CERTIFICATION OF APPROVAL

DESIGN OF A REAL CSTR BASED ON SAPONIFICATION AND RESIDENCE TIME DISTRIBUTION EXPERIMENTAL STUDIES

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.

OLIVER DENIS PAMBA

ABSTRACT

The Chemical Reactor Engineering has proven to be an important part of chemical engineering; it provides expertise to the industrial sector on Reactor Engineering and Chemical Processes, and concentrates on the development of novel reactor modelling and optimization of chemical processes. Its technology has gain tremendous applications in industry. Three ideal contacting patterns are, 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 types of reactors, depending on its application for the ease of cleaning, maintenance and requires less labor cost.

This project requires the student to analysis the ideal and the real behaviour of a methanol and ethanol model in a Continuous Stirred Tank Reactor. Thus, the research project illustrates the overall performance of a CSTR in terms of Reactor's conversion, residence time distribution and yield. Thus, the main objective of this research project is to conduct an empirical and analytical study on a real and ideal behaviour of a CSTR, which is often treated as an ideal reactor. However, the theoretical principle of an ideal and a perfect mixing in CSTR is hardly achieved in any industrial application due to some limitations such as dead zone creation and channeling. Thus, this study consists of three main parts as illustrated below;

1. Derivation of mathematical equation such as rate of reaction for the Saponification reaction
2. Determination of reaction rate constant from the concentration data and tracer analysis (experimental study).
3. Simulation and calculation on the experimental data obtained by using Microsoft Excel and FEMLAB.

Three main experiments are conducted, in which the first experiment is to determine the reaction rate constant of reaction, which is the saponification reaction. Secondly, to determine the effect of an adequate mixing on reaction rate constant and the third being the determination of the RTD value, which is determined by either step change input and pulse input. The RTD experiment is conducted using the CSTR dynamics, tank in series and the CSTR with hot water circulation equipment and experimental data are analyzed, the three equipments are used separately and their RTD values are compared just to further understand their performance and responds in the saponification process.
Finally, the study illustrated that the conversion in a real reactor is higher comparatively due to dead zone creation and bypassing. The conversions for the ideal reactor is 43 % for ethanol synthesis and 52 % for methanol synthesis, and for the real reactor modeled are as shown in table 4.

FEMLAB is used to model and analysis the mechanism of ethanol and methanol production in a CSTR under the ideal and real operating conditions. Temperature and concentration profile of the reactant generated by the FEMLAB modeling package is monitored, and conversion and yield of ethanol and methanol obtained from conducting an experiment is studied and the results are used for comparison with previous research. The concentration profile shows that the concentration of the reactant decreases from 0.05mole/L to 0.0484 mole/L, forming the desired product with respect to the residence time distribution of the reactant inside the reactor. While the temperature profile showing the temperature increases at the start of the reaction to show that this is an exothermic reaction. But when reactant is consuming gradually, the temperature started to decrease indicating that there is not enough reactant to produce the desired product.

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NOMENCLATURE

A, B, …	reactants
$a, b, \ldots$	stoichiometry coefficients for reacting substances A, B, … (-)
$C, C_A, C_B, \ldots$	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 (-)
σ	Standard deviation (min)
σ^2	variance of a tracer curve or distribution function (min^2)
τ	space time (min)

CHAPTER 1

INTRODUCTION

.1 BACKGROUND OF STUDY

Methanol is (CH_3OH) is a volatile colourless alcohol, derived originally as wood alcohol, used as a racing fuel and as a solvent. Also called methyl alcohol, and lethal if consumed. Used to make methoxide in biodiesel production. Methanol absorbs water from the air.

It has similar chemical and physical properties as that of ethanol. However, chemically oriented, it is methane with a hydroxyl radical or ions (OH) replacing single hydrogen molecule. It is also used as a fuel additive for gasoline in the form of methyl tertiary butyl ether (MTBE), and it's an oxygenate that minimizes ground level ozone emission. However, methanol is also used in varieties of industrial process such as food processing and chemical catalyst.

Ethanol, also known as ethyl alcohol or grain alcohol, is a flammable, colorless chemical compound, one of the alcohols that are most often found in alcoholic beverages. In common parlance, it is often referred to simply as alcohol. Its chemical formula is C_2H_5OH, or C_2H_6O.

Ethanol for use in alcoholic beverages is produced by fermentation; it is a product of sugar metabolism in certain species of yeast in the absence of oxygen. The process of culturing yeast under conditions to produce alcohol is termed as brewing. Yeasts grow in the presence of up to about 20% alcohol, but the concentration of alcohol in the final product can be increased by distillation.

The primary source of methanol and ethanol are from natural gas and other non-petroleum sources such as coal and biomass. The cost of producing methanol and ethanol are based on the type of source and the method of production. Due to their high demand in today's market, researchers currently are focusing on how to reduce their production cost by finding easier, economically sounding, a renewable alternatives sources and method of producing them. Some of these alternative sources and methods are the steam reforming of natural gas to produce a synthesis gas, which consist of carbon monoxide, hydrogen, and reaction of alcohol with carboxylic acid. The gas is then catalyst to produce methanol, ethanol, and steam.

Thus, this Final Year Research Project focus mainly on comparing and analyzing an ideal and a real behaviour of a CSTR base on a Saponification reaction (reaction of ethyl acetate and methyl acetate with sodium hydroxide to produce ethanol and methanol) and Residence Time Distribution. Thus, the main reactor employed in this research project is the CSTR, which consists of a well -stirred tank containing baffles. A substrate stream is continuously pumped into the reactor at the same time as the product stream is removed. If the reactor is behaving in an ideal manner, there is total back-mixing and the product stream is identical with the liquid phase within the reactor and invariant with respect to time. Some molecules of substrate may be removed rapidly from the reactor, whereas others may remain for substantial periods. It is easily constructed, versatile and cheap reactor, which allows simple catalyst charging and replacement. Its well-mixed nature permits straightforward control over the temperature and pH of the reaction and the supply or removal of gases. CSTR have high efficiency for mixing.

Its main advantage is that there is very little resistance to the flow of the substrate stream, which may contain colloidal or insoluble substrates.

However, CSTR is often treated as an ideal reactor but in reality non-ideality in common occurrence. The design of a real reactor requires creatively and in-depth knowledge of reactor study. In designing an optimum reactor, factors such as dead zone and channeling, which are the main factors in determining the optimum design parameters, must be taken into consideration. In addition, initial reactant concentration, temperature, and pressure will also affect the reaction kinetics.

However, an ideal CSTR has complete back -mixing resulting in a minimisation of the substrate concentration, and a maximizations of the product concentration, relative to the final conversion, at every point within the reactor the effectiveness factor being uniform throughout. The deviations from ideal CSTR behaviour occur when there is a less effective mixing regime and are generally overcome by increasing the stirrer speed, decreasing the solution viscosity or biocatalyst concentration or by more effective reactor baffling.

.2 PROBLEM STATEMENTS

Knowing the importance of Methanol and Ethanol not only to oil and Gas industries but as well in daily life, many researchers have been focusing on the most efficient and effective ways to synthesize them in the cheapest way which can safe energy and be able to obtain the highest conversion of the reactants into the desired product. However, this project requires student to model a Continuous Stirred Tank Reactor per the below stated conditions. Under an Ideal and a real operating condition to indicate the concentration and temperature profile of the reaction with respect to Reactor's Conversion and RTD by Saponification Reaction (Hydrolysis of Ester).

.3 OBJECTIVES OF THE PROJECT

1. To determine alternative routes of producing Methanol and Ethanol
2 To determine the external-age residence time distribution (RTD) function, E(t) from experimental data.
3 To determine the effects of initial reactant concentration, flow rate, and reactor temperature on the design of a real CSTR
4 To simulate a CSTR for the production of Methanol under adiabatic condition and non-adiabatic condition
5 To study of a real reactor based on models developed and RTD data
6 To compare a reaction conversions between the ideal and real reactors

.4 SCOPE OF STUDY

The design approaches is from the design of chemical reactors based on microscopic heat and mass transfer principles. It includes simultaneous consideration of kinetics and heat transfer, both critical to the performance of real chemical reactors.

However, the production of Methanol and Ethanol in CSTR under Ideal and Real condition will be analyzed by using FEMLAB. The temperature and concentration profile of the reactant will be monitored. In addition, conversion and yield of the reactants will be studied at the specified condition and the results will be analyzed and compared with any pre-set values. Based on the result of the analysis, the efficiency and effectiveness of the modeled CSTR in producing Methanol and Ethanol by Saponification reaction will be determine.

.5 THE RELEVANCY AND FELIXIBILITY OF THE PROJCET

This project consists of three main parts as stated below:

1. Derivation of a mathematical formulation for the process from experimental data
2. Simulating the Mechanism of the Methanol and Ethanol production in CSTR under a non-adiabatic condition
3. Using FEMLAB to illustrate the profiles for the effect of temperature, flow rate and concentration on the reactor.

CHAPTER 2

LITREATURE REVIEW

.1 SAPONIFICATION REACTION

Saponification is the hydrolysis of an ester under basic conditions to form an alcohol and the salt of the acid, it is commonly used to refer to the reaction of a metallic alkali (base) with a fat or oil to form soap.

Thus, the Saponification reaction of Methanol synthesis, Ethanol synthesis and their stoichiometry are as follows:

$NaOH$	+	CH_3COOCH_3	$\longrightarrow$	CH_3COONa	+	CH_3OH
Sodium Hydroxide		Methyl Acetate		Sodium Acetate		Methanol

$NaOH$	+	$CH_3COOCH_2CH_3$	$\longrightarrow$	CH_3COONa	+	$CH_3\,CH_2OH$
Sodium Hydroxide		Ethyl Acetate		Sodium Acetate		Ethanol

Saponification Reaction OR Ester Hydrolysis

$RCOOR$	+	HO^-	$\longrightarrow$	$RCOO^-$	+	ROH
Ester		Hydroxide		Carboxylate		Alcohol
Ion						

The Saponification reaction is theoretically in second order reaction overall, first order in each reactant with the reaction kinetic of:

$$r_A = -k\,[NaOH]\,[CH_3COOCH_3] \tag{1}$$

$$r_A = -k\,[NaOH]\,[CH_3COOCH_2CH_3] \tag{2}$$

The mechanism of the basic hydrolysis of esters was first analyzed by Bender, Swarts and many researchers. This reaction is theoretically a second order reaction overall, first order with respect to each reactant with the reaction kinetics as shown above.

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 REACTION MECHANISM

One of the main factors in doing this project was the overall understanding reaction rates in the reaction mechanism. The reaction mechanism is a description of the molecular scale process by which reactants are turned into products. These mechanisms consist of a sequence of elementary steps, each of which involves a collision between chemical spices, which might be atoms, molecules or even free radicals. Each reactive collision produces a product or a reaction intermediate. A reaction intermediates are an identifiable.

.3 REACTOR PERFORMANCE ANALYSIS

The performance of a chemical reactor is often related to the extent of reaction that occurs in it, and by the amount of reactant that is processed in a given time interval for a given reactor capacity or volume. The primary measure gives an indication of the fraction of reactant that have converted into products, while the secondary measures gives an indication of the overall production rate of the desired product and this reaction scenario is term conversion. Conversion, which is denoted by X, is defined as shown below:

$$X = \frac{\text{(Moles of spices that have reacted)}}{\text{(Moles of same spices initially present)}}$$

4 RATE OF REACTION

In any reactor performance analysis, the rate of reaction is the primary or main objective. The rate of reaction is defined as the measure of how quickly a reaction occurs. When a specific reaction condition such as reaction temperature and reactant concentration, the rate of reaction determines how long it will take to achieve a certain conversion of reactant into products. The rate of reaction is expressed in terms of disappearance of a reactant or the rate of formation of product. It usually measured in variety of units such as mol/s. However, they are mostly expressed in terms of a unit volume (e.g. $mol/m^3.s$), a unit mass catalyst (e.g. mol/kg.s), and catalyst surface area (e.g. $mol/m^2.s$).

However, chemical reactions are mostly conducted in the presence of a catalyst. And a catalyst is a substance which promote or increases the rate of reaction by providing an alternative reaction pathway between reactants and products. This path usually has smaller activation energy than the uncatalyzed reaction. Moreover, in an ideal case reaction the catalyst only participates in the chemical reaction but is not ultimately changed although the catalyst may lose its activity over certain time of promoting the reaction towards desired product. Catalysts are of two main types such as homogenous catalyst, in which the catalyst and the reactants are in the same phase, and a heterogeneous catalyst, in which the catalyst and the reactants are of different phase. However, the catalyst used in this research is temperature, which was used for increasing the rate of reaction by providing heat into the reaction.

.5 ORDER OF REACTION

If the macroscopic (observed, empirical or phenomenological) rate of reaction ($-r_A$) for any reaction can be expressed by an empirical differential rate equation (or rate law) which contains a factor of the form as shown below:

$$Reaction\ Rate = k\,[A]^{\alpha}\,[B]^{\beta} \qquad (3)$$

This expression illustrates the full the dependence of the rate of reaction on the concentrations [A], [B]. Where α, β are constant exponents (independent of concentration and time) and k is independent of [A] and [B] etc. (rate constant, rate coefficient), then the reaction is said to be of order a with respect to A, of order b with respect to B, and of (total or overall) order $n = \alpha + \beta$ The exponents α, β, can be positive or negative integral or rational non-integral numbers. They are the reaction orders with respect to A, B, and are sometimes called 'partial orders of reaction.

Orders of reaction deduced from the dependence of initial rates of reaction on concentration are called 'orders of reaction with respect to concentration'; orders of reaction deduced from the dependence of the rate of reaction on time of reaction are called 'orders of reaction with respect to time'.

Chemical reactions are classified based on their reaction kinetics. The general reaction form is:

$$aA + bB \rightarrow cC + dD$$

Reactions are categorized as zero-order, first-order, second-order, or mixed-order (higher-order) reactions.

.5.1 Zero-Order Reactions

Zero-order reactions (order = 0) have a constant rate. This rate is independent of the concentration of the reactants. The rate law is:

Rate = k, with k having the units of M/sec.

.5.2 First-Order Reactions

A first order reaction (order = 1) has a rate proportional to the concentration of one of the reactants. A common example of a first-order reaction is the phenomenon of radioactive decay. The rate law is:

Rate = $k[A]$ (or B instead of A), with k having the units of sec^{-1}

5.3 Second-Order Reactions

A second-order reaction (order = 2) has a rate proportional to the concentration of the square of a single reactant or the product of the concentration of two reactants:

Rate = $k[A]^2$ (or substitute B for A or k multiplied by the concentration of A times the concentration of B), with the units of the rate constant $M^{1}sec^{-1}$

.5.4 Mixed-Order or Higher-Order Reactions

Mixed-order reactions have a fractional order for their rate:

e.g. rate = $k\,[A]^{1/3}$

However, the order of a reaction is dependence on the concentration of a specific reactant, i.e. how many molecules of the reactant are involved in the reaction, and the rate of a reaction is proportional to the product of the concentrations of the individual reactants raised to the power of the order for the reactant.

.6 FACTORS THAT AFFECT REACTION RATE

2.6.1 Concentration of Reactants

A higher concentration of reactants leads to more effective collisions per unit time, which leads to an increasing reaction rate (except for zero order reactions). Similarly, a higher concentration of products tends to be associated with a lower reaction rate. Use the partial pressure of reactants in a gaseous state as a measure of their concentration.

2.6.2 Temperature

Usually, an increase in temperature is accompanied by an increase in the reaction rate. Temperature is a measure of the kinetic energy of a system, so higher temperature implies higher average kinetic energy of molecules and more collisions per unit time. A general rule of thumb for most (not all) chemical reactions is that the rate at which the reaction proceeds will approximately double for each 10°C increase in temperature. Once the temperature reaches a certain point, some of the chemical species may be altered (e.g., denaturing of proteins) and the chemical reaction will slow or stop.

2.6.3 Medium

The rate of a chemical reaction depends on the medium in which the reaction occurs. It may make a difference whether a medium is aqueous or organic; polar or non-polar; or liquid, solid, or gaseous.

2.6.4 Presence of Catalysts and Competitors

Catalysts (e.g., enzymes) lower the activation energy of a chemical reaction and increase the rate of a chemical reaction without being consumed in the process. Catalysts work by increasing the frequency of collisions between reactants, altering the orientation of reactants so that more collisions are effective, reducing intermolecular bonding within reactant molecules, or donating electron density to the reactants. The presence of a catalyst helps a reaction to proceed more quickly to equilibrium. Aside from catalysts, other chemical species can affect a reaction. The quantity of hydrogen ions (the pH of aqueous solutions) can alter a reaction rate. Other chemical species may compete for a reactant or alter orientation, bonding, electron density, etc., thereby decreasing the rate of a reaction.

.7 VELOCITY DISTRIBUTION IN A CIRCULAR TUBE

The flow of the Sodium Hydroxide solution and the aqueous solution of both Methyl and Ethyl Acetate from the Tanks into the Continuous Stirred Tank Reactor can be of a Laminar or Turbulent type. However, for this particular process the flow has been considered to be a turbulent, in which the velocity in fluctuating with time chaotically at each point of the tube.

MODE OF HEAT TRANSFER

Heat transfer is the movement of energy due to a temperature difference. There are three physical mechanisms or modes of heat transfer; conduction, convection, radiation. Heat normally flows from an area of higher temperature to a region of lower temperature. Heat can be made to flow from a cooler area to a hotter area, but this is not a spontaneous phenomena, work must be done on the system. Commonly found examples of this are refrigerators and heat pumps.
The conduction mode of heat transfer occurs when there is a temperature difference in a stationary medium. On a molecular level, the high temperature area has a higher vibrational energy, and this energy is transferred molecule to molecule to the cooler region. There is no movement in the bulk media. An example of this is when the experiment is run at higher temperature. When the solution is heated, the inside wall of the CSTR temperature is raised. The increased vibrational energy is diffused through the wall until the warmth of the solution is felt on the outside surface.

Convection occurs when heat is transferred due to diffusion and bulk motion, most commonly between a fixed surface and a moving fluid, liquid or gas. Convection is further subdivided into free convection and forced convection. For free convection, the flow of the fluid is induced by buoyancy forces, whereas in forced convection the fluid flow is due to some outside means such as a fan, blower, or pump. An example of free convection is the draft felt by an oven door. At the oven door surface, heat is diffused into the air. The increased temperature of the air causes it to expand. As it expands, it has a lower density than the cooler surrounding air causing it to rise. As the air moves up, heat is transported away from the oven door. An example of forced convection can be found under the hood with the car radiator. Air is forced by a fan over the fins of the radiator which has been heated by the engine coolant. Heat is diffused into the air as it comes into contact with the surface of the radiator, and is then transported away by the bulk motion of the air flow (Neil B.Farnam, 1965).

9 RELATIONSHIP BETWEEN CONDUCTIVITY AND CONCENTRATION

The Conductivity of s solution is the ability of the solution to conduct an electric current between two electrodes. In solution, the current flows by ion transport. Therefore, an increasing concentration of ions in the solution will result in higher conductivity values (Vernier 1996). The probe is actually measuring *resistance*, defined as the reciprocal of conductance. When resistance is measured in ohms, conductance is measured using the SI unit, *siemens* (S). Since the siemens is a very large unit, aqueous samples are commonly measured in microsiemens, μs.

Therefore, the conductivity of a solution is proportional to its ion concentration. In some situations however, conductivity may not correlate directly to concentration. The graphs below illustrate the relationship between conductivity and ion concentration for two common solutions. Notice that the graph is linear for both sodium chloride solution, and sodium hydroxide solution. Ionic interactions can alter the linear relationship between conductivity and concentration in some highly concentrated solutions.

For this research project, all the conductivity data taken are in (mS) unit, in order to convert the data into concentration value, the correlation between the conductivity and the concentration for sodium hydroxide and sodium chloride. A few samples are prepared, with fixed volume of water (0.5L) while changing the mass of the samples (NaCl and NaOH) and the conductivity values are taken. The conductivity values are recorded for each increasing mass of the samples. A graph of concentration versus conductivity is plotted as shown in figure, and the equation obtained is to be used for further calculation. Even though an already equations have been developed to convert the conductivity values to concentration by the Armfield software, however for the research purposes only, the experiments are conducted.

.10 CONTINUOUS STIRRED TANK REACTOR (CSTR)

A continuous Stirred Tank Reactor, also known as a perfectly mixed flow reactor always have inlet and outlet streams. These reactors are some time classified as a homogenous or a heterogeneous reactor. They are often operated at a steady state, that is, the mass flowrate into the reactor is equal to the mass out of the reactor, and the temperature and concentrations at all points in the reactor are assumed to be constant, although this is not always achieved is industrial application due to certain factors such as ambient temperature and the preset operating condition.

However, unsteady state operating condition may be used under certain circumstances and will prevail during startup, shutdown or after any change in certain operating variables. In addition, these reactors vary widely in configuration and are mostly classified according to their internal flow patterns such as ideal flow patterns and a non-ideal flow patterns.

However, in an ideal perfectly mixed reactor, the mixing inside the reactor is assumed to be complete, thus both the temperature and concentration of all of the chemical spices are the same at every point inside the reactor. As a result of this uniform composition distribution is that the temperature and the composition of the effluent steam is the same as that in the reactor.

These reactors are usually consists of stirred tank, baffles at the wall to enhance turbulence and hence the level of mixing as shown below. They also consist of impellers and the common types used in industrial applications are the propeller and the Rushton turbines. Sizing of the tank and their impellers owes a lot of experience and empirical data.

In addition, continuous stirred tank reactors are commonly used for liquid phase reactions, although it's also used for some gas phase reactions. However, perfectly mixing is mostly achieved in a liquid phase reactions where the flowing fluid has a low viscosity and simple flow pattern behaviour. Moreover, reactions involving highly viscous non-Newtonian fluids usually require a considerably special consideration, and perfect mixing is rarely conducted in stirred tank reactors.

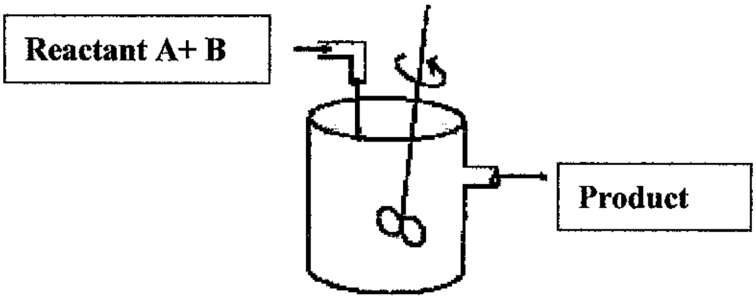


Figure 1: A Continuous Stirred Tank Reactor (Levenspiel, 1999)

The classical single-phase homogeneous CSTR model was first introduced through the famous work of Bodenstein and Wolgast (1908) in order to determine reaction rates in flowing fluid from measured exit conversion. These ideal CSTR equations containing only one mode (exit concentration or temperature) are based on the a priori assumption of perfect mixedness at all scales starting from macro (reactor) down to micro (local diffusion), which may not be satisfied in many practical cases. Nevertheless, over the years this model has become the most popular one among the chemical engineering practitioners due to its simplicity and ease of computation. It has also been extended to multiphase gas–liquid or gas–liquid–solid reactors on the basis of heuristic arguments. However, the incapability of these classical CSTR equations to capture the influence of finite mixing effects on the reactor performance posed one of the greatest challenges to chemical engineers.

Since in this project, CSTR is the preferred reactor used in the production of Methanol by Saponification Reaction, and CSTR is often treated as an ideal reactor as mentioned before, although in reality non-ideality in common occurrence. Then, an ideal CSTR has complete backmixing resulting in a minimisation of the substrate concentration, and a maximisation of the product concentration, relative to the final conversion, at every point within the reactor the effectiveness factor being uniform throughout.

Therefore, Reaction kinetics is the most important parameter in designing this reactor. 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) as shown below:

Irreversible bimolecular type second order reaction

$$A + B \longrightarrow \text{Product(s)}$$

With corresponding rate equation

$$-r_A = -\frac{dCA}{dt} = -\frac{dCB}{dt} = kC_AC_B \tag{4}$$

Noting that the amount of A and B that have reacted at any time t are equal and given by $C_{AO}X_A$, where XA is the conversion of the reactant A, the equation may be written as:

$$-r_A = C_{AO}\frac{dxA}{dt} = k[(C_{AO} - C_{AO}X_A)(C_{BO} - C_{AO}X_A)] \tag{5}$$

By assuming $M = C_{BO}/C_{AO}$ be the initial molar ratio of the reactant, then

$$r_A = C_{AO}\frac{dxA}{dt} = k\,C_{AO}^2(1 - X_A)(M - X_A) \tag{6}$$

By integrating equation (6) yield:

$$\int_0^{XA} \frac{dXA}{(1-XA)(M-XA)} = C_{AO}k\int_0^1 dt \tag{7}$$

After integrating the equation (7), then the final result in a number of different forms are

$$\ln\frac{1-X_B}{1-X_A} = \ln\frac{M-X_A}{M(1-X_B)} = \ln\frac{C_B C_{BO}}{C_B C_A} = C_{AO}(M-1)kt = (C_{BO} - C_{AO})kt \tag{8}$$

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.

11 RESIDENCE TIME DISTRIBUTION (RTD)

The residence time is the length of time that a chemical spices spends in the reactor. However, not all the molecules that enter the reactor spend the same length of time in the reactor, and thus for any given reactor there exist a distribution of residence time. Thus, this distribution residence time is termed the Residence Time Distribution (RTD), However, the average length of time that molecules spend in the reactor is termed the Mean Residence Time Distribution, t_m.

The concept of residence time distribution (RTD) is applied to incompressible fluids in closed-closed systems under nonsteady conditions, the residence time distribution expressed as a function of a residence time, is independent of the volume and/or the flow rate. Thus, RTD is defined as the period of time a molecule or atom spent to pass through the reactor. Some of the molecules usually leave quickly and some overstay. This concept was first being studied and proposed by MacMullin and Weber back in 1930s and in 1953 respectively, and the organizational structure to the subject was prepared by P.V. Danckwerts. However, Residence time distribution (RTD) curve is mainly used to characterize the behavior of reaction systems, especially continuous reactors at steady state, (Levenspiel, 1962; Fogler, 1992 ;) The measurement of RTD is based on the injection of a tracer material in the system and subsequent determination of the tracer concentration in the fluid leaving the system. Two different methods are used:

11.1 Injection of the tracer in a very short time interval at the entrance of the system (pulse injection).

11.2 Introduction of a concentration change in the form of a step function and © introduction of a periodic concentration fluctuation in the inflow.

From the information obtained from any of these methods, the behavior of a certain element of fluid can be known when steady-state conditions are considered.

However, the above methods are considered usually when the inlet flow into a Continuous Stirred Tank Reactor (CSTR) is the same and the system volume remains constant. Even though the system is considered to be operating at a steady state, in many occasions the flow is not constant and the volume is variable. When this scenario happens, two phenomena affect the model flow;

11.3 The inlet flow is the same as the outlet flow, for any time, although the flow varies with time, therefore, the volume of the system is constant.

11.4 As the inlet flow is different from the outlet flow, the volume of the system also changes.

Therefore, when a tracer injection is used in this type of system, the RTD will be modified by random flow and/or volume changes. Nevertheless, in spite of these phenomena, the system flow can be approximately characterized as that a reduced time is independent of the volume and/or the flowrate.

Generally, the feed into a CSTR is introduced at any given time and the feed material (The Tracer) is completely mixed with the material already in the reactor. Since, material is being withdrawn continuously from reactor, then some of the atoms entering the CSTR leave it immediately, 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:

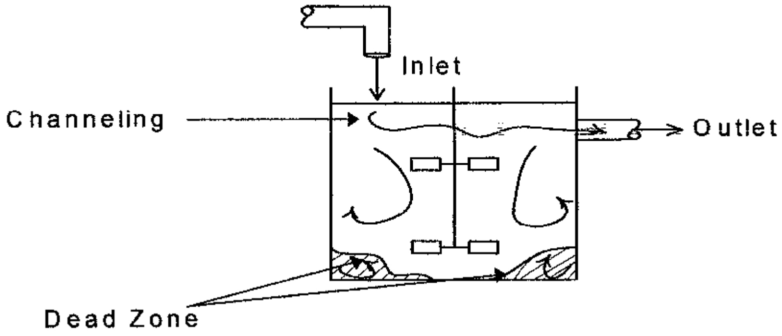


Figure 2: CSTR with Dead Zones and Channeling (Levenspiel, 1999)

12 MEASURING OF RTD IN A CSTR

The residence time distribution is usually measured an inert tracer. A tracer is a material that is non-reactive, non-adsorbing and has properties that closely resemble the spices for which it is desired to have the residence time distribution. The tracer always has a distinguished feature that makes it possible to measure its concentration easily. It might a coloured dye whose concentration can be measured using a spectrometer or a radioactive species that is monitored by using scintillation counting. If a simple system of a fixed volume with one entrance and one exit is considered, and a finite quantity of tracer is injected into the inlet of the system.

The tracer molecules flow through the system and exit over some period of time (RTD principle) until finally all of the tracer molecules leave the system. Depending on the flow pattern inside the system, the time at which the tracer molecules exit the system may change, and thus the residence time of the tracer molecules has distribution, which depends on the flow pattern in the system. Thus, the residence time distribution is determined by measuring the concentration of the tracer in the effluent system.

.13 RESIDENCE TIME AND MIXING

The existing relationship between the thermodynamic, transport, and kinetics behaviour of any chemical reactor is governed by two main factors, which are classified as follows:

2.13.1 *The amount of time that reactants spend in a reactor*

The factor illustrate that the longer that reactants can spend in the reactor, the more chance there is for them to react and be converted into the desired product. This time, which the molecules spend within the reactor, is termed Residence Time, and the distribution of residence times for feed molecules is an important factor in determining the extent of reaction. Thus, the residence time is in fact a key parameter in flow reactor performance (Fogler, 1999).

2.13.2 *The extent of mixing within the reactor*

The extent of reaction is also a major factor in analyzing/determining the performance of a reactor. For any reaction involving more than one molecule it is necessary that molecular collisions occur at a first step; therefore the concentration at the molecular level is important. However, the degree of mixing depends not only on the reactor configuration and operating condition but also on the fluid and reactants properties. Mixing is a complex phenomenon that is analyzed at several levels or scales, but ultimately it is the mixing at the molecular level that determines the extent of reaction (Fogler, 1999).

14 MODELLING THE RESIDENCE TIME DISTRIBUTION

In analyzing reactors performance, it is always to use the RTD data to predict reactor performance. Thus, in this project, the RTD data was used to model the reactor.

The approach followed was to develop a model flow system which has the same RTD as the pre-existing system. This was done based on the fact that the conversion equation was able to be written for the model system, and thus the performance of the real system was predicted. Since empirical models with one or two adjustable parameters are often used to model the RTD in vessels, then the more adjustable parameters that are used in a model the better the correlation between a predicted and observed RTD will be (R. E. Hayes). However, the adjustable parameters in RTD models are often related to the moments of the RTD and are usually expressed in terms of the dimensionless moments about the mean. The moments about the mean are selected so that the mean residence time is not a variable, and quite often the mean residence time is known or is calculated for other data.

For example, for a constant density fluid the mean residence time is defined by the ratio of the reactor volume to the volumetric flowrate as shown below:

$$t_m = \text{(Reactor Volume) / (Volumetric Flowrate)} = \frac{V}{v_o}$$

15 SEGREGATION MODEL

Segregation is the process by which an entering fluid of different ages into a perfectly mixed CSTR does not mix together at all. 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. Even though in a perfectly mixed reactor, the entering fluid is assumed to be distributed immediately and evenly throughout the reacting system. This mixing as well is assumed to take place even on a very small scale, and the elements of the different ages mix together thoroughly to form a completely micromixed fluid. Microfluid is a fluid in which molecules are free to move every where in the reacting system, and it describe how molecules of different ages mix with one another in a reaction system. However, micromixing is of two main extremes as shown.

I. Mixing in which all molecules of the same age school remain together as they move through the reaction system and are not mixed until they reach a stage of complete segregation

II. Mixing in which molecules of different age types are entirely mixed at the molecular level as soon as they enter the reaction system.

The above main two extremes of micromixing yield the upper and lower limit of conversion in a non-ideal reaction system. However, the stage of complete micromixing and segregation are the limits of micromixing of a reacting mixture (Fogler, 1999). Since the concept of mixing quality is better and easily defined in a CSTR, then, a CSTR is mainly considered while designing a segregation model. Segregated flow through a reaction system is considered to be consisting of a continuous series of globules as shown in figure 3a & 3b. However, in segregation model, globules behave as batch reactors operated for different times.

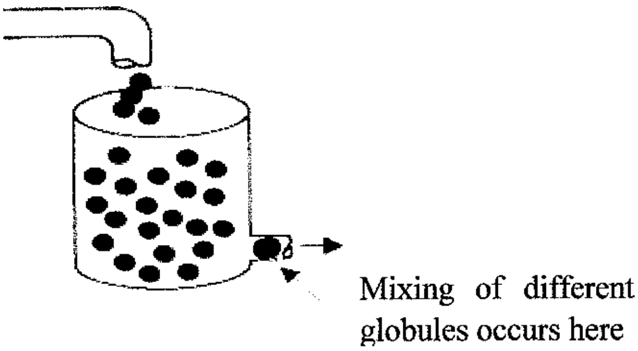


Figure 3a: Globules inside a CSTR. (Fogler, 1999)

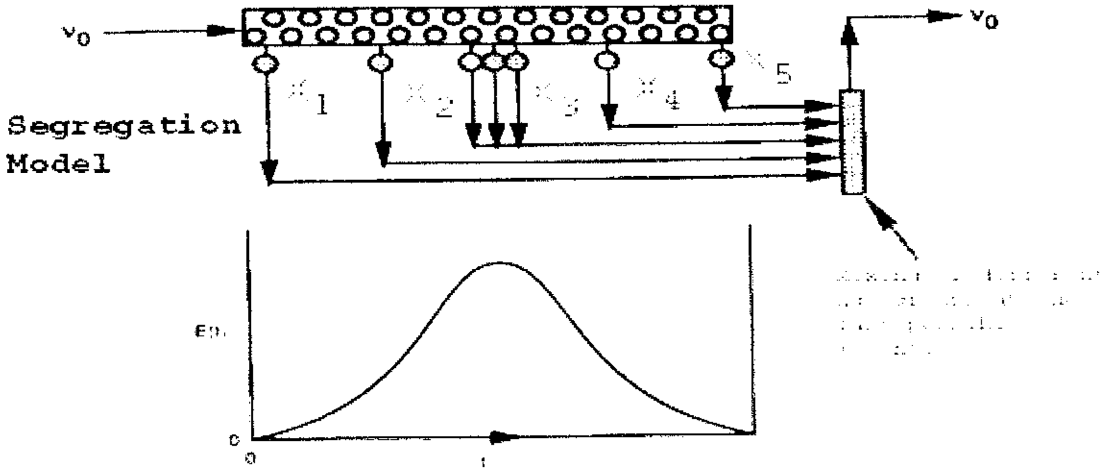


Figure 3b: Mixing occurs at the latest possible point. Each little batch reactor (globule) exiting the real reactor at different time will have different conversion, X. (Fogler, 1999).

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

$$d\bar{X} = X(t)\cdot E(t)dt$$

$$\bar{X} = \int_0^\infty X(t)E(t)dt \tag{8}$$

For second order reaction:

$$A + B \rightarrow C + D$$

For a batch reactor, $$-\frac{dN_A}{dt} = -r_A V = V k C_{A0}^2 (1-X)^2$$

This on arrangement becomes:

$$X = \frac{kC_{A0}t}{1+kC_{A0}t} \tag{9}$$

16 MAXIMUM MIXEDNESS

Maximum mixedness model is a model in which mixing takes place at the earliest possible point as shown in Figure 4, 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 Maximum mixedness in which reactors consist of side entrance, mixing occurs at the earliest possible moment consistent with the RTD. This effect is the maximum mixedness.

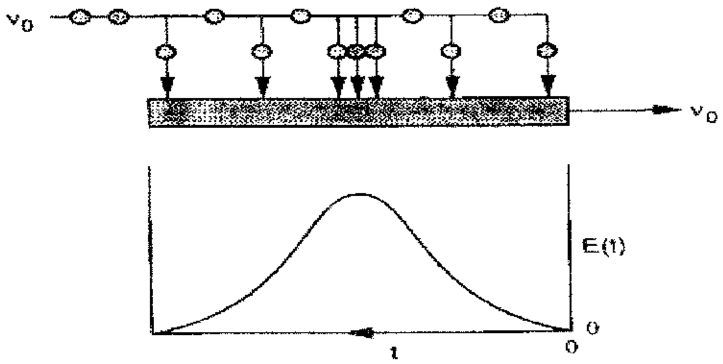


Figure 4: Mixing occurs at the earliest possible moment (Levenspiel, 1999).

If the life expectancy of the fluid in the reactor at that point is termed λ, Then, λ will decrease and become zero at the exit point as the globules moves down the reactor. The conversion of maximum mixedness model can be calculated using the Euler method for numerical integration for second order system:

$$X_{i+1} = X_i + (\Delta\lambda)\left[\frac{E(\lambda_i)}{1-F(\lambda_i)}X_i - kC_{A0}(1-X_i)^2\right] \tag{10}$$

17 TANKS IN SERIES MODEL

The tanks in series model consist of N equally sized perfectly mixed stirred tank reactors in series. The value of N is usually selected so as to match as closely as possible an expected RTD. Thus, in this project, three equally sized tank reactors in series through which a constant density flowing fluid giving an equal space time (mean residence time) for each reactor were used. At time zero, a pulse tracer was injected into the first reactor. This tracer instantaneously becomes uniformly distributed in the first tank, giving an initial concentration of C_0. The overall mathematical analyses are as shown below:

Thus, the principle of tanks in series model is to describe non-ideal reactor and calculate conversion. The analysis of RTD is used to determine the number of tanks in series that will give approximately the same RTD as the non-ideal reaction system.

The real reactor is modeled as a number of equally sized tanks-in-series. Each tank behaves as an ideal CSTR. The number of tanks necessary, n (our one parameter), is determined from the E(t) curve as shown in appendix B.

For n tanks in series, E(t) is;

$$E(t) = \frac{t^{n-1} e^{-t/\tau_i}}{(n-1)!\,\tau_i^{\,n}}$$

Where; $\tau_i = \frac{\tau}{n}$

It can be shown that $t_m = \tau = n\tau_i$

In dimensionless form $\theta = \frac{t}{\tau} = \frac{t}{n\tau_i}$ Thus, $\theta n = \frac{t}{\tau_i}$

$$E(\theta) = \tau E(t) = \frac{n(n\theta)^{n-1} e^{-n\theta}}{(n-1)!}$$

$$\sigma_\theta^{\ 2} = \frac{\sigma^2}{\tau^2} = \frac{\int_0^\infty (t-\tau)^2 E(t) d\tau}{\tau^2}$$

$$\sigma_\theta^{\ 2} = \frac{\sigma^2}{\tau^2} = \int_0^\infty (\theta - 1)^2 E(\theta) d\theta$$

Carrying out the integration for the n tanks-in-series E(t).

$$\sigma_\theta^{\ 2} = \frac{\sigma^2}{\tau^2} = \frac{1}{n}$$

Therefore; $$n = \frac{\tau^2}{\sigma^2} \qquad (11)$$

The conversion of a first order reaction is given as shown below.

$$X = 1 - \frac{1}{(1 + \tau_i k)^n} \qquad (12)$$

$$\tau_i = \frac{\tau}{n}$$

18 REAL CSTR MODELED BY USING BYPASSING AND DEAD SPACE

The main objective in designing this type of reactor is to model a real reactor with combinations of an ideal CSTR of volume v_S, a dead zone of volume V_d, and a bypass with a volumetric flowrate v_0 as shown in figure 5.

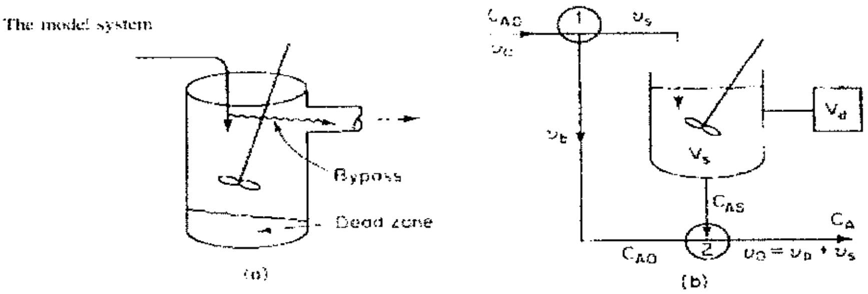


Figure 5: Real CSTR modeled using ideal CSTR, bypass and dead space (http://www.engin.umich.edu/~cre/course/lectures/thirteen)

This model is used for calculating the conversion for the below shown chemical reaction, assuming the order of the reaction is a first order reaction.

$$A \longrightarrow B$$

The bypass stream and effluent stream from the reaction volume are mixed at joint 2. From a balance on species A around this point is driven as shown below.

$$C_{AO}V_b + C_{AS}V_s = C_A(V_b + V_s)$$

Therefore, the concentration of A leaving the reactor as follows,

$$C_A = \frac{V_b C_{AO} + C_{AS}V_S}{V_b + V_s} = \frac{V_b C_{AO} + C_{AS}V_S}{v_0} \tag{13}$$

$$\begin{aligned} v_0 &= v_s + v_b \\ v_b &= \beta v_0 \\ V &= V_d + V_s \\ V_s &= \alpha V \end{aligned}$$

Where; α = the fraction of volume that is well-mixed (alpha)

$$\alpha = \frac{V_s}{V}$$

β = the fraction of the stream that is bypassed (beta)

$$\beta = \frac{V_b}{V_0}$$

$$V_s C_{AO} - V_s C_{AS} + r_{AS} V_s = 0$$
$$(1-\beta) C_{AO} - (1-\beta) C_{AS} + r_{AS} \alpha \tau = 0$$

$$\Rightarrow -r_{AS} = k C_{AS}$$

Combining

$$C_{AS} = \frac{(1-\beta) C_{AO}}{(1-\beta) + \alpha \tau K}$$

$$V_o C_A = V_s C_{As} + V_b C_{AO}$$
$$C_A = (1-\beta) C_{As} + \beta C_{AO}$$

Therefore ;

$$\frac{C_A}{C_{AO}} = \beta + \frac{(1-\beta)^2}{(1-\beta) + \alpha \tau K} = 1 - x \qquad (14)$$

9 REAL CSTR MODELED AS TWO CSTR INTERCHANGE

This model is modeled from two CSTR interchange, which has a considerable material transfer between the two interchange reactors. It has a highly agitated region in the vicinity of the impeller, while there exist a region with a less agitation in the outside the agitated region. Both the inlet and the outlet channels of the interchange reactors are connected to the highly agitated region. Figure 6a& 6b, shows a real reaction system and a modeled reaction system of two interchange reactors.

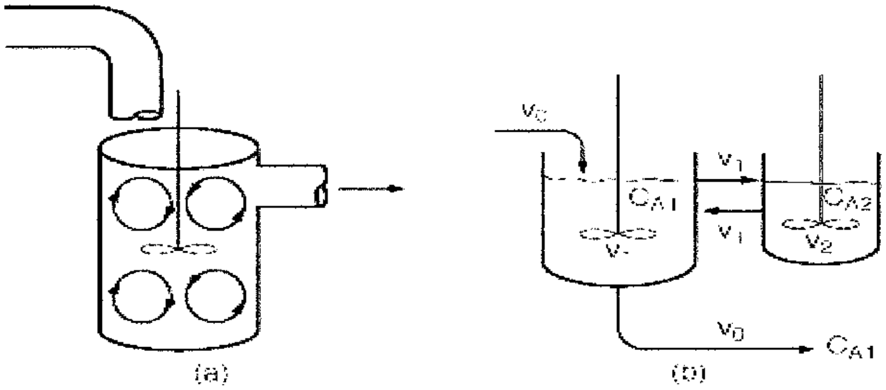


Figure 6: Model of a real CSTR as two CSTRs interchange (Fogler, 1999)

Assumptions:

The volume of Reactor 1 $=V_1$

The volume of Reactor 2 $=V_2$

β = fraction of the total flow which exchanges between reactor 1 and reactor 2

α = fraction of the total volume V occupied by the highly agitated region

Where;

$$\alpha = \frac{V_1}{V}$$

$$\beta = \frac{V_1}{v_o}$$

$$\textit{Therefore} \; ;$$

$$V_2 = (1-\alpha)V$$

Then, the space time is given as follows: $\tau = \dfrac{V}{v_0}$

If a first order reaction is considered, then, the exit concentration from reactor 1 and conversion after derivation is as shown below.

$$C_{A1} = \frac{C_{A0}}{1+\beta+\alpha\tau k - [\beta^2/[\beta+(1-\alpha)\tau k]} \quad \text{(Exit Concentration from reactor 1 after recycles)}$$

$$X = 1 - \frac{C_{A1}}{C_{A0}} = \frac{(\beta+\alpha\tau k)[\beta+(1-\alpha)\tau k]-\beta^2}{(1+\beta+\alpha\tau k)[\beta+(1-\alpha)\tau k]-\beta^2} \quad \text{(Conversion for the two CSTR model)}$$

0 FEMLAB

FEMLAB is a modelling package for the simulation of any physical process that can be described with partial differential equations (PDEs). It features state-of-the-art solvers, which addresses complex problems quickly and accurately, while it's intuitive structure is designed to provide ease of use and flexibility. The FEMLAB graphical user interface combines the ability to run ready made application in a variety of physics fields with equation based modelling.

Thus, this application is a mathematical tool used for describing and solving partial differential equations. However, the applications used in this research project describe the exothermic reaction of ethyl/methyl acetate with sodium hydroxide (ester hydrolysis) in a continuous stirred tank reactor. The system is described by four differential equations on a two dimensional surface. The surface represents a cross-section of the tubular reactor in the z-r-plane. Because of axial symmetry, the borders of the two dimensional surface represent the inlet, outlet, center, and wall of the reactor. The partial differential equations represent two mass balances, one energy balance, and one ordinary differential equation describes the axial variations of heat flux to the cooling jacket. Parameters such as flow rate and activation energy are used to describe the conditions of the reactor. Changing these parameter values allows users to explore and analyze the performance of the reactor.

The main object of this application is for the user to solve the system, change the parameters, and observe the results for several different conditions. There are two different sets of equations. One set of equations for turbulent flow, and one set for laminar flow. The gas phase model uses the set of equations for turbulent flow, while the liquid phase model uses either set, depending on the value of the Reynolds number.

Running the application solves the system of partial differential equations and displays the solution as colored graphs, showing the concentration and temperature profiles of a cross-section of the reactor. However, the solution may not be completely satisfactory sometimes. There may be negative concentrations, large variations in small areas, or other unreasonable results. This problem may sometimes arise from the parameters of the reaction that cause the equations to become stiff, but in most cases the reason is that FEMLAB is not able to solve the system correctly in its current form. The model will need some altering to achieve a satisfactory solution.

1 HEAT TRANSFER ACROSS THE REACTION SYSTEM (CSTR)

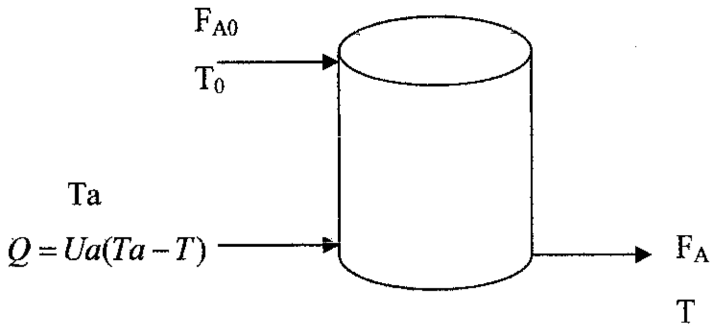


Figure 7: Heat transfer between CSTR and ambient

Mole balance for an adiabatic CSTR shown in figure 7:

$$V = \frac{F_{A0}X}{-r_A}, \frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

$$-r_A = kC_A{}^2 = kC_{A0}{}^2(1-X)^2$$

$$C_A = C_{A0}(1-X), F_{A0} = C_{A0}v_0, \tau = \frac{V}{v_0}$$

$$V = \frac{F_{A0}X}{kC_A{}^2(1-X)^2}, \tau = \frac{1}{kC_{A0}}\frac{X}{(1-X)^2}$$

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

$$\tau kC_{A0} - 2\tau kC_{A0}X + \tau kC_{A0}X^2 = X$$

$$\tau kC_{A0}X^2 - X(2\tau kC_{A0} + 1) + \tau kC_{A0} = 0$$

$$X = \frac{(2\tau kC_{A0} + 1) - \sqrt{(2\tau kC_{A0} + 1)^2 + 4(\tau kC_{A0})^2}}{2\tau kC_{A0}}$$

$$X = \frac{2\tau kC_{A0} + 1 - \sqrt{4(\tau kC_{A0})^2 + 4\tau kC_{A0} + 1 - 4(\tau kC_{A0})^2}}{2\tau kC_{A0}}$$

$$X = \frac{2\tau kC_{A0} + 1 - \sqrt{4\tau kC_{A0} + 1}}{2\tau kC_{A0}}$$

$$Assume, M = \tau kC_{A0}$$

$$X_{MB} = \frac{(2M+1) - \sqrt{4M+1}}{2M}$$

Energy balance for an adiabatic CSTR shown in figure 7:

Assume the amount of heat added into the reaction system per a unit mole of reactant A is given by the general equation of energy balance as shown below, the heat added and lost to the surrounding is due to temperature difference between the ambient and the reaction.

General Energy Balance equation:

$$Q - W_s + \sum F_{i0}E_{i0}\big|_{in} - \sum F_iE_i\big|_{out} = \frac{dE_{system}}{dt} \qquad (15)$$

$$E_i = H_i - PV_i,$$
$$H_i = U_i - P_iV_i \Rightarrow E_i = U_i$$

$$H_i = H_i^o(T_R) + \int_{T_R}^{T} \Delta C_p dt$$

$$\Delta H_R(T) = \Delta H_R^{\,o}(T_R) + \Delta C_p(T - T_R) \qquad (16)$$

Adding Equation 15 and 16 and rearranging gives the following,

$$Q - W_s - F_{A0}X[\Delta H_R{}^o(T_R) + \Delta C_p(T - T_R)] = F_{A0}\sum \Theta_i \Delta C_p (T - T_{i0})$$

(17)

Solving equation (17) with respect to T for an adiabatic state gives the following.

$$T = T_0 - \frac{X[\Delta H_R{}^o(T_R) + \Delta C_p(T - T_R)]}{\sum \Theta_i C_{pi} + X\Delta C_p} = T_0 - \frac{X[\Delta H_R(T_0)]}{\sum \Theta_i C_{pi} + X\Delta C_p} \qquad (18)$$

For constant heat capacities, equation (18) with respect to conversion X is given as follows:

$$X = \frac{\sum \Delta C_p (T - T_{i0})}{-\Delta H_R} \qquad (19)$$

If the work done on the reacting fluid is assumed to be zero, then differentiating equation (17) with respect to volume V and rearranging gives the following.

$$\frac{dQ}{dV} - [F_{A0}X[\Delta H_R{}^o(T_R) + \Delta C_p(T - T_R)]]\frac{dX}{dV} = F_{A0}\sum \Theta_i \Delta C_p (T - T_{i0})\frac{dT}{dV} \qquad (20)$$

Where,

$$\frac{dQ}{dV} = Ua(Ta - T)$$

If the work term is neglected and the value of $\frac{dQ}{dV}$ is substituted into equation (20) and rearrange, then the equation will be as follows:

From mole balance, $\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$.

$$\frac{dT}{dV} = \frac{Ua(Ta - T) + (rA)(-\Delta H_R(T_R))}{F_{A0}\sum \Theta_i C_{pi} + X\Delta C_p)} \qquad (21)$$

Where;

ΔC_p: Change in specific heat capacity between the un-reacted reactant and the completely converted product stream

Ti0: Initial temperature of the reaction system

ΔH_R: Heat of reaction per mole of entering reactant A, and temperature T

W_s: Work done on the reacting fluid (Ws = 0)

F_{A0}: Molar flowrate

CHAPTER 3

METHODOLOGY / PROJECT WORK

PROCEDURE IDENTIFICATION

This Project is divided into three interconnected parts as shown below.

Experimentation on Saponification Reaction of Methyl Acetate and Ethyl Acetate at various initial reactant concentrations and temperature modeling of a real Methanol and Ethanol Reactor by thoroughly considering the effect of dead zone and channeling, whereby the residence time distribution (RTD) function will be employed in characterizing the non-ideality of the reactor; Simulation of a transient Saponification reaction by using FEMLAB

In the first part of the project, three experiments are conducted as shown below;

1. Determination of Rate Constant in CSTR
2. Determination of an inadequate mixing effect on reaction rate
3. Determination of RTD Values (Dynamic Behaviour of CSTR)

However, the main applications to be studied are;

Production of Methanol by using the following principles

1. Segregation model
2. Maximum Mixedness
3. Real CSTR with bypass and dead-space

Production of Ethanol by using the following principles

1. Tanks in series
2. Real CSTR modeled as two CSTR interchange

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 also be calculated from these data.

In the second and the third part, which is the real reactor modeling and simulating parts, 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.

TOOLS/EQUIPMENT/SOFTWARE REQUIRED

No	Equipment	Frequency of usage (hours per Week)	Remarks
1	CSTR With Hot Water	10 –16	Usable
2	Tanks in Series	10 –16	Usable
3	CSTR dynamic	10 –16	Usable
4	Gas chromatography (GCMS)	1 –2	Usable
5	FEMLAB	5 –10	Usable

CHEMICALS/MATERIALS REQUIRED

No	Chemicals/Materials	Quantity	Purity (%)
1	NaOH	100L of 0.1M solution	99.0
2	Ethyl Acetate	100L of 0.1M solution	99.0
3	Methyl Acetate	100L of 0.1M solution	99.0
4	Methanol	2L of 0.1M solution	99.8
5	Ethanol	2L of 0.1M solution	99.8
6	Dichloromethane	2L of 0.1M solution	99.5
7	NaCl (Solid)	1kg	98.0
8	Distilled Water	100L	Distilled

TANKS IN SERIES

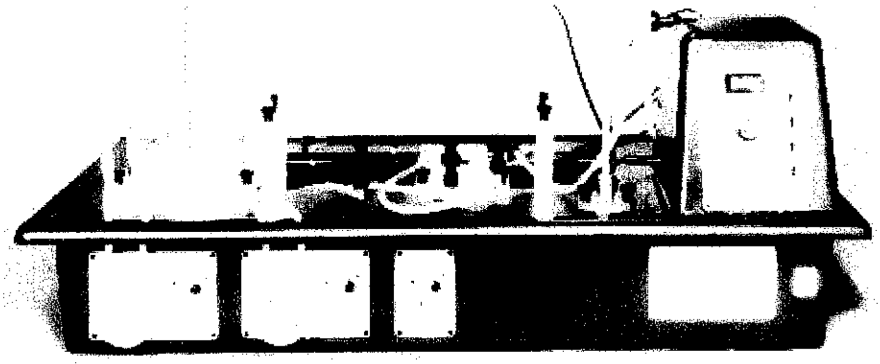


Figure 8: Equipment for Tanks in series (Armfield) (*www.armfield.co.uk/pdf_files/cex.pdf*).

3.4.1 TECHNICAL DESCRIPTION

The Armfield Stirred Tank Reactors in Series unit is designed to follow the dynamics of the perfectly mixed multi-stage process. Dynamic behaviour can be studied as can multi-stage chemical reaction. Bench mounted and self contained, the unit requires only being connected to a single phase electrical supply for operation. There are three reactor vessels connected in series, each containing a propeller agitator driven by a variable speed electric motor. Two reagent vessels and two variable speed feed pumps feed reagents into the first reactor in line. For certain experiments the feed can be connected to the third reactor and a dead-time coil, also positioned on the vacuum formed plinth. Each reactor and the exit port of the dead-time coil are fitted with conductivity probes for monitoring the process. Conductivity is displayed on a digital meter on the console through a selector switch and all four probes can be connected to the optional Armfield data logging accessory.

CSTR WITH HOT WATER CIRCULATION

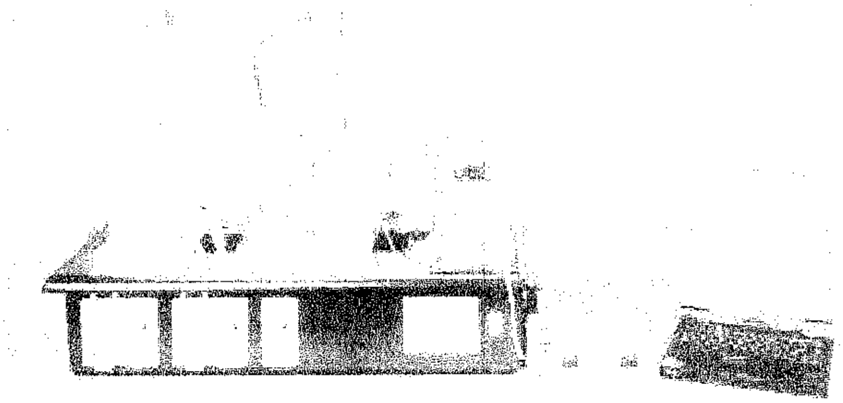


Figure 9: CEX fitted with CEM MKII CSTR with hot water circulation (Lab Manual).

3.5.1 TECHNICAL DESCRIPTION

The series of three reactors is designed to fit interchangeably onto the common Chemical Reactors Service Unit (CEX). Each reactor is mounted on a PVC base which attaches to the service unit by means of thumbnuts.

The appropriate services such as reagent feed pumps, hot water circulator and instrumentation for conductivity and temperature measurement are connected to the reactor. For temperature control, the CEM Mkll and CEB Mkll reactors employ submerged coils through which the heater water is circulated, the CET Mkll reactor coil is itself submerged in the temperature controlled water within the reactor vessel. CEM Mkll and CEB Mkll reactors each incorporate a stirrer driven by a lid-mounted electric motor to provide efficient mixing.

The reactor volume is adjustable with a maximum of 1.5 liters and a minimum of 0.4 liters. The reactor is equipped with a variable speed turbine agitator and baffle arrangement to ensure thorough mixing. A submerged stainless steel coil is used for operating the reactor at different temperatures. Quick release connectors allow easy supply of heat transfer medium to the coil and reagent from the feed pumps of the service unit. Glands in the lid allow fitting of the conductivity and temperature probes of the service unit. Operation at temperatures below ambient is possible.

CHAPTER 4

RESULTS AND DISCUSSION

SAPONIFICATION REACTION ANALYSIS

Saponification is the hydrolysis of an ester under basic conditions to form alcohol and the salt of the acid. However, saponification commonly used to refer to the reaction of a metallic alkali (base) with a fat or oil to form soap. In hydrolysis of an ester, as the reaction proceeds, hydroxide ions are consumed and acetate ions are produced. Hydroxide ion has a very much larger specific conductance than acetate ion. Hence, the alkaline hydrolysis of ethyl acetate and methyl acetate is monitored by following the change in the periodic conductivity readings of the reaction mixture with time. The rate constants is then determined at three different temperatures of 25°C, 30°C and 40°C, so that the activation energy for the reaction is obtained from a plot of lnk versus 1/T.

$$A + B \longrightarrow C + D$$

Assumed a saponification reaction takes place between reactant A and B, in which reactant A and B are acetates (can be ethyl or methyl acetate) and sodium hydroxide which reacts to form product C and D, then the rate law for the saponification reaction illustrates the relationship between reaction rate and concentration (i.e: $-r_A = [k_A(T)][\text{fn } C_A, C_B, \ldots]$). The algebraic equation that relates $-r_A$ to the species concentration is called the kinetics expression or *rate law*. The specific rate of reaction, k_A, like the reaction rate $-r_A$, is always referred to the particular species in the reactions and normally should be subscripted with respect to that species.

The reaction rate constant *k* is determined experimentally as shown in figure 11, not truly a constant but merely independent of the concentrations of the species involved in the reaction. The quantity *k* is also referred to as the specific reaction rate (constant). It is almost always strongly dependent on temperature. In the gas phase, it depends on the catalyst and may be a function of total pressure. In the liquid systems it can also be a function of total pressure, and in addition can depend on other parameters, such as ionic strength and choice of solvent. These other variables normally exhibit much less effect on the specific reaction rate than does temperature , so for the purpose of the material presented here it will be assumed that k_A depends only on temperature. This assumption is valid in most laboratory and industrial reactions and seems to work quite well.

Arrhenius suggested that the temperature dependence of the specific reaction rate, k_A, could be correlated by an equation shown below.

$$k_A = Ae^{-E_a/RT} \qquad \textit{Arrhenius equation}$$

Where

A = pre-exponential factor or frequency factor

E = activation energy, J/mol or cal/mol

R = gas constant = 8.314 J/mol.K = 1.987 cal/mol.K

T = absolute temperature, K

The Arrhenius equation has been verified empirically to give the temperature behavior of most reaction rate constants within experimental accuracy over fairly large temperature ranges. The activation energy E_a has been equated with a minimum energy that must be possessed by reacting molecules before the reaction will occur. From the kinetics theory of gases, the factor e^{-EaRT} gives the fraction of the collisions between molecules that together have this minimum energy E. Although this might be an acceptable elementary explanation, some suggest that E_a is nothing more than empirical parameter correlating the specific reaction rate to the temperature. Nevertheless, postulation of the Arrhenius equation remains the greatest single step in chemical kinetics, and retains its usefulness today, nearly a century later. The activation energy is determined experimentally by carrying out the reaction at several different temperatures. After taking the natural logarithm of Arrhenius equation

$$\ln k_A = \ln A - \frac{E_a}{R(T)}$$

It can be seen that a plot of lnk_A versus $1/T$ should be a straight line whose slope is proportional to the activation energy as shown in figure 12.

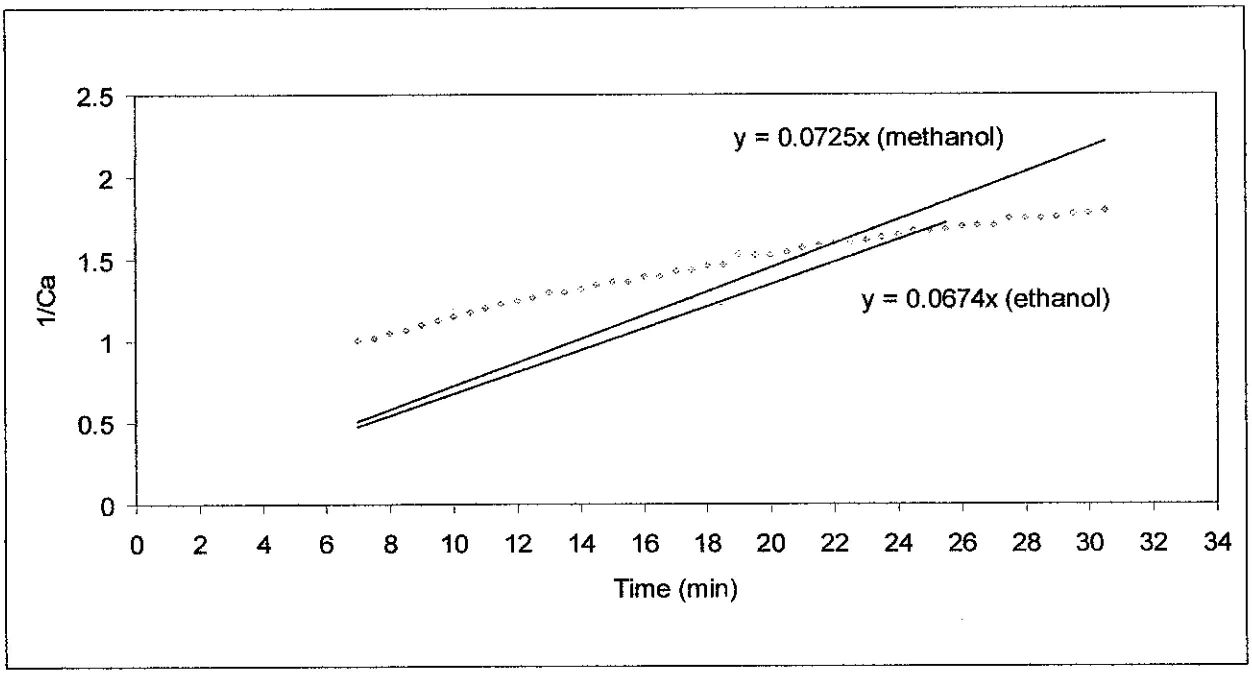


Figure 10: plot of 1/Ca vs. time for the calculation of rate constant "k" (1^{st} order Rxn) at temperature of 25°C.

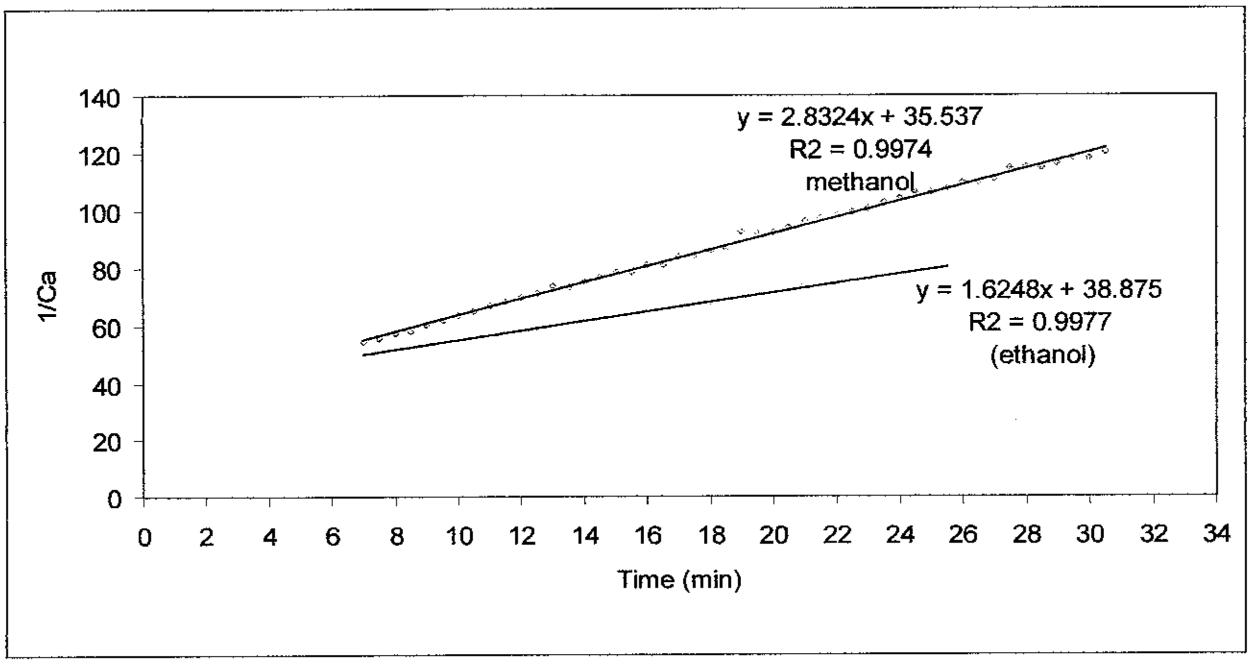


Figure 11: plot of 1/Ca vs. time for the calculation of rate constant "k" (2^{nd} order Rxn) at temperature of 25°C.

Since figure 11 shows a smooth graph with straight line whose slope = 1.6248 for ethanol production and 2.8324 for methanol production. The slope value is the rate constant *k* value. Thus, it is proved that the saponification of both ethyl and methyl acetate is in second order reaction.

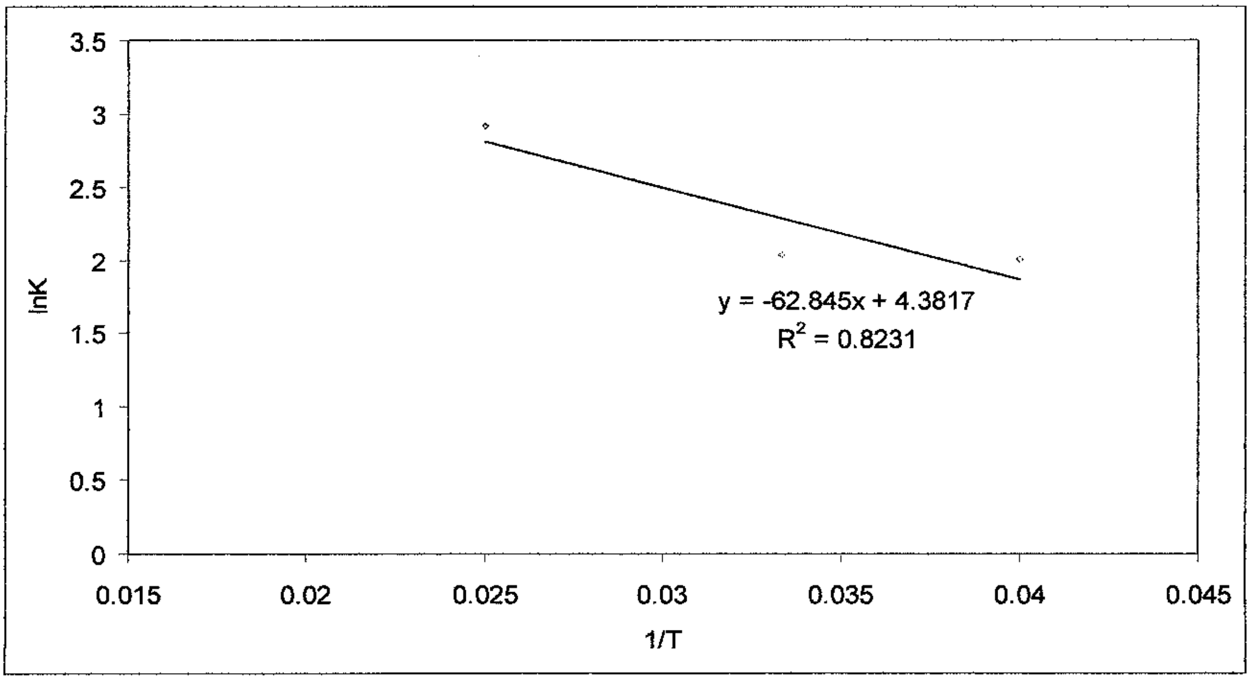


Figure 12: plot of lnk vs. 1/T for the calculation of activation energy "E_a" at temperature of 25°C, 30°C, and 40°C.

$$slope = \frac{-E_a}{R} = -62.845$$

$$E_a = (62.845)(8.314) = 510\frac{J}{mol}$$

$$\ln A = 4.3817$$

$$A = 78.0$$

RESIDENCE TIME DISTRIBUTION FUNCTION

The Residence Time Distribution of the tracer molecules which is obtained from the experimental data analysis is as shown below. This profile which is also the residence time distribution function is expressed by a density function denoted by E(t). This profile is the measurement of the fraction molecules that have a residence time t. This profile is described in terms of probability that the residence time of the tracer molecules lies between time t and t + dt.

The data analysis of step input shows that there is an increase in the conductivity values as the tracer is being injected continuously. While the pulse input illustrate that there is an increase in the conductivity value on the few minutes (two minutes) and then the value started decreasing until it become stable at very low values. The principle behind the deviation is that for the step input, the tracer is being injected continuously to the reactor which filled in with deionised water. At certain point, the conductivity values become stable as shown in figure 13, the conductivity values which is converted to concentration values are plotted against time and after almost 45 minutes, the values started to stabilize. From figure 13, the concentration values increased for the first two minutes and then decreased. However, Pulse input test presence the best way to visualize how the tracer test really works in terms of showing the time the molecule or material has spent within the reactor before exiting. The values started to decrease as time goes by due to the fact that the deionised water is continuously being fed. As the time increases, the sodium chloride molecule is replaced by water molecule and in exits the reactor, and as time passes by, all sodium chloride has been removed or left the reactor, and thus the final concentration of sodium chloride in the reactor approaches zero.

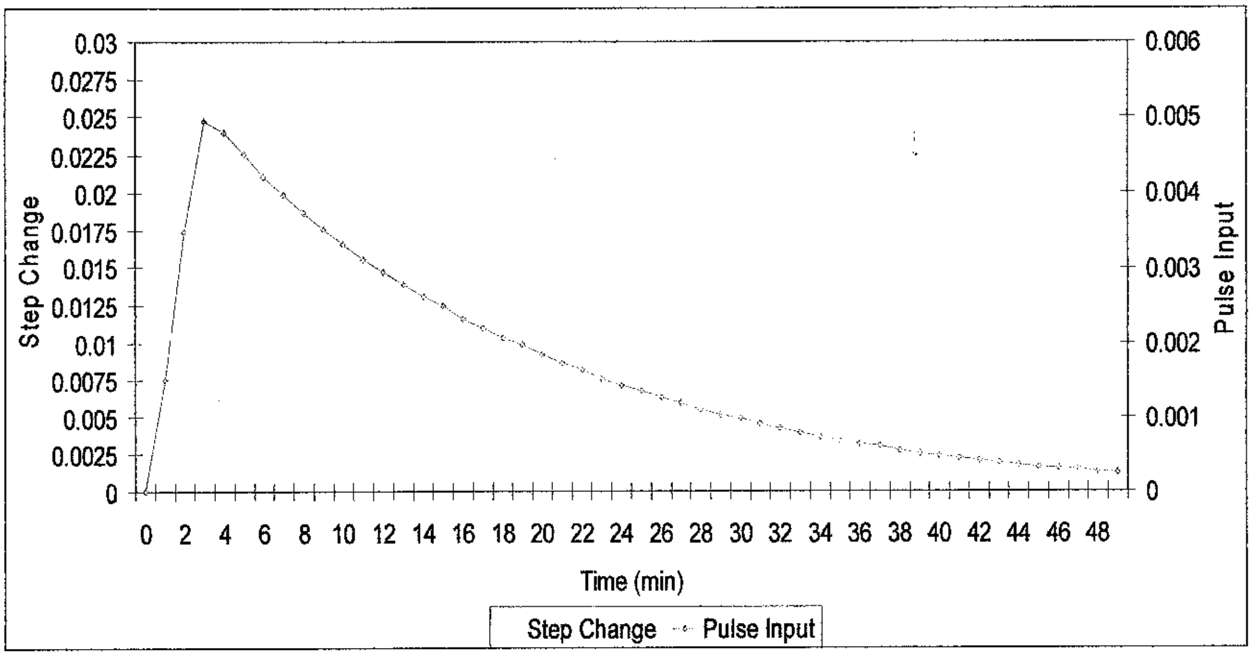


Figure 13: Step Input and Pulse Input Concentration Profile of Sodium Chloride

The residence time distribution is usually measured in an inert tracer. The tracer molecules flow through the system and exit over some period of time (RTD principle) until finally all of the tracer molecules leave the system. Depending on the flow pattern inside the system, the time at which the tracer molecules exit the system may change, and thus the residence time of the tracer molecules has distribution, which depends on the flow pattern in the system. Thus, the residence time distribution is determined by measuring the concentration of the tracer in the effluent system as in equation (22).

Since Pulse Input gives the best way to visualize how the tracer test really works in terms of showing the time the molecule or material has spent within the reactor before exiting, then, E(t) is calculated from the pulse input test:

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

Because all of the molecules must enter and eventually leave the system, it follows from the probability additional rule that:

$$\int_0^\infty E(t)dt=1 \tag{23}$$

Where, the denominator of equation (22) is the integral of the area under the curve as shown in figure 14. The cumulative distributed function, which gives the fraction of molecules with residence times from time zero to time t, is correlated by the following function in equation (24):

$$\int_0^t E(t)\,dt = F(t) \qquad (24)$$

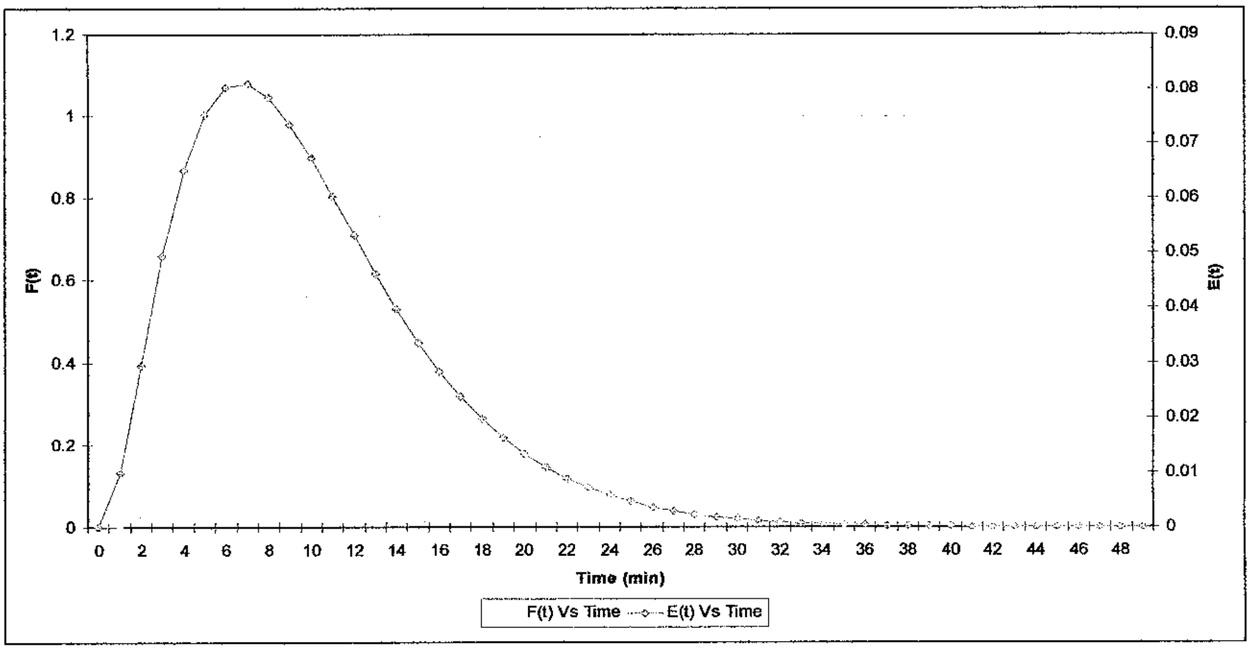


Figure 14: Residence Time Distribution function E(t) and Accumulative Distribution function F(t) for a Pulse Input of a flow system.

Space time, which is also known as the average residence time, τ is defined as in the below shown equation (25).

$$\tau = \frac{V}{v_o} \qquad (25)$$

However, theoretically illustrated by Fogler, 1999 shows that at any RTD value exists for any type of a stirred tank reactor, ideal or non-ideal, the τ is equal to the mean residence time, t_m. However, it is an emphasis that for the space time to be equal to the mean residence times the condition of temperature and pressure under which the feed flowrate is specified must be the same, and the space time data are frequently given with the feed conditions at the reactor inlet temperature and pressure.

Where the mean residence time is the average time the effluent molecules spent in the reactor as can be illustrated as per below equation (26).

$$t_m = \frac{\int_0^\infty t\,E(t)\,dt}{\int_0^\infty E(t)\,dt} = \int_0^\infty t\,E(t)dt \qquad (26)$$

Since; $\tau = \frac{V}{v_o} = t_m$; Therefore: $V = v_0 t_m$

Where the mean residence time, t_m, is the area under the graph shown as in Figure 15, and it can also be calculated by using the numerical integration as in APPENDIX A .

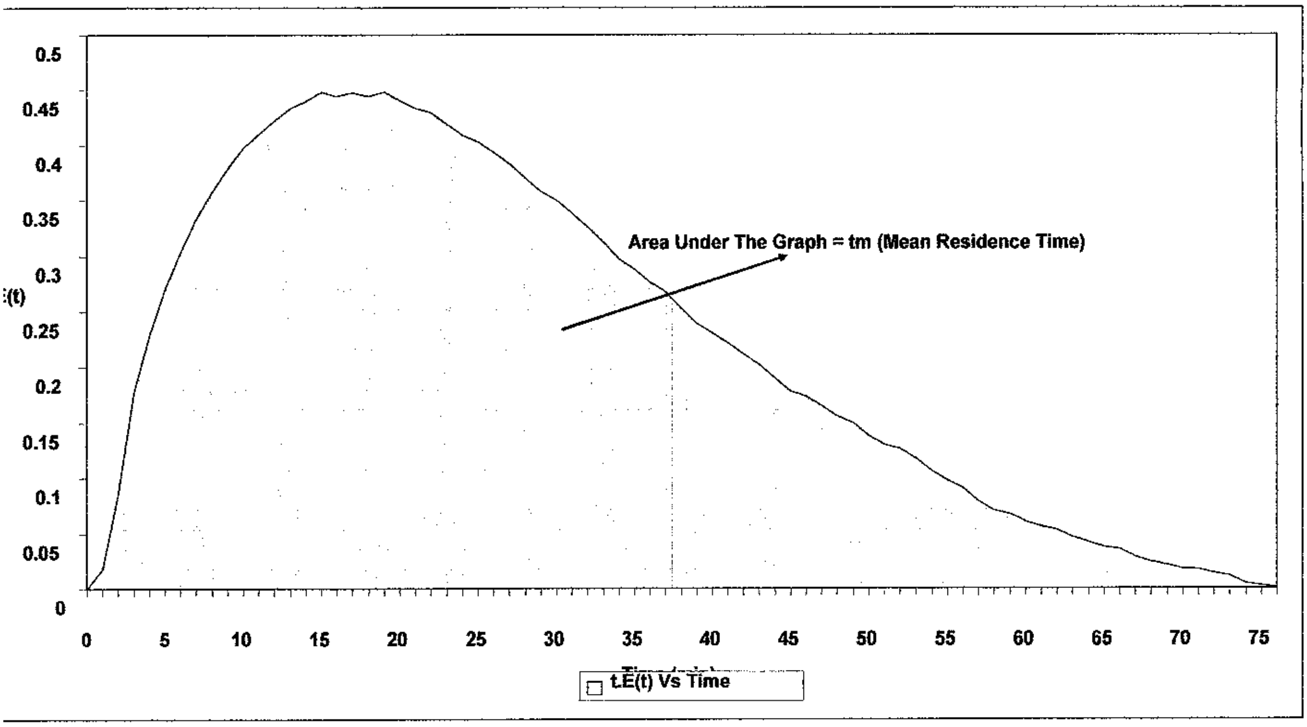


Figure 15: Graph. t.E(t) versus time (min). Note that the area under the graph is the mean residence time. Mean residence time just the space time,τ.

Since for a constant density system the mean residence time is equal to the space time, then calculating the mean residence time in the two different ways can be used to check on the accuracy of the experimental data used in calculating the RTD. In terms of accumulative distribution function, the mean residence time is therefore equal:

$$t_m = \int_0^\infty t.E(t)dt$$

Rather than computing the moments about the origin, it is commonly computed about the residence time, and these moments are called the central moments. The variance, σ^2, of the residence time distribution is the second central moment and is defined as in equation (27):

$$\sigma^2 = \int_0^\infty (t - t_m)^2 E(t)dt \qquad (27)$$

Moreover, the variance, σ^2, of the residence time distribution measures the spread of the distribution of molecules about the mean and the greater the value of this moment, the greater a distribution's spread. This is illustrated based on the below figure 16:

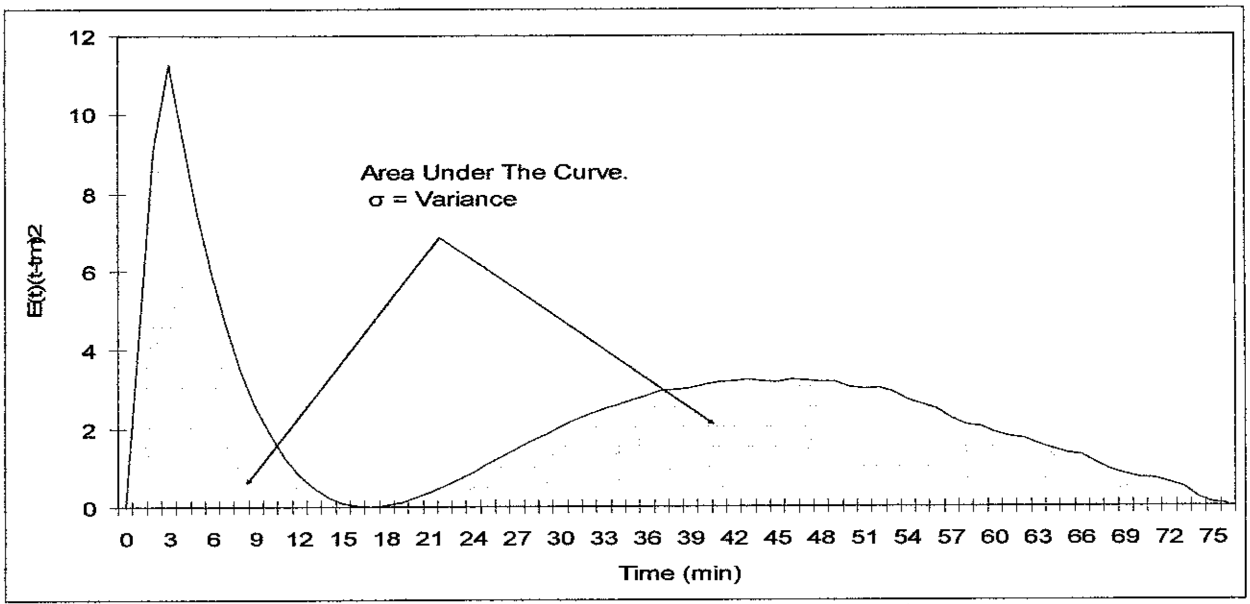


Figure 16: Graph for calculating the variance, σ^2.

The calculated parameters from the RTD experimental data correlation/analysis are as tabulated below in table1.

Table 1: Calculated Values of Space Time

PARAMETERS	**VALUES (min)**
$\tau_{\text{theoretical}}$	16.67
$\tau_{\text{mean}} = t_m$	16.80
σ_{variance}	12.988
E(t)	1.05

IDEAL REACTOR MODEL

The overall performance of the reactor was analyzed/measured based on the below tabulated process and kinetic parameters, which were calculated from the experimental data of ethanol and methanol production.

Table 2: The experimental rate Constant obtained at different temperature

Rate Constant	**Equipment Used**	**Temperature (°C)**	**Main Product**	**Values** (L/mol.s)	**Values** (L/mol.min)
K (L/mol.min)	Tanks In Series	25	Ethanol	0.0271	1.6246
K (L/mol.min)	Tanks In Series	25	Methanol	0.0472	2.832
K (L/mol.min)	CSTR With HWC	25	Ethanol	0.0751	4.506
K (L/mol.min)	CSTR With HWC	25	Methanol	0.1241	7.45
K (L/mol.min)	CSTR With HWC	30	Methanol	0.1275	7.65
K (L/mol.min)	CSTR With HWC	40	Methanol	0.3099	18.594

Table 3: Process and Kinetic Parameters

No	**PROCESS PARAMETERS**	**VALUES**	**REMARK**
I	Reactor's Volume (L)	1.0	Constant
II	$C_{A0} = C_{B0}$ (mol/L)	0.05	Constant
III	V_0 (L/min)	0.06	Constant
No	**KINETIC PARAMETERS**	**VALUES**	**REMARK**
1	K (L/mol.min)	1.625	Ethanol Production
2	K (L/mol.min)	2.832	Methanol Production
3	Reaction Order	2nd Order	For both
4	$-r_A$	$1.625C_A^2$	Ethanol Production
5	$-r_A$	$2.832C_A^2$	Methanol Production

The conversion of reactant A is the measure of the fraction of reactant that has converted into products. Thus, conversion of A, which is denoted by $X_{A,}$ relates the amount of reactant A, that is converted to product with respect to its residence time. Based on the mole balance equation, the reaction conversion of the second order system which has been assumed to be an ideal system is as shown:

$$V = \frac{F_{A0}X}{kC_A^2} \tag{28}$$

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

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

Where conversion is defined as in equation (29):

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

Thus, solving the above equation (29) for conversion, X_A, illustrate,

- Saponification process for Ethanol synthesis

$$X = \frac{(1+2\tau kC_{A0}) - \sqrt{(1+2\tau kC_{A0})^2 - (2\tau kC_{A0})^2}}{2\tau kC_{A0}} = \underline{\mathbf{0.43}} \textbf{ or } \underline{\mathbf{43\%}}$$

- Saponification process for Methanol synthesis

$$X = \frac{(1+2\tau kC_{A0}) - \sqrt{(1+2\tau kC_{A0})^2 - (2\tau kC_{A0})^2}}{2\tau kC_{A0}} = \underline{\mathbf{0.53}} \textbf{ or } \underline{\mathbf{53\%}}$$

4.4 REAL REACTOR MODELS

4.4.1 Conversion in a segregated model

The conversion in a segregated tank reactor is calculated by using the batch reactor mole balance and the residence time distribution. This is because the packages of fluid, which are small in comparison to the size of the reactor but at the same time, contain a significantly large number of reactant molecules are admitted to a stirred tank in which there is a sufficient level of mixing, and are assumed to be perfectly mixed at the macro scale. However, each package moves inside the reactor without intermingling with the fluid in other packages, and each package is seen as small as batch reactor. The time that the batch spends in the stirred tank determines its outlet conversion, and this time is usually given by RTD. The initial concentration of reactants in the packages is the same as the inlet concentration to the stirred tank, and the outlet concentration from the stirred tank is the average of the concentration of reactants in all the exiting packages, which is calculated using the batch reactor mole balance as shown below in equation (30). However, for a second order system, the segregation model is actually the highest bound and maximum mixedness is the lowest bound. This is proven by the below shown relation:

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

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

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

$$d\bar{X} = X(t) \cdot E(t)dt$$

$\bar{X} = \int_0^\infty X(t)E(t)dt$: Is the area under the below shown graph.

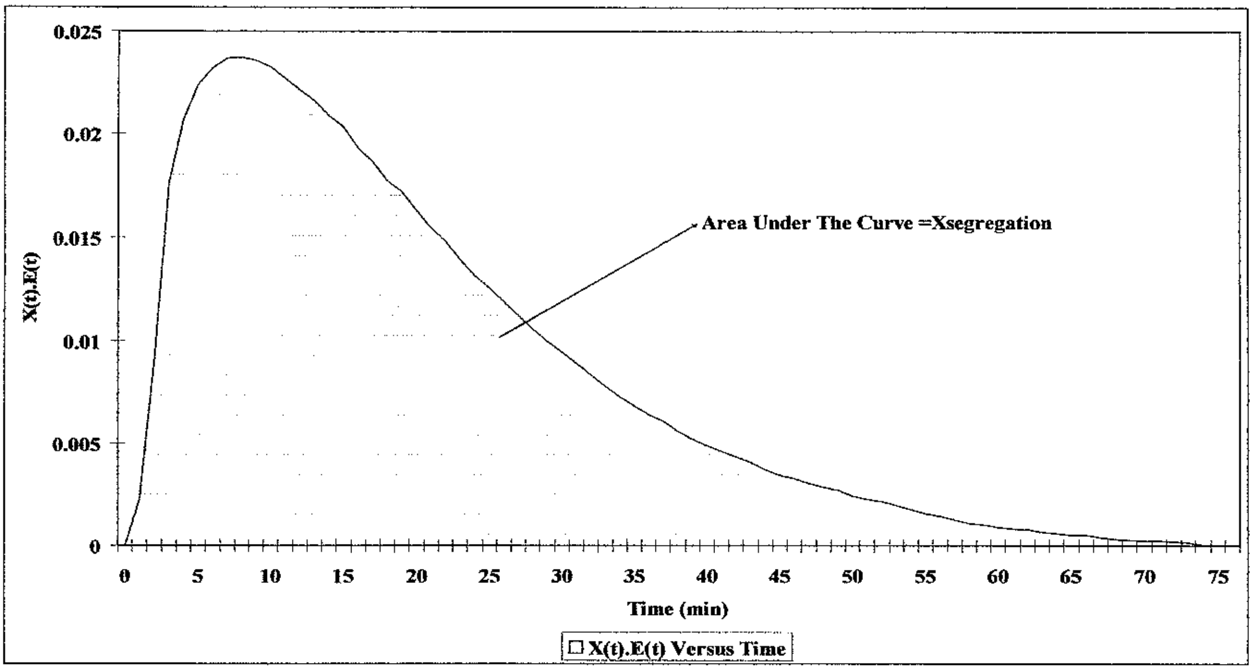


Figure 17: Profile of X(t).E(t) versus time (min). The area under the graph is the mean conversion, $\overline{X}$ OR the Segregation Conversion.

For second order reaction:

$$A + B \rightarrow C + D$$

For a batch reactor,

$$-\frac{dN_A}{dt} = -r_A\, V = V\, k\, C_{A0}^2 (1-X)^2 \tag{30}$$

This on arrangement becomes:

- Saponification process for Ethanol synthesis

$$X = \frac{kC_{A0}t}{1+kC_{A0}t} = \underline{\underline{\mathbf{0.511}}}\ \mathbf{or}\ \underline{\underline{\mathbf{51.1\%}}}$$

- Saponification process for Methanol synthesis

$$X = \frac{kC_{A0}t}{1+kC_{A0}t} = \underline{\underline{\mathbf{0.633}}}\ \mathbf{or}\ \underline{\underline{\mathbf{63.3\%}}}$$

The above conversion's values are calculated based on the empirical formula (numerical integration) illustrated in the APPENDIX A.

MAXIMUM MIXEDNESS

The conversion in a maximum mixedness model is calculated by performing a mole balance that considers all of the streams. This is done by defining an alternative variable, λ, which is termed as the residual life, or the residence time remaining for an entering particle. Particles that enter at the reactor exit have a residual time of zero. Residual time is nothing more than the residence time for entering side stream particles. Even though all particles at a given λ have the same time left in the reactor, but they have different ages. The concentration at the reactor outlet is driven from the mole balance equation illustrated by Euler method, which is used in performing the numerical integration for the conversion of maximum mixedness. The respective calculation for the conversion is as illustrated in the last column of the table. The conversion of maximum mixedness model then is calculated based on Euler method for numerical integration for second order system as follows:

- Saponification process for Ethanol synthesis

$$X_{i+1} = X_i + (\Delta\lambda)\left[\frac{E(\lambda_i)}{1-F(\lambda_i)}X_i - kC_{A0}(1-X_i)^2\right] = \underline{\mathbf{0.505}}\ \mathbf{or}\ \underline{\mathbf{50.5\%}}$$

- Saponification process for Methanol synthesis

$$X_{i+1} = X_i + (\Delta\lambda)\left[\frac{E(\lambda_i)}{1-F(\lambda_i)}X_i - kC_{A0}(1-X_i)^2\right] = \underline{\mathbf{0.599}}\ \mathbf{or}\ \underline{\mathbf{59.9\%}}$$

TANKS IN SERIES MODEL

The principle of tanks in series model is to describe non-ideal reactor and calculate conversion. The analysis of RTD is used to determine the number of tanks in series that will give approximately the same RTD as the non-ideal reaction system.

To determine the number of tanks in series, the variance is needed since it is computed as the second normalized moment a bout the mean residence time. Therefore, the mean residence time which is the first normalized moment is computed as the area under the curve shown in figure 15:

Where the mean residence time is illustrated as follows;

$$t_m = \int_0^\infty t.E(t)dt$$

Form the graph, the mean residence time is calculated by a numerical integration as shown in appendix A:

$t_m = \tau = 16.789699 =$ **<u>16.80 min</u>**

The variance, which is the second normalized moment about the mean residence time, is the area under curve of graph of figure and is computed by numerical integration of the experimental data. Therefore, the second normalized moment (variance) is calculated by a numerical integration as shown in appendix A:

$$\sigma_\theta^{\,2} = \frac{\sigma^2}{\tau^2} = \frac{1}{n}$$

Therefore; $n = \dfrac{\tau^2}{\sigma^2}$

σ = <u>12.988 min</u>

$$n = \frac{(16.80)^2}{(12.98)^2} = 1.70$$

Since only integers are acceptable, then, the number of tanks is **2 tanks**. The number of tanks in series that should be used to model the system of mean residence time, $\mathbf{t_m}$ =

16.80min, would consist of two tanks in series, each with a volume **50%** of the volume of the real system. And because the tanks in series model are restricted to an integer number of tanks, the match between the model and the observed RTD will not be perfect.

Conversion for a second order reaction carried out in two tanks in series is calculated as shown below.

Assume (V_1=V_2=V/2, and $\tau_1\tau_2$= τ/2).

$$V_2 = \frac{(C_{A0} - C_{A1})v_0}{kC_A^{\ 2}}$$

$$\tau_2 kC_A^{\ 2} + C_{A1} - C_{A0} = 0$$

$$C_{A1} = \frac{-1 + \sqrt{1 + 4\tau_2 kC_{A0}}}{2\tau_2 k}$$

$$C_{A2} = \frac{-1 + \sqrt{1 + 4\tau_2 kC_{A1}}}{2\tau_2 k}$$

$$X = 1 - \frac{C_{A2}}{C_{A0}}, \tau_2 = \frac{\tau}{2}$$

Saponification process for Ethanol synthesis

Where; **k = 1.625L/mol.min**

τ = 16.67min

τ_2= (16.67/2) = 8.335min

$$C_{A1} = \frac{-1 + \sqrt{1 + 4\tau_2 kC_{A0}}}{2\tau_2 k} = \mathbf{0.034M}$$

$$C_{A2} = \frac{-1 + \sqrt{1 + 4\tau_2 kC_{A1}}}{2\tau_2 k} = \mathbf{0.025M}$$

$$X = 1 - \frac{C_{A2}}{C_{A0}}, \tau_2 = \frac{\tau}{2}$$

$$X = 1 - \frac{C_{A2}}{C_{A0}} = \underline{\mathbf{0.50\ or\ 50\%}}$$

Saponification process for Methanol synthesis

Where; **k = 2.832/mol.min**

τ = 16.67min

τ₂= (16.67/2) = 8.335min

$$C_{A1} = \frac{-1+\sqrt{1+4\tau_2 k C_{A0}}}{2\tau_2 k} = \mathbf{0.030M}$$

$$C_{A2} = \frac{-1+\sqrt{1+4\tau_2 k C_{A1}}}{2\tau_2 k} = \mathbf{0.020M}$$

$$X = 1 - \frac{C_{A2}}{C_{A0}}, \tau_2 = \frac{\tau}{2}$$

$$X = 1 - \frac{C_{A2}}{C_{A0}} = \underline{\mathbf{0.60\ or\ 60\%}}$$

REAL CSTR MODELED BY USING BYPASSING AND DEAD SPACE

The conversion of the real CSTR modeled by using bypass and dead as shown in figure 5 is calculated as below.

$$A \longrightarrow B$$

The bypass stream and effluent stream from the reaction volume are mixed at joint 2 of figure 5. The mole balance on species A around this point is driven as shown below.

$$in \quad = \quad out$$

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

Therefore, the concentration of A leaving the reactor as follows,

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

Where;

α = the fraction of volume that is well-mixed (alpha)
β = and the fraction of the stream that is bypassed (beta)

Let $\alpha = \frac{v_s}{v}$ and $\beta = \frac{\upsilon_b}{\upsilon_0}$

Mole balance on CSTR on reactor volume V_s:

$$\begin{array}{ccccccc} in & - & out & + & generation & = & accumulation \\ \upsilon_s C_{A0} & - & \upsilon_s C_{As} & + & r_{As} V_s & = & 0 \end{array}$$

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

$$\begin{array}{ccccc} in & - & out & = & accumulation \end{array}$$

$$\upsilon_s C_{T0} - \upsilon_s C_{Ts} = V_s \frac{dC_{Ts}}{dt} \tag{31}$$

Mole balance around junction 2 from figure 5:

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

Integrating equation (31) and substitution of α, β and combination of the equation yields:

$$\ln \frac{C_{T0}}{C_{T0} - C_T} = \ln \frac{1}{1-\beta} + \left(\frac{1-\beta}{\alpha} \right) \frac{t}{\tau} \tag{32}$$

Since there are two unknown parameters (α and β), the tracer experiments and the RTD data analysis are used to plot the $\ln \left[\frac{C_{T0}}{C_{T0} - C_T} \right]$ profile and a straight line graph is obtained whose slope is the value of $\left(\frac{1-\beta}{\tau\alpha} \right)$ as shown in the figure 18:

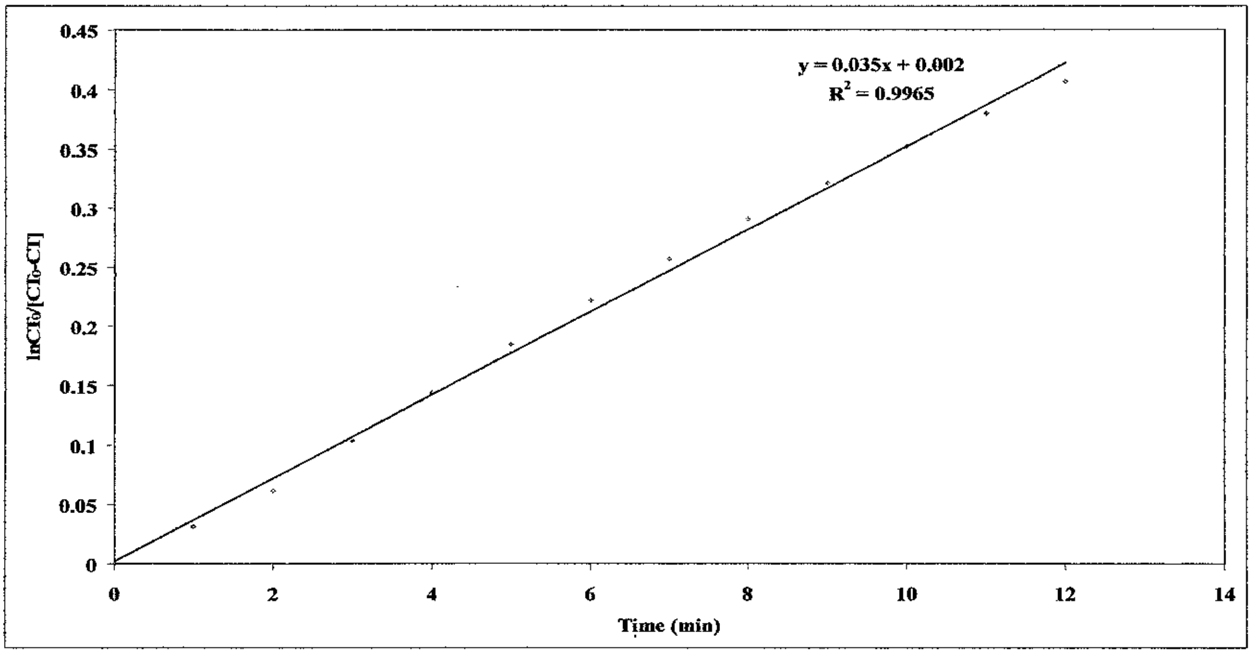


Figure 18: Profile of $\ln\left[\frac{C_{T0}}{C_{T0}-C_T}\right]$ *versus time (min). The slope of the graph is the value of* $\left(\frac{1-\beta}{\tau\alpha}\right)$.

The following illustrations are obtained from the graph.

Slope $= \left(\frac{1-\beta}{\tau\alpha}\right) = 0.035$. Intersection $= \ln\left(\frac{1}{1-\beta}\right) = 0.002$

Therefore: the value of β= 0.002, and α= 1.71.

Therefore, the conversion is determined as follows:

Mole balance on reactor volume V_s:

$$\upsilon_s C_{A0} - \upsilon_s C_{As} + r_{As} V_s = 0$$

Where the Rate Law is given by:

$$r_A = -kC_{AS}C_{BS} = -kC^2_{AS}.$$

Solving the above equations for the value of the final concentration, C_{AS}, exiting reactor volume Vs illustrate:

$$v_s C_{A0} - v_s C_{AS} - KC_{AS}{}^2 V_s = 0$$

Where,

$$\alpha = \frac{v_s}{v};$$

v_s= (vα) = 0.06*1.71 =0.1026/min

V_s = (vτα) = (1.71*16.67*0.06) = 1.71 L/min.

$$\tau_s = \frac{V_s}{v_s} = \left(\frac{1.71}{0.1026}\right) = 16.67\,\text{min}$$

Therefore, solving for C_{AS}, gives:

- Saponification process for Ethanol synthesis

$$C_{AS} = \frac{-1+\sqrt{1+4\tau_s kC_{AO}}}{2\tau_s k} = 0.028M$$

Where; $C_{A0} = 0.05$

k = **1.625 L/mol.min**

- Saponification process for Methanol synthesis

$$C_{AS} = \frac{-1+\sqrt{1+4\tau_s kC_{AO}}}{2\tau_s k} = 0.024M$$

Where; $C_{A0} = 0.05$

k = **2.832 L/mol.min**

Mole balance around junction point 2 illustrates the following:

in – *out* = *accumulation*

And since there is no accumulation, then:

In = out

$$v_b C_{A0} + v_s C_{AS} = v_0 C_A$$

- Saponification process for Ethanol synthesis

$$C_A = \frac{v_0 - v_s}{v_0} C_{A0} + \frac{v_s}{v_0} C_{AS} = \underline{\mathbf{0.0124M}}$$

- Saponification process for Methanol synthesis

$$C_A = \frac{v_0 - v_s}{v_0} C_{A0} + \frac{v_s}{v_0} C_{AS} = \underline{\mathbf{0.00554M}}$$

The Conversion for the system denoted by, X, calculated from the real CSTR modeled by using bypass and dead space is as follows:

- Saponification process for Ethanol synthesis

$$X = 1 - \frac{C_A}{C_{A0}} = \underline{\mathbf{0.75}}\ \mathbf{Or}\ \underline{\mathbf{75.0\%}}$$

- Saponification process for Methanol synthesis

$$X = 1 - \frac{C_A}{C_{A0}} = \underline{\mathbf{0.89}}\ \mathbf{Or}\ \underline{\mathbf{89.0\%}}$$

REAL CSTR MODELED AS TWO CSTR INTERCHANGE

Determination of the Parameters α and β from figure 19.

The determination of these parameters in the model is not straightforward, and they are usually calculated by nonlinear regression using the predicted tracer response curve directly. Exceptions do exist to this general rule, though. The two-CSTRs with-interchange model described earlier (shown in Figure 6 in simplified form).

A mole balance on a tracer pulse injected at t = 0 for each of the tanks is as follows:

Rate in – Rate out = Accumulation

Reactor 1:

$$v_1 C_{T2} - (v_0 C_{T1} + v_1 C_{T1}) = V_1 \frac{dC_{T1}}{dt} \tag{33}$$

Reactor 2:

$$v_1 C_{T1} - v_1 C_{T2} = V_2 \frac{dC_{T2}}{dt} \tag{34}$$

Where; $V_1 = \alpha V$, $v_1 = \beta v_0$, $V_2 = (1-\alpha)V$, $v_2 = v_1$, $\theta = \frac{t v_0}{V} = \frac{t}{\tau}$

C_{T1} = the tracer concentrations in reactors 1, with $C_{T10} = N_{T0}/V_1$

C_{T2} = the tracer concentrations in reactors 2, with $CT_{20} = 0$.

Substituting these values in equations (33 and 34), the following two coupled differential equations, which describes the unsteady behavior of the tracer, are

$$\alpha \frac{dC_{T1}}{d\theta} = \beta C_{T2} - (1+\beta) C_{T1} \tag{35}$$

$$(1-\alpha) \frac{dC_{T2}}{d\theta} = \beta C_{T1} - \beta C_{T2} \tag{36}$$

Differentiating Equation (33) with respect to θ and then multiply through by (1 - α) to get the following.

$$\alpha(1-\alpha)\frac{d^2C_{T1}}{d\theta^2}=\beta\left[(1-\alpha)\frac{dC_{T2}}{d\theta}\right]-(1-\alpha)(1+\beta)\frac{dC_{T1}}{d\theta} \tag{37}$$

Substituting Equation (34) in (37) for the bracketed term gives the following.

$$\alpha(1-\alpha)\frac{d^2C_{T1}}{d\theta^2}=\beta(\beta C_{T1}-\beta C_{T2})-(1-\alpha)(1+\beta)\frac{dC_{T1}}{d\theta} \tag{38}$$

Solving Equation (33) with respect to βC_{T2} gives the following.

$$\beta C_{T2}=\alpha\frac{dC_{T1}}{d\theta}+(1+\beta)C_{T1} \tag{39}$$

Combining Equations (38) and (39) and rearranging gives the following.

$$\frac{\alpha(1-\alpha)}{1+\beta-\alpha}\frac{d^2C_{T1}}{d\theta^2}+\frac{dC_{T1}}{d\theta}+\frac{\beta C_{T1}}{1+\beta-\alpha}=0 \tag{40}$$

Equation (40) is the form of: $a\frac{d^2C_{T1}}{d\theta^2}+b\frac{dC_{T1}}{d\theta}+cC_{T1}=0$

Assumed the initial operating conditions of the reactor at θ = 0 are:

$C_{T1}=C_{T10}$, and $C_{T2}=C_{T20}=0$.

Then equation (33) is: $\left(\frac{dC_{T1}}{d\theta}\right)_0=\frac{-1+\beta}{\alpha}C_{T10}$

(41)

Integrating equation (41) with respect to θ gives the following;

$$d\left(\frac{C_{T1}}{C_{T10}}\right)_0 = \frac{-1+\beta}{\alpha}\theta \qquad (42)$$

Therefore, the plot of $d\left(\frac{C_{T1}}{C_{T10}}\right)_0$ vs. θ is a polynomial trendline shown in figure 19, in which the area under the graph being the value of α.

Differentiating the polynomial equation in the figure 17 assuming x = 0, gives the following.

$$y = -0.0023x^3 + 0.0244x^2 - 0.0884x + 0.1124 \qquad (43)$$

$$\frac{dy}{dx} = -0.0069x^2 + 0.0488x - 0.0884$$
$$x = 0$$
$$Slope = \frac{-1+\beta}{\alpha} = \frac{dy}{dx} = -0.0884$$

Integrating equation (43) at x = 4.56, when the final concentration = 0, gives the following.

$$y = -0.0023x^3 + 0.0244x^2 - 0.0884x + 0.1124$$

$$\int(-0.0023x^3 + 0.0244x^2 - 0.0884x + 0.1124)dx$$

$$\left[-0.000575x^4 + 0.00813x^3 - 0.0442x^2 + 0.1124x\right]_0^{4.56} = \alpha = 0.12$$

Therefore, $Slope = \dfrac{-1+\beta}{\alpha} = -0.0884$ and $\beta = -0.0884 * 0.12 + 1 = 0.99$

Thus, $\alpha = 0.12$, and $\beta = 0.99$

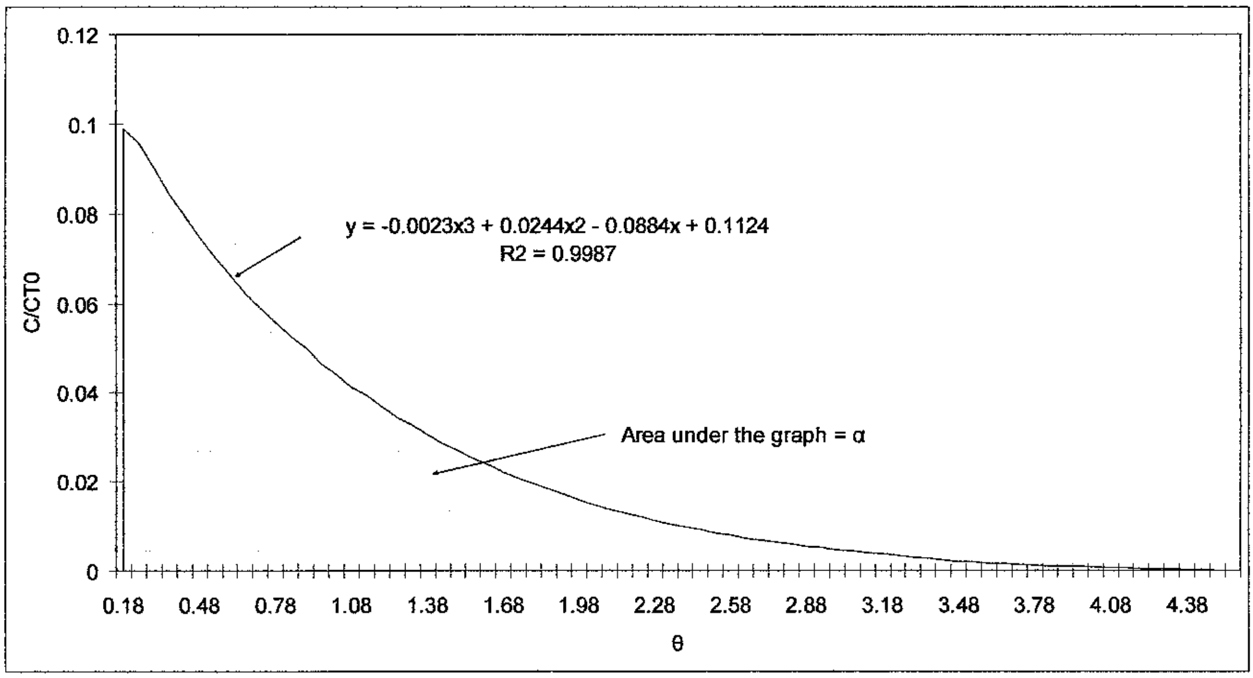


Figure 19: Profile of $\dfrac{C_{T1}}{C_{T10}}$ *versus θ.*

The conversion of figure 6 is calculated as follows:

Mole balance for the Top outlet

Reactor 1:

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

$$(v_0 C_{A0} + v_1 C_{A2}) - (v_0 C_{A1} + v_1 C_{A1}) + r_{A1} V_1 = 0 \tag{44}$$

Where;

$$r_{A1} = -kC_{A1}^{2}, \frac{1}{\tau} = \frac{v_0}{V}, \alpha = \frac{V_1}{V}, and \beta = \frac{v_1}{v_0}$$

Divide equation (44) by V:

$$(\frac{v_0}{V}C_{A0} + \frac{v_1}{V}C_{A2}) - (\frac{v_0}{V}C_{A1} + \frac{v_1}{V}C_{A1}) - kC_{A1}^{2}\frac{V_1}{V} = 0$$

$$kC_{A1}^{2}\alpha + C_{A1}(\frac{1}{\tau} + \frac{v_1}{V}) - (\frac{1}{\tau}C_{A0} + \frac{v_1}{V}C_{A2}) = 0 \qquad (45)$$

Divide equation (45) by v_0:

$$\frac{kC_{A1}^{2}\alpha}{v_0} + C_{A1}(\frac{1}{\tau v_0} + \frac{\beta}{V}) - (\frac{1}{\tau v_0}C_{A0} + \frac{\beta}{V}C_{A2}) = 0 \qquad (46)$$

$$C_{A1} = \frac{-(\frac{1}{\tau v_0} + \frac{\beta}{V}) + \sqrt{\left(\frac{1}{\tau v_0} + \frac{\beta}{V}\right)^2 + \frac{4\alpha k}{v_0}\left(\frac{1}{\tau v_0}C_{A0} + \frac{\beta}{V}C_{A2}\right)}}{\frac{2k\alpha}{v_0}} \qquad (47)$$

Reactor 2: $in \quad - \quad out \quad + Generation \quad = \quad accumulation$

$$v_1 C_{A1} - v_1 C_{A2} + r_{A1}V_2 = 0$$

$$V = V_1 + V_2 \Rightarrow 1 = \frac{V_1}{V} + \frac{V_2}{V} \Rightarrow 1 = \alpha + \frac{V_2}{V} \Rightarrow V_2 = (1-\alpha)V$$

$$v_1 C_{A1} - v_1 C_{A2} - kC_{A1}{}^2 V_2 = 0 \tag{48}$$

Divide equation (48) by v_0: $$kC_{A1}{}^2(1-\alpha)V + \beta C_{A2} - \beta C_{A1} - = 0$$

Therefore: $$C_{A2} = \frac{-\beta + \sqrt{\beta^2 + 4k\beta(1-\alpha)VC_{A1}}}{2k(1-\alpha)V}$$

Functions: $$f_1 = a_1 x_1{}^2 + b_1 x_1 - C_{1a} - C_{1b} x_2 = 0$$
$$f2 = a_1 x_1{}^2 + b_1 x_1 - C_{1a} - C_{1b} x_2 = 0$$

$$C_{Ai} = \frac{-1 + \sqrt{1 + 4k\tau C_{A0}}}{2k\tau}$$

$$V_1 = \alpha V,\ \ v_1 = \beta v_0,\ \ V_2 = (1-\alpha)V,\ \ v_2 = v_1$$

The constants are calculated as shown below;

$$a_1 = \frac{k\alpha}{\tau},\quad a_2 = k(1-\alpha)\tau,\ b_1 = \left(\frac{\frac{1}{v_0}}{\tau} + \frac{\beta}{V}\right),\quad b_2 = \beta,\ \ C_1 = \left(\frac{\frac{C_{A0}}{v_0}}{\tau}\right),\ C_2 = \frac{\beta}{V}$$

The Conversion for the system denoted by, X, calculated from the two CSTR interchange is as follows:

- Saponification process for Ethanol synthesis

$$C_{A1} = \frac{-(\frac{1}{\tau v_0} + \frac{\beta}{V}) + \sqrt{\left(\frac{1}{\tau v_0} + \frac{\beta}{V}\right)^2 + \frac{4\alpha k}{v_0}\left(\frac{1}{\tau v_0}C_{A0} + \frac{\beta}{V}C_{A2})\right)}}{\frac{2k\alpha}{v_0}} = \mathbf{0.029M}$$

$$C_{A2} = \frac{-\beta + \sqrt{\beta^2 + 4k\beta(1-\alpha)VC_{A1}}}{2k(1-\alpha)V} = \mathbf{0.002058M}$$

$$C_{Ai} = \frac{-1 + \sqrt{1 + 4k\tau C_{A0}}}{2k\tau} = \mathbf{0.028M}$$

$$X_1 = 1 - \frac{C_{A1}}{C_{A0}} = \mathbf{0.42\ or\ 42\%}$$

$$X_2 = 1 - \frac{C_{A2}}{C_{A1}} = \mathbf{0.93\ or\ 93\%}$$

$$X_{Ideal} = 1 - \frac{C_{Ai}}{C_{A0}} = \mathbf{0.44\ or\ 44\%}$$

- Saponification process for Methanol synthesis

$$C_{A1} = \frac{-(\frac{1}{\tau v_0} + \frac{\beta}{V}) + \sqrt{\left(\frac{1}{\tau v_0} + \frac{\beta}{V}\right)^2 + \frac{4\alpha k}{v_0}\left(\frac{1}{\tau v_0}C_{A0} + \frac{\beta}{V}C_{A2})\right)}}{\frac{2k\alpha}{v_0}} = \mathbf{0.026M}$$

$$C_{A2} = \frac{-\beta + \sqrt{\beta^2 + 4k\beta(1-\alpha)VC_{A1}}}{2k(1-\alpha)V} = \mathbf{0.00182M}$$

$$C_{Ai} = \frac{-1 + \sqrt{1 + 4k\tau C_{A0}}}{2k\tau} = \mathbf{0.024M}$$

$$X_1 = 1 - \frac{C_{A1}}{C_{A0}} = \mathbf{0.48\ or\ 48\%}$$

$$X_2 = 1 - \frac{C_{A2}}{C_{A1}} = \mathbf{0.931\ or\ 93.1\%}$$

$$X_{Ideal} = 1 - \frac{C_{Ai}}{C_{A0}} = \mathbf{0.52\ or\ 52\%}$$

Mole balance for the Bottom outlet

Reactor 1:

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

$$(v_0 C_{A0} + v_1 C_{A2}) - v_1 C_{A1} + r_{A1} V_1 = 0 \qquad (48)$$

Divide equation (48) by v_0:

$$(C_{A0} + \frac{v_1}{v_0} C_{A2}) - \frac{v_1}{v_0} C_{A1} - k C_{A1}{}^2 \frac{V_1}{v_0} = 0$$

$$k C_{A1}{}^2 \alpha + \beta C_{A1} - C_{A0} - \beta C_{A2} = 0$$

$$C_{A1} = \frac{-\beta + \sqrt{\beta^2 + 4k\alpha(C_{A0} + \beta C_{A2})}}{2k\alpha} \qquad (49)$$

Reactor 2:

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

$$v_1 C_{A1} - (v_1 C_{A2} + v_0 C_{A2}) - k C_{A1}{}^2 V_2 = 0$$

$$Where; V_2 = (1-\alpha)V$$

Therefore;

$$v_1 C_{A1} - (v_1 C_{A2} + v_0 C_{A2}) - k C_{A1}{}^2 (1-\alpha)V = 0 \tag{50}$$

Divide equation (50) by v_0:

$$k C_{A1}{}^2 (1-\alpha)\tau + \beta C_{A2} + C_{A2} - \beta C_{A1} = 0$$

$$C_{A2} = \frac{\beta C_{A1} - k C_{A1}{}^2 (1-\alpha)\tau}{(\beta+1)} \tag{51}$$

Functions:

$$a_1 C_{A1}{}^2 + b_1 C_{A1} - c_1 C_{A0} - b_1 C_{A2} = 0$$

$$a_2 C_{A2}{}^2 + b_1 C_{A2} - c_1 C_{A2} - b_1 C_{A1} = 0$$

$$C_{Ai} = \frac{-1 + \sqrt{1 + 4k\tau C_{A0}}}{2k\tau}$$

$V_1 = \alpha V$, $v_1 = \beta v_0$, $V_2 = (1-\alpha)V$, $v_2 = v_1$

The constants are calculated as shown below;

$a_1 = k\alpha\tau$, $a_2 = k(1-\alpha)\tau$, $b_1 = \beta$, $C_1 = 1$

- Saponification process for Ethanol synthesis

$$C_{A1} = \frac{-\beta + \sqrt{\beta^2 + 4k\alpha(C_{A0} + \beta C_{A2})}}{2k\alpha} = \mathbf{0.0281M}$$

$$C_{A2} = \frac{\beta C_{A1} - kC_{A1}{}^2(1-\alpha)\tau}{(\beta+1)} = \mathbf{0.0017M}$$

$$C_{Ai} = \frac{-1 + \sqrt{1 + 4k\tau C_{A0}}}{2k\tau} = \mathbf{0.028M}$$

$$X_1 = 1 - \frac{C_{A1}}{C_{A0}} = \mathbf{0.438 \text{ or } 43.8\%}$$

$$X_2 = 1 - \frac{C_{A2}}{C_{A1}} = \mathbf{0.94 \text{ or } 94\%}$$

$$X_{Ideal} = 1 - \frac{C_{Ai}}{C_{A0}} = \mathbf{0.44 \text{ or } 44\%}$$

- Saponification process for Methanol synthesis

$$C_{A1} = \frac{-\beta + \sqrt{\beta^2 + 4k\alpha(C_{A0} + \beta C_{A2})}}{2k\alpha} = \mathbf{0.0261M}$$

$$C_{A2} = \frac{\beta C_{A1} - kC_{A1}{}^2(1-\alpha)\tau}{(\beta+1)} = \mathbf{0.0011M}$$

$$C_{Ai} = \frac{-1 + \sqrt{1 + 4k\tau C_{A0}}}{2k\tau} = \mathbf{0.024M}$$

$$X_1 = 1 - \frac{C_{A1}}{C_{A0}} = \mathbf{0.478 \text{ or } 47.8\%}$$

$$X_2 = 1 - \frac{C_{A2}}{C_{A1}} = \mathbf{0.958 \text{ or } 95.8\%}$$

$$X_{Ideal} = 1 - \frac{C_{Ai}}{C_{A0}} = \mathbf{0.52 \text{ or } 52\%}$$

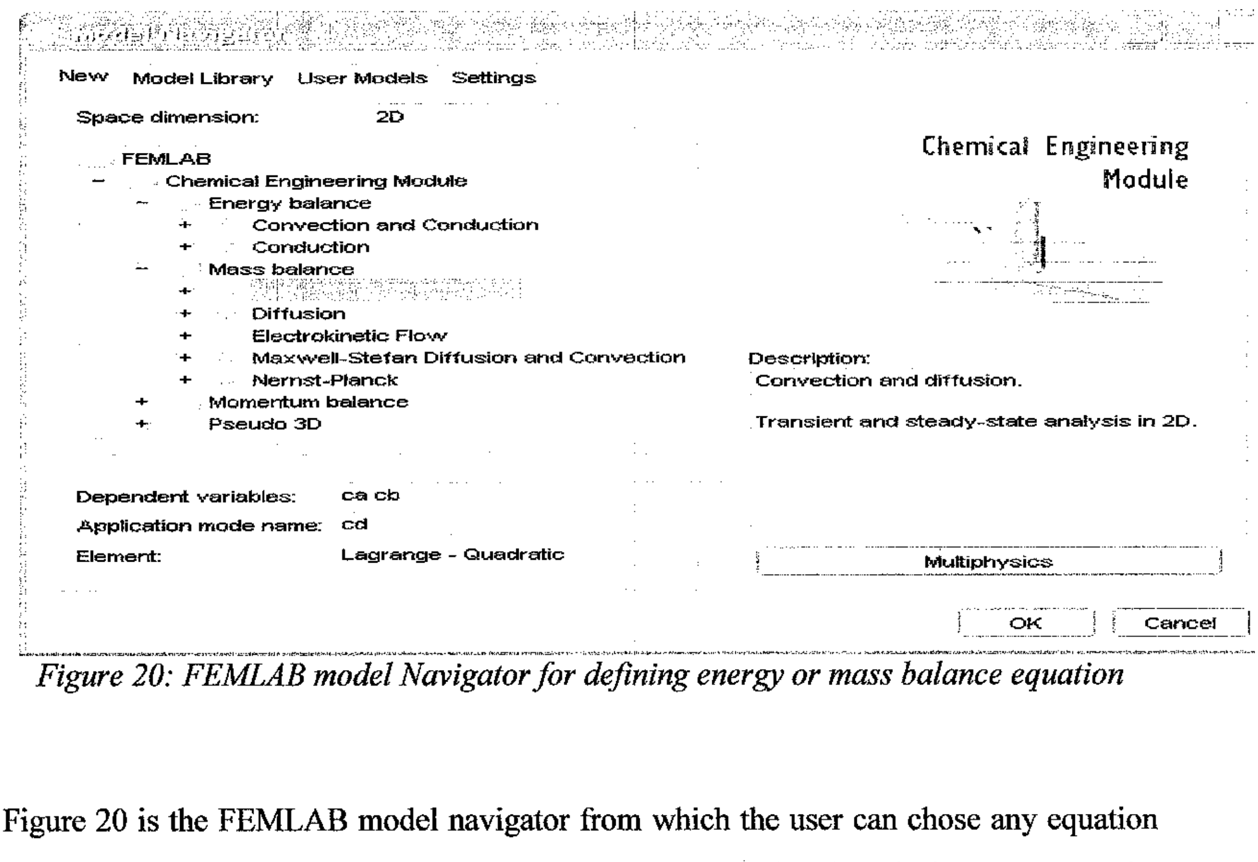
Based on the above analysis on the ideal and real reactors, it is observed that the conversion of the real reactor is higher in comparison to the ideal reactors' conversion as in table 4:

Table 4: Comparison between the conversion of ideal and real CSTR

MODEL	CONVERSION (%)	DEVIATION (%)	SYNTHESIS
	43	-	Ethanol
	52	-	Methanol
Model	51.1	16.1	Ethanol
Model	63.3	21.7	Methanol
ixedness	50.5	14.8	Ethanol
ixedness	59.9	15.2	Methanol
ypass-Dead Space	54.0	22.7	Ethanol
ypass-Dead Space	60.0	15.4	Methanol
ies Model (2 Tanks in Series)	50.0	13.6	Ethanol
ies Model (2 Tanks in Series)	60.0	15.4	Methanol
nterchange (Top outlet) Reactor 1	42.0	- 4.5	Ethanol
nterchange (Top outlet) Reactor 1	48.0	- 7.7	Methanol
nterchange (Top outlet) Reactor 2	93.0	116.3	Ethanol
nterchange (Top outlet) Reactor 2	93.1	79.0	Methanol
nterchange (bottom outlet) Reactor1	43.8	- 0.45	Ethanol
nterchange (bottom outlet) Reactor1	47.8	- 8.1	Methanol
nterchange (bottom outlet) Reactor2	94.0	118.6	Ethanol
nterchange (bottom outlet) Reactor2	95.8	84.2	Methanol

FEMLAB

FEMLAB is a modelling package for the simulation of any physical process that can be described with partial differential equations (PDEs). It contains ready-to-use predefined equations for momentum balances like the Navier-Stokes equations, Darcy's law and the Brinkman equations for porous media flow. In addition, it also contains predefined sets of equations for heat and balances, which can be easily coupled to the above mentioned momentum balances. It also includes a model library with examples from the fields of chemical reaction engineering, electrochemical engineering, fluid dynamics in reactors and unit operation equipment, heat balances in equipment for unit operations and much more.



Space dimension: 2D

- FEMLAB
  - − Chemical Engineering Module
    - − Energy balance
      - + Convection and Conduction
      - + Conduction
    - − Mass balance
      - +
      - + Diffusion
      - + Electrokinetic Flow
      - + Maxwell-Stefan Diffusion and Convection
      - + Nernst-Planck
    - + Momentum balance
    - + Pseudo 3D

Description:
Convection and diffusion.

Transient and steady-state analysis in 2D.

Dependent variables: ca cb
Application mode name: cd
Element: Lagrange - Quadratic

Figure 20: FEMLAB model Navigator for defining energy or mass balance equation

Figure 20 is the FEMLAB model navigator from which the user can chose any equation of state for modelling in either 2 dimensional or 3 dimensional analysis to measure the performance of a reactor at any pre-specified operation condition such as steady or unsteady state. However, for this research project, conduction and convection mode of heat transfer was chosen while convection and diffusion mode of mass transfer was chosen for modelling and investigating the performance of the ideal or real behaviour of a CSTR. The profiles obtained from modelling the experimental data are as shown below.

4.8.1 Concentration Profile

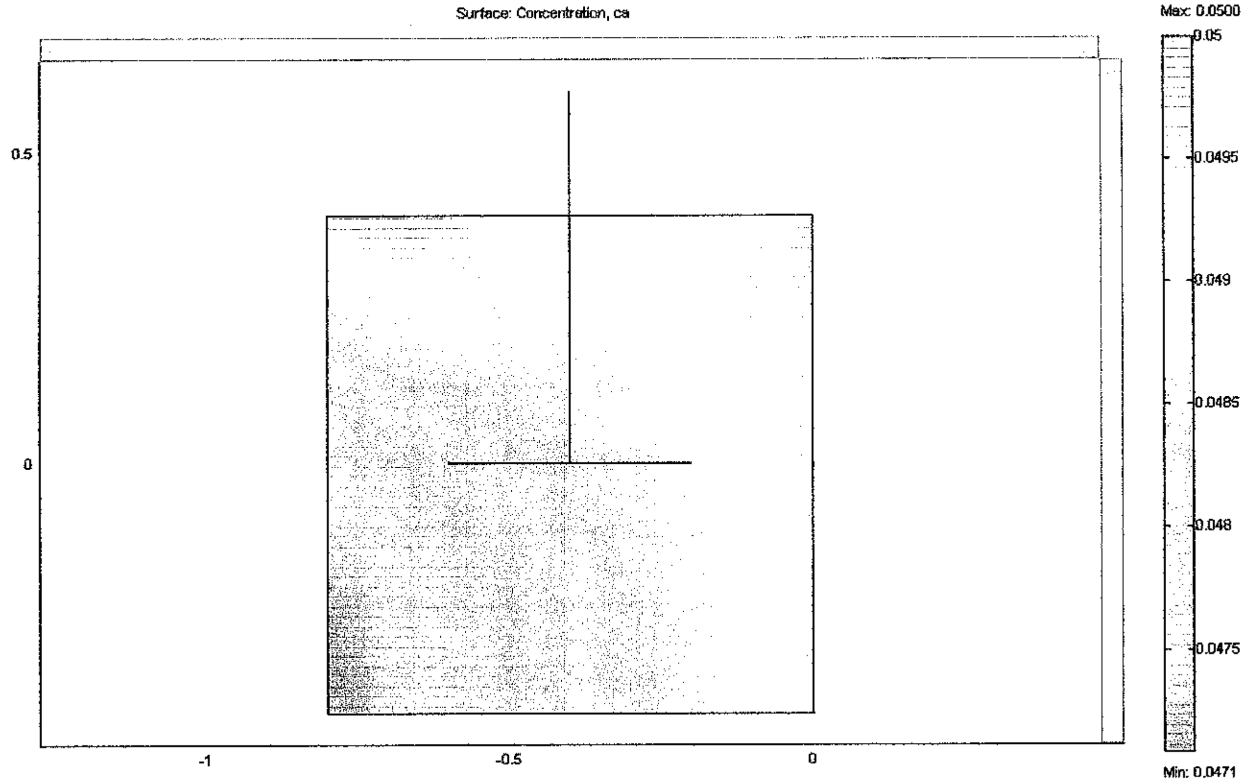


Figure 21: 2D solve mode for a surface Concentration distribution

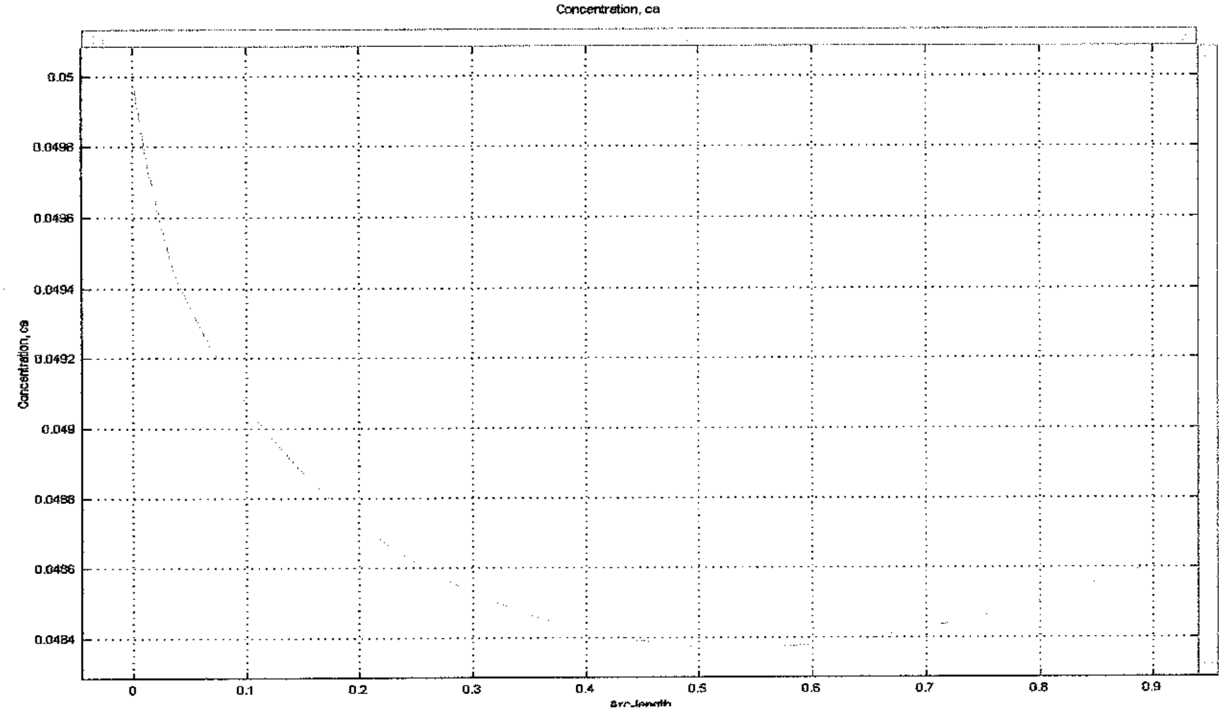


Figure 22: Concentration Profile

Figure 22 shows the concentration of profile of reactants changed with respect to their residence time distribution within the reactor. Sodium hydroxide reacted with methyl/ethyl acetate to produce methanol/ethanol and sodium acetate as the main by-product. The curve of the reactant concentration starts to decrease from 0.050 mole/L to around 0.0484 mole/L, which shows the conversion of the reactant into the desired product in the reaction system.

4.8.2 Temperature Profile

The CSTR model with a hot water circulation is equipped with a cooling jacket outside the reactor which plays a major role like a heat exchanger in supplying heat to the reaction system when the system is required to operate at a temperature higher than the room temperature. Since the saponification reaction of ethyl and methyl acetate with sodium hydroxide is an exothermic reaction, heat is released from the system into the ambient indicating that exothermicity of the process. Thus, the cooling jacket is allowed to supply heat into the reaction system only when the system is required to operate at higher temperature than the ambient, and when this is done, the temperature of the reactant inside the reactor initially at room temperature increases due to the temperature gradient between the system and the ambient.

CHAPTER 5

CONCLUSIONS

This project has proven to be a major and very sufficient study in illustrating and analyzing the overall performance of an ideal and a real Reactor with respect to their residence time distribution and conversion. However, the experimental data analysis and calculation reveals that alkaline hydrolysis of ethyl acetate and methyl acetate with sodium hydroxide is a 2nd order reaction. And the reaction rate constants "k" obtained from the experimental data as shown in the table 3 is proportional to the operating temperature. As temperature increase, k value increases. And the activation energy, E_a, which is defined as minimum energy that must be possessed by reacting molecules before the reaction will occur is determined using Arrhenius equation. Activation energy, E_a for particular reaction that use the same reacting species is the same.

The main objective of the research project is the illustration of an ideal and a real behaviour of CSTR based on saponification process and residence time distribution. A real CSTR experienced non-ideality behaviour due to creation of the dead zone and channeling. However, RTD, which is determined from either *pulse input* or *step input,* is the main factor used in measuring the degree of bypass as well as channeling. The two methods have their advantages and disadvantages in determining E (t) but reveals similar result.

From the RTD experimental data analysis, a few real reactors are modeled such as the two CSTR interchange, tanks in series, the zero adjustable parameters which are segregation and maximum mixedness model and the two adjustable parameters which is the CSTR modeled by using bypass and dead space 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 conversions for the ideal reactor is 43 % for ethanol synthesis and 53 % for methanol synthesis, and for the real reactor modeled are as shown in table 4.

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 main objectives of the study have been successfully accomplished.

RECOMMENDATIONS

In conclusion, the author would like to say that the material presented in this report is only an introduction to the area of reactor's performance analysis and more details can be found in some of the reverences cited. As stated in the earlier part of the report, the residence time distribution can be used as a tool for the diagnosis of non-ideal reactor behaviour, and can be combined with mixing model to estimate reactor conversion. However, this approach is appropriate for flowing systems in turbulence flow where the feed is mixed prior to entering the reactor vessel. In cases such as a fed batch reactor, the RTD approach is not very useful, and in situations where mixing is important more sophisticated models should be used.

Moreover, the author would like to recommend that the saponification process also be done for other types of reactors such as batch reactor and Plug flow reactor to further understand the conversion of reactants, which can help in predicting different routes of producing liquid ethanol and methanol in industries due to their high market demand.

- Analysis of dispersion Model for CSTR as well as other types of reactors.
- Analysis of RTD with multiple reactions.
- Development of material and energy balance simulation for a CSTR.
- Calibration of the pumps and the control values prior to any experiment
- Consider using other types of reaction process other than Saponification to optimize the cost of chemicals

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APPENDIX A:

RESULTS RELATIONSHIPE BETWEEN CONDUCTIVITY AND CONCENTRATION

Table 5: Calibration between Concentration and Conductivity of Sodium Chloride

Mass of NaCl (g)	Molarity (M)	Volume (L)	Conductivity Λ (ms)
4.06	0.146464646	0.5	7750
5.72	0.206349206	0.5	10600
8.65	0.312049062	0.5	15520
9.004	0.324819625	0.5	15990
10.015	0.361291486	0.5	17610
11.005	0.397005772	0.5	19350
12.026	0.433838384	0.5	21200
13.004	0.469119769	0.5	22700
14.008	0.505339105	0.5	24400
15.014	0.541630592	0.5	25900
16.051	0.579040404	0.5	27300
17.018	0.613924964	0.5	28700
18.021	0.650108225	0.5	30400
19.001	0.68546176	0.5	31900
20.015	0.722041847	0.5	33100

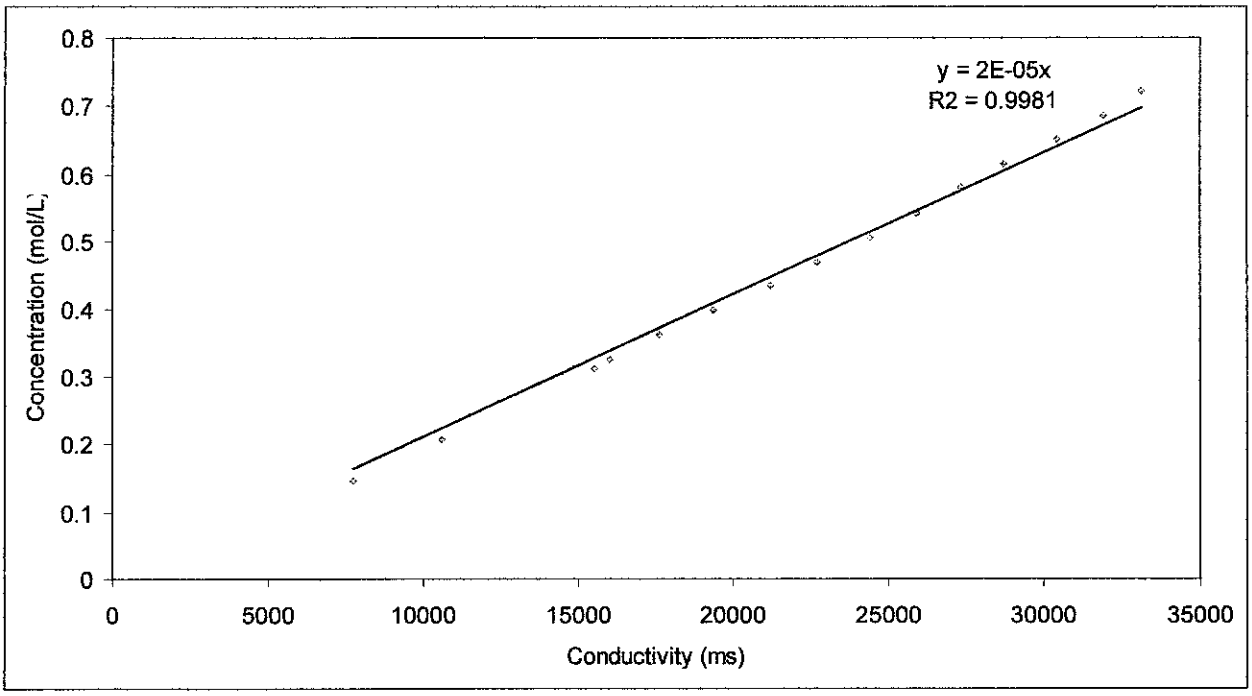


Figure 23: Trend of Concentration versus Conductivity of Sodium Chloride

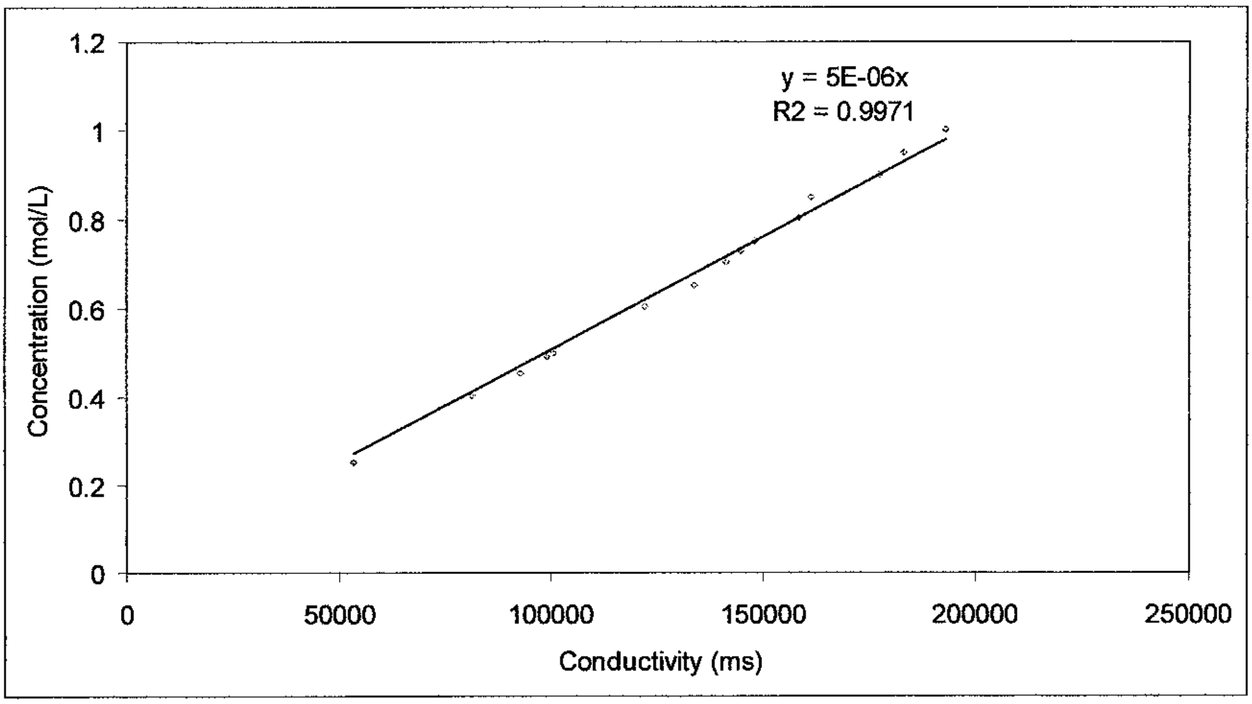


Figure 24: Trend of Concentration versus Conductivity of Sodium Hydroxide

Table 6: Calibration between Concentration and Conductivity of Sodium Hydroxide

Mass of NaOH (g)	Molarity (M)	Volume (L)	Conductivity Λ (ms)
5.066	0.2533	0.5	53600
8.08	0.404	0.5	81200
9.097	0.45485	0.5	92800
9.866	0.4933	0.5	98900
10.006	0.5003	0.5	100500
12.09	0.6045	0.5	121900
13.05	0.6525	0.5	133800
14.088	0.7044	0.5	141100
14.605	0.73025	0.5	144600
15.032	0.7516	0.5	147900
16.089	0.80445	0.5	158400
17.019	0.85095	0.5	161300
18.005	0.90025	0.5	177300
19.005	0.95025	0.5	182900
20.034	1.0017	0.5	193000

The above figure 23 and 24 shows the relationship between concentration and conductivity of Sodium Chloride and Sodium Hydroxide. The graph clearly shows that concentration is directly proportional to the conductivity of the Sodium Chloride and Sodium Hydroxide solution. As the concentration increases the conductivity will increase as well.

However, equation of straight line obtained from the graph is used to convert the conductivity values of the NaCl and NaOH solutions of the step change test and pulse input test into Concentration values.

Numerical Integration:

- For N+1 points, where N is an integer,

$$\int_{x_o}^{x_N} f(x)dx = \frac{3}{8}h[f_o + 3f_1 + 3f_2 + 2f_3 + \ldots\ldots\ldots\ldots\ldots + 3f_{N-1} + f_N\ ]$$

Where, $h = \frac{x_N - x_o}{N}$

- For N+1 points, where N is an even number,

$$\int_{x_o}^{x_N} f(x)dx = \frac{h}{3}[f_o + 4f_1 + 2f_2 + 4f_3 + 2f_4 + \ldots\ldots\ldots + 4f_N + f_N\ ]$$

Where, $h = \frac{x_N - x_o}{N}$

CALCULATION OF RESIDENCE TIME DISTRIBUTION

$$E(t) = \frac{C(t)}{Area - under - the - graph} = \frac{C(t)}{\int_0^\infty C(t)dt}$$

Numerical Integration:

- For N+1 points, where N is an integer,

$$\int_{x_o}^{x_N} f(x)dx = \frac{3}{8}h[f_o + 3f_1 + 3f_2 + 2f_3 + \ldots\ldots\ldots\ldots\ldots + 3f_{N-1} + f_N\ ]$$

Where, $h = \frac{x_N - x_o}{N}$

$$\int_0^\infty C(t)dt$$

- For N+1 points, where N is an even number,

$$\int_{x_o}^{x_N} f(x)dx = \frac{h}{3}[f_o + 4f_1 + 2f_2 + 4f_3 + 2f_4 + \dots\dots\dots\dots + 4f_N + f_N\ ]$$

Where, $h = \frac{x_N - x_o}{N}$

CALCULATION OF MEAN RESIDENCE TIME DISTRIBUTION

$$t_m = \int_0^\infty t.E(t)dt$$

- For N+1 points, where N is an even number,

$$\int_{x_o}^{x_N} f(x)dx = \frac{h}{3}[f_o + 4f_1 + 2f_2 + 4f_3 + 2f_4 + \dots\dots\dots\dots + 4f_N + f_N\ ]$$

Where, $h = \frac{x_N - x_o}{N}$

CALCULATION OF SEGREGATION CONVERSION

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

- For N+1 points, where N is an even number,

$$\int_{x_o}^{x_N} f(x)dx = \frac{h}{3}[f_o + 4f_1 + 2f_2 + 4f_3 + 2f_4 + \dots\dots\dots\dots + 4f_N + f_N\ ]$$

Where, $h = \frac{x_N - x_o}{N}$

CALCULATION OF VARIANCE

$$\sigma^2 = \int_0^\infty (t - t_m)^2 E(t)dt$$

- For N+1 points, where N is an even number,

$$\int_{x_o}^{x_N} f(x)dx = \frac{h}{3}[f_o + 4f_1 + 2f_2 + 4f_3 + 2f_4 + \ldots\ldots\ldots\ldots + 4f_N + f_N\ ]$$

Where, $h = \frac{x_N - x_o}{N}$

PREPARATION OF SOLUTIONS

i) To prepare 0.1M NaOH solution:

To determine the mass of Sodium Hydroxide needed for 0.1M NaOH solution

$$Molecular\ \ Weight\,, MW_{NaOH} = 40\,{}^{g}\!/_{mol}$$
$$Molarity\,, M = 0.1M\left({}^{mol}\!/_{L}\right)NaOH$$
$$Volume\,, V = 5.0L$$
$$M = \frac{n}{V}$$
$$Number\ \ of\ \ moles\,, n = M \cdot V$$
$$n = \left(0.1\,{}^{mol}\!/_{L}\right)\cdot(5.0L)$$
$$n = 0.5mol$$
$$n = \frac{mass\,, m}{MW_{NaOH}}$$
$$m = n \cdot MW$$
$$m = (0.5mol)\cdot\left(40\,{}^{g}\!/_{mol}\right)$$
$$m = 20g$$

ii) To prepare 0.1M Ethyl Acetate solution:

To determine the volume of Ethyl Acetate needed for 0.1M Ethyl Acetate solution:

$$Molarity, M = 0.1M\left(^{mol}/_{L}\right) CH_3C0_2C_2H_5$$

$$Volume, V = 5.0L$$

$$M = \frac{n}{V}$$

$$number\ of\ moles, n = M \cdot V$$

$$n = \left(0.1\,^{mol}/_{L}\right) \cdot (5.0L)$$

$$n = 0.5mol$$

$$Molecular\ Weight, MW_{CH_3C0_2C_2H_5} = 88.11\,^{g}/_{mol}$$

$$n = \frac{mass, m}{MW_{CH_3C0_2C_2H_5}}$$

$$m = n \cdot MW$$

$$m = (0.5mol) \cdot \left(88.11\,^{g}/_{mol}\right)$$

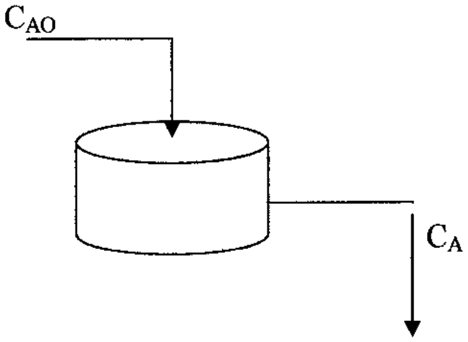
$$m = 44.055g$$

$$given: \quad 1L = 0.9kg$$

$$\therefore V = [44.055g] \cdot \left[\frac{1kg}{10^3 g}\right] \cdot \left[\frac{1L}{0.9kg}\right]$$

$$V = 0.05L = 50mL$$

SAPONIFICATION REACTION TAKING PLACE IN A CSTR



Material Balance for CSTR

In + *Generation* = *Out* + *Accumulation*

ads to:

$$v.C_0 + (-k.C.V) = v.C \Rightarrow v.C_0 = (v + kV)C \Rightarrow C = \frac{C_0}{\left(1 + \frac{kV}{v}\right)}$$

$$F_{A0} = F_A + \underbrace{G_A}_{=r_A V} + \underbrace{\frac{dN_A}{dt}}_{=0} \qquad \Rightarrow r_A V = F_{A0} - F_A$$

$$= F_{A0} - F_{A0}(1 - X_A) = F_{A0} X_A$$

ce; $F_{A0} = v_0 C_{A0}$

$$\Rightarrow r_A = \frac{v_0}{V} C_{A0} X_A$$

Space time:

$$\Rightarrow \tau = \frac{V}{v_0} = \frac{C_{A0} X_A}{r_A}$$ (Mean residence time)

If volume V of the reactor is considered constant, then concentration C_{A0} of inlet stream

$$C_A = C_{A0}(1 - X_A)$$

Substituting for τ:

$$\tau = \frac{C_{A0} X_A}{r_A} \qquad \Rightarrow C_A = C_{A0} - r_A \tau$$

Therefore:

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

Integrating the above equation illustrates the follow:

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = k\int_0^1 dt \qquad -\ln\frac{C_A}{C_{A0}} = kt$$

Plotting equation of $-\ln\frac{C_A}{C_{A0}}$ versus time gives a linear graph, whose slope of the straight line is the reaction rate constant *k*.

However, if the reaction is considerate to be a second order reaction, the rate of reaction is as follows:

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

Integrating the above equation with respect to C_A gives:

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = \frac{1}{C_A}\left(\frac{X_A}{1-X_A}\right) = kt$$

Thus, plotting a graph of $\frac{1}{C_A}$ versus time will give a linear trend with a straight whose slope is k, and intercept $= \frac{1}{C_{A0}}$.

MODELING OF CSTR UNDRE IDEAL/REAL CONDITION PER BELOW MENTIONED CONDITIONS

The main assumptions used in the approach of modeling the CSTR reactor are as follows

- Equimolar solution of the reactants
- The solution is perfectly mixed
- Steady state
- Constant volume

By running Hysys modeling package with the Saponification reaction of Methyl Acetate with sodium hydroxide to produce Methanol, the below tabulated physical properties are obtained:

Parameters	**Expression**	**Value**
Mass Density	ρ (kg/m3)	1510
Dynamic Viscosity	μ (N.s/m2)	0.53331E-3
Specific Heat Capacity	Cp (kJ/kgc)	5.18
Thermal Conductivity	K (W/mk)	0.649
Temperature (T_0)	(k)	298
Pressure	P (atm)	1.0

The calculated average velocity of the mixture = (flowrate)/(Area) = $(0.06/\pi *R*R)$

Where R = d/2 = (0.089/2) = 0.0445m

Therefore, Average Velocity = 9.645m/s

$$\mathrm{Re} = \frac{\rho V d}{\mu} = \left(\frac{1510 * 9.645 * 0.089}{0.00053331} \right) = 2430465.5$$

Since the Renold number is greater than 2000, therefore, the flow is in turbulence region.

$$\mathrm{Pr} = \frac{C_p \mu}{k} = \left(\frac{5.18 * 0.00053331}{0.649} \right) = 0.0043$$

$$Nu = 0.023 * \mathrm{Re}^{0.8} * \mathrm{Pr}^{0.4} = 334$$

$$h = \frac{kNu}{d} = \left(\frac{0.649 * 334}{0.089} \right) = 2435.6 W / m^2 k.$$

APPENDIX B:

t (min)	CT1 (M)	E(t)	$\boxed{t_m = \int_0^\infty t.E(t)\,dt}$
0	0	0	0
1	0.001508255	0.054134918	0.07217989
2	0.003487255	0.125166021	0.166888028
3	0.004949255	0.118427162	0.710562971
4	0.004789255	0.171897955	0.458394547
5	0.004517255	0.162135216	1.080901442
6	0.004219255	0.100959516	0.605757098
7	0.003980255	0.142860985	1.333369198
8	0.003740255	0.134246804	0.715982955
9	0.003520255	0.084233647	1.516205655
10	0.003322255	0.119243772	0.794958477
11	0.003114255	0.111778148	1.639412834
12	0.002942255	0.070403101	0.844837209
13	0.002790255	0.100149003	1.735916051
14	0.002627255	0.094298538	0.880119689
15	0.002501255	0.059850729	1.795521858
16	0.002324255	0.083423134	0.889846764
17	0.002203255	0.079080151	1.792483423
18	0.002065255	0.049417998	0.889523961
19	0.001975255	0.070896679	1.796049195
20	0.001843255	0.066158879	0.882118387
21	0.001728255	0.041354167	1.736875012
22	0.001634255	0.058657363	0.860307987
23	0.001523255	0.054673304	1.676647985
24	0.001426255	0.034127826	0.819067822
25	0.001348255	0.04839213	1.613070998
26	0.001264255	0.045377166	0.786537552
27	0.001186255	0.028385038	1.532792071

28	0.001105255	0.039670271	0.740511732
29	0.001032255	0.037050125	1.432604814
30	0.000975255	0.023336171	0.700085129
31	0.000913255	0.032778926	1.354862285
32	0.000851255	0.030553596	0.651810049
33	0.000790255	0.018909439	1.248022965
34	0.000731255	0.026246505	0.594920789
35	0.000687255	0.024667239	1.151137811
36	0.000641255	0.015344125	0.552388497
37	0.000605255	0.02172406	1.071720302
38	0.000554255	0.019893547	0.503969848
39	0.000512255	0.012257377	0.956075375
40	0.000481255	0.0172734	0.460623995
41	0.000452255	0.01623252	0.887377736
42	0.000421255	0.010079903	0.423355925
43	0.000394255	0.014150759	0.811310186
44	0.000361255	0.012966309	0.380345068
45	0.000332255	0.007950286	0.715525733
46	0.000316255	0.01135115	0.348101937
47	0.000294255	0.010561517	0.661855055
48	0.000271255	0.006490661	0.311551716
49	0.000256255	0.009197605	0.600910179
50	0.000231255	0.008300294	0.276676474
51	0.000214255	0.005126749	0.522928367
52	0.000203255	0.007295306	0.252903955
53	0.000186255	0.006685135	0.472416222
54	0.000164255	0.003930335	0.21223807
55	0.000148255	0.005321223	0.390223033
56	0.000135255	0.004854622	0.18123921
57	0.000116255	0.002781777	0.31712259
58	0.000102255	0.003670172	0.141913308
59	9.52548E-05	0.003418925	0.268955417

60	8.42548E-05	0.002016072	0.120964326
61	7.62548E-05	0.002736969	0.222606793
62	7.12548E-05	0.002557507	0.105710275
63	6.22548E-05	0.00148965	0.187695888
64	5.42548E-05	0.001947335	0.083086314
65	4.82548E-05	0.001731981	0.150105015
66	4.52548E-05	0.001082869	0.071469362
67	3.62548E-05	0.001301272	0.116246954
68	2.92548E-05	0.001050025	0.04760113
69	2.52548E-05	0.000604303	0.083393881
70	2.12548E-05	0.000762886	0.035601325
71	2.02548E-05	0.000726993	0.068822015
72	1.62548E-05	0.000388949	0.028004325
73	1.32548E-05	0.000475746	0.04630596
74	5.25478E-06	0.000188607	0.009304601
75	2.25478E-06	5.3953E-05	0.008092952
76	1.25478E-06	1.50124E-05	0.00114094
		E(t) = **1.049599**	**t_m=16.789699**

VARIANCE CALCULATION

t (min)	σ (Variance)
0	0
1	17.99549999
2	18.25214281
3	45.03922296
4	18.74563247
5	30.04841203
6	11.75346501
7	18.25538746
8	6.914498738
9	10.22249612
10	3.664759563

11	4.995829583
12	1.61513277
13	1.917762394
14	0.489247247
15	0.383406457
16	0.03468314
17	0.004663253
18	0.072388894
19	0.461814401
20	0.454557042
21	1.466140414
22	1.061590204
23	2.811508216
24	1.774252454
25	4.349422873
26	2.566219274
27	5.918294506
28	3.323597779
29	7.365142419
30	4.072443098
31	8.825514133
32	4.712449305
33	9.937812441
34	5.182713009
35	10.90670393
36	5.662529342
37	11.8311047
38	5.966430982
39	12.09306575
40	6.203661772
41	12.68601001
42	6.40637585

43	12.96171567
44	6.400174344
45	12.6540103
46	6.45684964
47	12.85213081
48	6.322441572
49	12.7233961
50	6.103062989
51	12.00012629
52	6.02964514
53	11.68727338
54	5.441966868
55	10.35884008
56	4.975817979
57	8.995534484
58	4.155341316
59	8.122041093
60	3.764268924
61	7.132725684
62	3.484980166
63	6.361972733
64	2.893497129
65	5.367369968
66	2.622334032
67	4.374137489
68	1.835790017
69	3.294560518
70	1.439990264
71	2.848607895
72	1.185585382
73	2.004222122
74	0.411542332

75	0.365632986
76	0.052631245
	σ= 12.98814935

MAXIMUM MIXDNESS (Conversion)

t (min)	X(t) (Ethanol)	X(t) (Methanol)
0	0.000000	0.000000
1	0.081240	0.141600
2	0.122602	0.198503
3	0.143205	0.221567
4	0.178631	0.269909
5	0.211585	0.312365
6	0.244156	0.352852
7	0.272384	0.385875
8	0.297385	0.413765
9	0.318253	0.435663
10	0.335568	0.452774
11	0.353067	0.470396
12	0.369127	0.486209
13	0.383418	0.499824
14	0.396166	0.511604
15	0.408703	0.523318
16	0.420262	0.533924
17	0.430488	0.542986
18	0.440396	0.551823
19	0.448935	0.559087
20	0.455862	0.564517
21	0.462459	0.569753
22	0.468491	0.574476
23	0.473565	0.578195

24	0.478471	0.581890
25	0.483744	0.586184
26	0.488803	0.590324
27	0.493168	0.593723
28	0.497668	0.597388
29	0.501795	0.600688
30	0.505708	0.603811
31	0.509746	0.607160
32	0.513279	0.609963
33	0.516280	0.612200
34	0.519134	0.614339
35	0.521741	0.616254
36	0.524240	0.618109
37	0.526599	0.619861
38	0.528535	0.621171
39	0.529921	0.621898
40	0.531309	0.622703
41	0.532471	0.623305
42	0.533526	0.623846
43	0.534193	0.623992
44	0.534552	0.623840
45	0.534685	0.623491
46	0.534675	0.623041
47	0.534668	0.622656
48	0.534427	0.622051
49	0.533910	0.621180
50	0.533253	0.620202
51	0.532433	0.619090
52	0.531591	0.618005
53	0.530520	0.616700
54	0.529130	0.615073
55	0.527712	0.613467

56	0.526069	0.611647
57	0.524101	0.609499
58	0.522317	0.607620
59	0.520243	0.605444
60	0.518114	0.603248
61	0.515473	0.600499
62	0.512873	0.597850
63	0.510021	0.594954
64	0.507067	0.591988
65	0.503892	0.588808
66	0.500291	0.585177
67	0.496424	0.581291
68	0.492201	0.577048
69	0.487564	0.572382
70	0.482598	0.567401
71	0.477001	0.561750
72	0.471041	0.555758
73	0.465410	0.550240
74	0.469092	0.555788
75	0.483517	0.573689
	0.505188	**0.599423**

SEGREGATION MODEL: TANKS IN SERIES @ TEMPERATURE OF 25C

	Ethanol			Methanol		
t (min)	X(t)	X(t)E(t)	Conversion	X(t)	X(t)E(t)	Conversion
0	0	0	0	0	0	0
1	0.075187275	0.001356752	0.005427009	0.12403644	0.002238234	0.0089529
2	0.139858937	0.005835196	0.011670391	0.220698254	0.009207974	0.0184159
3	0.196076855	0.011610413	0.046441651	0.298147108	0.017654358	0.0706174
4	0.245396921	0.014061076	0.028122153	0.361593463	0.020719059	0.0414381
5	0.289015286	0.015619852	0.062479408	0.414519906	0.022402758	0.0896110
6	0.327866649	0.016550629	0.033101258	0.459342561	0.023187501	0.0463750
7	0.362691989	0.017271512	0.069086047	0.497790277	0.023704937	0.0948197
8	0.394086282	0.017634941	0.035269883	0.531132783	0.023767626	0.0475352
9	0.422532771	0.017795738	0.071182953	0.560323602	0.02359905	0.0943962
10	0.44842802	0.017824083	0.035648166	0.586092715	0.023295969	0.0465919
11	0.472100512	0.017590174	0.070360694	0.609008445	0.022691279	0.0907651
12	0.493824661	0.017383394	0.034766787	0.629519858	0.022160075	0.0443201
13	0.513831494	0.017153237	0.068612949	0.647986483	0.021631733	0.0865269
14	0.532316902	0.016732235	0.03346447	0.664699571	0.020893399	0.0417867
15	0.549448074	0.016442434	0.065769735	0.679897567	0.020346182	0.0813847
16	0.565368567	0.015721606	0.031443212	0.69377756	0.019292366	0.0385847
17	0.580202342	0.015294163	0.061176652	0.706503874	0.018623478	0.0744939
18	0.594056994	0.014678554	0.029357107	0.718214608	0.017746364	0.0354927
19	0.607026369	0.014345384	0.057381538	0.729026664	0.017228523	0.0689140
20	0.619192688	0.013655031	0.027310063	0.739039666	0.016298012	0.0325960
21	0.630628301	0.013039554	0.052158216	0.748339038	0.015473469	0.0618938
22	0.641397117	0.012540888	0.025081776	0.756998445	0.014801177	0.0296023
23	0.651555803	0.011874236	0.047496945	0.765081752	0.013943182	0.0557727
24	0.661154784	0.011281888	0.022563775	0.772644598	0.01318434	0.0263686
25	0.670239077	0.010811432	0.043245729	0.779735683	0.01257769	0.0503107
26	0.678848995	0.010268081	0.020536163	0.786397813	0.011894835	0.0237896
27	0.687020751	0.009750555	0.039002221	0.792668768	0.011249967	0.0449998
28	0.694786961	0.009187462	0.018374925	0.798582017	0.010559988	0.0211199
29	0.702177086	0.008671916	0.034687665	0.804167319	0.0099315	0.0397259
30	0.709217796	0.008275214	0.016550428	0.80945122	0.009444746	0.0188894
31	0.715933301	0.007822508	0.031290033	0.814457474	0.008899014	0.0355960
32	0.722345624	0.007356752	0.014713504	0.819207405	0.008343244	0.0166864
33	0.728474843	0.006887525	0.027550101	0.823720209	0.007788043	0.0311521
34	0.734339302	0.006424613	0.012849227	0.828013209	0.007244151	0.0144883
35	0.739955792	0.006084222	0.024336888	0.832102082	0.006841887	0.0273675
36	0.745339717	0.005718293	0.011436586	0.83600105	0.006413852	0.0128277
37	0.750505227	0.005434674	0.021738694	0.839723041	0.006080731	0.0243229
38	0.755465349	0.005009628	0.010019257	0.84327984	0.005591942	0.0111838
39	0.760232095	0.004659226	0.018636902	0.846682203	0.005189051	0.0207562
40	0.764816557	0.004403661	0.008807321	0.849939976	0.004893784	0.0097875
41	0.769228994	0.004162175	0.0166487	0.853062184	0.004615783	0.0184631
42	0.773478911	0.003898296	0.007796592	0.856057117	0.004314486	0.0086289
43	0.777575124	0.003667759	0.014671038	0.8589324	0.004051515	0.0162060
44	0.781525824	0.003377835	0.00675567	0.861695065	0.003724335	0.0074486
45	0.785338628	0.003121833	0.012487333	0.864351601	0.003435921	0.0137436
46	0.789020634	0.002985431	0.005970861	0.866908007	0.003280134	0.0065602

47	0.792578457	0.002790277	0.011161108	0.86936984	0.003060621	0.01224248
48	0.796018277	0.002583342	0.005166685	0.871742253	0.002829092	0.00565818
49	0.799345868	0.002450689	0.009802757	0.874030031	0.002679661	0.0107186
50	0.802566634	0.002220513	0.004441026	0.876237624	0.002424343	0.00484868
51	0.805685638	0.002065274	0.008261096	0.878369174	0.002251589	0.00900635
52	0.808707629	0.00196659	0.00393318	0.880428544	0.002140999	0.00428199
53	0.811637062	0.001808635	0.007234538	0.88241934	0.001966364	0.00786545
54	0.814478127	0.001600586	0.003201172	0.88434493	0.001737886	0.00347577
55	0.817234762	0.001449563	0.005798251	0.886208466	0.001571904	0.00628761
56	0.819910676	0.001326785	0.002653571	0.888012901	0.001436989	0.00287397
57	0.822509363	0.001144019	0.004576075	0.889761002	0.001237558	0.0049502
58	0.825034118	0.001009339	0.002018678	0.891455366	0.001090598	0.0021811
59	0.827488054	0.00094304	0.003772159	0.893098435	0.001017812	0.0040712
60	0.829874107	0.000836543	0.001673086	0.894692502	0.000901882	0.0018037
61	0.832195056	0.000759231	0.003036923	0.896239728	0.00081766	0.0032706
62	0.834453531	0.000711373	0.001422747	0.897742147	0.000765327	0.0015306
63	0.83665202	0.000623159	0.002492637	0.899201677	0.000669748	0.0026789
64	0.838792881	0.00054447	0.001088941	0.90062013	0.000584603	0.0011692
65	0.840878351	0.000485462	0.001941847	0.901999216	0.000520748	0.0020829
66	0.842910553	0.000456381	0.000912762	0.903340551	0.0004891	0.0009782
67	0.844891502	0.000366478	0.001465911	0.904645663	0.000392397	0.0015695
68	0.846823111	0.000296395	0.00059279	0.905916002	0.000317078	0.0006341
69	0.848707203	0.000256438	0.001025753	0.907152938	0.000274098	0.0010963
70	0.850545509	0.00021629	0.000432579	0.908357771	0.000230991	0.0004619
71	0.852339678	0.000206548	0.000826193	0.909531736	0.000220408	0.0008816
72	0.85409128	0.000166099	0.000332198	0.910676004	0.000177103	0.0003542
73	0.855801814	0.000135715	0.000542859	0.911791687	0.000144594	0.0005783
74	0.857472706	5.39084E-05	0.000107817	0.912879844	5.73918E-05	0.0001147
75	0.859105319	2.31757E-05	9.27026E-05	0.91394148	2.46549E-05	9.86198E-
76	0.860700953	1.29212E-05	1.29212E-05	0.914977554	1.3736E-05	1.3736E-0
		SUM = X =	**0.511166546**		SUM = X =	**0.633030**