

REACTION KINETICS

- 10.1 Plug Flow Reactor
- 10.2 Dynamic and Steady State Behaviour of a CSTR
- 10.3 Reaction Kinetics Study of Saponification Reaction in a CSTR and Series CSTRs
- 10.4 Esterification

*For millions of years mankind lived just like animals.
Then, something happened which unleashed the power
of our imagination.
We learned to talk.*

DAVID GILMOUR / POLLY SAMSON

10.1 PLUG FLOW REACTOR

Keywords: *Tubular reactor, plug flow reactor, saponification, integral method, differential method.*

10.1.1 Object

The object of this experiment is to study the behaviour of a plug-flow reactor by performing a series of experiments on the saponification of ethyl acetate.

10.1.2 Theory

In a tubular reactor, the feed enters at one end of a cylindrical tube and the product stream leaves at the other end. The long tube and the lack of provision for stirring prevents complete mixing of the fluid in the tube. Hence the properties of the flowing stream will vary from one point to another, namely in both radial and axial directions.

In the ideal tubular reactor, which is called the “plug flow” reactor, specific assumptions are made about the extent of mixing:

1. no mixing in the axial direction, i.e., the direction of flow
2. complete mixing in the radial direction
3. a uniform velocity profile across the radius.

The absence of longitudinal mixing is the special characteristics of this type of reactor. It is an assumption at the opposite extreme from the complete mixing assumption of the ideal stirred tank reactor.

The validity of the assumptions will depend on the geometry of the reactor and the flow conditions. Deviations, which are frequent but not always important, are of two kinds:

1. mixing in longitudinal direction due to vortices and turbulence
2. incomplete mixing in radial direction in laminar flow conditions

Mass Balance

For a time element Δt and a volume element ΔV , the mass balance for species 'i' is given by the following equation:

$$Q_A C_A \Big|_v \Delta t - Q_A C_A \Big|_{v+\Delta v} \Delta t - r_A \Delta V \Delta t = 0 \quad (10.1.1)$$

where Q_A : molar feed rate of reactant A to the reactor, mol/sec

C_A : concentration of reactant A

r_A : rate of disappearance of reactant A, mol/lit•sec

The conversion, X, is defined as:

$$X = (\text{initial concentration} - \text{final concentration}) / (\text{initial concentration})$$

Since the system is at steady state, the accumulation term in Equation (10.1.1) is zero.

Equation (10.1.1) can be written as:

$$-Q_A \Delta C_A - r_A \Delta V = 0 \quad (10.1.2)$$

Dividing by ΔV and taking limit as $\Delta V \rightarrow 0$

$$dC_A/dV = -r_A/Q_A \quad (10.1.3)$$

This is the relationship between concentration and size of reactor for the plug flow reactor. Here rate is a variable, but varies with longitudinal position (volume in the reactor, rather than with time). Integrating,

$$-dV/Q_A = dC_A/r_A \quad (10.1.4)$$

At the entrance: $V = 0$

$$C_A = C_{A0}$$

At the exit: $V = V_R$ (total reactor volume)

$$C_A = C_A \text{ (exit conversion)}$$

$$-\frac{V_R}{Q_A} = \int_{C_{A0}}^{C_A} \frac{dC_A}{r_A} \quad (10.1.5)$$

10.1.3 Apparatus

The apparatus used in this experiment is shown in Figures 10.1.1 and 10.1.2:

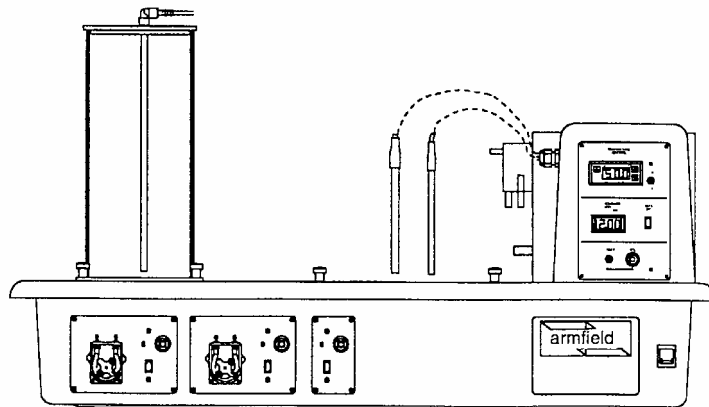


Figure 10.1.1 - Chemical reactor service unit.

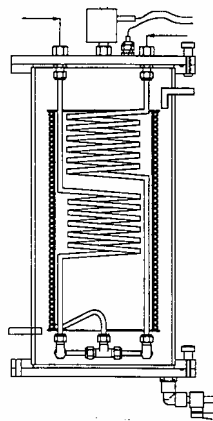


Figure 10.1.2 - Tubular reactor.

10.1.4 Experimental Procedure

1. Prepare 5 lt of 0.05 N ethyl acetate and 0.05 N NaOH solutions. Then pour these solutions into the feed tanks.
2. Adjust the temperature of PFR.
3. Adjust the apparatus to constant flowrate.
4. Record the conductivity when steady state is reached.
5. Repeat the same procedure for different flowrates.

10.1.5 The Conductivity and Concentration Relations

It has been determined that the degree of conversion of the reagents affects the conductivity of the reactor contents so that recording the conductivity with respect to time helps to calculate the amount of conversion with the help of formulas that are provided below.

$$C_{A0} = \frac{Q_A}{Q_A + Q_B} C_{\text{tank1}} \qquad C_{B0} = \frac{Q_B}{Q_A + Q_B} C_{\text{tank2}} \quad (10.1.6)$$

where A=NaOH, B=EtAc in the reaction: $A + B \rightarrow C + D$

$$C_{\infty} = C_{B0} \quad \text{for} \quad C_{B0} < C_{A0}$$

$$C_{\infty} = C_{A0} \quad \text{for} \quad C_{B0} \geq C_{A0}$$

$$\Lambda_{C_{\infty}} = 0.070 C_{\infty} [1 + 0.0284(T-294)] \quad \text{for } T \geq 294K \quad (10.1.7)$$

$$\Lambda_{C_{A0}} = 0.195 C_{A0} [1 + 0.0184(T-294)] \quad \text{for } T \geq 294K \quad (10.1.8)$$

$$\Lambda_0 = \Lambda_{C_{A0}} \quad \text{assuming } C_0 = 0$$

$$C_{A_{\infty}} = 0 \quad \text{for} \quad C_{A0} < C_{B0}$$

$$C_{A_{\infty}} = C_{A0} - C_{B0} \quad \text{for} \quad C_{A0} \geq C_{B0}$$

$$\Lambda_{C_{A_{\infty}}} = 0.195 C_{A_{\infty}} [1 + 0.0184(T-294)] \quad \text{if } C_{A0} \neq 0. \quad (10.1.9)$$

$$\Lambda_{\infty} = \Lambda_{C_{\infty}} + \Lambda_{C_{A_{\infty}}} \quad (10.1.10)$$

$$C_A = (C_{A\infty} - C_{A0}) \left(\frac{\Lambda_0 - \Lambda_1}{\Lambda_0 - \Lambda_\infty} \right) + C_{A0} \quad (10.1.11)$$

$$C_C = C_{C\infty} \left(\frac{\Lambda_0 - \Lambda_1}{\Lambda_0 - \Lambda_\infty} \right) \quad \text{for } C_{C0} = 0 \quad (10.1.12)$$

$$X_A = \frac{C_{A0} - C_A}{C_{A0}} \quad (10.1.13)$$

10.1.5 Report Objectives

You may assume that the saponification reaction of ethyl acetate with NaOH is second order (overall).

1. Evaluate the data using the Integral Method. Calculate conversion.
2. Evaluate the rate constant using the Differential Method.
3. Compare the results of the two methods.

10.1.6 References

1. Denbihh, K. G., and J. C. R. Turner, *Chemical Reactor Theory*, 2nd edition, Cambridge University, 1971.
2. Levenspiel, O., *Chemical Reaction Engineering*, 2nd edition, John Wiley and Sons, 1972.
3. Perry, R. H., and D. Green, *Perry's Chemical Engineer's Handbook*, 6th edition, McGraw-Hill, 1984.
4. Smith, J. M., *Chemical Engineering Kinetics*, 3rd edition, McGraw-Hill, 1981.

10.2 DYNAMIC AND STEADY STATE BEHAVIOR OF A CSTR

Keywords: *Continuous stirred tank reactors, saponification, mathematical modelling, differential equations.*

10.2.1 Object

The object of the experiment is to study the dynamics of a CSTR during different stages of its continuous operation by using the saponification of ethyl acetate reaction.

10.2.2 Theory

Continuous stirred tank reactors are used very commonly in industrial processes. For this type of reactor, mixing is complete, so that the temperature and the composition of the reaction mixture are uniform in all parts of the vessel and are the same as those in the exit stream.

Three stages of the continuous operation of a CSTR can be modelled.

1. From beginning to overflow
2. From overflow to steady state
3. Steady state operation

The first and second stages are transient and they produce differential equations. The third stage is represented by a steady state model which contains algebraic equations.

Stage One

This stage is semibatch. There is no output because the reactor contents do not yet reach the overflow level. A material balance on either NaOH or ethyl acetate (both reactants are at the same concentration and flow rate) gives:

$$\text{rate of accumulation} = \text{rate of input} - \text{rate of consumption}$$

$$\frac{d}{dt}(VC) = FC_0 - VkC^2 \quad (10.2.1)$$

or

$$V \frac{dC}{dt} + C \frac{dV}{dt} = FC_0 - VkC^2 \quad (10.2.2)$$

But 'V' is a function of time, and since the system is of constant density and flow rate, a total mass balance gives:

$$\frac{dV}{dt} = F \quad \text{or} \quad V = Ft$$

since at $t = 0$, $V = 0$. Equation (10.2.2) becomes

$$\frac{dC}{dt} = \frac{C_0}{t} - \frac{C}{t} - kC^2 \quad (10.2.3)$$

Equation (10.2.3) is subject to $C = C_0$ at $t = 0$.

Stage Two

The second stage is continuous but not yet steady. The concentration is changing with time but the volume of the reactants is constant. A material balance takes the form:

rate of accumulation = rate of input - rate of output - rate of consumption

$$V \frac{dC}{dT} = FC_0 - FC - kVC^2 \quad (10.2.4)$$

and therefore

$$\frac{dC}{dT} = \frac{C_0}{\tau} - \frac{C}{\tau} - kC^2 \quad (10.2.5)$$

where $T = t - \tau$ is time in minutes and
 $\tau = V/F$ is time constant.

At steady state, $C = C_s$, which is a particular solution to Equation (10.2.5).

Stage Three

This is the easiest stage to model. A material balance requires that

rate of input = rate of output + rate of consumption

$$FC_0 = FC_s + kVC_s^2 \quad (10.2.6)$$

and

$$k\tau C_s^2 + C_s - C_0 = 0 \quad (10.2.7)$$

10.2.3 Apparatus

The apparatus used in this experiment is shown in Figures 10.2.1 and 10.2.2.

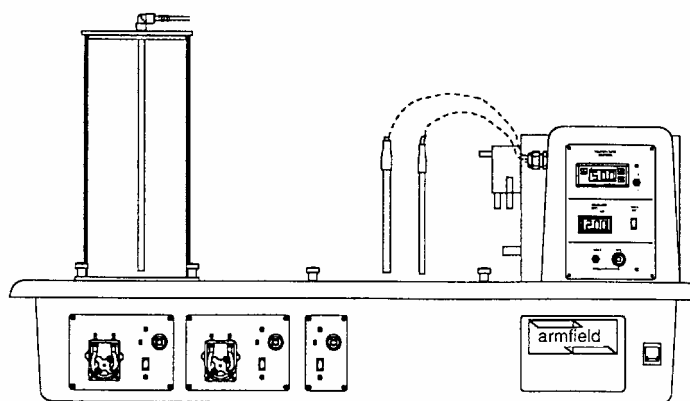


Figure 10.2.1 - Chemical reactor service unit.

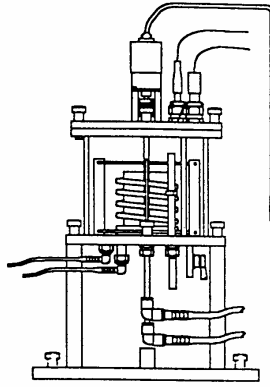


Figure 10.2.2 - Continuous stirred tank reactor.

10.2.4 Experimental Procedure

1. Make up 5 litre batches of 0.05 M sodium hydroxide and 0.05 M ethyl acetate.
2. Remove the lids of the reagent vessels and carefully fill the reagents to a level approximately 50 mm from the top. Refit the lids.
3. Adjust the set point of the temperature controller to 18 °C.
4. Using the calibration graph for each of the feed pumps, set the pump speed control to give 50 ml/min flow rate.
5. Set the agitator speed controller to 7.0
6. Switch on the feed pumps and agitator motor.
7. Collect the conductivity data for 45 minutes.

10.2.5 Report Objectives

You may assume that the saponification reaction of ethyl acetate with NaOH is second order overall.

1. Prepare a spreadsheet to calculate sodium hydroxide concentration, sodium acetate concentration and the degree of conversion of sodium hydroxide and sodium acetate for each of the conductivity data taken over the period of the experiment.

2. Draw sodium hydroxide concentration versus time, sodium acetate concentration versus time, and the degree of conversion of sodium hydroxide versus time and sodium acetate versus time graphs.
3. Calculate the specific rate constant (k) from material balance and compare it with the one obtained from Arrhenius equation.
4. By using the material balance at steady state, find the sodium hydroxide concentration and compare it with the experimental one.
5. Derive all of the equations you use in the theory part.

10.2.6 References

1. Fogler, H. S., *Elements of Chemical Reaction Engineering*, 2nd edition, Prentice-Hall Inc., 1992.
2. Levenspiel, O., *Chemical Reaction Engineering*, 2nd edition, Cambridge University, 1971.
3. Smith, J. M., *Chemical Engineering Kinetics*, 3rd edition, McGraw Hill, 1981.

10.3 REACTION KINETICS STUDY OF SAPONIFICATION REACTION IN SERIES CSTR'S

Keywords: *CSTR, CSTR in series, saponification, and conversion.*

10.3.1 Object

The object of this experiment is to find the efficiencies in three series stirred tank reactors. This way, the reaction mechanisms in CSTRs can be comprehended in a better way by studying the effect of the number of reactors used to carry out a specific reaction.

10.3.2 Theory

10.3.2.1 *Continuous Reactors*

In continuously operated chemical reactors, the reactants are pumped at constant rate into the reaction vessel and chemical reaction takes place while the reactant mixture flows through. The reaction products are continuously discharged to the subsequent separation and purification stages. The extent of the required separation and purification process depends on the efficiency of the reactor, and so the selection of the correct type of the reactor for a given duty is most important since the economics of the whole process could hinge on this choice. Normally, the efficiency of a chemical reactor is measured by its ability to convert the reactants into the desired products with the exclusion of unwanted by-products; this is measured by yield. However, additional factors such as safety, ease of control and stability of the process must also be considered. Many of these factors depend on the size and shape of the reactor. The size of reactor for a purposed feed rate depends on the reaction kinetics of the materials undergoing chemical change and on the flow conditions in the reactor. The flow conditions are determined by the cross sectional area of the path through which the reaction mixture flows; i.e. on the shape of the reactor. Thus, it is apparent that size and shape are interrelated factors, which must be taken together when considering the continuous reactors. The extreme types of continuous reactors are:

- i. Stirred tank reactor
- ii. Plug flow reactor

A. Continuous Stirred Tank Reactors

This type of reactor consists of one or more cylindrical tanks. Normally the tanks are arranged with their axes vertical, although this is not essential. The stirring of the contents of each tank is affected by an agitator which is mounted on a shaft inserted through the vessel lid. In addition, the tank is fitted with the auxiliary equipment necessary to maintain the desired reaction temperature and pressure conditions.

The well-stirred tank reactor is used almost exclusively for liquid phase reactions, although instances of gaseous reactions have been reported. In normal operation, a steady continuous feed of reactants is pumped into the vessel and since there is usually negligible density change on reaction, an equal volume of the reactor contents is displaced through an overflow pipe situated near the top of the vessel.

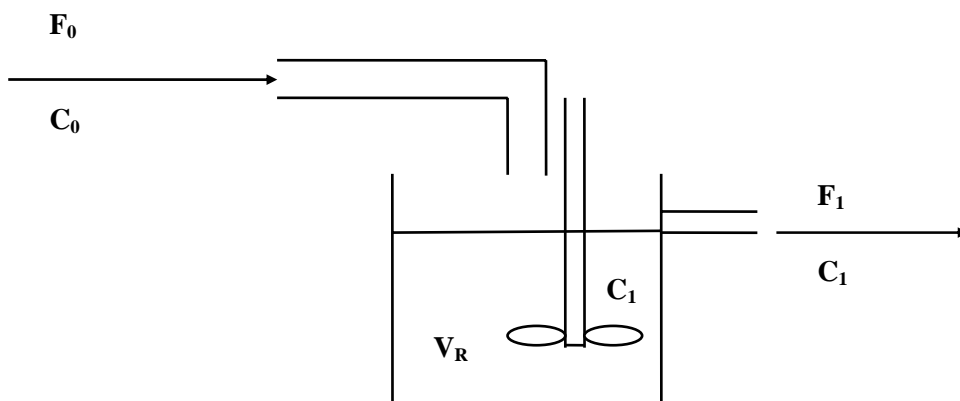


Figure 10.3.1 - Single continuous stirred tank reactor.

Considering the single stirred tank reactor shown in Figure 10.3.1, it is assumed that the design of the agitator is such that the whole of the vessel contents are completely mixed and at both a uniform temperature and composition. This premise of complete mixing then implies that the reactor outlet stream is identical in temperature and composition to the bulk reactor contents. Then, for an effective reactor volume 'V', molar input and output 'F', and moles N the mass balance for component A is:

$$F_{A0} - F_{A1} + r_A V_R = \frac{dN_A}{dt} \quad (10.3.1)$$

For irreversible reactions, the reaction rate term is:

$$r = kC_1^n \quad (10.3.2)$$

The reaction rate 'r' is constant with reactor position and also with time when steady state operation has been established. Hence under steady state operation, Equation (10.3.1) is an algebraic equation, the right hand side vanishes.

Single Tanks with Simple Reactions

For a first order reaction:

$$C_0 = C_1 \left(1 + \frac{kV}{F} \right) \quad (10.3.3)$$

V_R / Q is the space time and will be given the symbol 'τ'. Hence,

$$\frac{C_1}{C_0} = \frac{1}{(1 + k\tau)} \quad (10.3.4)$$

Since the input and the outlet volumetric flow rates are equal, the fractional conversion 'x' may be written:

$$x = 1 - \frac{C_1}{C_0} = 1 - \frac{1}{1 + k\tau} \quad (10.3.5)$$

and as is usual with first order reactions the result is independent of the feed concentration.

For a second order reaction:

$$C_0 = C_1 + k\tau C_1^2 \quad (10.3.6)$$

and the positive root of this quadratic gives:

$$C_1 = \frac{\sqrt{-1 + (1 + 4k\tau C_0)}}{2k\tau} \quad (10.3.7)$$

and hence,

$$x = 1 + \frac{-1 + \sqrt{(1 + 4k\tau C_0)}}{2k\tau} \quad (10.3.8)$$

The values of 'C₁' and 'x' are seen to be no longer dependent of the feed concentration, while on extension to non-integral reaction orders the algebraic equations are also likely to require numerical iteration for their solution.

Unsteady – State Behavior

Under unsteady – steady state conditions the mass balance equation turns out to be an ordinary differential equation that is to be solved numerically in order to simulate the theoretical behavior of concentration and conversion with respect to time. For a second order reaction this equation is derived from the equation (10.3.1) substituting the expressions of concentration, space time, and conversion.

$$\frac{dx}{dt} = kC_{A0}(1-x)^2 - \frac{x}{\tau} \quad (10.3.9)$$

where x = conversion of reactant A

C_{A0} = Initial concentration of A

k = Reaction rate constant

τ = Space time (V/v_0)

v_0 = Constant volumetric flow rate

Multiple Tank Cascade with Simple Reactions (CSTR in Series)

A major shortcoming of a single stirred tank is that all of the reaction takes place at the low final reactant concentration and hence requires an unduly large reactor hold-up. If a number of smaller well-stirred reactors are arranged in series, only the last one will have a reaction rate governed by the final reactant concentration and all of the others will have higher rates. Hence, for a given duty the total reactor hold-up will be less than for a single tank. This saving in reactor volume increases as the required fractional conversion increases and also as the number of installed

tanks increases. In fact, all of the desirable features of the CSTR may be retained while the low hold-up characteristics of a plug flow tubular reactor may be approached, i.e., the order of five to ten tanks in cascade are likely to give a close approximation to plug flow. It is a matter of economics to balance the cost of a number of tanks against their reduced size.

There are other operational advantages in carrying out reactions in series of stirred tanks. For example if one vessel in the cascade has to be put out of commission for any reason, it may be by-passed and production continued at a slightly reduced rate whereas failure of a single CSTR would entail complete loss in production.

The analysis of a cascade of CSTRs affecting simple reactions may be made but allowing the possibility of different temperatures in each tank, and hence different rate constants. In a similar fashion, also tank sizes and hence space times can be varied.

B. Plug Flow Reactor

The plug flow reactor (ideal tubular flow reactor) is a reactor in the form of a cylindrical tube through which feed enters at one end and exits at the other end. In an actual tubular reactor, there is incomplete mixing in both radial and axial directions, whereas in ideal tubular reactor there is assumed to be complete mixing perpendicular to the direction of flow (i.e. the radial direction) and no mixing in the direction of flow.

In the plug flow, the residence time in the reactor is the same for all elements of fluid, i.e., the reaction proceeds as the reactants in a plug progress along the reactor tube. However, no interchange of material in the plug with material in the other leading or following plugs occurs. There is ideally no back-mixing in the reactor and there exists a uniform velocity profile across the radius. Concentrations vary along the longitudinal direction, but not the radial direction. Except when isothermal operation is possible, temperature will also vary with the axial direction.

10.3.2.2 The Conductivity and Concentration Relations

It has been determined that the degree of conversion of the reagents affects the conductivity of the reactor contents so that recording the conductivity with respect to time helps to calculate the amount of conversion with the help of formulas that are provided below.

$$C_{A0} = \frac{Q_A}{Q_A + Q_B} C_{\text{tank1}} \quad C_{B0} = \frac{Q_B}{Q_A + Q_B} C_{\text{tank2}} \quad (10.3.10)$$

where A=NaOH, B=EtAc in the reaction: $A + B \rightarrow C + D$

$$C_{\infty} = C_{B0} \quad \text{for} \quad C_{B0} < C_{A0}$$

$$C_{\infty} = C_{A0} \quad \text{for} \quad C_{B0} \geq C_{A0}$$

$$\Lambda_{C_{\infty}} = 0.070 C_{\infty} [1 + 0.0284(T-294)] \quad \text{for } T \geq 294\text{K} \quad (10.3.11)$$

$$\Lambda_{C_{A0}} = 0.195 C_{A0} [1 + 0.0184(T-294)] \quad \text{for } T \geq 294\text{K} \quad (10.3.12)$$

$$\Lambda_0 = \Lambda_{C_{A0}} \quad \text{assuming } C_0 = 0.$$

$$C_{A_{\infty}} = 0 \quad \text{for} \quad C_{A0} < C_{B0}$$

$$C_{A_{\infty}} = C_{A0} - C_{B0} \quad \text{for} \quad C_{A0} \geq C_{B0}$$

$$\Lambda_{C_{A_{\infty}}} = 0.195 C_{A_{\infty}} [1 + 0.0184(T-294)] \quad \text{if } C_{A0} \neq 0. \quad (10.3.13)$$

$$\Lambda_{\infty} = \Lambda_{C_{\infty}} + \Lambda_{C_{A_{\infty}}} \quad (10.3.14)$$

$$C_A = (C_{A_{\infty}} - C_{A0}) \left(\frac{\Lambda_0 - \Lambda_1}{\Lambda_0 - \Lambda_{\infty}} \right) + C_{A0} \quad (10.3.15)$$

$$C_C = C_{C_{\infty}} \left(\frac{\Lambda_0 - \Lambda_1}{\Lambda_0 - \Lambda_{\infty}} \right) \quad \text{for } C_{C0} = 0 \quad (10.3.16)$$

$$X_A = \frac{C_{A0} - C_A}{C_{A0}} \quad (10.3.17)$$

$$X_c = \frac{C_C}{C_{C_{\infty}}} \quad \text{for} \quad C_{C0} = 0 \quad (10.3.18)$$

To calculate the specific rate constant k, the overall mass balance may be written as:

Rate of change within the reactor = Input – Output + Accumulation

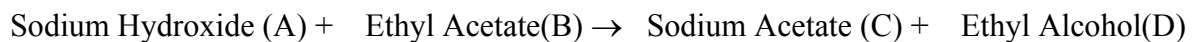
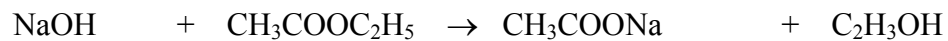
ie. for a reactant A in a reactor operating at steady state the volume may be assumed constant and

$$k = \frac{Q}{V} \frac{(C_{A0} - C_A)}{C_A^2} \quad (10.3.19)$$

$$k = \frac{(Q_A + Q_B)}{V} \frac{(C_{A0} - C_A)}{C_A^2} \quad \text{lt / mol.s} \quad (10.3.20)$$

The steady state concentration of NaOH in reactor (C_A) may be used to calculate the specific rate constant (k).

10.3.2.3 Saponification Reaction



The reaction can be considered equimolar and first order with respect to both sodium hydroxide and ethyl acetate i.e. second order overall, within the limits of concentration (0-0.1M) and temperature (20- 40⁰C) studied.

The reaction carried out in a Continuous Stirred Tank Reactor or series CSTRs eventually reaches steady state when a certain amount of conversion of the starting reagents has taken place.

The steady state conditions will vary depending on concentration of reagents, flow rate, volume of reactor and temperature of reaction.

10.3.3 Apparatus

The apparatus used in this experiment is shown in Figures 10.3.2 .

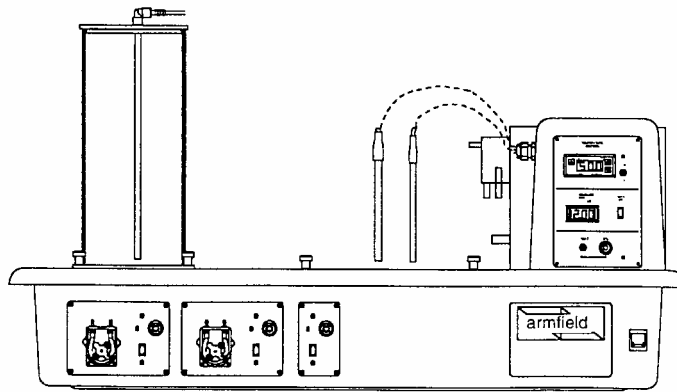


Figure 10.3.2 - Chemical reactor service unit.

10.3.4 Experimental Procedure

1. The calibration of the each of the pumps is necessary before the experiment begins unless the calibration graphs are available.
2. Make up 5.0 liter batches of 0.05M sodium hydroxide and 0.05M ethyl acetate.
 - It is essential when handling these chemicals to wear protective clothing, gloves and safety spectacles.
3. Remove the lids of the reagent tanks and carefully fill with the reagents to a level approximately 50 mm from the top. Refit the lids.
4. Put the thermometer in one of the reactors to record the temperature during the experiment.
5. Using the calibration graph for each of the feed pumps, set the pump speed control to give 50 ml / min flow rate.
6. Set the agitator speed controller to 7.0.
7. Switch on both feed pumps and agitator motor, and begin taking readings.
8. Collect the conductivity data for 30 minutes in 30 seconds intervals.

10.3.5 Report Objectives

1. Find the overall reaction rate constant and reaction rate constants for each CSTR.
2. Find the sodium hydroxide conversion corresponding to each datum taken.
3. Draw conversion VS time graphs for each reactor set (CSTR in series)
4. Write the overall mass balance.

5. Solve the differential equations numerically to find the conversions.
6. Compare the conversions obtained from numerical solution with measured ones, showing experimental and theoretical conversion on the same graphs.

10.3.6 References

1. Cooper, A.R., and G.V. Jeffreys, *Chemical Kinetics and Reactor Design*, Oliver & Boyd, Norwich, 1971.
2. Fogler, H.G., *The Elements of Chemical Reaction Engineering*, 2nd edition, Prentice Hall, New York, 1992.
3. Perry, R.H., and D. Green, *Perry's Chemical Engineers' Handbook*, 6th edition, Mc Graw-Hill, New York, 1988.
4. Smith, J.M., *Chemical Engineering Kinetics*, 3rd edition, McGraw-Hill, Tokyo, 1981.

10.4 ESTERIFICATION

Keywords: *Esterification reaction, batch reactor, rate constant, Arrhenius Equation, frequency factor, activation energy*

10.4.1. Object

The object of the experiment is to investigate the esterification reaction of phthalic anhydride with 2-ethyl hexanol in a batch reactor and to determine the rate constants by using the integral method of data analysis.

10.4.2. Theory

Chemical kinetics is the study of the rate and mechanism by which one chemical species is converted to another. The 'rate' is the mass, or moles, of a product produced or reactant consumed per unit time. The mechanism is the sequence of individual chemical events whose overall result produces the observed reaction. For chemical engineering purposes determination of the reaction rate is important in designing reactors and calculating conversions.

In general, chemical reactors have been classified in two ways:

- a) according to the type of operation
- b) according to design features

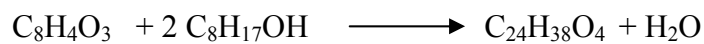
The former classification is mainly for homogeneous reactions and divides reactors into batch, continuous, and semicontinuous types.

In batch reactors, all the reactants are taken in at the beginning and processed according to the predetermined course of action during which no material is fed into or removed from the reactor. Usually it is in a form of a tank with or without agitation and is used primarily in a small-scale production. Most of the basic kinetic data for reactor design are obtained from this type.

Esterification

Esterification is the reaction to form an ester using various reactants such as carboxylic acids with alcohols, carboxylic acids via acid chlorides, anhydrides with alcohols and acid chlorides with alcohols. Acids are used in esterification reactions as catalysts.

Phthalic anhydride reacts with 2-ethyl hexanol in the presence of sulphuric acid, as the catalyst, to give di-octyl phthalate and water. The reaction equation is as follows:



Rate Equation

The rate of a reaction at any time t is given by:

$$\text{rate} = - \frac{d[A]}{dt} \quad (1)$$

That is, the rate of reaction is equal to the rate of decrease in the concentration of A (reactant) with time. The relationship between the rate and the concentration is called the rate equation:

$$- \frac{d[A]}{dt} = k [A]^n \quad (2)$$

where

k : rate constant

$[A]$: concentration of species A

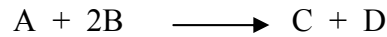
n : order of the reaction

The rate equation states how the rate of a reaction varies with the concentration of the reactants.

Integral Method of Data Analysis

To determine the reaction order by the integral method, the reaction order is guessed and the differential equation used to model the batch system is integrated. If the order assumed is correct, the plot of $\ln(C_B/C_A)$ vs. t data should be linear.

For the reaction:



$$-R_A = -\frac{dC_A}{dt} = k C_A^\alpha C_B^\beta \quad (3)$$

for $\alpha = \beta = 1$

$$\begin{array}{lll} t = 0 & C_A = C_{A0} & C_B = C_{B0} \\ t = t & C_A = C_A & C_B = C_B \end{array}$$

$$-2 \frac{dC_A}{dt} = -\frac{dC_B}{dt} \quad (4)$$

$$2(C_{A0} - C_A) = (C_{B0} - C_B) \quad (5)$$

$$C_B = C_{B0} - 2(C_{A0} - C_A) \quad (6)$$

Substituting (6) in (3):

$$-\frac{dC_A}{dt} = k C_A (C_{B0} - 2C_{A0} + 2C_A) \quad (7)$$

$$\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A (C_{B0} - 2C_{A0} + 2C_A)} = k \int_0^t dt \quad (8)$$

Integrating Equation (8) yields:

$$\ln \frac{C_B}{C_A} = k(C_{B0} - 2C_{A0})t + \ln \frac{C_{B0}}{C_{A0}} \quad (9)$$

The Arrhenius Equation

The rate constant depends strongly on temperature. This behavior is described by the Arrhenius equation:

$$k(T) = A \times e^{\frac{-E}{RT}}$$

where

A : frequency factor (pre-exponential factor)

E : activation energy

10.4.3. Apparatus

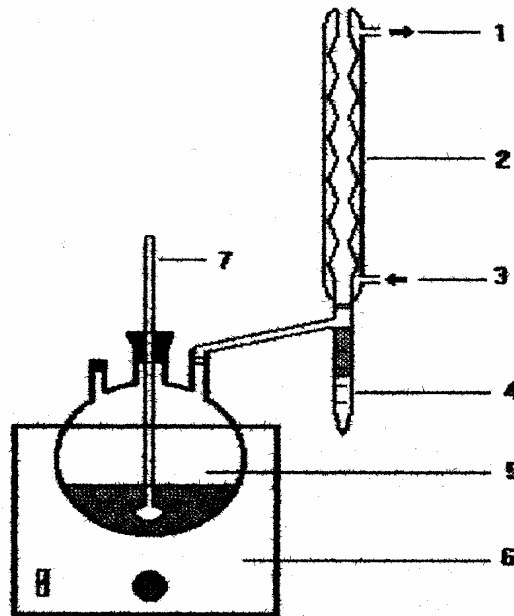


Figure Batch reactor equipment

1. Water inlet
2. Condenser
3. Water outlet
4. Water collector
5. Reactor
6. Heater
7. Thermometer

Figure 10.4.1 – Batch reactor equipment.

10.4. 4. Experimental Procedure

1. Put 200 ml. 2-ethyl hexanol, 74 g phthalic anhydride and 20 ml. sulfuric acid into the reactor.
2. Add boiling chips.
3. Set up the heater to 300 °C.
4. Record the temperature and water level every 1 minute.
5. Repeat the same procedure by setting up the heater to 120 °C.

10.4.5 Report Objectives

1. Derive Equation (9) and find the rate constants at two temperatures.
2. Discuss how the rate constant changes with temperature.
3. Calculate frequency factor (A) and activation energy (E) for the reaction.
4. Discuss how the reaction proceeds in a batch reactor and the advantages of the batch reactor to obtain kinetic data.

10.4.6 References

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