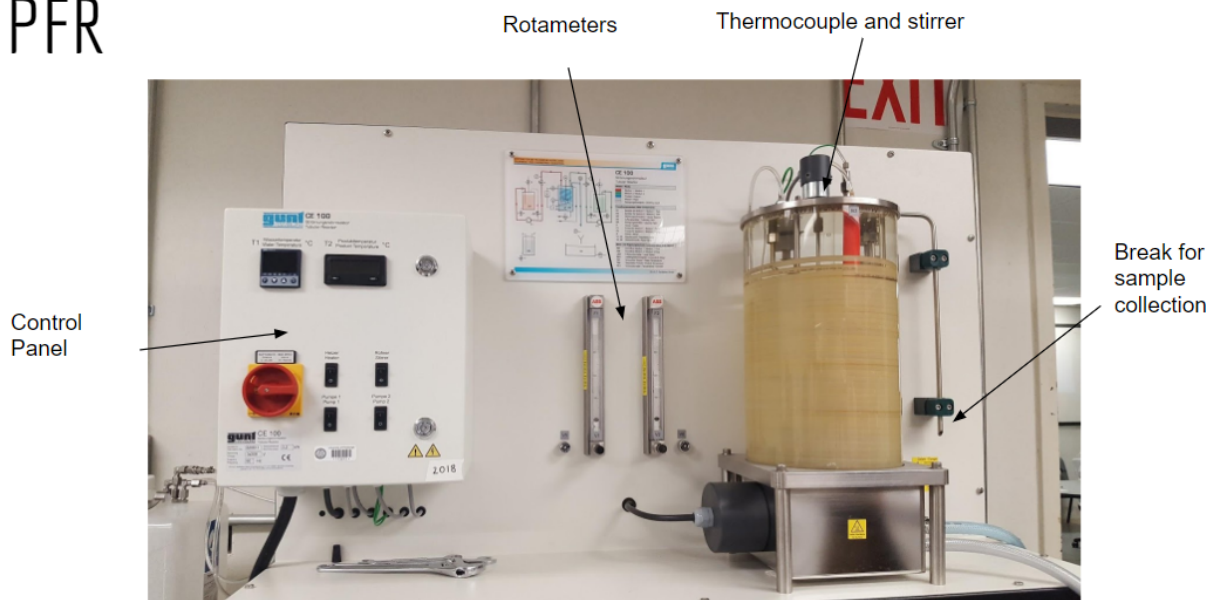


Figure 4: Diagram of the PFR

The sixth and final reactor mentioned in experimentation is the PFR reactor. As mentioned previously, the PFR is an open system, so it functions with a continuous feed and exit flow like the CSTR. Unlike the CSTR, the PFR reacts in a long thin 1L tube rather than a large well-mixed tank. In Figure 4, the tube can be seen in a water tank so that it is controlled at the desired reaction temperature. This tank is mixed with a stirrer for even distribution and has a thermocouple at the top for temperature readings. On the left, the control panel can be seen. This is where the stirrer can be engaged and the heater can be set to a desired temperature. In the very left bottom corner, the reactant tank or the source of the feed flow is just visible. In the center, the rotameters are seen as a method of controlling the flow rate of the feed. Finally on the right, there is a break in the system where samples of the exit stream can be taken and measured. Because the tube is long and thin, the conductivity must be measured manually through samples of the exiting stream.

## 2.2 Experimental Variables

The reactants used for the saponification reaction are ethyl acetate and sodium hydroxide. They react to form ethanol and sodium acetate. The initial feed concentrations for each reactant is 0.1M, and after addition to the reactors it is 0.05M. The batch reactor operated at room temperature (22C), 30C, 35C, 40C, and 45C and each batch will run for 20 minutes with a conduction measurement every 10 seconds for the first three minutes and every 20 seconds for the last 17. The old CSTR operated at a range from room temperature, 35C, and 45C with flow rates of 2x80 mL/min, 2x60 mL/min, 2x40 mL/min. The PFR like the CSTR, operated at room temperature, 35C, and 45C. The flow rates used for the PFR are 2x130 mL/min, 2x100 mL/min, and 2x80 mL/min. The new CSTR ran at room temperature using flow rates of 2x76.7 mL/min, 2x52.2 mL/min, and 33.1 mL/min.

### 3.0 Results

#### 3.1 Thermodynamic Analysis

For the thermodynamic analysis the thermodynamic data found in Table 1 was used to calculate estimates for the heat of reaction and the standard Gibbs free energy change of the saponification reaction. The heat of reaction, the Gibbs free energy, as well as the entropy of the saponification reaction are included in Table 2.

Table 1: Thermodynamic Data for the Saponification Reaction

Compound	Formula	Standard $\Delta H$ -formation (kJ/mol)	Standard $\Delta G$ -formation (kJ/mol)	Standard Molar Entropy (J/mol-K)
Sodium Hydroxide	NaOH	-427.0	-380.7	64.0
Ethyl Acetate	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	-479.0	-332.7	259.0
Sodium Acetate	C <sub>2</sub> H <sub>3</sub> NaO <sub>2</sub>	-709.3	-607.7	138.1
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	-277.7	-174.1	161.0

The heat of reaction is dependent on the heat of formation values for each species in the reaction, and is obtained from

$$\Delta H_{\text{Rxn}} = [\Delta H_{\text{f Ethanol}} + \Delta H_{\text{f Sodium Acetate}}] - [\Delta H_{\text{f ethyl acetate}} + \Delta H_{\text{f sodium hydroxide}}] \quad (1)$$

$\Delta H_{\text{Rxn}}$  denotes the heat of reaction and  $\Delta H_{\text{f}}$  is the heat of formation for each species. The Gibbs free energy change depends on the Gibbs free energy formation values for each species and is modeled by

$$\Delta G_{\text{Rxn}} = [\Delta G_{\text{f Ethanol}} + \Delta G_{\text{f Sodium Acetate}}] - [\Delta G_{\text{f ethyl acetate}} + \Delta G_{\text{f sodium hydroxide}}]. \quad (2)$$

$\Delta G_{\text{Rxn}}$  is the Gibbs free energy change and  $\Delta G_{\text{f}}$  is the Gibbs free energy of formation for each species.

Table 2: Calculation of Thermodynamic Properties for the Saponification Reaction

$\Delta H_{\text{Rxn}}$ (kJ/mol)	$\Delta S_{\text{Rxn}}$ (kJ/mol-K)	$\Delta G_{\text{Rxn}}$ (kJ/mol)
-81.0	-0.0239	-73.926

The saponification reaction was conducted at five different temperatures: room temperature, 30C, 35C, 40C, 45C. Room temperature was approximated as 22C. The estimated Gibbs free energy change of the reaction was used to calculate the equilibrium constant  $K_{\text{eq}}$ . In turn, the equilibrium constant was used to estimate the equilibrium conversion, X, for the reaction. The equilibrium constant is dependent on the Gibbs free energy change and the temperature of the reaction and is calculated using

$$K_{\text{eq}} = \exp(-\Delta G_{\text{Rxn}} / R * T) \quad (3)$$

where  $K_{\text{eq}}$  is the equilibrium constant,  $\Delta G_{\text{Rxn}}$  is the Gibbs free energy change, R is the gas constant, and T is the temperature. The equilibrium conversion depends on the equilibrium constant and is modeled with

$$X = \text{sqrt}(k_{\text{eq}}) / (\text{sqrt}(k_{\text{eq}}) + 1) \quad (4)$$

where X is the estimated equilibrium conversion and  $K_{\text{eq}}$  is the equilibrium constant. The calculated results for  $K_{\text{eq}}$  and X are displayed in Table 3.

Table 3: Calculation of the Equilibrium Constant and Equilibrium Conversion for Different Temperatures

Temperature (°C)	Temperature (K)	$K_{\text{eq}}$	Estimated Equilibrium Conversion
23	296	$1.177 \times 10^{12}$	0.9999
30	303	$6.195 \times 10^{11}$	0.9999
35	308	$3.986 \times 10^{11}$	0.9999
40	313	$2.602 \times 10^{11}$	0.9999
45	318	$1.721 \times 10^{11}$	0.9999

### 3.2 Batch Reactor

The saponification reaction was studied with the batch reactor operating at room temperature (22C), 30C, 35C, 40C, and 45C. The conductivity of the batch reactor was recorded over the course of 20 minutes and was used to measure the reaction rate coefficient, activation energy, and productivity of the batch reaction.

Equation 5 was used to calculate the specific conductance of the reactants,

$$\lambda_{\text{species}} = (K_{\text{species std}} + \alpha_{\text{species}} * (T - T_{\text{species std}})) / C_{\text{species std}} \quad (5)$$

where K is the species reference conductivity, with the species being sodium hydroxide and sodium acetate,  $\alpha$  is the species alpha value, T is the temperature of the reaction, with T standard being the reference temperature of the species, and C standard being the reference concentration of the species.

The specific conductance for the reactants and the conductance throughout the reaction were used to calculate the conversion of the reactants into the product,

$$X = (k - \lambda_{\text{NaOH}} * C_{0 \text{ NaOH}}) / (-\lambda_{\text{NaOH}} * C_{0 \text{ NaOH}} + \lambda_{\text{NaAc}} * C_{0 \text{ NaOH}}) \quad (6)$$

where k is the conduction of the reaction at a given time,  $\lambda$  is the specific conductance of the indicated species, and  $C_0$  is the initial concentration of the indicated species. The conversions at different temperatures over time are shown in Figures 5, 6, and 7.

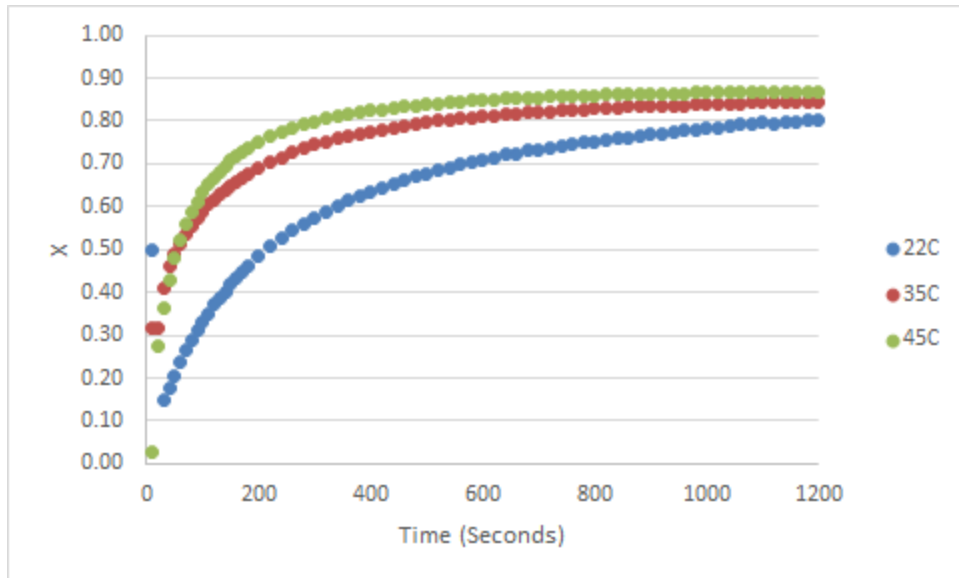


Figure 5: Conversion vs. Time for Lab Session 1 for Batch Reactor

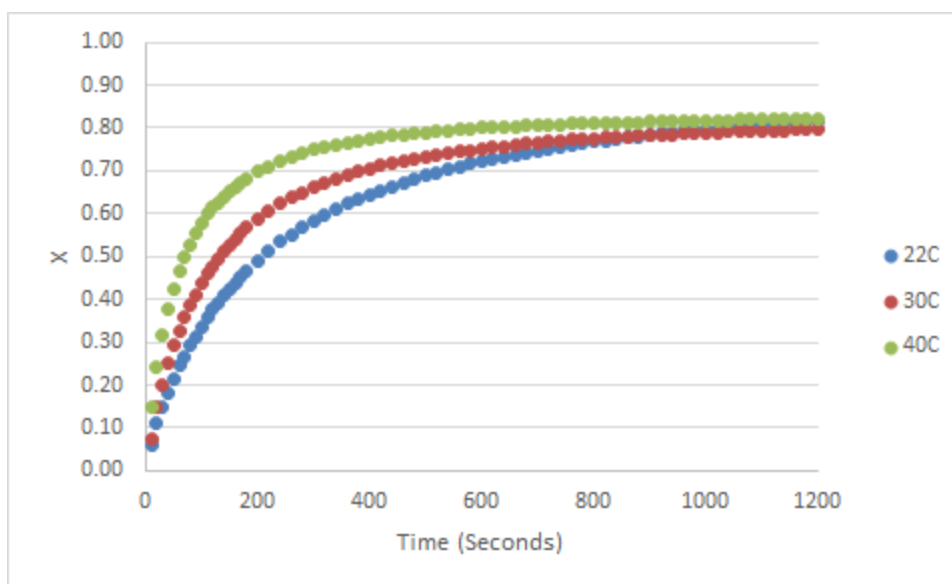


Figure 6: Conversion vs. Time for Lab Session 2 for Batch Reactor

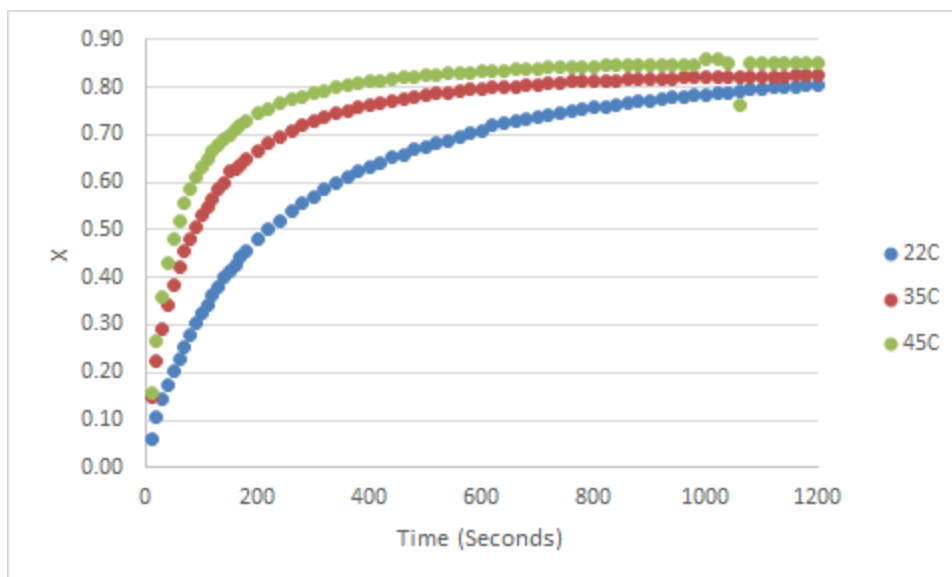


Figure 7: Conversion vs. Time for Lab Session 3 for Batch Reactor

The conversion and initial concentration of sodium hydroxide was used to calculate the concentration of sodium hydroxide throughout the reaction, as shown in Equation 7,

$$C_{\text{NaOH}} = C_{0 \text{ NaOH}}(1-X), \quad (7)$$

where  $X$  is the conversion of the reactant to the product, and  $C_0$  is the initial concentration of the reactant.

The rate coefficient ( $k$ ) was derived from the integrated rate law for a 2nd order reaction, as shown in Equation 8,

$$1/C_{\text{NaOH}} = k \cdot t + 1/C_{0 \text{ NaOH}}, \quad (8)$$

where  $C_{\text{NaOH}}$  is the concentration of the sodium hydroxide,  $k$  is the reaction rate coefficient,  $t$  is the time, and  $C_{0 \text{ NaOH}}$  is the initial concentration of sodium hydroxide. By plotting the inverse concentration against time, the slope indicates the reaction rate coefficient, as shown in Figure 8, 9, and 10.

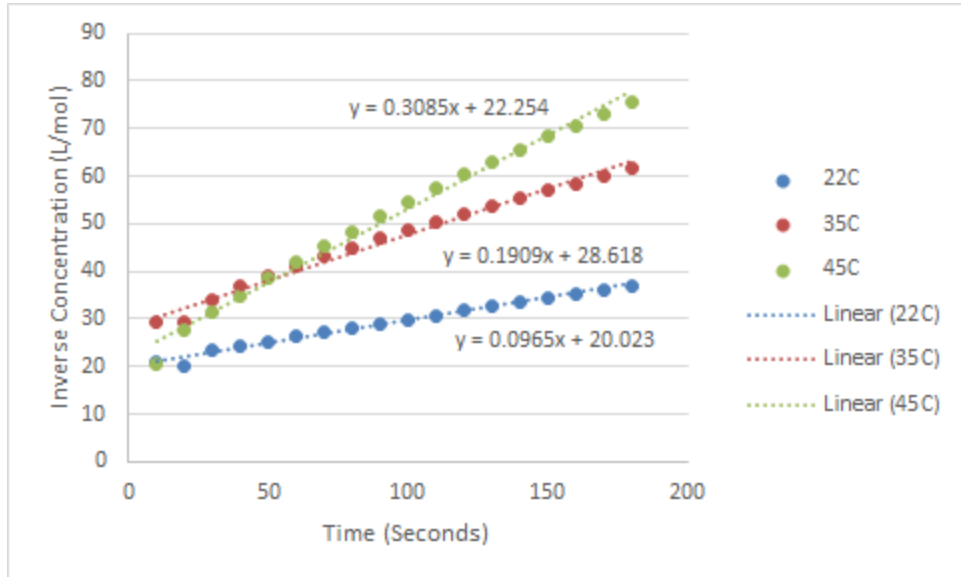


Figure 8: Inverse Concentration vs. Time for Lab Session 1 for Batch Reactor



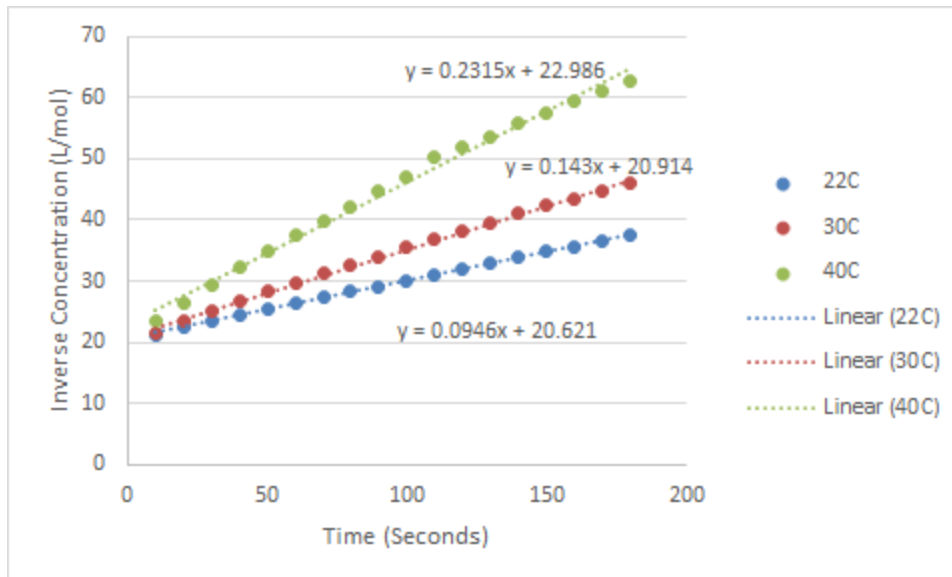


Figure 9: Inverse Concentration vs. Time for Lab Session 2 for Batch Reactor

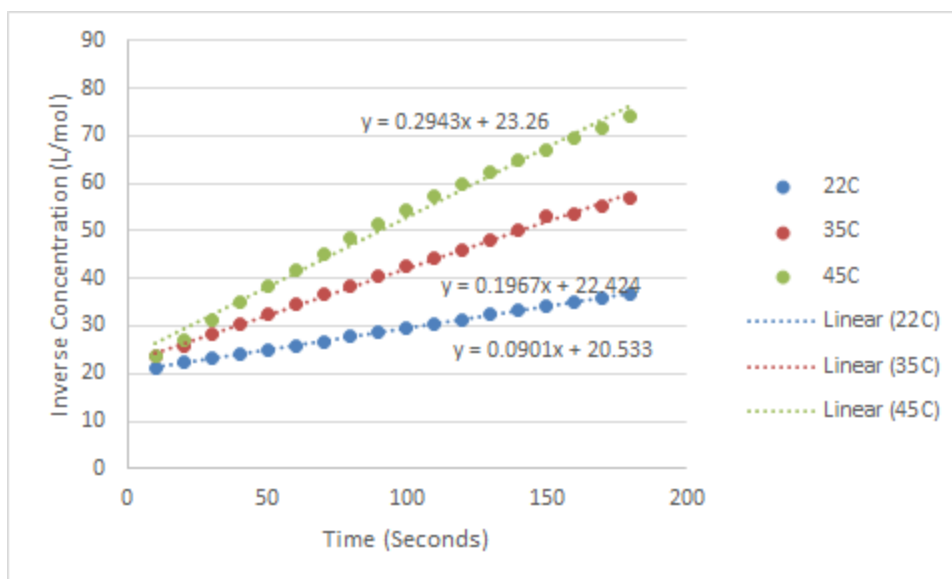


Figure 10: Inverse Concentration vs. Time for Lab Session 3 for Batch Reactor

The reaction rate coefficients at the different batch reactor temperatures are shown in Table 4.

Table 4: Reaction Rate Coefficient for Batch Reactor

Temperature (C)	Reaction Rate Coefficient (L/mol-sec)
22 (First Session)	0.0965
22 (Second Session)	0.0946
22 (Third Session)	0.0901
30	0.143
35 (First Session)	0.191
35 (Third Session)	0.197
40	0.232
45 (First Session)	0.309
45 (Third Session)	0.294

The activation energy of the reaction was derived using the Arrhenius equation, Equation 9,

$$k = k_0 \cdot \exp(-E/RT) , \quad (9)$$

where  $k_0$  is the pre-exponential exponent,  $E$  is the activation energy,  $R$  is the universal gas constant, and  $T$  is the temperature of the reaction. The activation energy of the reaction was calculated by plotting the natural log of the  $k$  value against the inverse temperature. The slope of the plot is equivalent to the negative of the activation energy multiplied by the universal gas constant. The activation energy for the first lab session was found to be 39.42 kJ/mol, the second session was found to be 38.16 kJ/mol, and the third session was found to be 40.45 kJ/mol. The slope data is shown in Figure 11.

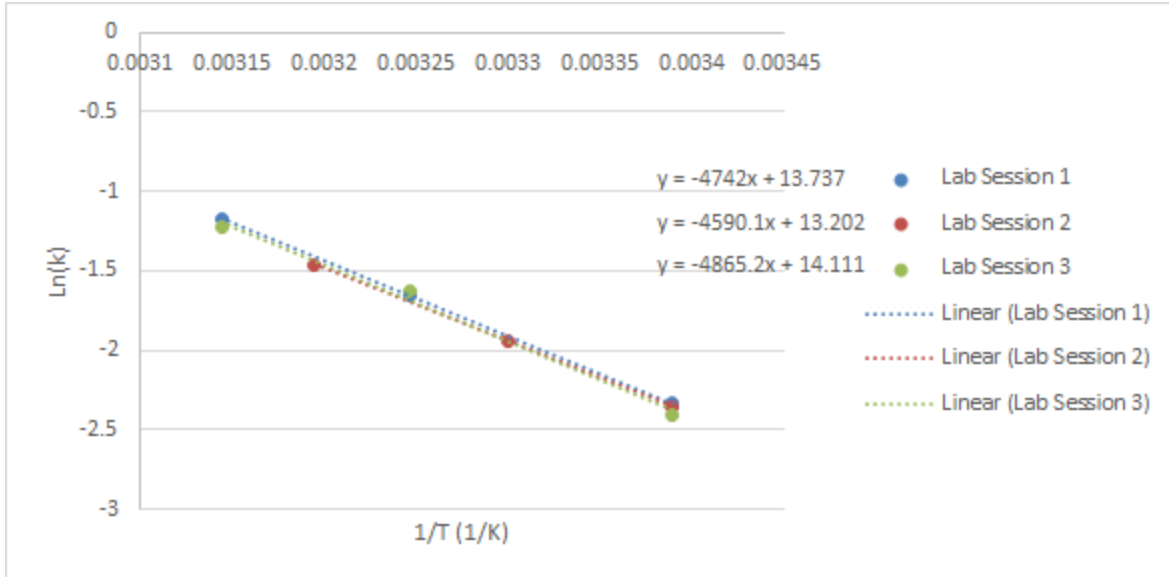


Figure 11: Natural Log of k vs. Inverse Temperature for Batch Reactor

Assuming a simultaneous charging rate of 100 mL/min for both reactants and a discharge rate of 200 mL/min and no cleaning time, a productivity at 70% conversion was found using Equation 10,

$$P = C_{0\text{NaOH}} * X/t, \quad (10)$$

where  $C_0$  is the initial concentration of sodium hydroxide,  $X$  is the conversion of 0.7, and  $t$  is the time it takes for a full batch process to occur, including charging time, reaction time, discharge time, and cleaning time. Since the solution had a volume of 1 L, the charging and discharging time were calculated by dividing the volume by the rates. The productivities at different temperatures are shown in Table 5.

Table 5: Productivity for Batch Reactor

Reaction Time (Minutes)	Temperature (C)	Charging Time (Min)	Discharging Time (Min)	Productivity (mol NaAc/L-min)
9.33	22 (First Session)	5	5	$1.81 \times 10^{-3}$
8.67	22 (Second Session)			$1.87 \times 10^{-3}$
9.33	22 (Third Session)			$1.81 \times 10^{-3}$
6.33	30			$2.14 \times 10^{-3}$
3.67	35 (First Session)			$2.56 \times 10^{-3}$
4.00	35 (Third Session)			$2.50 \times 10^{-3}$
3.33	40			$2.63 \times 10^{-3}$
2.33	45 (First Session)			$2.84 \times 10^{-3}$
2.50	45 (Third Session)			$2.80 \times 10^{-3}$

### 3.3 Old CSTR

For experimental session 1, the old CSTR was run at three temperatures: room temperature, 35C and 45C while maintaining a constant flow rate of 2x60mL/min. For session 2, the old CSTR was run at three temperatures, room temperature, 35C and 45C, while maintaining a constant flow rate of 2x80mL/min. For session 3, the old CSTR was again run at the same three temperatures, room temperature, 35C and 45C, while maintaining a constant flow rate of 2x32mL/min. Temperature and conductivity were collected to calculate the residence time, conversion, reaction rate coefficient, activation energy, and steady state productivity. The measured data along with specific conductance of NaOH and NaAc (Equation 5) were used to calculate conversion (Equation 6). The conversion was then plotted against the reaction temperature, shown in Figure 12.

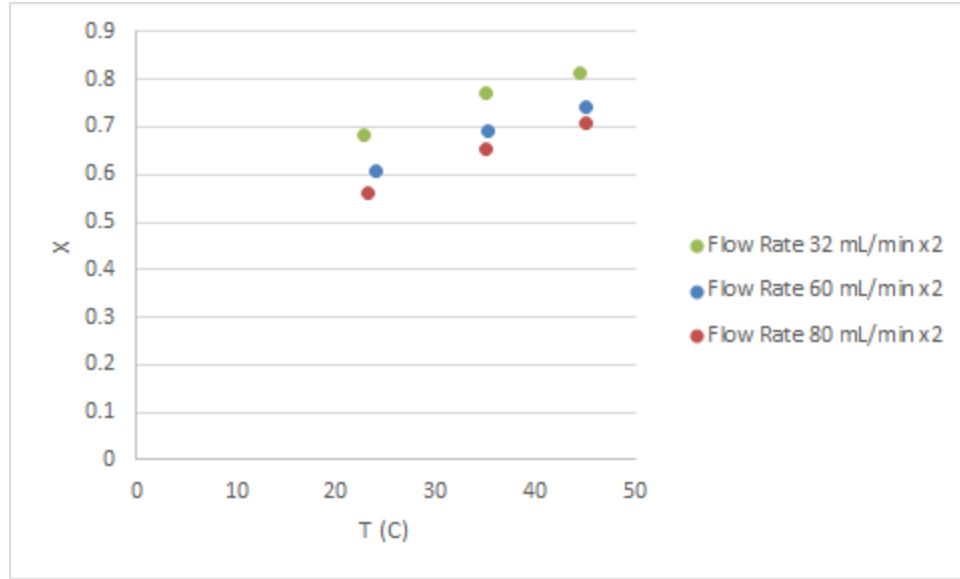


Figure 12: Conversion vs. Temperature for Old CSTR

For all of the studied flow rates the conversion increased with the temperature. Utilizing the volume of the reactor and the flow rate of the reactants, the residence time of the reactor was calculated using the following Equation 11,

$$\tau = V / F_{\text{NaOH+EtAc}} \quad (11)$$

where V is the volume of the CSTR and  $F_{\text{NaOH+EtAc}}$  is the volumetric flow rate of sodium hydroxide and ethyl acetate. The residence time results are found in Table 6.

Table 6: Residence Time for Old CSTR

Flow rate mL/min x 2	Residence Time (min)
32	26.09
60	13.92
80	10.44

As the flow rate increased, the residence time decreased. The reaction rate coefficient was calculated using Equation 12,

$$k = (C_{0\text{NaOH}} * X_{\text{NaOH}}) / (C_{0\text{NaOH}})^2 * (1 - X_{\text{NaOH}})^2 * (\tau_{\text{CSTR}}) \quad (12)$$

where  $C_{0\text{NaOH}}$  is the initial concentration of sodium hydroxide,  $X_{\text{NaOH}}$  is the conversion of sodium hydroxide, and  $\tau_{\text{CSTR}}$  is the residence time of the CSTR. The reaction rate coefficient for each flow rate and temperature is listed in Table 7.

Table 7: Reaction Rate Coefficients for Old CSTR

Temperature (C)	Flow Rate (mL/min x 2)	k (L/(mol-sec))
22	32	0.086
	60	0.095
	80	0.092
35	32	0.189
	60	0.174
	80	0.175
45	32	0.294
	60	0.264
	80	0.269

The reaction rate coefficients rose as the temperature also rose. For the 2x60 mL/min and 2x80 mL/min flow rates, the increase in flow rate had very little effect on the reaction rate coefficient. However, for the 2x32 mL/min flow rate, the reaction rate coefficient was much less consistent. For the data at 22C, the reaction rate coefficient at the 2x32 mL/min flow rate is lower than the reaction rate coefficients for the other two flow rates. For the 35C and 45C trials the 2x32 mL/min flow rate reaction rate coefficient again differed from the other two flow rates, however this time it was higher than the other two.

To calculate the activation energy, the natural log of k was plotted vs. the inverse temperature, in accordance with Equation 9. The slope was then measured. The slope of the plot is equivalent to the negative of the activation energy multiplied by the universal gas constant R. The results can be found in Table 8.

Table 8: Activation Energy for Old CSTR

Flow rate (mL/min x 2)	Activation Energy (kJ/mol)
32	44.62
60	37.95
80	38.34

The activation energy estimates for the last two flow rates were extremely similar. The activation energy for the 2x32mL/min flow rate is higher than the other two values.

The productivity of the reaction in the CSTR was calculated using

$$P = C_{0\text{NaOH}} * X/\tau \quad (13)$$

where  $C_0$  is the initial concentration of sodium hydroxide. The results are listed in Table 9.

Table 9: Productivity for Old CSTR

Residence Time (min)	Temperature (C)	Productivity (mol NaAc/L-min)
10.44	22	$2.68 \times 10^{-3}$
	35	$3.13 \times 10^{-3}$
	45	$3.40 \times 10^{-3}$
13.92	22	$2.19 \times 10^{-3}$
	35	$2.48 \times 10^{-3}$
	45	$2.66 \times 10^{-3}$
26.09	22	$1.30 \times 10^{-3}$
	35	$1.48 \times 10^{-3}$
	45	$1.56 \times 10^{-3}$

### 3.4 New CSTR

Table 10 shows the results for the steady-state conversion, which was calculated with Equation 6 except for the series CSTR which used

$$X_{\text{NaOH}} = 1 - (1 - X_{\text{NaOH}}) * (1 - X_{\text{NaOH} 2}) \quad (14)$$

where X is the conversion. The combined series during session 2 showed the highest conversion at 53.7% while also proving that the series reactors were always higher than the single reactor conversions during each session.

Table 10: Conversion for New CSTR

Reactor Type	Flow Rate (mL/min)	Conversion
Single Reactor	153	0.335
	66.2	0.427
	52.2	0.389
Reactor 1	153	0.263
	66.2	0.365
	52.2	0.32
Reactor 2	153	0.217
	66.2	0.270
	52.2	0.241
Combined Series	153	0.423
	66.2	0.537
	52.2	0.484

The residence time vs. volumetric flow rate, Table 11, presents the correlation between the flow rate and residence time. The residence time was calculated with Equation 11 for all reactors except for the overall series time which combined the two reactors using

$$\tau_{\text{CSTR}} = \tau_{\text{CSTR} 1} + \tau_{\text{CSTR} 2}. \quad (15)$$



where  $\tau$  is residence time. The table shows that the residence time is nearly the same for both the single and series reactors without any dependence on flow rate. The residence time is 12.09 minutes for both reactor designs during session 2. However, a smaller flow rate does increase the residence time. According to the table, when the flow rate was decreased the residence time increased from 5.22 to 12.09 minutes for both reactors.

Table 11: Residence Time for New CSTR

Reactor Type	Flow Rate (mL/min)	Residence Time (min)
Single Reactor	153	5.22
	66.2	12.1
	52.2	15.33
Reactor 1	153	2.61
	66.2	6.04
	52.2	7.66
Reactor 2	153	2.61
	66.2	6.04
	52.2	7.66
Combined Series	153	5.22
	66.2	12.1
	52.2	15.33

Table 12 shows the productivity and how the flow rate affects both CSTR reactor types. The series reactor has the overall best production with a  $4.05 \times 10^{-3}$  M/min during the first session with the larger flow rate. There is a directly proportional relationship for productivity; when the flow rate decreases the productivity also decreases. This is proven by the drop with the single CSTR reactor from  $3.2 \times 10^{-3}$  M/min to  $1.77 \times 10^{-3}$  M/min when the flow rate decreased from 153 to 66.2 mL/min. This trend continued within the third trial also when the flow rate was

decreased to 52.2 L/min and dropped the productivity to  $1.27 \times 10^{-3}$  mol NaAc/L min. These trends were also common in the combined series reactors.

Table 12: Productivity for New CSTR

Reactor Type	Flow Rate (mL/min)	Productivity (mol NaAc/L min)
Single Reactor	153	$3.2 \times 10^{-3}$
	66.2	$1.77 \times 10^{-3}$
	52.2	$1.27 \times 10^{-3}$
Combined Series	153	$4.05 \times 10^{-3}$
	66.2	$2.22 \times 10^{-3}$
	52.2	$1.58 \times 10^{-3}$

### 3.5 PFR

The saponification reaction was studied with the PFR at flow rates of 80mL/min, 100mL/min, and 130mL/min for each reactant at room temperature (22C), 35C, and 45C. Conductivity of the product stream and temperature were measured and used to calculate conversion, residence time, reaction rate coefficient, activation energy, and productivity. The measured values along with the specific conductance for sodium hydroxide and sodium acetate (calculated with Equation 5) and the initial concentration of sodium hydroxide were used to calculate conversion using Equation 6. These results are shown in Figure 13.

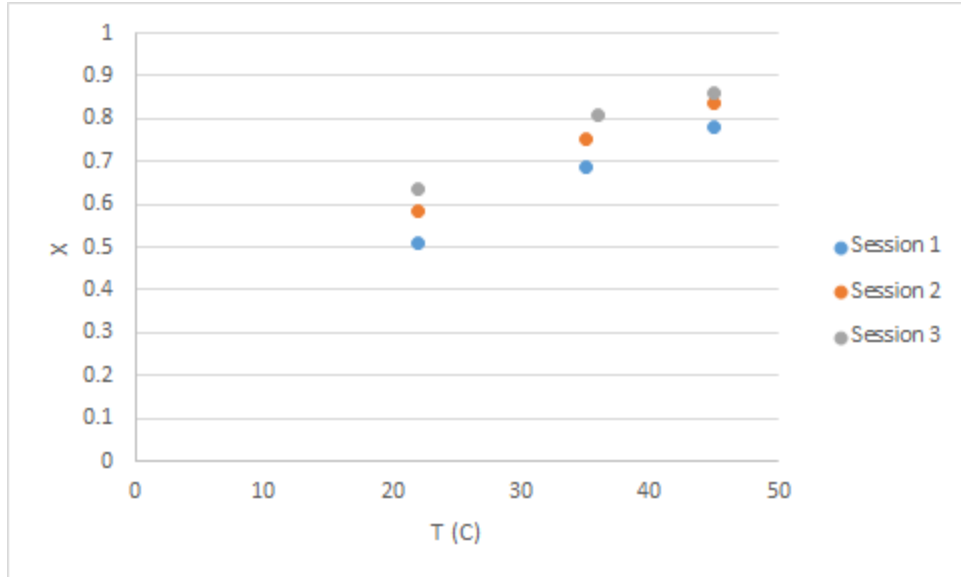


Figure 13: Conversion vs. Temperature for PFR

For all flow rates studied, the conversion increased as the temperature increased.

Residence time was calculated using Equation 11. The results for each flow rate are shown in Table 13.

Table 13: Residence Time for PFR

Flow rate (mL/min x 2)	Residence Time (min)
130	3.85
100	5.00
80	6.25

As the flow rate decreased, the residence time increased.

The reaction rate coefficient was calculated using the equation

$$k = u/L * (1/C_{NaOH} - 1/C_{0NaOH}), \quad (16)$$

where  $k$  is the reaction rate coefficient,  $L$  is the length of the tube in the reactor,  $C_{NaOH}$  is the concentration of sodium hydroxide,  $C_{0NaOH}$  is the initial concentration of sodium hydroxide, and  $u$  is the linear velocity. The concentration of sodium hydroxide is calculated as

$$C_{NaOH} = C_{0NaOH} * (1 - X), \quad (17)$$

where X is the conversion of sodium hydroxide in the reactor. The linear velocity is calculated as

$$u = F / (0.25 \cdot \pi \cdot D^2), \quad (18)$$

where F is the volumetric flow rate in the reactor and D is the inner diameter of the tube in the reactor. The reaction rate coefficients for each flow rate and temperature are displayed in Table 14.

Table 14: Reaction Rate Coefficients for PFR

Temperature (C)	Flow Rate (mL/min x 2)	k (L/(mol-sec))
22	130	0.090
	100	0.094
	80	0.093
35	130	0.189
	100	0.204
	80	0.344
45	130	0.309
	100	0.344
	80	0.331

The reaction rate coefficients increased as the temperature increased, and are not affected greatly by the change in flow rate.

The activation energy was calculated by plotting the natural log of k vs. the inverse temperature and measuring the slope, as calculated for the other reactors with Equation 9. Table 15 shows the results.

Table 15: Activation Energy for PFR

Flow rate mL/min x 2	Activation Energy (kJ/mol)
130	41.8
100	44.0
80	43.3

All flow rates produced similar values for the activation energy. The productivity for the reaction was calculated using Equation 13. Table 16 displays the results.

Table 16: Productivity for PFR

Residence Time (min)	Temperature (C)	Productivity (mol NaAc/L-min)
3.85	22	$6.62 \times 10^{-3}$
	35	$8.91 \times 10^{-3}$
	45	$1.01 \times 10^{-2}$
5.00	22	$5.85 \times 10^{-3}$
	35	$7.53 \times 10^{-3}$
	45	$8.38 \times 10^{-3}$
6.25	22	$5.09 \times 10^{-3}$
	35	$6.45 \times 10^{-3}$
	45	$6.89 \times 10^{-3}$

For each temperature the smaller residence times produced larger productivities. As temperature increased, productivity increased for each residence time.

### 3.6 Statistical Analysis

A 95% confidence test was performed using the acquired activation energy and reaction rate coefficient data for all three trials of the Batch, Old CSTR, and PFR reactors at 22C (room temperature), 35C, and 45C. In order to find the the 95% confidence interval the mean, sample standard deviation, standard error, and t-statistic were calculated. The values of each statistical parameter, the confidence intervals, and the k-values and activation energies are displayed in Table 17.

Table 17: Statistical Analysis of Reaction Rates and Activation Energies

	Session	k (22C) (L/mol-sec)	k (35C) (L/mol-sec)	k (45) (L/mol-sec)	E <sub>A</sub> (kJ/mol)
Batch	1	0.0965	0.191	0.309	39.42
	2	0.0946	N/A	N/A	38.16
	3	0.0901	0.197	0.294	40.45
OCSTR	1	0.086	0.189	0.294	44.62
	2	0.095	0.174	0.264	37.95
	3	0.092	0.175	0.269	38.34
PFR	1	0.090	0.189	0.309	41.8
	2	0.094	0.204	0.344	44
	3	0.093	0.344	0.331	43.3
$\bar{x}$	N/A	0.0924	0.2079	0.3018	40.89
S	N/A	0.0032	0.0559	0.0277	2.626
S $\bar{x}$	N/A	0.0011	0.0198	0.0098	0.8754
t <sub>stat</sub>	N/A	2.306	2.365	2.365	2.306
95% Confidence Interval	N/A	(0.0899 , 0.0948)	(0.1611 , 0.2546)	(0.2786 , 0.3249)	(38.87 , 42.92)

## 4.0 Analysis

### 4.1 Thermodynamic Analysis

The estimated heat of reaction for the saponification reaction is -81.0 kJ/mol, which means the reaction is exothermic. The Gibbs free energy change of the reaction is -73.926 kJ/mol, meaning that the reaction is spontaneous.

Upon observation of the data two trends are noticed in Table 3. As the temperature of the saponification reaction increased the equilibrium constant decreased. This follows the understanding that an increase in temperature in exothermic reactions decreases the equilibrium constant. This is because an exothermic reaction, which releases heat energy, would thermodynamically favor a lower reaction temperature. Regardless of the equilibrium constant, and thus regardless of the temperature, the estimated equilibrium conversion was always approximately 0.9999 or 99.99%.

### 4.2 Batch Reactor

The technical objective for batch saponification was to evaluate the dependence of conversion versus time, reaction rate coefficient, and productivity on reaction temperature. The experimental data indicated that increasing the reaction temperature increases the rate of conversion, reaction rate coefficient, and productivity. Over the course of 20 minutes, the conversions varied from 0.03 to 0.87 across all the temperatures, as shown in Figures 5, 6, and 7, and was modelled by Equations 5 and 6.

The reaction rate coefficient increased as temperature increased from 0.0901 L/mol-sec at room temperature to 0.309 L/mol-sec at 45C, as shown in Table 4. This is modelled by the Arrhenius equation, Equation 9. Similarly, the productivity increased as temperature increased, ranging from  $1.81 \times 10^{-3}$  mol/L-min at room temperature to  $2.84 \times 10^{-3}$  mol/L-min at 45 C, as shown in Table 5. The productivity was modelled using Equation 10. These observations, along with the increase in the conversion and the increase in the reaction rate coefficient can be explained by the fact that increasing temperature gives more energy to the reactants, thus allowing for more collisions to occur.

The literature values for the reaction rate coefficient of this reaction are shown in Table 18. The Arrhenius equation was used to extrapolate and interpolate from the given values to the temperatures measured. The calculated values appear to vary marginally from the measured values. At room temperature, the percent difference between the literature and calculated values was 7.48% for the first session, 9.46% for the second session, and 14.32% for the third session. At 35C, the percent difference was 10.89% for the first session and 7.80% for the third session, and at 45C, the difference was 14.13% for the first session and 19.08% for the third session. This variation is most likely due to a variety of factors, including variations in the environment's temperature and the fact that the method of pouring the reactants into the batch reactor quickly then beginning the timer can leave room for error in timing the progress of the reaction.

Table 18: Literature Values for Reaction Rate Coefficient [2]

Temperature (C)	Reaction Rate Coefficient (L/mol-sec)
22	0.104
35	0.213
45	0.356

The literature activation energy value of 41.4 kJ/mol is slightly higher than the three measured values of activation energies for each session. The percent difference between the literature activation energy and the measured activation energy was 4.90% for the first session, 8.14% for the second session, and 2.32% for the third session. The variation from the literature value is most likely due to the same reasons for the variation in the reaction rate coefficient.

### 4.3 Old CSTR

For the Old CSTR the two variables that were changed were the reaction temperature and flow rate of the entering reactants. Through this change in variables, the conversion ranged from 0.56 to 0.81. As the temperature was increased from 22C to 45C, the conversion also increased



from 0.56 to 0.81. This is expected as with a higher temperature, the molecules are moving faster and undergoing more frequent collisions, resulting in more reactions and a higher conversion. As the flow rate increased from 2x22 mL/min to 2x80 mL/min at 45C, the conversion decreased from 0.81 to 0.68. A similar decrease was seen across all temperatures. This is expected since as the reactant moves faster through the reactor, it has less time to react, thus reducing the conversion.

As the flow rate of the reactants increased, the residence time with the reactor decreased. This is explained by Equation 11, which mathematically shows the inverse relationship of reactant flow rate to residence time.

The reaction rate coefficient was also calculated for the various temperatures and flow rates. Predictably, the coefficient increased from 0.086 (L/(mol-sec)) to 0.294 (L/(mol-sec)) as the temperature of the reaction was also increased from 22C to 45C. Mechanistically, this can be explained by the kinetic energy of the molecules. Since temperature is a measure of the kinetic energy of molecules, the higher the temperature, the faster the movement, and the greater number of collisions. This means that even before the concentration reactant is increased, the rate of reaction is increased by a higher temperature, resulting in a higher reaction rate coefficient. In contrast, the flow rate did not have a large effect on the reaction rate or its coefficient. This can be explained by the fact that flow rate does not affect the concentration of the reactants. While there are more reactants present overall, they are present in equally greater quantities with the same proportion of solvent, resulting in no change to the reaction rate.

The literature values given for the reaction rate coefficient align fairly well with the values that were calculated. The literature values are displayed in Table 18. The experimental reaction rate coefficients for 22C, 35C and 45C that are the furthest from the literature values had a percent difference of 17%, 18%, and 26%, respectively. While these percentages are higher than ideal, the differences are most likely explained by the challenges in precise temperature control that affected the Old CSTR, and upon which the reaction rate coefficient is extremely dependent.

The activation energies displayed in Table 8 are very close to each other in value. This makes sense as the activation energy of an reaction should stay constant, regardless of flow rate

or temperature. The percent difference for the experimental activation energies for 22C, 35C, and 45C were 7.7%, 8.3%, and 7.4%, respectively. These percent difference are quite low, and the error is most likely a result of the troubles with temperature control mentioned above.

The productivity of the Old CSTR can be found in Table 9. This varied from both the change in temperature and the change in flow rate of the reactants. As the temperature increased from 22C to 45C, the productivity increased from  $1.30 \times 10^{-3}$  mol NaAc/L-min to  $3.40 \times 10^{-3}$  mol NaAc/L-min. This is because as the temperature rose, more product was produced due to the higher conversion that the temperature rise drove. As the residence time rose, the productivity of the reactor dropped. This is due to the fact that a lowered residence time results in a lowered conversion, dropping the productivity. The most productive system had a productivity of  $3.40 \times 10^{-3}$  mol NaAc/L-min with a flow rate 80 mL/min and temperature of 45C.

#### 4.4 New CSTR

Three separate factors were used to compare how the CSTRs in series and the single CSTR performed. Conversion, residence time vs. flow rate, and productivity were calculated for both mechanisms and were placed side-by-side to see the comparisons.

From the results section, it shows that the conversion for the series reactors were much larger than the single reactor, close to 20% for the 66.2 mL/min flow rate. This was the common occurrence with the same flow rate for both reactor assemblies. Reactors in series have a higher conversion due to the conversion continuing to increase in the second reactor after starting in the first reactor. This causes an increase in the conversion, making it higher than the single CSTR starting conversion. The flow rate change from the two sessions suggests that even with different flow rates, the reactor series will have a higher conversion than the single reactor.

Another observation from the conversions is that when the flow rate was lower, the conversion was higher. When the flow rate was decreased from 153 to 66.2 and 52.2 mL/min the conversion jumped almost 20% higher in reactor 2 and the combined reactor series. This shows a considerably higher conversion and could show a trend; that if the flow rate is high, there will be a lower conversion. This happens because the CSTR has higher conversion at higher residence time, which as discussed above is tied to the flow rate.

Table 11, it shows that the residence time more than doubles when the flow rate is decreased from 153 mL/min to 66.2 mL/min. While the residence time doubles with the flow rate decrease, the single CSTR and the series CSTR have identical residence times. The single CSTR has a 15.33 minute residence time for the third session just as the series CSTR.

The effectiveness of how something is produced is productivity and it plays a significant role to the deciding factor of what production process to use. As shown in Table 12, the decrease in flow rate causes a decrease in productivity. The initial experiment, at a flow rate of 153 mL/min, has a productivity of  $3.2 \times 10^{-3}$  mol NaAc/L min, when the flow rate was decreased to 52.2 L/min, the productivity decreased to  $1.27 \times 10^{-3}$  mol NaAc/L. The table also shows that productivity was higher for the reactor series than the single reactor. The productivity for the single reactor, at a flow rate of 153 mL/min, was  $3.2 \times 10^{-3}$  mol NaAc/L min and for the series reactors the productivity was  $4.05 \times 10^{-3}$  mol NaAc/L min. This shows that the series CSTR is the more favorable process for our reaction due to a higher conversion and higher productivity than with the single CSTR.

#### 4.5 PFR

For the PFR, the results varied based on temperature and flow rate. Conversion ranged from 0.50 to 0.86 and increased as the temperature increased, as displayed in Figure 11. As temperature increased from 22C to 45C, the conversion increased from 0.51 to 0.78 for the 130mLx2 flow rate, from 0.59 to 0.84 for the 100mLx2 flow rate, and from 0.64 to 0.86 for the 80mLx2 flow rate. This makes sense, because as the temperature increases the reactants have more energy and collide more often, thus reacting more. Conversion decreased as flow rate increased. Between a flow rate of 130mLx2 and 80mLx2, conversion changed from 0.51 to 0.64 for 22C, from 0.69 to 0.81 for 35C, and from 0.78 to 0.86 for 45C. This is because the residence time decreased, lessening reaction time as discussed above. Residence time, as displayed in Table 13, is independent of temperature, and it decreases as flow rate increases, due to its relationship to flow rate discussed above.

The reaction rate coefficient varied based on both temperature and flow rate, as shown in Table 14. As the temperature increased, the rate coefficient also increased from 0.090

(L/mol-sec) to 0.331 (L/mol-sec), due to the increased kinetic energy. The variations of  $k$  based on flow rate vary by very little, between 4% and 17% at different temperatures; the two flow rates produce the same value measured to one significant figure. This is because  $k$  is determined by the Arrhenius equation, where the only variable for a given reaction is temperature.

The literature values given for  $k$  align well with the calculated values. These literature values are displayed in Table 18. When rounded to one significant figure, the calculated values and the literature values are the same. This indicates these measurements are fairly reliable.

The activation energy, displayed in Table 15, is independent of temperature and flow rate. This is expected since the activation energy should be independent of both temperature and flow rate, as it is only a function of the reaction not the conditions. The activation energy was calculated by using the reaction rate coefficient and the temperature. Since the rate coefficient varied very little for each flow rate, the activation energy did not vary by much. The range was 41.8 (kJ/mol) to 43.3 (kJ/mol), meaning a difference in values of only 3%.

The literature value for the activation energy is 41.4 kJ/mol [2]. This value is within 1-6% for each trial. This increases the confidence in the measured values.

Productivity varied based on both residence time and temperature, as displayed in Table 16. As residence time increased, productivity decreased from  $1.01 \times 10^{-2}$  to  $5.09 \times 10^{-3}$ . This is because as the time in the reactor increases, the reactor produces less product. Productivity increased as temperature increased to 35C. This is because as temperature increases, conversion increases, and thus the amount of product produced increases. The most productive system had a flow rate of 100 mL/min and temperature of 45C and had a productivity value of  $5.07 \times 10^{-3}$  mol NaAc/L-min.

#### 4.6 Overall Reactor Analysis

As a whole, the reactors displayed a lot of very similar trends. The first one that was examined across all the reactors was that of conversion. The first variable that was varied to see how it affected conversion was temperature. Which the exception of the new CSTR which didn't vary temperature, the conversion of all the reactors increased, from the lowest conversion of 0.51 at room temperature in the PFR to the highest conversion of 0.86 at 45C in the PFR . The cause

of this increase is due to the increased kinetic energy of the molecules, as discussed above. The other variable that was varied while conversion was observed was the flow rate into the reactors. The varying of the flow rate allowed the amount of time that reactants spent in the reactor to be changed. This was observed across all the reactors besides the batch reactor, as the batch reactor had a fixed reaction time. The conversion increased as the reaction time increased from the lowest conversion of 0.51 at 3.51 minutes at room temperature of reacting in the PFR to the highest conversion of 0.86 at 6.25 minutes at 45C of reacting in the PFR .

The next analyzed trend was that of the reaction rate coefficient. The reaction rate coefficient was found in a very similar way to the conversion, varying temperature and reaction time for the same reactors as mentioned above. However, the reaction rate coefficient only increased when temperature increased, rising from the lowest  $k$  of 0.086 L/mol-sec at room temperature in the old CSTR to the highest  $k$  of 0.344 at 45C in the PFR. The reasons that the reaction rate coefficient only increased for temperature and not reaction time were discussed above.

The final analyzed trend was that of productivity. Productivity takes into account both the amount of product made through the conversion, and how long it takes to make it by taking the flow rate into the reactor into account. Both the temperature of the reaction and the flow rates of the reactants had an effect of the productivity. The lowest productivity of  $1.27 \times 10^{-3}$  mol NaAc/L-min was found in the New CSTR, in it's single reactor and highest residence time. The highest productivity of  $1.01 \times 10^{-2}$  mol NaAc/L-min was found in the PFR at 45C and a residence time of 3.85 minutes.

After considering each of the trends discussed above, the PFR stands out as the most opportune reactor to use for the production of sodium acetate from sodium hydroxide and ethyl acetate. With the highest overall conversion, and highest overall productivity, the PFR is certainly the best choice. Therefore, the PFR is indeed the ideal reactor, and more specifically, the PFR operating at 45C is optimal due to the comparisons and analysis above.

#### 4.7 Statistical Analysis

According to the confidence intervals found in Table 17 there is a 95% probability that the true value for  $k$  (22C) falls within the range 0.0899 and 0.0948 L / mol-sec, and there is a 95% probability that the true value for  $k$  (35C) is within 0.1611 and 0.2546 L/mol-sec. In addition, the actual value of  $k$  (45C) has a 95% probability of existing in the range 0.2786 to 0.3249 L/mol-sec. Finally, there is a 95% probability that the actual value of the activation energy falls within 38.87 and 42.92 kJ/mol.

Based on the reaction rate coefficient literature values found in Table 18, only the literature value for  $k$  (35C) at 0.213 L/mol-sec exists within the corresponding confidence interval. The literature value for  $k$  (22C) is 0.104 L/mol-sec which is slightly above the upper bound of the 95% confidence interval. In addition, the literature value for  $k$  (45C) of 0.356 is also slightly above the upper bound of the corresponding 95% confidence interval. For the activation energy for the saponification reaction the literature value is 41.4 kJ/mol. 41.4 kJ/mol is within the 95% confidence interval for activation energy.

## 5.0 Conclusion

In all, the batch reactors, CSTR, and PFR showed to be great tools for understanding of the saponification process. Many trends were revealed through the myriad technical objectives, and by studying them, conclusions were determined about the functionality of the reactors and the process of saponification. The first noteworthy trend is that as the temperature increased, the conversion, and with it the productivity, increased as well. This increase in temperature provided more kinetic energy to the molecules allowing them to overcome the activation energy more often during collisions. The other main trend noticed through the experimentation was that an increase in the flow rate for the CSTR and the PFR caused the conversion to decrease while the productivity still increased. While this may seem counterintuitive, the reasoning behind this lies in the ratios. The increase in flow rate allowed less exposure in the reactor for the reactants to react which overall lowered the conversion. Because the residence time was lowered by the flow rate however, the productivity was still able to increase due to the way it is defined. Productivity is defined as having the conversion in the numerator and the residence time in the denominator so while the overall conversion may have decreased, the productivity can still increase so long as the residence time decreases more comparatively to the conversion, assuming the initial concentration of the compared experiments were held constant. In other words, if the ratio of conversion to residence time increases, the productivity increases even if both numbers decrease.

Overall, these trends help us better understand the process of saponification and allow us to continue honing the process to increase efficiency and productivity. Saponification is a big part of the chemical industry, and by improving upon the current methods, it can be even easier for people all around the United States as well as the world to receive commodities like soap that are a product of saponification. As noted previously the acquired values of  $k$  (22) and  $k$  (45) vary from the literature values significantly, explaining the discrepancy between the 95% confidence intervals and the literature values.

## 6.0 References

- [1] Statista, “U.S. population: Do you use bar soap”, 2017. [Online]. Available: <https://www.statista.com/statistics/275225/us-households-usage-of-bar-soap/> [Accessed: 7-Mar-2018]
- [2] Das et. Al, *International Journal of Chemical Kinetics*, Vol. 43, November 2011



## 7.0 Appendix

### 7.1 Sample Calculations

#### 7.11 Thermodynamic Analysis

##### **Heat of Reaction**

$$\Delta H_{\text{Rxn}} = [\Delta H_{\text{f Ethanol}} + \Delta H_{\text{f Sodium Acetate}}] - [\Delta H_{\text{f ethyl acetate}} + \Delta H_{\text{f sodium hydroxide}}]$$

$$\Delta H_{\text{f Ethanol}} = -277.7 \text{ kJ/mol}$$

$$\Delta H_{\text{f Sodium Acetate}} = -709.3 \text{ kJ/mol}$$

$$\Delta H_{\text{f ethyl acetate}} = -479.0 \text{ kJ/mol}$$

$$\Delta H_{\text{f sodium hydroxide}} = -427.0 \text{ kJ/mol}$$

$$\Delta H_{\text{Rxn}} = [-277.7 \text{ kJ/mol} + -709.3 \text{ kJ/mol}] - [-479.0 \text{ kJ/mol} + -427.0 \text{ kJ/mol}] = -81.0 \text{ kJ/mol}$$

##### **Gibbs Free Energy**

$$\Delta G_{\text{Rxn}} = [\Delta G_{\text{f Ethanol}} + \Delta G_{\text{f Sodium Acetate}}] - [\Delta G_{\text{f ethyl acetate}} + \Delta G_{\text{f sodium hydroxide}}]$$

$$\Delta G_{\text{f Ethanol}} = -174.1 \text{ kJ/mol}$$

$$\Delta G_{\text{f Sodium Acetate}} = -607.7 \text{ kJ/mol}$$

$$\Delta G_{\text{f ethyl acetate}} = -332.7 \text{ kJ/mol}$$

$$\Delta G_{\text{f sodium hydroxide}} = -380.7 \text{ kJ/mol}$$

$$\Delta G_{\text{Rxn}} = [-174.1 \text{ kJ/mol} + -607.7 \text{ kJ/mol}] - [-332.7 \text{ kJ/mol} + -380.7 \text{ kJ/mol}] = -68.4 \text{ kJ/mol}$$

##### **Equilibrium Constant**

$$K_{\text{eq}} = \exp(-\Delta G_{\text{Rxn}} / R * T)$$

$$\text{At } T = 30 \text{ }^{\circ}\text{C} = 303 \text{ K}$$

$$\Delta G_{\text{Rxn}} = -68.4 \text{ kJ/mol}$$

$$R = 0.008314 \text{ kJ/ mol K}$$

$$T = 303 \text{ K}$$

$$K_{\text{eq}} = \exp(68.4 \text{ kJ/mol} / 0.008314 \text{ kJ/ mol K} * 303 \text{ K}) = 6.195 \times 10^{11}$$

### Estimated Equilibrium Conversion

$$X = \sqrt{K_{eq}} / (\sqrt{K_{eq}} + 1)$$

$$\text{At } T = 30\text{ }^{\circ}\text{C} = 303\text{ K}$$

$$K_{eq} = 6.195 \times 10^{11}$$

$$X = \sqrt{6.195 \times 10^{11}} / (\sqrt{6.195 \times 10^{11}} + 1) = 0.9999 = 99.99\%$$

### 7.12 Batch Reactor

#### Temperature Corrected Lambda Values

$$\lambda_{\text{species}} = [\kappa_{\text{species, standard}} + \alpha_{\text{species}}(T - T_{\text{species, standard}})] / C_{\text{species, standard}}$$

For sodium hydroxide at 22C,

$$\kappa_{\text{species, standard}} = 21.1\text{ mS}$$

$$\alpha_{\text{species}} = 0.4006\text{ mS/C}$$

$$T = 22\text{C}$$

$$T_{\text{species, standard}} = 20.9\text{ }^{\circ}\text{C}$$

$$C_{\text{species, standard}} = 0.1\text{ mol/L}$$

$$\lambda_{\text{NaOH}} = [21.1\text{ mS} + 0.4006\text{ mS/C} * (22\text{C} - 20.9\text{C})] / 0.1\text{ mol/L} = 215.4\text{ mS-L/mol}$$

#### Conversion

$$X = (\kappa - \lambda_{\text{NaOH}} * C_{0\text{NaOH}}) / (-\lambda_{\text{NaOH}} * C_{0\text{NaOH}} + \lambda_{\text{NaAc}} * C_{0\text{NaOH}})$$

$$\kappa = 7.06\text{ mS}$$

$$\lambda_{\text{NaOH}} = 215.4\text{ mS-L/mol}$$

$$C_{0\text{NaOH}} = 0.05\text{ mol/L}$$

$$\lambda_{\text{NaAc}} = 66.35\text{ mS-L/mol}$$

$$X = (7.06\text{ mS} - 215.4\text{ mS-L/mol} * 0.05\text{ mol/L}) / (-215.4\text{ mS-L/mol} * 0.05\text{ mol/L} + 66.35\text{ mS-L/mol} * 0.05\text{ mol/L}) = 0.50$$

#### Reaction Rate Coefficient

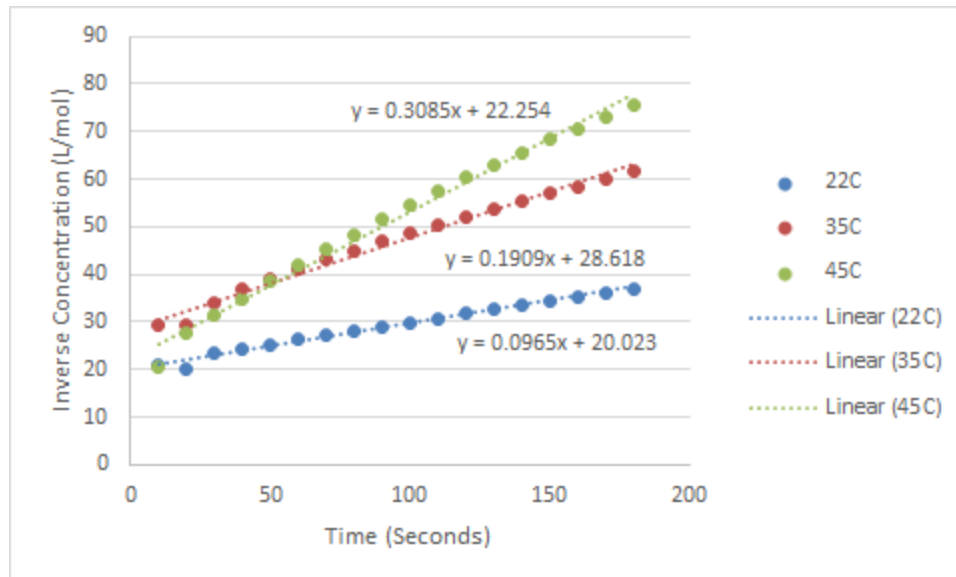


Figure A1: Inverse Concentration vs. Time for Lab Session 1 for Batch Reactor

$k = \text{slope}$

For reaction at 22C

$k = 0.309 \text{ L/mol}$

### Activation Energy

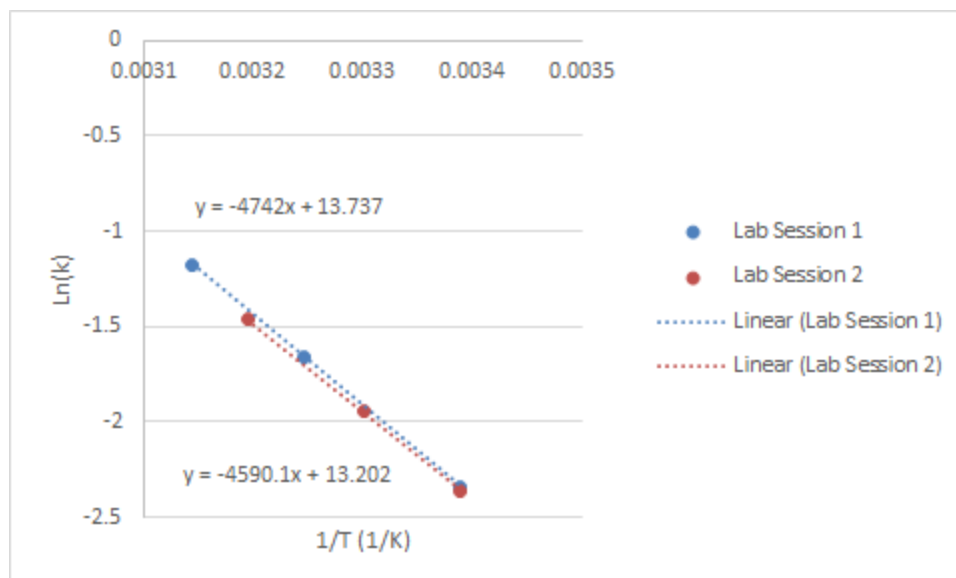


Figure A2: Plot of ln(k) vs 1/T to Calculate Activation Energy for Batch Reactor

$$E_a = -\text{slope} \cdot R$$

For Lab Session 1

$$\text{slope} = -4742 \text{ K}$$

$$R = 8.314 \text{ J/mol-K}$$

$$E_a = 4742 \text{ K} \cdot 8.314 \text{ J/mol-K} = 39424 \text{ J/mol} = 39.42 \text{ kJ/mol}$$

### Productivity

$$P = C_{0 \text{ NaOH}} \cdot X/t$$

$$C_{0 \text{ NaOH}} = 0.05 \text{ mol/L}$$

$$X = 0.70$$

For 22C First Trial

$$t = 19.33 \text{ min}$$

$$P = 0.05 \text{ mol/L} \cdot 0.70 / 19.33 \text{ min} = 1.81 \times 10^{-3} \text{ mol/L-min}$$

### 7.13 Old CSTR

#### Temperature Corrected Lambda Values

$$\lambda_{\text{species}} = [\kappa_{\text{species, standard}} + \alpha_{\text{species}}(T - T_{\text{species, standard}})] / C_{\text{species, standard}}$$

For sodium hydroxide at 23.96 C,

$$\kappa_{\text{species, standard}} = 21.2 \text{ mS}$$

$$\alpha_{\text{species}} = 0.3528 \text{ mS/C}$$

$$T = 23.96 \text{ C}$$

$$T_{\text{species, standard}} = 21.1 \text{ C}$$

$$C_{\text{species, standard}} = 0.1 \text{ mol/L}$$

$$\lambda_{\text{NaOH}} = [21.2 \text{ mS} + 0.3528 \text{ mS/C} \cdot (23.96 \text{ C} - 21.1 \text{ C})] / 0.1 \text{ mol/L} = 222.09 \text{ mS-L/mol}$$

### Conversion

$$X = (\kappa - \lambda_{\text{NaOH}} \cdot C_{0 \text{ NaOH}}) / (-\lambda_{\text{NaOH}} \cdot C_{0 \text{ NaOH}} + \lambda_{\text{NaAc}} \cdot C_{0 \text{ NaOH}})$$

For 60 mL/min x 2 at 24.311C,

$$\kappa=6.545 \text{ mS}$$

$$\lambda_{\text{NaOH}}=223.33 \text{ mS-L/mol}$$

$$C_{0\text{NaOH}}=0.05 \text{ mol/L}$$

$$\lambda_{\text{NaAc}}=71.32 \text{ mS-L/mol}$$

$$X=(6.545 \text{ mS} - 223.33 \text{ mS-L/mol} * 0.05 \text{ mol/L})/(-223.33 \text{ mS-L/mol} * 0.05 \text{ mol/L} + 71.32 \text{ mS-L/mol} * 0.05 \text{ mol/L}) = 0.61$$

### **Residence Time**

$$\tau=V/F_{\text{NaOH+NaAc}}$$

For 60\*2 mL/min

$$V=1670 \text{ mL}$$

$$F_{\text{NaOH+NaAc}}=120 \text{ mL/min}$$

$$\tau=1670 \text{ mL}/(120 \text{ mL/min})=13.92 \text{ min}$$

### **Reaction Rate Coefficient**

$$k=(C_{0\text{NaOH}} * X_{\text{NaOH}})/(C_{0\text{NaOH}})^2 * (1-X_{\text{NaOH}})^2 * (\tau_{\text{CSTR}})$$

For 60 mL/min x 2 at 24.311C,

$$C_{0\text{NaOH}}=0.05 \text{ mol/L}$$

$$X_{\text{NaOH}}= 0.61$$

$$\tau_{\text{CSTR}}=13.92 \text{ min} =835.2 \text{ sec}$$

$$k=(0.05 \text{ mol/L} * 0.61)/(0.05 \text{ mol/L})^2 * (1-0.61)^2 * (13.92 \text{ min})=5.96 \text{ M}^{-1} * \text{Min}^{-1}$$

### **Activation Energy**

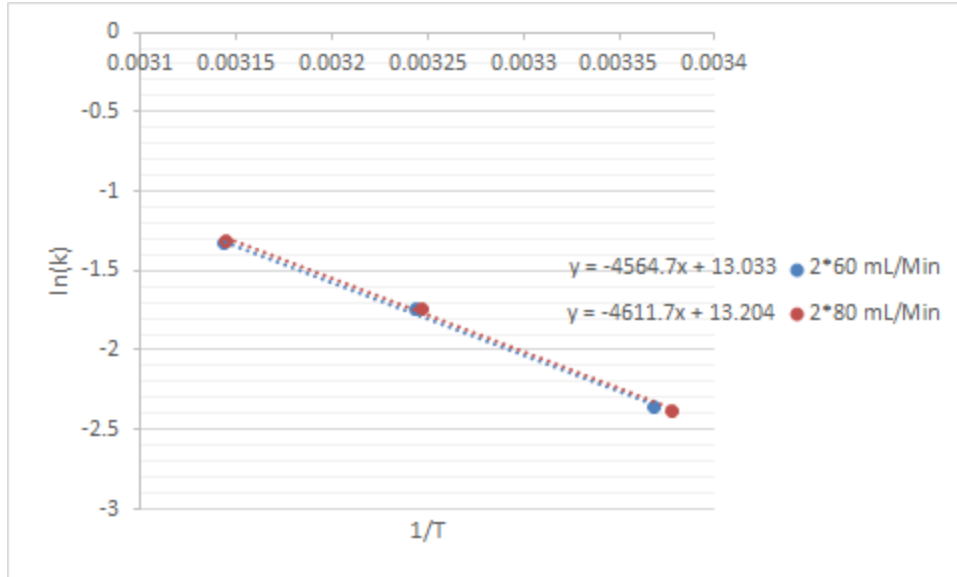


Figure A3: Plot of  $\ln(k)$  vs  $1/T$  to Calculate Activation Energy for Old CSTR

$$E_a = -\text{slope} \cdot R$$

For 60 mL/min x 2

$$\text{slope} = -4564.7 \text{ K}$$

$$R = 8.314 \text{ J/mol-K}$$

$$E_a = 4564.7 \text{ K} \cdot 8.314 \text{ J/mol-K} = 37950.9 \text{ J/mol} = 37.95 \text{ kJ/mol}$$

### Productivity

$$P = C_{0\text{NaOH}} \cdot X / \tau$$

For 80 mL/min x 2 at 23.1°C

$$C_{0\text{NaOH}} = 0.05 \text{ mol/L}$$

$$X = 0.56$$

$$\tau = 10.44 \text{ min}$$

$$P = 0.05 \text{ mol/L} \cdot 0.56 / 10.44 \text{ min} = 2.68 \times 10^{-3} \text{ mol/L-min}$$

### 7.14 New CSTR

#### Temperature Corrected Lambda Values

$$\lambda_{\text{species}} = [\kappa_{\text{species, standard}} + \alpha_{\text{species}}(T - T_{\text{species, standard}})] / C_{\text{species, standard}}$$

For sodium hydroxide,

$$\kappa_{\text{species, standard}} = 19.9 \text{ mS}$$

$$\alpha_{\text{species}} = 0.4151 \text{ mS/C}$$

$$T = 21.4^\circ\text{C}$$

$$T_{\text{species, standard}} = 20.5^\circ\text{C}$$

$$C_{\text{species, standard}} = 0.1 \text{ mol/L}$$

$$\lambda_{\text{NaOH}} = [19.9 \text{ mS} + 0.4151 \text{ mS/C} \cdot (21.4^\circ\text{C} - 20.5^\circ\text{C})] / 0.1 \text{ mol/L} = 202.7 \text{ mS-L/mol}$$

### Conversion for Single Reactor

$$X = (\kappa - \lambda_{\text{NaOH}} \cdot C_{0\text{NaOH}}) / (-\lambda_{\text{NaOH}} \cdot C_{0\text{NaOH}} + \lambda_{\text{NaAc}} \cdot C_{0\text{NaOH}})$$

$$\kappa = 7.85 \text{ mS}$$

$$\lambda_{\text{NaOH}} = 202.79 \text{ mS/M NaOH}$$

$$C_{0\text{NaOH}} = 0.05 \text{ mol/L}$$

$$\lambda_{\text{NaAc}} = 66.02 \text{ mS/M NaAc}$$

$$X = (7.85 \text{ mS} - 202.79 \text{ mS/M NaOH} \cdot 0.05 \text{ M}) / (-202.79 \text{ mS/M NaOH} \cdot 0.05 \text{ M} + 66.02 \text{ mS/M NaAc} \cdot 0.05 \text{ M}) = 0.335$$

### Conversion 2<sup>nd</sup> Series Reactor

$$X_{\text{NaOH}} = (\kappa - \lambda_{\text{NaOH}} \cdot C_{\text{NaOH}} - \lambda_{\text{NaAc}} \cdot C_{\text{NaAc}}) / (C_{\text{NaOH}} \cdot (\lambda_{\text{NaAc}} - \lambda_{\text{NaOH}}))$$

$$\kappa = 7.26$$

$$\lambda_{\text{NaOH}} = 202.79 \text{ mS/M NaOH}$$

$$C_{\text{NaOH}} = 0.0369 \text{ mol/L}$$

$$\lambda_{\text{NaAc}} = 66.02 \text{ mS/M NaAc}$$

$$C_{\text{NaAc}} = 0.0132 \text{ mol/L}$$

$$X = (7.26 \text{ mS} - 202.7359 \text{ mS/M NaOH} \cdot 0.0369 \text{ M NaOH} - 66.016 \text{ mS/M NaAc} \cdot 0.0132 \text{ M NaAc}) / (0.0369 \text{ M NaOH} \cdot (66.016 \text{ mS/M NaAc} - 202.7359 \text{ mS/M NaOH}))$$

$$= 21.7\%$$

### Combined Series Reactor

$$X = 1 - (1 - X_{\text{NaOH}})(1 - X_{\text{NaOH}2})$$

$$X_{\text{NaOH}} = .2628$$

$$X_{\text{NaOH}2} = .1888$$

$$X = 1 - (1 - .2628)(1 - .1888) = 0.402$$

### Residence Time Single CSTR

$$\tau_{\text{CSTR}} = V/F_{\text{NaOH+NaAc}}$$

$$V = .8 \text{ L}$$

$$F_{\text{NaOH+NaAc}} = .1534 \text{ L/min}$$

$$\tau_{\text{CSTR}} = .8 \text{ L} / .1534 \text{ L/min} = 5.215 \text{ min}$$

### Single CSTR Productivity

$$P = (C_{0\text{NaOH}} * X_{\text{NaOH}}) / \tau_{\text{CSTR}}$$

$$C_{0\text{NaOH}} = 0.05 \text{ mol/L}$$

$$X_{\text{NaOH}} = .334$$

$$\tau_{\text{CSTR}} = 5.215 \text{ min}$$

$$P = (.05 \text{ M NaOH} * .334) / 5.215 \text{ min} = 3.2 \times 10^{-3} \text{ M NaOH/min}$$

### 7.15 PFR

#### Temperature Corrected Lambda Values

$$\lambda_{\text{species}} = [\kappa_{\text{species, standard}} + \alpha_{\text{species}}(T - T_{\text{species, standard}})] / C_{\text{species, standard}}$$

For sodium hydroxide at 22C,



$$\kappa_{\text{species, standard}} = 23.4 \text{ mS}$$

$$\alpha_{\text{species}} = 0.4041 \text{ mS/C}$$

$$T = 22 \text{ C}$$

$$T_{\text{species, standard}} = 21.7 \text{ C}$$

$$C_{\text{species, standard}} = 0.1 \text{ mol/L}$$

$$\lambda_{\text{NaOH}} = [23.4 \text{ mS} + 0.4041 \text{ mS/C} * (22\text{C} - 21.7\text{C})] / 0.1 \text{ mol/L} = 235.2 \text{ mS-L/mol}$$

### Conversion

$$X = (\kappa - \lambda_{\text{NaOH}} * C_{0\text{NaOH}}) / (-\lambda_{\text{NaOH}} * C_{0\text{NaOH}} + \lambda_{\text{NaAc}} * C_{0\text{NaOH}})$$

For 130 mL/min x 2 at 22C,

$$\kappa = 7.06 \text{ mS}$$

$$\lambda_{\text{NaOH}} = 235.2 \text{ mS-L/mol}$$

$$C_{0\text{NaOH}} = 0.05 \text{ mol/L}$$

$$\lambda_{\text{NaAc}} = 66.02 \text{ mS-L/mol}$$

$$X = (7.06 \text{ mS} - 235.2 \text{ mS-L/mol} * 0.05 \text{ mol/L}) / (-235.2 \text{ mS-L/mol} * 0.05 \text{ mol/L} + 66.02 \text{ mS-L/mol} * 0.05 \text{ mol/L}) = 0.56$$

### Residence Time

$$\tau = V/F$$

For 130 mL/min

$$V = 1 \text{ L} = 1000 \text{ mL}$$

$$F = 260 \text{ mL/min}$$

$$\tau = 1000 \text{ mL} / (260 \text{ mL/min}) = 3.85 \text{ min}$$

### Reaction Rate Coefficient

$$k = u/L * (1/C_{\text{NaOH}} - 1/C_{0\text{NaOH}})$$

$$C_{\text{NaOH}} = C_{0\text{NaOH}} * (1 - X)$$

$$u = F / (0.25 * \pi * D^2)$$

For 130 mL/min x 2 at 22C

$$X=0.51$$

$$L=22.6 \text{ m}$$

$$C_{0\text{NaOH}}=0.05 \text{ mol/L}$$

$$F=130 \text{ mL/min}=2.16667 \times 10^{-6} \text{ m}^3/\text{sec}$$

$$D=0.75 \text{ cm}=0.0075 \text{ m}$$

$$u=(2.16667 \times 10^{-6} \text{ m}^3/\text{sec})/(0.25 \times \pi \times (0.0075 \text{ m})^2)=0.098 \text{ m/s}$$

$$C_{\text{NaOH}}=(0.05 \text{ mol/L}) \times (1-0.51)=0.025 \text{ mol/L}$$

$$k=0.098 \text{ m/s} / 22.6 \text{ m} \times (1/0.025 \text{ mol/L} - 1/0.05 \text{ mol/L})=0.0901 \text{ L/mol-sec}$$

### Activation Energy

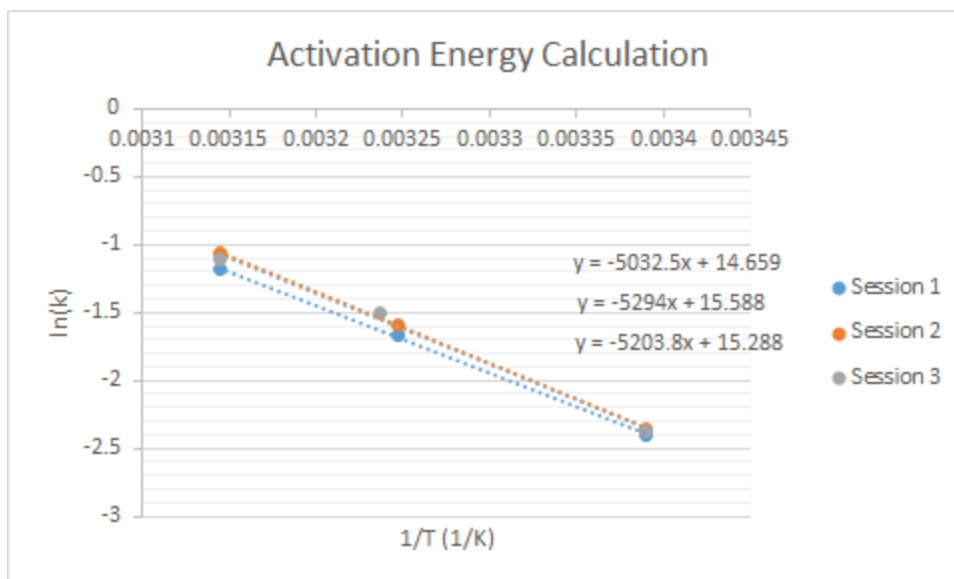


Figure A4: Plot of  $\ln(k)$  vs.  $1/T$  to Calculate Activation Energy for PFR

$$E_a = -\text{slope} \times R$$

For 130 mL/min x 2

$$\text{slope} = -5294 \text{ K}$$

$$R=8.314 \text{ J/mol-K}$$

$$E_a = 5294 \text{ K} \times 8.314 \text{ J/mol-K} = 35300 \text{ J/mol} = 35.3 \text{ kJ/mol}$$

### Productivity

$$P = C_{0\text{NaOH}} * X / \tau$$

For 130 mL/min at 22C

$$C_{0\text{NaOH}} = 0.05 \text{ mol/L}$$

$$X = 0.56$$

$$\tau = 3.85 \text{ min}$$

$$P = 0.05 \text{ mol/L} * 0.56 / 3.85 \text{ min} = 6.62 \times 10^{-3} \text{ mol/L-min}$$

### 7.15 Statistical Analysis

#### **95% Confidence Interval for Reaction Rate Coefficient**

$$95\% \text{ Confidence Interval} = \bar{x} \pm t_{\text{stat}} * S\bar{x}$$

For k(35)

$$\bar{x} = 0.2079$$

$$S\bar{x} = 0.0198$$

$$t_{\text{stat}} = 2.365$$

$$95\% \text{ Confidence Interval} = 0.2079 \pm 2.365 * 0.0198$$

$$95\% \text{ Confidence Interval} = (0.1611, 0.2546)$$

#### **95% Confidence Interval for Activation Energy**

$$95\% \text{ Confidence Interval} = \bar{x} \pm t_{\text{stat}} * S\bar{x}$$

For  $E_A$

$$\bar{x} = 40.89$$

$$S\bar{x} = 0.8754$$

$$t_{\text{stat}} = 2.306$$

$$95\% \text{ Confidence Interval} = 40.89 \pm 2.306 * 0.8754$$

$$95\% \text{ Confidence Interval} = (38.87, 42.92)$$