Semi-Batch Reactive Distillation of Consecutive Reaction : The Saponification Reaction of Diethyl Adipate with Sodium Hydroxide Solution

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ABSTRACT

This research presents a new study in reactive distillation by using consecutive reaction: the saponification reaction of diethyl adipate (DA) with sodium hydroxide solution .

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 . Also , the percentage purity of the intermediate product was recorded . The results showed that increasing mole ratio of DA to NaOHsolution increases the conversion and percentage purity to a maximum value within the range of study . The effect of NaOH solution concentration decreases the conversion and percentage purity to specified value within the range of study . The effect of batch time on conversion and percentage purity , when NaOH solution concentration (3 N) is as follows : the increasing in batch time decreases the conversion and percentage purity to specified value within the range of study . When NaOH solution concentration (8 N) increasing batch time decreases the conversion , while percentage purity increases with increasing batch time to a maximum value within the range of study . The maximum attainable conversion within the studied range of parameters was eighteen fold of the base case , while the maximum percentage purity was (99.40 %) .

Empirical equation was obtained using statistical analysis of experimental results . The empirical results of relative conversion was drawn . The empirical graphs showed linear variation .

Key words: consecutive reaction, the saponification reaction, diethyl adipate with sodium hydroxide solution, sodium monoethyladipate.

التقطير التفاعلي شبه ذوالدفعات لتفاعل متسلسل : صوبنة ثنائي أثيل أديبيت مع محلول هيدروكسيد الصوديوم

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الخلاصة

يقدم هذا البحث دراسة جديدة في التقطير التفاعلي بإستخدام تفاعل متسلسل: تفاعل صوبنة ثنائي أثيل أديبيت مع محلول هيدروكسيد الصوديوم .تمت دراسة تأثير ثلاثة عوامل من خلال تصميم تجارب بتطبيق تصميم مفكوك 2^3 . هذه العوامل كانت : النسبة المولية لثنائي أثيل أديبيت إلى محلول هيدروكسيد الصوديوم (0,1 و 1) , تركيز محلول هيدروكسيد الصوديوم (3 عيارية و 8 عيارية) , و زمن الدفعة (1,5ساعة و3,5 ساعة) . إن نسبة تحول ثنائي أثيل أديبيت إلى صوديوم أحادي أثيل أديبيت (المركب الوسطي) كانت تأثير تلك العوامل الذي تم تتبعه . كذلك سجلت نسبة نقاوة المركب الوسطي . لقد بينت النتائج

إن زيادة النسبة المولية لثنائي أثيل أديبيت إلى محلول هيدروكسيد الصوديوم تزيد من نسبة التحول و نسبة النقاوة إلى قيمة عليا ضمن حدود الدراسة . إن تأثير تركيز محلول هيدروكسيد الصوديوم تقلل من نسبة التحول و نسبة النقاوة إلى قيمة معينة ضمن حدود الدراسة . ان تأثير زمن الدفعة على نسبة التحول ونسبة النقاوة , عندما تركيز محلول هيدروكسيد الصوديوم (3 عيارية),هو كما يلي: زيادة زمن الدفعة تقلل نسبة التحول ونسبة النقاوة إلى قيمة معينة ضمن حدود الدراسة .عندما تركيز محلول هيدروكسيد الصوديوم (8 عيارية) زيادة زمن الدفعة تقلل نسبة التحول . بينما نسبة النقاوة تزداد بزيادة زمن الدفعة إلى قيمة عليا ضمن حدود الدراسة . إن أكبر نسبة تحول تم الحصول عليها خلال المدى المدروس للمتغيرات كانت ثمانية عشر ضعفا أكثر من الحالة المرجعية , بينما أعظم نسبة نقاوة كانت (99,40 %) . تم الحصول على معادلة تجريبية باستخدام التحليل الإحصائي للنتائج العملية . رسمت النتائج التجريبية لنسبة التحول نسبة الحالة المرجعية . أظهرت الرسوم التجريبية تغيرخطي.

الكلمات الرئيسية: تفاعل متسلسل, تفاعل الصوبنة, ثنائي اثيل اديبيت مع محلول هيدروكسيد الصوديوم, صوديوم احادي اثيل اديبيت.

1. INTRODUCTION

Reactive distillation (RD) is a process which includes a combination of reaction and separation in a single unit. The concept of combining these two important functions for enhancing the process overall performance is not new in chemical engineering world. The production of ammonia from soda ash by classic Solvay process of the 1860s may be cited as possibly the first commercial applying of this technique**,Sundmacher and Kienle,2002**. Many old operations have made usage of this concept.The combination of reaction and distillation is possible , of course only if the conditions of both operations can be combined. This means that the reaction have to show data for reasonable conversion at temperature and pressure levels that are compatible with separation conditions. The type of catalysis is also important. Homogeneous catalysis is possible in more cases , but requires a separation step for catalyst recycling. This can be eliminated in heterogeneous catalysis , but here special constructions are necessary to fix the catalyst in the reaction zone. If everything harmonizes , considerable advantages arise : for the production of methyl acetate via RD for example , only one column is needed instead of a reactor and nine columns. RD can be used with many chemical processes including acetylation ,**Mufrod, et al.,2013**, amination , esterification , etherification , hydrolysis , hydration , dehydration , hydrogenation , isomerization , etc..

The general utility of RD (till now) is increasing the conversion of reversible reactions , **Laybenand Ching Yu,2008**. This depends on the withdrawal of the product (or one of the products) by evaporation from the reacting mixture. This technique accelerates the forward reaction.RD also provides compactness to the chemical plant and cost effectiveness.

This research presents a new study in RD of a consecutive reaction. The consecutive reaction proposed is the saponification reaction of diethyl adipate with sodium hydroxide solution. This reaction takes place in two steps. The distillation process has the role of withdrawing the intermediate product(SMA) by evaporation from the reacting mixture before the second conversion occurs. This technique is useful in producing the intermediate product(when it is the desired product)as it is the case in many industrial and petroleum processes.

2. KINETICS OF REACTIONS

Saponification reaction of diethyl adipate as studied byNewberger and Kadlec **,Newberger and Kadlec,1973**, represents second order , irreversible , consecutive homogeneous reaction in the liquid phase .

The chemical reactions are represented as follows , **Newberger and Kadlec,1973**:

$(CH_2)_4(COOC_2H_5)_2+NaOH\xrightarrow{k1} (CH_2)_4(COONa)(COO\ C_2H_5) + C_2H_5OH$

Diethyl adipate Sodiumhydroxide Sodium monoethyl adipate Ethanol

$(CH_2)_4(COONa)(COOC_2H_5)+NaOH\xrightarrow{k2} (CH_2)_4(COO\ Na)_2+ C_2H_5OH$

Sodiummonoethyladipate Sodiumhydroxide Disodium adipate Ethanol

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

$E_1 = 42.2$ MJ / Kmole , $E_2 = 25.0$ MJ / Kmole

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 :

$\Delta H_1 = - 45.2 \pm 3.4$ MJ / Kmole

$\Delta H_2 = - 68.0 \pm 4.2$ MJ / Kmole

These quantities were found to contribute at most 0.5 K temperature rise in their tubular reactor , **Newberger and Kadlec,1973**.

3. METHODOLOGY

3.1 Experimental Work

1-Sodium hydroxide solution (NaOH) was prepared and standardized using indicators ,**Vogel,1961**, and pH – meter .

2-Experiments were conducted to compare the case of using distillation with that of without distillation .

3-Measured amounts (20 - 27 ml.) of diethyl adipate (DA) and sodium hydroxide "NaOH" solution (56 – 332 ml.) were mixed in (500 – ml.) distillation flask which was shielded .

4-Keeping the temperature at constant value (50 ℃) and providing good mixing (500 rpm) for the reacting mixture using magnetic stirrer .

5-After a planned period of time (1.5 hr.) the reaction was stopped and flask contents which consist of two layers were transferred immediately to a (500 – ml.) separating funnel .

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

7-FTIR measurement was done for each layer which showed the existence of sodium monoethyladipate (SMA) in the two layers with higher concentration in the upper layer . The unreacted diethyl adipate (DA) was noticed to appear in the two layers too with higher concentration in the upper layer than that of the lower layer .

8-Atomic absorption measurement was done for the upper layer to measure the concentration of sodium monoethyladipate (SMA) .

9-The conversion of diethyl adipate (DA) to sodium monoethyladipate (SMA) was calculated . Relative conversion (conversion of DA to SMA relative to base case* conversion) was adopted to show the enhancement of conversion with respect to base case . Also , the purity of upper layer relative to the lower layer was calculated.

3.2 Experimental Work

1-Sodium hydroxide (NaOH) solution , was prepared and standardized .

2-According to the design of experiment (Table 1) ,(Montgomery,2001) three factors were intended to study (feed mole ratio , sodium hydroxide (NaOH) solution concentration, and batch "distillation" time) within the ranges fixed in Table 2 .

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

4-Heating the mixture till boiling . The distillate began to appear approximately at 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-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 .

9- After that atomic absorption was made for the upper layer to measure the concentration of sodium monoethyladipate (SMA) .

10-The conversion(using Eq. (1))and relative conversion (usingEq. (2))were calculated as in the case of without distillation . The percentage purity of distillate upper layer which contains SMA was also calculated(using Eq. (3)) .

11-In order to characterize the final product , i.e disodium adipateDSA (**see Fig. 1**)the measurement of somephysical properties were performed as illustrated in **Table 3** .

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*Base case : is the experiments that carried out at lower values of all the parameters , which is regarded as base (reference) case .

3.3 Illustrations of Relative Conversion and Percentage Purity Calculations

Sodium monoethyladipate (SMA) concentration = sodium (Na) concentration in distillate upper layer

Conversion of diethyl adipate (DA) to (SMA)= $\frac{moles\ of\ reacted\ DA\ to\ SMA}{moles\ of\ DA\ in\ feed} * 100$ (1)

Relative conversion= $\frac{conversion\ of\ DA\ to\ SMA}{base\ case\ (run1) conversion}$ (2)

%Purity= $\frac{wt.of\ distillate\ upper\ layer}{wt.of\ total\ distillate} * 100$(3)

4. RESULTS

4.1 Experimental Results

Fig. 2 shows the variation of sodium monoethyladipate (SMA) concentration with feed mole ratio represented by (x_1) . Two curves were drawn for the same NaOH solution concentration (x_2 = 3 N) and different distillation time (x_3 = 1.5 and 3.5 hr.) . From this figure , it is clear for the two curves that SMA concentration was direct proportional with feed mole ratio in the range (x_1 = 0.1 – 0.3) . The two curves have a maximum SMA concentration at (x_1 = 0.3) . After that, increasing feed mole ratio in the range (x_1 = 0.3 – 1) caused 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,1973**. 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 SMA concentration for the curve of shorter distillation time (t = 1.5 hr.) at (x_1 = 0.1 – about 0.8) was higher than that of longer distillation time (t = 3.5 hr.) . At feed mole ratio (x_1 = 0.3) SMA concentration for the curve of shorter distillation time (106.10 ppm.) , while for the curve of longer distillation time (50.33 ppm.) viz has its half concentration value . This is because longer distillation time activated the second reaction (i.e SMA consumption increased) , meanwhile the other products (ethanol) as well as (water) continued to accumulate in the distillate . So SMA concentration with respect to the upper layer of distillate reduced .

Fig. 3 also shows the variation of SMA concentration with feed mole ratio (x_1) . Again two curves were drawn for the same NaOH solution concentration (x_2 = 8 N) and different batch time (x_3 = 1.5 and 3.5 hr.) . From this figure , it is clear that the two curves have the same trend of variation as in **Fig. 2** with wide difference between them . The peak of the curve of shorter distillation time (119.82 ppm.) was higher than the corresponding one of **Fig. 2**. The peak of the curve of longer distillation time (15.77 ppm.) was lower than the corresponding one of **Fig. 2** .

This is because increasing NaOH solution concentration activated both the first and second reactions . For (1.5 hr.) duration SMA accumulation was greater than its consumption , so SMA concentration increased with increasing NaOH solution concentration . For (3.5 hr.) duration SMA consumption was greater than its accumulation , so SMA concentration decreased with increasing NaOH solution concentration .

Fig. 4 illustrates the variation of SMA concentration with NaOH solution concentration represented by (x_2) . The curve was drawn for feed mole ratio ($x_1 = 0.3$) and distillation time ($t = 2.5$ hr.), i.e. the center points of each parameter . From this figure , it is clear that SMA concentration decreased with increasing NaOH solution concentration in the range ($x_2 = 3 – 5.5$ N) . The curve has a minimum value of SMA concentration (8.67 ppm.) at ($x_2 = 5.5$ N) . After that SMA concentration increased with increasing NaOH solution concentration in the range ($x_2 = 5.5 – 8$ N) . As explained before , increasing NaOH solution concentration stimulated both reactions . Also , as explained before in **Figs. 2** and **3** , for ($t = 1.5$ hr.) and ($x_1 = 0.3$) NaOH solution concentration ($x_2 = 8$ N) gave higher SMA concentration than NaOH solution concentration ($x_2 = 3$ N) , while for ($t = 3.5$ hr.) NaOH solution concentration ($x_2 = 3$ N) gave higher SMA concentration than NaOH solution concentration ($x_2 = 8$N) . For ($t = 2.5$ hr.) and ($x_1 = 0.3$) SMA concentration for NaOH solution concentration ($x_2 = 8$ N) was higher than its concentration for NaOH solution concentration ($x_2 = 3$ N) . It can be concluded that SMA concentration increased with increasing NaOH solution concentration during (1.5 – 2.5 hr.) , while SMA concentration decreased with increasing NaOH solution concentration during (2.5 – 3.5 hr.) .

Fig. 5 explains the variation of SMA concentration with batch (distillation) time represented by (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 increasing distillation time in the range ($t = 1.5 – 2.5$ hr.) decreased SMA concentration progressively .The curve has a minimum in SMA concentration (10.55 ppm.) at ($t = 2.5$ hr.) . After that, SMA concentration increased with increasing distillation time in the range ($t = 2.5 – 3.5$ hr.) . This can be explained as follows : the increasing in distillation time in the range ($t = 1.5 – 2.5$ hr.) for ($x_2 = 3$ N) decreased SMA concentration because of increasing SMA consumption by means of activating the second conversion reaction, meanwhile other products (ethanol) as well as (water) continued to accumulate in distillate upper layer so SMA concentration decreased progressively . The increasing in SMA concentration with increasing distillation time in the range ($t = 2.5 – 3.5$ hr.) was because of decreasing SMA consumption . Also , from this figure it is clear that SMA concentration for shorter distillation time (106.10 ppm.) was higher than SMA concentration for longer distillation time (50.33 ppm.) as explained in **Fig. 2** at ($x_1 = 0.3$) .

Fig. 6 shows the variation of SMA concentration with batch time (x_3) and feed mole ratio ($x_1 = 0.3$) . The curve was drawn for NaOH solution concentration ($x_2 = 8$ N) . As explained previously , increasing NaOH solution concentration stimulated the two reactions (first and second conversion reactions) . From this figure , it is clear that when distillation time increased in the range ($t = 1.5 - 2.5$ hr.) SMA concentration increased . The curve has a maximum SMA concentration (152.37 ppm.) at ($t = 2.5$ hr.) , this is on the contrary to **Fig. 5** which has a minimum value at ($t = 2.5$ hr.) . This means higher SMA production be at ($t = 2.5$ hr.) for ($x_2 = 8$ N) , while higher SMA consumption be at ($t = 2.5$ hr.) for ($x_2 = 3$ N) . After that, SMA concentration decreased when distillation time increased in the range ($t = 2.5 - 3.5$ hr.) . Also, it is clear from this figure (1.5 hr.) distillation time gave higher SMA concentration (119.82 ppm.) than (3.5 hr.) distillation time (15.77 ppm.)as explained in **Fig. 3**.

Fig. 7 explains the variation of relative conversion with feed mole ratio (x_1) . The curves were drawn for the same NaOH solution concentration (x_2 = 3 N) , and different batch time (x_3 = 1.5 and 3.5 hr.) . 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 range (x_1 = 0.3 – 1) decreased relative conversion . The increasing in relative conversion with increasing feed mole ratio in the range (x_1 = 0.1 – 0.3) was because of the increasing in SMA concentration in this range of feed mole ratios as shown in **Fig. 2**. The decreasing in relative conversion for the range (x_1 = 0.3 - 1) is due to the decreasing in SMA concentration. The curves have the same trend of variations as in **Fig. 2** . Relative conversion is a function of SMA concentration, weight of distillate upper layer , and DA volume . It varies proportionally with SMA concentration and the weight of the upper layer and it varies inversely with DA volume . 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) . This was because SMA concentration for (t = 1.5 hr.) was higher than its concentration for (t = 3.5 hr.) as shown in **Fig. 2**. It was noticed thatat feed mole ratios approximately above (x_1 = 0.6) the variation of relative conversion with feed mole ratio becomes linear .

Fig. 8 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) . This curve has this behaviour due to increasing then decreasing in SMA concentration as shown in **Fig. 3** . This curve has the same trend of variation as the curve of shorter distillation time in **Fig. 7** . The peak of the curve of shorter distillation time (2.76) is lower than the corresponding one of **Fig. 7** . This appears in contradiction with **Figs. 2**and**3** . This is because of lower weight of distillate upper layer and higher volume of DA . 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 for the range (x_1 = 0.55 - 1) was because of increasing in weight of upper layer distillate and increasing SMA concentration . The peak for the curve of longer distillation time (0.62) is lower than the corresponding one of **Fig.7**.This is because of lower weight of distillate upper layer and higher volume of DA as mentioned above.

Fig. 9 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 decreasingthenincreasing of SMA concentration with NaOH solution concentration as shown in **Fig. 4**.

Fig. 10 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 due to the decreasingthen increasing of SMA concentration with distillation time as shown in **Fig. 5** .

Fig. 11 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 in **Fig. 6**.

Fig. 12 illustrates the variation of percentage purity of distillate upper layer with feed mole ratio (x_1) . The two curves were drawn for the same NaOH solution concentration (x_2 = 3 N) and different batch time (x_3 = 1.5 and 3.5 hr.) . From this figure , obvious that the percentage purity for the two curves increased with increasing feed mole ratio in the range (x_1 = 0.1 – 0.3) . The two curves have a maximum value of percentage purity at (x_1 = 0.3) . After that the percentage purity decreased with increasing feed mole ratio in the range (x_1 = 0.3 – 1) . Percentage purity is a function of weight of distillate upper layer and unreacted DA weight in distillate . It is proportionally varies with the weight of distillate upper layer and inversely varies with the weight of unreacted DA in distillate . The increasing in percentage purity with increasing feed mole ratio in the range (x_1 = 0.1 – 0.3) was because stimulating the first conversion reaction (DA consumption increased so the appearance of unreacted DA in distillate decreased and SMA concentration in distillate increased) as explained in **Fig. 2** . The decreasing in percentage purity with increasing feed mole ratio in the range (x_1 = 0.3 - 1) was because stimulating the second conversion reaction (i.e SMA concentration in distillate decreased) as explained in **Fig. 2** . So the weight of upper layer distillate decreased and percentage purity decreased . Also , it is clear from this figure that the percentage purity for the curve of longer distillation time was higher than that of shorter distillation time . For the curve of (t = 3.5 hr.) at (x_1 = 0.3) the percentage purity (98.52 %) , while it is (97.5 %) for the curve of (t = 1.5 hr.) . This is because the accumulation of (ethanol) as well as (water) increased in the distillate for longer distillation time . So the weight of distillate upper layer increased with respect to unreacted DA layer (distillate lower layer) so that percentage purity of distillate upper layer increased .

Fig. 13 also illustrates the variation of percentage purity with feed mole ratio (x_1) .The batch time for the two curves was different (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 the two curves have the same trend of variation of **Fig. 12** . The peak for the curve of longer distillation time (98.01 %) was lower than the corresponding one of **Fig.12** . Also the peak for the curve of shorter distillation time (97.08 %) was lower than the corresponding one of **Fig. 12** . This is because for (x_2 = 8 N) both first and second reactions were highly activated ,so the accumulation of ethanol and water is much more than for (x_2 = 3 N)for (t = 1.5 hr.) as well as for (t = 3.5 hr.) . So the accumulated distillate for (t = 1.5 and 3.5 hr.) is much more than that for(x_2 = 3 N) in **Fig. 12**. The conclusion , that the maximum percentage purity occurred in low NaOH solution concentration (x_2 = 3 N) for both distillation time (1.5 hr. and 3.5 hr.) .**Fig. 14** shows the variation of percentage purity with NaOH solution concentration (x_2) . The curve was drawn for feed mole ratio (x_1 = 0.3) and batch time (t = 2.5 hr.) . From this figure, it is obvious that the percentage purity decreased with increasing NaOH solution concentration in the range (x_2 = 3 –

5.5 N) . The curve has a minimum percentage purity (95.34 %) at (x_2 = 5.5 N) . After that, the percentage purity increased with increasing NaOH solution concentration in the range (x_2 = 5.5 – 8 N) . This behaviour can be discussed through the decreasing then increasing of SMA concentration in **Fig. 4**.This result is fairly coincident with the conclusion of **Fig. 13**.

Fig. 15 illustrates the variation of percentage purity 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 percentage purity decreased with increasing distillation timein the range (x_3 = 1.5 – 2.5 hr.) . The curve has a minimum value of percentage purity (97.21 %) at (t = 2.5 hr.) . After that the percentage purity increased with increasing distillation time in the range (t = 2.5 – 3.5 hr.) . The discussion of the curve may be accomplished through **Fig. 5** as the decreasing SMA concentration led to decreasing percentage purity . Then increasing SMA concentration led to increasing percentage purity .

Fig. 16 also illustrates the variation of percentage purity with distillation time (x_3) and feed mole ratio (x_1 = 0.3) . The curve was drawn for NaOH solution concentration (x_2 = 8 N) . From this figure , it is obvious that the percentage purity increased with increasing distillation time in the range (t = 1.5 – 2.5 hr.) . The curve has a maximum percentage purity (99.40 %) at (t = 2.5 hr.) . After that the percentage purity decreased with increasing distillation time in the range (t = 2.5 – 3.5 hr.) . The curve can be discussed through the curve of**Fig. 6**. Increasing SMA concentration in the range (1.5 – 2.5 hr.) led to increasing percentage purity . Then decreasing SMA concentration in the range (2.5 – 3.5 hr.) led to decreasing percentage purity .

4.2 Empirical Equation and Figures

The empirical equation obtained from the statistical manipulation of the design of experiments results is:

$$y = (0.5329)\,x_1 + (1.5376)\,x_2 + (0.6561)\,x_3 + (0.2304)\,x_1x_2 + (0.2809)\,x_1x_3 + (0.2704)\,x_2x_3 + (0.2304)\,x_1x_2x_3 \qquad (4)$$

The empirical equation shows neither significance interaction between the parameters nor significance of any parameter except x_2 because all coefficients are < 1 except that for x_2 (1.5376). This indicates that NaOH solution concentration is the most effective parameter on the conversion .

Applying the parameters in the empirical equation, Eq. (4) within the range of parameters studied produced **Figs. 17-21** . **Figs. 17-21**, generally show the linear trend of variation . The reason of linearity is the absence of interactions between the variables (parameters studied , i.e feed mole ratio , sodium hydroxide solution concentration , and batch time) . The close looking of these results with experimental results shows that the empirical equation may well applied on this system at high values of feed mole ratios , high values of sodium hydroxide solution concentration , and low values of batch time . The empirical relation accounts for the general relation or trend of variation and not details . Therefore ; the peaks didn't appear in empirical figures .

5. 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 and purity were also influenced by it . Increasing feed mole ratio caused increasing in the concentration of SMA , conversion of DA to SMA , and percentage purity of SMA in the distillate 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 , conversion , and percentage purity decreased .

2-Increasing sodium hydroxide solution concentration (x_2) increased the concentration of SMA , as well as the conversion and percentage purity with other parameters (x_1 and x_3) were 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 , conversion , and percentage purity .

3-Increasing in batch time (x_3) caused decreasing the concentration of SMA and percentage purity till it reached (2.5 hr.) . After this value with other factors made fixed ($x_1 = 0.3$ and $x_3 = 3$ N) , the concentration of SMA and percentage purity increased with increasing x_3 . For the set of parameters ($x_1 = 0.3$ and $x_3 = 8$ N) increasing x_3 made increasing in the concentration of SMA and percentage purity till ($x_3 = 2.5$ hr.) . After this value SMA concentration and percentage purity decreased with increasing x_3 .

4-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 ($x_3 = 2.5$ hr.) . Then the conversion increased with increasing x_3 . For the set of parameters ($x_1 = 0.3$ and $x_2 = 8$ N) the increasing x_3 made steady decreasing in the conversion of DA to SMA .

5-The empirical equation well represented the system in the range of high values of x_1 and x_2 and low values of x_3 .Also , it showed no interactions between the parameters and independence on the two parameters ($x_1$andx_3). In other words, it is dependent on x_2 only.

6-The empirical figures showed a linear relationships between the effect (conversion) and the parameters (x_1 , x_2 , and x_3) . It was concluded that the empirical equation didn't consider the detailed behaviour of the function (conversion) . On the contrary , it took into account the global effect of the parameters as a whole .

7- The maximum conversion obtained in this study was 18.58 fold of that for the base case which corresponds to the set of parameters ($x_1 = 0.3$, $x_2 = 3$ Nand$x_3 = 1.5$ hr.).In other words , it corresponds to the center point of x_1, the low value of x_2 and the low value of x_3.The percentage purity for this set of parameters was %97.50 . Although the maximum percentage purity obtained was %99.40 which corresponds to($x_1 = 0.3$, $x_2 = 8$ Nand$x_3 = 2.5$ hr.), the calculated relative conversion for this set was only 2.40.

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Table 1 . 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 2 . Variation range of parameters.

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) , (hr.)	1.5	2.5	3.5

Table 3 . Some physical properties of DSA.

Physical property	**Measured**	**Published , [*]**
Density , g / cm^3	1.4428(using gas pycnometry) 1.4852(using ultra – pycnometry)	1.7
Melting point , ℃	≥ 250	250

Figure 1 . Disodium adipate from experimental work (with distillation) .

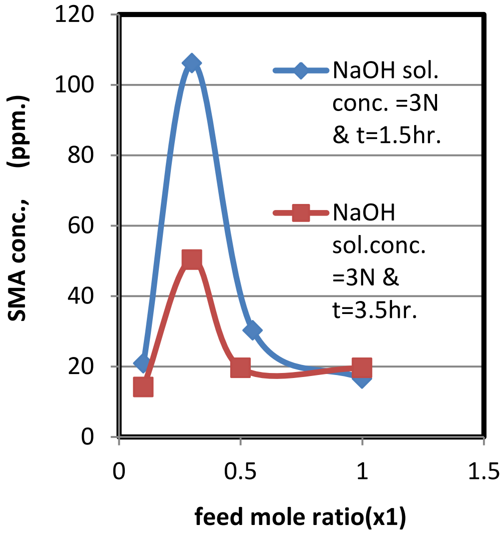

Figure 2 . SMA concentration , (ppm.) vs. feed mole ratio (x_1) for NaOH sol. conc. = 3N and t = (1.5 & 3.5 hr.) .

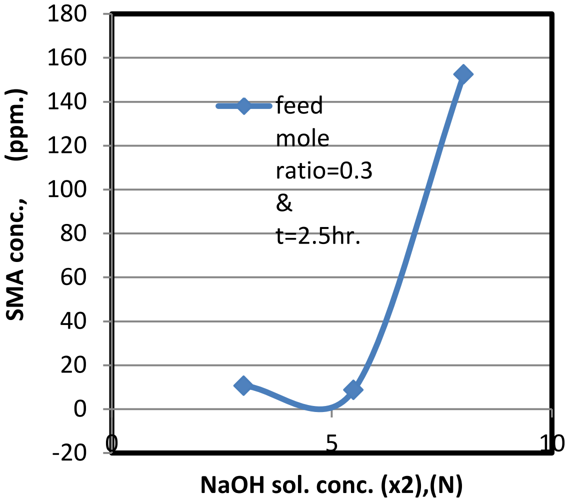

Figure 4 . SMA concentration , (ppm.) vs. NaOH solution concentration (x_2) , (N) for feed mole ratio = 0.3 and t = 2.5 hr.

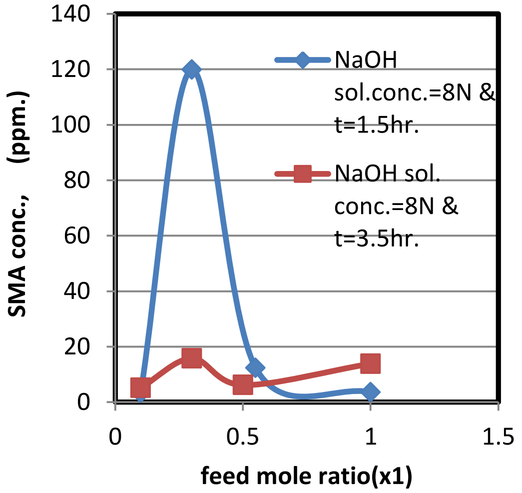

Figure 3 . SMA concentration , (ppm.) vs. feed mole ratio(x_1) for NaOH sol. conc. = 8 N and t = (1.5 & 3.5 hr.)

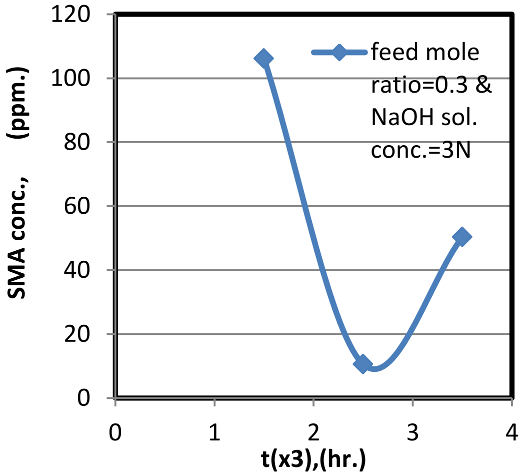

Figure 5 . SMA concentration , (ppm.) vs. t (x_3) , (hr.) for feed mole ratio = 0.3 and NaOH sol. conc. = 3 N .

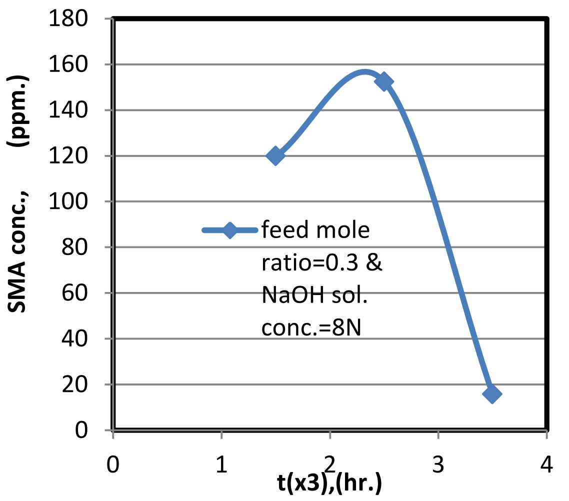

Figure 6 . SMA concentration , (ppm.) vs. t (x_3) , (hr.) for feed mole ratio = 0.3 and NaOH sol. conc.= 8 N .

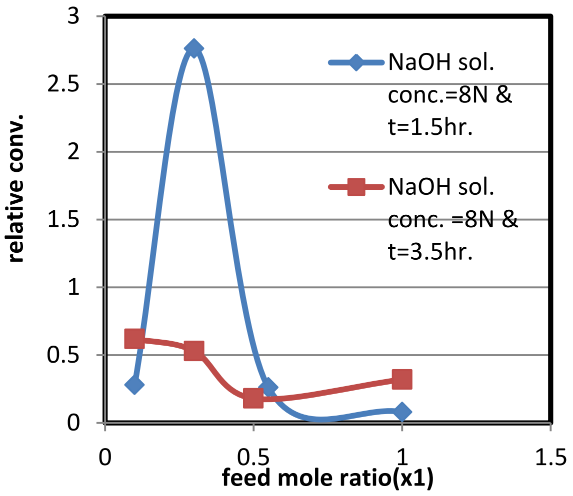

Figure 8 . Relative conversion vs. feed mole ratio (x_1) for NaOH sol. conc.= 8 N and t = (1.5 & 3.5 hr.) .

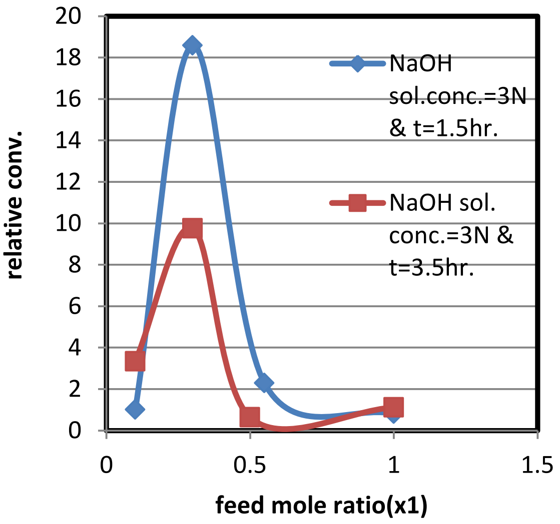

Figure 7 . Relative conversion vs. feed mole ratio (x_1) for NaOH sol. conc. = 3 N and t = (1.5 & 3.5 hr.) .

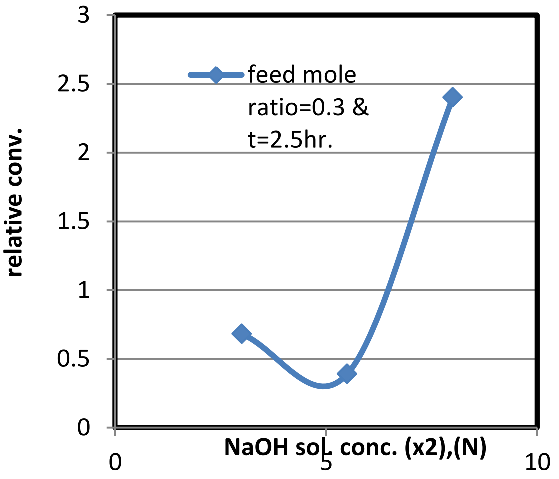

Figure 9 . Relative conversion vs. NaOH solution concentration (x_2) , (N) for feed mole ratio = 0.3 and t = 2.5 hr.

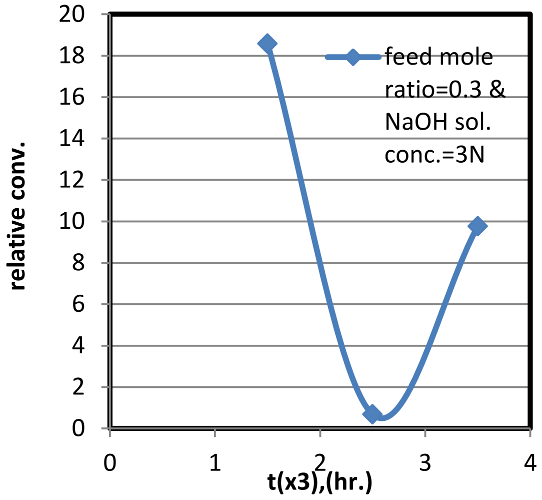

Figure 10 . Relative conversion vs. t (x_3) , (hr.) for feed mole ratio = 0.3 and NaOH sol. conc. = 3 N .

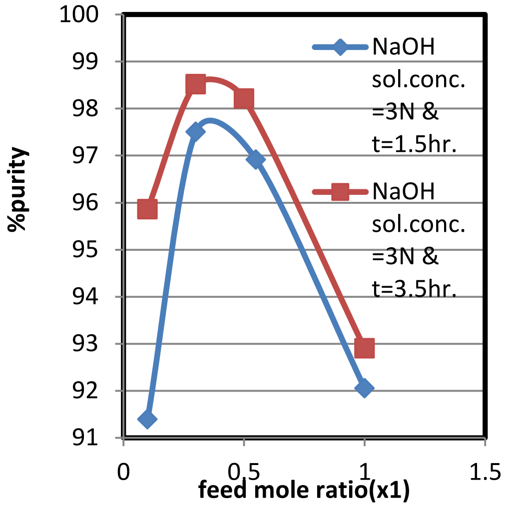

Figure 12 .% purity vs. feed mole ratio (x_1) for NaOH sol. conc. = 3 N and t = (1.5 & 3.5 hr.) .

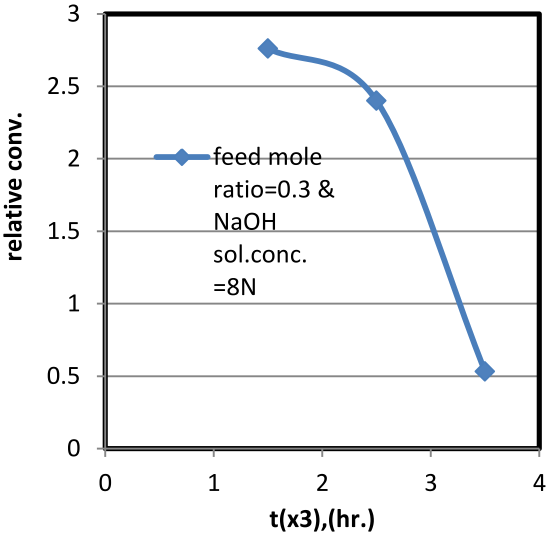

Figure 11 . Relative conversion vs. t (x_3) , (hr.) for feed mole ratio = 0.3 and NaOH sol. conc.= 8 N .

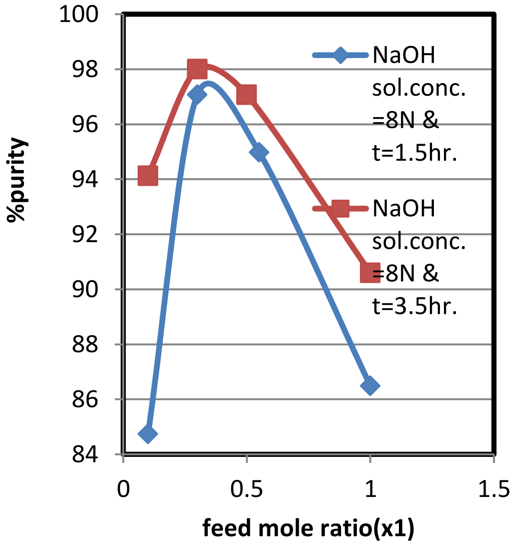

Figure 13 . % purity vs. feed mole ratio (x_1) for NaOH sol. conc. = 8 N and t = (1.5 & 3.5 hr.) .

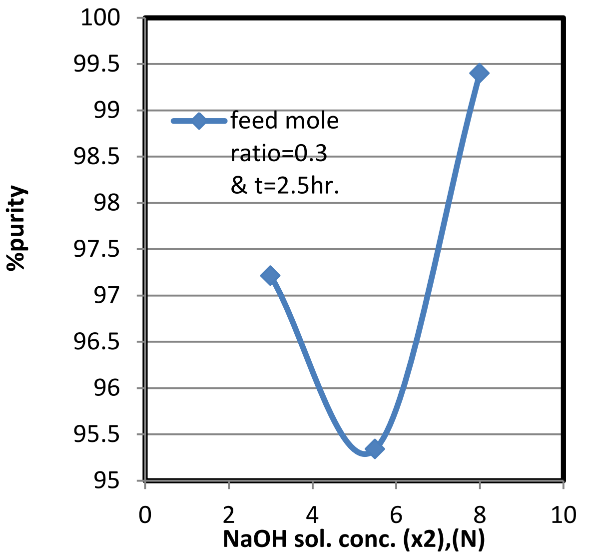

Figure 14 .% purity vs. t (x_3) , (hr.) for feed mole ratio = 0.3 and t = 2.5 hr.

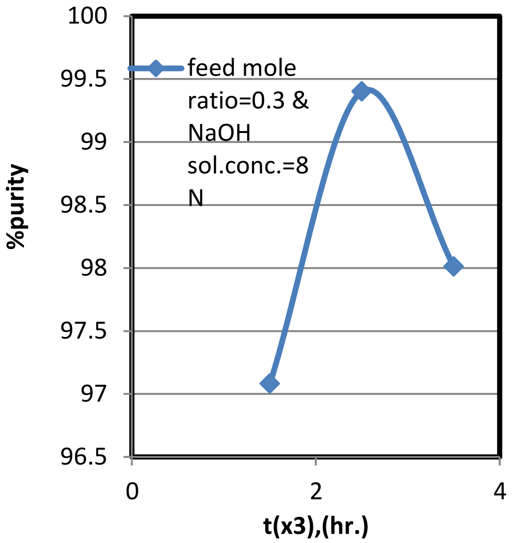

Figure 16 . % purity vs. t(x_3) , (hr.) for feed mole ratio = 0.3 and NaOH sol. conc. = 8 N.

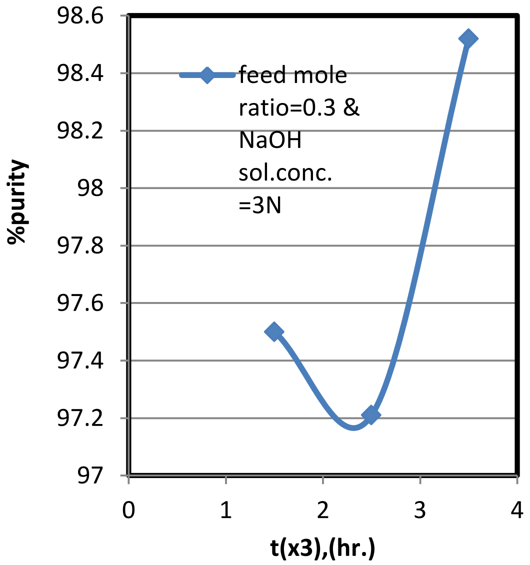

Figure 15 . % purity vs. t(x_3) , (hr.) for feed mole ratio = 0.3 and NaOH sol. conc. = 3 N.

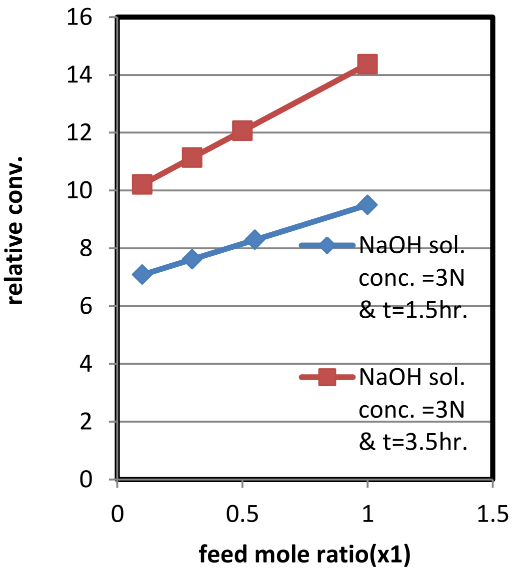

Figure 17 . Relative conversion vs. feed mole ratio (x_1) for NaOH sol. conc. = 3 N and t = (1.5 & 3.5 hr.) .

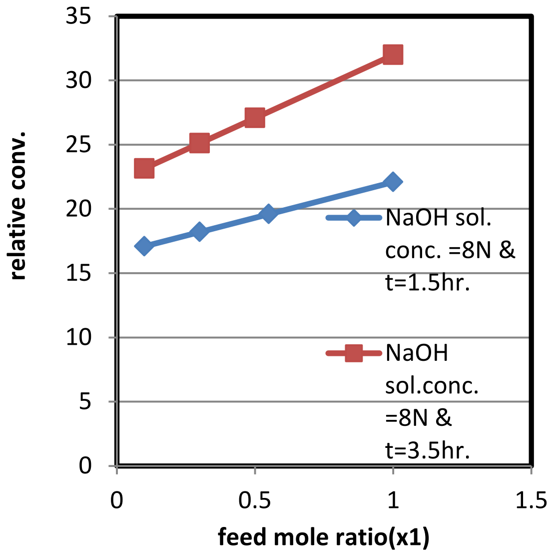

Figure 18 . Relative conversion vs. feed mole ratio (x_1) for NaOH sol. conc. = 8 N and t = (1.5 & 3.5 hr.) .

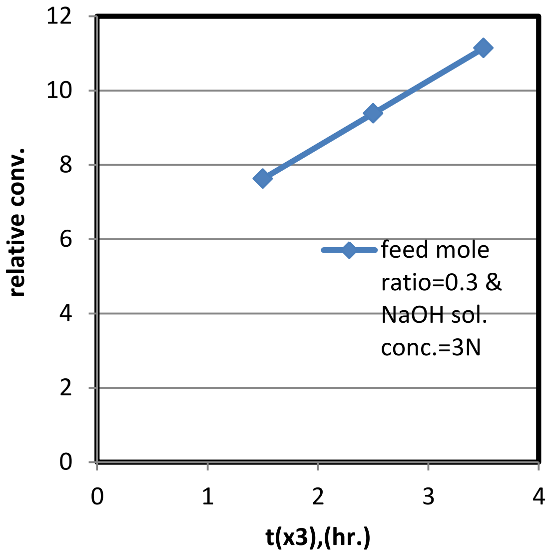

Figure 20 . Relative conversion vs. t (x_3) , (hr.) for feed mole ratio = 0.3 and NaOH sol. conc. = 3 N .

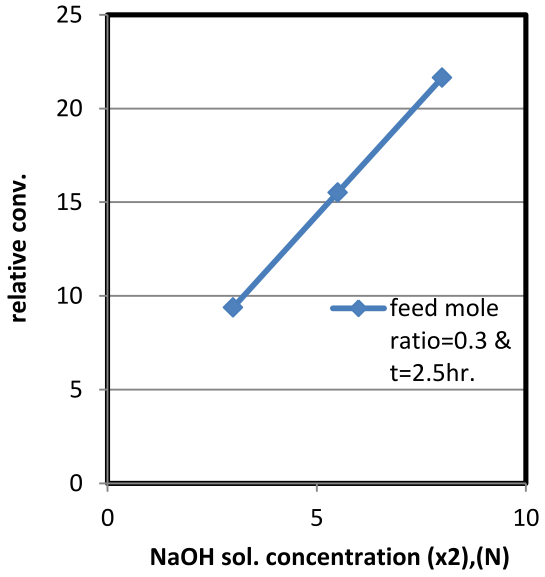

Figure 19. Relative conversion vs. NaOH sol. conc. (x_2) , (N) for feed mole ratio = 0.3 and t = 2.5 hr.

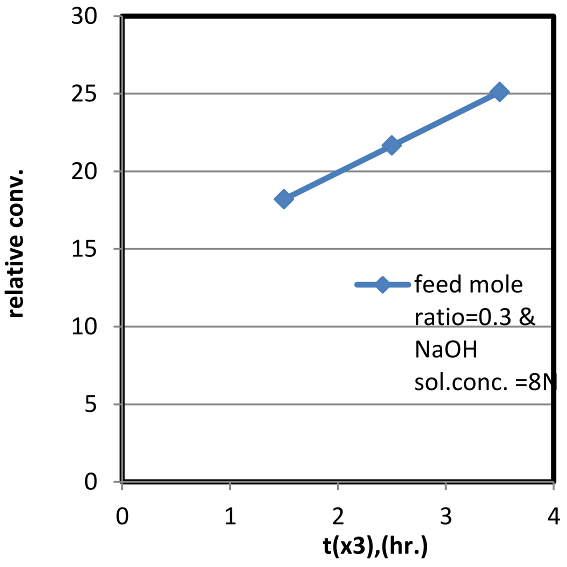

Figure 21 . Relative conversion vs. t (x_3) , (hr.) for feed mole ratio = 0.3 and NaOH sol. conc. = 8 N .