Statistical Studies of a Real Continuous Stirred Tank Reactor (CSTR) Based on Experimental Data

by

Azwa Hashima Khamthani

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JANUARY 2005

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CERTIFICATION OF APPROVAL

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Approved by,

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

AZWA HASHIMA KHAMTHANI

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ABSTRACT

Reactor engineering is the most unique part of chemical engineering and its technology has gain tremendous applications in industry. Three ideal contacting patterns – batch, mixed flow and plug flow reactors are often studied and treated to make real reactors approach ideality as closely as possible. The three reacting patterns are easy to treat and simple to find their performance equation. Mixed flow reactor or Continuous Stirred Tank Reactor (CSTR) is a type of reactor that is widely used mainly in food and beverages production, chemical neutralization, and other industries. It is preferable compared to other reactors, depending on its application for the ease of cleaning and maintenance and requires less labor cost.

The objective of the study is to conduct statistical studies on a real CSTR. CSTR is often treated as 'ideal reactor', in which this statement is untrue because in real life perfect mixing in CSTR is hardly to be achieved because of dead zone creation and channeling. This study consists of two main parts; the first part is conducting experiments to obtain the reaction rate constant from the concentration data and tracer analysis. The second part is to do simulation and calculation on the experimental data obtained by using Microsoft Excel and MATLAB.

The experiment conducted is to determine the reaction rate constant of the saponification reaction. The experiments on determining the RTD value are also conducted. There are two methods on determining it – step and pulse input. The experiment is conducted using the CSTR dynamics equipment and experimental data are analyzed. From the study, it was proved that the conversion in an ideal reactor is higher compared to the conversion in real reactors due to dead zone creation and bypassing. The conversion for the ideal reactor is 0.496, and for the real reactor modeled which are segregation model, maximum mixedness model and real CSTR with dead-space and bypass model are 0.479, 0.470 and 0.480 respectively.

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NOMENCLATURE

A, B, ...	reactants
a, b, ...	stoichiometric coefficients for reacting substances A, B, ... (-)
C, C_A, C_B, ...	concentration of reactants A, B, ...(mol/L or mol/m^3)
C_{A0}, C_{B0}	initial concentration of reactants A, B, ... (mol/L or mol/m^3)
C_{As}	ideal concentration of reactant A in a real CSTR with dead-space and bypass model (mol/L)
C_{T0}	initial concentration of tracer (mol/L)
C_{Ts}	ideal concentration of tracer T in a real CSTR with dead-space and bypass model (mol/L)
$E(t)$	exit age distribution function or residence time distribution of particle inside reactor (min^{-1})
$F(t)$	cumulative distribution function (dimensionless)
F_{A0}	initial feed flow rate of component A (mol/min or kg/min)
F_A	feed flow rate for component A (mol/min or kg/min)
k	reaction rate constant (mol/L)$^{1-n}$ min^{-1}
n	order of reaction (-)
N_A	moles of component A
r_A	rate of reaction of component A or consumption of component A
t	time (min)
t_m	reactor holding time or mean residence time of fluid in a flow reactor (min)
T	temperature (K)
υ	volumetric flow rate (L/min)
υ_0	initial volumetric flow rate (L/min)

υ_b	bypass volumetric flow rate in a real CSTR with dead-space and bypass model (L/min)
υ_s	ideal volumetric flow rate in a real CSTR with dead-space and bypass model (L/min)
V	volume of a reactor (L)
V_d	dead zone volume in a real CSTR with dead-space and bypass model (L)
V_s	ideal CSTR volume in a real CSTR with dead-space and bypass model (L)
X_A	conversion or fraction of A converted (-)
X_{seg}	conversion of reactant in segregation model (-)
X_{mm}	conversion of reactant in maximum mixedness model (-)

Greek symbols

α	ratio between ideal CSTR volume in a real CSTR with dead-space and bypass model to total volume of the reactor (-)
β	ratio of bypass stream in a real CSTR with dead-space and bypass model (-)
δ	Dirac delta function (min^{-1})
σ	Standard deviation (min)
σ^2	variance of a tracer curve or distribution function (min^2)
τ	space time (min)

ABBREVIATIONS

CSTR	continuous stirred tank reactor
MFR	mixed flow reactor
RTD	residence time distribution

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

In the majority of industrial chemical processes, a reactor is the key equipment that is designed to produce economically desired products from raw materials. Thus, the design and operation of chemical reactors is crucial to the whole success of industry. Reactors will vary, depending on the nature of the feed materials and products. Besides considering the thermodynamics factor, kinetics (rate law and mechanism) and material and energy balances in designing a reactor, understanding the 'non-ideal' behavior is necessary as in real practice, the observe behavior such as perfect mixing (ideal reactor) in reactors like Continuous Stirred Tank Reactor (CSTR) is just an assumption in order to analyze the reactor performance.

In many CSTR, deviation from ideal flow patterns can be caused by short-circuiting (channeling) of fluid, inadequate mixing and stagnant region (dead zone) creation which subsequently lowers the performance of the reactors. Residence time distribution (RTD) concept is introduced in real reactor design as it is the only way the 'real behavior' of a reactor could be modeled and observed.

This Final Year Research Project is mainly to conduct statistical studies of a real CSTR. Statistical studies, as its name depicts is an analytical studies and solving problem. In the recent years, more and more studies are conducted on RTD, whether mathematically or experimentally. However, it is observed that there is less number of studies based on real reactors. Most of the studies are always take care of the ideality of a CSTR. Thus, this study is motivated by the lack of real reactor's studies, besides to reduce errors of conducting experiments. Experiments could be very easy and very tricky and difficult, as much time required in order to get good results and furthermore, experiments need to be conducted at least three times to get the accurate data. In other way, simulating the data by using Microsoft Excel and MATLAB is highly favorable in this study. Besides reducing the number of experiments need to be conducted, it will also reducing the chemicals usage from the laboratory; besides strengthening the technical skills on simulation.

RTD function, E(t) is the main subject in the studies in order to measure the characteristic of the mixing occurs in the reactor. The RTD is to be determined from experimental data by injecting an inert chemical (tracer) into the reactor at some time $t = 0$ and the tracer concentration, C at the effluent stream are to be measured. Inert chemical or atom is a nonreactive species that is easily detectable. In addition to that, the tracer should have similar physical properties to those of reacting mixture and completely soluble in the mixture. It should not adsorb on the walls or other surfaces in the reactor. There are many types of tracer used for RTD experiment such as colored and radioactive materials. In this project, tracer used is sodium chloride as it reflects the sodium hydroxide properties. The two most used methods of injection are *pulse input* and *step input.* The reaction conversions between the ideal and real reactors can also be developed using the segregation and maximum mixedness models. These models represent the lower and upper limits of the real values of conversion. Other models that could be used to study the real reactor are CSTR with dead-space and bypass model and Two CSTR interchange (with exit at the top and bottom).

1.2 PROBLEM STATEMENT

One of the jobs of a chemical engineer is to scale-up the laboratory experiments to pilot-plant operation or to full-scale production. Since pilot plat costs highly, engineers have modeled and designed a full-scale plant from the operation of a laboratory-bench-scale unit. Analyzing the laboratory data; considering a thorough understanding of the chemical kinetics and transport limitation, reactors could be designed, using its respective design equation.

Since CSTR is widely used in industry, people often misjudge the functionality of it. It is often treated as an ideal reactor. Theoretically, for the sake of calculation and explanation, a CSTR is assumed to be in well mixed system. The density change with reaction is usually small and can be neglected. However, in reality, it is hard to achieve this ideal condition in a real reactor. Thus, in that way, the design of real reactors demands creativity and indepth knowledge of reactor engineering. As far as CSTR is concerns, factors such as dead zone creation and channeling are likely to play major roles in determining the optimum parameters. Dead zone is where there is no reaction occurs at certain regions of the reactor. These regions exist due to the limitation of the CSTR in where the reactants or mixture inside the CSTR do not reach the mixer; or there is little or no exchange of materials with the well-mixed regions. Channeling also occurs due to the design of the reactor itself, for example the outlet of the reactor could be on the top right. There is a tendency that the reactants entering the reactor will not being mixed by the mixer or agitator due to the velocity inside the reactor. Since the mixer is already stirring with a certain speed, thus, channeling and bypassing of reactants without being mixed with the well-mixed region might occur.

These two main factors will be studied extensively in order to incorporate the theoretical and practical aspects of reactor design.

1.3 OBJECTIVES & SCOPE OF STUDY

The research is aimed to develop statistical studies of a real CSTR. The studies will consist of the following:

1. Calculation of the external-age residence time distribution (RTD) function, E(t) from experimental data.

2. Developing models of real reactors such as segregation model, maximum mixedness model, CSTR with dead-space and bypass model and two CSTR interchanges.

3. Study of a real reactors based on models developed and RTD data.
4. Comparison of reaction conversions between the ideal and real reactors.

CHAPTER 2
LITERATURE REVIEW / THEORY

2.1 CONTINUOUS STIRRED TANK REACTOR (CSTR)

CSTR is a type of ideal steady state flow reactor which also known as mixed reactor, backmix reactor or mixed flow reactor (MFR). As its name suggest, it is a reactor in which the contents are well stirred and uniform throughout. Thus, the exit stream from this reactor has the same composition as the fluid within the reactor (Levenspiel, 1999). CSTR consist of a tank with a stirring propeller that is fed and drained by pipes containing reactants and products respectively ***(Figure 1)***. The composition is identical everywhere since the concentration changes instantly at the entrance where mixing occurs. Reaction occurs at the entrance point and nothing else happen in the reactor because nothing is changing.

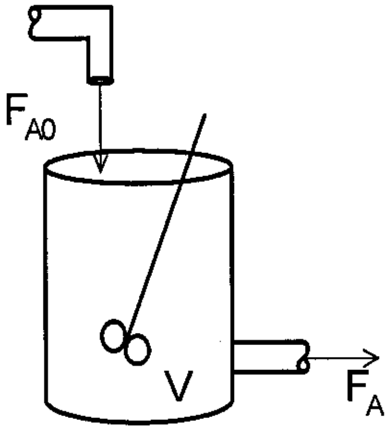


Figure 1: Continuous Stirred Tank Reactor

The overall material balance of a reaction:

$$[input]+[generation]=[output]+\cancelto{=0}{[accumulation]} \qquad (1)$$

The accumulation term is zero since the composition is uniform throughout the system. The uniform composition is achieved by assuming a perfect or well mixing system.

Introducing the terms into equation (1):

$$F_{A0}+(-r_A)\cdot V=F_{A0}-F_{A0}X_A+0 \qquad (2)$$

which on rearrangements become:

$$\frac{V}{F_{A0}}=\frac{X_A}{-r_A}=\frac{\tau}{C_{A0}} \qquad (3)$$

CSTR has been used widely in the organic chemicals industry for medium and large scale of production. It can be made into a continuous process yielding constant product quality, ease of automatic control and low manpower requirements. CSTR is generally inexpensive to be constructed and cleaning the tank is an easy task because of its open nature which makes it particularly important in polymerization reactions. In this type of reactor, the reactants entering will be diluted immediately; which in many cases favors the desired reaction and suppresses the unwanted products. Since fresh reactants are rapidly mixed into a larger volume, the temperature of the tank is readily controlled and hot spots are likely less to occur.

2.2 RATE LAW, $-r_A$

Reaction kinetics is the most important parameter in reactor design. It is found by experiment that rates almost have power-dependences on the densities such as concentration of chemical species. The rate law is determined from experimental observation and relates the rate of reaction at a particular point to the species concentration at the same point. In simple words, rate law is the product of a *reaction rate constant k* and a function of the concentrations (Fogler, 1999):

$$-r_A = k_A(T) \cdot f(C_A, C_B, C_C, \ldots\ldots) \tag{4}$$

Reaction rate constant, k is not truly a constant, but is independent of concentrations of the species involved in the reaction and dependent on temperature.

2.3 SAPONIFICATION REACTION

Saponification reaction of ethyl acetate can also be called as alkaline hydrolysis of ethyl acetate. The stoichiometry of the reaction is:

$$NaOH + CH_3COOCH_2CH_3 \rightarrow CH_3CH_2OH + NaOOCH_3 \tag{5}$$

The mechanism of the basic hydrolysis of esters was first being proposed by Day and Ingold and analyzed by Bender, Swarts and many investigators. The reaction is theoretically in second order reaction overall, first order in each reactant with the reaction kinetic of:

$$-r_A = k[NaOH][CH_3COOCH_2CH_3] \tag{6}$$

According to mechanism established by fellow researchers, the second order rate equation is applicable only when the concentration of the addition complex C is very small and when the reverse reaction rate is negligible in comparison with the forward reaction rate.

2.4 INTERPRETATION OF EXPERIMENTAL DATA

Rate equation could be determined by theoretical considerations or simply by the result of curve-fitting procedure from experimental data. In any case, the value of the rate constant of the equation can only be found by experiment as predictive models are inadequate. There are two procedures of analyzing kinetic data, *differential* and *integral* method (Levenspiel, 1999):

1. Differential method
    - The fit of rate expression is tested to the data directly without any integration.

2. Integral method
    - A particular form of rate equation is guessed and plot of certain function of concentration versus time is predicted after mathematical integration and manipulation (the plot should yield straight line satisfactorily).

2.5 RESIDENCE TIME DISTRIBUTION (RTD)

RTD is the period of time a molecule or atom spent to pass through the reactor. Some of the molecules will leave quickly and some will overstay. The concept was first being proposed by MacMullin and Weber back in 1930s and in 1953 respectively; P.V. Danckwerts prepared the organizational structure to the subject by defining most of the distribution.

In CSTR, feed is introduced at any given time and the material will become completely mixed with the material already in the reactor. Some of the atoms entering the CSTR leave it almost immediately, because material is being withdrawn continuously from reactor and other atoms remain inside almost forever because the material is never removed from reactor at one time. As shown in ***Figure 2***, in many continuous tank reactors, the inlet and outlet pipes are close together and it was realized that some channeling or short-circuiting must occur; thus most of tanks are modeled with bypass stream. Dead zones or stagnant regions were also virtually observed. In these regions, there were little or no exchange of materials with the well-mixed regions, and hence basically there is no reaction occurs in this particular point [3]. RTD describes the characteristics of the mixing that occur in chemical reactor, in which different type of reactor will have different type of RTD.

The actual RTD is defined as:

$$\tau = \frac{V}{\upsilon_0} \tag{7}$$

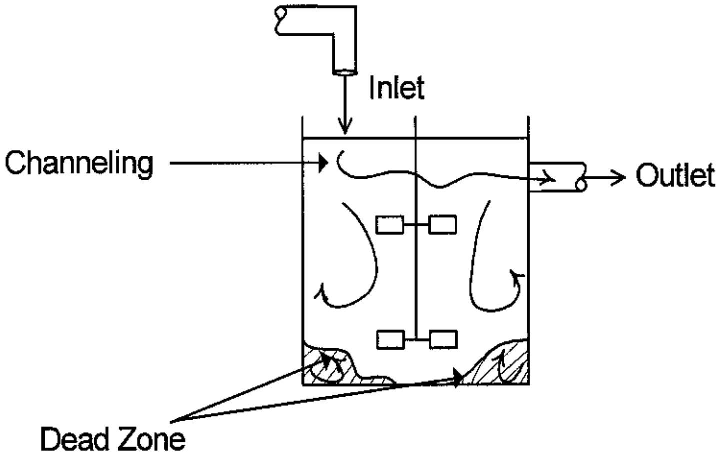


Figure 2: CSTR with Dead Zones and Channeling

2.6 EXPERIMENTAL DETERMINATION OF RTD

Residence time is the time it takes for a fluid element to pass through the reactor in different paths between time t and $t + dt$. The function $E(t)$ can be determined experimentally, either using *pulse input* or *step input* method:

1. *Pulse input* - tracer is suddenly injected on one shot (in the shortest time) into the feed stream and the outlet concentration $C(t)$ is measured.

2. *Step input* - tracer is introduced continuously and the outlet tracer concentration versus t is measured.

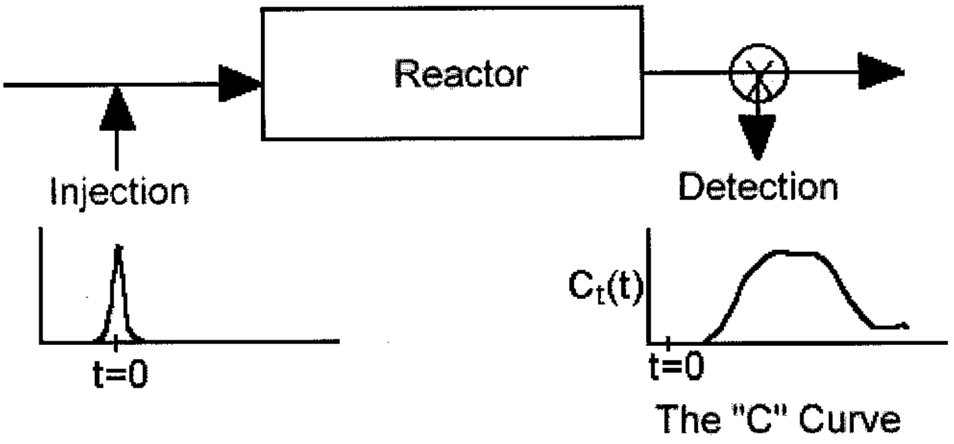


Figure 3: RTD Measurement for Pulse Injection. (From H. S. Fogler, Elements of Chemical Reaction Engineering, 3rd Edition, Prentice-Hall International Inc., 1999).

The data obtained from the tracer test is used to obtain the E (t) curve. The $E(t)$ obtained is then being used to characterize the real reactors and to predict the exit conversions and concentrations when reaction occurs in these reactors. From the RTD, the fraction of molecules exiting the reactor that has spent time *t* or less in the reactor, $F(t)$ (cumulative distributive function) can be determined (Fogler, 1999).

2.7 MODELLING OF REACTOR FROM RTD

RTD function alone is not sufficient enough to predict or study the reactor performance since it only tells how long the various fluid elements have been in the reactor but not the exchange matter between the elements (mixing). Thus, the state of aggregation and earliness of mixing concept are introduced. Flowing material is in some particular state of aggregation, whether it is in *microfluids* or *macrofluids*. *Macromixing* in reactor distributes the residence time whereas *micromixing* specifies how molecules of different ages mix with each other. Uniform mixing is impossible to be achieved in real reactors as the fluid elements can mix with each other either early or late in their flow through the vessel. These two concepts are very important for a system with two entering reactant streams.

The RTD is not a complete description of structure for a particular reactor or systems or reactors. Thus, there are several models for predicting reaction conversion from RTD data in nonideal reactors (Fogler, 1999):

1. Zero adjustable parameters – segregation and maximum mixedness model.
2. One adjustable parameter – tanks-in-series and dispersion model.
3. Two adjustable parameters – real reactor modeled as combinations of ideal reactors (CSTR with dead-space and bypass model and two CSTR interchange).

In the study, the zero adjustable parameters and two adjustable parameters are applied in order to predict the reaction conversion and compare between the ideal and real CSTR.

2.7.1 Segregation Model

The real CSTR is modeled as a number of small batch reactors, each spending different times in the reactor. All molecules that spend the same length of time in the reactor remain together in the same globule. Mixing of different age groups occurs at the last possible moment at the reactor exit. As shown in ***Figure 4***, in segregation model, globules behave as batch reactors operated for different times.

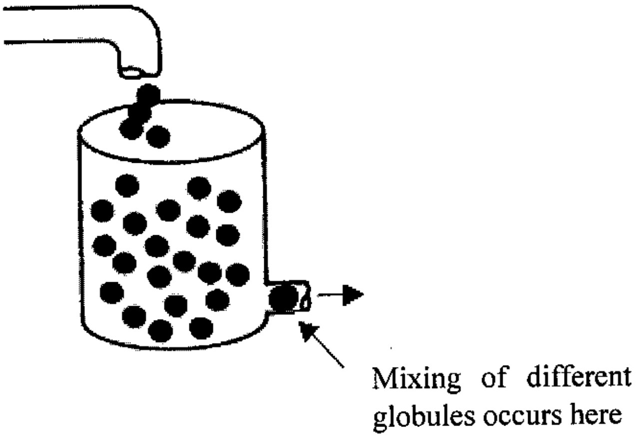


Figure 4: Globules inside a CSTR. (From H. S. Fogler, Elements of Chemical Reaction Engineering, 3rd Edition, Prentice-Hall International Inc., 1999).

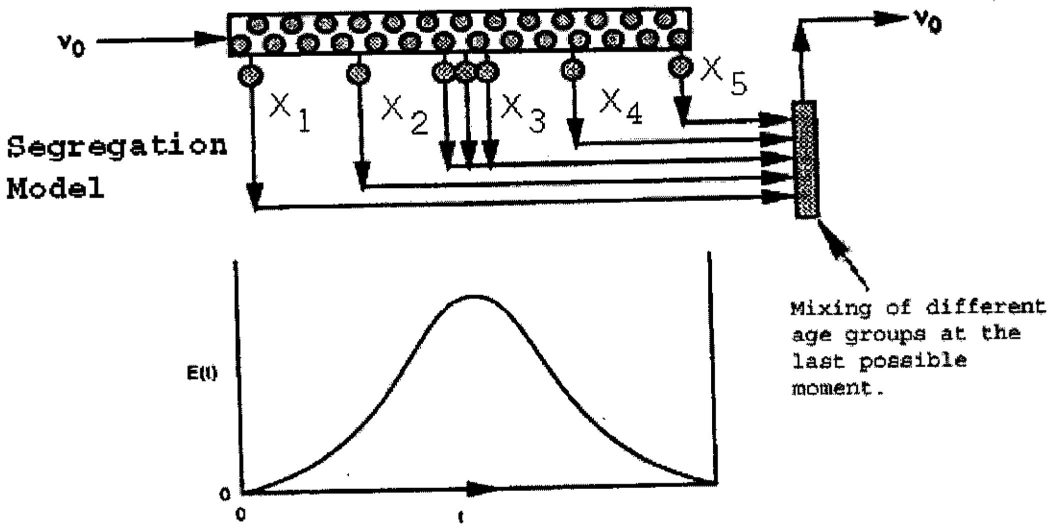


Figure 5: Mixing occurs at the latest possible point. Each little batch reactor (globule) exiting the real reactor (plug flow reactor) at different time will have different conversion, *X*. (From H. S. Fogler, Elements of Chemical Reaction Engineering, 3rd Edition, Prentice-Hall International Inc., 1999).

The mean conversion, $\overline{X}$ of the effluent stream the conversions of various globule in the exit stream is average:

$$d\overline{X} = X(t)\cdot E(t)dt \tag{8}$$

$$\bar{X} = \int_0^\infty X(t)E(t)dt \tag{9}$$

For second order reaction:

$$A + B \rightarrow C + D \tag{10}$$

For a batch reactor,

$$-\frac{dN_A}{dt} = -r_A V = V k C_{A0}^2 (1 - X)^2 \tag{11}$$

Which on arrangement becomes:

$$X = \frac{kC_{A0}t}{1 + kC_{A0}t} \tag{12}$$

2.7.2 Maximum Mixedness Model

Maximum mixedness model is where the mixing occurs at the earliest possible point. As pictured in Figure 6, the globules at the far left corresponds to the molecules that spend a long time in the reactor whereas the far right corresponds to the molecules that channel through the reactor (Fogler, 1999). In the reactor with side entrances, mixing occurs at the earliest possible moment consistent with the RTD. This effect is the maximum mixedness.

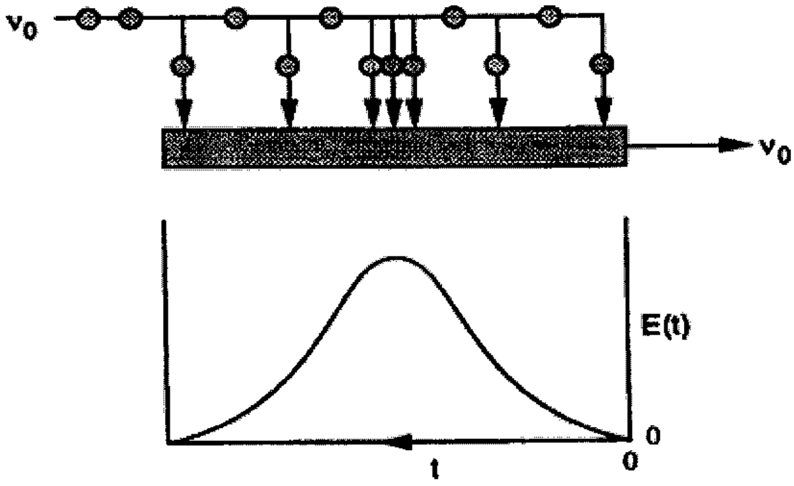


Figure 6: Mixing at the earliest possible point. (From H. S. Fogler, Elements of Chemical Reaction Engineering, 3rd Edition, Prentice-Hall International Inc., 1999).

A new term is introduced here, which is λ, the life expectancy of the fluid in the reactor at that point. λ decreases and become zero at the exit point as the globules moving down the reactor. The conversion of maximum mixedness model can be calculated using the Euler method for numerical integration for second order system:

$$X_{i+1} = X_i + (\Delta\lambda)\left[\frac{E(\lambda_i)}{1-F(\lambda_i)}X_i - kC_{A0}(1-X_i)^2\right] \qquad (13)$$

2.7.3 Real CSTR with Dead-Space and Bypass Model

As far as the study is concern, creativity and engineering judgment are necessary for model formulation in a real reactor design. In order to model a real reactor by combinations and taking into account the adjustable parameters, namely α and β. A tracer experiment is used to evaluate the model parameters.

A real CSTR is believed to be modeled as a combination of an ideal CSTR of volume V_s, a dead zone of volume V_d, and a bypass stream with volumetric flowrate of υ_b (***Figure 7***).

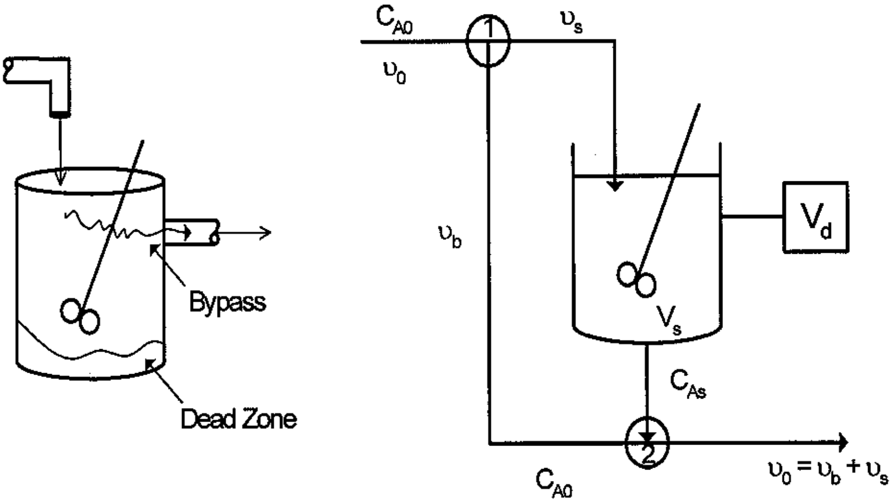


Figure 7: (a) Real system; (b) model system.

For a second order reaction as in equation(7), from Figure 7, the bypass stream and effluent stream from the reaction volume are mixed at point 2. Thus, the balance at junction 2:

$$\begin{aligned} &in \quad = \quad out \\ &C_{A0}\upsilon_b + C_{As}\upsilon_s = C_A(\upsilon_b + \upsilon_s) \end{aligned} \tag{14}$$

Solving for the concentration of A leaving the reactor,

$$C_A = \frac{\upsilon_b C_{A0} + C_{As}\upsilon_s}{\upsilon_b + \upsilon_s} = \frac{\upsilon_b C_{A0} + C_{As}\upsilon_s}{\upsilon_0} \tag{15}$$

Let $\alpha = \frac{V_s}{V}$ and $\beta = \frac{\upsilon_b}{\upsilon_0}$

Mole balance on CSTR on reactor volume V_s:

$$\begin{aligned} &in \quad - \quad out \quad + \quad generation \quad = \quad accumulation \\ &\upsilon_s C_{A0} \; - \; \upsilon_s C_{As} \quad + \quad r_{As}V_s \quad = \quad 0 \end{aligned} \tag{16}$$

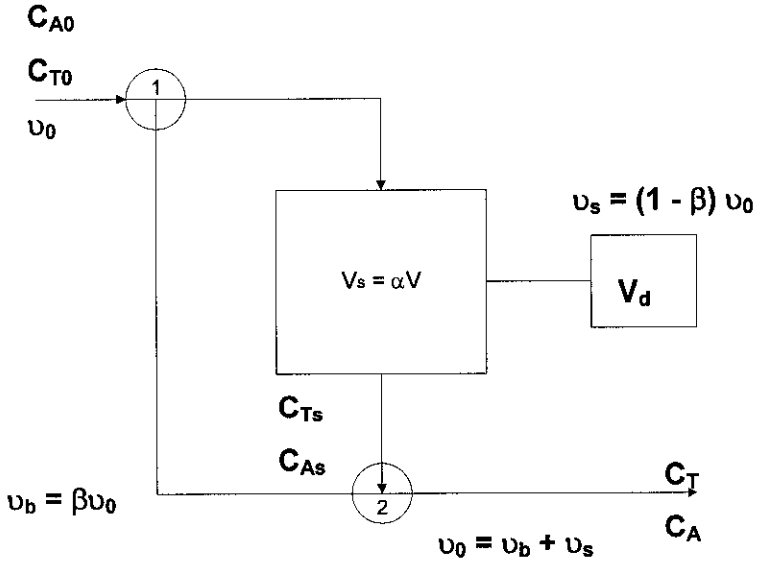


Figure 8: Model system: CSTR with dead volume and bypassing with tracer injected as a positive-step input.

From Figure 8, as the tracer is being injected, the unsteady-state balance on the non-reacting tracer T in the reactor volume Vs is

$$in \quad - \quad out \quad = \quad accumulation$$

$$\upsilon_s C_{T0} - \upsilon_s C_{Ts} = V_s \frac{dC_{Ts}}{dt} \tag{17}$$

Balance around junction 2 from Figure 8:

$$C_T = \frac{\upsilon_b C_{T0} + C_{Ts}\upsilon_s}{\upsilon_0} \tag{18}$$

Integrating equation (16) and substitution of α and β and combination of equation (17) yields:

$$\ln \frac{C_{T0}}{C_{T0}-C_T} = \ln \frac{1}{1-\beta} + \left(\frac{1-\beta}{\alpha}\right)\frac{t}{\tau} \tag{19}$$

CHAPTER 3

METHODOLOGY / PROJECT WORK

3.1 PROCEDURE IDENTIFICATION

The project is divided into two interconnected parts. The first part is conducting experiments and the latter part is real reactor modeling. In the experiments part, two experiments are conducted; **CSTR in Series** to determine the reaction rate constant, *k* and **CSTR Dynamics** to calculate the RTD value. The method used for this experiments are based on the Chemical Engineering Laboratory II manuals, obtained from the respective technicians. The rate constant, *k* is to be predicted from the concentration data. The RTD function, *E(t)* is determined from the *pulse input* or *step input* and the other useful information such as cumulative distribution function, *F(t)* can be calculated from these data.

In the second part, which is the real reactor modeling, all data obtained from experiments are used to simulate and model real reactors; together with reaction conversion determination. The conversion between an ideal and a real CSTR is then compared.

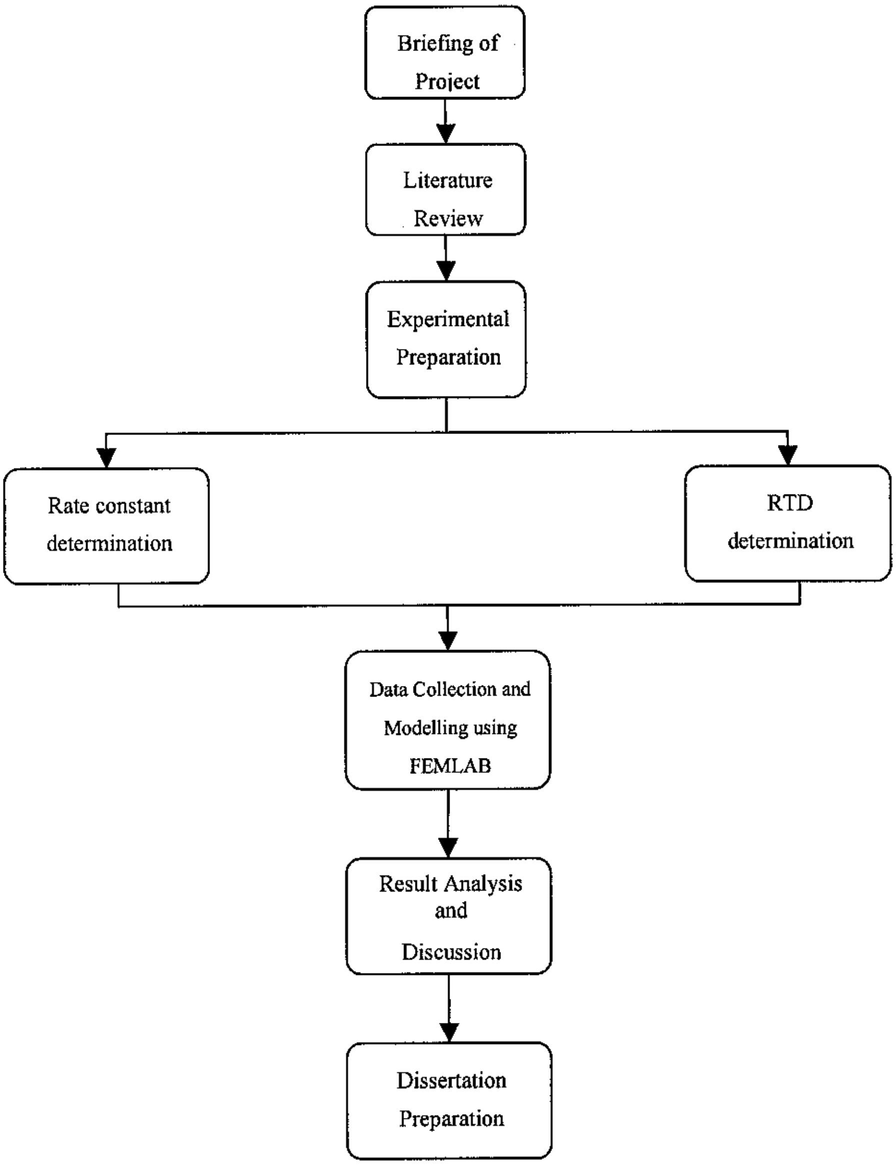


Figure 9: Process Flow of the Final Year Research Project

3.2 EXPERIMENTS

CSTR in series Model No: CEP MkII (Armfield Ltd.) as shown in **Figure 10** is used in order to conduct the experiment on determining the reaction rate constant. The system consists of two feed tanks and three equal sized reactors (volume of 1.5 liter); each reactor is equipped with a variable speed turbine agitator and baffle arrangement to ensure thorough mixing. The reactants are pumped through Pump 1 and 2 and mixed at the mixing point prior to enter the reactor. The reactors have a variable speed agitator (%) and conductance probe to measure the conductivity in units of milliSiemens (mS). Liquid level in the reactor is determined by the location of an overflow discharge line connected to the side of the reactor. All reactor effluent is drained for disposal. All conductivity data will be tabulated through the software (CEP Reactors in Series).

Solutions of sodium hydroxide and ethyl acetate are used as the reactants for the reaction rate constant experiment and deionized water and sodium chloride is used for the tracer experiment. In experiment of CSTR in series, the concentration used is 0.10 M for both sodium hydroxide and ethyl acetate; and 0.05 M of sodium chloride for CSTR Dynamics.

Theoretically, the reaction is in second order and in the following section, the determination of second order will be explained. Since both sodium hydroxide and ethyl acetate are strong electrolytes, the measurement of electrical conductance can be used to follow the reaction progression. Because the hydroxide ion is a higher conductivity than the acetate ion, there is a net decrease in conductance as the reaction occurs.

There are actually three reactors in the system, as shown in **Figure 10**. However, only the first tank will be taken into consideration for analysis since Tank 2 are the overflow of Tank 1 and Tank 3 are the overflow of Tank 2. Thus, the reactants only enter the first tank; that is where the reaction occurs first.

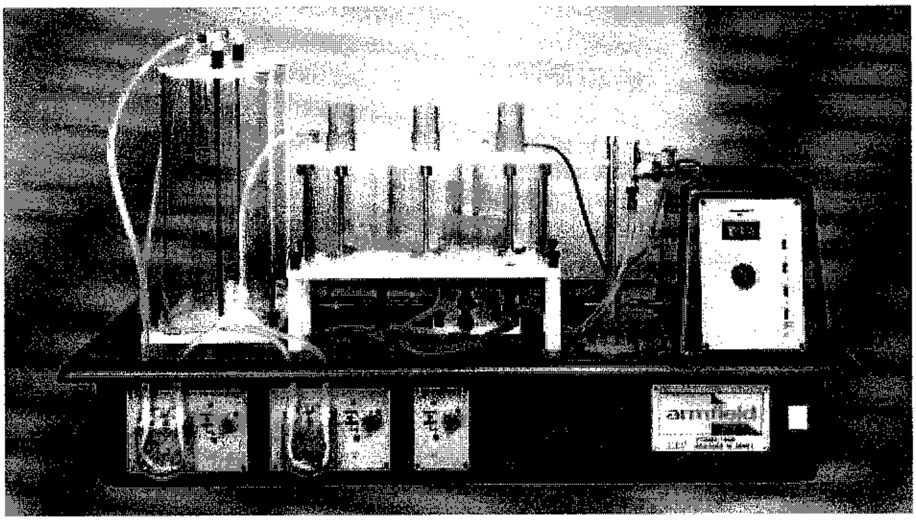


Figure 10: Equipment for CSTR in series (Armfield) (Source from www.armfield.co.uk/pdf_files/cex.pdf).

3.2.1 CSTR in series

10 L batches of 0.10 M of NaOH and 0.10 M of ethyl acetate is prepared and put in the feed tank. The equipment is switched on first before opening the software. The overview diagram of the system is displayed and the feed concentration is inserted to be 0.10 M. The feed flowrate and stirrer speed is adjusted at the equipment and the value is set to be 60 ml/min and 62% (check value at software while adjusting). The reactants are then being pumped through pump P1 and P2 and ensured the tube to be bubble air-free to maintain the flowrate. The process and instrumentation diagram of the system is shown in ***Figure 11***. In this study, the effect of temperature is not going to be covered, thus the temperature of the system is maintained to be 25°C. Pump 1 and Pump 2 will be switched on simultaneously in order to supply the reactants at the same time. From ***Figure 11***, it is shown that the reactants will meet at point V-3 and thus the reaction will occur first here. The conductivity data will be taken until steady state is reached in the reactor. Usually this will take time approximately 45 to 50 minutes in which the conductivity data will be stabilized at one point. The sampling rate of the software is set to be 30 seconds interval. When the experiment is finished, all reactants and mixtures inside the reactors are drained.

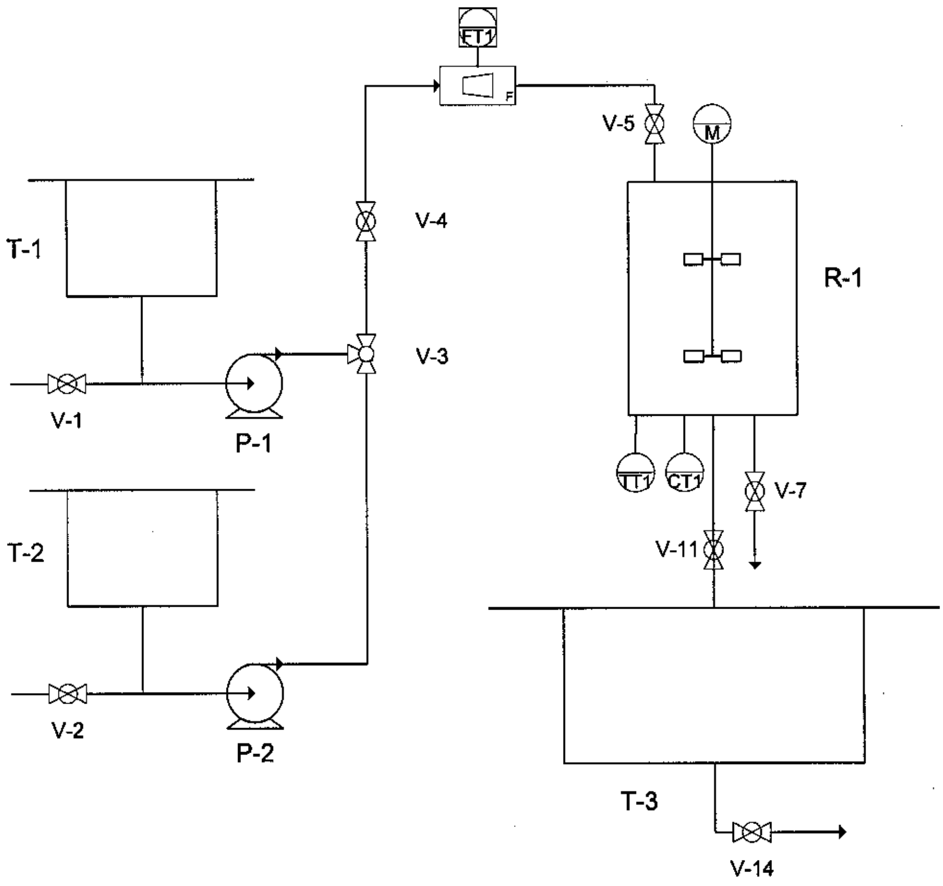


Figure 11: Piping & Instrument Diagram (P&ID) of the CSTR System

3.2.2 CSTR Dynamics

CSTR Dynamics is used in order to determine the RTD data. The system is the same shown in Figure 8, except that the tank is filled with deionized water (Tank 1) and 0.05 M of sodium chloride (Tank 2). Two experiments will be conducted, *pulse input test* and *step change test*. The deionized water will be filled in first in the reactor with flowrate of 150 mL/min until it reached the total volume of the reactor, which is 1.5 L. The stirrer speed is adjusted to be 200 rpm. The deionized water will be pumped until all conductivity readings are stable at low values and the values are recorded at time t_0.

The pump P1 is then switched off and pump P2 is simultaneously switched on to pump the sodium chloride. For the step change test, the conductivity values are recorded until readings are almost constant. For pulse input test, pump P2 is operated for 2 minutes and then switch to pump P1 and again the conductivity data is taken until all readings are almost constant. All liquids in reactors are drained by opening the drainage valve.

3.2.3 Relationship between Conductivity and Concentration

Since all data taken are in conductivity (mS) value, in order to convert the data into concentration value, an experiment is conducted in order to obtain a correlation between conductivity and concentration for sodium hydroxide and sodium chloride. A few samples are prepared, with initial concentration of 0.10 M and the conductivity values are taken. The concentration is then increased to a certain values and again the conductivity values are recorded for each increasing concentration. A graph of concentration versus conductivity will be plotted and the equation obtained is to be used for further calculation. Equations have been developed to convert the conductivity values to concentration by the Armfield software, however for the research purposes, the experiments are conducted.

3.2.4 Safety and Maintenance Aspect

In the laboratory, there are safety procedures to be followed. Prior to conducting the experiments, a laboratory logbook needs to be filled up. There is a risk assessment form inside the logbook to be completed for safety purposes. Before starting up the experiment, all safety precautions such as fire extinguisher, safety shower and eye wash station in the lab should be observed and if possible the functionality of the control measures are tested first. The protective clothing (lab coat), covered shoes, and gloves need to be worn throughout the lab session.

As for the CSTR in series experiment, since sodium hydroxide and ethyl acetate are corrosive and may damage the tubing and rig in the long run, any liquids inside the reactors are drained off and the tubing and reactor are cleaned properly. Any spillage from the unit is wiped off immediately. As there is the presence of electrical source, all cables are always plugged into appropriate sockets before switching on the main power on the control panel. All cables are inspected for any damage to avoid electrical shock.

3.3 TOOLS/EQUIPMENT/SOFTWARE REQUIRED

The project consists of three parts; experiments, simulation and data analysis and modeling. As mentioned previously, the equipments used in the experiments are CSTR in series and CSTR dynamics. These equipments are readily available at the chemical engineering laboratory of UTP. For the sample preparation, there are a few common apparatus used such as magnetic stirrer, digital balance, volumetric flask, beaker, Buchner funnel, plate and containers.

The chemicals consumed are 40 g of NaOH for 10 L 0.10 M NaOH (99% purity), 98.91 mL of 99% purity of ethyl acetate for 0.10 M ethyl acetate and 58.44 g of 99.5% purity NaCl for 0.10 M NaCl. These chemical are also available at the laboratory. Sodium chloride is supplied by HmbG Chemicals and sodium hydroxide is supplied by Merck KgaA, a company from Germany. The ethyl acetate solution is supplied by Systerm.

For the simulation and data analysis, tools used are Microsoft Excel and MATLAB. It is the simplest yet accurate means of analyzing the data since the project requires loads of calculation. The latter part is the real reactor modeling using FEMLAB. It is the last part in which the concentration profile of the real CSTR is to be shown using FEMLAB for steady state and transient system.

CHAPTER 4

RESULTS AND DISCUSSION

This particular section encompasses the results obtained and achieved, basically from the experiments conducted. In the rate constant determination, the CSTR in series equipment is run for about 1 hour and the conductivity data is collected. The experiment is done three times in order to get an average values to increase the accuracy. The Armfield software has already converted the value of conductivity of sodium hydroxide. However the calibration experiment is also done in order to compare the values. It is shown that the values of concentration obtained from the calibration curve and Armfield software are almost similar ***(APPENDIX I)***.

For the saponification reaction of ethyl acetate, the stoichiometric balance can be simplified as

$$A + B \rightarrow C + D, \qquad (20)$$

where A is the sodium hydroxide, B is the ethyl acetate, C is the ethyl alcohol and D is the sodium acetate. The rate of reaction is influenced by the composition and the energy of the material. Basically for simplification, the term inside the bracket used is concentration (moles per volume) which is usually expressed in moles per liter. Thus rate of reaction of the saponification reaction becomes

$$-r_A = kC_A C_B \qquad (21)$$

The negative value of rate of reaction is deviated from the fact that the reactants are disappearing during the reaction to form products.

4.1 RATE CONSTANT, *k*

Experiment of CSTR in series is conducted in order to determine the *k* value. The experiment is conducted three runs to get the average value of *k* to increase the accuracy. Theoretically the saponification reaction is in second order reaction. In order to determine to what order is the reaction, the guess of first order and second order reaction is conducted by using integral method.

From **Figure 12** plotted, it is shown that the data does not fit well for the respective equation. The data does not give a straight line graph that intercepts at the origin. Thus, the first order kinetics cannot reasonably represent the data.

The equation of first order kinetics is: $-\ln\frac{C_A}{C_{A0}} = kt$

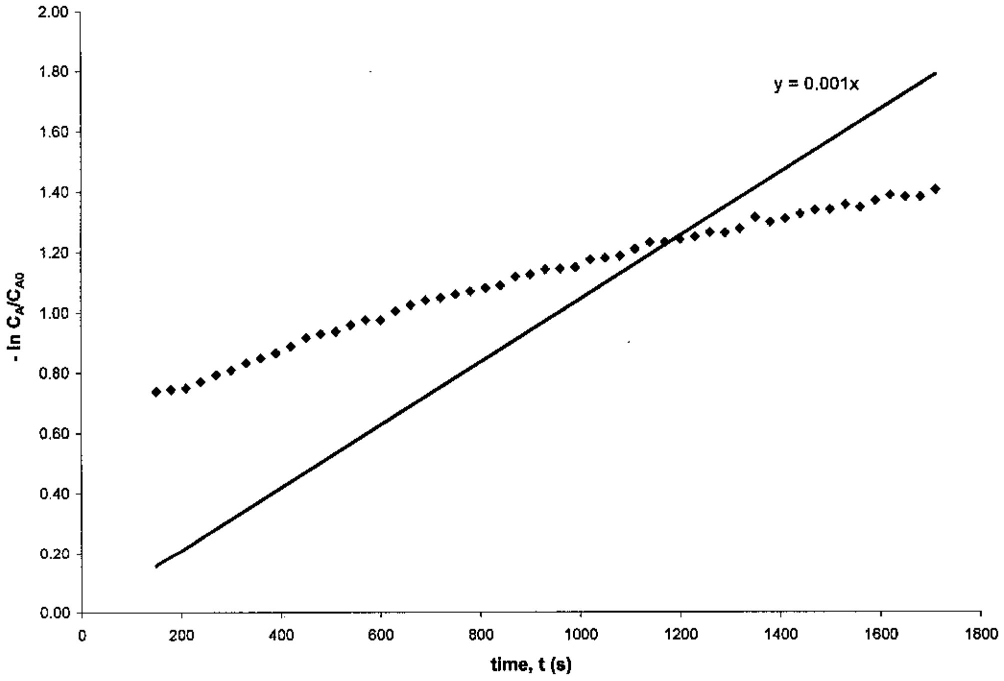


Figure 12: Fitting the experimental data with the equation of First Order Kinetics.

As in **Figure 13**, the graph should be straight line with the slope = 0.0261. The slope value is the *k* value. Thus, it is proved that the saponification of ethyl acetate is in second order reaction.

From the graph:

$$slope = k = 0.0261\frac{L}{mol.s} = 1.566\frac{L}{mol.\min}$$

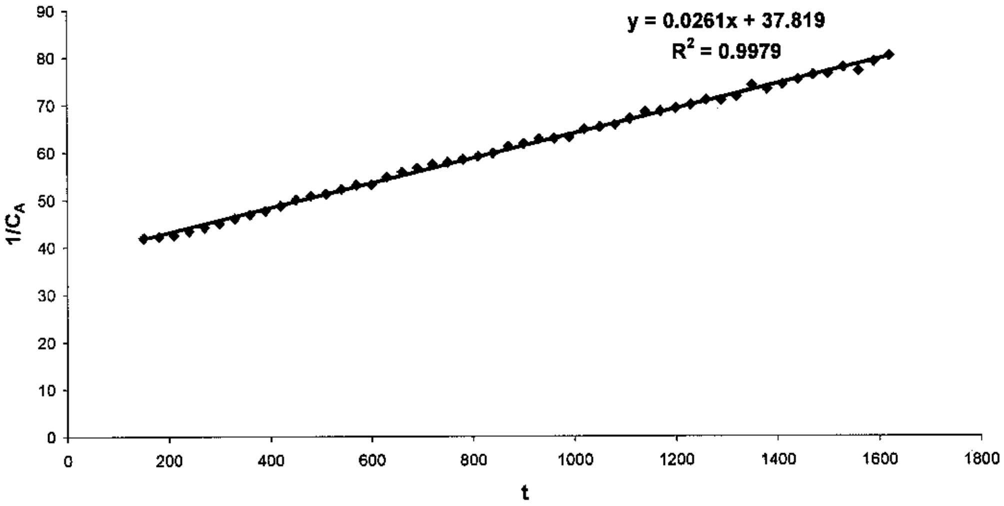


Figure 13: Fitting the experimental data with the equation of Second Order Kinetics.

See APPENDIX I for complete data and calculation.

4.2 RTD DATA ANALYSIS

From the data of step input, there is an increase of conductivity value as the tracer is being injected continuously. For the pulse input, it is observed that there is an increase of conductivity value on the first two minutes and then the value is decreasing until it become stable at very low values. The phenomenon is that for the step input, the tracer is being injected continuously to the reactor which filled in with deionized water. At certain point, the conductivity values become stable. As observed in ***Figure 14***, the conductivity values which have been converted to concentration values are plotted against time and after almost 50 minutes, the values are starting to stabilize. From Figure 15, as mentioned above, the concentration values increased for the first two minutes and then decreased. Pulse input test is the best way to visualize how the tracer test really works in terms of showing the time the molecule or material has spent inside the reactor before coming out. The values started to decrease as time goes by because the deionized water is being fed continuously. Imagine at time increases, the sodium chloride molecule has been replaced by the water molecule and in exits the reactor, until after a very long time, all sodium chloride has been removed or left the reactor.

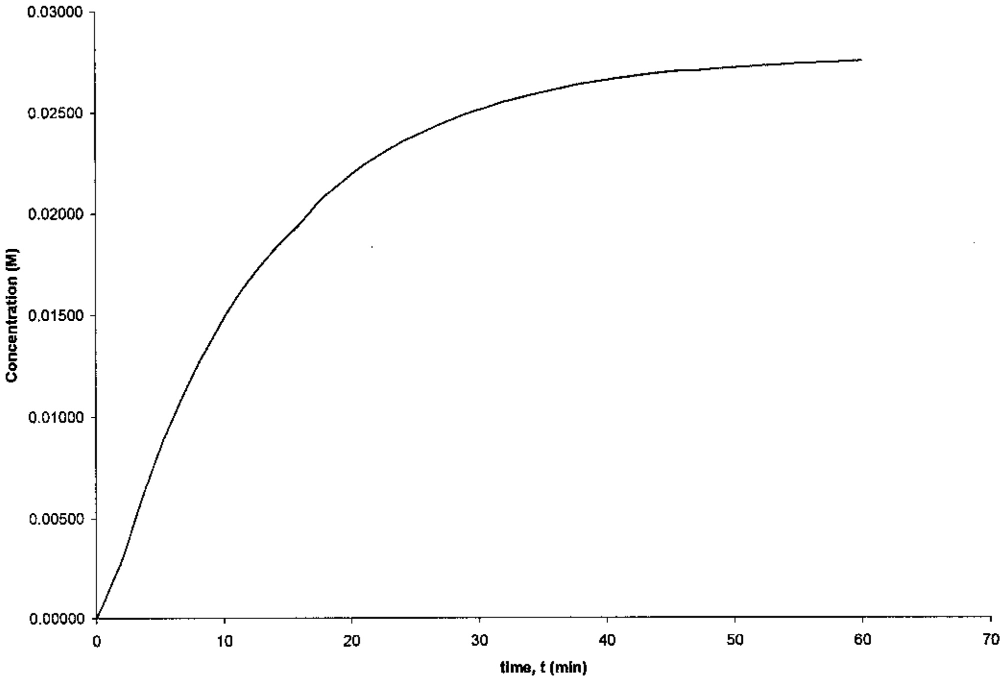


Figure 14: Graph Concentration of sodium chloride (M) versus time (min) for Step Change Data.

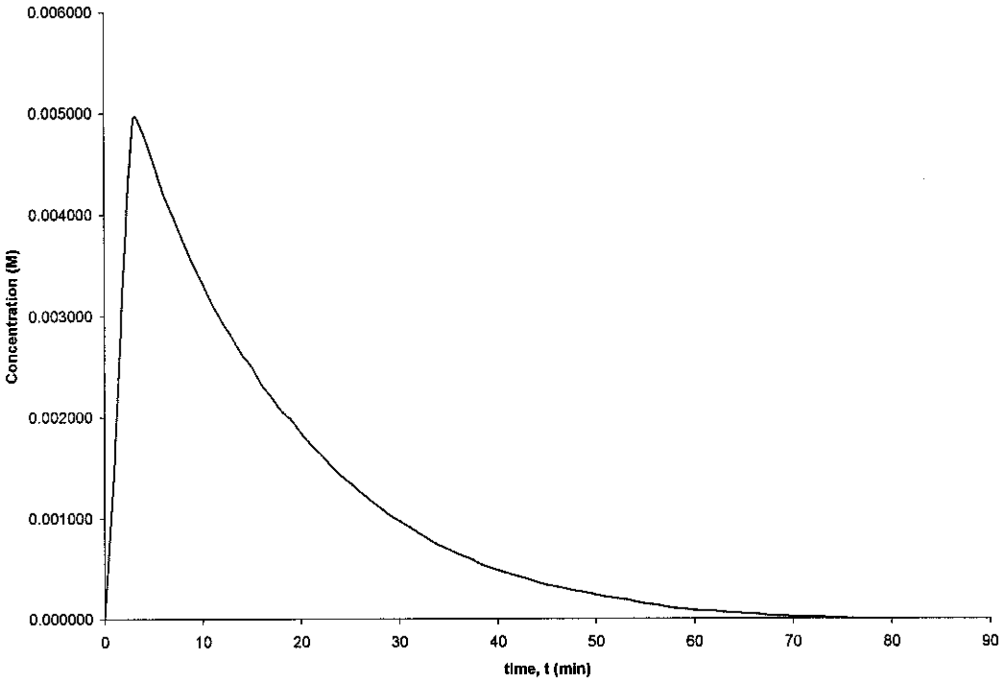


Figure 15: Graph Concentration of sodium chloride (M) versus time (min) for Pulse Input Data.

RTD or *E(t)* is calculated from the pulse input test:

$$E(t)=\frac{C(t)}{\int_0^\infty C(t)\,dt} \tag{22}$$

The denominator which is the integral is the area under the C-curve. The plot is as ***Figure 16.***

The fraction of the exit stream that has resided in the reactor that have spent a time t or less is called as cumulative distributive function, *F(t)* and is correlate as:

$$\int_0^t E(t)\,dt \quad = F(t) \tag{23}$$

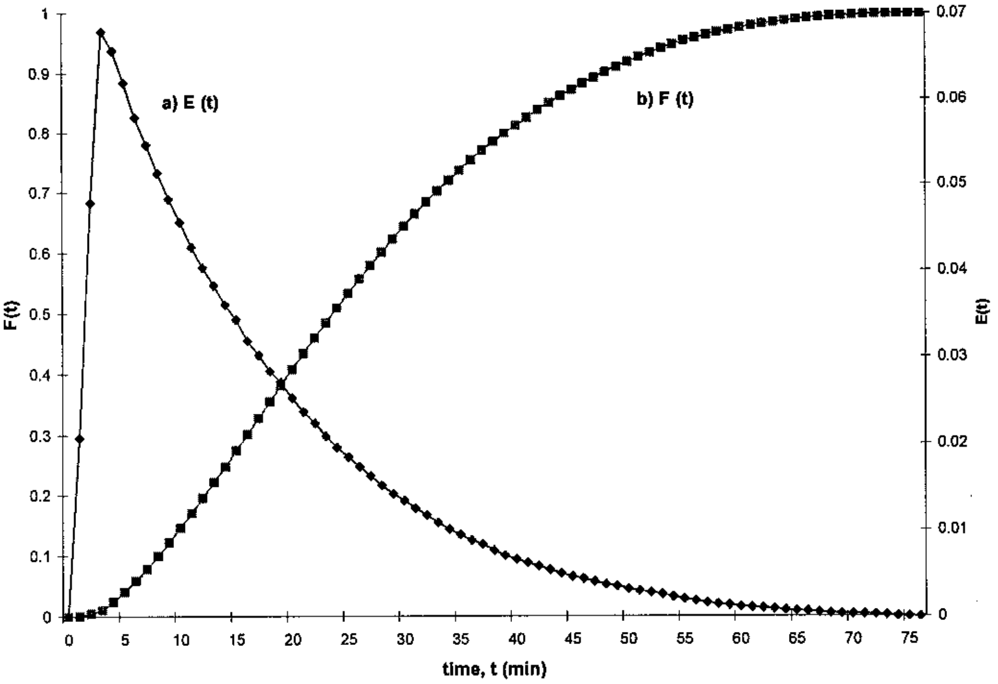


Figure 16: Graph: (a) Residence time distribution, E(t) versus time (min); and (b) cumulative distributive function, F(t) versus time (min).

Space time or average residence time, τ is defined as in equation (7). Theoretically, at any RTD or no matter what RTD exists for a particular reactor, ideal or non-ideal, the τ is equal to the mean residence time, t_m. The mean residence time is the average time the effluent molecules spent in the reactor, which is also called as the first moment of the RTD function.

$$t_m = \frac{\int_0^\infty t\,E(t)\,dt}{\int_0^\infty E(t)\,dt} = \int_0^\infty t\,E(t)dt \tag{24}$$

The t_m is the area under the graph shown as in **Figure 17**, and it can also be calculated using the numerical integration as in **APPENDIX II.**

The actual residence time can also be calculated using:

$$\tau = \frac{\sum t_i C_i}{\sum C_i} \tag{25}$$

From the correlation above, the calculated τ are tabulated as in Table 1 below.

Table 1 Calculated values for τ

τ	Values (min)
$\tau_{\text{theoretical}}$	25.00
τ_{actual}	16.06
τ_{mean}	16.07

Usually RTDs are compared using their moments instead of trying to compare their entire distributions (e.g., Wen and Fan) (Fogler, 1999). The second moment about the mean is the variance, σ^2 or the square of the standard deviation. From **Figure 18**, the variance can be calculated from area under the graph or:

$$\sigma^2 = \int_0^\infty (t - t_m)^2 \, E(t)\, dt \tag{26}$$

Using the numerical integration, the σ^2 = **165.36 min^2**, thus σ = **12.86 min**.

See *APPENDIX II* for complete data and calculation.

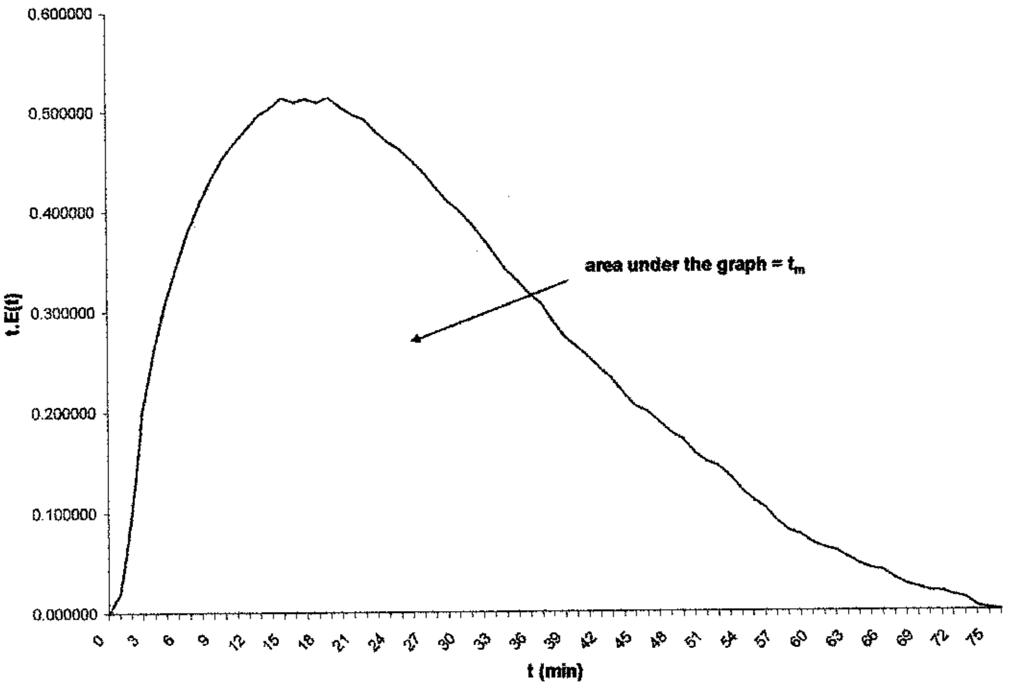


Figure 17: Graph t.E(t) versus time (min). Note that the area under the graph is the mean residence time. Mean residence time just the space time, τ.

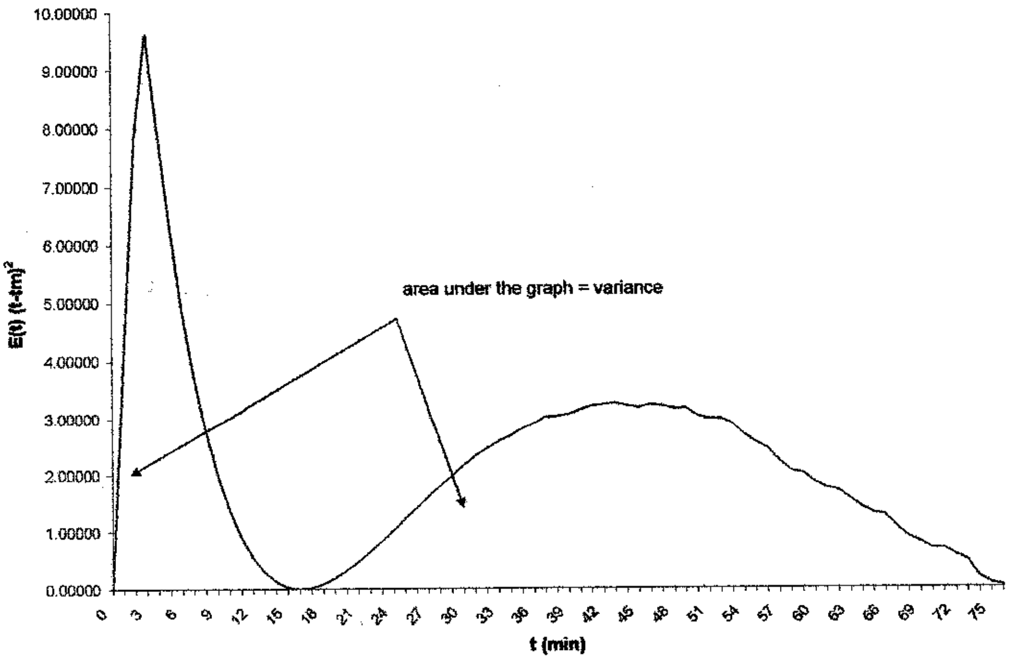


Figure 18: Graph for calculating the variance, σ^2. Variance is the second moment of the mean; also an indication of the "spread" of the distribution. The greater the value of this moment, the greater a distribution's spread.

4.3 IDEAL REACTOR MODEL

The parameters of the second order system are as in table below:

Table 2 Parameters for CSTR system

PROCESS PARAMETERS	
Volume (L)	1.5
$C_{A0} = C_{B0}$ (mol/L)	0.05
υ_0 (L/min)	0.06
KINETICS PARAMETERS	
k (L/mol.min)	1.566
Reaction order	2nd order
$-r_A$	$1.566C_A^2$

Conversion of A, X_A is how much amount of the reactant A is converted to product. Based on equation (2), the reaction conversion of a second order system, assuming ideal system:

$$V = \frac{F_{A0}X}{kC_A^2} \tag{27}$$

For constant density, $\upsilon = \upsilon_0$, $F_{A0}X = \upsilon_0(C_{A0} - C_A)$, then

$$\tau = \frac{V}{\upsilon_0} = \frac{C_{A0} - C_A}{kC_A^2} \tag{28}$$

Definition of conversion:

$$\tau = \frac{X}{kC_{A0}(1-X)^2} \tag{29}$$

Solving equation (29),

$$X = \frac{(1 + 2\tau kC_{A0}) - \sqrt{(1 + 2\tau kC_{A0})^2 - (2\tau kC_{A0})^2}}{2\tau kC_{A0}} = \underline{\mathbf{0.496}} \text{ or } \underline{\mathbf{49.6\%}}$$

4.4 REAL REACTOR MODELS

4.4.1 Segregation Model

For second order system, the segregation model is actually the *highest bound* and maximum mixedness is the *lowest bound.* This is proven by:

If $n > 1$, then $\dfrac{\partial^2(-r_A)}{\partial C_A^2} > 0$ and $X_{seg} > X_{mm}$

If $n < 0$, then $\dfrac{\partial^2(-r_A)}{\partial C_A^2} > 0$ and $X_{seg} > X_{mm}$

If $0 > n < 1$, then $\dfrac{\partial^2(-r_A)}{\partial C_A^2} < 0$ and $X_{seg} < X_{mm}$

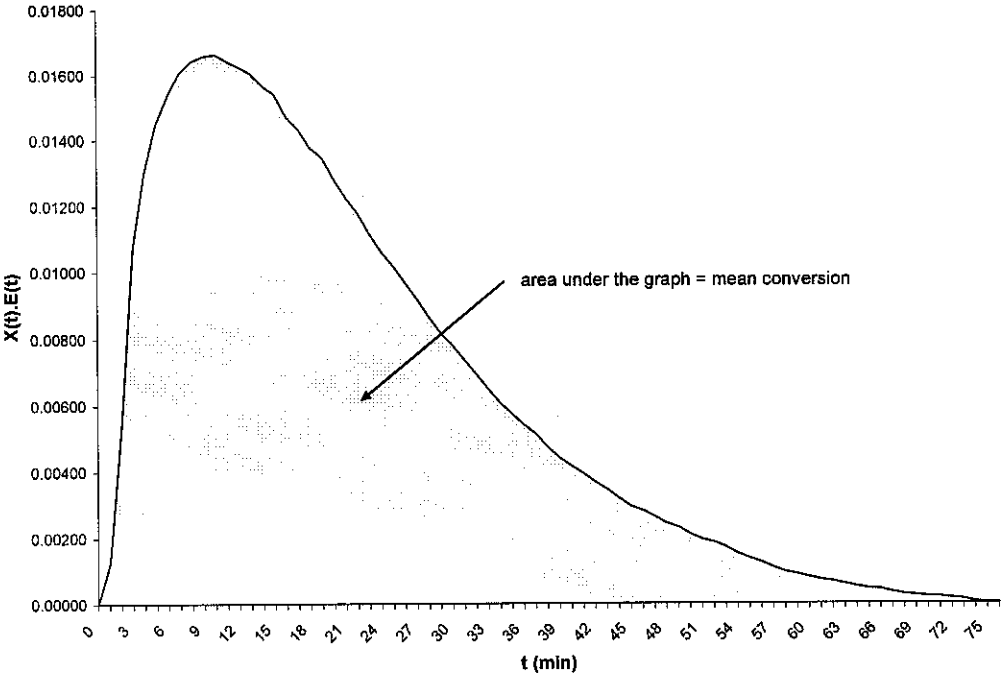
Segregation model is treated as batch reactor, thus the batch reactor equation to find conversion for second order reaction is

$$X = \frac{kC_{A0}\,t}{1 + kC_{A0}\,t} \tag{30}$$

The complete calculations are performed in APPENDIX III. The numerical integration is used to calculate the mean conversion, $\overline{X}$.

The conversion for this system if the fluid were completely segregated is

$\overline{X}$ = **<u>0.479</u> or <u>47.9%</u>**



Plots of X(t).E(t) versus time (min). The area under the graph is the mean conversion, $\overline{X}$.

4.4.2 Maximum Mixedness Model

Euler method is used to perform the numerical integration for the conversion of maximum mixedness. The respective calculation for the conversion is performed in the last column of the table in **APPENDIX IV**.

The conversion for a condition of maximum mixedness in this reactor is
X = **0.470** or **47.0%**

Thus, it is obtained and proved that for the second order reaction; segregation model is the highest bound of conversion whereas the maximum mixedness is the lowest bound of conversion. There is little difference in the conversions for the two conditions of complete segregation (47.9%) and maximum mixedness (47.0%). With bounds this narrow, there would not be much point in modeling the reactor to improve the predictability of conversion.

4.4.3 Real CSTR with Dead-space and Bypass Model

A real CSTR as mentioned above would have dead space creation and bypass stream. These two parameters are important in order to design a real reactor. As in ***Figure** 7*, V_s is the ideal CSTR volume and V_d is the dead volume. The two parameters introduced, which are not being introduced on the analysis of segregation and maximum mixedness are α and β. α is the ratio of ideal CSTR volume to total volume, V and β is the fraction of bypass stream.

These two parameters are unknown, and thus in order to determine the values, tracer experiments and RTD data are used. From equation (19), by plotting $\ln\left[\dfrac{C_{T0}}{C_{T0}-C_T}\right]$ as a function of *t*, a straight line graph is obtained as in ***Figure 20***.

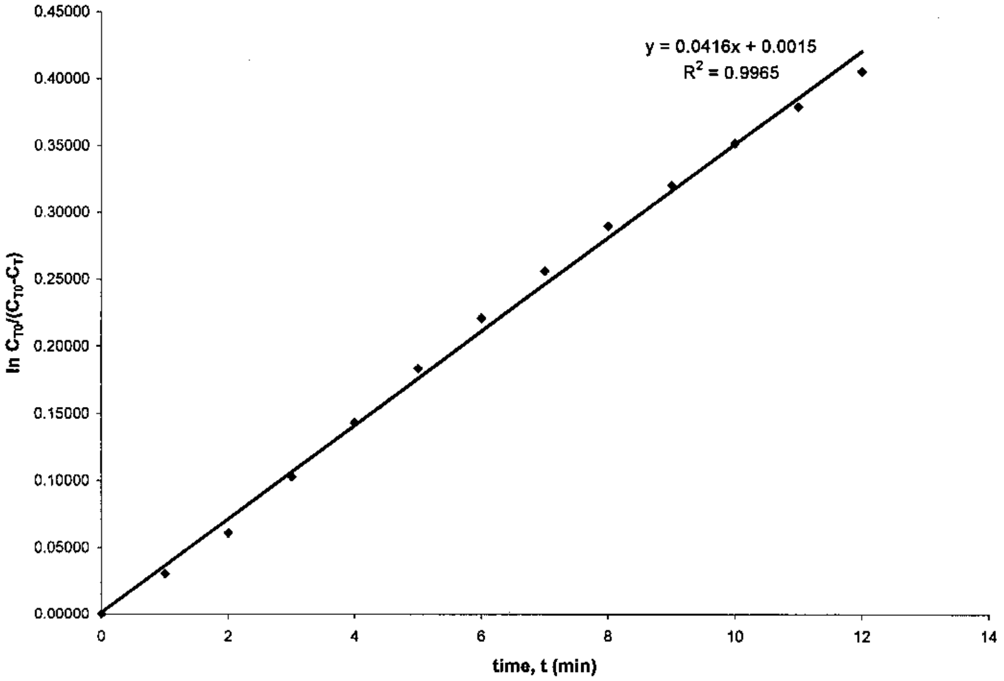


Figure 19: Response to Step Input.

From the graph,

Slope = $\dfrac{(1-\beta)}{\alpha\tau} = 0.0416$

Interception = $\ln\left[\dfrac{1}{1-\beta}\right] = 0.0015$

This will give the values of: α = **0.96** and β = **0.0015**

To determine the reaction conversion:

1. **Balance on reactor volume Vs:**

$$\upsilon_s C_{A0} - \upsilon_s C_{As} \quad + \quad r_{As} V_s \quad = \quad 0 \qquad (16)$$

2. **Rate law:**

For equimolar feed $\therefore C_{As} = C_{Bs}$

$$-r_{As} = kC_{As}C_{Bs} = kC_{As}^2 \qquad (31)$$

3. **Combining equation (16) and (31) will give**

$$\upsilon_s C_{A0} - \upsilon_s C_{As} \quad - \quad kC_{As}^2 V_s \quad = \quad 0$$

Solving for C_{As}

$$C_{As} = \frac{-1+\sqrt{1+4\tau_s kC_{A0}}}{2\tau_s k} \qquad (32)$$

4. **Balance around junction point 2:**

$$in \quad = \quad out$$

$$\upsilon_b C_{A0} + \upsilon_s C_{As} = \upsilon_0 C_A$$

Solving for C_A,

$$C_A = \frac{\upsilon_0 - \upsilon_s}{\upsilon_0} C_{A0} + \frac{\upsilon_s}{\upsilon_0} C_{As} \qquad (33)$$

5. Parameter evaluation:

$$\upsilon_s = (0.96)(0.06\,L/\min) = 0.0576\,L/\min$$

$$V_s = (\alpha\tau)\upsilon_0 = (24)(0.06\,L/\min) = 1.44\,L/\min$$

$$\tau_s = \frac{V_s}{\upsilon_s} = 25\,\min$$

Solving for C_{As} from equation (32) and C_A from equation (33),

C_{As} = **0.025 M**

C_A = **0.026 M**

Thus, conversion for the system is:

$$X = 1 - \frac{C_A}{C_{A0}} = \underline{\mathbf{0.480}} \text{ or } \underline{\mathbf{48.0\%}}$$

Based on the above analysis on the ideal and real reactors, it is observed that the conversion of the ideal reactor is much higher compared to the real reactors' conversion as in table below:

Table 3 Comparison of the conversion between the ideal and real CSTR

CSTR	Conversion, X
Ideal reactor	0.496
Segregation Model	0.479
Maximum Mixedness Model	0.470
Real CSTR with dead-space and bypass Model	0.480

The lower value of conversion in a real reactor is led by a few factors such as non-ideal flow inside the reactors, inadequate mixing or earliness of mixing, dead zone creation, channeling and bypassing and lastly fluid recycling. These factors cause ineffective contacting between the mixtures inside the reactor and cause lower conversion to be achieved.

CHAPTER 5

CONCLUSIONS & RECOMMENDATIONS

Statistical studies of a real CSTR is a newly method of studying the behavior of a real reactor, compared to conducting experiments which consumed much time and high accuracy in terms of sample preparation and conducting the experiments. This study requires indepth knowledge of a reactor besides knowing the reaction kinetics and thermodynamics.

From the experiments conducted, it is verified that alkaline hydrolysis of ethyl acetate with sodium hydroxide is 2nd order reaction. The rate equation obtained from experimental data is k = 1.566 L/mol.min. The theoretical value of this reaction is varied, depending on the temperature of the reaction and also the concentration used. Compared to the literature research, there is no one fix value for the reaction rate constant as the purity of the chemicals used are also taken into consideration.

The purpose of the research project is to develop statistical studies for a real CSTR. Nonideality behavior occurs in real CSTR, consisting of stagnant zone creation and channeling. Thus in doing such, the RTD function E(t) is to be determined first from either *pulse input* or *step input* as it is the governing key factor in the analysis. The two methods have their advantages and drawbacks in determining E(t) but in the end, the results obtained is similar.

From the RTD data, a few real reactors are modeled such as the zero adjustable parameters which are segregation and maximum mixedness model and two adjustable parameters which is the dead space and bypass model. The RTD function alone is not necessarily sufficient to describe reactor performance as many vessel models will give the same RTD, but conversion calculation will lead to different results. Thus, it is suffice to say that RTD in reactor behavior, modeling is subject to potential error and require certain amount of experience. Based on the calculation performed, it is achieved that the reaction conversion inside a real reactor is lower compared to the one in ideal reactor. The conversion in the ideal reactor is 0.496 and it is higher than conversion in the real reactors. The conversion of the segregation model, maximum mixedness model and real CSTR with dead-space and bypass model are 0.479, 0.470 and 0.480 respectively. This is due to a few factors such as dead zone creation and bypassing. These factors lead to the ineffectiveness of contacting between the mixtures inside the reactors and lower the conversion value. Hence, the objectives of the study is achieved and accomplished.

5.1 RECOMMENDATIONS

Based on the conversion achieved, it is quite hard to see the difference between each model as the conversion values are almost similar and has little difference. It is believed that the concentration used for the reactants is quite small which is 0.05 M. This value will give a lower conversion as shown from the calculation. In the future, the author should be more careful in terms of choosing the right concentration of reactants for the sake of project research.

The less accuracy of data could be caused by the data obtained from the experiments itself. The idea of the research is to study the real CSTR, provided with the information obtained from the ideal CSTR. The author has chosen two different type of CSTR for the study because during the Chemical Engineering Laboratory II, there are two systems on CSTR, one on CSTR in series and another one is CSTR Dynamics. These two CSTR, even though it has the same mechanism, but in terms of limitation, one could be differ from another one by a few factors such as dimension of the reactor and different type of stirrer. For the CSTR in series, the stirrer has got only one impeller whereas the CSTR dynamics has two impellers. It could be assumed and expected that the reaction occurring inside the CSTR dynamics is more 'well-mixed' compared to the CSTR in series because the upper part which is near to the inlet of the reactor is also being mixed together. It can be said that in CSTR dynamics the bypassing stream and dead zones are reduced. In the future, the author should think of using the same system for both experiments – for the reaction rate determination and for the tracer analysis.

This study is a good piece of work especially in order to clarify to people that there is no such ‘ideal’ reactor in real life. In the future, it is suggested that the real reactor study either batch, CSTR or PFR or even packed-bed reactor is done using modeling totally. There are a lot of good software such as FEMLAB, FLUENT and MATLAB to model how real reactor works, in terms of concentration profile and temperature profile.

Previous studies on the saponification reaction conducted are the difference in conversion between batch reactor and CSTR for the saponification of methyl acetate and the temperature profile also being observed. Perhaps in the future, a lot more studies in reactors should be done because it is the most unique part of engineering. Reaction engineering is the heart of chemical engineering.

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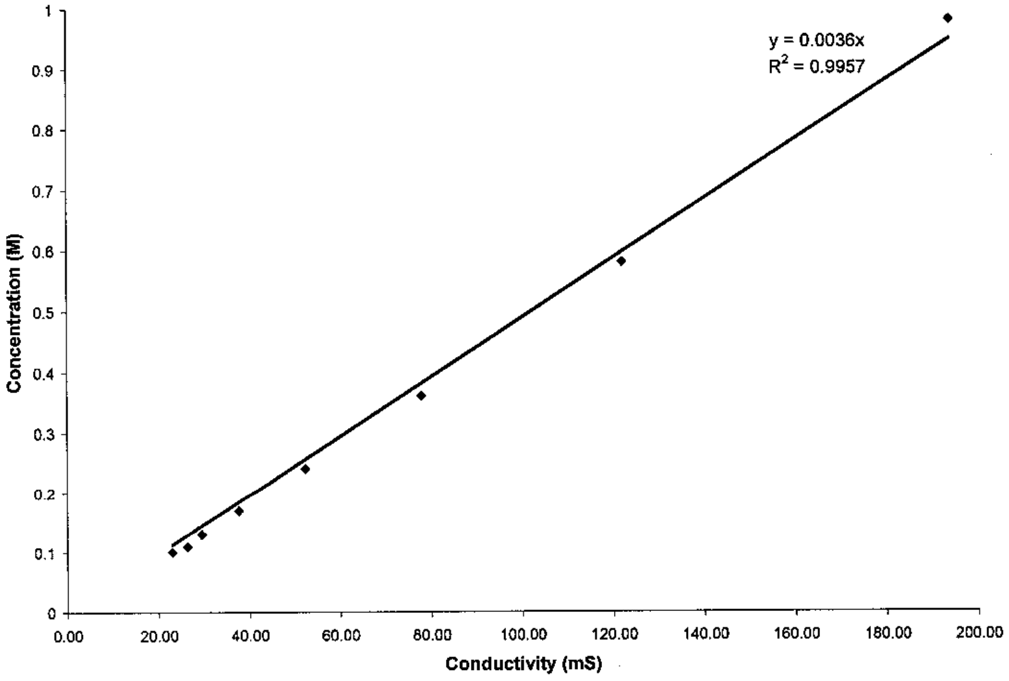
APPENDICES

APPENDIX I

Data:

1. Correlation between conductivity and concentration of sodium hydroxide

Mass NaOH (g)	Molarity (M)	Volume (L)	Λ (mS)
2.000	0.1	0.5	23.03
2.200	0.11	0.5	26.30
2.640	0.13	0.5	29.47
3.432	0.17	0.5	37.63
4.805	0.24	0.5	52.23
7.207	0.36	0.5	77.83
11.532	0.58	0.5	121.87
19.604	0.98	0.5	193.77



Graph above showed the relationship between concentration and conductivity of sodium hydroxide. It is obtained that the conductivity is directly proportional to concentration. As the concentration of sodium hydroxide is increased, the conductivity will also increase. By using the straight linear equation obtained, the conductivity values for sodium hydroxide can be converted to concentration values. Compared to the data obtained from Armfield software, the values are almost similar.

The conversion equation from conductivity to concentration from Armfield is:

Initial concentration of sodium hydroxide: $\Lambda_0 = 0.195[1 + 0.0284(T - 294)]a_0$

Final concentration of sodium hydroxide: $\Lambda_{a\infty} = 0.195[1 + 0.0284(T - 294)]a_\infty$

Thus, the concentration of sodium hydroxide:

$$a_1 = (a_\infty - a_o)\frac{\Lambda_o - \Lambda_1}{\Lambda_o - \Lambda_\infty} + a_o$$

2. Conductivity and concentration of experiment CSTR is series

Stirrer speed = 62%

Temperature = 25 °C

Elapsed Time	Λ Tank 1 (mS)	Λ Final sod acetate (mS)	Λ Initial NaOH (mS)	NaOH conc (mol/dm^3)	- ln C_A/C_{A0}	1/C_A
0	4.37	0.00389	0.01045	0.00362	2.62444	276.47925
30	5.50	0.00389	0.01045	0.01222	1.40777	81.84289
60	6.39	0.00389	0.01045	0.01898	0.96725	52.68236
90	6.89	0.00390	0.01046	0.02283	0.78343	43.80773
120	7.01	0.00389	0.01045	0.02374	0.74364	42.12627
150	7.03	0.00390	0.01046	0.02387	0.73885	41.89798
180	7.00	0.00389	0.01045	0.02368	0.74530	42.22405
210	6.98	0.00389	0.01044	0.02355	0.75013	42.45596
240	6.92	0.00389	0.01045	0.02309	0.77073	43.31151
270	6.88	0.00390	0.01047	0.02264	0.79297	44.17009
300	6.82	0.00389	0.01045	0.02225	0.80830	44.94027
330	6.75	0.00389	0.01045	0.02173	0.83195	46.01600
360	6.70	0.00389	0.01045	0.02136	0.84921	46.81676
390	6.66	0.00390	0.01047	0.02102	0.86636	47.56464
420	6.59	0.00389	0.01045	0.02054	0.88823	48.67980
450	6.53	0.00389	0.01048	0.02002	0.91661	49.95145
480	6.47	0.00389	0.01044	0.01969	0.92935	50.78955
510	6.46	0.00389	0.01044	0.01954	0.93692	51.17564

540	6.42	0.00390	0.01047	0.01917	0.95888	52.17566
570	6.37	0.00389	0.01045	0.01883	0.97511	53.09815
600	6.37	0.00389	0.01045	0.01883	0.97510	53.09801
630	6.30	0.00390	0.01046	0.01829	1.00482	54.66412
660	6.25	0.00390	0.01046	0.01792	1.02535	55.79778
690	6.22	0.00390	0.01047	0.01766	1.04135	56.62401
720	6.17	0.00388	0.01042	0.01744	1.04848	57.32804
750	6.17	0.00390	0.01047	0.01731	1.06085	57.77666
780	6.14	0.00389	0.01045	0.01712	1.07026	58.39862
810	6.12	0.00390	0.01046	0.01696	1.08076	58.97703
840	6.08	0.00388	0.01043	0.01676	1.08938	59.68254
870	6.04	0.00390	0.01047	0.01634	1.11829	61.19250
900	6.03	0.00390	0.01046	0.01621	1.12559	61.68059
930	5.99	0.00389	0.01045	0.01593	1.14223	62.75662
960	5.99	0.00390	0.01046	0.01592	1.14409	62.83272
990	5.98	0.00390	0.01046	0.01584	1.14877	63.12750
1020	5.93	0.00390	0.01047	0.01545	1.17441	64.72478
1050	5.91	0.00389	0.01045	0.01534	1.18025	65.18877
1080	5.89	0.00389	0.01044	0.01523	1.18614	65.65945
1110	5.86	0.00390	0.01047	0.01493	1.20866	66.98016
1140	5.82	0.00390	0.01047	0.01461	1.23075	68.43132
1170	5.81	0.00390	0.01046	0.01458	1.23189	68.59890
1200	5.80	0.00390	0.01047	0.01446	1.24097	69.13429
1230	5.77	0.00389	0.01045	0.01430	1.25049	69.93233
1260	5.74	0.00389	0.01045	0.01410	1.26420	70.94323
1290	5.74	0.00389	0.01044	0.01412	1.26217	70.84611
1320	5.73	0.00390	0.01047	0.01396	1.27557	71.61458
1350	5.69	0.00388	0.01052	0.01351	1.31374	74.01345
1380	5.69	0.00390	0.01047	0.01367	1.29709	73.17239
1410	5.66	0.00389	0.01045	0.01348	1.30936	74.17258
1440	5.64	0.00390	0.01047	0.01329	1.32465	75.21762
1470	5.63	0.00390	0.01047	0.01313	1.33801	76.17977
1500	5.62	0.00390	0.01046	0.01309	1.33944	76.38764
1530	5.58	0.00389	0.01044	0.01285	1.35591	77.80911
1560	5.60	0.00389	0.01045	0.01298	1.34657	77.03489
1590	5.55	0.00388	0.01043	0.01267	1.36904	78.94074
1620	5.53	0.00389	0.01045	0.01246	1.38747	80.25108
1650	5.55	0.00390	0.01047	0.01255	1.38218	79.67137
1680	5.55	0.00390	0.01047	0.01255	1.38218	79.67137

1710	5.50	0.00389	0.01045	0.01224	1.40551	81.71214
1740	5.52	0.00390	0.01046	0.01235	1.39788	80.98527
1770	5.52	0.00390	0.01047	0.01233	1.40010	81.11221
1800	5.53	0.00389	0.01045	0.01244	1.38967	80.37556
1830	5.51	0.00390	0.01047	0.01225	1.40615	81.60414
1860	5.54	0.00389	0.01045	0.01254	1.38153	79.77528
1890	5.51	0.00390	0.01046	0.01227	1.40392	81.47583
1920	5.52	0.00389	0.01045	0.01239	1.39346	80.73308
1950	5.52	0.00389	0.01045	0.01237	1.39567	80.85890
1980	5.51	0.00388	0.01043	0.01235	1.39503	80.96576
2010	5.52	0.00389	0.01045	0.01237	1.39568	80.85923
2040	5.50	0.00390	0.01046	0.01220	1.41000	81.97219
2070	5.52	0.00389	0.01045	0.01237	1.39567	80.85890
2100	5.51	0.00389	0.01045	0.01229	1.40170	81.34808
2130	5.49	0.00390	0.01047	0.01211	1.41835	82.60612
2160	5.51	0.00390	0.01046	0.01227	1.40392	81.47566
2190	5.53	0.00389	0.01045	0.01244	1.38967	80.37556
2220	5.51	0.00389	0.01049	0.01218	1.41506	82.12112
2250	5.48	0.00388	0.01052	0.01188	1.44251	84.19046
2280	5.50	0.00389	0.01045	0.01222	1.40776	81.84255
2310	5.53	0.00390	0.01046	0.01242	1.39189	80.50092
2340	5.50	0.00388	0.01043	0.01228	1.40105	81.45508
2370	5.48	0.00390	0.01047	0.01201	1.42676	83.24976
2400	5.49	0.00389	0.01045	0.01216	1.41163	82.21293
2430	5.49	0.00389	0.01048	0.01207	1.42284	82.87017
2460	5.48	0.00390	0.01047	0.01203	1.42451	83.11639
2490	5.48	0.00390	0.01046	0.01205	1.42225	82.98311
2520	5.49	0.00390	0.01047	0.01209	1.42060	82.73802
2550	5.49	0.00390	0.01047	0.01209	1.42059	82.73785
2580	5.50	0.00389	0.01045	0.01222	1.40777	81.84289
2610	5.48	0.00388	0.01043	0.01213	1.41326	82.45509
2640	5.49	0.00390	0.01046	0.01212	1.41611	82.47464
2670	5.49	0.00389	0.01045	0.01214	1.41387	82.34375
2700	5.50	0.00390	0.01046	0.01220	1.41000	81.97219
2730	5.49	0.00389	0.01045	0.01216	1.41162	82.21242
2760	5.49	0.00390	0.01046	0.01212	1.41611	82.47464
2790	5.51	0.00390	0.01046	0.01227	1.40392	81.47566
2820	5.51	0.00389	0.01045	0.01229	1.40170	81.34808
2850	5.50	0.00389	0.01045	0.01222	1.40776	81.84255

2880	5.49	0.00389	0.01045	0.01214	1.41387	82.34375
2910	5.46	0.00389	0.01045	0.01192	1.43239	83.88344
2940	5.49	0.00390	0.01046	0.01212	1.41610	82.47447
2970	5.49	0.00390	0.01046	0.01212	1.41611	82.47464
3000	5.48	0.00389	0.01045	0.01207	1.42000	82.85008
3030	5.48	0.00389	0.01045	0.01209	1.41776	82.71834
3060	5.48	0.00389	0.01044	0.01211	1.41550	82.58616
3090	5.48	0.00390	0.01046	0.01205	1.42226	82.98328
3120	5.48	0.00389	0.01045	0.01207	1.42000	82.85043
3150	5.48	0.00390	0.01047	0.01201	1.42677	83.25010
3180	5.47	0.00389	0.01045	0.01200	1.42618	83.36374
3210	5.49	0.00388	0.01043	0.01220	1.40711	81.95034
3240	5.49	0.00390	0.01046	0.01212	1.41611	82.47481
3270	5.45	0.00389	0.01045	0.01185	1.43865	84.40967
3300	5.48	0.00388	0.01043	0.01213	1.41326	82.45509
3330	5.49	0.00389	0.01044	0.01218	1.40938	82.08236
3360	5.46	0.00390	0.01046	0.01190	1.43467	84.01963
3390	5.48	0.00390	0.01046	0.01205	1.42225	82.98311
3420	5.48	0.00390	0.01047	0.01203	1.42451	83.11639
3450	5.48	0.00390	0.01046	0.01205	1.42226	82.98328
3480	5.47	0.00389	0.01045	0.01200	1.42618	83.36374

Using Integral Method:

1. First order reaction

Suppose the hydrolysis of ethyl acetate is guessed to be first order reaction, thus equation (8) becomes

$$-r_A = \frac{-dC_A}{dt} = kC_A \tag{12}$$

Integrating and separating equation (11),

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = k\int_0^t dt$$

$$-\ln\frac{C_A}{C_{A0}} = kt \tag{13}$$

A plot of $-\ln\frac{C_A}{C_{A0}}$ versus t will give a straight line through the origin with the slope of k.

2. <u>Second order reaction</u>

Suppose the hydrolysis of ethyl acetate is second order reaction, thus equation (8) becomes

$$-r_A = \frac{-dC_A}{dt} = kC_A^2 = kC_{A0}^2(1-X_A)^2 \qquad (16)$$

which on integration yields,

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = \frac{1}{C_{A0}}\frac{X_A}{1-X_A} = kt \qquad (17)$$

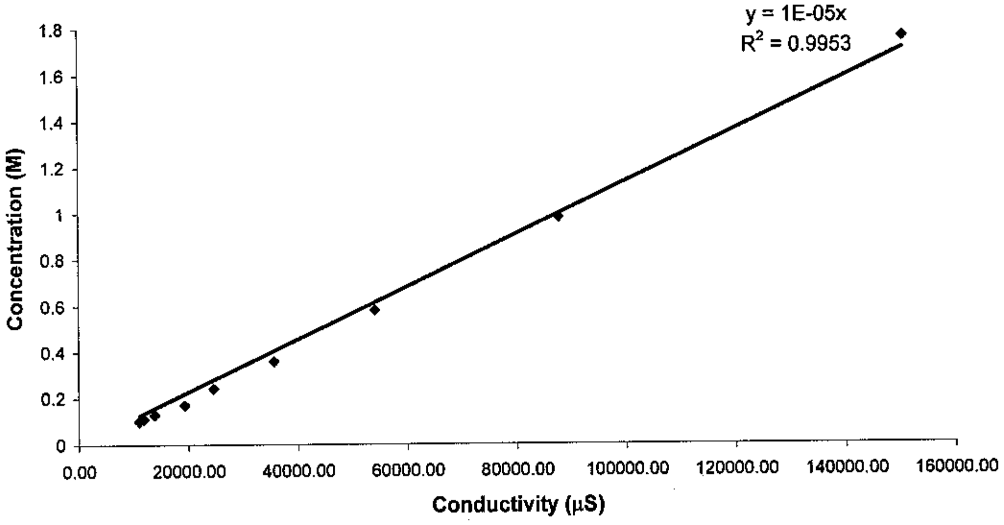
Plot $\frac{1}{C_A}$ versus t will give straight with slope $= k$ and intercept $\frac{1}{C_{A0}}$.

APPENDIX II

Data:

1. Correlation between Concentration and Conductivity of sodium chloride

Mass NaCl (g)	Molarity (M)	Volume (L)	Λ (mS)
2.922	0.1	0.5	10956.67
3.214	0.11	0.5	11806.67
3.857	0.13	0.5	13770.00
5.014	0.17	0.5	19283.33
7.020	0.24	0.5	24600.00
10.530	0.36	0.5	35600.00
15.848	0.58	0.5	54000.00
28.641	0.98	0.5	87666.67
51.554	1.76	0.5	150500.00



Graph above showing the relationship between concentration and conductivity of sodium chloride. Based on the graph, it is seen that the conductivity is directly proportional to concentration. As the concentration of the sodium chloride increased, the conductivity value of it will also increase. By using the equation of straight line obtained from the graph, the conductivity values of the step change test and pulse input test can be converted to concentration values.

2. Step Change Test and Pulse Input Concentration

t (min)	STEP CHANGE		PULSE INPUT	
	Λ (µS)	Concentration (M)	Λ (µS)	Concentration (M)
0	0	0.00000	0	0.000000
1	150.2	0.00150	150.8	0.001508
2	294.5	0.00295	348.7	0.003487
3	489.4	0.00489	494.9	0.004949
4	667.5	0.00668	478.9	0.004789
5	838.7	0.00839	451.7	0.004517
6	990.5	0.00991	421.9	0.004219
7	1129.8	0.01130	398.0	0.003980
8	1257.8	0.01258	374.0	0.003740
9	1370.6	0.01371	352.0	0.003520
10	1481.9	0.01482	332.2	0.003322
11	1578.3	0.01578	311.4	0.003114
12	1666.9	0.01667	294.2	0.002942
13	1747.0	0.01747	279.0	0.002790
14	1821.4	0.01821	262.7	0.002627
15	1887.7	0.01888	250.1	0.002501
16	1950.4	0.01950	232.4	0.002324
17	2023.2	0.02023	220.3	0.002203
18	2087.1	0.02087	206.5	0.002065
19	2139.9	0.02140	197.5	0.001975
20	2191.4	0.02191	184.3	0.001843
21	2238.8	0.02239	172.8	0.001728
22	2279.9	0.02280	163.4	0.001634
23	2318.1	0.02318	152.3	0.001523
24	2355.2	0.02355	142.6	0.001426
25	2383.0	0.02383	134.8	0.001348
26	2412.6	0.02413	126.4	0.001264
27	2440.2	0.02440	118.6	0.001186
28	2466.6	0.02467	110.5	0.001105
29	2490.6	0.02491	103.2	0.001032
30	2513.0	0.02513	97.5	0.000975
31	2532.9	0.02533	91.3	0.000913
32	2551.7	0.02552	85.1	0.000851
33	2566.8	0.02567	79.0	0.000790

34	2583.4	0.02583	73.1	0.000731
35	2598.2	0.02598	68.7	0.000687
36	2613.5	0.02614	64.1	0.000641
37	2626.4	0.02626	60.5	0.000605
38	2638.7	0.02639	55.4	0.000554
39	2649.5	0.02650	51.2	0.000512
40	2659.9	0.02660	48.1	0.000481
41	2668.7	0.02669	45.2	0.000452
42	2676.9	0.02677	42.1	0.000421
43	2685.2	0.02685	39.4	0.000394
44	2692.3	0.02692	36.1	0.000361
45	2698.5	0.02699	33.2	0.000332
46	2704.5	0.02705	31.6	0.000316
47	2705.3	0.02705	29.4	0.000294
48	2710.7	0.02711	27.1	0.000271
49	2716.3	0.02716	25.6	0.000256
50	2720.1	0.02720	23.1	0.000231
51	2723.6	0.02724	21.4	0.000214
52	2728.6	0.02729	20.3	0.000203
53	2733.2	0.02733	18.6	0.000186
54	2735.4	0.02735	16.4	0.000164
55	2740.4	0.02740	14.8	0.000148
56	2743.5	0.02744	13.5	0.000135
57	2745.0	0.02745	11.6	0.000116
58	2747.9	0.02748	10.2	0.000102
59	2751.2	0.02751	9.5	0.000095
60	2753.2	0.02753	8.4	0.000084
			7.6	0.000076
			7.1	0.000071
			6.2	0.000062
			5.4	0.000054
			4.8	0.000048
			4.5	0.000045
			3.6	0.000036
			2.9	0.000029
			2.5	0.000025
			2.1	0.000021
			2.0	0.000020
			1.6	0.000016

			1.3	0.000013
			0.5	0.000005
			0.2	0.000002
			0.1	0.000001

3. RTD Data Analysis from Pulse Input

t (min)	Concentration (V)	E(t)	t.E(t)	$(t-t_m)^2 E(t)$	F(t)
0	0.000000	0.000000	0.000000	0.00000	0.000000
1	0.001508	0.020667	0.020667	3.90442	0.001077
2	0.003487	0.047788	0.095576	7.86986	0.004981
3	0.004949	0.067824	0.203473	9.63814	0.010605
4	0.004789	0.065632	0.262526	7.95392	0.024288
5	0.004517	0.061904	0.309519	6.31050	0.040420
6	0.004219	0.057820	0.346919	4.87734	0.058502
7	0.003980	0.054544	0.381811	3.73256	0.078402
8	0.003740	0.051255	0.410043	2.77665	0.099774
9	0.003520	0.048240	0.434163	2.00575	0.122402
10	0.003322	0.045527	0.455268	1.39528	0.146131
11	0.003114	0.042676	0.469439	0.91244	0.170598
12	0.002942	0.040319	0.483829	0.55549	0.195816
13	0.002790	0.038236	0.497067	0.29970	0.221723
14	0.002627	0.036002	0.504029	0.12828	0.247993
15	0.002501	0.034275	0.514129	0.03262	0.274790
16	0.002324	0.031850	0.509593	0.00013	0.301350
17	0.002203	0.030191	0.513252	0.02175	0.328101
18	0.002065	0.028300	0.509401	0.08775	0.354651
19	0.001975	0.027067	0.514267	0.19338	0.381455
20	0.001843	0.025258	0.505153	0.32463	0.407784
21	0.001728	0.023682	0.497314	0.47895	0.433704
22	0.001634	0.022393	0.492654	0.65523	0.459381
23	0.001523	0.020872	0.480060	0.83405	0.484402
24	0.001426	0.019543	0.469028	1.02254	0.508848
25	0.001348	0.018474	0.461846	1.22575	0.532920
26	0.001264	0.017323	0.450389	1.42118	0.556394
27	0.001186	0.016254	0.438850	1.61557	0.579267
28	0.001105	0.015144	0.424021	1.79325	0.601367
29	0.001032	0.014143	0.410152	1.96730	0.622744

30	0.000975	0.013362	0.400861	2.15724	0.643637
31	0.000913	0.012512	0.387882	2.32049	0.663854
32	0.000851	0.011663	0.373205	2.46234	0.683306
33	0.000790	0.010827	0.357280	2.58182	0.701927
34	0.000731	0.010018	0.340615	2.67955	0.719680
35	0.000687	0.009415	0.329528	2.80699	0.736855
36	0.000641	0.008785	0.316248	2.90305	0.753338
37	0.000605	0.008291	0.306778	3.02186	0.769328
38	0.000554	0.007592	0.288510	3.03785	0.784365
39	0.000512	0.007017	0.273654	3.06942	0.798628
40	0.000481	0.006592	0.263677	3.14057	0.812371
41	0.000452	0.006194	0.253974	3.20302	0.825608
42	0.000421	0.005770	0.242325	3.22748	0.838238
43	0.000394	0.005400	0.232184	3.25795	0.850340
44	0.000361	0.004947	0.217684	3.21088	0.861685
45	0.000332	0.004550	0.204747	3.16818	0.872357
46	0.000316	0.004331	0.199211	3.22756	0.882740
47	0.000294	0.004029	0.189371	3.20686	0.892610
48	0.000271	0.003714	0.178270	3.15021	0.901901
49	0.000256	0.003508	0.171911	3.16516	0.910862
50	0.000231	0.003166	0.158289	3.03216	0.919112
51	0.000214	0.002933	0.149572	2.97703	0.926907
52	0.000203	0.002782	0.144666	2.98801	0.934447
53	0.000186	0.002549	0.135100	2.89230	0.941489
54	0.000164	0.002248	0.121368	2.69017	0.947815
55	0.000148	0.002028	0.111556	2.55741	0.953629
56	0.000135	0.001850	0.103607	2.45416	0.959029
57	0.000116	0.001590	0.090615	2.21570	0.963752
58	0.000102	0.001398	0.081077	2.04465	0.967978
59	0.000095	0.001302	0.076814	1.99625	0.971981
60	0.000084	0.001151	0.069071	1.84829	0.975581
61	0.000076	0.001042	0.063535	1.74926	0.978893
62	0.000071	0.000973	0.060328	1.70773	0.982037
63	0.000062	0.000850	0.053530	1.55690	0.984827
64	0.000054	0.000740	0.047363	1.41442	0.987296
65	0.000048	0.000658	0.042758	1.31027	0.989524
66	0.000045	0.000617	0.040703	1.27910	0.991646
67	0.000036	0.000493	0.033056	1.06468	0.993369
68	0.000029	0.000397	0.027026	0.89167	0.994777

69	0.000025	0.000343	0.023640	0.79857	0.996009
70	0.000021	0.000288	0.020146	0.69638	0.997059
71	0.000020	0.000274	0.019461	0.68804	0.998074
72	0.000016	0.000219	0.015788	0.57066	0.998896
73	0.000013	0.000178	0.013006	0.48039	0.999574
74	0.000005	0.000069	0.005071	0.19131	0.999839
75	0.000002	0.000027	0.002056	0.07919	0.999946
76	0.000001	0.000014	0.001042	0.04095	1.000000

Numerical Integration:

1. For $N+1$ points, where $(N/3)$ is an integer,

$$\int_{X_0}^{X_N} f(X)dX = \tfrac{3}{8}h\left[f_0 + 3f_1 + 3f_2 + 2f_3 + \ldots\ldots + 3f_{N-1} + f_N\right]$$

where, $$h = \frac{X_N - X_0}{N}$$

2. For $N+1$ points, where N is even,

$$\int_{X_0}^{X_N} f(X)dX = \frac{h}{3}\left[f_0 + 4f_1 + 2f_2 + 4f_3 + 2f_3 + \ldots\ldots + 4f_N + f_N\right]$$

where, $$h = \frac{X_N - X_0}{N}$$

APPENDIX III

Data:

t (min)	$E(t)$ (min^{-1})	$X(t)$	$X(t).E(t)$ (min^{-1})	$X(t)$ $E(t)\ \Delta t$
0	0.00000	0.00000	0.00000	0.00000
1	0.01719	0.07261	0.00125	0.00125
2	0.03976	0.13540	0.00538	0.00538
3	0.05643	0.19022	0.01073	0.01073
4	0.05460	0.23850	0.01302	0.01302
5	0.05150	0.28135	0.01449	0.01449
6	0.04810	0.31964	0.01538	0.01538
7	0.04538	0.35405	0.01607	0.01607
8	0.04264	0.38515	0.01642	0.01642
9	0.04013	0.41339	0.01659	0.01659
10	0.03788	0.43915	0.01663	0.01663
11	0.03550	0.46274	0.01643	0.01643
12	0.03354	0.48443	0.01625	0.01625
13	0.03181	0.50444	0.01605	0.01605
14	0.02995	0.52295	0.01566	0.01566
15	0.02851	0.54012	0.01540	0.01540
16	0.02650	0.55611	0.01474	0.01474
17	0.02512	0.57102	0.01434	0.01434
18	0.02354	0.58496	0.01377	0.01377
19	0.02252	0.59802	0.01347	0.01347
20	0.02101	0.61029	0.01282	0.01282
21	0.01970	0.62183	0.01225	0.01225
22	0.01863	0.63270	0.01179	0.01179
23	0.01736	0.64297	0.01116	0.01116
24	0.01626	0.65268	0.01061	0.01061
25	0.01537	0.66188	0.01017	0.01017
26	0.01441	0.67060	0.00966	0.00966
27	0.01352	0.67888	0.00918	0.00918
28	0.01260	0.68676	0.00865	0.00865
29	0.01177	0.69426	0.00817	0.00817
30	0.01112	0.70140	0.00780	0.00780
31	0.01041	0.70823	0.00737	0.00737
32	0.00970	0.71474	0.00693	0.00693

33	0.00901	0.72097	0.00649	0.00649
34	0.00833	0.72694	0.00606	0.00606
35	0.00783	0.73266	0.00574	0.00574
36	0.00731	0.73814	0.00539	0.00539
37	0.00690	0.74340	0.00513	0.00513
38	0.00632	0.74845	0.00473	0.00473
39	0.00584	0.75331	0.00440	0.00440
40	0.00548	0.75799	0.00416	0.00416
41	0.00515	0.76249	0.00393	0.00393
42	0.00480	0.76682	0.00368	0.00368
43	0.00449	0.77100	0.00346	0.00346
44	0.00412	0.77504	0.00319	0.00319
45	0.00379	0.77893	0.00295	0.00295
46	0.00360	0.78269	0.00282	0.00282
47	0.00335	0.78633	0.00264	0.00264
48	0.00309	0.78985	0.00244	0.00244
49	0.00292	0.79325	0.00232	0.00232
50	0.00263	0.79654	0.00210	0.00210
51	0.00244	0.79973	0.00195	0.00195
52	0.00231	0.80282	0.00186	0.00186
53	0.00212	0.80582	0.00171	0.00171
54	0.00187	0.80873	0.00151	0.00151
55	0.00169	0.81155	0.00137	0.00137
56	0.00154	0.81429	0.00125	0.00125
57	0.00132	0.81695	0.00108	0.00108
58	0.00116	0.81954	0.00095	0.00095
59	0.00108	0.82205	0.00089	0.00089
60	0.00096	0.82450	0.00079	0.00079
61	0.00087	0.82688	0.00072	0.00072
62	0.00081	0.82919	0.00067	0.00067
63	0.00071	0.83145	0.00059	0.00059
64	0.00062	0.83364	0.00051	0.00051
65	0.00055	0.83578	0.00046	0.00046
66	0.00051	0.83787	0.00043	0.00043
67	0.00041	0.83990	0.00034	0.00034
68	0.00033	0.84188	0.00028	0.00028
69	0.00029	0.84382	0.00024	0.00024
70	0.00024	0.84570	0.00020	0.00020
71	0.00023	0.84754	0.00019	0.00019

72	0.00018	0.84934	0.00015	0.00015
73	0.00015	0.85110	0.00013	0.00013
74	0.00006	0.85282	0.00005	0.00005
75	0.00002	0.85449	0.00002	0.00002
76	0.00001	0.85613	0.00001	0.00001
			SUM	0.47863

APPENDIX IV

Data:

t (min)	Concentration (M)	E(t) (min^{-1})	λ	E(λ)	1-F(λ)	E(λ)/[1-F(λ)]	X (t)
0	0.00000	0.00000	76	0.00001	0.00004	0.29382	0.00000
1	0.00151	0.01719	75	0.00002	0.00010	0.23690	0.07830
2	0.00349	0.03976	74	0.00006	0.00027	0.21404	0.12627
3	0.00495	0.05643	73	0.00015	0.00049	0.30243	0.15902
4	0.00479	0.05460	72	0.00018	0.00097	0.18839	0.16630
5	0.00452	0.05150	71	0.00023	0.00171	0.13318	0.18940
6	0.00422	0.04810	70	0.00024	0.00261	0.09185	0.21562
7	0.00398	0.04538	69	0.00029	0.00370	0.07703	0.24399
8	0.00374	0.04264	68	0.00033	0.00511	0.06472	0.26995
9	0.00352	0.04013	67	0.00041	0.00687	0.05972	0.29421
10	0.00332	0.03788	66	0.00051	0.00866	0.05923	0.31564
11	0.00311	0.03550	65	0.00055	0.01102	0.04964	0.33362
12	0.00294	0.03354	64	0.00062	0.01360	0.04528	0.35183
13	0.00279	0.03181	63	0.00071	0.01632	0.04331	0.36879
14	0.00263	0.02995	62	0.00081	0.01918	0.04221	0.38402
15	0.00250	0.02851	61	0.00087	0.02233	0.03880	0.39752
16	0.00232	0.02650	60	0.00096	0.02561	0.03740	0.41052
17	0.00220	0.02512	59	0.00108	0.02906	0.03728	0.42237
18	0.00207	0.02354	58	0.00116	0.03283	0.03542	0.43275
19	0.00198	0.02252	57	0.00132	0.03685	0.03589	0.44262
20	0.00184	0.02101	56	0.00154	0.04099	0.03755	0.45106
21	0.00173	0.01970	55	0.00169	0.04525	0.03729	0.45771
22	0.00163	0.01863	54	0.00187	0.05000	0.03740	0.46367
23	0.00152	0.01736	53	0.00212	0.05495	0.03859	0.46886
24	0.00143	0.01626	52	0.00231	0.06007	0.03853	0.47285
25	0.00135	0.01537	51	0.00244	0.06572	0.03713	0.47639
26	0.00126	0.01441	50	0.00263	0.07167	0.03675	0.48017
27	0.00119	0.01352	49	0.00292	0.07789	0.03747	0.48368
28	0.00111	0.01260	48	0.00309	0.08436	0.03663	0.48643
29	0.00103	0.01177	47	0.00335	0.09129	0.03672	0.48927
30	0.00098	0.01112	46	0.00360	0.09863	0.03653	0.49173
31	0.00091	0.01041	45	0.00379	0.10647	0.03555	0.49399
32	0.00085	0.00970	44	0.00412	0.11470	0.03588	0.49648
33	0.00079	0.00901	43	0.00449	0.12345	0.03639	0.49852
34	0.00073	0.00833	42	0.00480	0.13273	0.03616	0.50007
35	0.00069	0.00783	41	0.00515	0.14249	0.03617	0.50155
36	0.00064	0.00731	40	0.00548	0.15272	0.03591	0.50287
37	0.00061	0.00690	39	0.00584	0.16355	0.03569	0.50416
38	0.00055	0.00632	38	0.00632	0.17506	0.03608	0.50542
39	0.00051	0.00584	37	0.00690	0.18704	0.03688	0.50633
40	0.00048	0.00548	36	0.00731	0.19965	0.03660	0.50674
41	0.00045	0.00515	35	0.00783	0.21298	0.03678	0.50724
42	0.00042	0.00480	34	0.00833	0.22709	0.03670	0.50760
43	0.00039	0.00449	33	0.00901	0.24195	0.03723	0.50796
44	0.00036	0.00412	32	0.00970	0.25755	0.03767	0.50800
45	0.00033	0.00379	31	0.01041	0.27390	0.03800	0.50782

46	0.00032	0.00360	30	0.01112	0.29117	0.03818	0.50749
47	0.00029	0.00335	29	0.01177	0.30930	0.03804	0.50711
48	0.00027	0.00309	28	0.01260	0.32833	0.03837	0.50684
49	0.00026	0.00292	27	0.01352	0.34826	0.03883	0.50643
50	0.00023	0.00263	26	0.01441	0.36916	0.03904	0.50584
51	0.00021	0.00244	25	0.01537	0.39099	0.03931	0.50522
52	0.00020	0.00231	24	0.01626	0.41372	0.03930	0.50453
53	0.00019	0.00212	23	0.01736	0.43746	0.03969	0.50392
54	0.00016	0.00187	22	0.01863	0.46216	0.04031	0.50319
55	0.00015	0.00169	21	0.01970	0.48778	0.04039	0.50223
56	0.00014	0.00154	20	0.02101	0.51434	0.04085	0.50135
57	0.00012	0.00132	19	0.02252	0.54174	0.04157	0.50033
58	0.00010	0.00116	18	0.02354	0.57002	0.04130	0.49909
59	0.00010	0.00108	17	0.02512	0.59910	0.04192	0.49812
60	0.00008	0.00096	16	0.02650	0.62889	0.04213	0.49696
61	0.00008	0.00087	15	0.02851	0.65931	0.04325	0.49583
62	0.00007	0.00081	14	0.02995	0.69033	0.04339	0.49429
63	0.00006	0.00071	13	0.03181	0.72125	0.04410	0.49287
64	0.00005	0.00062	12	0.03354	0.75189	0.04461	0.49127
65	0.00005	0.00055	11	0.03550	0.78216	0.04539	0.48962
66	0.00005	0.00051	10	0.03788	0.81172	0.04666	0.48779
67	0.00004	0.00041	9	0.04013	0.84048	0.04775	0.48557
68	0.00003	0.00033	8	0.04264	0.86814	0.04912	0.48311
69	0.00003	0.00029	7	0.04538	0.89440	0.05074	0.48030
70	0.00002	0.00024	6	0.04810	0.91900	0.05234	0.47708
71	0.00002	0.00023	5	0.05150	0.94157	0.05470	0.47352
72	0.00002	0.00018	4	0.05460	0.96173	0.05677	0.46932
73	0.00001	0.00015	3	0.05643	0.97897	0.05764	0.46473
74	0.00001	0.00006	2	0.03976	0.99246	0.04006	0.46038
75	0.00000	0.00002	1	0.01719	0.99883	0.01721	0.46473
76	0.00000	0.00001	0	0.00000	1.00000	0.00000	0.47029

APPENDIX V

Data:

t (min)	Concentration (M)	ln $C_{T0}/[C_{T0}-C_T]$
0	0.00000	0.00000
1	0.00150	0.03050
2	0.00295	0.06071
3	0.00489	0.10301
4	0.00668	0.14329
5	0.00839	0.18361
6	0.00991	0.22077
7	0.01130	0.25613
8	0.01258	0.28976
9	0.01371	0.32037
10	0.01482	0.35152
11	0.01578	0.37930
12	0.01667	0.40554
13	0.01747	0.42986
14	0.01821	0.45300
15	0.01888	0.47408
16	0.01950	0.49443
17	0.02023	0.51859
18	0.02087	0.54029
19	0.02140	0.55858
20	0.02191	0.57675
21	0.02239	0.59377
22	0.02280	0.60877
23	0.02318	0.62291
24	0.02355	0.63684
25	0.02383	0.64741
26	0.02413	0.65878
27	0.02440	0.66951
28	0.02467	0.67988
29	0.02491	0.68939
30	0.02513	0.69836
31	0.02533	0.70639
32	0.02552	0.71404
33	0.02567	0.72023
34	0.02583	0.72708
35	0.02598	0.73322
36	0.02614	0.73961
37	0.02626	0.74503
38	0.02639	0.75023
39	0.02650	0.75481
40	0.02660	0.75924
41	0.02669	0.76301
42	0.02677	0.76654
43	0.02685	0.77011
44	0.02692	0.77319
45	0.02699	0.77588

46	0.02705	0.77849
47	0.02705	0.77884
48	0.02711	0.78119
49	0.02716	0.78364
50	0.02720	0.78531
51	0.02724	0.78684
52	0.02729	0.78904
53	0.02733	0.79107
54	0.02735	0.79204
55	0.02740	0.79425
56	0.02744	0.79562
57	0.02745	0.79629
58	0.02748	0.79757
59	0.02751	0.79904
60	0.02753	0.79993