



## Saponification of Diethyl Adipate with Sodium Hydroxide Using Reactive Distillation

**Dr.Raghad Fareed Kassim Almilly**

Lecturer

Department of Chemical Engineering  
College of Engineering – University of Baghdad  
Email: rfkalm@yahoo.com

**Dr.Asrar Abdullah Alobaidy**

Lecturer

Department of Chemical Engineering  
College of Engineering – University of Baghdad  
Email: asrar-alobaidy@yahoo.com

**Maha Hadi Alhassani**

Assistant Professor

Department of Chemical Engineering  
College of Engineering – University of Baghdad  
Email: Maha@yahoo.com

### ABSTRACT

This research presents a new study in reactive distillation by adopting a consecutive reaction. The adopted consecutive reaction was the saponification reaction of diethyl adipate with NaOH solution. The saponification reaction occurs in two steps. The distillation process had the role of withdrawing the intermediate product i.e. monoethyl adipate from the reacting mixture before the second conversion to disodium adipate occurred. It was found that monoethyl adipate appeared successfully in the distillate liquid. The percentage conversion from di-ester to monoester was greatly enhanced (reaching 86%) relative to only 15.3% for the case of reaction without distillation. This means 5 times enhancement. The presence of two layers in both the distillate and residual liquids was noticed, the upper (water) layer and the lower (ester) layer. However, water layer was dominant in the distillate. The percentage excess of NaOH solution was calculated with respect to the concentration of monoester (9%-79%) and it was found that increasing the concentration of NaOH solution (until 40%) led to increase in the percentage conversion to monoester. It also led to get a pure monoester in the distillate and made the residual liquid appear as one layer. Maximum conversion had been occurred in the range (40%-60%). After 60% the percentage conversion lowered noticeably.

**Key words:** reactive distillation, consecutive reactions, saponification reaction, monoethyl adipate, diethyl adipate.

### صوبنة ثنائي اثيل ادبييت مع هيدروكسيد الصوديوم باستخدام التقطير التفاعلي

مها هادي الحسني  
استاذ مساعد  
كلية الهندسة / جامعة بغداد  
قسم الهندسة الكيمياوي

د. اسرار عبد الله العبيدي  
مدرس  
كلية الهندسة / جامعة بغداد  
قسم الهندسة الكيمياوي

د. رغد فريد قاسم الملي  
مدرس  
كلية الهندسة / جامعة بغداد  
قسم الهندسة الكيمياوي

### الخلاصة

يقدم هذا البحث دراسة جديدة في التقطير التفاعلي باعتماد التفاعل المتسلسل. ان التفاعل المتسلسل المعتمد هو تفاعل صوبنة ثنائي اثيل ادبييت مع محلول هيدروكسيد الصوديوم. ان تفاعل الصوبنة يحدث بخطوتين. وان دور عملية التقطير هو في سحب المركب الوسيط اي احادي اثيل ادبييت من المزيج المتفاعل قبل حدوث التحول الثاني الى ثنائي صوديوم ادبييت. لقد ظهر احادي اثيل ادبييت بنجاح في السائل المتقطر. ان النسبة المئوية للتحول من الاستر الثنائي الى الاستر الاحادي قد تحسنت بصورة كبيرة ( وصولا الى 86%) نسبة الى 15,3% فقط في حالة التفاعل بدون التقطير. هذا يعني التحسن لخمسة اضعاف.

لقد لوحظ وجود طبقتين في كلا السائلين المتقطر والمتبقي. الطبقة العلوية ( الماء ) والطبقة السفلية ( الاستر ) . ولوان طبقة الماء كانت هي السائدة في السائل المتقطر. تم احتساب النسبة المئوية للزيادة في محلول هيدروكسيد الصوديوم بالنسبة الى تركيز الاستر الاحادي(9%-79%) ولقد وجد ان الزيادة في محلول هيدروكسيد الصوديوم( الى حد 40%) يؤدي الى زيادة النسبة المئوية للتحويل الى الاستر الاحادي. كما تؤدي الى الحصول على الاستر الاحادي نقيا في السائل المتقطر وظهور السائل المتبقي كطبقة واحدة. ان اعظم تحول حصل في المدى (40%-60%). بعد 60% انخفضت النسبة المئوية للتحويل بصورة ملحوظة .

الكلمات المفتاحية: التقطير التفاعلي , التفاعلات المتسلسلة , تفاعل الصوبنة , احادي اثيل ادبييت , ثنائي اثيل ادبييت .

## 1. INTRODUCTION

The technique of reactive distillation was described to be useful for equilibrium-limited reactions such as esterification and ester hydrolysis reactions, **Edreder , et al. ,2010**. That is conversion can be increased far beyond what is expected by the equilibrium due to the continuous removal of reaction products from the reactive zone. This helps in reducing capital and investment costs and may be important for sustainable development due to a lower consumption of resources.

Reactive distillation was used with reversible, liquid phase reactions such as the production of ethylene glycol ,**Okasinsld , and Doherty , 1998** . A model was presented to show the difference between the kinetics of the reaction without and with the boiling of the reaction mixture in a staged reactive distillation column.

Catalytic distillation is a branch of reactive distillation which combines the processes of distillation and catalysis to selectively separate mixtures within solutions. Its main function is to maximize the yield of catalytic organic reactions, such as the refining of gasoline , **Babich , and Moulijn , 2003** .

The design and operation for reactive distillation systems are considerably more complex than those involved for either conventional reactors or conventional distillation columns. The development of models for design of reactive distillation columns was proposed, **Taylor, and Krishna, 2000. Huss and et al., and Huss, et al., 2003**, presented a hierarchy of methods, models , and calculation techniques that support the design of reactive distillation columns. The approach was illustrated for the production of methyl acetate. They showed the existence of both minimum and maximum reflux. A narrow range of reflux ratios produced high conversions and high purity methyl acetate.

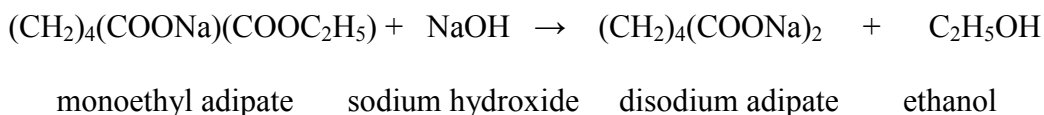
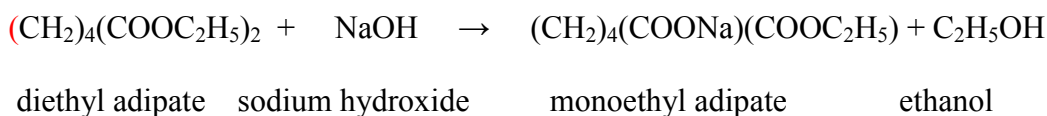
**Huerta-Garrido and Rico-Ramirez , 2004** , presented a simplified methodology for the analysis and design of reactive batch distillation columns based on the McCabe-Thiele method for reactive continuous columns and on the concept of a reactive difference point.

A reactive distillation column for the synthesis of methyl tert-butyl ether (MTBE) was simulated using a steady – state equilibrium stage model, **Jacobs, and Krishna, 1993. Gildert , et. al.,2011**, presented advances in process technology through catalytic distillation . A number of recently commercialized catalytic distillation applications were described, such as:

- Butadiene selective hydrogenation.
- Pentadiene selective hydrogenation.
- C<sub>4</sub> acetylene conversion.
- Benzene saturation.

In this research, the reactive distillation technique is applied to a consecutive reaction for the first time. Saponification reaction of diethyl adipate with sodium hydroxide solution was proposed as the consecutive reaction. In this reaction the di-ester converts to disodium adapted by two steps. The first step converts diethyl adipate to monoethyl adipate (which represents the

intermediate product) . The second step converts monoethyl adipate to disodium adipate (which represents the final product). The chemical reactions were represented as follows, **Newberger and Kadlec , 1973** :



The objective of this research is to prove that reactive distillation technique can be applied to enhance the conversion of the intermediate product of a consecutive reaction. This can be done by removing the intermediate product from the reaction zone using distillation before converting to the final product. This technique may be applied in many industrial reactions where the intermediate product is the desired product.

## 2. EXPERIMENTAL WORK

Because diethyl adipate material is not available in laboratories neither in market, it should be prepared in laboratory, **Micovic , 2013** . So, the experimental work was split into two parts.

### 2.1 Part I – Preparation of Diethyl Adipate

#### 2.1.1 Materials

Adipic acid (Hopkin & Williams LTD), ethanol (Medical grade 96% purity, Al-Tharthar Co. LTD) , toluene ( Analyt GCC ) , sulfuric acid ( commercial grade).

#### 2.1.2 Equipment

500 ml- distillation flask , condenser ,heater, (0-300°C) thermometers, 500 ml - receiving flask , Büchner suction tube and Büchner flask of 250 ml, 100 ml- graduated cylinder , 50ml- pycnometer , pipet , buret , sample flasks of 25- and 50-ml , refractometer ( Model Optika , no. 2WAJ SN 281006 , Italy ).

#### 2.1.3 Procedure

73 grams of adipic acid is weighed and transferred to the 500 ml - distilling flask . Then 180 cc of ethanol , 90 cc of toluene are added. Few drops of concentrated sulfuric acid are added as a catalyst.

The flask is connected with a condenser. It is heated. An azeotropic mixture of alcohol, toluene , and water begins to distill at approximately 70°C . Distillation is continued until the thermometer in the neck of the flask rises to 80°C . Then heating is suspended.

That was the first part of preparation . The second part begins when the residual liquid in the flask is again heated under vacuum using Büchner suction tube and flask (calibrated using U-tube manometer). Alcohol and toluene distil first . Then the temperature rises and diethyl adipate begins to distill at 137°C. The yield was 78 ml of diethyl adipate.

The FTIR of the ester was performed, as well as its density, refractive index, and boiling point were measured. The density was measured using pycnometer and was found to be  $1.124 \text{ g/cm}^3$  at  $10^\circ\text{C}$  (the ambient temperature). This was satisfactory when compared with the published value of  $1.009 \text{ g/cm}^3$  at  $25^\circ\text{C}$ , **Perry's Handbook, 1984**. Also the refractive index was measured for the prepared amount of ester using the refractometer. It was found to be 1.429. This was again satisfactory when compared with the published value of 1.427, **Langs Handbook, 1934**. The boiling point was recorded to be  $137^\circ\text{C}$ . Again it was fair enough with published  $138^\circ\text{C}$ . These results were reliable to proceed in this research and accomplish the second part of it.

## 2.2 Part II – Saponification of Diethyl Adipate with Sodium Hydroxide using Reactive Distillation

### 2.2.1 Materials

The materials used are: diethyl adipate (prepared in the laboratory), sodium hydroxide solution (Aldrich mark) standardized against standard HCl solution (commercial grade) (standardization of HCl is due to, **Vogel, 1961**).

### 2.2.2 Equipment

The apparatus used consists of (500 ml- distilling flask) connected with adapter, condenser, receiver, and receiving flask to collect the condensate, as shown in **Fig.1**. A thermometer is put in one of the flask's opening to measure the temperature of the boiling liquid. Another thermometer is put in the adapter's opening to measure the temperature of the rising vapour.

### 2.2.3 Procedure

Measured amounts (10 – 50 ml) of prepared diethyl adipate were mixed with standard sodium hydroxide solution of changeable excess amounts (150-350 ml) in the distilling flask and heated. The distillate began to appear at  $100^\circ\text{C}$ . The temperature was found to be constant at  $100^\circ\text{C}$ . After about one hour the distillation was stopped. The distillate and residual liquids were transferred to separating funnels. They were left to separate into two layers. Each layer was transferred to a flask and analysed using FTIR, and titration against standard hydrochloric acid. The conversion to monoester for the distillate was calculated. Results are tabulated in **Table 1**. The refractive index of distillate upper layer was also measured as shown in **Table 2**.

## 3. RESULTS and DISCUSSIONS

**Figs. 2-14** show FTIR analyses results. **Fig. 2** shows FTIR analysis for diethyl adipate alone. It has a peak at 1735 which indicates ester carbonyl group (C=O) existence. **Figs. 3 and 4** illustrate the existence of unreacted diethyl- with monoethyl adipate in both the upper and lower layers. The conversion to monoester was found to be 74.1%. These results corresponded to 9% excess of NaOH solution. **Figs. 5 and 6** show the results using 15% excess of NaOH solution. They show the presence of both mono- and diester with noticeable reversed concentrations in the two layers of distillate. It has been found that the conversion of di-ester to monoester was increased to 78.9%. This is because increasing NaOH concentration (one of the reactants), leads to increase the extent of reaction. Also, the reaction is irreversible in alkaline solution due to the stabilizing effect caused by resonance of the carbonyl group, **Newberger and Kadlec, 1973**. At higher value of percentage excess of NaOH solution, i.e. 19%, the conversion to monoester was clearly enhanced, reaching 87.5%. This was explained by **Figs. 7 and 8**. Also, it is obvious that monoester appears purely in **Fig. 7** which represents the upper (water) layer of distillate. That's means gaining the intermediate (desired) product at higher

yield and purity . These results are summarized in **Table 1**.

FTIR analyses were carried out for residual liquids. The presence of monoester in the residue was noticed for different values of percentage excess of NaOH solution. FTIR analyses for upper and lower layers of residue are shown in **Figs. 9-14**. It was noticed that mono- and di-ester presented in the two layers .Concentration of monoester cannot be detected by titration of these layers , since NaOH solution presented in these layers in excess values as the second reactant . It was also noticed that at 19% excess of NaOH solution , there was only one layer in the residual liquid as shown in **Figs. 13 and 14**. Increasing percentage excess of NaOH to 79% led to lowering the conversion to mono-ester to 86% as shown in **Table 1**. Another experiment was conducted without distillation to compare the conversion between the two cases , i.e the reaction without distillation and the reactive distillation .It was difficult to calculate monoester concentration using titration in this experiment since monoester and unreacted NaOH solution were being in the same mixture . Therefore; GC analysis and atomic absorption were carried out to indicate the presence of monoester and to measure the quantity of it as illustrated in **Figs. 15 and 16**. It was shown by atomic absorption that the conversion of di-ester to monoester was only 15.3% using 79% of NaOH solution (calculated with respect to monoester). A summary of these results are tabulated in **Table 2**. The dependence of the conversion from di-ester to monoester on the %excess of NaOH solution is drawn in **Fig. 17**. It can be noticed that the curve has second degree shape which indicates the presence of maximum conversion. This means that the increase of percentage excess of NaOH solution increases conversion to approximately 100% at about 40% excess NaOH then further increasing of percentage excess of NaOH (above 60%) lowers the conversion .This can be discussed as follows: at low values of percentage excess of NaOH solution , the conversion increases with increasing NaOH molecules (increasing the concentration of one of reactants), but when percentage excess of NaOH solution increases further, the molecules are hindered to transfer causing reduced values of conversion. The refractive indices of the distillate upper layers were measured . The values were found to be near to that of water (1.3331) , **Langs Handbook , 1934**, as shown in **Table 3**. The explanation of these results is that the ester is slightly soluble in water , **Perry's Handbook , 1984** , so it was appeared as a dispersed phase in water and the refractive index fixed to that of water.

#### 4. CONCLUSIONS

-The technique of reactive distillation is used to increase the conversion of an intermediate product of consecutive reactions.

-Increasing percentage excess of reactant (certain limit) increases the conversion of the intermediate product of a consecutive reaction in the distillate.

-The purity of the intermediate product is increased with increasing percentage excess of the reactant.

#### ACKNOWLEDGMENT

Raghad F. Almilly , Asrar A. Alobaidy , and Maha H. Alhassani are thankful for Prof. Dr. Ahlam Marouf Al-Azzawi / Chemical Department / College of Science / Baghdad University for her valuable guidance in testing the samples and explaining the results.



## REFERENCES

- -Babich , I.V., and Moulijn , J.A., 2003, *Science and Technology of Novel Processes for Deep Desulfurization of Oil Refinery Streams : A Review* , Fuel , 82 , PP. 607-631.
- -Doherty , M. F. , and Malone , M.F. , 1999, *Recent Advances in Reactive Distillation* , AIChE Annual Meeting , paper 203C , Nov. 3 , PP. 1-24.
- -Gildert , G.R. , Rock , K. , and McGuirk , T. , 2011 , *Advances in Process Technology Through Catalytic Distillation* , CDTECH , 12141 Wickchester , TX , USA 77079 .
- -Huerta – Garrido , M . E . , and Rico – Ranirez , V .,2004, *Simplified Design of Batch Reactive Distillation Columns* , Ind. Eng. Chem. Res., Vol. 43, PP. 4000-4011.
- -Huss , R.S. , Chen , F., Malone , M. F. , and Doherty , M. F. , 2003, *Reactive Distillation for Methyl Acetate Production* , Computers and Chemical Engineering , Vol. 17 , PP. 1855-1866.
- -Jacobs , R., and Krishna , R., 1993, *Multiple Solutions in Reactive Distillation for Methyl tert-Butyl Ether Synthesis* , Ind. Eng. Chem. Res. , Vol. 32 , PP. 1706-1709.
- -Micovic , V.M.,2013, *Ethyl Adipate* , Organic Syntheses , CV 2 , 264.
- -Newberger , M.R. , and Kadlec , R.H. , 1973, *Kinetics of the Saponification of Diethyl Adipate* , AIChE Journal , Vol. 19 , No. 6 , PP. 1272-1275.
- -Okasinsld M.J., and Doherty ,M.F., 1998, *Design Method for Kinetically Controlled , Staged Reactive Distillation Column*, Ind. Eng. Chem. Res. , Vol. 37, No. 7 , PP. 2821-2834.
- -Perry , R.H., and Don , G., 1984, *Perry's Chemical Engineers Handbook*, 6<sup>th</sup> ed., McGraw- Hill, USA.
- Taylor , R. , and Krishna , R. , 2000 , *Modeling Reactive Distillation* , Chemical Engineering Science , Vol. 55 , Issue 22, Nov. , PP. 5183-5229.
- Vogel, A.I.,1961, *Quantitative Inorganic Analysis* , 3<sup>rd</sup> ed. , Longmans.

## NOMENCLATURE

- A limiting reactant (ester)
- B excess reactant (NaOH solution)
- C concentration (mol . l<sup>-1</sup>)

## Subscripts

- o initial ( C<sub>Ao</sub> initial conc. of reactant A)



Figure 1. Apparatus photo.

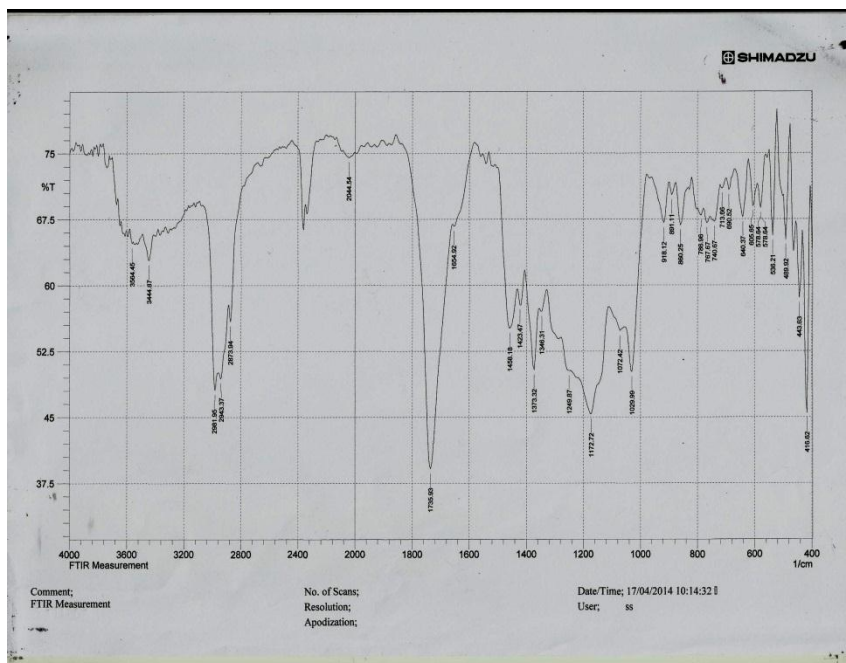
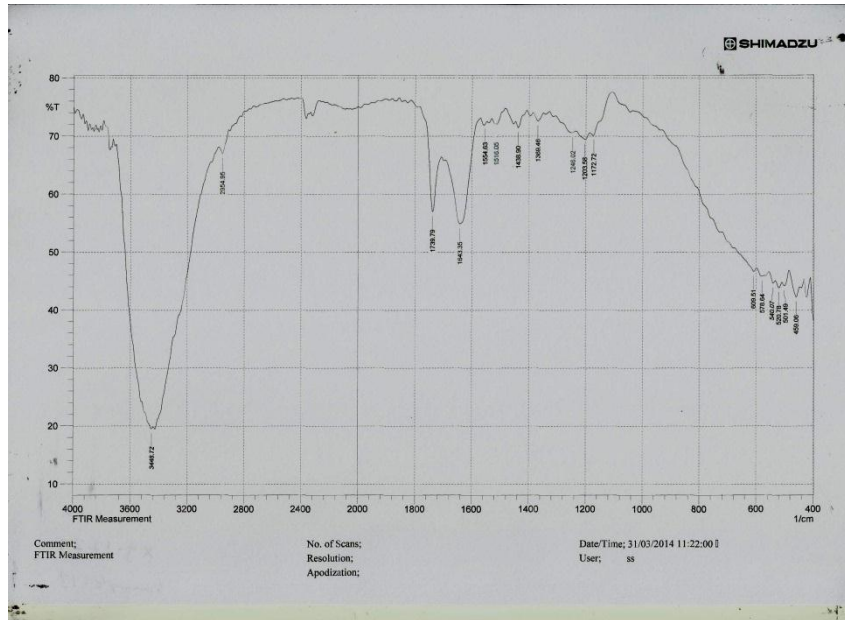
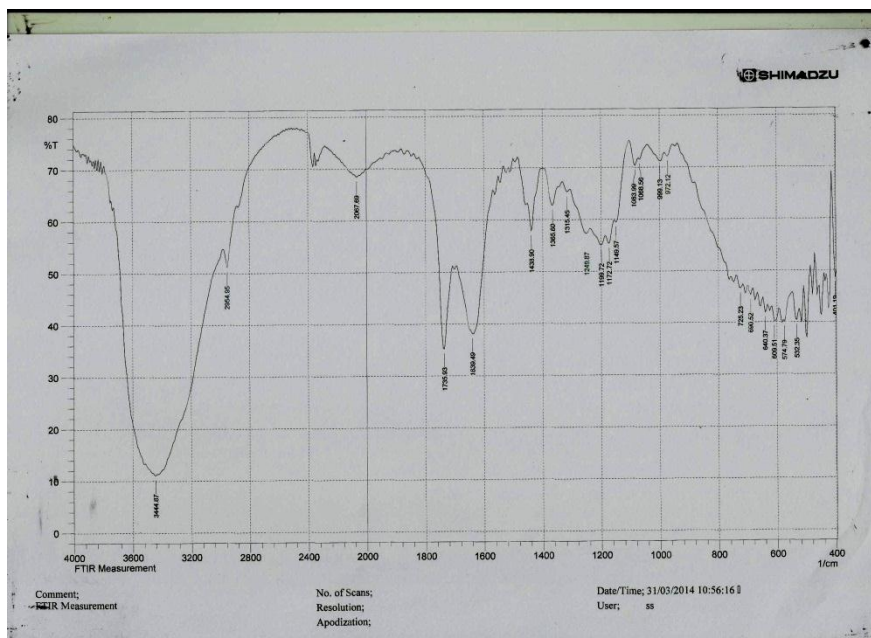


Figure 2. FTIR measurement for diethyl adipate .

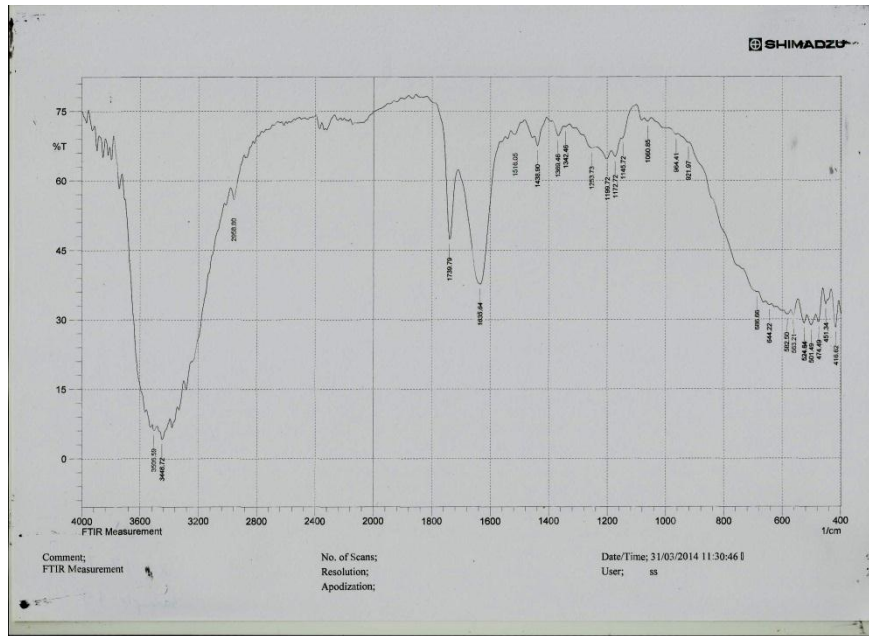


**Figure 3.** FTIR measurement for upper layer of distillate with  $C_{A0}=0.58 \text{ mol.l}^{-1}$ ,  $C_{B0}=0.63 \text{ mol.l}^{-1}$  and 9 % excess of NaOH solution.

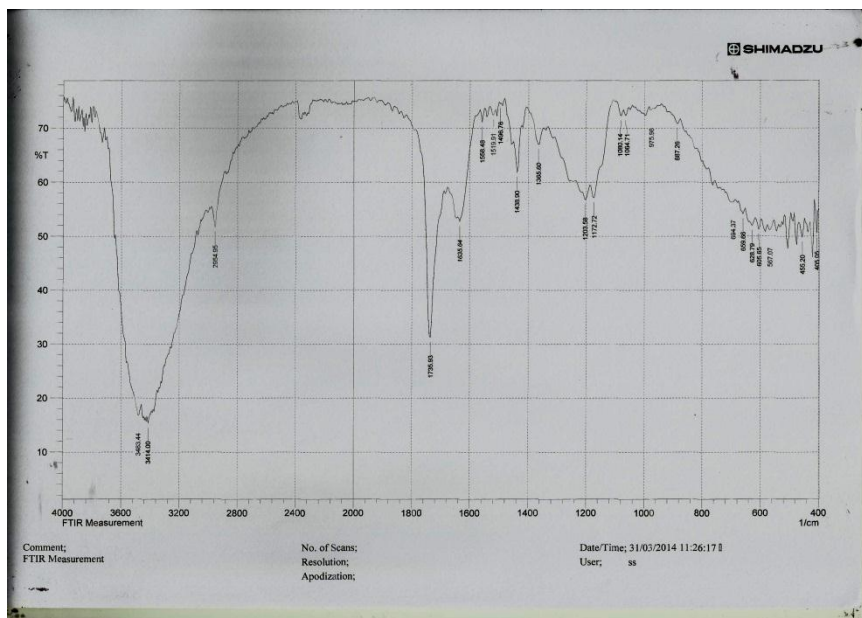


**Figure 4.** FTIR measurement for lower layer of distillate with  $C_{A0}=0.58 \text{ mol.l}^{-1}$ ,  $C_{B0}=0.63 \text{ mol.l}^{-1}$  and 9% excess of NaOH solution.

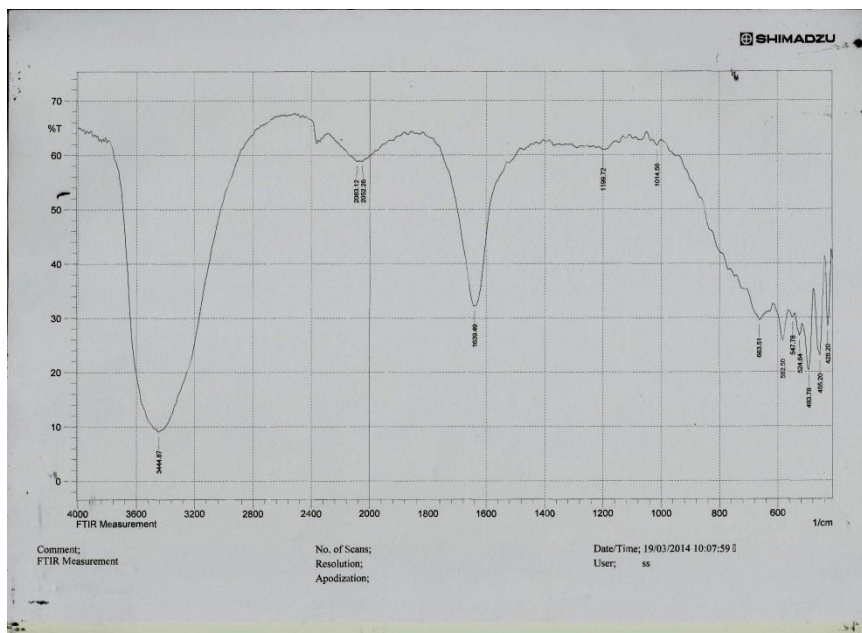




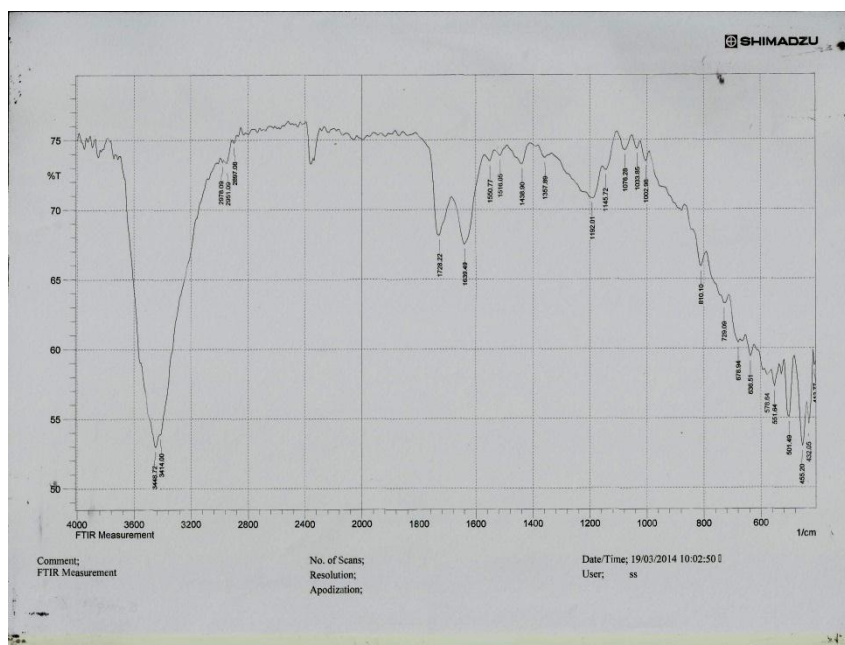
**Figure 5.** FTIR measurement for upper layer of distillate with  $C_{A0}=0.5553 \text{ mol.l}^{-1}$ ,  $C_{B0}=0.6384 \text{ mol.l}^{-1}$  and 15% excess of NaOH solution.



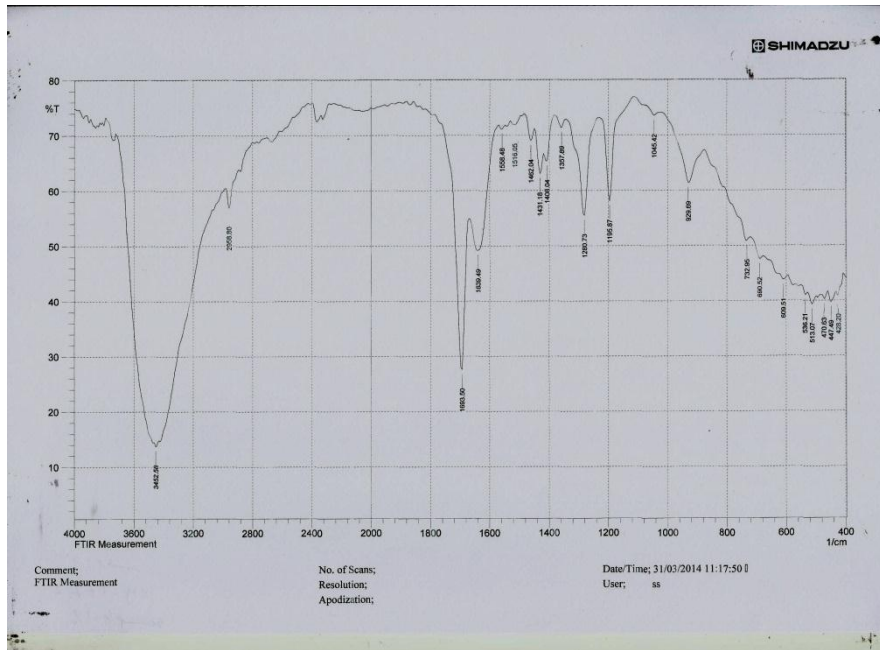
**Figure 6.** FTIR measurement for lower layer of distillate with  $C_{A0}=0.5553 \text{ mol.l}^{-1}$ ,  $C_{B0}=0.6384 \text{ mol.l}^{-1}$  and 15% excess of NaOH solution.



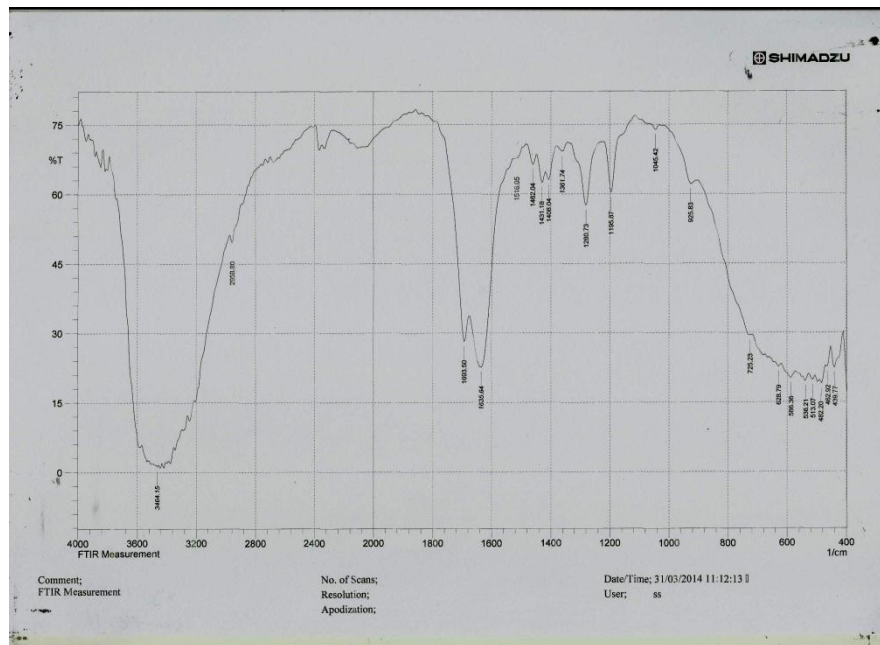
**Figure 7.** FTIR measurement for upper layer of distillate with  $C_{A0}=0.32 \text{ mol.l}^{-1}$ ,  $C_{B0}=0.38 \text{ mol.l}^{-1}$  and 19% excess of NaOH solution.



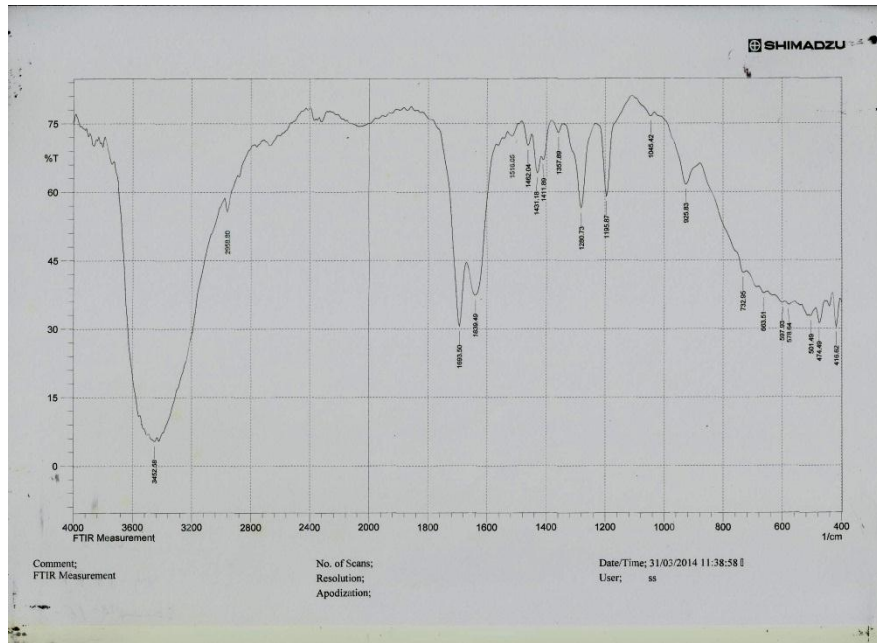
**Figure 8.** FTIR measurement for lower layer of distillate with  $C_{A0}=0.32 \text{ mol.l}^{-1}$ ,  $C_{B0}=0.38 \text{ mol.l}^{-1}$  and 19% excess of NaOH solution.



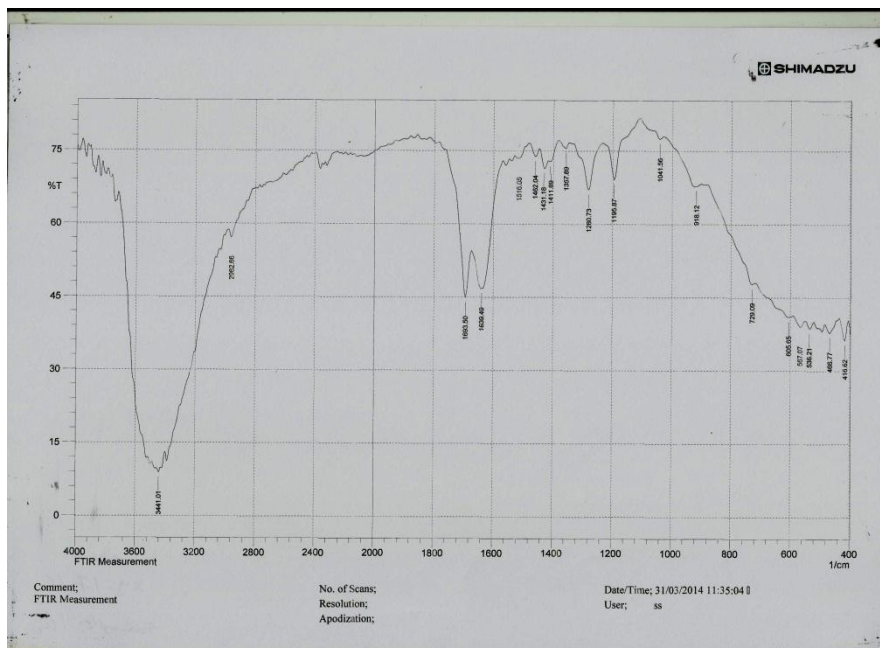
**Figure 9.** FTIR measurement for upper layer of residue with  $C_{A0}=0.58 \text{ mol.l}^{-1}$ ,  $C_{B0}=0.63 \text{ mol.l}^{-1}$  and 9 % excess of NaOH solution.



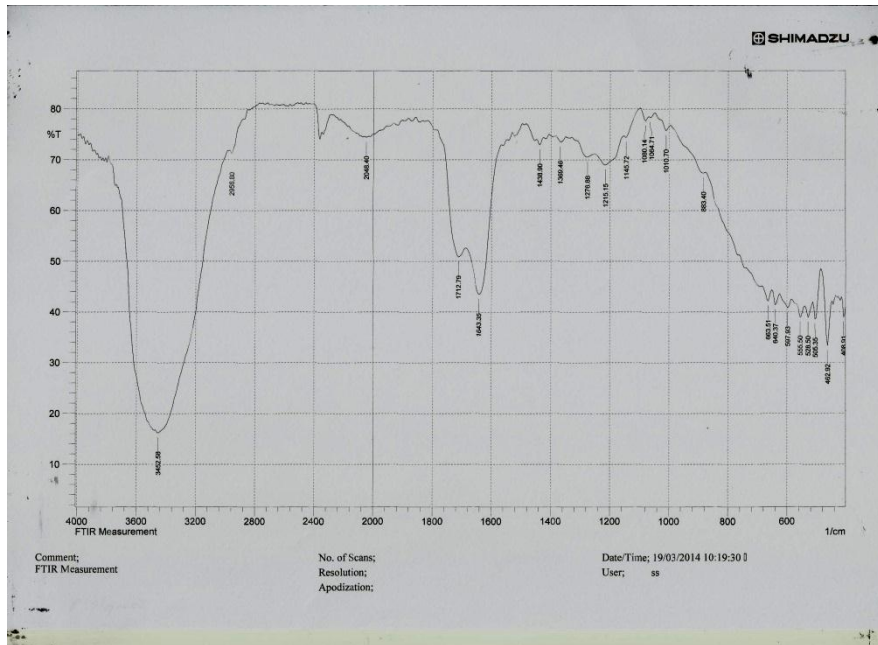
**Figure 10.** FTIR measurement for lower layer of residue with  $C_{A0}=0.58 \text{ mol.l}^{-1}$ ,  $C_{B0}=0.63 \text{ mol.l}^{-1}$  and 9 % excess of NaOH solution.



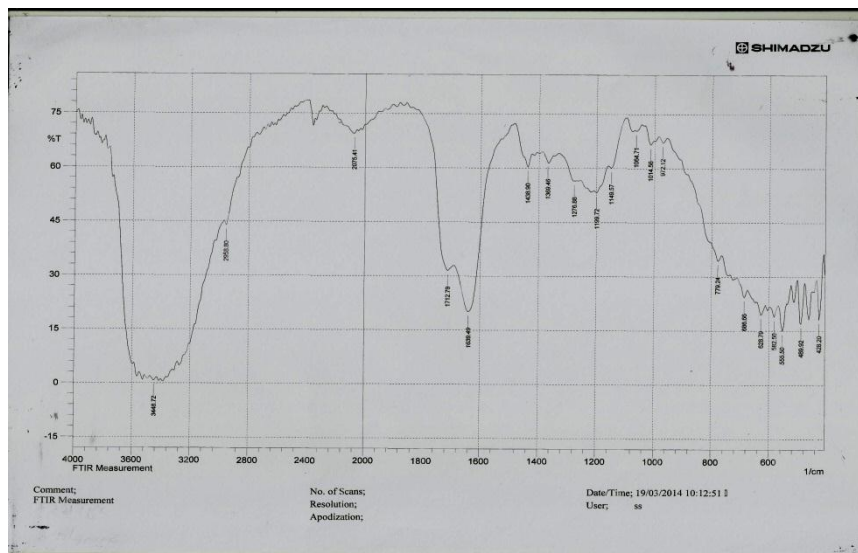
**Figure 11.** FTIR measurement for upper layer of residue with  $C_{A0}=0.5553 \text{ mol.l}^{-1}$ ,  $C_{B0}=0.6384 \text{ mol.l}^{-1}$  and 15 %excess of NaOH solution.



**Figure 12.** FTIR measurement for lower layer of residue with  $C_{A0}=0.5553 \text{ mol.l}^{-1}$ ,  $C_{B0}=0.6384 \text{ mol.l}^{-1}$  and 15%excess of NaOH solution.



**Figure 13.** FTIR measurement for upper layer of residue with  $C_{A_0}=0.32 \text{ mol.l}^{-1}$ ,  $C_{B_0}=0.38 \text{ mol.l}^{-1}$  and 19 %excess of NaOH solution.



**Figure 14.** FTIR measurement for lower layer of residue with  $C_{A_0}=0.32 \text{ mol.l}^{-1}$ ,  $C_{B_0}=0.38 \text{ mol.l}^{-1}$  and 19 %excess of NaOH solution.

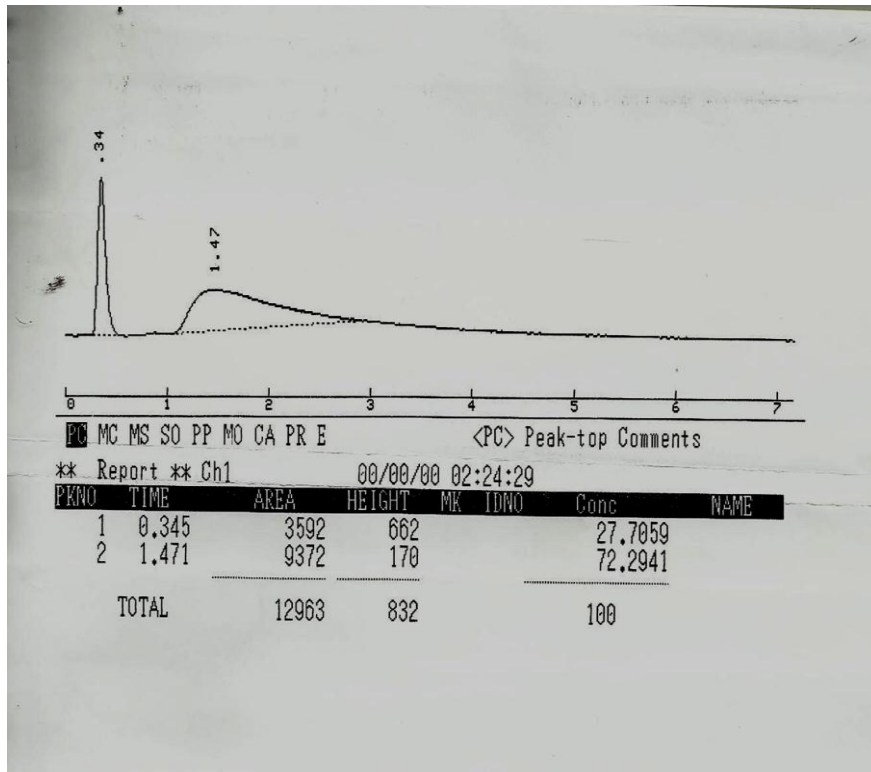


Figure 15. GC analysis of diethyl adipate sample saponified without distillation ( $C_{A0}=0.094$  mol.l<sup>-1</sup> and  $C_{B0}=0.24$  mol.l<sup>-1</sup>).

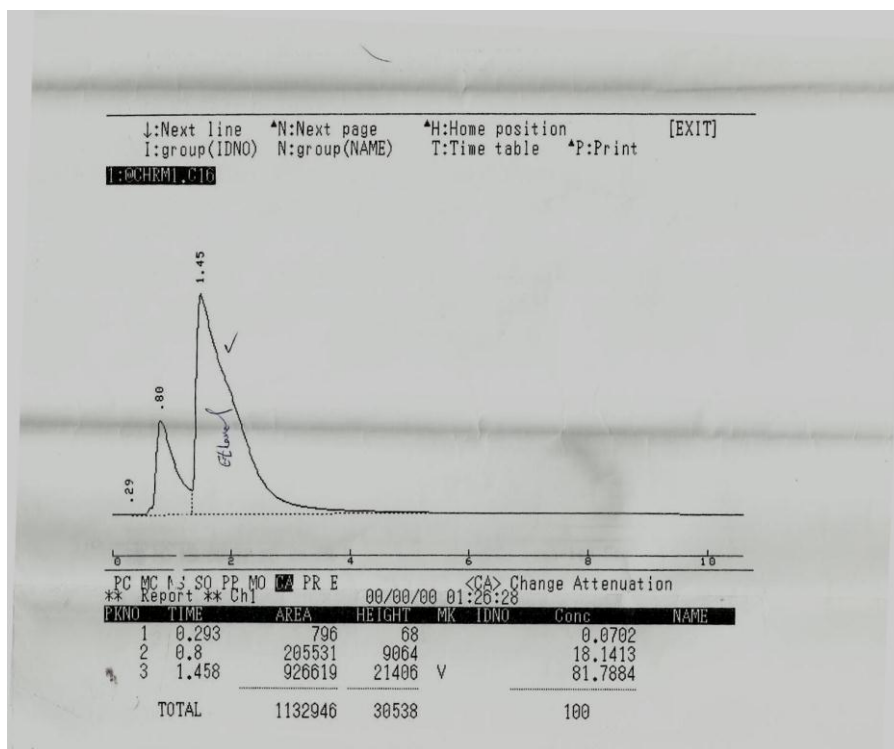
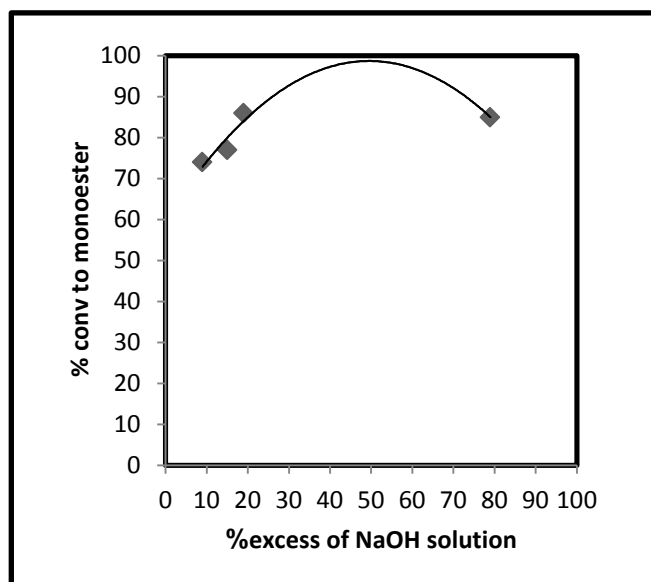


Figure 16. GC analysis of ethyl group as standard.



**Figure 17.** The dependence of the conversion (from di-ester to monoester) on %excess of NaOH solution in reactive distillation of saponification of diethyl adipate.

**Table 1.** Percentage conversion to monoester in distillate.

$C_{Ao}$ (mol.l <sup>-1</sup> )	$C_{Bo}$ (mol.l <sup>-1</sup> )	%excess of NaOH sol.	%conversion in distillate
0.58	0.63	9	74.1
0.5553	0.6384	15	78.9
0.32	0.38	19	87.5
0.094	0.24	79	86

**Table 2.** Summary of experimental results.

Technique	%excess of NaOH sol.	%conversion to monoester
without distillation	79	15.3
with distillation	9	74.1
	15	78.9
	19	87.5
	79	86

**Table 3.** Refractive index variation with initial reactants concentrations and percentage excess of NaOH solution.

$C_{Ao}$ (mol.l <sup>-1</sup> )	$C_{Bo}$ (mol.l <sup>-1</sup> )	%excess of NaOH sol.	RI of upper layer of distillate
0.58	0.63	9	1.3383
0.5553	0.6384	15	1.3380
0.32	0.38	19	1.3380
0.094	0.24	79	1.339