Iraqi Journal of Chemical and Petroleum Engineering
Vol.17 No.1 (March 2016) 99- 108
ISSN: 1997-4884

Iraqi Journal of Chemical and Petroleum Engineering

University of Baghdad
College of Engineering

Study in Kinetics of Saponification Reaction of Diethyl Adipate with Sodium Hydroxide Solution under Reactive Distillation

Raghad fareed kasim* and rouaa ali shokorr**
College of engineering-University of Baghdad
*email:rfkalm@yahoo.com
****** email:hu.iraq91@gmail.com

Abstract

This research presents a new study in kinetics under reactive distillation by using consecutive two – step reaction : the saponification reaction of diethyl adipate with sodium hydroxide solution . The distillation process takes the role of withdrawing the intermediate product (sodium monoethyladipate SMA) which otherwise converts to the final product of low purity.The effect of three parameters were studied through a design of experiments applying 2^3 factorial design. These parameters were : the mole ratio of DA to NaOH solution (0.1 and 1) , NaOH solution concentration (3 N and 8 N) , and batch time (1.5 hr. and 3.5 hr.) . The conversion of DA to sodium monoethyladipate(SMA)(intermediate product) was the effect of these parameters which was detected .The results showed that increasing mole ratio of DA to NaOHsolution increases the conversionto a maximum value within the range of study.The effect of NaOH solution concentration decreases the conversion to a specified value within the range of study . The effect of batch time on conversion was decreasing the conversion to a specified value within the range of study . The maximum attainable conversion within the studied range of parameters was eighteen fold of thebase case.Reaction rate constant k and the order of reaction n of first reaction weredetrminedusing the differential method . The study attempted to determine n and k under the maximum conversion condition obtained in this system which corresponds to : feed mole ratio of diethyl adipateDA to NaOH solution of 0.3,NaOH solution concentration of3 Nandtime of1.5 hr.The study showed that the reaction order was 1.5and reaction rate constant was 0.8m^3/kmol.s at a temperature of 100 ℃.

Key Words: reactive distillation, kinetic study, consecutive reaction, saponification reaction.

Introduction

Separation is one of the most significant processes in chemical engineering. From ancient times to recent days, separation processes have been implemented in almost every chemical process. The distillation process is the most suitable separation process in the chemical and petroleum industries. Reactors are also essential parts of any chemical industry. Reactor effluents do not usually meet the specification criteria due to the process of the unconverted materials.

Therefore, it is quite common in industry to see reactors followed by a separation section with recycles. From this point of view, it is important to study and investigate the reactor / Separation / recycle system. One aspect of studying this system is the reactor combined with the separation unit. This is referred to as reactive distillation [1]. It involves simultaneous chemical reaction and distillation [2]. RD has been used in industry from many decades, but its area of application has grown essentially in the past decade [3]. There are many documented success references involving the industrial implementations of RD. The implementations of RD in the petroleum and chemical industries have been increased quickly in the past decade. One such example is the production of methyl acetate by the Eastman plant. In this case a single RD column replaced the conventional flow sheet consisting of eleven major operation units with an assortment of pumps, heat exchangers, and controllers. The result was a five-doubles reduction in energy consumption and capital investment over the conventional design for methyl acetate production [4].

For esterification reactions: when carboxylic acid treated with an alcohol, an ester is formed. Saponification reaction is a kind of esterification reaction that can be conducted under reactive distillation (RD). The general utility of RD is increasing the conversion of reversible reactions [5]. RD depends on the withdrawal of the product (or one of the products) by evaporation from the reacting mixture. This technique accelerates the forward reaction .In previous research of the investigators [6], it was shown that the maximum conversion obtained for this system was 18.58fold of that for the base case (the base case is the experiment that carried out at lower values of all the parameters, which is regarded as base or reference case).

The maximum conversion value corresponded to the set of parameters (under study): feed mole ratio of DA to NaOH solution (x_1) = 0.3, NaOHsolution concentration (x_2) = 3 N, and distillation time (x_3) = 1.5 h.

Newberger and Kadlec [7], studied the kinetic of saponification reaction of diethyl adipate with sodium hydroxide solution in a batch isothermal system at temperature of 293.1 K. They determined reaction order and reaction rate constant for the two consecutive reactions which can be represented as follows:

$$(CH_2)_4(COOC_2H_5)_2 + NaOH \overset{k1}{\Rightarrow} (CH_2)_4(COONa)(COO\,C_2H_5) + C_2H_5OH \quad ... (1)$$

$$(CH_2)_4(COONa)(COOC_2H_5) + NaOH \overset{k2}{\Rightarrow} (CH_2)_4(COO\,Na)_2 + C_2H_5OH \quad ... (2)$$

They found that the rate constant of the first reaction (k_1) to be 9.3 m^3 / kmole . s , while that of the second reaction (k_2) to be 7.7 m^3 / kmole . s . These values were obtained at temperature 293.1 K . It is obvious that $k_1 > k_2$ i.e. the first reaction is faster than the second.

They also found that the frequency factors of Arrhenius equation , and the activation energies of the two reactions were:

$a_1 = 4.87 * 10^6\ m^3$ / kmole . s
$a_2 = 3.49 * 10^6\ m^3$ / kmole . s
$E_1 = 42.2$ kJ / mole
$E_2 = 25.0$ kJ / mole

It is obvious that $E_1 > E_2$, so the first reaction has a higher energy barrier than the second reaction.

In addition, they determined the heats of the two reactions to be:

$\Delta H_1 = - 45.2 \pm 3.4$ kJ / mole
$\Delta H_2 = - 68.0 \pm 4.2$ kJ / mole

These quantities were found to contribute at most 0.5 K in temperature rising in tubular reactor which they used.

Table 1, The reaction order and reaction rate constant values for diethyl adipate with sodium hydroxide solution at (293.1 K) temperature [8]

Investig-ator	C_A kmol. /m^3	C_B kmol. /m^3	Reaction order	k_1 , m^3/ Kmol.s	k_2 , m^3/ kmol.s
Ingold (1931)	0.002	0.002	2	3.52	0.704
Westhe-imer (1942)	0.01	0.01	2	5.20	1.83
Westhe-imer (1942)	0.005 –0.011	0.005–0.011	2	5.7 – 6.1	-----
Frost and Schwe-mer (1952)	0.01	0.01 – 0.02	2	-----	1.7 – 2.2
Newber-ger and Kadlec (1973)	0.02	0.05	2	9.3	7.7

They also compared their results with some former ones that were published as given in Table (1).

The reaction system can be represented by:
$A + B \rightarrow C + D$
$C + B \rightarrow E + D$
Where:
A: refers to diethyl adipate (DA)
B: refers to sodium hydroxide solution
C: refers to sodium monoethy ladipate (SMA)
D: refers to ethanol
E: refers to disodium adipate (DSA)

From Eq. (1), the kinetic study of the first reaction depended on measuring SMA concentration (i.e. C_C).

$$r_C = \frac{dCc}{dt} = k\, C_A\, C_B \qquad \ldots (3)$$

Eq. (3) represents the rate equation.

In order to apply the differential method r_A must be determined. From Eq. (4) we see that r_C can be converted to r_A.

$$\frac{rC}{no.of\ moles\ of\ C} = \frac{-rA}{no.of\ moles\ of\ A} \qquad \ldots (4)$$

As the stoichiometric number of C and A is the same, therefore; $-r_A = r_C$ numerically. So r_A can be determined directly from calculating r_C as shown later.

Experimental Work

1- Materials

Diethyl adipate, sodium hydroxide pellets. Hydrochloric acid HCl ,borax , methyl red , methyl orange for sodium hydroxide solution standardisation.

2- Procedure

1- According to the design of experiment Table (2) ,(Montgomery[9]) three factors were intended to study (feed mole ratio , sodium hydroxide (NaOH) solution concentration, and batch "distillation" time) within the ranges set in the Table(3).

2- Sodium hydroxide (NaOH) solution with (3N concentration), was prepared and standardized using indicators, (Vogel [10]) and pH-meter.

3- Measured amounts (12 – 129 ml.) of diethyl adipate (DA) and sodium hydroxide "NaOH" solution (31 – 332 ml.) was mixed in (500 – ml.) distillation flask which was shielded.

4- Heating the mixture till boiling. The distillate began to appear at approximately about 100 ^{0}C.

5- The distillate was collected in receiving conical flask. It was noticed that it was composed of two layers.

6- The distillate was transferred to a (500 - ml.) separating funnel.

7- The weight and volume of each layer were measured.

8- Relative conversions were also determined for the center values of the parameters shown in Table (3).Additional experiments were performed to get sufficient data for plotting.

3- Test Method

FTIR measurement was done for each layer which showed that sodium monoethyladipate (SMA) appeared in the dominate upper layer. The unreacted diethyl adipate (DA) appeared in the impaired lower layer.

Atomic absorption was made for the upper layer to measure the concentration of SMA (C_C)as given in Table (4).

Table 2, Design of experiments

Feed mole ratio (x_1) , (mol. DA / mol. NaOH)	NaOH solution concentration (x_2) , (N)	Time(x_3), (hr)
0.1	3	1.5
1	3	1.5
0.1	8	1.5
1	8	1.5
0.1	3	3.5
1	3	3.5
0.1	8	3.5
1	8	3.5

Table 3, Ranges of parameters studied

Factor	Low value (-)	Centre value (0)	High value (+)
Feed mole ratio (x_1) , (mole DA / mole NaOH solution)	0.1	0.55	1
NaOH solution concentration (x_2) , (N)	3	5.5	8
Time (x_3) , (h)	1.5	2.5	3.5

Results and Discussion

From SMA concentration, relative conversion (conversion of DA to SMA relative to base case conversion) was calculated. The variation of relative conversion with feed mole ratio x_1 were drawn for NaOH solution concentration x_2 = 3 N , and different batch time x_3 = 1.5 and 3.5 h as shown in Fig. (1).From this figure , it is obvious that for the two curves the relative conversion proportionally increased with increasing feed mole ratio in the range x_1 = (0.1 - 0.3) . The two curves have a maximum relative conversion at x_1 = 0.3 which seems to be the best value in our range of feed mole ratios. After that increasing, feed mole ratio in the rangex$_1$ = (0.3 – 1) decreased relative conversion. The increasing in relative conversion with increasing feed mole ratio in the rangex$_1$ = (0.1 – 0.3) was because of the increasing in SMA concentration in this range of feed mole ratios.

The decreasing in relative conversion for the rangex_1 = (0.3 – 1) was due to the decreasing in SMA concentration.

This can be explained as follows: the rate of first conversion reaction (SMA production) is higher than the rate of second conversion reaction (SMA consumption), Newberger and Kadlec [7]. The increasing in feed mole ratio in the range (x_1 = 0.1 – 0.3) activated the first conversion reaction (i.e SMA production increased) and its concentration in distillate increased. Higher increasing in feed mole ratio in the range (x_1 = 0.3 – 1) activated the second conversion reaction (i.e. SMA consumption increased) so its concentration in distillate decreased.

Also, it is clear from this figure that the relative conversion for the curve of shorter distillation time (t = 1.5 hr.) at (x_1 = 0.15 – about 0.8) was higher than that of longer distillation time (t = 3.5 hr.). At (x_1 = 0.3) relative conversion for the curve of shorter distillation time was (18.58), while for the curve of longer distillation time was (9.76). Fig. 2 also explains the variation of relative conversion with feed mole ratio (x_1) and different batch time (x_3 = 1.5 and 3.5 hr.). The two curves were drawn for the same NaOH solution concentration (x_2 = 8 N).

From this figure, it is clear that for the curve of shorter distillation time, relative conversion increased with feed mole ratios in the range (x_1 = 0.1 - 0.3).

The curve has a maximum value of relative conversion (2.76) at (x_1 = 0.3). After that the relative conversion decreased when feed mole ratio increased in the range (x_1 = 0.3 – 1).

The peak of the curve of shorter distillation time (2.76) is lower than the corresponding one of Fig. 1.This is because of lower weight of distillate upper layer and higher volume of DA .Relative conversion is a function of SMA concentration, weight of distillate upper layer, and DA volume as shown in Eq. (5):

$$\text{Relativeconv.}=\frac{conversion of DA to SMA}{base case(run1) conversion}\ldots\ (5)$$

For the curve of longer distillation time it is clear that the relative conversion decreased when feed mole ratio increased in the range (x_1 = 0.1 - 0.55).

The curve has a minimum value of relative conversion (0.18) at (x_1 = 0.55). Then relative conversion increased somewhat till (x_1 = 1).

The decreasing in relative conversion with feed mole ratio in the range (x_1 = 0.1 – 0.55) because of decreasing in weight of distillate upper layer and increasing in DA volume. The increasing in relative conversion in the range (x_1 = 0.55 - 1) was because of increasing in weight of upper layer distillate and increasing SMA concentration.

The peak of the curve of longer distillation time (0.62) is lower than the corresponding one of Fig. 1.This is because of lower weight of distillate upper layer and higher volume of DA as mentioned above.

Fig. 3 shows the variation of relative conversion with NaOH solution concentration (x_2). The curve was drawn for feed mole ratio (x_1 = 0.3) and batch time (x_3 = 2.5 hr.). From this figure, it is clear that the relative conversion decreased with increasing NaOH solution concentration in the range (x_2 = 3 – 5.5 N) . The curve has a minimum value of relative conversion (0.39) at (x_2 = 5.5 N) . After that the relative conversion increased when NaOH solution concentration increased in the range (x_2 = 5.5 – 8 N) . The behaviour of this curve was due to the decreasing then increasing of SMA concentration with NaOH solution concentration.

Fig. 4 explains the variation of relative conversion with distillation time (x_3). The curve was drawn for feed mole ratio (x_1 = 0.3) and NaOH solution concentration (x_2 = 3 N). From this figure, it is clear that the relative conversion decreased when distillation time increased in the range (t = 1.5 – 2.5 hr.).

The curve has a minimum value of relative conversion (0.68) at (t = 2.5 hr.) . After that, the relative conversion increased with increasing distillation time in the range (t = 2.5 – 3.5 hr.). This behaviour is due to the decreasing then increasing of SMA concentration with distillation time.

Fig. 5 also explains the variation of relative conversion with distillation time (x_3), and feed mole ratio (x_1 = 0.3). The curve was drawn for NaOH solution concentration (x_2 = 8N).

From this figure, it is clear that the relative conversion decreased with increasing distillation time. This can be attributed to the decreasing in SMA concentration as discussed before.

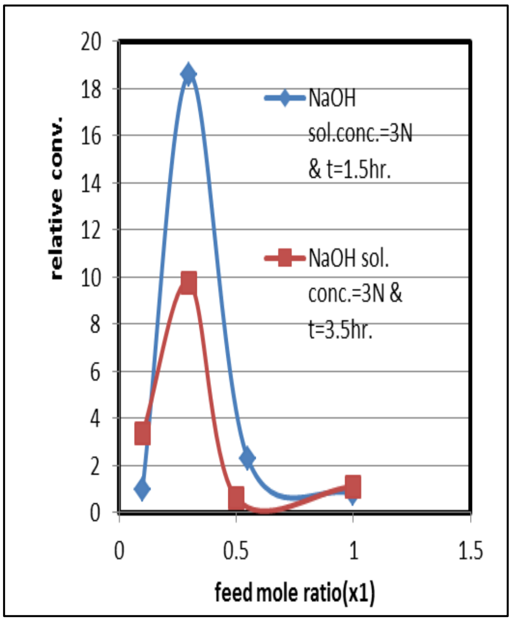

Fig. 1, Relative conversion vs. feed mole ratio (x_1) for NaOH sol. conc. = 3 N and t = (1.5 & 3.5 hr.).

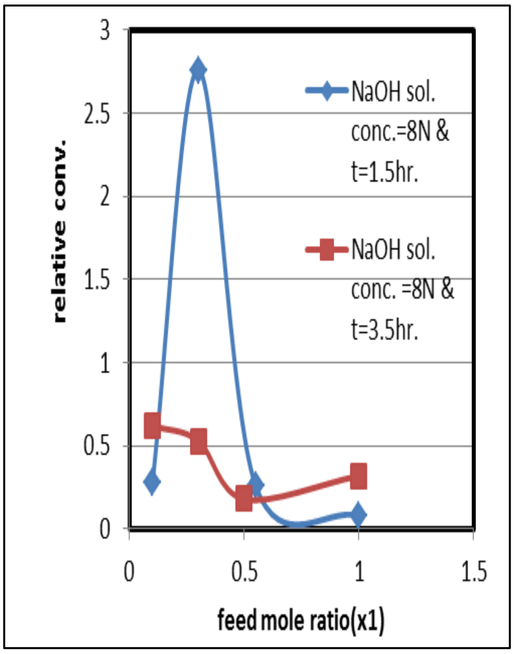

Fig. 2, Relative conversion vs. feed mole ratio (x_1) for NaOH sol. conc. = 8 N and t = (1.5 & 3.5 hr.).

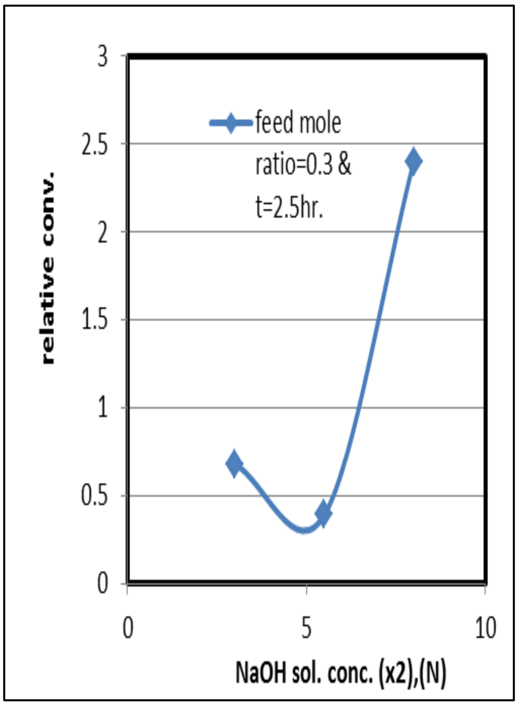

Fig. 3, Relative conversion vs. NaOH solution concentration (x_2), (N) for feed mole ratio = 0.3 and t = 2.5 hr.

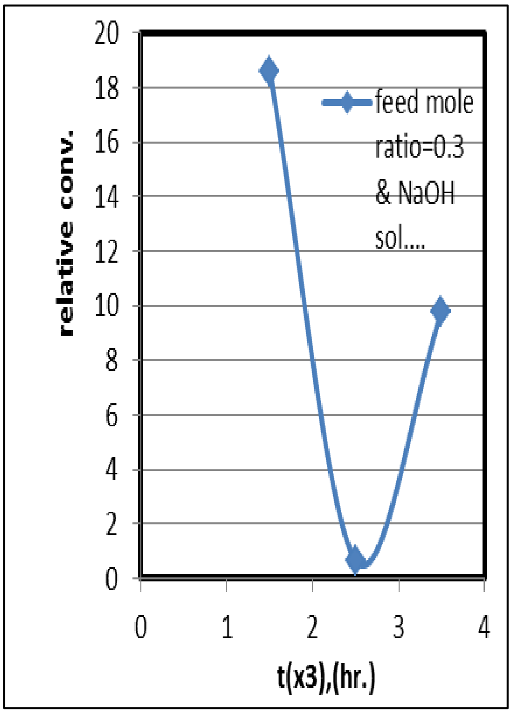

Fig. 4, Relative conversion vs. t (x_3), (hr.) for feed mole ratio = 0.3 and NaOH sol. conc. = 3 N.

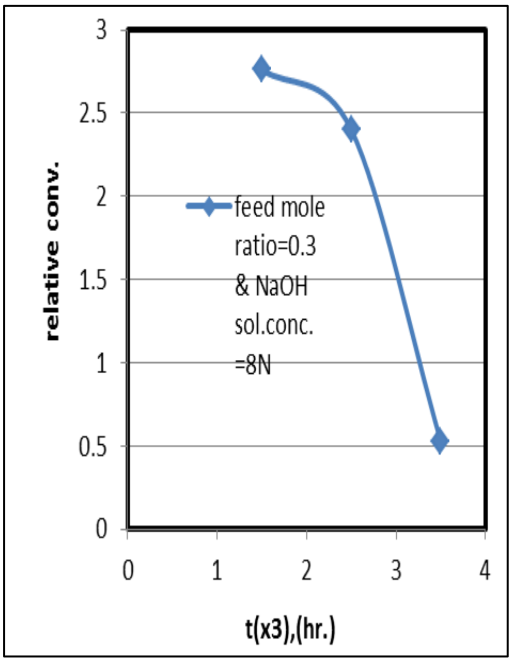

Fig. 5, Relative conversion vs. t (x_3), (hr.) for feed mole ratio = 0.3 and NaOH sol. conc. = 8N.

Table 4, shows SMA concentration in distillate upper layer with distillation time for the maximum - conversion set of parameters (i.e. Feed mole ratio = 0.3 and NaOH sol. conc. = 3 N).

t , hr.	C_C , ppm.
0	0
1.5	106.10
2.5	10.55
3.5	50.31

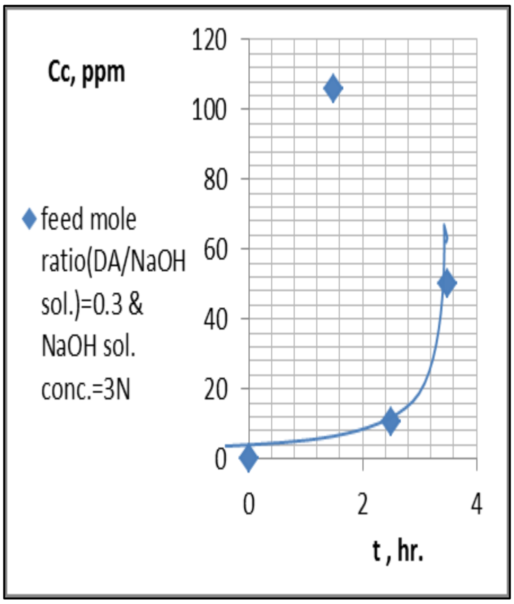

Fig. 6, SMA concentration in distillate (ppm.) versus time(hr.) for feed mole ratio=0.3 and NaOHsol. Conc. =3N .

Table 5, shows values of diethyl adipate concentration (limiting reactant) (C_A), and reaction rate ($-r_A$) with their logarithms.

Cc , ppm	C_A , ppm	Log C_A	$-r_A= dC_C/dt = r_C$	Log $-r_A$
0	0	-----	-----	-----
2.01	2.07	0.32	4.14	0.62
4	4.13	0.62	4.51	0.65
106.10	109.48	-----	-----	-----
10.55	10.89	1.04	56	1.75
50.31	51.91	1.72	100	2

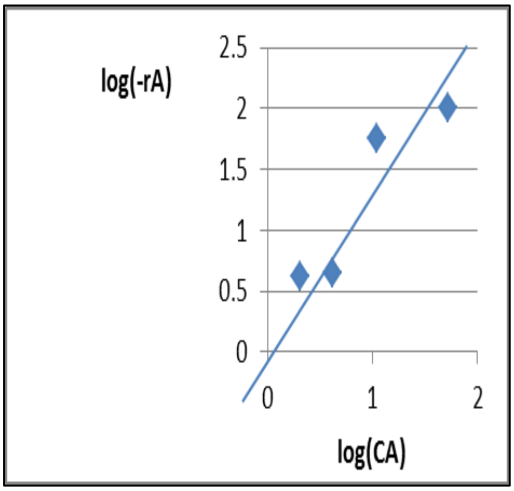

Fig. 7, Plot of log(-r_A) vs log(C_A) for determining reaction order (n) and rate constant (k).

SMA concentration (Cc) versus batch time (t) data was plotted as shown in Fig. (6) .The slopes of the curve at different values of C_C were determined .These slopes represented the rate of reaction r_C which are listed in Table (5).From Eq. (6) diethyl adipate concentration (C_A) was calculated from sodium monoethyladipate concentration (C_C).

$$C_A=C_C*\frac{DA\ molecular\ weight(202.25)}{SMA\ molecular\ weight(196)} \quad \ldots (6)$$

The results are shown in Table (5). Also in Table (5) the logarithms of these values were obtained. Fig, (7) shows a plot of log(-r_A) versus log C_A.

A linear relation was obtained. The slope of this relationship represents n (order of reaction) and the intercept representslog (k) Levenspiel [11].

From Eq. (7) and Eq. (8) the resulting values of n and k are 1.5 and 0.8 m^3/kmole. s respectively.

$$n = \frac{2.5-0.4}{2-0.6} = 1.5 \quad \ldots (7)$$

$$\text{Log k} = -0.1 \rightarrow k=0.8\ m^3/\text{kmole.s} \quad \ldots (8)$$

Reaction rate constant (k) for saponification of diethyl adipate as calculated by Newberger and Kadlec (1973) was (9.3 m^3/kmole.s) at temperature of (293.1 K) and initial concentrations of DA and NaOH solution of (0.02 and 0.05) respectively as given in Table (1).

In this study reaction rate constant was (0.8 m3/kmole.s) at temperature about (100°C) (the distillation temperature). This was in fair agreement with Arrhenius equation Eq. [9] which shows that the rate constant is inversely proportional with temperature.

$$k = a\exp\left(\frac{-E}{RT}\right) \quad \ldots (9)$$

Or in logarithmic form:

$$\ln(k) = \ln(a) - \left(\frac{E}{RT}\right)$$

It is obvious that: $\ln(k)\ \alpha\ \frac{1}{T}$

So increasing temperature till boiling is essential to achieve reactive distillate, but this technique will retard the magnitude of the reaction - rate (k) for this reaction . This issue is a matter of balancing between the rate of reaction and gaining of a valuable intermediate product.

Conclusions

From this study the following items can be concluded:

1- Feed mole ratio x_1 obviously affected the concentration of SMA in the distillate. Accordingly the conversion was influenced by it. Increasing feed mole ratio caused increasing in the concentration of SMA, and conversion of DA to SMA in the range (0.1 - 0.3) , when the other factors x_2 (NaOH solution concentration) and x_3 (batch time) were fixed at specified values . In the range (0.3 –1)of x_1 the concentration , and conversion decreased.

2- Increasing sodium hydroxide solution concentration x_2 increased the conversion with other parameters x_1 and x_3 fixed. That was attributed to the effect of NaOH as a reactant which accelerated the reactions with increasing in its concentration. Although, there were some ranges x_2 = (3 – 5.5 N) of NaOH solution concentration which caused decreasing in SMA concentration, and conversion.
3- The conversion of DA to SMA for $x_1 = 0.3$ and $x_2 = 3$ N showed decreasing with increasing batch time x_3 till $x_3 = 2.5$ h . Then the conversion increased with increasing x_3.
4- The conversion of DA to SMA for $x_1 = 0.3$ and $x_2 = 8$ N showed decreasing with increasing batch time x_3.
5- The maximum conversion obtained in this study was 18.58 fold of that for the base case.The maximum conversion corresponds to the set of parameters ($x_1 = 0.3$, $x_2 = 3$ Nand$x_3 = 1.5$ h).
6- The order of reaction and reaction rate constant at maximum conversion set of parameters were 1.5 and 0.8m^3/kmole.s, respectively.
7- Reaction rate constant determined in reactive distillation system is of lower value than that with ordinary operated system. This affirms Arrhenius equation outputs.

Abbreviation

RD= Reactive Distillation
DA= Diethyl Adipate
SMA= Sodium MonoethylAdipate
DSA= Di-Sodium Adipate

Nomenclature

a= Pre-exponential (frequency) factor (m^3/kmole.s)
R= Perfect gas law constant (J/mole.K)
E= Activation energy (kJ/mole)
C_A= Concentration of DA (kmole/m^3)
C_B= Concentration of NaOH soln. (kmole/m^3)

References

1- Al – Arfaj , M. , " Quantitative heuristic design of reactive distillation " , Chemical department , College of Engineering , University of Lehigh , 1999 .
2- Lone , S. R. , and Ahmad , S. A. , "Modelling and Simulation of Ethyl Acetate Reactive Distillation Using Aspen Plus" , International Journal of Scientific & Engineering Research , Vol. 3 , No. 8 , PP. (1 – 5) , 2012 .
3- Al – Arfaj , M. , and Luyben , W. L. , "Comparison of Alternative Control Structures for an Ideal Two –Product Reactive Distillation Column " , Industrial Chemical Engineering Research , Vol. 39 , No. 9 , PP. (3298 – 3307) , 2000 .
4- Munshi , B. , and Kumar , S. , " Modelling and Simulation of ethyl acetate reactive distillation column using ASPEN PLUS " , Thesis , Chemical Department , College of Engineering , University of Technology, Iraq , 2010.
5- Luyben , W. L. , and Yu ,C. , (2008) , " Reactive Distillation Design and Control " , WILEY , United States of America , 1-574.
6- Kasim , R. F. , and Shokorr , R. A. , (2015) , " Semi- Batch Reactive Distillation of Consecutive Reaction :The Saponification of Diethyl Adipate with Sodium Hydroxide Solution " , Baghdad University, Chemical Engineering , 1-133.

7- Newberger , M. R. , and Kadlec , R. H. , (1973) , " Kinetics of the Saponification of Diethyl Adipate " , AIChE Journal , No. 6 , Vol. 19 , 1272 – 1275.

8- Ingold , C. K. , (1973) " The Mechanism and Constitutional FactorsControlling the Hydrolysis of Carboxylic Esters " , Westheimer , F. H. , W. A. Jones , and R. A. Lad , " Electrostatic Influence of Substituents on Reactor Rates " , Frost , A. A. , and W. C. Schweimer , " The Kinetics of Competitive Consecutive Second Order Reactions – The Saponification of Ethyl Adipate and Ethyl Succinate " , cited in Newberger , M. R. , and Kadlec , R. H. , " Kinetics of the Saponification of Diethyl Adipate " , AIChE Journal , No. 6 , Vol. 19 , 1272 – 1275.

9- Montgomery, D. C., 2001, DESIGNANDANALYSISOFEXPERIMENTS, 5th ed., John Wiley &Sons (Asia) Pte. Ltd., Singapor.

10- Vogel , A. I. , (1961) , "QUANTITATIVE INORGANIC ANALYSIS INCLUDING ELEMENTARY INSTRUMENTAL ANALYSIS " , LONGMANS , GREEN AND CO LTD 48 Grosvenor Street , 3rd ed. , London , 1-1216 .

11- Levenspiel, O., (1999), “CHEMICAL REACTION ENGINEERING”, John Wiley & Sons, United States of America, 3rd ed., 1-668.